

Semiconducting Niobium Oxyiodide Cluster Compounds from Heterogenous Solid-State Reactions

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List of Abbreviations

CBM	conduction band minimum
DFT	density functional theory
DTA	differential thermal analysis
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
EDX	energy dispersive X-ray spectroscopy
ELF	electron localisation function
SEM	scanning electron microscopy
TXRF	total reflection X-ray fluorescence
UV	ultraviolet
VBM	valence band maximum
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Summary

In this thesis, the reduction of NbI_4 with $\text{Li}_2(\text{CN}_2)$ in the presence of Li_2O was investigated. In this system, a heterogeneous reaction takes place involving both, a solid and a gaseous phase. The gaseous phase exhibit behaviour characteristic close to a non-equilibrium system, as it is highly sensitive on the reaction conditions and results in the formation of a variety of cluster compounds. A comparable situation is found in the W-O-I system in halogen lamps, where multiple phases coexist under very similar conditions.¹

The system described here displays an even broader structural chemistry. No fewer than ten different cluster-containing compounds could be isolated from a single type of reaction mixture. For many reactions, mixtures of compounds are obtained, which separate into three distinct zones within the ampoule: the bottom of the ampoule with the highest temperature, a central zone at intermediate temperature, and the top of the ampoule with the lowest reaction temperature.

The top zone of the ampoule contains the unavoidable side products NbOI_2 and NbI_5 . The bottom zone is represented by the metathesis salt LiI , amorphous powder and two new compounds with a novel cluster core; $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$. All other new compounds are found in the central zone, their formation depending sensitively on the reaction conditions.

All newly discovered compounds are black in colour, which often is caused by small band gaps. Their structural connectivity ranges from isolated molecular units to one-dimensional strings, two-dimensional layers, and three-dimensional frameworks. In many cases, the electronic properties as well as the electronic structures were investigated.

The identified cluster cores contain between four and ten metal atoms with attached and integrated oxygen atoms. A rectangular $[\text{Nb}_4\text{O}]$ core is present in four compounds with the general formula $\text{Nb}_4\text{OI}_{12-x}$, which differ in iodide content, valence electron count and connectivity. These include the molecular compound $\text{Nb}_4\text{OI}_{12}$, two modifications of $\text{Nb}_4\text{OI}_{11}$ featuring string-like connectivity, and a layered structure in $\text{Nb}_4\text{OI}_{10}$.

In addition to the rectangular core, a butterfly-shaped $[\text{Nb}_4\text{O}]$ cluster core with two attached $[\text{NbO}]$ units was characterised in $\text{Nb}_6\text{O}_3\text{I}_{15}$. In this compound, the cluster cores are connected to four neighbouring clusters, forming a three-dimensional framework.

For cluster containing five metal atoms, a square-pyramidal $[\text{M}_5\text{O}_4]$ core with oxygen atoms located at the edges was identified in $\text{Nb}_5\text{O}_4\text{I}_{11}$ as well as in three modifications of tantalum

compounds. The connectivity between neighbouring clusters gives rise to corrugated layered structures with van der Waals gaps between the layers.

This $[\text{Nb}_5\text{O}_4]$ cluster core also forms the basis of the $[\text{Nb}_7\text{O}_5]$ core found in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$. Both structures exhibit three-dimensional networks, differing in their connectivity and thereby forming channels that are accessible either for I^- or $(\text{NbI}_6)^-$ units.

Extension of the $[\text{Nb}_7\text{O}_5]$ core by an additional niobium atom at one edge of the $[\text{Nb}_5\text{O}_4]$ basis leads to the $[\text{Nb}_8\text{O}_5]$ core found in the layered structure of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. Within the channels between the layers, molecular NbI_5 units are incorporated.

Furthermore, the structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ contains $[\text{Nb}_{10}\text{O}_4]$ cluster cores, which are connected into one-dimensional strings by an additional niobium atom. This cluster core shows a close structural relation to the core found in $\text{Nb}_6\text{O}_3\text{I}_{15}$.

As nearly all these compounds originate from the same gaseous phase, this heterogenous system represents a special case of a state close to non-equilibrium conditions, resulting in pronounced sensitive with respect to the reaction parameters.

Zusammenfassung

In dieser Arbeit wird die Reduktion von NbI_4 mit $\text{Li}_2(\text{CN}_2)$ in Anwesenheit von Li_2O untersucht. In diesem System findet eine heterogene Reaktion statt, an der sowohl eine feste als auch eine gasförmige Phase beteiligt sind. Die gasförmige Phase zeigt ein Verhalten, das für ein Nichtgleichgewichtssystem charakteristisch ist, da sie hochgradig empfindlich gegenüber den Reaktionsbedingungen ist und zur Bildung einer Vielzahl von Clusterverbindungen führt. Eine vergleichbare Situation findet sich im W–O–I-System in Halogenlampen, in dem unter sehr ähnlichen Bedingungen mehrere Phasen koexistieren.

Das hier beschriebene System weist eine noch breitere Strukturchemie auf. Nicht weniger als zehn verschiedene clusterhaltige Verbindungen konnten aus einem einzigen Typ von Reaktionsgemisch isoliert werden. Bei vielen Reaktionen entstehen Gemische von Verbindungen, die sich in drei klar unterscheidbare Zonen innerhalb der Ampulle aufteilen: den Boden der Ampulle mit der höchsten Temperatur, eine zentrale Zone bei mittlerer Temperatur und den oberen Bereich der Ampulle mit der niedrigsten Reaktionstemperatur.

Die obere Zone der Ampulle enthält die unvermeidbaren Nebenprodukte NbOI_2 und NbI_5 . Die untere Zone wird durch das Metathesesalz LiI , amorphes Material sowie zwei neue Verbindungen mit einem neuartigen Clusterkern repräsentiert: $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ und $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$. Alle weiteren neuen Verbindungen finden sich in der zentralen Zone, wobei ihre Bildung stark von den Reaktionsbedingungen abhängt.

Alle neu identifizierten Verbindungen haben eine schwarze Farbe, was häufig mit kleinen Bandlücken in Zusammenhang steht. Ihre strukturelle Vernetzung reicht von isolierten molekularen Einheiten über eindimensionale Ketten und zweidimensionale Schichten bis hin zu dreidimensionalen Gerüststrukturen. In vielen Fällen wurden sowohl die elektronischen Eigenschaften als auch die elektronische Struktur untersucht.

Die identifizierten Clusterkerne enthalten vier bis zehn Metallatome mit angebundenen und integrierten Sauerstoffatomen. Ein rechteckiger $[\text{Nb}_4\text{O}]$ -Kern tritt in vier Verbindungen mit der allgemeinen Formel $\text{Nb}_4\text{OI}_{12-x}$ auf, die sich in ihrem Iodidgehalt, der Anzahl der Valenzelektronen und ihrer Vernetzung unterscheiden. Dazu zählen die molekulare Verbindung $\text{Nb}_4\text{OI}_{12}$, zwei Modifikationen von $\text{Nb}_4\text{OI}_{11}$ mit kettenartiger Verknüpfung sowie eine Schichtstruktur in $\text{Nb}_4\text{OI}_{10}$.

Neben dem rechteckigen Kern konnte in $\text{Nb}_6\text{O}_3\text{I}_{15}$ auch ein Butterfly-artiger $[\text{Nb}_4\text{O}]$ -Clusterkern mit zwei angelagerten $[\text{NbO}]$ -Einheiten charakterisiert werden. In dieser

Verbindung sind die Clusterkerne mit vier benachbarten Clustern verknüpft und bilden ein dreidimensionales Gerüst.

Für Cluster mit fünf Metallatomen wurde ein quadratisch-pyramidaler $[M_5O_4]$ -Kern mit an den Kanten positionierten Sauerstoffatomen in $Nb_5O_4I_{11}$ sowie in drei Tantal-Modifikationen identifiziert. Die Verknüpfung mit benachbarten Clustern führt zu gewellten Schichtstrukturen mit van-der-Waals-Lücken zwischen den Schichten.

Dieser $[Nb_5O_4]$ -Clusterkern bildet auch die Basis des $[Nb_7O_5]$ -Kerns, der in $Li_3Nb_7O_5I_{15}$ und $Li_3Nb_7O_5I_{14}(NbI_6)$ gefunden wird. Beide Strukturen zeigen dreidimensionale Netzwerke, die sich in ihrer Vernetzung unterscheiden und dadurch Kanäle ausbilden, die entweder für I^- - oder für $(NbI_6)^-$ -Einheiten zugänglich sind.

Die Erweiterung des $[Nb_7O_5]$ -Kerns durch ein weiteres Niobatom an einer Kante der $[Nb_5O_4]$ -Basis führt zum $[Nb_8O_5]$ -Kern, der in der geschichteten Struktur von $Nb_8O_5I_{17}(NbI_5)$ vorkommt. In den Kanälen zwischen den Schichten sind molekulare NbI_5 -Einheiten eingebaut. Darüber hinaus enthält die Struktur von $Nb_{11}O_6I_{24}$ $[Nb_{10}O_4]$ -Clusterkerne, die durch ein zusätzliches Niobatom zu eindimensionalen Ketten verknüpft sind. Dieser Clusterkern zeigt eine enge strukturelle Verwandtschaft zu dem Kern in $Nb_6O_3I_{15}$.

Da nahezu alle diese Verbindungen aus derselben gasförmigen Phase hervorgehen, stellt dieses heterogene System einen Sonderfall eines Zustands nahe dem Nichtgleichgewicht dar, welches eine ausgeprägte Sensitivität gegenüber den Reaktionsparametern besitzt.

List of Publications

Publication 1:

The Rectangular Niobium Oxyiodide Cluster Nb₄OI₁₀ – A Narrow Band-Gap Semiconductor

Jan Beitzberger, Markus Ströbele, Fabian Strauß, Marcus Scheele, Carl P. Romao, and Hans-Jürgen Meyer

Eur. J. Inorg. Chem. **2024**, 27, e202400329

Publication 2:

The family of tetranuclear Nb₄OI_{12-x} clusters (x = 0, 1, 2): from the molecular Nb₄OI₁₂ cluster to extended chains and layers

Jan Beitzberger, Mario Martin, Marcus Scheele, Patrick Schmidt, Markus Ströbele, and Hans-Jürgen Meyer

Dalton Trans. **2025**, 54, 5486-5493

Publication 3:

Structural Modifications of M₅O₄I₁₁ (M = Nb, Ta) Cluster Networks from Heterogeneous Solid-State Reactions

Fabian Grahlow, Jan Beitzberger, Mario Martin, Eric Juriatti, Heiko Peisert, Marcus Scheele, Markus Ströbele, Carl P. Romao and Hans-Jürgen Meyer

Dalton Trans. **2025**, 54, 16593-16604

Publication 4:

Niobium oxyiodide cluster compounds Li₃Nb₇O₅I₁₅ and Nb₈O₅I₁₇(NbI₅) with expanding cluster architectures and multicenter Nb–Nb bonding

Jan Beitzberger, Markus Ströbele, Patrick Schmidt, Carl P. Romao, and Hans-Jürgen Meyer

Dalton Trans. **2025**, 54, 14376-14383

Publication 5:

Zero Indirect Band Gap and Flat Bands in a Niobium Oxyiodide Cluster Material

Jan Beitzlberger, Mario Martin, Marcus Scheele, Marek Matas, Carl P. Romao, Markus Ströbele,
and Hans-Jürgen Meyer

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Publication 6:

Niobium oxyiodide clusters from heterogeneous solid-state reactions: the example of
 $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$

Jan Beitzlberger, Patrick Schmidt, and Hans-Jürgen Meyer

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Scientific Contribution

Publication 1:

The Rectangular Niobium Oxyiodide Cluster Nb₄OI₁₀ – A Narrow Band-Gap Semiconductor

The manuscript was written in collaboration with Prof. H.-J. Meyer. Dr. M. Ströbele performed the structure solution and refinement. I planned and carried out the synthesis. I measured and analysed the DRIFTS measurements. The electronic conductivity measurements and the writing of this part were performed by Dr. F. Strauß in collaboration with Prof. M. Scheele. The electronic band structure calculations and the writing in this section were performed by Dr. C. P. Romao.

Publication 2:

The family of tetranuclear Nb₄OI_{12-x} clusters (x = 0, 1, 2): from the molecular Nb₄OI₁₂ cluster to extended chains and layers

The manuscript was written in collaboration with Prof. H.-J. Meyer. Dr. M. Ströbele and P. Schmidt solved the structures and did the refinement. I planned and carried out the synthesis. The electronic conductivity measurements and the writing of this part were performed by M. Martin in collaboration with Prof. M. Scheele.

Publication 3:

Structural Modifications of M₅O₄I₁₁ (M = Nb, Ta) Cluster Networks from Heterogeneous Solid-State Reactions

The manuscript was written by F. Grahlow in collaboration with me and Prof. H.-J. Meyer. F. Grahlow planned and conducted the experimental syntheses and preparations of the tantalum compounds, while I synthesised and measured the niobium compound. F. Grahlow prepared the conductivity measurements and carried them out together with M. Martin, who evaluated the data and co-wrote that section with Prof. M. Scheele. The DRIFTS measurements were performed in collaboration with F. Grahlow. F. Grahlow prepared the samples for the XPS measurements, which were performed by E. Juriatti, who co-wrote that part with Prof. H. Peisert. Dr. M. Ströbele carried out the structure refinements. Dr. C. P. Romao performed the calculations and wrote the corresponding section.

Publication 4:

Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicenter Nb–Nb bonding

The manuscript was written in collaboration with Prof. H.-J. Meyer and P. Schmidt. Dr. M. Ströbele and P. Schmidt did the structure solution and refinement. I planned and carried out the synthesis. The electronic band structure calculations, the electron localisation function calculations and the writing in this section were performed by Dr. C. P. Romao.

Publication 5:

Zero Indirect Band Gap and Flat Bands in a Niobium Oxyiodide Cluster Material

The manuscript was written in collaboration with Prof. H.-J. Meyer and C. P. Romao. Dr. M. Ströbele did the structure solution and refinement. I planned and carried out the synthesis. The electronic conductivity measurements and the writing of this part were performed by M. Martin in collaboration with Prof. M. Scheele. The electronic band structure calculations, the theoretical concepts and the writing in this section were done by M. Matas and Dr. C. P. Romao.

Publication 6:

Niobium oxyiodide clusters from heterogeneous solid-state reactions: the example of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$

The manuscript was written by Prof. H.-J. Meyer and me in collaboration with P. Schmidt. P. Schmidt did the structure solution and refinement. I planned and carried out the synthesis.

1. Introduction

1.1 Ternary Metal Oxyhalides

Metal halides, despite their wide variety in composition and properties, commonly feature halide ligands coordinating a cationic metal centre, often in an octahedral geometry. The structures of these metal halides vary significantly, ranging from three-dimensional frameworks (e.g. CuCl), to layered structures (e.g. CdCl_2), to one-dimensional chain-like motifs (e.g. ZrCl_4) and even to discrete molecular species (e.g. WCl_6).² The dimensional reduction correlates closely with the number of halide ligands coordinating the metal centre.

Interestingly, such a dimensional reduction can also occur the other way around by replacing the halide ligands with heteroanions of higher negative charge. An example for this is the gradual substitution of chloride by oxygen in tungsten halides. Starting with WCl_6 , a molecular compound, the replacement of two chlorides by one oxygen yields WOCl_4 .³ This compound exhibits a one-dimensional, string-like connectivity facilitated by shared oxygen atoms. Replacing two additional chlorides with another oxygen leads to WO_2Cl_2 , which adopts a layered structure, again due to oxygen bridging.⁴ Finally, the complete replacement of all six chlorides with three oxygen atoms results in WO_3 , a fully connected three-dimensional framework.⁵

Metal oxyhalides often exhibit lower sublimation points than the corresponding halides or oxides. This property makes them attractive as potential transport agent in chemical vapor transport reactions like in the van Arkel-de Boer process⁶. A notable application of this principle is found in halogen lamps with tungsten filament, where the efficiency of light emission and the compact size of the bulb are optimised by introducing a small amount of oxygen and iodide. The resulting oxyhalide species enable a regenerative cycle that prolongs filament life and maintains bulb clarity.^{1a}

Metal oxyhalides are not only useful for improving processes such as chemical vapor transport, but also serve directly as efficient phosphor materials. A notable example is LaOCl doped with Sb^{3+} , which exhibits strong blue and green light emission under UV excitation.⁷ The presence of two emissions arise from two distinct phases; one phase where the LaOCl lattice is uniformly doped with Sb^{3+} (responsible for blue emission) and another phase with a higher local concentration of antimony (resulting in green emission). Beyond UV excitation, some metal oxyhalides are capable of photon upconversion to emit visible light upon excitation with near-

infrared radiation. For instance, YOCl co-doped with Yb³⁺ and Er³⁺ emits red light when excited with 1550 nm or 980 nm, due to efficient upconversion processes mediated by energy transfer between Yb³⁺ and Er³⁺ ions.⁸ In contrast, when the material is doped solely with Er³⁺ and excited at 980 nm, the emission shifts to orange with a reduced upconversion efficiency.

Doped materials are not only valuable in light-emitting applications, but are also used in electronic technologies. A well-known example is fluorine-doped SnO₂, a widely used transparent conductive oxide. Its combination of good electrical conductivity and optical transparency makes it an ideal candidate for applications such as touchscreens, flat-panel displays, and photovoltaic cells.⁹ Additionally, some 3d transition metal oxides are being explored as potential electrode materials for batteries. Compounds such as FeOCl and TiOF₂ have attracted interest due to their layered structures and favourable redox properties, which may support reversible ion intercalation and high energy storage capacity.¹⁰

Although metal oxyhalides offer numerous potential applications, those derived from group 5 and 6 elements are comparatively underrepresented in practical use. Nevertheless, a considerable number of ternary metal oxyhalides from these groups have been crystallographically characterised (Table 1), highlighting their structural diversity and chemical richness, even if their functional applications remain less explored.

Table 1. Crystallographic characterised, ternary metal oxyhalides of groups 5 and 6.

<i>M-O-X</i> Compound	Oxidation State of <i>M</i>	Synthesis	Appearance	Year of Publication
Vanadium				
VOF ₃	+V	V ₂ O ₅ + F ₂	pale yellow solid	2007 ¹¹
VO ₂ F	+V	V ₂ O ₅ + VOF ₃	orange solid	2015 ¹²
VOCl	+III	VCl ₃ + V ₂ O ₃	brown solid	1969 ¹³
VOCl ₂	+IV	V ₂ O ₅ + 3 VCl ₃ + VOCl ₃	green solid	1981 ¹⁴
VOCl ₃	+V	V ₂ O ₃ + 3 Cl ₂	orange-yellow liquid	1983 ¹⁵
VOBr	+III	3 VBr ₃ + As ₂ O ₃	violet solid	1969 ¹³
VOBr ₂	+IV	V ₂ O ₃ + 2 Br ₂	dark brown solid	1981 ¹⁴

Niobium

$\text{Nb}_2\text{O}_2\text{F}_3$	+III/IV	$4 \text{ Nb} + 4 \text{ SnO} + 3 \text{ SnF}_2$	black solid	2014 ¹⁶
$\text{NbO}_x\text{F}_{3-x}$ ($x = 0-2$)	+III-V	$2 \text{ Nb} + 3 \text{ NbF}_5^{(1)}$	black to white solid	1971 ¹⁷
NbOF_3	+V	$\text{NbO}_2\text{F} + \text{NbF}_5$	slight greyish solid	2002 ¹⁸
$\text{Nb}_3\text{O}_5\text{F}_5$	+V	$5 \text{ NbO}_2\text{F} + \text{NbF}_5$	blueish solid	2006 ¹⁹
NbO_2F	+V	$\text{Nb}/\text{Nb}_2\text{O}_5 + \text{aq. HF}$	white solid	1956 ²⁰
$\text{Nb}_3\text{O}_7\text{F}$	+V	$\text{Nb}_2\text{O}_5 + \text{NbO}_2\text{F}$	white solid	1964 ²¹
$\text{Nb}_{17}\text{O}_{42}\text{F}$	+V	$8 \text{ Nb}_2\text{O}_5 + \text{NbO}_2\text{F}$	white solid	1966 ²²
$\text{Nb}_{31}\text{O}_{77}\text{F}$	+V	$15 \text{ Nb}_2\text{O}_5 + \text{NbO}_2\text{F}$	white solid	1966 ²²
$\text{Nb}_3\text{O}_2\text{Cl}_5$	+III	$5 \text{ NbCl}_5 + 2 \text{ Nb}_2\text{O}_5 + 6 \text{ Nb}$	dark brown solid	2000 ²³
$\text{Nb}_{10}\text{O}_7\text{Cl}_{16}$	+III	$16 \text{ NbCl}_5 + 7 \text{ Nb}_2\text{O}_5 + 20 \text{ Nb}$	black solid	2003 ²⁴
NbOCl_2	+IV	$2 \text{ NbCl}_5 + \text{Nb}_2\text{O}_5 + \text{Nb}$	dark brown/black solid	1997 ²⁵
NbOCl_3	+V	$\text{Nb}_2\text{O}_5 + \text{CCl}_4$	white solid	1959 ²⁶
$\text{Nb}_3\text{O}_7\text{Cl}$	+V	$\text{Nb}_2\text{O}_5 + \text{NbOCl}_3$	white solid	1964 ²⁷
NbOBr_2	+IV	$2 \text{ NbOBr}_3 + \text{InBr}$	black solid	2006 ²⁸
NbOBr_3	+V	$2 \text{ Nb}_2\text{O}_5 + 6 \text{ Nb} + 15 \text{ Br}_2$	yellow/brown solid	2008 ²⁹
NbO_2Br	+V	$4 \text{ Nb}_2\text{O}_5 + 2 \text{ Nb} + 5 \text{ Br}_2$	yellow solid	1966 ³⁰
NbOI_2	+IV	$\text{Nb}_2\text{O}_5 + 3 \text{ Nb} + 5 \text{ I}_2$	black solid	1978 ³¹
NbOI_3	+V	$2 \text{ Nb}_2\text{O}_5 + 6 \text{ Nb} + 15 \text{ I}_2$	black solid	2007 ³²
NbO_2I	+V	$4 \text{ Nb}_2\text{O}_5 + 2 \text{ Nb} + 5 \text{ I}_2$	red solid	1966 ³⁰

⁽¹⁾ Oxygen contamination

Tantalum

TaOF ₃	+V	TaO ₂ F + TaF ₅	white solid	2002 ¹⁸
TaO ₂ F	+V	Ta + aq. HF	white solid	1956 ²⁰
Ta ₃ O ₇ F	+V	Ta ₂ O ₅ + TaO ₂ F	white solid	1975 ³³
TaOCl ₂	+IV	Ta ₂ O ₅ + Ta + 2 TaCl ₅	black solid	2022 ³⁴
TaO ₂ Cl	+V	2 Ta + 4 Ta ₂ O ₅ + 5 Cl ₂	yellowish solid	1966 ³⁰
Ta ₃ O ₇ Cl	+V	14 Ta ₂ O ₅ + 2 Ta + 5 Cl ₂	greyish-white solid	1966 ³⁰
TaOBr ₂	+IV	Ta ₂ O ₅ + Ta + 2 TaBr ₅	black solid	2022 ³⁴
TaO ₂ Br	+V	2 Ta + 4 Ta ₂ O ₅ + 5 Br ₂	yellow solid	1966 ³⁰
TaOI ₂	+IV	Ta ₂ O ₅ + 3 Ta + 5 I ₂	black solid	1995 ³⁵
TaO ₂ I	+V	2 Ta + 4 Ta ₂ O ₅ + 5 I ₂	red solid	1966 ³⁰

Chromium

CrOF ₃	+V	CrO ₂ F ₂ + XeF ₂	brick red solid	1986 ³⁶
CrOF ₄	+VI	CrO ₂ F ₂ + KrF ₂	purple solid	2019 ³⁷
CrO ₂ F ₂	+VI	CrO ₃ + 2 HF	violet-red solid	2007 ¹¹
CrOCl	+III	Cr ₂ O ₃ + CrCl ₃	violet/green solid	1962 ³⁸
CrOCl ₃	+V	CrO ₂ Cl ₂ + BCl ₃	dark-red solid	2013 ³⁹
CrO ₂ Cl ₂	+VI	CrO ₃ + 2 HCl	red liquid	2006 ⁴⁰
CrOBr	+III	3 CrBr ₃ + As ₂ O ₃	greyish-violet solid	1966 ⁴¹

Molybdenum

MoO _{2.4} F _{0.6}	+V/VI	4 MoO ₃ + Mo + 3 HF	dark blue solid	1971 ⁴²
Mo ₄ O _{11.2} F _{0.8}	+V/VI	14 MoO ₃ + Mo + 3 HF	dark blue solid	1971 ⁴²
MoOF ₄	+VI	2 Mo + 4 F ₂ + O ₂	white solid	1968 ⁴³
MoO ₂ F ₂	+VI	Na ₂ MoO ₂ F ₄ ·2H ₂ O + O ₂	white solid	2010 ⁴⁴

MoOCl ₂	+IV	MoO ₃ + 2 MoCl ₃	golden yellow solid	1997 ²⁵
Mo ₂ OCl ₈	+V	H ₂ MoO ₄ + 4 SOCl ₂	dark red solid	1988 ⁴⁵
MoOCl ₃	+V	9 MoCl ₅ + 5 Sb ₂ O ₃	black solid	1970 ⁴⁶
MoOCl ₄	+VI	MoO ₃ + 2 SOCl ₂	dark green solid	1980 ⁴⁷
MoO ₂ Cl ₂	+VI	2 MoCl ₅ + 4 AlCl ₃ + 3 P ₂ O ₅	yellow solid	2023 ⁴⁸
MoOBr ₃	+V	MoO ₂ Br ₂ + PBr ₅	grey-black solid	1970 ⁴⁹
MoO ₂ Br ₂	+VI	LaBr ₃ + 2 MoO ₃	red solid	2011 ⁵⁰

Tungsten

WO _{3-x} F _x (<i>x</i> = 0-0.6)	+V/VI	WO ₃ + (C ₂ F ₄) _{<i>n</i>}	light green to blue	2020 ⁵¹
WOF ₄	+VI	2 W + O ₂ + 4 F ₂	white solid	1968 ⁵²
WOCl ₃	+V	3 WOCl ₄ + Al	green solid	2006 ⁵³
WOCl ₄	+VI	WO ₃ + 2 SOCl ₂	red solid	1966 ³
WO ₂ Cl ₂	+VI	WO ₃ + 2 HCl	white solid	1968 ⁴
WOB ₄	+VI	2 WBr ₆ + WO ₃	brown-black solid	1966 ³
WOI ₃	+V	2 W ₃ O + 2 O ₂ + 9 I ₂	grey-black solid	1987 ⁵⁴
W ₂ O ₃ I ₄	+V	WO ₂ I ₂	black solid	2021 ^{1b}
WO ₂ I ₂	+VI	W + 2 WO ₃ + 3 I ₂	black solid	2021 ^{1b}

Concerning the compounds in the Nb–O–I system, there are only three representatives: NbOI₂, NbOI₃ and NbO₂I.³⁰⁻³² All of them can be synthesised from Nb₂O₅, elemental Nb and I₂ at appropriate temperatures and the right molar proportions.⁵⁵ Especially NbOI₂ was investigated in terms of ferroelectricity⁵⁶ and applications for water splitting⁵⁷.

It is noteworthy that many known metal oxyhalides are found in their highest oxidation states, whereas only a limited number of examples display metal–metal bonding or cluster formation associated with low oxidation states.

1.2 Metal Cluster Compounds

The term “metal cluster” has been widely discussed and varying definitions were formulated to define, what a cluster is. An early definition by F. A. Cotton claims, that metal atom cluster compounds can be defined as materials containing “a finite group of metal atoms which are held together mainly, or at least to a significant extent, by bonds directly between the metal atoms, even though some nonmetal atoms may also be intimately associated with the cluster”.⁵⁸ This definition includes binuclear complexes with metal–metal bonds as well, like in the structure of $\text{Nb}_2\text{Se}_2\text{I}_6$.⁵⁹ In another definition, metal clusters are a network of at least three metal atoms, which are directly bond together or even form a ring.⁶⁰

Within this broad conceptual framework, niobium halides represent a particularly well-studied class of metal-rich compounds in which metal–metal interactions play a central role.⁶¹ Peierls-distorted NbX_4 exhibits a string-like connected structure with alternating short and long Nb–Nb contacts.⁶² The more reduced niobium halides are represented by Nb_3X_8 ,⁶³ $\text{Nb}_6\text{Cl}_{14}$ ⁶⁴ and Nb_6I_{11} ,⁶⁵ including triangular and octahedral metal clusters. Typical synthetic procedures for these compounds are based on reactions of the elements or by reducing niobium halides with elemental niobium.⁵⁵

These structural motifs highlight the fundamental interplay between metal–metal bonding and ionic interactions in metal cluster compounds. Hence, metal atom cluster compounds exhibit unique chemical and physical properties that have attracted extensive scientific interest. Since clusters are usually spatially separated from one another by halide ligands, the electrons involved in metal–metal interactions are often localised within the clusters, strongly influencing the electronic, magnetic, and structural behaviour of the material.

One of the most well-known and extensively studied metal atom clusters features an octahedral arrangement, typically represented by the $[\text{M}_6\text{X}_{12}]$ - and $[\text{M}_6\text{X}_8]$ -type architectures (M = transition metal, X = halogen), illustrated in Figure 1.⁶⁶ These clusters are predominantly formed by group 4 – 7 transition metals and may incorporate an interstitial atom at the centre of the octahedron (especially in the case of electron-deficient group 4 metals).⁶⁷ The structural difference between the two architectures results from the ratio of the ionic radii of the metal and the halide ions as well as the cluster electron count. When large metal cations are combined with small halide anions, the $[\text{M}_6\text{X}_{12}]$ -type is favoured, in which the halide ligands are capping all twelve edges of the octahedron. Conversely, when smaller metals are paired with larger halides, increased repulsion of the halide ions result in a face-capping coordination, giving rise to the $[\text{M}_6\text{X}_8]$ -type structure.

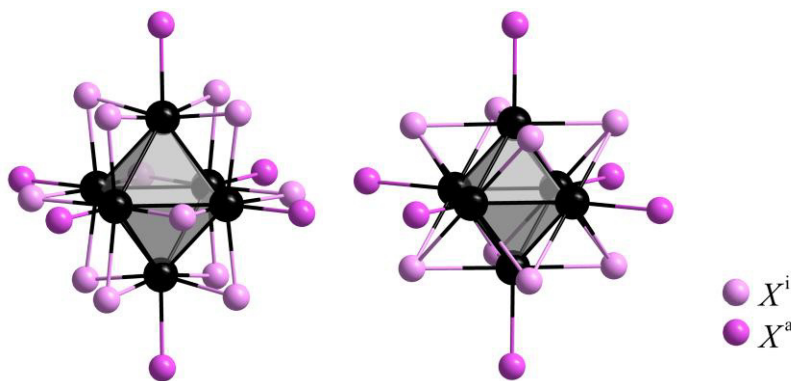


Figure 1. Octahedral clusters with $[M_6X_{12}]$ - and $[M_6X_8]$ -type architectures.

Once formed, metal clusters can undergo further chemical modification, including reactions like ligand exchange. For example, the outer ligands of $\text{Mo}_6\text{Cl}_{12}$ or $[(\text{Mo}_6\text{Cl}_8^i)\text{Cl}_2^a\text{Cl}_{4/2}^{a-a}]$ (i = inner, a = outer) can be substituted through hydrolysis in an alkaline solution, yielding the compound $(\text{Mo}_6\text{Cl}_8)(\text{OH})_4 \cdot 14\text{H}_2\text{O}$.⁶⁸ Mo_6X_{12} can also react with alkali metal salts, such as CsX , to form compounds like $\text{Cs}_2\text{Mo}_6\text{X}_{14}$ or $\text{Cs}_2[(\text{Mo}_6\text{X}_8^i)\text{X}_6^a]$.⁶⁹ This compound serves as a versatile precursor enabling subsequent substitution of the alkali metal cation, the outer ligands, or both.⁷⁰ The replacement of inorganic counterions with organic cations, such as tetrabutylammonium, can significantly enhance the luminescence properties of these octahedral clusters.⁷¹ Further improvements can be achieved by substituting the apical halide ligands with neutral or anionic organic ligands, allowing the adjustment of their photophysical behaviour for specific applications.⁷²

In addition to their luminescence, transition metal clusters can exhibit a range of other interesting physical properties. For instance, Nb_6I_{11} is an example of an octahedral cluster compound containing unpaired electrons, resulting in paramagnetic behaviour.⁷³ Other octahedral clusters, such as those found in the Chevrel phases, display superconducting properties at low temperatures.⁷⁴ A notable example is PbMo_6S_8 , which has a critical temperature of approximately 15 K and a remarkably high critical magnetic field, making it of interest for applications in superconducting materials and technologies.⁷⁵

Although octahedral clusters are the most prominent and extensively studied examples, there are also other quite stable cluster compounds. Notably, M_3 -type cluster compounds are observed for a variety of transition metals and in diverse chemical environment. These M_3 cluster ($M = \text{Ti, Nb, Ta, Mo, W}$ and Re) typically feature a trigonal cluster core and can be stabilised in five different anionic coordination environments (Figure 2).

The first three coordination types occur for (alkali) metal (chalco-)halides, with the most common configuration involving octahedral coordination of the metal atoms by halide ligands

(Figure 2a).^{63, 76} The other two halide-based configurations involve square pyramidal coordination. In one arrangement, the square pyramids are edge-sharing - as seen in compounds such as W_3I_x ($x = 8, 9, 12$)⁷⁷, presented in Figure 2b. In the second arrangement, the pyramids are corner-sharing, as in Re_3X_9 ($X = Cl, Br, I$)⁷⁸ and $\alpha-TcCl_3$ ⁷⁹ (Figure 2c). Two coordination types could just be observed involving chalcogen atoms. Therefore, the forth coordination type can be described as bicapped trigonal cluster with an octahedral coordination of the metal atoms and is represented by Nb_3SI_7 ⁸⁰ and $Nb_7S_2I_{19}$ ⁸¹ (Figure 2d). The last coordination type occurs in metal chalcogenides with the general formula $M_3Q_7X_4$ ($M = Mo, W$; $Q = S, Se, Te$; $X = Cl, Br, I$). While many of these combinations are known, relatively few have been characterised by single-crystal X-ray diffraction due to poor crystallinity.⁸² These compounds consist of $[M_3Q_7X_2X_{4/2}]$ -chains, where halide ligands either bridge to adjacent clusters or act as terminal ligands. One chalcogenide is capping as μ_3-Q the triangle, while three μ_2-Q_2 units are coordinating the edges of the $M-M$ bonds (Figure 2e).

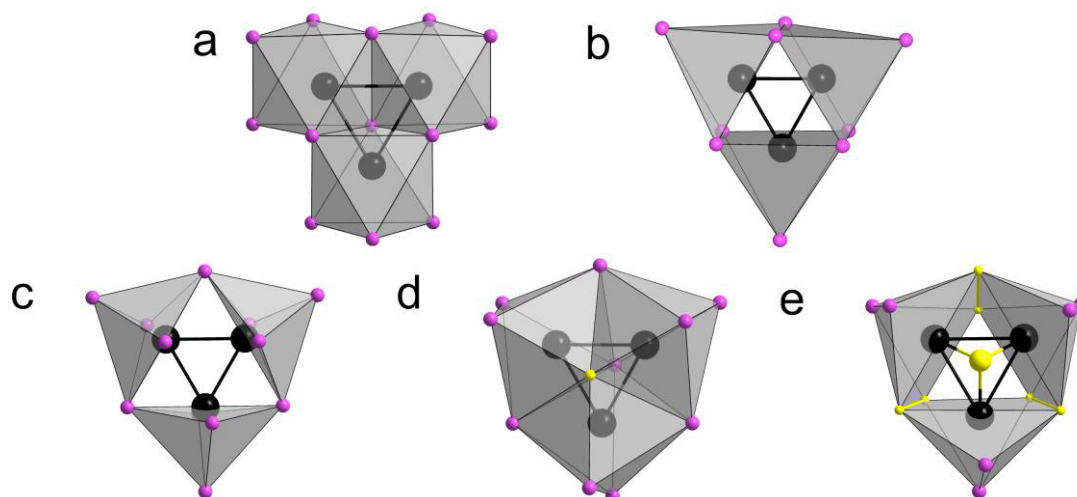


Figure 2. Anion environments of known trigonal M_3 cluster. Metal atoms are coloured in black, halides in pink and chalcogenides in yellow.

The expansion to ternary, heteroatomic metal halide clusters not only broadens the range of anionic arrangements within existing M_3 or M_6 cluster frameworks, as exemplified in compounds like Nb_3SI_7 ⁸⁰ or Nb_6SI_9 ⁸³, but also enables the formation of entirely new cluster geometries stabilised by the presence of heteroanions. The incorporation of such heteroanions has led to the discovery of numerous M_4 clusters in metal halide systems, displaying a variety of geometries, including square, rectangular, tetrahedral and butterfly-shaped motifs.⁸⁴ Moreover, the addition of an alkali halide to the reduction process can promote the formation of novel clusters compounds. An example is the ANb_4X_{11} ($A = Cs, Rb$; $X = Cl, Br$) family, resulting from the presence of an alkali halide during the synthesis.⁸⁵ M_5 cluster, though

relatively rare, are also known; typically occurring with a square pyramidal shape. Representative examples include clusters of molybdenum, technetium and tungsten.⁸⁶ For tungsten, M_5 clusters are either represented by various $[(W_5I_8^I)I_5^a]$ cluster compounds, interconnected through a diverse amount of iodide and polyiodide, or by $W_5Br_{12} \cdot SbBr_3$, which features a chain-like connectivity of W_5 clusters along with $SbBr_3$ units.^{77, 87} This compound highlights a synthetic strategy involving the reduction of a metal halide under moderate conditions using an uncommon reducing agent; in this case antimony.

For numerous non-octahedral cluster compounds, careful synthetic control is essential, as these clusters are often metastable and do not form under conventional reduction conditions. In such cases, the use of softer reducing agents is advantageous, as they facilitate the formation of thermodynamic labile intermediates in between the metal halide and the octahedral cluster compound.

Phosphorus serves as an effective example of such a softer reducing agent, as it enables the formation of Nb_4PX_{11} ($X = Cl, Br, I$)^{84d} or of the compounds $W_4(PCI)Cl_{10}$ and W_6PCl_{17} ⁸⁸ through reactions of red phosphorus with NbX_5 and WCl_6 , respectively. These reactions illustrate how subtle changes in reducing conditions can open access to previously unattainable cluster architectures.

Thus, the choice of reducing agent is a critical parameter in the synthesis of new cluster compounds, especially those beyond the conventional octahedral motif.

1.3 Reducing Agents

1.3.1 Industrial Reducing Agents

Reduction is a fundamental chemical process with widespread industrial importance. One of the most established examples is the production of elemental iron from ore in blast furnaces where carbon (in the form of coke) acts as reducing agent.⁸⁹ The production of other metals, e.g. aluminium, is often achieved through electrolytic reduction, as in the Hall-Héroult process, which involves the electrolysis of molten alumina dissolved in cryolite.⁹⁰ Electrolytic reduction is also essential in electrochemical deposition, where a thin layer of metal is deposited onto a surface to prevent corrosion, especially in the protection of less noble metals.⁹¹

Another major reducing agent, hydrogen, is widely applied in hydrogenation reactions, particularly in the petrochemical industry, food processing, and pharmaceutical synthesis.⁹² Moreover, hydrogen is an essential part in the production of ammonia through the Haber-Bosch-process.⁹³

Stronger reducing agents, such as alkali and alkaline earth metals, are more expensive but are employed when carbon or hydrogen are insufficient. For example, titanium is obtained from TiCl_4 via reduction with magnesium or calcium in the Kroll process.⁹⁴

While the reducing agents mentioned above are well-established and highly effective due to their strength, there are many cases in which milder reducing conditions are required. In such instances, weaker reducing agents become essential to access sensitive intermediates or metastable compounds, such as in the synthesis of non-octahedral metal clusters.

1.3.2 Less Commonly used Reducing Agents

In certain applications, it is essential to use reducing agents with a well-defined and moderate reduction potential to achieve selective and controlled reduction. One such example is the recycling of precious metals through cementation, where reducing agents like elemental zinc are used to reduce gold and silver ions from a cyanide leach liquor. The reduced metals can then be recovered through simple filtration.⁹⁵

Also, for cluster synthesis strong reducing agent are counterproductive, as the metal salt is reduced rapidly, frequently leading to the direct formation of the elemental metal rather than the desired cluster species. As a result, the synthesis of clusters is typically carried out by reacting a metal with elemental halide or with its corresponding metal halide (comproportionation reaction), allowing a more controlled pathway.^{63a, 65}

The synthesis of clusters in binary systems is usually limited to trigonal or octahedral geometries. However, introducing a heteroatom significantly expands the structural diversity (see also chapter 1.2). For instance, the compound $\text{Nb}_4\text{OI}_4\text{Te}_9$ features an M_4 cluster with a distorted-tetrahedral cluster core centred by oxygen.⁹⁶ Such non-octahedral clusters are typically metastable and decompose at elevated temperatures, eventually to the octahedral cluster or to the elemental metal. Therefore, to access metastable clusters, the synthesis must be performed under moderate conditions; with temperatures high enough for the reduction process, but low enough to avoid further decomposition. In this context, the use of reducing agents that are reactive at lower temperatures and possess moderate reduction potentials is a key requirement for the successful formation of complex cluster architectures.

Therefore, many less-common used reducing agents have been explored in synthetic reactions, gaining new and unusual cluster configurations. An example is the use of phosphorus as reducing agent for WX_6 (as mentioned before), which resulted in the formation of a non-octahedral W_6 cluster core in $\text{W}_6\text{PCl}_{17}$ and a PX capped, rectangular W_4 cluster in $\text{W}_4(\text{PX})\text{X}_{10}$ ($X = \text{Cl}, \text{Br}$).^{88, 97} The reduction of WBr_6 with antimony gained also novel cluster compounds. $\text{W}_4\text{Br}_{10} \cdot 2\text{SbBr}_3$ and W_4Br_{10} are both containing a tetrahedral W_4 cluster core, while the compound $\text{W}_5\text{Br}_{12} \cdot \text{SbBr}_3$ features a square-pyramidal W_5 core.^{87, 98} These compounds are formed at comparatively low temperatures (between 170 °C and 280 °C) and decompose to the thermodynamically more stable, octahedral W_6Br_{12} at around 350 °C. Further structural diversity has been achieved through the reaction of WCl_6 with antimony in the presence of NaCl , resulting in the formation of $\text{Na}_3\text{W}_3\text{Cl}_{13}$,^{76b} which contains a triangular W_3 cluster core which is also found in $\text{Sn}[\text{SnCl}][\text{W}_3\text{Cl}_{13}]$,⁹⁹ synthesised by reduction with elemental Sn .

Despite its importance, the reduction process, particularly in cluster formation, is still not fully understood. When strong reducing agents are used, the reactions proceed very rapidly, making it difficult to detect or isolate intermediate species. Additionally, the use of comproportionation reactions requires comparatively high temperatures and reaction times and lead to thermodynamic stable products. To gain deeper insight into the mechanism, softer reducing agents have been employed in an effort to trap and characterise intermediates structurally.

For this, the reactions of WCl_6 with 3d transition metals were investigated through differential thermal analysis (DTA) by A. Mos *et.al.*¹⁰⁰ A stepwise reduction pathway with a gradual incorporation of the transition metal into the WCl_6 structure was observed, continuing until no further metal could be introduced. At that point, excess transition metal was removed from the system in the form of transition metal chlorides, with $\text{MW}_6\text{Cl}_{14}$ as the final reduction product.

Another intriguing reduction pathway involves metathesis reactions with anions that possess intrinsic reducing nature toward d-block elements. Examples of such anions include N^{3-} , $(\text{N}_3)^-$, $(\text{C}_2)^{2-}$, $(\text{BN}_2)^{3-}$ and $(\text{CN}_2)^{2-}$, which decompose during the reaction within a reductive process.¹⁰¹

1.3.3 Non-Conventional Reduction Agents

Solid-state metathesis reactions are well-established pathways for synthesising carbides, nitrides, borides and related compounds. These reactions involve a metal (M) halide (X) reacting with an alkali or alkaline earth (A) compound (L) (see reaction (1)).¹⁰²



The formation of the corresponding alkali or alkaline earth halide is highly exothermic and the released energy accelerates the reaction towards the products. This type of reaction can also be performed using alkali hydrides, acetylides, nitridoborates and carbodiimides.¹⁰¹ For many d-block elements, the reaction with these alkali metal salts rely on high temperatures and are very exothermic. Consequently, instead of a classical metathesis reaction, the anion can decompose and can act as a non-conventional reducing agent, leading to the reduction of the corresponding metal halide, while the reducing agent decomposes to a neutral species (e.g. $(\text{C}_2)^{2-}$ to elemental carbon).

For carbodiimides ($(\text{CN}_2)^{2-}$), some d-block metals do not undergo reduction under moderate conditions. Known examples include carbodiimide complexes of certain 4d transition metals, as well as rare earth metals, zirconium, silver, and cadmium.¹⁰³ However, if the reductive nature predominates, the metal gets reduced, and the carbodiimide decomposes and the formation of a carbon nitride species, C_3N_4 , is formed.¹⁰¹

The reductive nature of these compounds is not yet fully understood, particularly in the context of their potential as reducing agents for cluster formation. Therefore, it is part of this work to investigate the advantage of such reduction processes to synthesis new cluster compounds.

2. Objective

Metal cluster compounds, whose structures and properties lie between those of metallic and salt-like materials, exhibit a range of unique and intriguing characteristics. Among the most prominent and extensively studied cluster motifs are the trigonal M_3 cluster, as found for example in M_3X_8 compounds, and the octahedral M_6 cluster, e.g. in M_6X_{12} systems.

M_6 clusters are thermodynamically highly stable and are typically synthesised via metallothermic reduction of metal halides in high oxidation states. In contrast, the formation of thermodynamically metastable cluster compounds generally requires lower reaction temperatures and the use of suitable reducing agents that are effective under such mild conditions.

Alkali carbodiimides have been shown to be effective starting materials in metathesis reactions with metal halides, leading to the formation of metal carbodiimides. This approach is particularly successful for rare-earth and 3d-transition-metal halides. When analogous reactions are performed with more noble metal halides, such as those of nickel or gold, reduction of the metal cation by the carbodiimide occurs, resulting in the formation of the elemental metal.

To explore this reductive nature in less noble metal systems, the reaction between niobium iodide and lithium carbodiimide was investigated. Following the initial discovery of an oxygen-stabilised niobium cluster formed in this reaction, the focus of this work was directed toward the reduction of niobium iodide in the presence of an oxygen source, with the aim of accessing novel oxygen-containing niobium cluster compounds.

3. Summary of the Main Results

The reaction of NbI_4 with $\text{Li}_2(\text{CN}_2)$ and Li_2O lead to the formation of multiple, previously unreported cluster compounds, all synthesised from one kind of reaction with small changes in the ratio of the educts. The crucial factor for the production of a defined compound is the choice of temperature program; in particular cooling rates, reaction durations and temperatures (Figure 3 gives an overview over the successful reaction pathways). Each obtained compound will be described one by one in the following chapters.

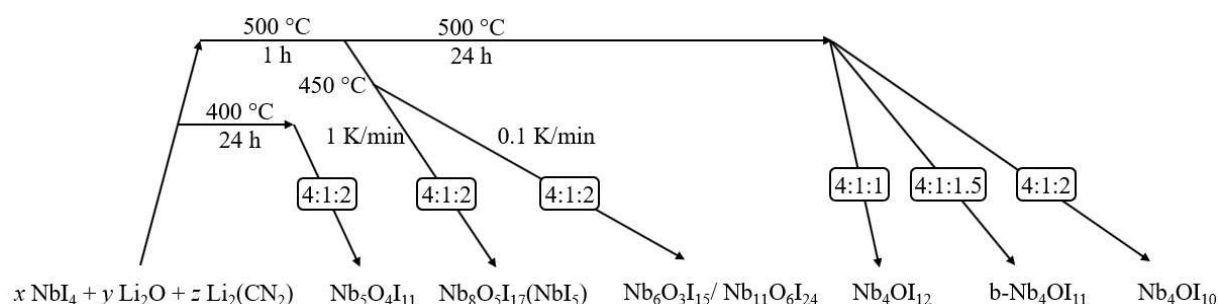


Figure 3. Overview of critical reaction conditions for the synthesised compounds, found on the wall of the ampoule.

3.1 The Rectangular Niobium Oxyiodide Cluster $\text{Nb}_4\text{OI}_{10}$ – A Narrow Band-Gap Semiconductor (Publication 1)¹⁰⁴

The synthesis of new, thermally labile cluster compounds requires moderate conditions and more complex reduction pathways. Formerly applied non-conventional reduction agents gained such compounds with the use of e.g. phosphorus or transition metals.^{88, 100} In this work the use of another soft reduction agent, lithium carbodiimide, resulted in new cluster compounds.

The first one is $\text{Nb}_4\text{OI}_{10}$, gained from the reaction of NbI_4 with $\text{Li}_2(\text{CN}_2)$ and Li_2O at 500 °C for 36 h and appear as black, plate-like crystals, which were used to perform single-crystal X-ray diffraction (XRD) and to solve the structure (Table S 1). The niobium atoms in this compound can be assumed to have the oxidation state +III, resulting in eight cluster electrons for metal-metal bonds. These metal-metal bonds result in a rectangular cluster core with an oxygen atom in the centre. The cluster core is surrounded by eight edge-bridging (i = inner) iodides and four terminal (a = outer) iodides, which are connecting to adjacent clusters (Figure 4). The resulting $[\text{NbOI}_8\text{I}_{4/2}^{\text{a-a}}]$ cluster can be derived from the octahedral Nb_6I_{11} by cutting off two (Nb–I) edges and centring the cluster with an oxygen atom. The cluster is connected to four adjacent clusters, forming a layered structure with a van der Waals gap in between (Figure 5).

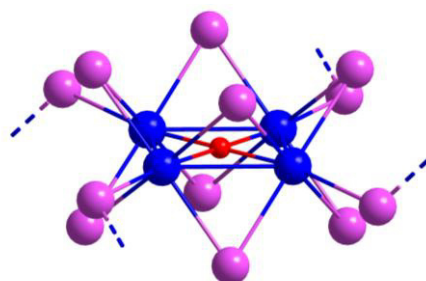


Figure 4. $[\text{Nb}_4\text{OI}_8\text{I}_{4/2}]$ fragment in the structure of $\text{Nb}_4\text{OI}_{10}$.

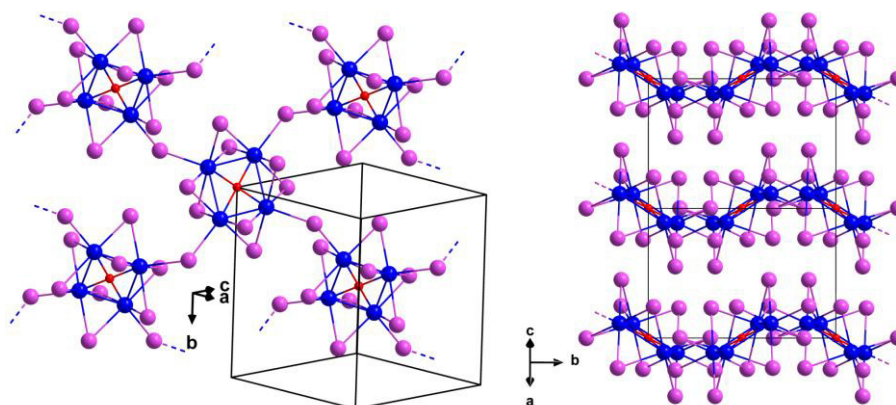


Figure 5. Layered connectivity in $\text{Nb}_4\text{OI}_{10}$ (left) and the stacking of the layers with a van der Waals gap in between (right).

In a reduction with carbodiimide, the formation of a N-centred cluster could be plausible. In order to figure out, if either nitrogen or oxygen is present, electron microprobe analysis was used. This results in a signal at the energy of oxygen (0.525 keV), but not in the range of nitrogen (0.392 keV).

Such a $[\text{Nb}_4\text{O}]$ cluster type has been reported before for some compounds, either with squared shape like in $\text{K}_4[(\text{Ti}_4\text{O})\text{I}_{12}]^{105}$, or rectangular ones like the $[\text{Nb}_4\text{OI}_8]^{2+}$ cation in $[\text{Nb}_4\text{OI}_8][\text{Mo}_6\text{I}_{14}]^{106}$.

Crystals of $\text{Nb}_4\text{OI}_{10}$ were measured in terms of their electric conductivity. Temperature dependent measurements reveal decreasing current with decreasing temperature, which is characteristic for semiconductors. Fitting the data between 300 K and 100 K revealed an activation barrier to transport of 0.6 eV. Additionally, a photocurrent was observed for illumination at 779 nm.

The calculated band structure (Figure 6) through density functional theory (DFT) calculations shows eight energy bands arise from two formula units of $\text{Nb}_4\text{OI}_{10}$ above the p-block orbitals. These bands near the Fermi energy are predominantly coming from Nb d orbitals and depict the ionic character of the Nb–I bonds. The obtained direct band gap of about 0.3 eV fits to a semiconducting behaviour. For understanding the rectangular shape, DFT calculations with a rectangular and a squared Nb_4 cluster were performed. The reduction in symmetry is compensated by a lowering of the energy of occupied orbitals and the accompanied energetic increase of unoccupied orbitals, which correspond to a pseudo-Jahn-Teller effect.

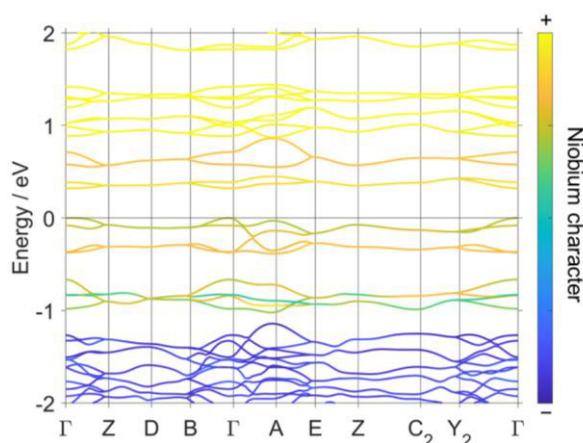


Figure 6. The DFT-calculated electronic band structure of $\text{Nb}_4\text{OI}_{10}$ with bands coloured by their niobium character. Special points in and paths through the Brillouin zone were chosen following the literature.¹⁰⁷

The band gap was also determined through a DRIFTS (diffuse reflectance infrared Fourier transformation spectroscopy) measurement, resulting in an optical band gap of 0.479 eV. This is slightly higher than the DFT calculations and lower than the conductivity measurements.

3.2 The Family of Tetranuclear Nb₄OI_{12-x} Clusters ($x = 0, 1, 2$): From the Molecular Nb₄OI₁₂ Cluster to Extended Chains and Layers (Publication 2)¹⁰⁸

Based on the rectangular [Nb₄O] in Nb₄OI₁₀, described in the previous section, a whole family of related structures was found by slight variations of the synthetic conditions. This study describes several [Nb₄O] cluster networks that were structurally characterised by single-crystal XRD (Table S 1) and vary in their connectivity, while maintain a similar iodide ligand environment.

Again, the reduction through carbodiimide, (CN₂)²⁻, plays a central role in the synthetic process. At elevated temperatures, carbodiimides tend to decompose to form C₃N₄ and thereby they can act as reducing agents.¹⁰¹

The parent compound, Nb₄OI₁₂, appears as a molecular structure with a van der Waals gap between the adjacent clusters. The structure can be described as [Nb₄OI₈^I₄^a] where the inner iodides are μ_2 -capping and the outer iodides are terminal. The cluster core is nearly rectangular and has six cluster electrons available for metal–metal bonds. The short Nb–Nb bond is in the range of 2.793(3)–2.807(3) Å, while the long bond is in the region of 3.029(7)–3.051(3) Å, considering more electron density in the short bonds. The isolated molecules are arranged in stacked layers with an ABCB sequence when looking along the *b* axis, but not with a closest packing behaviour (Figure 7).

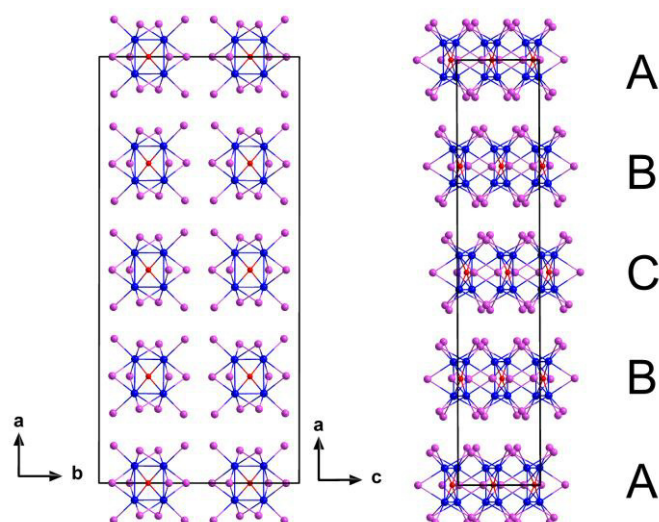


Figure 7. Section of the crystal structure of Nb₄OI₁₂ with the corresponding stacking sequence.

With one iodide atom less, the structure of Nb₄OI₁₁ exhibits a string-like connectivity and appears in two modifications, denoted as “a” and “b”. a-Nb₄OI₁₁ is represented by rectangular

[Nb₄O] cluster cores with a *trans* connection to two adjacent clusters. The crystal structure of the a-modification shows a superposition of two alternating layers of strings, which creates a layered structure of [Nb₄O] and [Nb₆O] cores (Figure 8, left). However, Nb2 is just occupied by 50 % and therefore two (Nb₄OI₈)I₂I_{2/2} chains appear, running in [011] and [01-1] direction (Figure 8, middle and right).

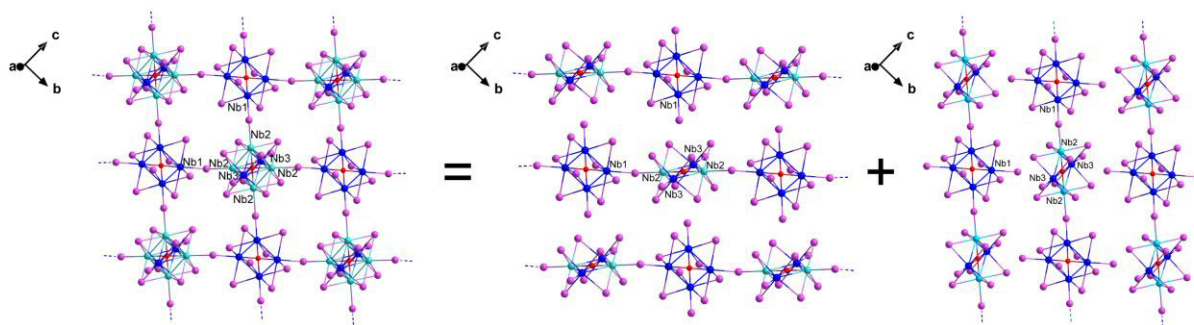


Figure 8. Cluster connectivity with all half occupied Nb2 positions (left) and the separated chains running in two different directions (right).

The second modification, b-Nb₄OI₁₁, features a string-like connectivity as well. In this case, the clusters are connected through alternating *cis* and *trans* iodide bridging (Figure 9, left). While the *trans* connected cluster is nearly the same as in a-Nb₄OI₁₁, the *cis* connectivity induces a distortion from the rectangular to a trapezoidal shape. The strings are running in [001] direction with a hexagonal arrangement (Figure 9, right).

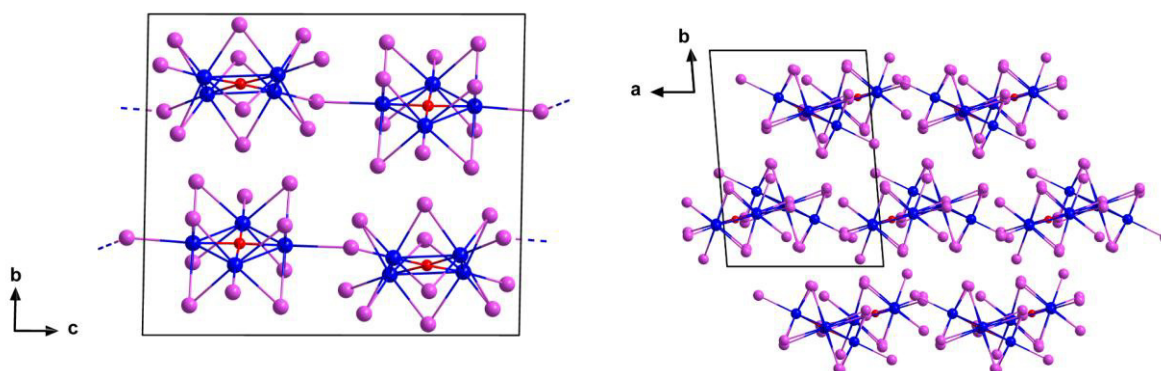


Figure 9. Alternating *cis* and *trans* connectivity (left) and the hexagonal arrangement of the strings (right).

Because of the string-like connectivity, Nb₄OI₁₁ can be expected as one-dimensional conductor. Hence the electrical conductivity was investigated. The temperature-dependent conductivity measurement indicates an Arrhenius-type, temperature-activated transport, as expected for semiconducting materials (Figure 10). The resulting activation energy was determined to be

$E_A = 0.2$ eV, which would lead, in case of an intrinsic position of the Fermi level, to a band gap around 0.4 eV. With an excitation of a 779 nm laser an initial photocurrent could be measured.

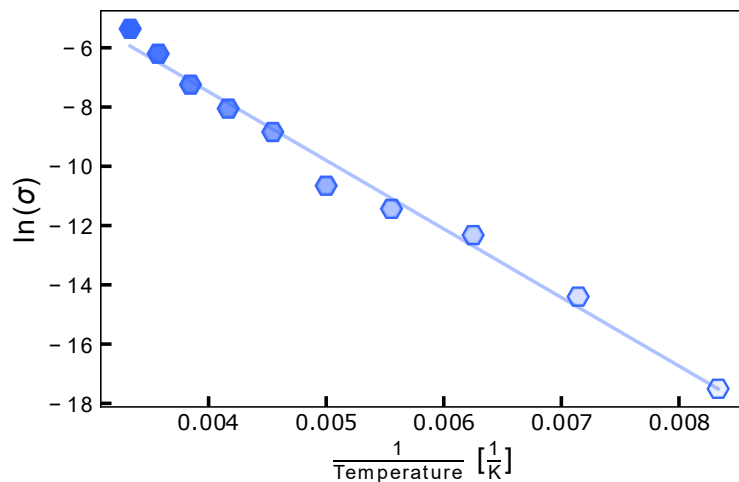


Figure 10. Arrhenius plot of the electrical conductivity measurements of b-Nb₄OI₁₁, with 20 K temperature steps between 120–300 K with a linear Arrhenius fit.

With the compound Nb₄OI₁₀, the family of Nb₄OI_{12-x} compounds is represented through four structures. Besides the connectivity, the main difference of the compounds includes the length of the short Nb–Nb bond (2.793(3)–2.807(3) Å for Nb₄OI₁₂ and 2.6232(2) Å for Nb₄OI₁₀) and the number of cluster electrons, available for metal–metal bonds (six for Nb₄OI₁₂, seven for a- and b-Nb₄OI₁₁, and eight for Nb₄OI₁₀).

3.3 Structural Modifications of $M_5O_4I_{11}$ ($M = \text{Nb, Ta}$) Cluster Networks from Heterogeneous Solid-State Reactions (Publication 3)¹⁰⁹

The use of $\text{Li}_2(\text{CN}_2)$ as reduction agent was not only investigated for niobium iodide, but for tantalum pentafluoride, TaI_5 . A similar reactivity in the presence of Li_2O could be observed, including the formation of LiI , amorphous C_3N_4 and N_2 , as well as a dark violet gas phase at temperatures above 300 °C. However, the reaction products differ from those gained for niobium iodide.

Some side phases appear from the reaction which could not be found for niobium. Beside the known tantalum oxyiodides TaOI_2 and TaO_2I , two new tantalum oxyiodides could be isolated with tantalum in the oxidation state +V. $\text{LiTa}_3\text{O}_2\text{I}_{12}$ features kinked strands of $[\text{Ta}_3\text{O}_2\text{I}_{10}\text{I}_{4/2}]$ -units separated by Li^+ . $\text{Ta}_2\text{O}_3\text{I}_4$ forms a layered structure with tantalum coordinated by three iodine and three oxygen atoms in an octahedral manner, with edge-sharing iodides and corner-sharing oxygens.

The cluster formation occurs in direct contact with TaO_2I side phase, suggesting it to may serve as a precursor for the cluster formation. The three observed cluster networks consist of a distorted square-pyramidal $[M_5O_4]$ cluster core with four μ_3 -oxygen atoms bridging the edges between the metal.

In the orthorhombic $o\text{-}M_5O_4I_{11}$ ($M = \text{Nb, Ta}$), each outer metal atom exhibits a distorted octahedral coordination by oxygen and iodine atoms and additional metal–metal bonding to the central metal atom (Figure 11, left). The cluster connectivity can be described as $[(\text{Ta}_5\text{O}_4)\text{I}_2^{\text{i}}\text{I}_4^{\text{a}}\text{I}_{10/2}^{\text{a-a}}]$ where two iodides are capping the pyramids apex edges (i), four iodides are terminal (a) with one above and three below the pyramid base and ten iodides are shared between the clusters at the corners of the base (a-a).

The clusters are connected to four adjacent clusters, forming extended, corrugated layers in the ac -plane (Figure 11, right). Along the a -axis, the Ta(2) atoms are linked by two bridging iodides across a mirror plane, while along the c -axis, Ta(3) and Ta(4) are connected via three iodides along a screw axis, producing a tilted layer structure, separated by a van der Waals gap.

A comparison with the niobium analogue shows similar metal–metal bond lengths due to the comparable ionic radii of Nb and Ta. However, the $\angle M(3)\text{--}M(1)\text{--}M(4)$ angle differs by about 6°, and the inter-cluster $M(3)\text{--}M'(4)$ distance is 11 pm shorter in $\text{Nb}_5\text{O}_4\text{I}_{11}$, leading to more pronounced corrugation in its layers.

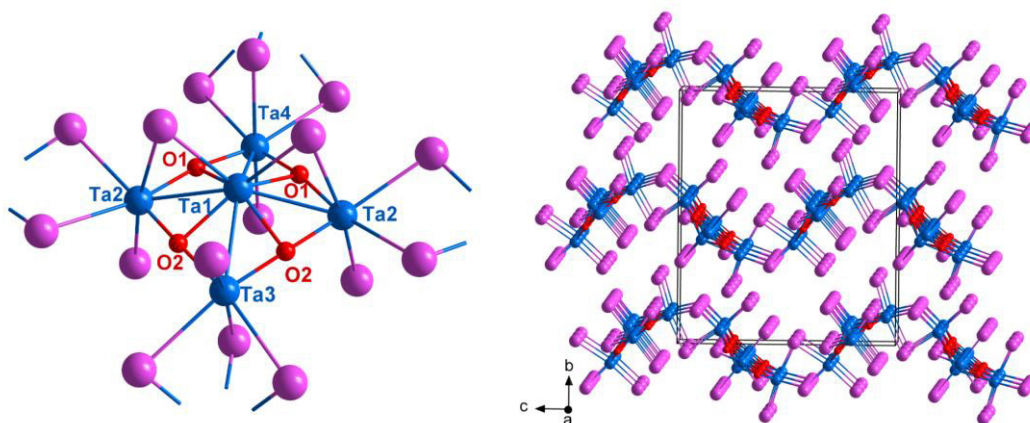


Figure 11. Building block of isotypic $M_5O_4I_{11}$ structures ($M = Nb, Ta$), corresponding to o - $Ta_5O_4I_{11}$ (left), and the resulting waved layer structure (right).

The second modification, the monoclinic m - $Ta_5O_4I_{11}$, contains a similar $[Ta_5O_4]$ cluster core, however more symmetric due to a different iodide environment (Figure 12, left). Therefore, the ligand coordination can be described as $[(Ta_4O_5)I_2^i I_5^a I_{8/2}^{a-a}]$, where the two capping, inner μ_2 -iodides (i) are located under the base of the pyramid, the five terminal iodides (a) are each bonded to one of the five Ta atoms on top of the pyramid, and eight outer iodides (a-a) are shared between the clusters.

The resulting layered structure shows a corrugation as well, as the surrounding clusters are each pointing to the opposite direction compared to the central cluster. This connectivity results in sinusoidal layers, separated by a van der Waals gap (Figure 12, right).

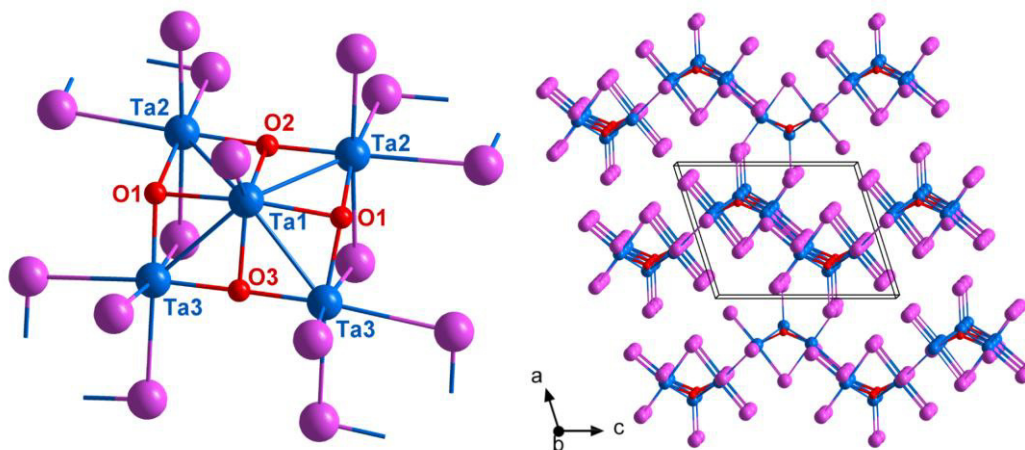


Figure 12. Building block of the m - $Ta_5O_4I_{11}$ structure (left), and the resulting waved layer structure (right).

The third modification, $Ta_5O_4I_{11}(TaI_5)$, is closely related to m - $Ta_5O_4I_{11}$, while incorporating $[TaI_5]$ units. Although the cluster connectivity pattern $[(Ta_4O_5)I_2^i I_5^a I_{8/2}^{a-a}]$ remains the same, the orientation of the surrounding clusters changes. While in m - $Ta_5O_4I_{11}$ all four adjacent clusters are inverted, in $Ta_5O_4I_{11}(TaI_5)$ there are two adjacent clusters pointing in the same direction and

two in the other direction. This results in a more pronounced corrugation of the layers, forming voids big enough to incorporate $[\text{TaI}_5]$ molecules (Figure 13).

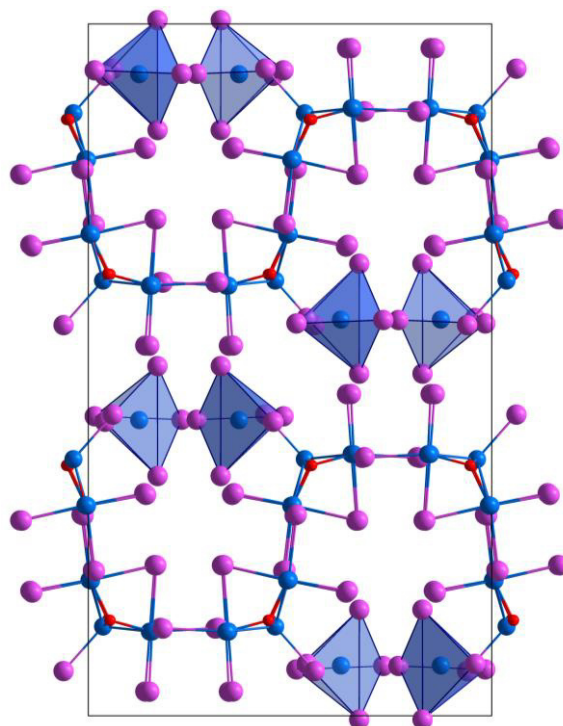


Figure 13. Section of the crystal structure of $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$ with the incorporated $[\text{TaI}_5]$ molecules shown as polyhedral.

The $[\text{TaI}_5]$ molecules adopt a trigonal bipyramid geometry, as it is well known for TaCl_5 and TaBr_5 in the gas phase.¹¹⁰ Such accommodation could be also observed for other materials. One example is the incorporation of $[\text{NbI}_5]$ molecules within $\text{Nb}_7\text{S}_2\text{I}_{19} \triangleq (\text{Nb}_3\text{SI}_7)_2(\text{NbI}_5)$.⁸¹ In this structure, $[\text{NbI}_5]$ units are located in hexagonal channels formed within Nb_3SI_7 layers, where the voids are generated by six surrounding $[\text{Nb}_3\text{SI}_4\text{I}_{6/2}]$ units.

All $M_5\text{O}_4\text{I}_{11}$ -based compounds contain a pentanuclear metal cluster core, but differ in their halide coordination and the presence of $[\text{TaI}_5]$ molecules in the structure. No interconversion between the modifications was observed; instead, at elevated temperatures (above 650 °C), the clusters tend to decompose under the formation of TaOI_2 .

The structural modifications were further examined using scanning electron microscopy (SEM). The orthorhombic *o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ displays well-defined, individual layers (Figure 14a-c), which suggests weaker interlayer interaction. In contrast, the monoclinic modification exhibits more block-like crystal morphologies (Figure 14d-f), indicating stronger interactions of the layers. In this process, the elemental composition was investigated via energy dispersive X-ray (EDX) spectroscopy, yielding a Ta:O:I ratio of 5:4.3(5):10.9(3). These results were confirmed

by total reflection X-ray fluorescence (TXRF) measurements, resulting in a Ta:I ratio of 5:11.3(2) and therefore verifying the composition from single-crystal XRD.

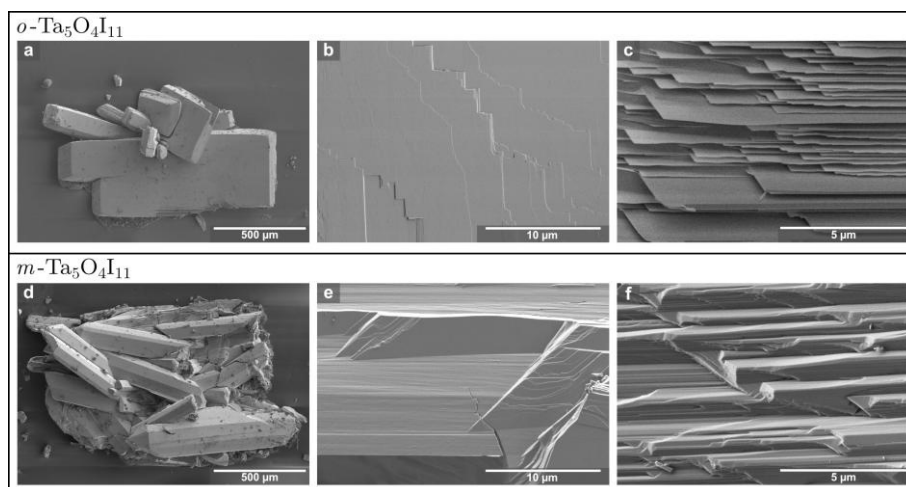


Figure 14. Scanning electron micrographs of o -Ta₅O₄I₁₁ crystals (a-c) and m -Ta₅O₄I₁₁ crystals (d-f), showing a layered morphology.

Regarding the electron distribution, the $[M_5O_4]$ cluster core contains six electrons available for metal–metal interactions. From a simple perspective, the oxidation states of tantalum could be suggested as one Ta³⁺ atom in the centre of the cluster and four Ta⁴⁺ atoms at the corners of the cluster. To verify this assignment, XPS was performed on o -Ta₅O₄I₁₁. The Ta 4f spectrum revealed two distinct doublets corresponding to the Ta 4f_{7/2} and Ta 4f_{5/2} signals of Ta⁴⁺ and Ta³⁺ species. The Ta⁴⁺:Ta³⁺ ratio of 4.14:1 aligns well with the proposed oxidation state distribution with a central Ta³⁺ atom and Ta⁴⁺ atoms at the corners.

Further insight into the electronic structure was obtained by determining the optical band gap using DRIFTS. For o -Ta₅O₄I₁₁, a direct band gap of 0.241 eV and an indirect band gap of 0.226 eV were determined, indicating semiconducting behaviour.

This semiconducting nature is further supported by temperature-dependent two-point current-voltage measurements. The resulting Arrhenius plots show thermally activated conductivity. From the slope of these plots, activation energies of $E_A = 0.10$ eV (o -Ta₅O₄I₁₁) and $E_A = 0.40$ eV (m -Ta₅O₄I₁₁) were calculated. Assuming intrinsic semiconducting behaviour, these activation energies correspond to estimated band gaps of approximately 0.2 eV for o -Ta₅O₄I₁₁ and 0.8 eV for m -Ta₅O₄I₁₁, consistent with the DRIFTS results.

3.4 Niobium Oxyiodide Cluster Compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with Expanding Cluster Architectures and Multicenter Nb–Nb Bonding (Publication 4)¹¹¹

The previously presented cluster compounds were found deposited on the wall in the central region of the ampoule, as the reactions took place in a furnace with temperature gradient. This observation supports the hypothesis that these species form via a gaseous intermediate. In addition to the wall deposit, a residual powder was also found at the hotter region at the bottom of the ampoule. Besides the metathesis salt LiI and amorphous C_3N_4 , the powder contained other compounds featuring cluster cores.

To gain deeper insight into the formation process, a series of reactions was conducted at various temperatures and reaction durations. A reaction carried out at 300 °C yielded an unidentified crystalline phase alongside LiI , NbOI_2 , and amorphous material. Upon heating to 400 °C, the unknown phase decomposed, resulting in the formation of two cluster compounds: the aforementioned $\text{Nb}_5\text{O}_4\text{I}_{11}$ and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, which will be described later on. Further elevation of the temperature to 500 °C, with a duration of 1 hour, led to the formation of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, which is reported in this section and shows structural similarities to $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. Prolonged heating at 500 °C for 24 hours resulted in the formation of $\text{Nb}_4\text{OI}_{10}$, which was discussed in section 3.1.

The participation of a reactive gaseous phase was further confirmed through quenching experiments. In these trials, the reaction mixture was rapidly cooled from 400 °C to room temperature by submersion in water. As a result, black droplets formed on the ampoule walls, which subsequently transformed into dark red, filamentous crystallites at room temperature. These crystallites were found to decompose after a short period.

The two newly identified compounds, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$ (named $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ from hereon), were structurally characterised by single-crystal XRD (Table S 1) and share a common structural motif, which is based on a $[\text{Nb}_7\text{O}_5]$ cluster core. This oxygen-stabilised niobium cluster consists of a central niobium atom surrounded by six additional niobium atoms arranged in a trigonal prismatic geometry. Notably, this configuration contrasts to other reported M_7 cluster cores, which typically exhibit alternative geometries. For instance, the $[\text{Os}_6\text{Au}]$ in $[\text{N}(\text{PPh}_3)_2][\text{Os}_6\text{Au}(\text{CO})_{20}\text{H}_2]$ is described as two butterfly-shaped units sharing a wing tip.¹¹² Other examples include an asymmetric $[\text{Fe}_6\text{Mo}]$ cluster core in

$[\text{Ph}_4\text{As}]_2[\text{MoFe}_6\text{S}_6(\text{CO})_{16}]^{113}$ and octahedral M_6 cluster containing an interstitial transition metal.¹¹⁴

In contrast, the current $[\text{Nb}_7\text{O}_5]$ can be described as an extended form of the $[\text{M}_5\text{O}_4]$ cluster core known from $\text{M}_5\text{O}_4\text{I}_{11}$ ¹⁰⁹, wherein two more Nb atoms (Nb3) and one oxygen atom (O3) are added at the top of the $[\text{Nb}_5\text{O}_4]$ base (Figure 15, left). The cluster core features six short Nb–Nb contacts between Nb1–Nb2 and Nb2–Nb3 (2.8050(4) Å and 2.7883(7) Å) and four long Nb–Nb distances for Nb1–Nb3 (3.0667(6) Å).

In terms of iodine coordination, the cluster can be described as $(\text{Nb}_7\text{O}_5\text{I}_4^{\text{i}})\text{I}_4^{\text{a-a}}\text{I}_{12/2}^{\text{a-a}}$, comprising four edge-capping (i), four terminal (a) and twelve bridging iodide ligands (a-a), which connect the six adjacent clusters to form a three-dimensional network (Figure 15, right).

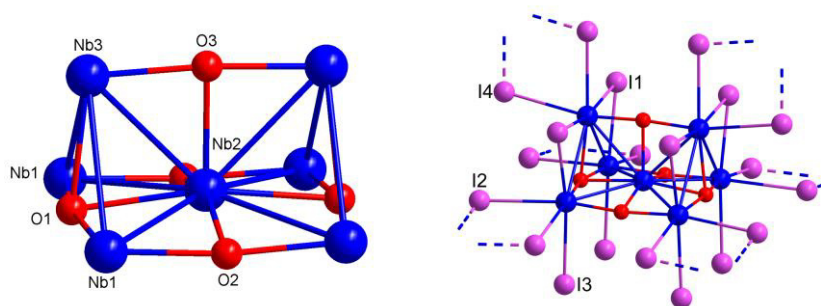


Figure 15. Structure of the $[\text{Nb}_7\text{O}_5]$ cluster core inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ (left) and the iodide environment (right).

Additionally, the compound is further stabilised by three lithium ions and an additional iodide anion. The lithium ions are coordinated by this additional I[−] and four iodide ligands in a square-pyramidal manner.

The second compound, $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$, features a $[\text{Nb}_8\text{O}_5]$ cluster core that is closely related to $[\text{Nb}_7\text{O}_5]$. This core arises from the addition of a single Nb atom at one edge of the $[\text{Nb}_5\text{O}_4]$ base (Figure 16, top left). The Nb–Nb distances to the central Nb2 atom (2.7911(3)–2.8600(7) Å) are comparable to those observed in the $[\text{Nb}_7\text{O}_5]$ core. However, the Nb–Nb distances between the outer Nb atoms are notably longer (2.9981(6)–3.1812(7) Å). The bond lengths involving the additional Nb5 (3.1418(7) Å) fall within a similar range as those between the outer Nb atoms.

The iodide environment also undergoes a notable change. It can be described as $(\text{Nb}_8\text{O}_5\text{I}_8^{\text{i}})\text{I}_5^{\text{a}}\text{I}_{8/2}^{\text{a-a}}$, comprising eight edge-capping, five terminal and eight bridging iodide ligands (Figure 16, bottom left). Due to the additional niobium atom, the number of connections to adjacent clusters is reduced from six (in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$) to four, resulting in the formation of a two-dimensional, layered structure (Figure 16, right).

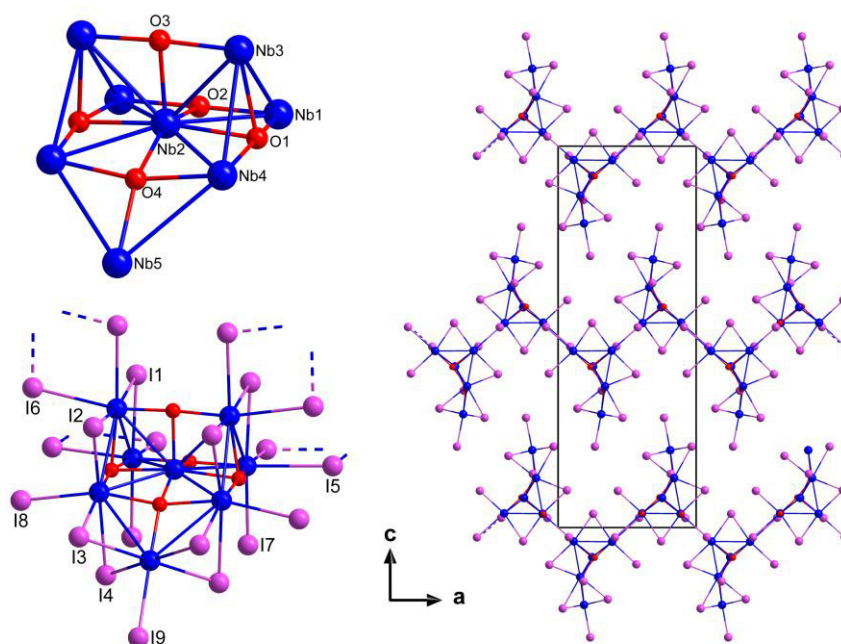


Figure 16. $[\text{Nb}_8\text{O}_5]$ cluster core (top left) and iodide environment (bottom left) and a section of the crystal structure, showing the layered behaviour with NbI_5 molecules omitted for clarity (right).

Between the layers, channels are present that accommodated NbI_5 units. These units exhibit a degree of disorder, due to the incorporation of excess iodine. The intercalation of discrete molecular species is uncommon, but several examples are well-documented in the literature. A prominent case is the incorporation of NbI_5 in $\text{Nb}_7\text{S}_2\text{I}_{19}$, which can be formulated as $(\text{Nb}_3\text{SI}_7)_2(\text{NbI}_5)$.⁸¹ In this compound, channels are formed by six $[\text{Nb}_3\text{S}]$ units, within which molecular NbI_5 units are accommodated. Another related example is the previously discussed $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$, where TaI_5 molecules are intercalated between the layers.¹⁰⁹

Regarding $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, its electronic structure was investigated through DFT calculation, focusing on the electronic band structure and the electron localisation function (ELF). The band structure analysis reveals seven bands that primarily originate from niobium–niobium bonding interactions (Figure 17, top). Several of these bands cross the Fermi level at multiple points, indicating delocalised electronic states. In addition to a significant contribution from niobium orbitals near the Fermi level, a notable contribution from oxygen orbitals is observed, suggesting some covalency in Nb–O bonds.

This interpretation is further supported by ELF calculations, which show electron density originating from the oxygen atoms (Figure 17, bottom). Moreover, electron density is also detected in the region between Nb1, Nb2 and Nb3, indicating the presence of three-centred bonding. The combined effects of oxygen admixture and three-centred bonding appear to play a critical role in stabilising the cluster core.

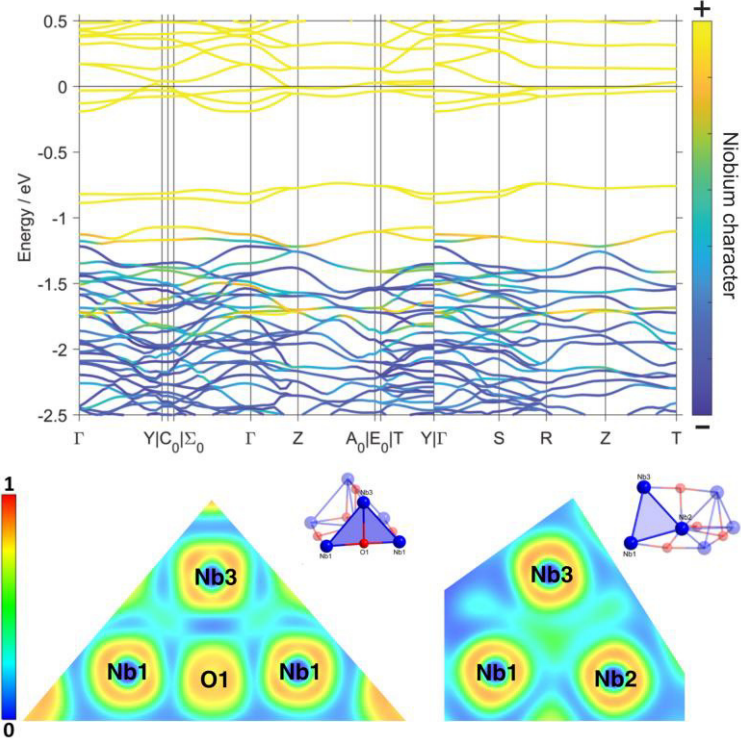


Figure 17. DFT-calculated electronic band structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ with bands coloured by their niobium character (top). Special points in and paths through the Brillouin zone were chosen following the literature.¹⁰⁷ Electron localisation functions of the $[\text{Nb}_7\text{O}_5]$ cluster core in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ (bottom).

3.5 Zero Indirect Band Gap and Flat Bands in a Niobium Oxyiodide Cluster Material (Publication 5)¹¹⁵

All of the cluster cores described so far come from the same kind of reaction, only varying the temperature program. Most of these compounds were found in the middle of the ampoule at the wall, suggesting a formation from a reactive gaseous phase. The diversification of cluster formation illustrates the potential of finding even more cluster cores from this reaction by other temperature programs.

Two compounds could be isolated by adjusting the cooling rate of the synthesis of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. $\text{Nb}_6\text{O}_3\text{I}_{15}$ and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ were determined by single-crystal XRD (Table S 1) and show unique cluster cores, not reported so far.

$\text{Nb}_6\text{O}_3\text{I}_{15}$ exhibit two slightly different oxygen-capped butterfly clusters, elongated by two opposing $[\text{NbO}]$ units (Figure 18) to yield $[\text{Nb}_4\text{O}(\text{NbO})_2]$ clusters. Regarding the butterfly fragment, the Nb–Nb distances of the edges (2.8850(7)–2.9184(7) Å) are slightly shorter than the Nb–Nb backbone (Nb2–Nb5 and Nb8–Nb8' with 2.9552(7) and 2.968(1) Å, respectively). This is contrary to the cluster with the pnictide-capped $[\text{Nb}_4\text{Pn}]$ core found in $\text{Nb}_4\text{PnX}_{11}$ ($\text{Pn} = \text{N}, \text{P}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), where the Nb–Nb backbone is shorter than the Nb–Nb connections at the edges. However, the comparison of the cluster cores is limited due to a variation of the connectivity pattern and the different amount of cluster electrons (nine for $\text{Nb}_6\text{O}_3\text{I}_{15}$ and six for $\text{Nb}_4\text{PnX}_{11}$).

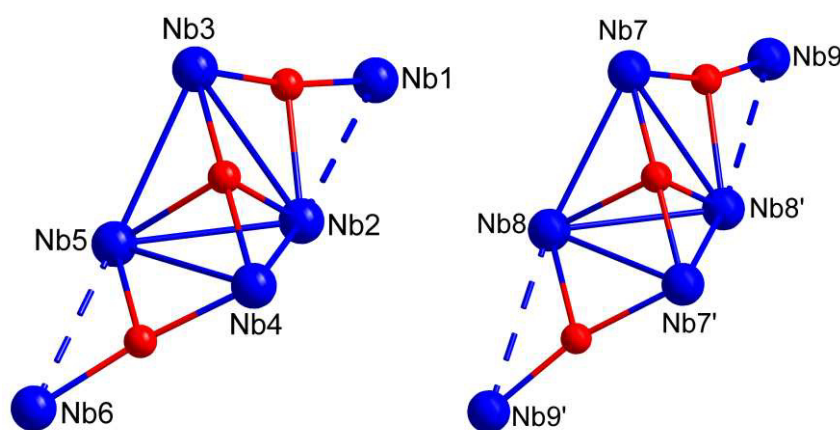


Figure 18. Two crystallographically distinct $[\text{Nb}_4\text{O}]$ clusters extended by two $[\text{NbO}]$ units in the structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$.

In $\text{Nb}_6\text{O}_3\text{I}_{15}$, each cluster is connected to four neighbouring clusters through two iodide bridges (Figure 19, left). Through a 180° rotation of the adjacent clusters, the compound creates a three-dimensional framework, with the $[\text{NbO}]$ elongation aligning in c -direction (Figure 19, right).

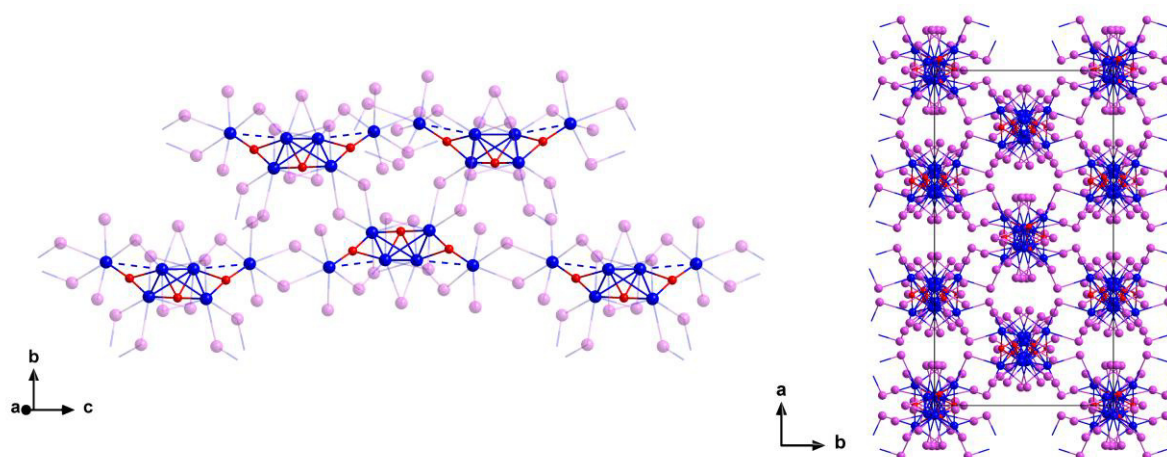


Figure 19. Connectivity inside $\text{Nb}_6\text{O}_3\text{I}_{15}$ with μ_2 -iodide bridges (left) and section of the crystal structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$, looking along the c -axis (right).

The cluster core of the second compound, $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, is based on a $[\text{Nb}_{10}\text{O}_4]$ core with two independent butterfly $[\text{Nb}_4\text{O}]$ fragments of the same type as found in $\text{Nb}_6\text{O}_3\text{I}_{15}$. A comparison of the cluster cores is shown in Figure 20, highlighting the related niobium oxide constitution. The two $[\text{Nb}_4\text{O}]$ fragments are interconnected by a pair of niobium atoms as (ONb_2O) , resulting in a $[(\text{Nb}_4\text{O})(\text{ONb}_2\text{O})(\text{Nb}_4\text{O})]$ or $[(\text{Nb}_4\text{O})_2(\text{Nb}_2\text{O}_2)]$ core.

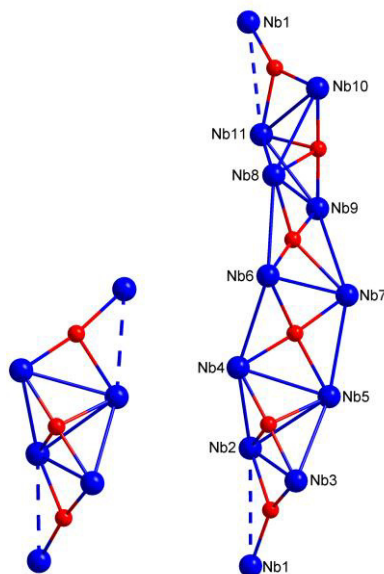


Figure 20. Similarities of the cluster cores in $\text{Nb}_6\text{O}_3\text{I}_{15}$ (left) and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ (right) with labelled niobium atoms.

In $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, the $[\text{Nb}_{10}\text{O}_4]$ cluster core is interconnected with two adjacent clusters through an additional niobium atom (Nb1) (Figure 21). The Nb–Nb distances to this additional niobium atom are quite long with 3.4230(9) Å and 3.5110(9) Å.

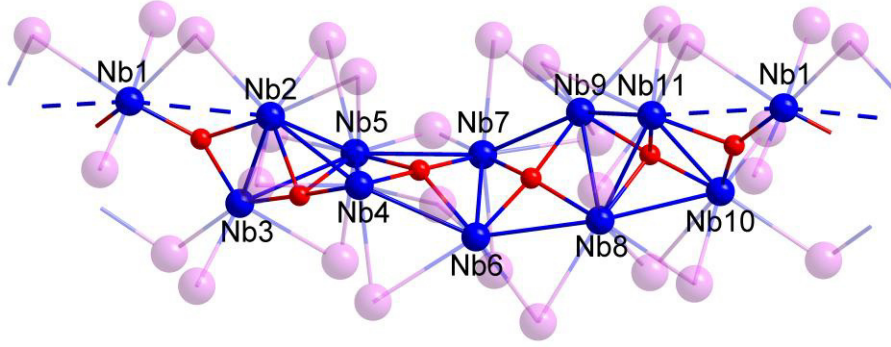


Figure 21. String-like connectivity of the clusters in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$.

The structure consists of cluster-strings running parallel in a hexagonal manner, directing along the b -axis. With the one-dimensionality, we were interested in the electronic properties of this compound.

The electrical conductivity at 300 K shows a value of $\sigma \approx 0.25 \frac{\text{S}}{\text{m}}$. The temperature dependent conductivity measurements between 60 K and 300 K result in an Arrhenius like behavior, typical for a semiconductor. The linear fit in the Arrhenius plot, depicted in Figure 22, indicate activation energies of 0.06 eV for crystal 1 (light blue) and 0.07 eV for crystal 2 (dark blue). In case of an intrinsic semiconductor, this would lead to a band gap of approximately 0.13 eV.

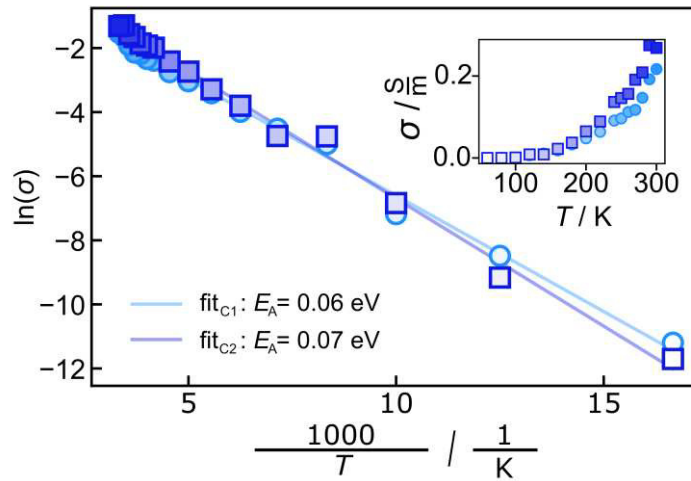


Figure 22. Arrhenius plot of the electrical conductivity from two $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ -crystals between 60 K–300 K (in 20 K steps between 60 K–240 K and 240 K–300 K in 10 K steps). The two lines represent linear fits, revealing activation energies of around 0.07 eV (light blue = crystal 1; dark blue = crystal 2). The inset shows the linear plot of conductivity against the temperature.

The DFT calculated electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ shows flat bands near the Fermi level with an indirect zero band gap between the valence band maximum (VBM) at D ($0 \frac{1}{2} \frac{1}{2}$) and the conduction band minimum (CBM) at E ($-\frac{1}{2} \frac{1}{2} \frac{1}{2}$) (Figure 23). Former experimentally realised zero band gap materials are all direct. The flat bands correspond to spatially localised

wavefunctions, which can enhance electronic correlation effects, such as unconventional superconductivity¹¹⁶ and the fractional quantum Hall effects.¹¹⁷

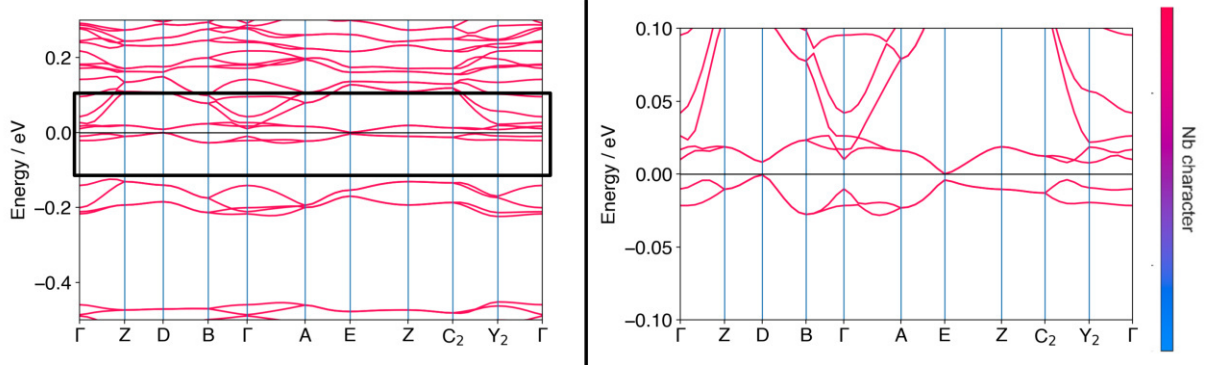


Figure 23. The electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, showing the band manifolds near the Fermi energy (left), and a closeup of the flat bands surrounding the Fermi energy and the indirect zero gap between D ($0 \frac{1}{2} \frac{1}{2}$) and E ($-\frac{1}{2} \frac{1}{2} \frac{1}{2}$) (right). Special points in and paths through the Brillouin zone were chosen following the literature.¹⁰⁷

Each structural unit in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ possesses an odd number of electrons, indicating intercluster interactions along the a and c direction. The maximally localised Wannier functions¹¹⁸, illustrating the localisation of the wavefunction, of the VBM and the CBM show a delocalisation of the electronic states over the $[(\text{Nb}_4\text{O})_2(\text{Nb}_2\text{O}_2)]$ units, with some reach into neighbouring clusters. This allows adjacent clusters to interact, forming a quantum singlet stage.

The origin of this unusual band gap can be associated with the helical shape of the cluster core. Local symmetry breaking, appearing in chiral or helical systems, move the VBM and the CBM to different points in the momentum states, creating an indirect gap.¹¹⁹ Although the structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ is achiral, there are two pairs of clusters with opposite helicity, resulting in an overall antiferrochiral¹²⁰ arrangement.

3.6 Niobium Oxyiodide Clusters from Heterogeneous Solid-State Reactions: The Example of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ (Publication 6)¹²¹

As previously discussed, there is a residual powder remaining at the bottom of the ampoule not undergoing transport in a gradient during the reaction. It consists of the metathesis byproduct LiI as well as amorphous phases such as C_3N_4 and the crystalline compound $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. This compound features a $[\text{Nb}_7\text{O}_5]$ cluster core within its structure. Instead of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, another crystalline compound can occur at the bottom of the ampoule. However, the crystallinity was insufficient to obtain high-quality crystals suitable to fully characterise the compound by single-crystal X-ray diffraction. As a result, only a structural proposal could be proposed, yielding the empirical formula $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$. The lithium content in this proposal was estimated based on the available voids in the structure, residual electron density and charge balance considerations, analogous to the confirmed structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. Rietveld refinement of crystalline powder (Figure 24) support the initial structure solution from single-crystal XRD and yielded in the structure proposal deposited with the CCDC number 2493985 (Table S 1).

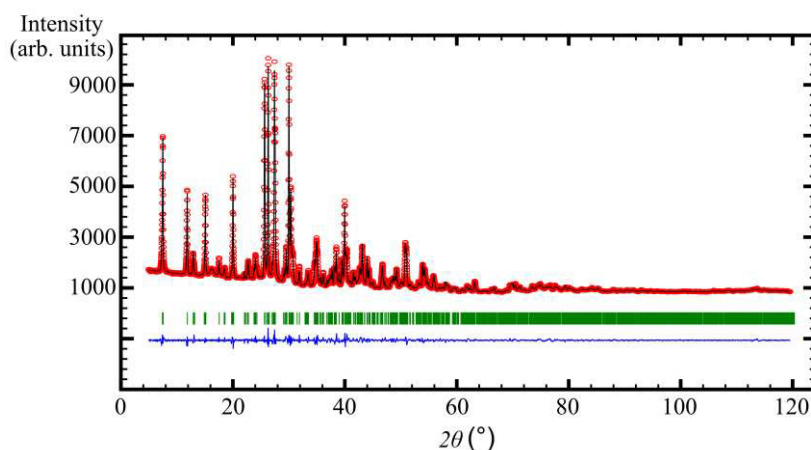


Figure 24. Powder X-ray diffraction pattern subjected to a Rietveld refinement for the crystal structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ at 298 K with the experimental (red) and calculated (black) intensities, with Bragg positions (green), and the difference curve (blue) shown.

As in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ is based on a $[\text{Nb}_7\text{O}_5]$ cluster core and has an identical iodide coordination environment (Figure 25). The Nb–Nb distances range from 2.71(1) Å to 3.097(9) Å and are therefore in good accordance with those found in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. The connectivity between adjacent clusters is realised by six pairs of $\text{I}^{\text{a-a}}$ bridges at each of the six corners of the $[\text{Nb}_7\text{O}_5]$ core, forming a three-dimensional network.

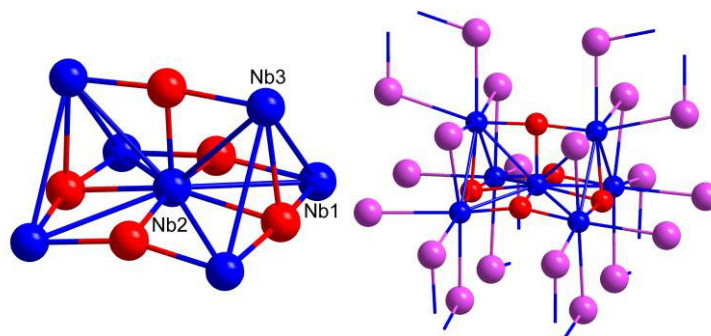


Figure 25. Structure of the $[\text{Nb}_7\text{O}_5]$ cluster core inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ (left) and the iodide environment (right).

This open framework results in large channels within the structure, sufficient to accommodate $(\text{NbI}_6)^-$ ions, unlike in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, where I^- occupy the interstitial spaces. These $(\text{NbI}_6)^-$ ions form distorted iodide octahedra with neighbouring octahedra shifted in c -direction (Figure 26, right, $(\text{NbI}_6)^-$ as blue octahedra). Such incorporations of molecules are also present in other structures. A close example is represented by $(\text{Ta}_6\text{Br}_{15})(\text{TaBr}_6)_{0.86}$ ¹²², where four $(\text{Ta}_6\text{Br}_{12}\text{Br}_{6/2})$ units are forming a bromide-bridged ring arrangement. The created channel is big enough to accommodate $(\text{TaBr}_6)^-$ molecules, stabilising the framework formation.

The voids for the lithium atoms include a square-pyramidal (Li1 and Li2) and a distorted octahedral (Li3) iodide environment (Figure 26, left). The square-pyramidal environment was also observed inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. The octahedrally surrounded Li3 atom is showing average Li–I distances of 3.05 Å.

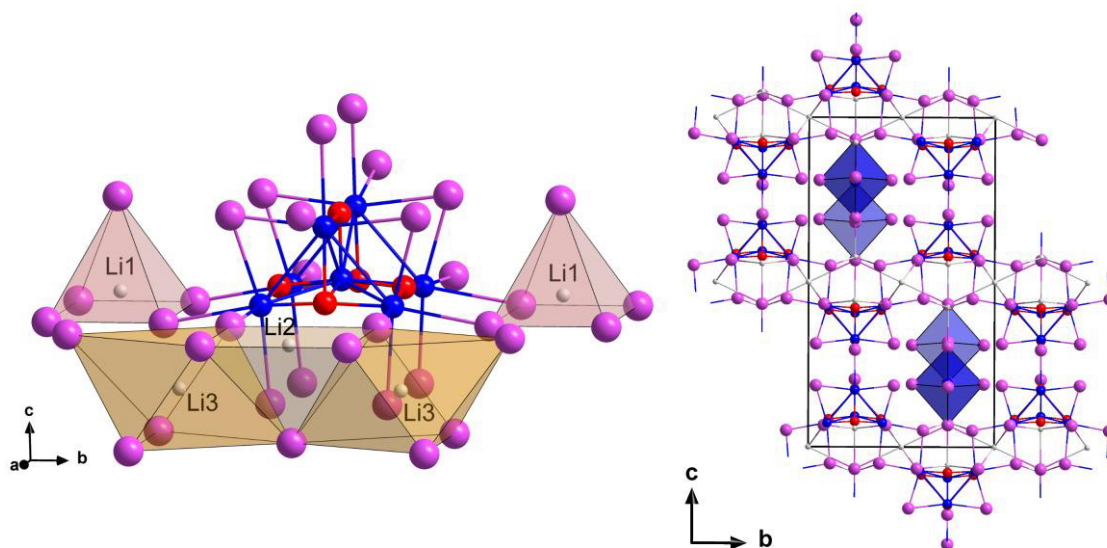


Figure 26. Iodide coordination of the lithium atoms inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ (left) and section of the crystal structure with $(\text{NbI}_6)^-$ octahedra (right).

In $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, each cluster is connected to six neighbouring clusters at each corner; two via iodide bridges at the top of cluster, and four in the horizontal plane of the $[\text{Nb}_5\text{O}_4]$ base. This results in a structural arrangement where the spatial organisation of the clusters mirrors the arrangement of the niobium atoms within the cluster itself (Figure 27, left).

In contrast, in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$, the $[\text{Nb}_7\text{O}_5]$ cluster core connects to only four adjacent clusters; two through two iodide bridges, and two through four iodide bridges. This kind of connectivity yields a tetrahedral arrangement of neighbouring clusters, leading to an overall diamond-like structural motif (Figure 27, right). Through the different connectivity pattern, the cavities inside the structure are big enough to accommodate $(\text{NbI}_6)^-$ anions.

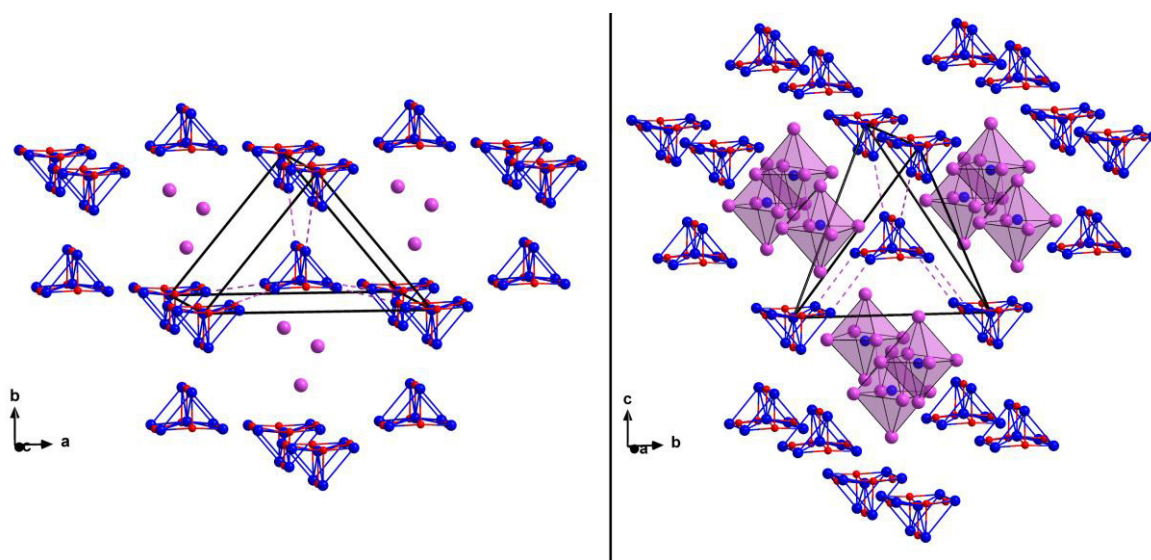


Figure 27. Comparison of the cluster arrangement in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ (left) and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ (right) with the created cavities for I^- (violet balls) and $(\text{NbI}_6)^-$ ions (violet polyhedra). Two iodide bridges, which connect the central cluster with six, respectively four adjacent clusters, are illustrated by pink, dashed lines.

4. Conclusion

Conventional synthetic approaches to metal halide cluster compounds are largely restricted to thermodynamically stable motifs, most prominently trigonal M_3 and octahedral M_6 clusters. The introduction of heteroanions and the transition from binary to ternary systems increases the structural diversity and allows access to additional cluster types; however, the commonly employed synthetic conditions (particularly the use of elemental metals as reducing agents) require high temperatures and long reaction times. Under such conditions, thermally labile intermediates are unlikely to persist and therefore remain inaccessible to structural characterisation.

In this work, an alternative synthetic strategy has been established that enables the formation and isolation of metastable cluster compounds under comparatively mild conditions. The use of lithium carbodiimide as a reducing agent allows reactions to proceed at significantly lower temperatures and gives rise to a heterogeneous reaction system involving solid precursors and a reactive gaseous phase. This gaseous phase, which appears at temperatures above approximately 300 °C, plays a decisive role in directing cluster formation and leads to a pronounced sensitivity of the product distribution with respect to the reaction parameters.

Using the Nb–O–I system as a model case, the reduction of niobium iodide in the presence of an oxygen source was shown to yield a remarkably broad range of cluster compounds with varying nuclearities and connectivities. Depending on temperature, reaction time, and reducing conditions, cluster cores containing four to ten niobium atoms were obtained, including rectangular $[\text{Nb}_4\text{O}]$, square-pyramidal $[\text{Nb}_5\text{O}_4]$, and more complex $[\text{Nb}_7\text{O}_5]$, $[\text{Nb}_8\text{O}_5]$, and $[\text{Nb}_{10}\text{O}_4]$ motifs (Figure 28). These cluster cores assemble into structural motifs ranging from isolated molecular units to one-, two-, and three-dimensional networks. The frequent occurrence of black colour of the crystals and small band gaps further highlights the electronical interesting properties of the synthesised compounds.

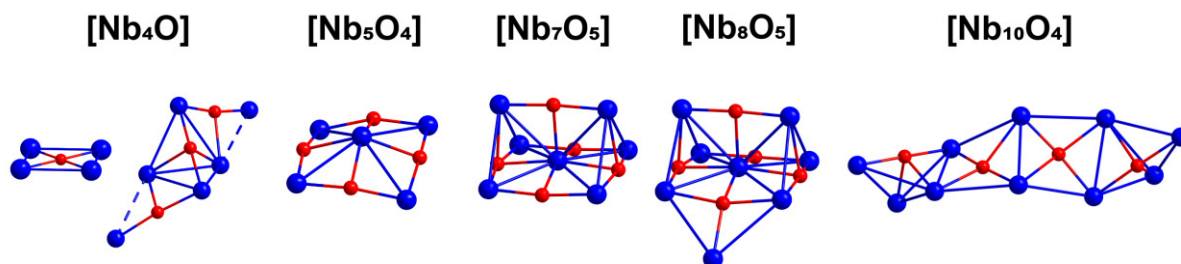


Figure 28. Overview of the cluster cores in the synthesised compounds.

The spatial separation of products within the reaction ampoule, combined with the coexistence of multiple cluster species formed from the same gaseous phase, indicates that this reaction system operates under conditions close to thermodynamic non-equilibrium. This near-non-equilibrium character enables access to cluster motifs that are not attainable by conventional high-temperature routes and underscores the importance of kinetic control in cluster chemistry. Although demonstrated here for the niobium–oxygen–iodine system, the underlying concept is not limited to this specific chemistry. The approach can, in principle, be extended to other early transition metals such as molybdenum or tungsten, to alternative heteroanions such as sulphur or phosphorus, and to different reducing agents. As such, this work establishes a versatile synthetic framework for accessing metastable metal cluster compounds and significantly expands the structural landscape of metal oxyhalide cluster chemistry.

5. References

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6. Appendix

Figures were used as shown in the published articles except those declared below:

- Figure 4:** The comparison to the $[\text{Nb}_6\text{I}_8\text{I}_{6/2}]^{3-}$ fragment in Nb_6I_{11} is omitted.
- Figure 5:** The layered connectivity and the stacking of the layers are displayed in two separated images in the publication.
- Figure 8:** The picture with both occupied Nb2 positions is extended, and the arrangement of the segments is different.
- Figure 9:** The *cis* and *trans* connectivity and the hexagonal arrangement are displayed in two separated images in the publication.
- Figure 11:** The building block and the waved layered structure of *o*- $\text{M}_5\text{O}_4\text{I}_{11}$ are displayed in two separated images in the publication.
- Figure 12:** The building block and the waved layered structure of *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ are displayed in two separated images in the publication.
- Figure 13:** The section of the crystal structure of $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$ is illustrated in a different way with the $[\text{TaI}_5]$ molecules as trigonal-bipyramidal polyhedral.
- Figure 14:** The images are rearranged compared to the figure in the publication.
- Figure 15:** The $[\text{Nb}_7\text{O}_5]$ cluster core and the iodide environment are displayed in two separated images in the publication.
- Figure 16:** The $[\text{Nb}_8\text{O}_5]$ cluster core, the iodide environment and the section of the crystal structure are displayed in three separated figures in the publication.
- Figure 17:** The electronic band structure and the electron localisation functions are displayed in two separated images in the publication.
- Figure 19:** The connectivity of the $\text{Nb}_6\text{O}_3\text{I}_{15}$ and the section of the crystal structure are displayed in two separated images in the publication.
- Figure 23:** The images are rearranged compared to the figure in the manuscript.

Figure 25: The cluster core of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ and the iodide environment are displayed in two separated images in the manuscript.

Figure 26: The iodide coordination of the lithium atoms and the section of the crystal structure with $[\text{NbI}_6]^-$ units are displayed in two separated images in the manuscript.

Figure 27: The images are rearranged compared to the figure in the manuscript.

Table S 1. Crystal data and structure refinement of Nb₄OI₁₀, a- and b-Nb₄OI₁₁, Nb₄OI₁₂, Nb₅O₄I₁₁, Li₃Nb₇O₅I₁₅, Nb₈O₅I₁₇(NbI₅), Nb₅O₃I₁₅, Nb₁₁O₆I₂₄ and Li₃Nb₇O₅I₁₄(NbI₆).

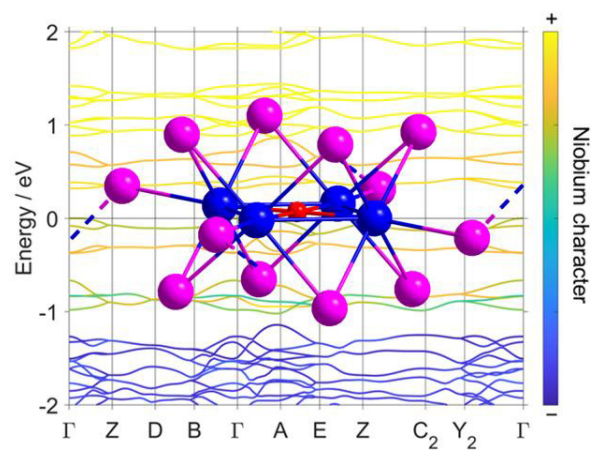
	Nb ₄ OI ₁₀	a-Nb ₄ OI ₁₁	b-Nb ₄ OI ₁₁	Nb ₄ OI ₁₂	Nb ₅ O ₄ I ₁₁
CCDC No.	2225618	2391069	2408695	2366237	2400835
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$C2/m$	$P\bar{1}$	$Pmc2_1$	$Pmc2_1$
Temperature (K)	150	220	150	270	150
Unit cell dimensions	$a = 10.0435(1) \text{ \AA}$	$a = 15.4442(3) \text{ \AA}$	$a = 10.1217(2) \text{ \AA}$	$a = 37.9189(8) \text{ \AA}$	$a = 9.7963(2) \text{ \AA}$
	$b = 10.6595(1) \text{ \AA}$	$b = 13.0449(2) \text{ \AA}$	$b = 13.9844(3) \text{ \AA}$	$b = 17.8026(4) \text{ \AA}$	$b = 17.8082(3) \text{ \AA}$
	$c = 10.0594(1) \text{ \AA}$	$c = 11.9078(2) \text{ \AA}$	$c = 16.3913(3) \text{ \AA}$	$c = 7.3403(2) \text{ \AA}$	$c = 15.2052(2) \text{ \AA}$
			$\alpha = 88.968(2)^\circ$		
	$\beta = 94.193(1)^\circ$	$\beta = 105.698(2)^\circ$	$\beta = 89.093(2)^\circ$		
			$\gamma = 85.329(2)^\circ$		
Volume ($\text{\AA}^3$)	1074.06(2)	2309.56(7)	2311.80(8)	4955.1(2)	2652.61(8)
Z	2	4	4	8	4
Wavelength ($\text{\AA}$)	0.71073	0.71073	0.71073	0.71073	1.54184
μ (mm^{-1})	16.433	16.624	16.607	16.744	117.683
R_{int}	0.0354	0.0189	0.020	0.0351	0.0339
R_1	0.0117	0.0150	0.0185	0.0517	0.0485
wR_2	0.0282	0.0314	0.0581	0.1414	0.1254
Goodness-of-fit F^2	1.093	1.430	1.037	1.086	1.025

	Li ₃ Nb ₇ O ₅ I ₁₅	Nb ₈ O ₅ I ₁₇ (NbI _{5.37})	Nb ₁₈ O ₉ I ₄₅ (Nb ₆ O ₃ I ₁₅)	Nb ₁₁ O ₆ I ₂₄	Li ₃ Nb ₇ O ₅ I ₁₄ (NbI ₆)
CCDC No.	2311571	2428720	2401147	2380623	2493985
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	<i>Cmcm</i>	<i>Pnma</i>	<i>C2/c</i>	<i>P2₁/c</i>	<i>Imma</i>
Temperature (K)	230	200	150	150	298
Unit cell dimensions	<i>a</i> = 14.5783(3) Å	<i>a</i> = 11.4282(4) Å	<i>a</i> = 26.9643(4) Å	<i>a</i> = 16.4086(1) Å	<i>a</i> = 13.5176(1)
	<i>b</i> = 17.6445(3) Å	<i>b</i> = 13.4336(6) Å	<i>b</i> = 14.3399(2) Å	<i>b</i> = 16.2749(2) Å	<i>b</i> = 13.4466(2)
	<i>c</i> = 13.5823(2) Å	<i>c</i> = 31.479(1) Å	<i>c</i> = 24.8587(4) Å	<i>c</i> = 18.8946(2) Å	<i>c</i> = 23.7811(3)
			$\beta = 95.744(1)^\circ$	$\beta = 91.713(1)^\circ$	
Volume (Å ³)	3493.7(1)	4848.1(3)	9563.7(2)	5043.52(9)	4322.56(9)
<i>Z</i>	4	4	4	4	4
Wavelength (Å)	1.54184	1.54184	0.71073	1.54184	1.54060
μ (mm ⁻¹)	122.292	128.729	16.616	135.138	128.992
<i>R_{int}</i>	0.0316	0.0589	0.0192	0.0236	<i>R_{Bragg}</i> = 2.734
<i>R</i> ₁	0.0197	0.0274	0.0284	0.0292	<i>R_p</i> = 3.143
<i>wR</i> ₂	0.0534	0.0516	0.0699	0.0745	<i>R_{wp}</i> = 4.2119
Goodness-of-fit <i>F</i> ²	1.060	1.036	1.034	1.020	<i>X</i> ² = 1.3461

7. Publications

Publication 1

The Rectangular Niobium Oxyiodide Cluster $\text{Nb}_4\text{OI}_{10}$ – A Narrow Band-Gap Semiconductor



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The Rectangular Niobium Oxyiodide Cluster $\text{Nb}_4\text{OI}_{10}$ – A Narrow Band-Gap Semiconductor

Jan Beitzberger,^[a] Markus Ströbele,^[a] Fabian Strauß,^[b] Marcus Scheele,^[b] Carl P. Romao,^[c] and Hans-Jürgen Meyer^{*[a]}

A metal-rich niobium oxyiodide was prepared by soft reduction of NbI_4 . The structure of the new compound $\text{Nb}_4\text{OI}_{10}$ was determined by single-crystal X-ray diffraction and contains a rectangular $\text{Nb}_4(\mu_4\text{-O})$ cluster that is interconnected into layers by iodide ligands. The local structure of the $\text{Nb}_4\text{OI}_{10}$ cluster

bears a close relationship to a defect Nb_6I_{11} structure. The two-dimensional van der Waals material $\infty^2[\text{Nb}_4\text{OI}_{8/4/2}]$ is a small band-gap semiconductor (<1 eV), as analysed by electrical conductivity measurements, photoresponse, experimental band gap determination, and band structure calculation.

Introduction

Metal-rich niobium halides are known to form cluster compounds with various architectures and oxidation states.^[1] Well-known examples include the Peierls-distorted chain structure of NbX_4 ,^[2] triangular niobium clusters in Nb_3X_8 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$)^[3] and the octahedral niobium cluster compounds $\text{Nb}_6\text{Cl}_{14}$ ^[4] and Nb_6I_{11} .^[5] Beyond these most common clusters, there exist numerous ternary niobium halide cluster compounds. Depending on the electronic structure and the coordination pattern, at least five known types of Nb_4 -clusters have already been reported. In $\text{CsNb}_4\text{X}_{11}$, the Nb_4 cluster occurs with a rhombic arrangement with ten cluster electrons for metal-metal bonding (Figure 1a).^[6] In $\text{Nb}_4\text{PnX}_{11}$, the cluster is represented by a butterfly motif that is μ_4 -capped by a pnictide (Pn), containing six cluster electrons (Figure 1b).^[7] The Nb_4 cluster, found in the structure of $\text{Nb}_4\text{Se}_4\text{I}_4$, has eight cluster electrons and forms a tetrahedron with selenide capped faces (Figure 1c).^[8] The structure of $[\text{Nb}_4\text{OCl}_8((\text{PhC})_4)_2]^{2-}$ contains a rectangular $\text{Nb}_4(\mu_4\text{-O})$ cluster with eight electrons for metal-metal bonding (Figure 1d).^[9] Finally, the fifth reported cluster pattern is a square niobium cluster, observed in $\text{Li}_4[\text{Nb}_4\text{S}_2(\text{SPh})_{12}]\cdot 4\text{THF}$ (Fig-

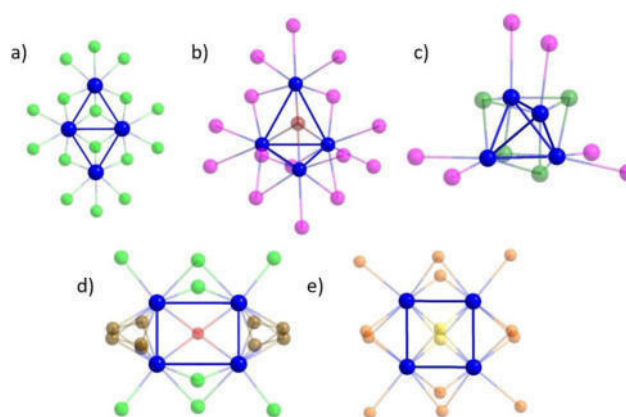


Figure 1. Characteristic Nb_4 -Cluster types in a) $\text{CsNb}_4\text{Cl}_{11}$,^[6] b) $\text{Nb}_4\text{PI}_{11}$,^[7] c) $\text{Nb}_4\text{Se}_4\text{I}_4$,^[8] d) $[\text{Nb}_4\text{OCl}_8((\text{PhC})_4)_2]^{2-}$,^[9] and e) $[\text{Nb}_4\text{S}_2(\text{SPh})_{12}]^{4-}$.^[10] Niobium atoms are shown in blue, chlorine in green, iodine in pink, phosphorus in dark red, selenium in dark green, oxygen in red, C–Ph in brown, S–Ph in orange, and sulphur in yellow.

ure 1e).^[10] A comparable variety of cluster patterns is reported for Mo_4 clusters.^[11]

Niobium oxyhalides (or oxide halides) show a great variety in their composition and properties. Metal atoms in the structures are typically surrounded by halide and oxide ions in an octahedral fashion. This arrangement allows for the formation of chains or layers, depending on the specific composition. In addition to variable halide/oxygen ratios and different oxidation states, there are examples of metal-metal bonding interactions within the niobium halide/oxygen system.^[12]

In many metal-oxide-halide systems, the condensed phases volatilize easily and can only be crystallized within a specific equilibrium window of temperature and composition. This observation highlights the sensitivity of these systems to changes in conditions, such as temperature and composition, which can significantly impact the formation of different phases. Understanding and controlling the equilibrium window is crucial for the successful crystallization and characterization of phases in metal-oxide-halide systems, of which the mostly

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comparable W–O–I system is a prominent example. Following the most recent findings, the reaction cascade in the transport of tungsten from cold-to-hot involves the sequential formation of W, WO₂, W₂O₃, WO₃, and finally W; a sequence which has been completely characterized no earlier than in 2021.^[13]

Niobium oxyhalides typically appear in three common structures, NbOX₂, NbOX₃ and NbO₂X with X=F, Cl, Br and I.^[14] In addition, there are also other compositions reported, including Nb₃O₇Cl, Nb₃O₅F₅ and Nb₃O₂Cl₅, to mention just some examples.^[15]

Among these, Nb₃O₂Cl₅ is a less common example of a niobium oxyhalide whose structure contains metal-to-metal bonding, forming a triangular cluster core. Some interesting magnetic and electrical conductivity properties of these compounds have been reported.^[16]

Herein we present the principal result of our study in the Nb–O–I system: The synthesis and structure of Nb₄OI₁₀. The employment of a soft reduction agent in the given reaction is an advancement upon our previous studies on the reduction with non-conventional reduction agents.^[17] The structure of the new compound Nb₄OI₁₀ was characterized by X-ray single-crystal diffraction techniques and its properties were analyzed by electrical conductivity measurements, band gap measurement, and DFT band structure calculations.

Results and Discussion

Synthesis and Crystal Structure

Black crystals of Nb₄OI₁₀ (Figure S1) were observed from the reaction of NbI₄ with Li₂(CN)₂ and Li₂O in a molar mixture of 4:2:1 after heating at 500 °C for 36 h. In this reaction, Li₂(CN)₂ serves as a soft reducing agent as has been described in the reduction of WCl₆,^[18] as well as in the analogous reduction of NbCl₅ by NaN₃,^[7] where the reduction agent is formed during the reaction.

The presence of the oxide ion in the given Nb–O–I system introduces a complex system of solid and gas phases, with dynamic phase equilibria.

The crystal structure of Nb₄OI₁₀ was solved and refined from recorded single-crystal X-ray diffraction data in the monoclinic space group *P*2₁/*n*. Some details of the measurement and refinement are collected in Table 1. A powder X-ray diffraction pattern of a crystalline sample of Nb₄OI₁₀ is shown in Figure S2.

The two distinct niobium atoms in Nb₄OI₁₀ can be assigned to the average oxidation state of +III, forming a rectangular Nb₄ cluster core, centered by an oxygen atom at the inversion center of the structure, displayed in Figure 2. Hence, the Nb₄O cluster contains a total of eight electrons which are available for metal-to-metal bonding.

The cluster core in Nb₄OI₁₀ is surrounded by eight edge-bridging (i=innen) iodide ligands, and four outer (a=außen) iodide ligands shared (a–a) between adjacent clusters as [Nb₄OI₈I_{4/2}ⁱ]^{a–a}. A closely related structure pattern of this arrangement of iodide ligands can be seen in the octahedral cluster Nb₆I₁₁, in which eight inner iodide ligands cap the Nb–Nb edges

Table 1. Crystallographic and refinement data of Nb₄OI₁₀.

CCDC No.	2225618
Space group	<i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	150
Unit cell dimensions (Å)	<i>a</i> = 10.0435(1) <i>b</i> = 10.6595(1) <i>c</i> = 10.0594(1)
Angle (°)	<i>β</i> = 94.193(1)
Volume (Å ³)	1074.06(2)
<i>Z</i>	2
Wavelength (Å)	0.71073
<i>μ</i> (mm ^{−1})	16.433
Calculated density (g/cm ³)	5.122
2 θ range for data collection	5.532 to 72.638
Total number of reflections	80092
Independent reflections	5209
Refined parameters	71
<i>R</i> 1	0.0117
<i>wR</i> 2	0.0282
Goodness-of-fit on <i>F</i> ²	1.093

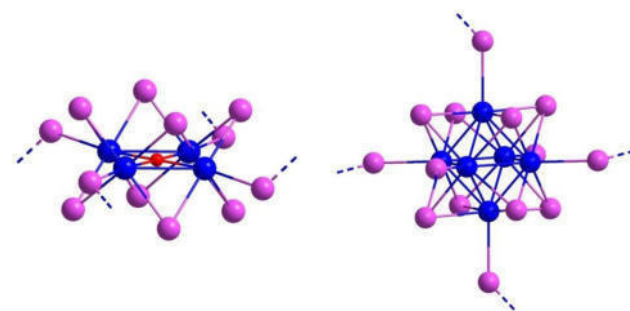


Figure 2. Comparison of the planar [Nb₄OI₈I_{4/2}]^{2−} fragment in the structure of Nb₄OI₁₀ (left) with the octahedral [Nb₆I₈I_{6/2}]^{3−} fragment in the structure of Nb₆I₁₁ (right). Niobium is shown in blue, iodine in pink and oxygen in red.

and six outer iodide ligands connect adjacent clusters following the connectivity formula [Nb₆I₈I_{6/2}^{a–a}], shown in Figure 2. Hence, the planar Nb₄ cluster can be derived from an octahedral cluster by cutting off two (Nb–I) edges of the octahedral Nb₆I₁₁ cluster.

The connectivity of adjacent clusters in the structure of Nb₄OI₁₀ by four outer iodide ligands forms a layered arrangement, displayed in Figure 3, that can be described as ∞²[Nb₄OI₈I_{4/2}]. Individual clusters in each layer are tilted relative to each other in two different ways, thereby increasing the filling fraction. The arrangement of adjacent layers, shown in Figure 4, includes significant anisotropy into the structure with the interaction between adjacent layers being mediated by van der Waals forces.

The presence and identity of a light interstitial atom (*Z*=B, C, N, ...) in a given cluster, for example in Zr₆ZCl₁₄, is typically verified by a NMR measurement. However, this technique is not suitable for the identification of the oxygen atom in Nb₄OI₁₀.

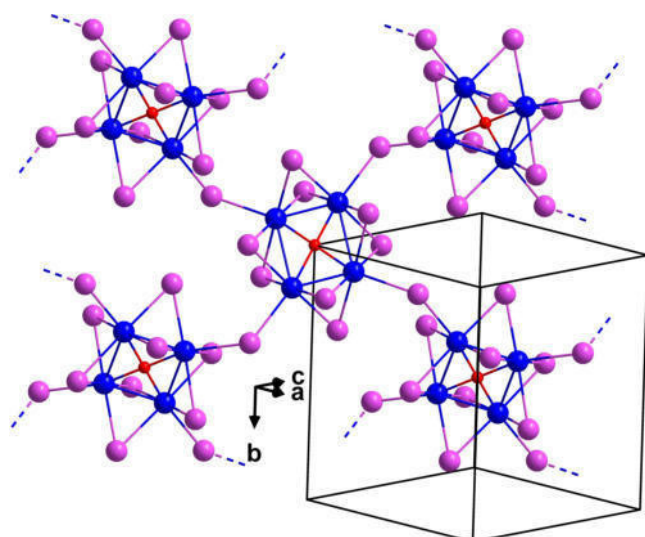


Figure 3. Section of one layer in the crystal structure of $\text{Nb}_4\text{OI}_{10}$ shown with the unit cell. The clusters are tilted relative to each other in two different directions. Niobium is shown in blue, iodine in pink and oxygen in red.

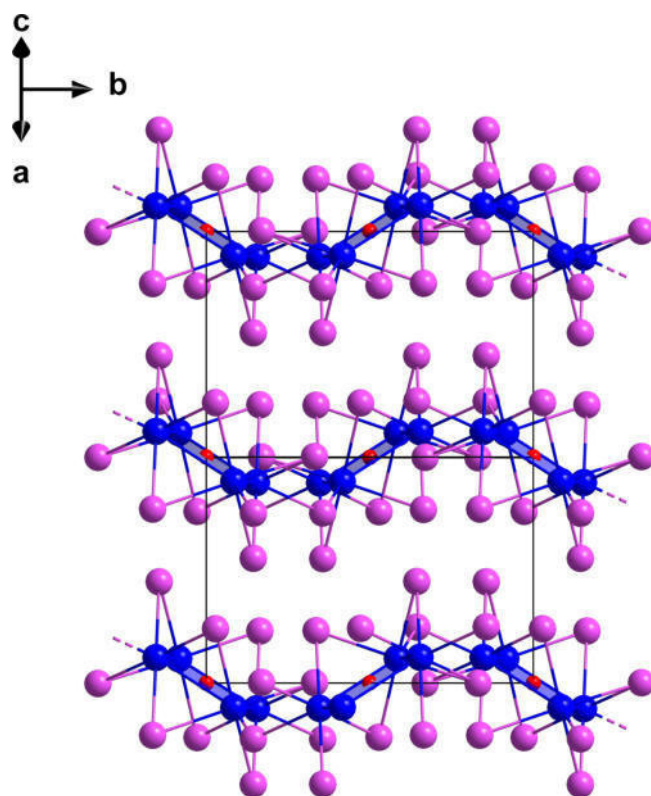


Figure 4. Visualization of layers in the structure of $\text{Nb}_4\text{OI}_{10}$, with the unit cell indicated by black lines.

Therefore, the presence of oxygen in the cluster was proven by means of electron microprobe analysis (Figure 5).

The emission of the characteristic X-ray O- $K_{\alpha 1}$ radiation has an energy around 0.525 keV.^[19] The electron microprobe analysis shows a signal at the expected energy for oxygen. The absence of nitrogen in the structure was analogously confirmed by the absence of a corresponding signal (see Figure S3).

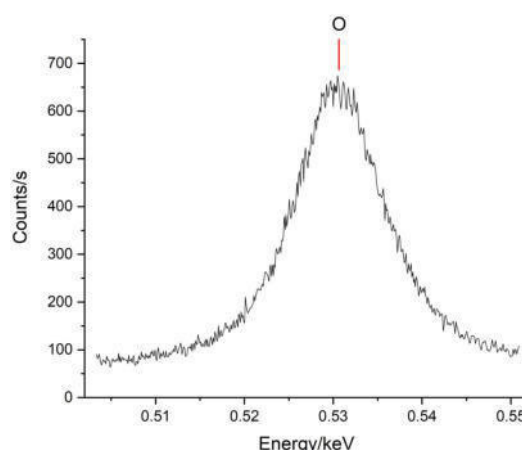


Figure 5. Electron microprobe analysis measurement of $\text{Nb}_4\text{OI}_{10}$ in the $K_{\alpha 1}$ -radiation energy range of oxygen.

An interesting feature in the structure $\text{Nb}_4\text{OI}_{10}$ is the presence of a rectangular Nb_4O cluster with Nb–Nb distances of 2.623(2) Å and 3.104(2) Å (Figure 6). The shorter distance can be described as a metal-to-metal bonding distance that is slightly shorter than corresponding distances in Nb_6I_{11} , ranging between 2.743 Å and 2.918 Å.

The characteristic Nb_4O -type cluster in the structure of $\text{Nb}_4\text{OI}_{10}$ has also been reported in other compounds, however with varying dimensions, either with square or rectangular shape. The Ti_4O cluster in $\text{K}_4[(\text{Ti}_4\text{O})\text{I}_{12}]$ adopts a square planar arrangement, electronic structure calculations revealed strong Ti–Ti and Ti–O σ -bonding with the absence of Ti–Ti multiple (π) bonding, representing an electronically localized material.^[20]

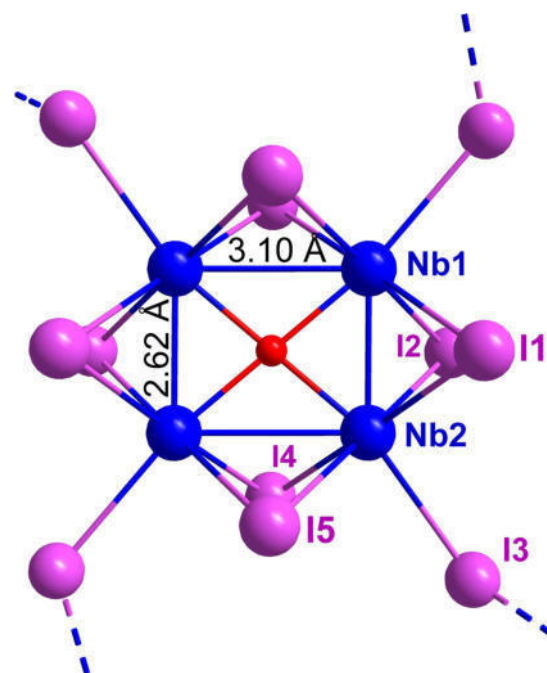


Figure 6. The rectangular niobium cluster core in $\text{Nb}_4\text{OI}_{10}$ with two distinct Nb–Nb bond lengths and the iodine environment.

A $[\text{Nb}_4\text{O}_8]^{2+}$ cation based on a rectangular Nb_4O core was reported in $[\text{Nb}_4\text{O}_8][\text{Mo}_6\text{I}_{14}]$, indicating the coexistence of a rectangular $[\text{Nb}_4\text{O}_8]^{2+}$ and an octahedral $[\text{Mo}_6\text{I}_{14}]^{2-}$ cluster in the structure.^[21] Nb–Nb distances in the $[\text{Nb}_4\text{O}_8]^{2+}$ cation were reported as 2.771(1) Å and 2.961(1) Å. Another rectangular cluster was reported in the $[\text{Nb}_4\text{OCl}_8(\text{PhC}_2)_2]^{2-}$ ion, with the shorter Nb–Nb distance at 2.61 Å. Both compounds contain eight cluster electrons. Molecular orbital theory calculations suggest Nb–Nb bonding, at least between pairs of niobium atoms.^[9]

The lack of a clear assignment of electron localization or distribution in the crystal structure of $\text{Nb}_4\text{OI}_{10}$ poses a challenge to gaining a deeper understanding of the microscopic electronic properties and potential of this compound.

Electrical Conductivity Measurements

Temperature-dependent conductivity measurements were conducted on two crystal specimens of $\text{Nb}_4\text{OI}_{10}$. Figure 7 shows I/U curves of two $\text{Nb}_4\text{OI}_{10}$ crystals, revealing ohmic behavior and a

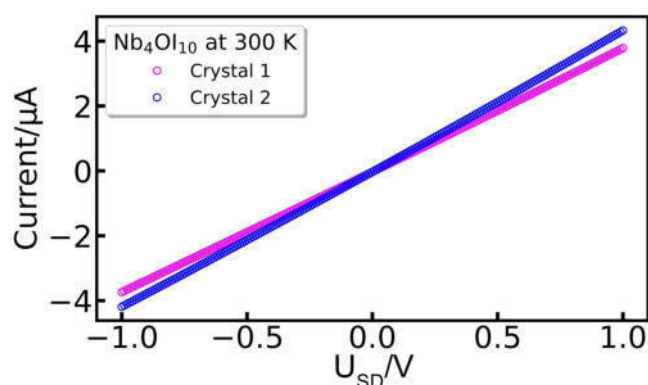


Figure 7. Dark current of two $\text{Nb}_4\text{OI}_{10}$ crystals at 300 K with an applied source-drain voltage U_{SD} from -1 V to 1 V.

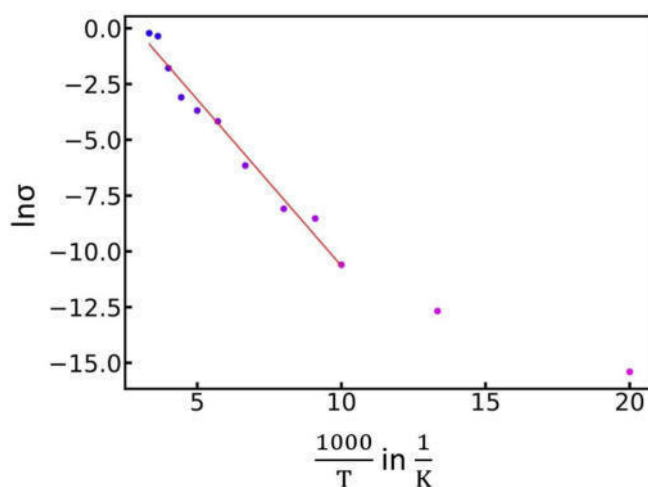


Figure 8. Arrhenius plot of the electrical conductivity of $\text{Nb}_4\text{OI}_{10}$ (Crystal 2) at temperatures in the range of 50 K to 300 K. The red line is a linear fit for the range between 100 K and 300 K.

conductivity of $\sigma = 0.8$ S/m (Crystal 1) as well as $\sigma = 1.2$ S/m (Crystal 2) at 300 K, respectively.

The conductivity at individual temperatures in the range from 50 K to 300 K are shown in Figure S4 and S5 and reveal decreasing currents for decreasing temperatures, characteristic for a semiconducting material. In Figure 8, this data is presented in an Arrhenius-like plot. Below 100 K, the conductivities tend to show a slower decline, which could be due to structural and/or electronic transitions. This behavior in the low temperature region appears to be reversible for both crystal specimens (1 and 2).

From fitting the data between 300 K and 100 K, we determine an activation barrier to transport of 0.6 eV, indicating as a first-order approximation a bandgap of approx. 0.3 eV under the assumption of an intrinsic position of the Fermi level.^[22]

Under illumination with a 779 nm CW-laser, the crystals show a photoresponse, displayed in Figure 9. A rapid, steep increase precedes a slower second component in this photocurrent. For the first rise, we credit photoexcited charge carriers; for the second, we attribute the effect to the crystal's concurrent heating. Strong temperature activation is present in the photocurrent, which varies from a few picoamperes at 50 K to several tens of nanoampere at room temperature.

Electronic Structure Calculations

The electronic structure of $\text{Nb}_4\text{OI}_{10}$ was calculated using density functional theory (DFT). The calculated electronic band structure is displayed in Figure 10; it shows eight energy bands split off above the p-block orbitals. The bands arise from two formula units $\text{Nb}_4\text{OI}_{10}$, resulting in a total of 16 cluster electrons that fully occupy these bands. These bands near the Fermi energy have predominantly Nb character, indicating a clear separation in energy being seen between the Nb d and I p orbitals (Figure S6) and the ionic character of the Nb–I bonding. The band structure analysis suggests the presence of a small (0.3 eV) direct band gap at the Γ point, characteristic of a semiconductor. This band gap value is slightly smaller than that

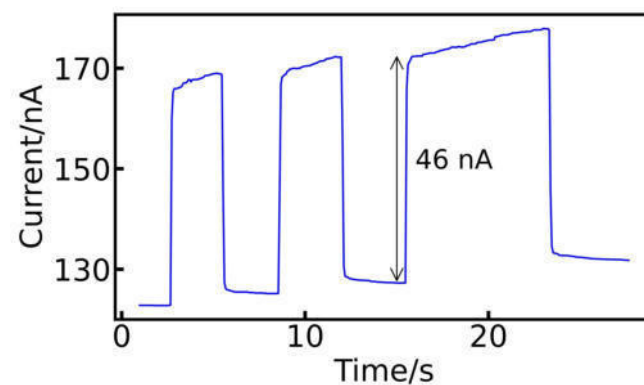


Figure 9. Photoresponse of a $\text{Nb}_4\text{OI}_{10}$ crystal toward a 779 nm laser at 300 K and with 200 mV bias applied.

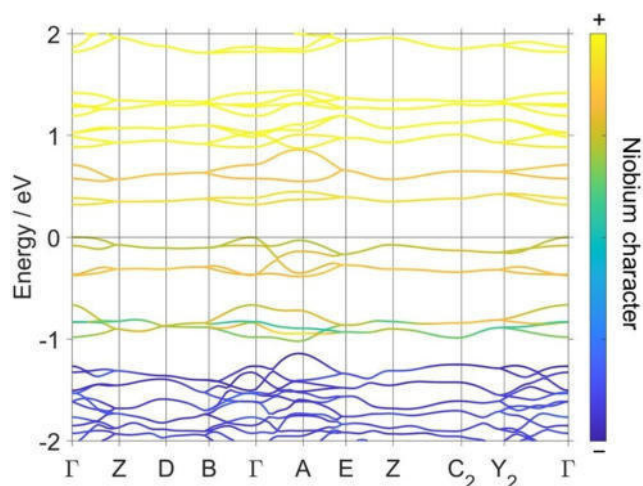


Figure 10. The DFT-calculated electronic band structure of Nb₄OI₁₀ with bands coloured by their niobium character. Special points in and paths through the Brillouin zone were chosen following the literature.^[23]

determined through DRIFT spectroscopy (0.48 eV, see below), as it is typically underestimated by DFT calculations.

The band curvature at the valence band maximum is fairly flat, suggesting electron localization.

In order to understand the origins of the rectangular distortion of the Nb₄ unit, DFT calculations of the electronic energy levels of an isolated [Nb₄OI₁₂]²⁻ cluster were performed with a rectangular Nb₄ geometry (as in the crystal structure) and with a square Nb₄ geometry. The driving force for the reduction in symmetry can be seen by comparison of energy splitting of the four highest occupied energy levels of an isolated [Nb₄OI₈]²⁻ unit, because these levels are most representative for metal-to-metal interactions. The decrease in energy of three highest energy molecular orbitals of the rectangular Nb₄ unit, displayed in Figure 11, is accompanied by an increase in energy of some of the unoccupied orbitals. Such shifts correspond to a pseudo-Jahn–Teller (or second-order Jahn–Teller) effect, wherein symmetry lowering is associated with increased hybridization of molecular orbitals.

Band Gap Determination by DRIFT

The Tauc-plot formalism was used for experimental determination of the band gap. The absorption coefficient was obtained by using Kubelka-Munk analysis, following

$F(R_{\infty}) = \frac{\alpha}{S} = \frac{(1-R_{\infty})^2}{2R_{\infty}}$, where $R_{\infty} = \frac{R_{\text{sample}}}{R_{\text{standard}}}$ is the reflectance of an infinitely thick specimen, α is the absorption and S is the scattering coefficient. For particle sizes greater than the wavelengths used in the measurement, the scattering coefficient is understood to be approximately independent of the frequency ($F(R_{\infty}) \sim \alpha$) and therefore $F(R_{\infty})$ could be used as a “pseudo-absorbance” coefficient.^[24]

The optical band gaps were obtained using the Tauc method with the relationship:

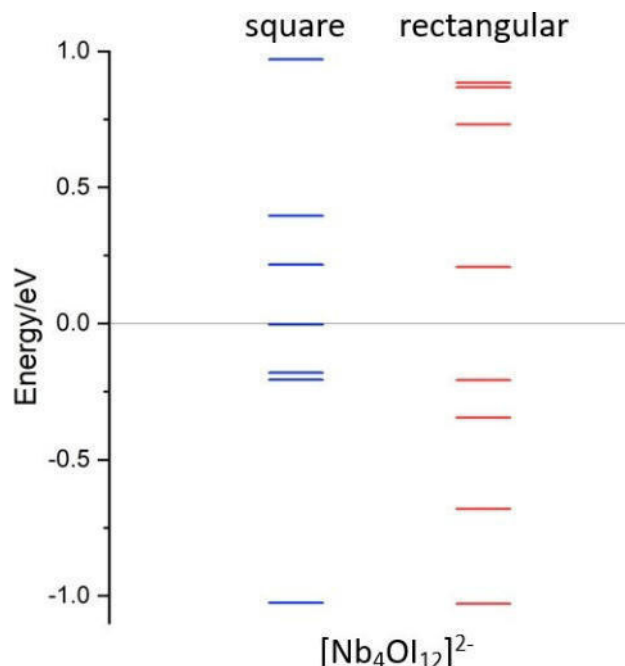


Figure 11. Metal-dominated MO energy levels of an isolated [Nb₄OI₁₂]²⁻ cluster with square and rectangular geometry of the Nb₄ unit. The Fermi level is drawn for the square cluster having eight electrons, with occupied energy levels of the corresponding rectangular cluster being lower in energy.

$$(\alpha \cdot h\nu)^{1/\beta} = A(h\nu - E_g)$$

where α is the absorption coefficient, $h\nu$ the photon energy, A and h constants, E_g the optical band gap and n is a parameter which depends on the nature of the electronic transition. The corresponding values for β of an allowed direct and indirect transition are $1/2$ and 2 .^[25] Substitution of α with $F(R_{\infty})$ yields in the Tauc equation:

$$(F(R_{\infty}) \cdot h\nu)^{1/\beta} = A(h\nu - E_g)$$

The band gap value was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the linear portion of the absorption edge in the $(F(R_{\infty}) \cdot h\nu)^{1/\beta}$ versus E plot. This optical band gap determination from DRIFT spectroscopy yields a direct band gap of 0.479 eV (Figure 12).

Conclusions

The chemistry of metal-rich transition metal halide clusters is primarily characterized by the presence of octahedral metal clusters, which are readily formed in classical reduction reactions. Recently, insights have been provided into the reduction of transition metal halides using unconventional reduction agents such as Mn, Fe, Co, Cu, and others. These studies have revealed a basic reduction mechanism that involves a reductive intercalation followed by metal halide elimination.^[17]

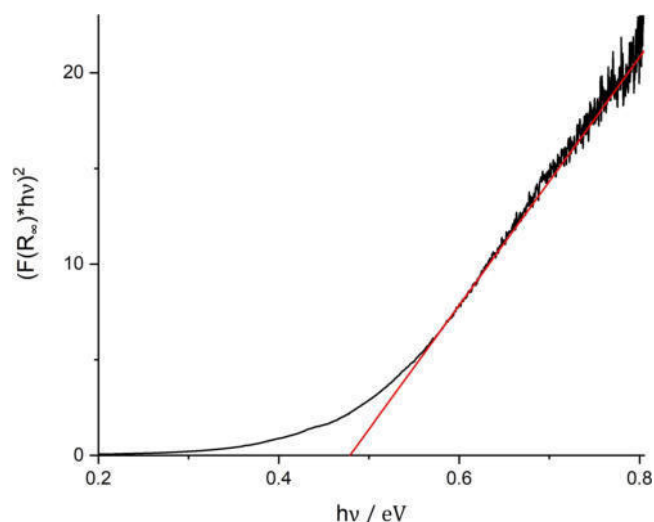


Figure 12. Tauc plot using $F(R_\infty)$ of $\text{Nb}_4\text{OI}_{10}$ for direct gap fitting (black) along with the linear extrapolation (red) to obtain the optical band gap.

The preparation of a metal-rich niobium oxyiodide through soft reduction described herein involves the use of a reducing agent to convert NbI_4 into the desired product $\text{Nb}_4\text{OI}_{10}$. The presence of oxygen in the reaction enables the formation of elusive phases in which solid $\text{Li}_2(\text{CN}_2)$ acts as a reduction agent.^[18] This process requires careful control of reaction conditions to ensure the formation of the desired product. The conditions involve a highly dynamic system whose equilibria depend on the temperature and on local concentrations, as has been previously shown for the W-O-I system.^[13]

By varying the synthetic conditions, four new metal-rich compounds have been characterized in the Nb-O-I system, each with their respective crystal structures. Among these compounds, $\text{Nb}_4\text{OI}_{10}$ stands out as the first example reported in this study. This discovery contributes to the expanding knowledge of the chemical behavior, properties, and potential applications of niobium-based materials.

Experimental Section

All manipulations of starting materials and products were performed in a glovebox under dry argon with moisture and oxygen levels below 1 ppm.

Synthesis

Li_2O (ABCR, 95%) was used as purchased. NbI_4 was synthesized as described in the literature.^[14] $\text{Li}_2(\text{CN}_2)$ was synthesized as described previously.^[26]

$\text{Nb}_4\text{OI}_{10}$ was synthesized from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol) and $\text{Li}_2(\text{CN}_2)$ (7.2 mg, 0.135 mmol) were encapsulated into a evacuated silica ampoule. The ampoule was heated from room temperature to 500 °C with a rate of 0.1 °C/min. The holding time was 36 h before the reaction was allowed to cool to room temperature with a rate of 2 °C/min. Plate-like crystals of $\text{Nb}_4\text{OI}_{10}$ were found on the wall at the upper part of the ampoule, along with some NbOI_2 and NbI_5

above. A powder pattern of the product was recorded (Figure S2). The estimated yield of $\text{Nb}_4\text{OI}_{10}$ was 28%. Crystals of $\text{Nb}_4\text{OI}_{10}$ appear black and can be handled in air for several days.

$\text{Nb}_4\text{OI}_{10}$ was also obtained when reacting NbI_4 with $\text{Pb}(\text{CN})_2$ (synthesized as described in the literature^[27]) and PbO (Merck, 99%) under the same reaction conditions, as confirmed in the recorded X-ray powder pattern of the reaction product (Figure S7).

Electron Microprobe Analysis (EMPA)

The presence of oxygen or nitrogen in the crystals was determined using a JEOL JXA-8230 electron microprobe at the University of Tübingen. For this purpose, single crystals of Nb_4OI_8 were fixed on a carbon tape sample holder. Analyses were carried out with an acceleration voltage of 15 kV and a probe current of 20 nA. For nitrogen the measured energy range was 0.3797–0.4064 keV, for oxygen 0.5034–0.551 keV.

Crystallography

A black plate-like single-crystal of $\text{Nb}_4\text{OI}_{10}$ was mounted on a Rigaku XtaLab Synergy-S X-ray diffractometer using MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation. The single crystal was kept under N_2 cooling at 150 K during the data collection. Corrections for absorption effects were applied with CrysAlisPro 171.41.64.93a (Rigaku Oxford Diffraction, 2020). The crystal structure was solved by the integrated space group and crystal-structure determination routine of SHELXT^[28] and full-matrix least-squares refinement with SHELXL-2014^[28] implemented in Olex2 1.3-ac4.^[29]

Reaction products were investigated by powder X-ray diffraction (PXRD) using a StadiP diffractometer (Stoe, Darmstadt) with Ge-monochromated $\text{Cu-K}_{\alpha 1}$ radiation and a Mythen1 Detector.

DRIFT (Diffuse Reflectance Infrared Fourier Transformation) Spectroscopy

Samples were measured at room temperature under inert conditions in diffuse reflectance with a Harrick Praying Mantis attachment using a Bruker Vertex 70 infrared spectrophotometer with a deuterated triglycine sulfate (DTGS) detector and KBr beam splitter. The background spectra were collected using pure dried KBr in powder form.

Density Functional Theory

Density functional theory (DFT) calculations were performed using the Abinit software package (v. 9).^[30] The Perdew–Burke–Ernzerhof exchange–correlation functional^[31] was used with the vdW–DFT–D3(BJ) dispersion correction of Grimme.^[32] A $3 \times 3 \times 3$ Monkhorst–Pack grid of k-points was used to construct the electronic structure of crystalline $\text{Nb}_4\text{OI}_{10}$.^[33] Plane-wave calculations were performed using the (PAW) method^[34] with an energy cutoff of 20 Ha outside of the PAW spheres and a 120 Ha cutoff inside them. PAW basis sets were used as received from the Abinit library.^[30] These computational parameters were chosen following convergence studies. Calculations of the electronic structure of the isolated clusters were performed in a cubic cell with 40 Bohr side lengths. The charge of the isolated anion was compensated by a uniform background charge.

Electrical Characterisation

Conductivity measurements were performed in a Lake Shore Cryotronics CRX-6.5 K probe station with a Keithley 2636B source meter unit. Plate-like Nb₄OI₁₀ crystals were contacted with silver paste on a silicon substrate with 770 nm oxide layer and transferred into the chamber under protective gas. The conductive silver pads at each end of the crystals were connected to the circuit with tungsten tips. The chamber was kept under vacuum ($<5 \cdot 10^{-5}$ mbar) and the temperature was varied between 50 K and 300 K. Before each measurement, sufficient time was allowed for the sample to reach the chosen temperature. Two-point conductivity measurements were performed by varying the applied source-drain voltage from -1 V to 1 V while detecting the current. For time-resolved photo-current measurements, using a picosecond pulsed laser driver (Taiko PDL M1, PicoQuant) together with a 779 nm laser head (pulse length <500 ps) the crystals were illuminated at 40 mW laser output power using the continuous wave mode under a constant bias of 1 V.

Supporting Information

Photograph of crystals, X-ray diffraction patterns of Nb₄OI₁₀, electron microprobe, electrical conductivity, and the calculated band structure of Nb₄OI₁₀.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: niobium halide · oxyiodide · crystal structure · semiconductor · cluster

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Supporting Information

The Rectangular Niobium Oxyiodide Cluster Nb₄OI₁₀ – A Narrow Band-Gap Semiconductor

Jan Beitzlberger, Markus Ströbele, Fabian Strauß, Marcus Scheele, Carl P. Romao, and Hans-Jürgen Meyer*

Supporting Information

The Rectangular Niobium Oxyiodide Cluster $\text{Nb}_4\text{OI}_{10}$ – A Narrow Band-Gap Semiconductor

Jan Beitzberger,^[a] Markus Ströbele,^[a] Fabian Strauß,^[b] Marcus Scheele,^[b] Carl P. Romao,^[c] and Hans-Jürgen Meyer^{*[a]}



Figure S1. Shape and dimensions of $\text{Nb}_4\text{OI}_{10}$ crystals.

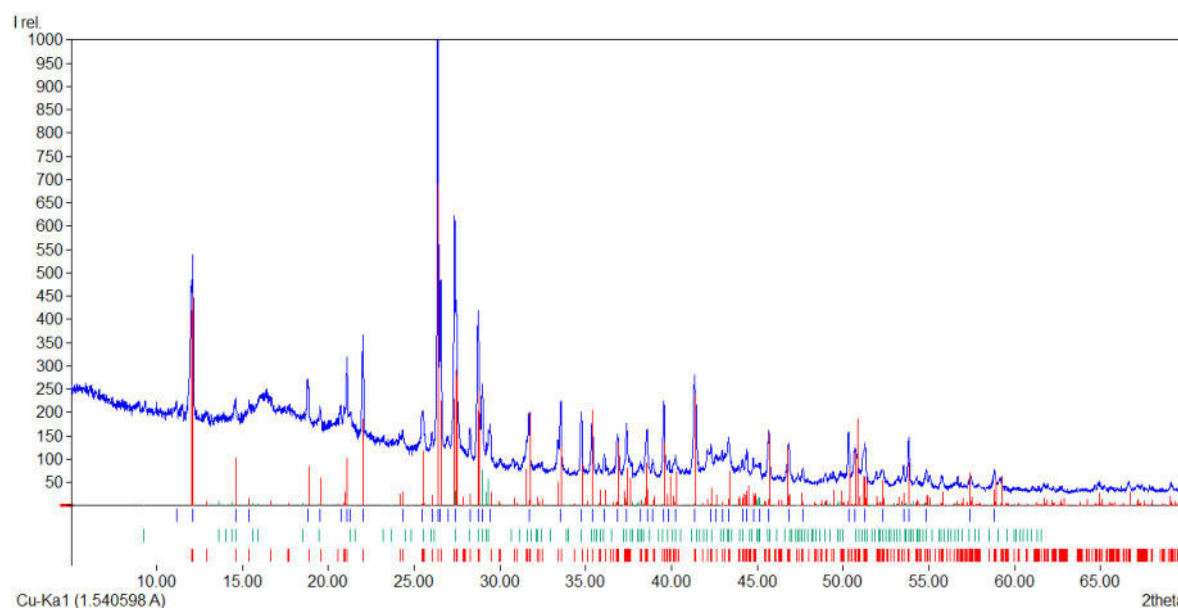


Figure S2. Measured powder X-ray diffraction pattern of $\text{Nb}_4\text{OI}_{10}$ with $\text{Cu-K}\alpha_1$ -radiation. In blue is the measured powder pattern, red corresponds to the calculated reflections single crystal X-ray measurement of $\text{Nb}_4\text{OI}_{10}$ and in green are the positions of the Bragg positions of coproduced NbI_5 ^[1].

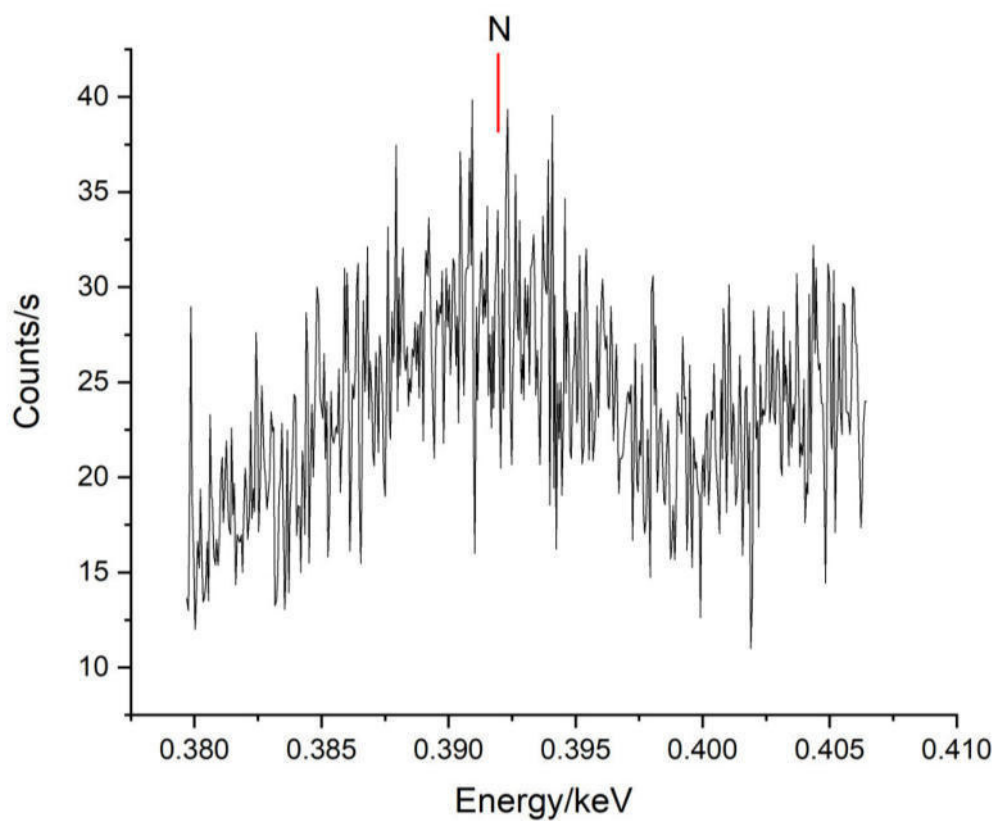


Figure S3. Electron microprobe measurement of Nb₄OI₁₀ in the K_{α1}-radiation energy range of nitrogen.

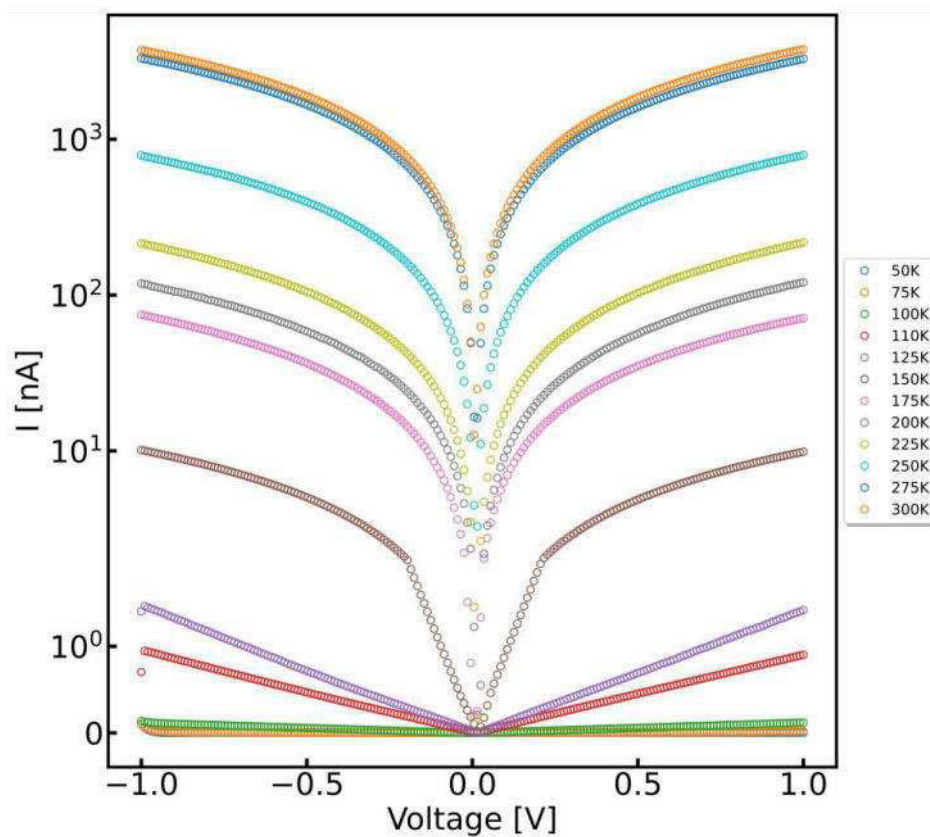


Figure S4. Source-Drain sweeps for different temperatures from 50 to 300 K.

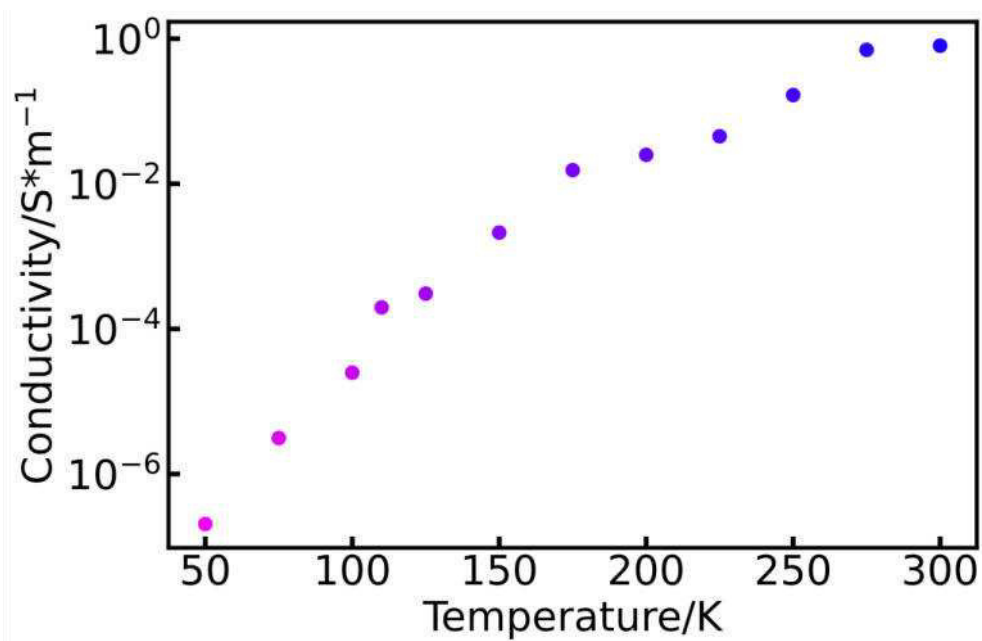


Figure S5. Electrical conductivity of a Nb₄OI₁₀ crystal at temperatures in the range of 50 K to 300 K.

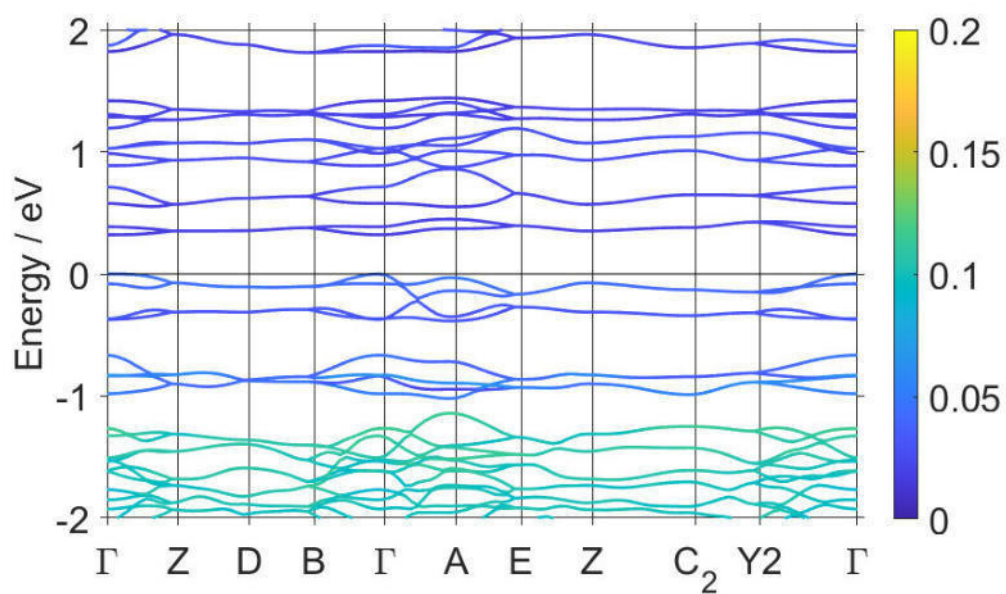


Figure S6. The DFT-calculated electronic band structure of Nb₄OI₁₀ with bands coloured by their iodine character.

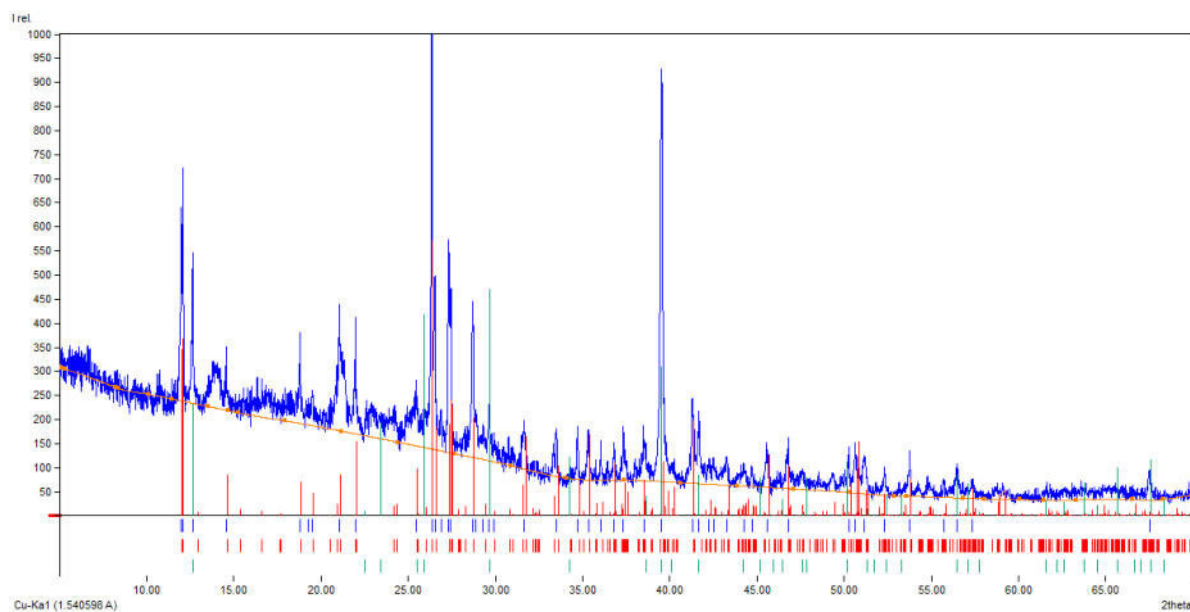
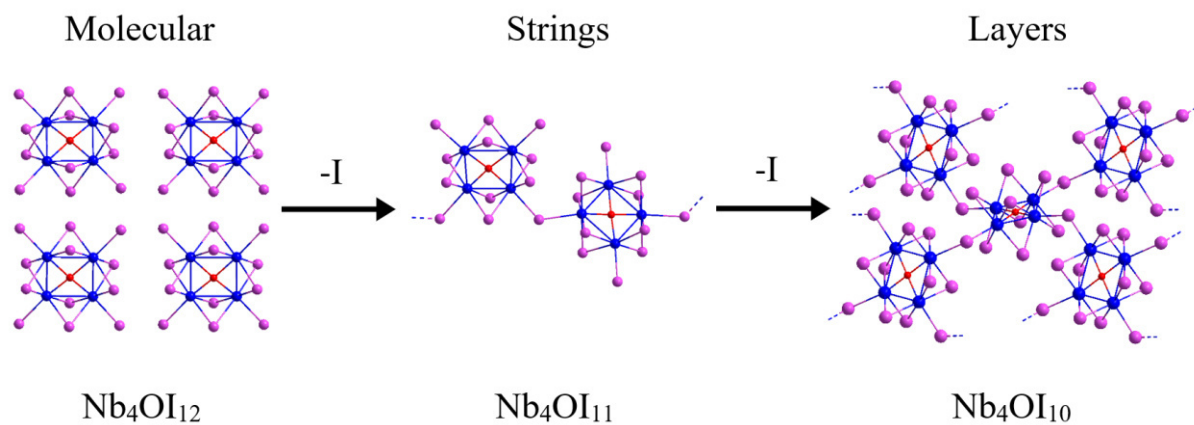


Figure S7. Measured powder X-ray diffraction pattern of Nb₄OI₁₀ with Cu-K_{α1}-radiation. In blue is the measured powder pattern, red correspond to the single crystal X-ray measurement of Nb₄OI₁₀ and green are Bragg positions of the metathesis salt PbI₂^[2].

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Publication 2

The family of tetranuclear $\text{Nb}_4\text{OI}_{12-x}$ clusters ($x = 0, 1, 2$): from the molecular $\text{Nb}_4\text{OI}_{12}$ cluster to extended chains and layers



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PAPER

[View Article Online](#)
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Unconventional reduction reactions in the Nb–O–I system have produced a number of niobium oxyiodides containing the oxygen-centered $[\text{Nb}_4\text{O}]$ cluster. Crystalline $\text{Nb}_4\text{OI}_{12}$ and two modifications of $\text{Nb}_4\text{OI}_{11}$ were structurally characterized by means of single-crystal X-ray diffraction studies. The new compounds can be classified as members of the $\text{Nb}_4\text{OI}_{12-x}$ family, together with the already known $\text{Nb}_4\text{OI}_{10}$. $\text{Nb}_4\text{OI}_{12}$ is represented by a molecular structure, in which the two modifications of $\text{Nb}_4\text{OI}_{11}$ are forming structures with iodido-bridged strings, that can be assigned to represent one-dimensional structures. Measurements of b- $\text{Nb}_4\text{OI}_{11}$ single crystals reveal semiconducting behaviour, with an electrical conductivity in the order of 10^{-3} S m^{-1} at 300 K and an electrical band gap estimated as 0.4 eV. The presence of varying numbers of cluster electrons in the given compounds is discussed in the light of second-order Jahn–Teller distortion.

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Introduction

Metal clusters display a broad variety in structural arrangements and oxidation states. A large number of transition metal (M) halide (X) clusters have been reported with the octahedral $[\text{M}_6]$ cluster core, being represented with $[\text{M}_6\text{X}_{12}]$ - and $[\text{M}_6\text{X}_8]$ -type architectures.¹ The $[\text{M}_6\text{X}_{12}]$ -type constitutes an octahedral M_6 cluster with twelve X atoms capping all edges of the M_6 core and is typically obtained for combinations of larger M and smaller X atoms. The $[\text{M}_6\text{X}_8]$ cluster constitutes an octahedral cluster with eight face-capping ligands of the M_6 cluster and is typically obtained for combinations of smaller M and larger X atoms. The well-known niobium cluster compounds $\text{Nb}_6\text{Cl}_{14}$ and Nb_6I_{11} are good examples of these two architectures, of which the latter can be described as $(\text{Nb}_6\text{I}_8)\text{I}^{a-a}_{6/2}$ (i = innen or inner; a = außen or outer), emphasizing the presence of an $[\text{M}_6\text{X}_8]$ cluster and a connectivity pattern in which six outer iodide ligands are shared between two clusters.^{2,3}

The connectivity between adjacent cluster cores and the number of cluster electrons being present has an important impact on the electronic properties of cluster compounds. A connectivity, where inner ligands simultaneously act as outer ones (i - a and a - i connectivity), is obtained in Chevrel phases like PbMo_6S_8 , which is showing superconducting properties as a result of metal-to-metal interactions between adjacent clusters.⁴

A successive dimensional reduction of cluster connectivities is exemplified when going from Nb_6I_{11} $[(\text{Nb}_6\text{I}_8)\text{I}^{a-a}_{6/2}]$ having six shared outer ligands in three dimensions, along to W_6I_{12} $[(\text{W}_6\text{I}_8)\text{I}^{a-a}_{4/2}]$ having four bridging apical ligands, creating layers, and finally to $\text{BiW}_6\text{Cl}_{15}$ $[\text{BiCl}_2(\text{W}_6\text{Cl}_8)\text{Cl}^a_4\text{Cl}^{a-a}_{2/2}]$ with two bridging apical ligands, creating a linear arrangement of clusters.^{3,5} Isolated clusters like W_6Cl_{18} $((\text{W}_6\text{Cl}_8)\text{Cl}^a_6)$ are held together by van der Waals forces.⁶

Metal-rich niobium iodides involve the compounds Nb_6I_{11} , Nb_3I_8 , NbI_3 , and NbI_4 .^{3,7} A promising approach for the expansion of this chemistry is the introduction of another anion to create a heteroanionic metal cluster compound. An early outcome of this approach was the insertion of an interstitial atom (Z) into the octahedral $[\text{M}_6\text{X}_{12}]$ -type cluster core to yield $[\text{M}_6\text{ZX}_{12}]$, mostly evident with the electron-poorer d-metals (M = Zr, Hf).⁸ The formation of an interstitially stabilized cluster is uncommon for $[\text{M}_6\text{X}_8]$ -type clusters, obviously due to an unfavorable short distance between the interstitial and the face-capping anion, causing repulsion. An exception is Nb_6I_{11} which can incorporate a hydrogen atom to form the interstitially stabilized compound $\text{Nb}_6\text{HI}_{11}$.⁹

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† Electronic supplementary information (ESI) available: IR spectra, X-ray diffraction pattern of b- $\text{Nb}_4\text{OI}_{11}$, photographs of crystals. CCDC 2366237, 2391069 and 2408695. For crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5dt00174a>

Generally, heteroanionic clusters can also be envisioned to constitute anion replacements in given architectures to induce a modified structure or connectivity pattern of clusters, as exemplified for $\text{Nb}_6\text{I}_9\text{S}$ (derived from Nb_6I_{11}), $\text{Nb}_3\text{X}_7\text{S}$ ($\text{X} = \text{Cl}$, Br , I) and $\text{ANb}_3\text{Br}_7\text{S}$ with $\text{A} = \text{Rb}$, Cs (derived from Nb_3X_8).¹⁰

The employment of oxide as a heteroanion unavoidably leads to the formation of oxyhalides NbOI_2 , NbOI_3 and NbO_2I .¹¹ However, it has been demonstrated that new oxyiodide cluster compounds can be obtained under certain conditions. A most recent example of a new oxyiodide cluster is $\text{Nb}_4\text{OI}_{10}$, which has been characterized as a small band-gap semiconductor showing photoresponse.¹² Its crystal structure can be easily derived from that of Nb_6I_{11} by cutting-off two $(\text{NbI}^{a-a}_{1/2})$ -groups of $(\text{Nb}_6\text{I}_8)\text{I}^{a-a}_{6/2}$. The resulting planar $[(\text{Nb}_4\text{OI}_8)\text{I}^{a-a}_{4/2}]$ cluster is allowing the presence of a surplus oxygen atom in the cluster center. The relaxation of inner iodide ligands in this structure is avoiding strong interanionic $\text{O}-\text{I}$ repulsions that would likely inhibit an oxygen centering in Nb_6I_{11} .

The preparation of niobium oxyiodide cluster compounds requires subtle control of reaction conditions and can otherwise lead to the crystallization of the thermodynamic more stable known niobium oxyiodides. Such conditions involve a highly dynamic system including elusive phases whose equilibria depend on the temperature and on local concentrations, as has been previously demonstrated with the newly discovered compound $\text{W}_2\text{O}_3\text{I}_4$ in the $\text{W}-\text{O}-\text{I}$ system.¹³ By varying the synthetic conditions, we herein describe the crystal structures of three tetranuclear niobium cluster compounds that we have characterized in the $\text{Nb}-\text{O}-\text{I}$ system. The previously reported $\text{Nb}_4\text{OI}_{10}$ and the herein described compounds are represented by a $[\text{Nb}_4\text{O}]$ cluster core that is interconnected in different ways following a dimensional reduction from layers ($\text{Nb}_4\text{OI}_{10}$) over strings ($\text{Nb}_4\text{OI}_{11}$) to isolated molecules ($\text{Nb}_4\text{OI}_{12}$).

Results and discussion

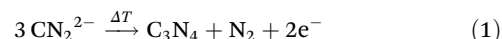
Synthesis and crystal structure

Recently, we have described the new cluster compound $\text{Nb}_4\text{OI}_{10}$ whose structure is based on a rectangular $[\text{Nb}_4\text{O}]$ core that is interconnected into layers by iodide ligands.¹² The crystal structure features a two-dimensional van der Waals material representing a small band gap semiconductor.

Slight variations of the synthesis conditions relative to those given for $\text{Nb}_4\text{OI}_{10}$ revealed the existence of a number of related compounds to exist in the $\text{Nb}-\text{O}-\text{I}$ system. These compounds are generated by changing the concentrations of reaction partners and by subtle variations of the temperature program of reactions. For a general understanding of this type of reaction we have to consider the chemical changes that occur on heating solid reactants in a heterogeneous solid-state reaction with the involvement of solid and gaseous phases. This has been already exemplified by the formation of niobium oxyiodides (NbOI_2 , NbOI_3 and NbO_2I) that were described previously.¹¹ For the preparation of reduced com-

pounds in the $\text{Nb}-\text{O}-\text{I}$ system, we are avoiding the classical pathway of a metallothermic reduction. Instead, we are exploring unconventional reduction agents with the employment of the carbodiimide ion $(\text{N}=\text{C}=\text{N})^{2-}$.

At elevated temperatures, carbodiimides have the tendency to decompose and to act as reducing agents. In this process, metal ions can be reduced, some even to form the metal state.¹⁴ The decomposition product of carbodiimide in such a reaction is not fully evidenced, as products appear X-ray amorphous. However, infrared spectra indicate the formation of C_3N_4 (Fig. S1 and S2†).¹⁵ A corresponding reduction mechanism could follow reaction (1).



All three compounds reported in this work crystallize as black, block-like crystals (Fig. 1). They were investigated by X-ray powder and single-crystal diffraction, providing X-ray intensity data for subsequent crystal structure determinations. The crystallographic data and refinement parameters of all tetranuclear cluster compounds are summarized in Table 1.

Syntheses of the new compounds are performed in evacuated/fused silica tubes at temperatures up to 500 °C. $\text{Nb}_4\text{OI}_{12}$ and $\text{b-Nb}_4\text{OI}_{11}$ were prepared from $\text{NbI}_4 : \text{Li}_2(\text{CN}_2) : \text{Li}_2\text{O}$ mixtures with 4 : 1 : 1 and 4 : 1.5 : 1 molar proportions, respectively. $\text{a-Nb}_4\text{OI}_{11}$ was synthesized by a reaction mixture of $\text{NbI}_4 : \text{K}_2\text{CN}_2 : \text{Cu}_2\text{O}$ in 4 : 1.5 : 1 molar ratio (see Experimental section for more details).

The $\text{Nb}_4\text{OI}_{12-x}$ system includes four structures with sum formulae $\text{Nb}_4\text{OI}_{12}$, $\text{Nb}_4\text{OI}_{11}$, and $\text{Nb}_4\text{OI}_{10}$. $\text{Nb}_4\text{OI}_{11}$ appears with two modifications, denoted as “a” and “b”.

The parent compound $\text{Nb}_4\text{OI}_{12}$ features a molecular structure based on the rectangular $[\text{Nb}_4\text{O}]$ cluster core with eight (μ_2 -) capping and four terminal iodide atoms, shown in Fig. 2. The unit cell contains eight molecules that interact through

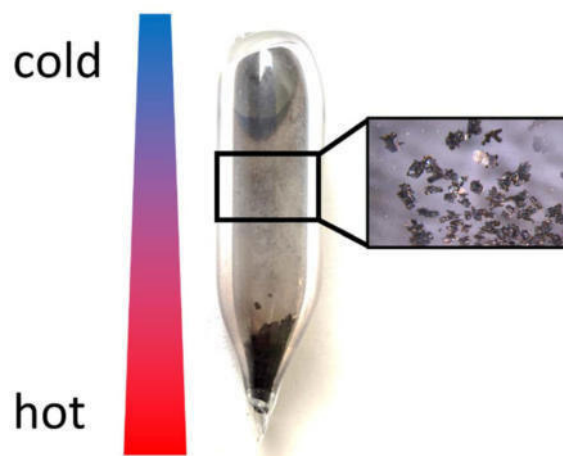


Fig. 1 A typical ampoule after the reaction is performed. The temperature gradient during the reaction is illustrated through the bar on the left side (red: hot region, blue cold region). The inset shows the reaction product $\text{b-Nb}_4\text{OI}_{11}$ (see also Fig. S4†).



Table 1 Crystal data and structure refinement parameters of Nb₄OI_{12-x} compounds

	Nb ₄ OI ₁₂	a-Nb ₄ OI ₁₁	b-Nb ₄ OI ₁₁	Nb ₄ OI ₁₀ ¹²
CCDC no.	2366237	2391069	2408695	2225618
Space group	<i>Pmc</i> 2 ₁	<i>C</i> 2/ <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	270	220	150	150
Unit cell dimensions	<i>a</i> = 37.9189(8) Å <i>b</i> = 17.8026(4) Å <i>c</i> = 7.3403(2) Å α = 90° β = 90° γ = 90°	<i>a</i> = 15.4442(3) Å <i>b</i> = 13.0449(2) Å <i>c</i> = 11.9078(2) Å α = 90° β = 105.698(2)° γ = 90°	<i>a</i> = 10.1217(2) Å <i>b</i> = 13.9844(3) Å <i>c</i> = 16.3913(3) Å α = 88.968(2)° β = 89.093(2)° γ = 85.329(2)°	<i>a</i> = 10.0435(1) Å <i>b</i> = 10.6595(1) Å <i>c</i> = 10.0594(1) Å α = 90° β = 94.193(1)° γ = 90°
Volume (Å ³)	4955.1(2)	2309.56(7)	2311.80(8)	1074.06(2)
<i>Z</i>	8	4	2	2
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	16.744	16.624	16.607	16.433
2 θ range for data collection	4.576 to 50.700	4.154 to 57.396	7.186 to 76.742	5.532 to 72.638
Total number of reflections	53 804	44 103	17 704	80 092
Independent reflections	9037	3115	17 704	5209
Refined parameters	418	91	290	71
<i>R</i> _{int}	0.0351	0.0189	0.020	0.0354
<i>R</i> ₁	0.0517	0.0150	0.0185	0.0117
<i>wR</i> ₂	0.1414	0.0314	0.0581	0.0282
Goodness-of-fit on <i>F</i> ²	1.086	1.430	1.037	1.093

van der Waals bonding. The crystal structure measurement was performed near room temperature because low-temperature measurements revealed incoherent scattering patterns, which could be likely indicative for the appearance of a phase-transition.

Three distinct Nb₄OI₁₂ molecules are present in the crystal structure. Each of them exhibits a (nearly) rectangular cluster core with six electrons being available for Nb–Nb bonding. The bond lengths of the cluster cores hold a small variability (Fig. 2). The short and the long interatomic distances of the cluster are in the range of 2.793(3)–2.807(3) Å and 3.029(7)–3.051(3) Å, suggesting more electron density in each shorter Nb–Nb contact. Regarding the crystal structure, the Nb₄OI₁₂ molecules are arranged in layers along the *ac*- and *bc*-planes (Fig. 3). When looking along the *b* axis (Fig. 3, right), the stacking of the molecules in the *a* direction could be explained as an ABCB sequence, although there is no closest packing of the molecules. The molecules are just arranging to each other in three different *bc*-planes (denoted in Fig. 3 as A, B and C) to reduce repulsion.

When departing from the molecular Nb₄OI₁₂ structure, the crystal structure of Nb₄OI₁₁ contains one iodide atom less and appears with two modifications. We denote these modifications with “a” and “b” because no conversion from one into the other structure could be discovered experimentally. The structure of a-Nb₄OI₁₁ is represented by a string-like connectivity of (Nb₄OI₈)I₂I_{2/2} cluster chains, in which each of the two distinct clusters is iodine bridged in a *trans* connection to the next cluster (Fig. 4). The [Nb₄O] cluster cores in this structure are as well in a rectangular shape, having two short (2.7368(6)–2.7584(7) Å) and two long (3.0375(6)–3.0423(6) Å) Nb–Nb distances.

The presence of Nb₂ atoms over all equivalent (8j) positions would create a layered structure with [Nb₄O]- and [Nb₆O]-cluster cores, shown in Fig. 5. However, the Nb₂ positions

(highlighted in light blue) are occupied by only $\frac{1}{2}$ resulting in a string connectivity. In fact, this picture (Fig. 5) represents a superposition of the alternating layers in the structure. The crystal structure of a-Nb₄OI₁₁ is characterized by two alternating layers of (Nb₄OI₈)I₂I_{2/2} that are stacked on top of each other along the [100] direction. The cluster strings within the alternating layers in the structure, each of them shown in Fig. 6, are running in two different directions ([011] and [01–1]). This arrangement affords an alternating occupation of Nb₂ positions in each layer. The adhesion between adjacent strings and layers in the structure can be described as van der Waals type, forming a hexagonal packing of strings.

Another modification of Nb₄OI₁₁ is denoted as b-Nb₄OI₁₁. The crystal structure of b-Nb₄OI₁₁ again features a string-like connectivity of two distinct [Nb₄O] clusters. However, the connectivity pattern *via* iodine atoms alternates with a *cis* and a *trans* connectivity of [Nb₄O] cores. Each *trans* connected cluster includes two short and two long Nb–Nb distance within the [Nb₄O] core. The same is true for the *cis* connected cluster. However, the *cis* connectivity induces a significant distortion to the cluster, specified in Table 2.

The unit cell of the crystal structure of b-Nb₄OI₁₁ is projected in Fig. 7. In contrast to the bidirectional arrangement of cluster strings in the structure of a-Nb₄OI₁₁, all cluster strings in b-Nb₄OI₁₁ are running parallel into one direction ([001]). A view on the projected *ab*-plane suggests that the separate strings are hold together by van der Waals interactions. The given arrangement of (Nb₄OI₈)I₂I_{2/2} chains be derived from a hexagonal packing of strings, which is a typical structure pattern observed for one-dimensional structures (Fig. 8).

Electrical conductivity of b-Nb₄OI₁₁

Crystal structures like those of a- and b-Nb₄OI₁₁ with one-dimensional connectivities may be expected to act as one-



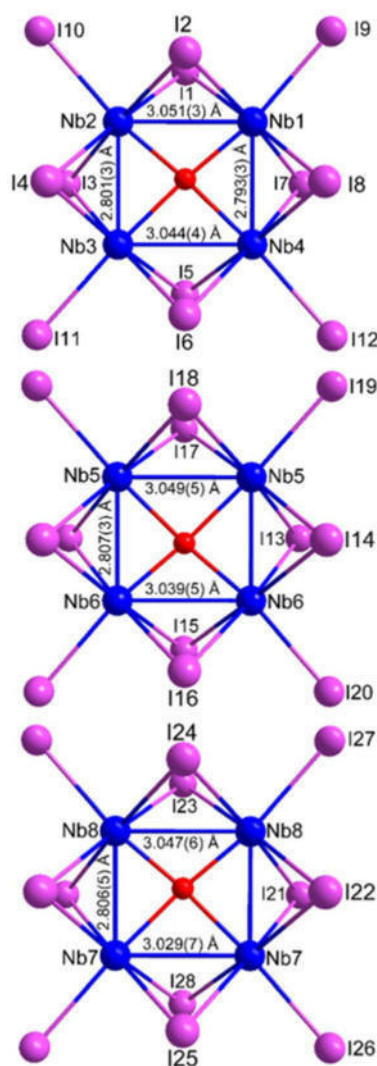


Fig. 2 Three distinct $\text{Nb}_4\text{OI}_{12}$ molecules with atom labels and Nb–Nb distances given.

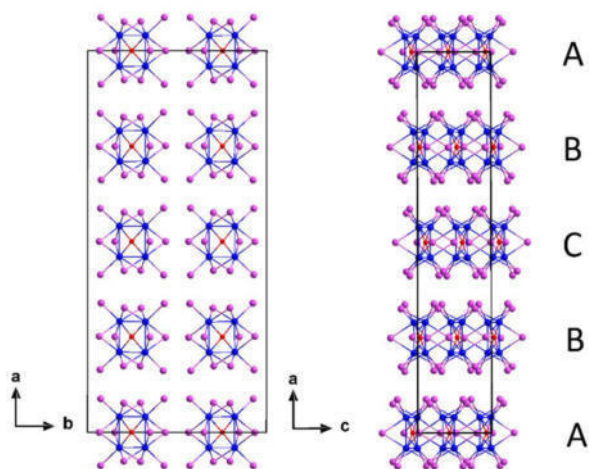


Fig. 3 Section of the crystal structure of $\text{Nb}_4\text{OI}_{12}$, looking along the c - and b -axis. Niobium atoms are coloured in blue, iodine in pink, and oxygen in red.

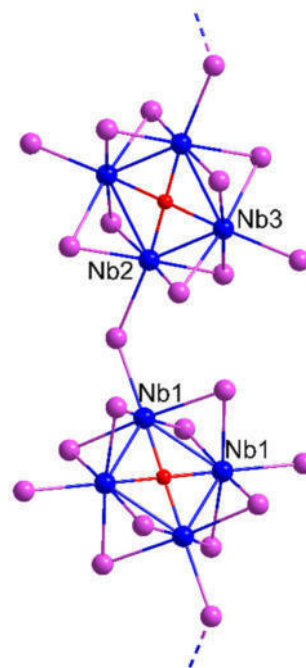


Fig. 4 String-like connectivity in the structure of $a\text{-Nb}_4\text{OI}_{11}$.

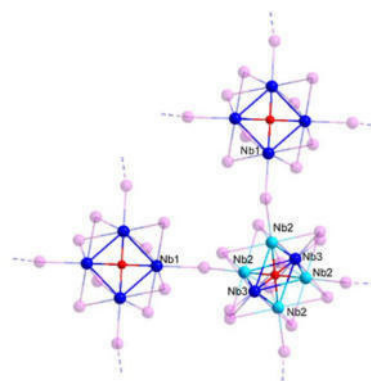


Fig. 5 Cluster connectivity in the structure of $a\text{-Nb}_4\text{OI}_{11}$ with the equivalent Nb2 positions coloured in cyan. Due to the half-occupation of Nb2 sites, only one pair of Nb2 atoms is present.

dimensional conductors. Hence, the electrical conductivity properties of single crystals of $b\text{-Nb}_4\text{OI}_{11}$ were investigated.

In Fig. 9, we display a two-point probe I – U sweep of a typical rod-shaped $b\text{-Nb}_4\text{OI}_{11}$ crystal from which we calculate the electrical conductivity as $\sigma = 4.5 \times 10^{-3} \text{ S m}^{-1}$ at 300 K.^{16,17}

The temperature-dependent conductivity measurement in Fig. 10 indicates an Arrhenius-type, temperature-activated transport, which is typical for semiconducting materials.^{12,17,18}

From this plot, we obtain an activation energy of $E_A = 0.2 \text{ eV}$. Thus, in a first-order approximation the energy difference of the Fermi level to the conduction band can be gauged as 0.2 eV. Under the assumption of an intrinsic position of the Fermi



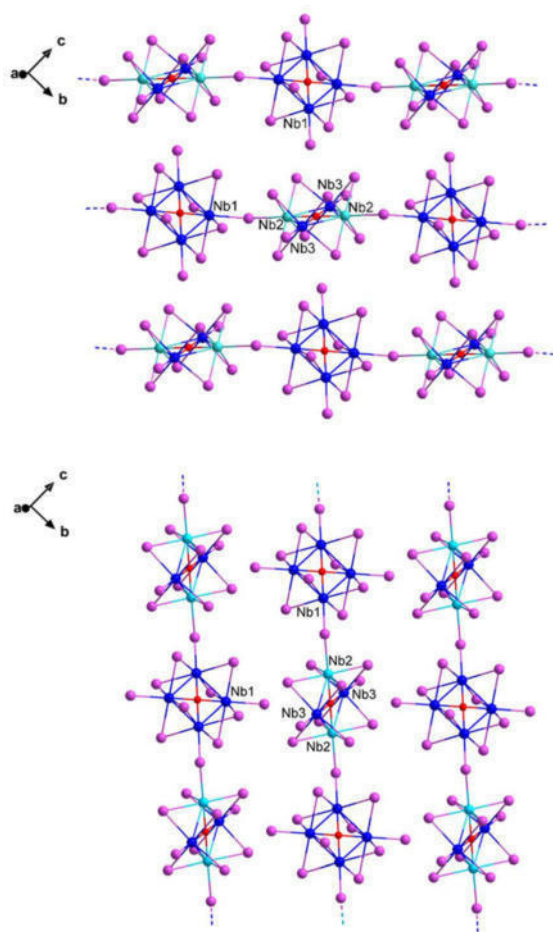


Fig. 6 Arrangement of individual cluster layers in the structure, based on string-like connectivities in the structure of a-Nb₄OI₁₁.

level, this would suggest an electrical band gap on the order of 0.4 eV.

The photoresponse at 300 K of b-Nb₄OI₁₁ toward optical excitation with a 779 nm laser in continuous wave mode is shown in Fig. 11. An initial fast photocurrent of ~65 nA is followed by a slower, second component under continuous excitation. We attribute this slow component to thermal excitation by heating the crystal with the laser. At lower temperature, the photocurrent decreases substantially, *e.g.* to 12.6 pA at 160 K.

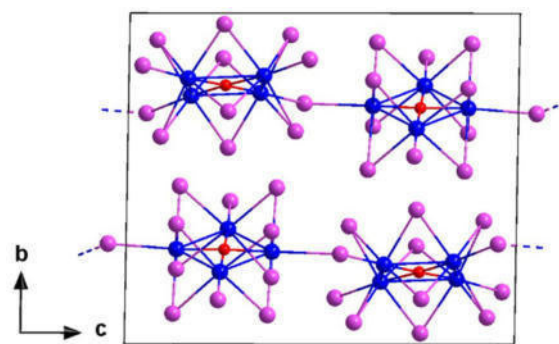


Fig. 7 Section of the crystal structure of b-Nb₄OI₁₁, looking along [100].

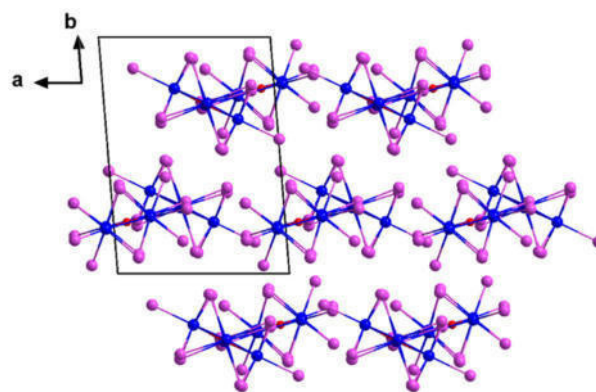


Fig. 8 Section of the crystal structure of b-Nb₄OI₁₁, following the [001] string direction.

Electronic properties of Nb₄OI_{12-x} compounds

One member of the Nb₄OI_{12-x} family was already described before as Nb₄OI₁₀.¹² Nb₄OI₁₀ appears with black, plate-like crystals with an electronic band gap near 0.4 eV, according to an experimental bandgap determination and band structure calculation. This compound contains (Nb₄OI₈)I_{4/2} units that are connected into layers, through four shared apical iodide atoms (Fig. 12). The cluster core itself is rectangular with Nb–Nb distances of 2.6232(2) Å and 3.1042(2) Å. This compound was reported with an electrical conductivity of $\sigma \approx 1 \text{ S m}^{-1}$ at 300 K.

Table 2 The Nb₄OI_{12-x} family with the respective number of cluster electrons of each compound, interatomic distances with average values ($\bar{\phi}$) and distance ranges along the short and long cluster edges, and angles within the [Nb₄O] cluster core

	Nb ₄ OI ₁₂ 6 cluster-e ⁻	a-Nb ₄ OI ₁₁ 7 cluster-e ⁻	b-Nb ₄ OI ₁₁ (<i>trans</i>) 7 cluster-e ⁻	b-Nb ₄ OI ₁₁ (<i>cis</i>) 7 cluster-e ⁻	Nb ₄ OI ₁₀ ¹² 8 cluster-e ⁻
short Nb–Nb (Å)	$\bar{\phi}$ 2.802 2.793(3)–2.807(3)	$\bar{\phi}$ 2.748 2.7368(6)–2.7584(7)	$\bar{\phi}$ 2.735 2.7329(8)–2.7369(8)	$\bar{\phi}$ 2.729 2.7288(8)–2.7299(8)	2.6232(2)
long Nb–Nb (Å)	$\bar{\phi}$ 3.044 3.029(7)–3.051(3)	$\bar{\phi}$ 3.040 3.0375(6)–3.0423(6)	$\bar{\phi}$ 3.054 3.0423(8)–3.0656(8)	$\bar{\phi}$ 3.056 2.9168(7)–3.1950(8)	3.1042(2)
small Nb–Nb–Nb (°)	89.81(9)–89.93(9)	87.47(2)	87.34(2)–87.88(2)	87.01(2)–87.14(2)	89.568(6)
large Nb–Nb–Nb (°)	90.11(8)–90.23(9)	92.53(1)	92.17(2)–92.60(2)	92.87(2)–92.97(2)	90.431(6)



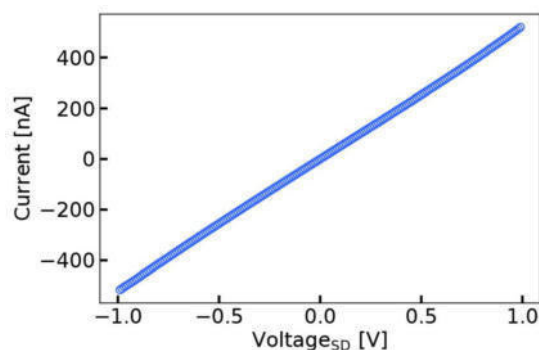


Fig. 9 I - U sweep in the dark of b-Nb₄OI₁₁ at 300 K.

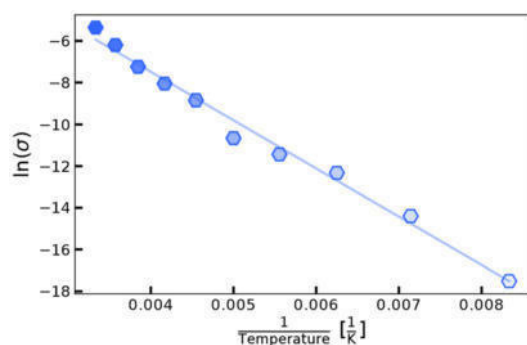


Fig. 10 Arrhenius plot of the electrical conductivity of b-Nb₄OI₁₁, with 20 K temperature steps between 120–300 K. The blue line represents a linear Arrhenius fit to the data.

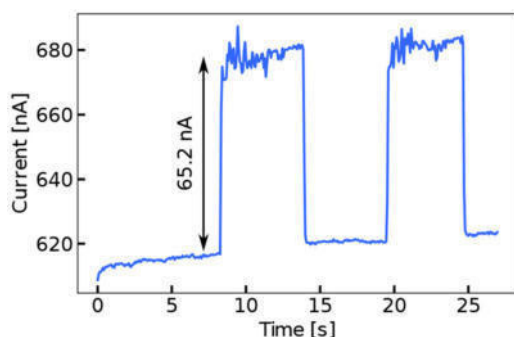


Fig. 11 Photoresponse of b-Nb₄OI₁₁ at 300 K toward a 779 nm laser illumination with 1 V bias applied.

Beside their different connectivities, the cluster compounds of the Nb₄OI_{12-x} family differ not only in their Nb–Nb bond lengths and Nb–Nb–Nb angles, but also by their numbers of cluster electrons, as summarized in Table 2.¹²

From Nb₄OI₁₂ to Nb₄OI₁₀ there is a difference of two electrons being available for niobium-to-niobium bonding. All compounds are forming nearly rectangular [Nb₄O] clusters in which the longer edges possess almost the same Nb–Nb distances (see Table 2). For the example of Nb₄OI₁₀ we already discussed the higher stability of a rectangular *versus* a square cluster core. The resulting symmetry lowering goes along with

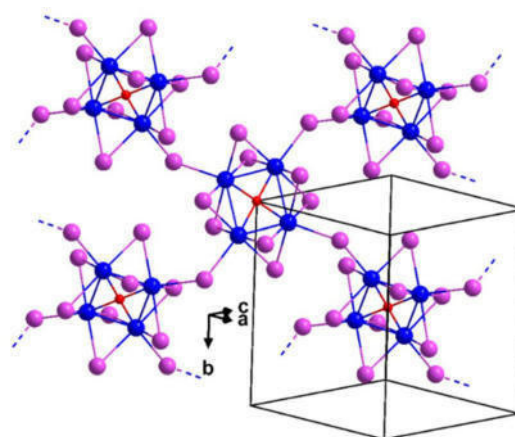


Fig. 12 Visualization of the connectivity of Nb₄OI₁₀.¹²

an increase in hybridization of molecular orbitals through a second-order Jahn–Teller distortion. In other words, the series of compounds are showing higher electron localization within the two shorter edges of [Nb₄O] cluster cores. The rectangular niobium arrangement hosts six electrons for Nb₄OI₁₂, seven electrons for Nb₄OI₁₁, and eight electrons for Nb₄OI₁₀, thereby undergoing a continuous shrinkage of the short Nb–Nb distance, with the values given in Table 2.

If there were less than six electrons for Nb–Nb bonding, the bond lengths should elongate even more. Such a compound is not yet known in the Nb–O–I system. However, the structure of Nb₄OTe₉I₄ contains an oxygen centered Nb₄ cluster core having four cluster electrons for Nb–Nb bonding.¹⁹ The cluster is distorted into a flattened tetrahedral shape with nearly equal Nb–Nb distances of 3.057(4) Å and 3.050(3) Å. These are quite close to the long distances present in the [Nb₄O] cluster cores presented in this work.

Conclusion

Cluster compounds can show a broad flexibility in their oxidation states. A well-established example is the binary tungsten-iodide system, with more than 20 different structures being reported.²⁰ The addition of oxygen leads into the W–O–I system, that is well-known because WO₂I₂ is a prominent compound in chemical vapor transport (CVT) reactions.¹³ The thermal treatment of WO₂I₂ leads to W₂O₃I₄ first, and then to WO₂. All oxides and oxyiodides in this system appear under discrete temperature conditions.

An even broader chemistry is now discovered in the Nb–O–I system for Nb₄OI_{12-x} ($x = 0, 1, 2$) compounds, with their rectangular [Nb₄O] cluster cores appearing in layers, strings, and in isolated molecules. The distinct connectivity patterns in the crystal structures involve different semiconducting properties.

These compounds could not be prepared in conventional reduction attempts through metallothermic reduction. In contrast, comparably soft reduction conditions were successful, with the carbodiimide ion as reducing agent. Hence, the formation of compounds in the Nb–O–I system involves uncon-



ventional reduction reactions in heterogeneous solid-state reactions. The product formation involves subtle equilibrium conditions related to small changes in temperature and local concentrations. These conditions appear fairly complex and are further complicated by other new compounds that exist in the given Nb–O–I system besides the herein described tetranuclear cluster compounds. The discovery of compounds with pentanuclear and heptanuclear niobium clusters in the Nb–O–I system will be reported shortly.

Experimental section

Materials and methods

Manipulations of starting materials and products were performed in a glovebox under dry argon with moisture and oxygen levels below 1 ppm. Reaction partners were charged into silica tubes ($V \approx 1.5 \text{ cm}^3$). Li_2O (ABCR, 95%) and Cu_2O (Sigma-Aldrich, 99.99%) were used as purchased. NbI_4 , $\text{Li}_2(\text{CN}_2)$ and $\text{K}_2(\text{CN}_2)$ were synthesized as described in the literature.²¹ $\text{Nb}_4\text{OI}_{10}$ was synthesized as described before.¹²

Syntheses

$\text{b-Nb}_4\text{OI}_{11}$ and $\text{Nb}_4\text{OI}_{12}$ were synthesized from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol), and $\text{Li}_2(\text{CN}_2)$ (5.4 mg, 0.101 mmol ($\text{b-Nb}_4\text{OI}_{11}$) or 3.6 mg, 0.067 mmol ($\text{Nb}_4\text{OI}_{12}$)) were encapsulated into fused silica ampoules. The ampoules were heated from room temperature to 500 °C with a rate of 0.1 °C min^{-1} . The holding time was 24 h before the reactions were allowed to cool to room temperature with a rate of 5 °C min^{-1} for $\text{b-Nb}_4\text{OI}_{11}$ and a rate of 10 °C min^{-1} for $\text{Nb}_4\text{OI}_{12}$. Block-like crystals of $\text{b-Nb}_4\text{OI}_{11}$ and $\text{Nb}_4\text{OI}_{12}$ were found on the wall of the ampoule, along with some NbOI_2 and NbI_5 at the top of the ampoule. The products were collected mechanically. The compounds are sensitive to moisture. A powder XRD pattern of $\text{b-Nb}_4\text{OI}_{11}$ is shown in Fig. S3.† Examples of crystal specimens of $\text{b-Nb}_4\text{OI}_{11}$ and $\text{Nb}_4\text{OI}_{12}$ can be seen in Fig. S4 and S5.†

$\text{a-Nb}_4\text{OI}_{11}$ was synthesized from NbI_4 , Cu_2O and $\text{K}_2(\text{CN}_2)$. For this purpose, NbI_4 (100.7 mg, 0.168 mmol), Cu_2O (6 mg, 0.042 mmol), and $\text{K}_2(\text{CN}_2)$ (7.4 mg, 0.063 mmol) were encapsulated into a fused silica ampoule. The ampoule was heated from room temperature to 500 °C with a rate of 0.1 °C min^{-1} . The holding time was 24 h before the reaction was allowed to cool to room temperature with a rate of 5 °C min^{-1} . Block-like crystals of $\text{a-Nb}_4\text{OI}_{11}$ were found on the wall of the ampoule, along with some NbOI_2 and NbI_5 at the top of the ampoule. The product was collected mechanically. The compound is sensitive to moisture.

Instrumentation

X-ray diffraction

Black block-shaped single-crystals of $\text{a-Nb}_4\text{OI}_{11}$, $\text{b-Nb}_4\text{OI}_{11}$, and $\text{Nb}_4\text{OI}_{12}$ were mounted on a Rigaku XtaLab Synergy-S X-ray diffractometer using $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The single-crystal

was kept under N_2 cooling at 270 K for $\text{Nb}_4\text{OI}_{12}$, at 220 K for $\text{a-Nb}_4\text{OI}_{11}$ and at 150 K for $\text{b-Nb}_4\text{OI}_{11}$ during the data collection. Corrections for absorption effects were applied with CrysAlisPro (Rigaku Oxford Diffraction, 2020). The crystal structure was solved by the integrated space group and crystal structure determination routine of ShelXT²² and refined by full-matrix least-squares refinement with ShelXL–2019/3²² implemented in Olex2.²³

Reaction products were investigated by powder X-ray diffraction (PXRD) using a StadiP diffractometer (Stoe, Darmstadt) with $\text{Ge}[111]$ -monochromated $\text{Cu-K}\alpha_1$ radiation and a mythen1 detector.

Electrical conductivity

Conductivity measurements were performed in a Lake Shore Cryotronics CRX–6.5 K probe station with a Keithley 2636B source meter unit. Block-shaped $\text{b-Nb}_4\text{OI}_{11}$ crystals were contacted with silver paste on a silicon substrate with 770 nm oxide layer and transferred into the chamber under protective gas. The conductive silver pads at each end of the crystals were connected to the circuit with tungsten tips. The chamber was kept under vacuum ($<5 \times 10^{-5}$ mbar) with 20 K temperature steps between 120 K and 300 K during the measurements. Two-point conductivity measurements were performed by varying the applied source–drain voltage from -1 V to 1 V while detecting the current. For time-resolved photocurrent measurements, using a picosecond pulsed laser driver (Taiko PDL M1, PicoQuant) together with a 779 nm laser head (pulse length $<500 \text{ ps}$) the crystals were illuminated at 40 mW laser output power using the continuous wave mode under a constant bias of 1 V .

Data availability

Crystallographic data have been deposited at the CCDC under 2366237 ($\text{Nb}_4\text{OI}_{12}$), 2391069 ($\text{a-Nb}_4\text{OI}_{11}$), and 2408695 ($\text{b-Nb}_4\text{OI}_{11}$).†

Data are available within the article.

The data that support the findings of this study are available on request from the corresponding author, H.-J. Meyer.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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Supporting Information

The Family of tetranuclear $\text{Nb}_4\text{OI}_{12-x}$ Clusters ($x = 1, 2$): From the molecular $\text{Nb}_4\text{OI}_{12}$ cluster to extended chains and layers

Jan Beitzberger,^a Mario Martin,^b Marcus Scheele,^b Patrick Schmidt,^a Markus Ströbele,^a and H.-Jürgen Meyer^{*a}

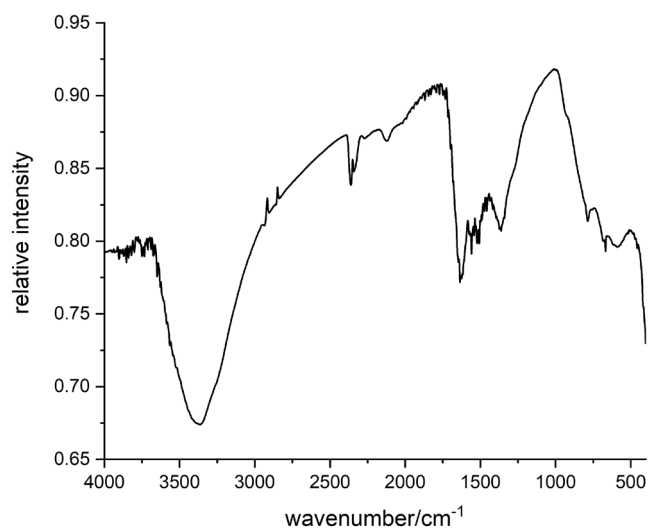


Figure S1. IR spectrum of the residual powder after the reduction of carbodiimide.

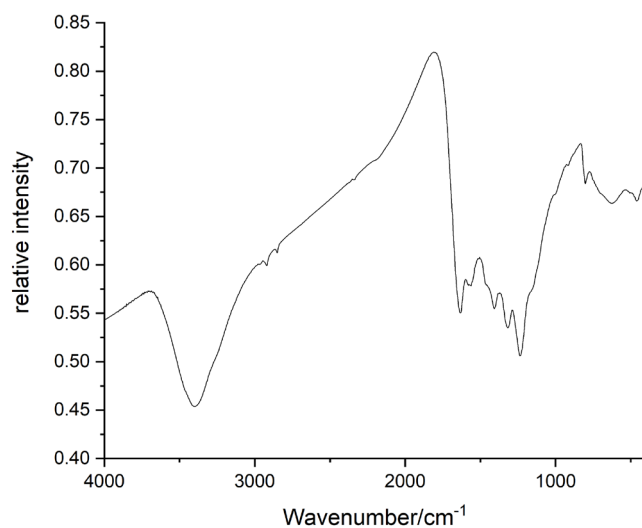


Figure S2. IR spectrum of the reaction product of amorphous C_3N_4 , made by a literature method.^[1]

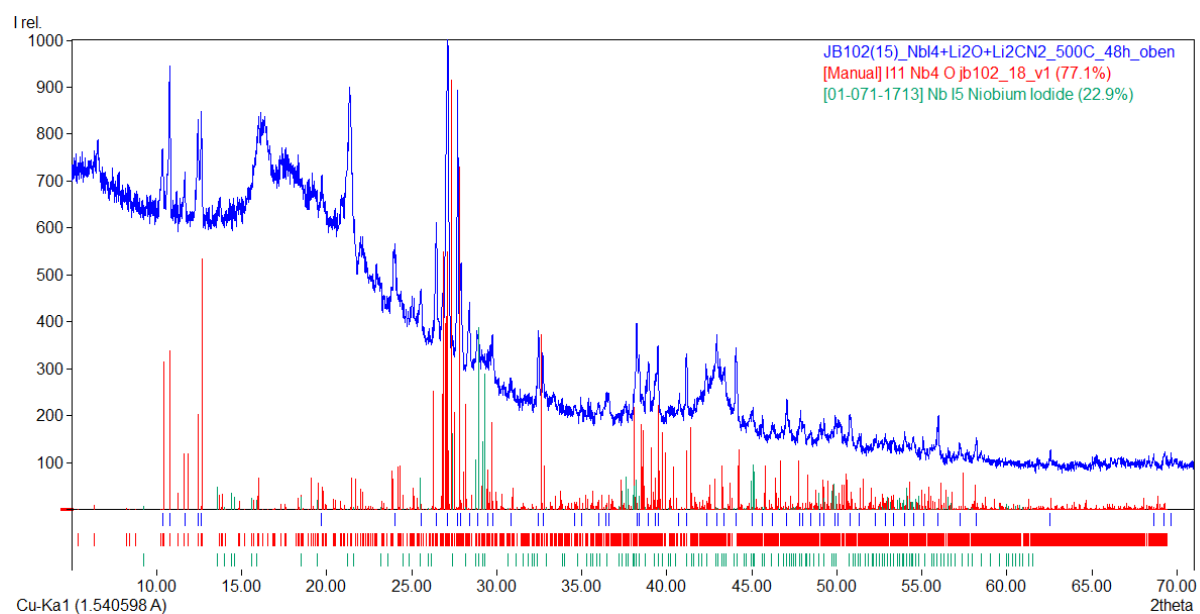


Figure S3. Measured powder X-ray diffraction pattern of $b\text{-Nb}_4\text{OI}_{11}$ with $\text{Cu-K}\alpha_1$ -radiation. In blue is the measured powder pattern, red corresponds to the calculated reflections of the single crystal X-ray measurement of $b\text{-Nb}_4\text{OI}_{11}$ and in green are the Bragg positions of coproduced NbI_5 .

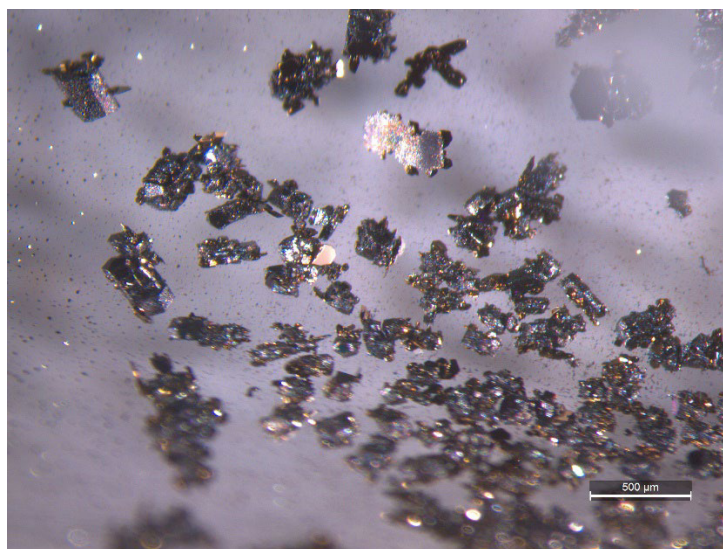


Figure S4. Example of black $b\text{-Nb}_4\text{OI}_{11}$ crystals along with some NbI_5 (golden plates).

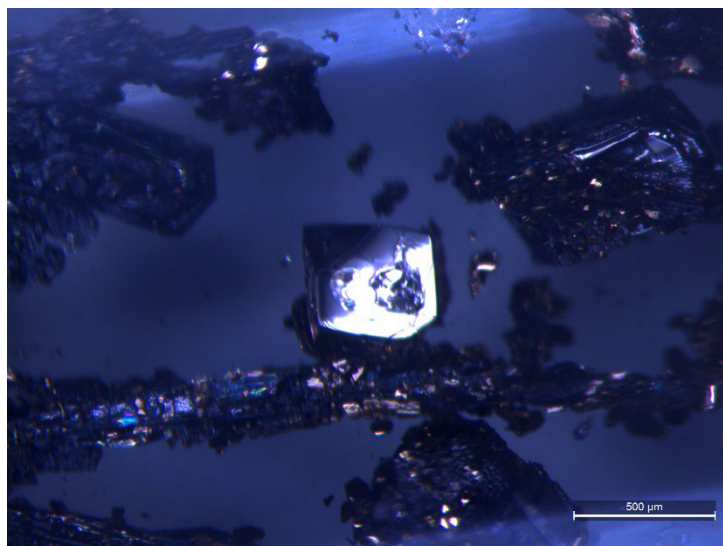
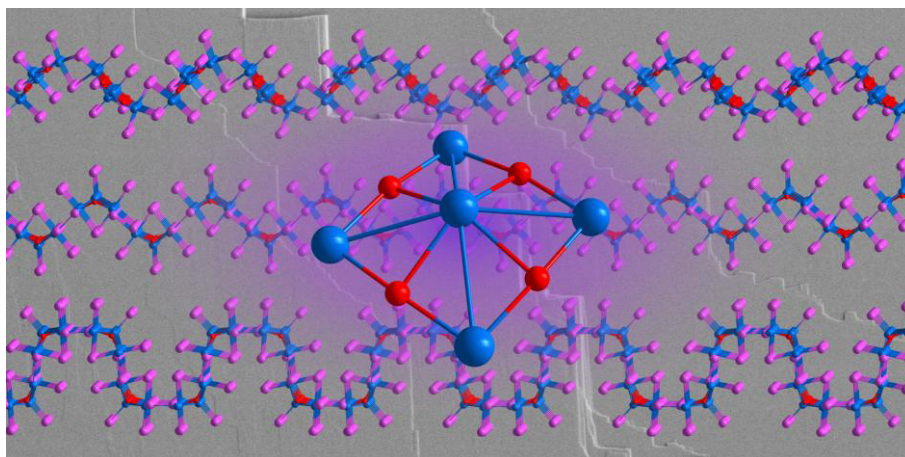


Figure S5. Example of a black Nb₄OI₁₂ crystal along with some b-Nb₄OI₁₁ aside.

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Publication 3

Structural Modifications of $M_5O_4I_{11}$ ($M = \text{Nb}, \text{Ta}$) Cluster Networks from Heterogeneous Solid-State Reactions



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Structural modifications of $M_5O_4I_{11}$ ($M = Nb, Ta$) cluster networks from heterogeneous solid-state reactions

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The cluster compounds $M_5O_4I_{11}$ ($M = Nb, Ta$) and $Ta_5O_4I_{11}(Ta_5)$ were obtained from heterogeneous solid-state reactions and structurally characterised by single-crystal X-ray diffraction. Their crystal structures are based on the novel $[M_5O_4]$ cluster core with metal (M) atoms arranged following the motif of a square pyramid. Iodide ligands contribute to different connectivities in the structures, resulting in (van der Waals type) waved layer structures. Two structural modifications exist for $Ta_5O_4I_{11}$, denoted as *o*- $Ta_5O_4I_{11}$ and *m*- $Ta_5O_4I_{11}$, and the compound $Ta_5O_4I_{11}(Ta_5)$ encloses $[Ta_5]$ molecules within voids of the structure. The two-dimensional nature of the structures and the presence of metal-to-metal bonding motivated investigations of the electronic properties through optical band-gap measurements, electrical conductivity studies, electronic band structure calculations, and X-ray photoelectron spectroscopy.

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Introduction

The chemistry of reduced niobium and tantalum halides is characterised by metal cluster compounds that are usually achieved through solid-state synthesis at elevated temperatures.¹ These compounds display a wide range of structural motifs and oxidation states, with a pronounced tendency to form clusters featuring octahedral M_6 ($M = Nb, Ta$) cores.² Many transition metal (M) halide (X) clusters crystallise in either the $[M_6X_{12}]$ - or $[M_6X_8]$ -structural types.^{3–6} The $[M_6X_{12}]$ structure consists of twelve halide ligands bridging the edges of an M_6 octahedron which generally favours combinations of larger metal atoms with smaller halides. In contrast, $[M_6X_8]$ clusters, in which eight halides cap the faces of the octahedron, tend to form when smaller metal atoms are paired with larger halide ions. Due to the spatial separation of adjacent clusters by outer ligands, these crystalline materials typically exhibit semiconducting behaviour with poor electrical conductivity.^{7,8} The chemistry of binary niobium halide clusters is further enriched by triangular Nb_3 clusters present in

Nb_3X_8 ($X = Cl, Br, I$), as well as Peierls-distorted NbX_4 .^{9,10} Metal-rich tantalum halides exist as Ta_6X_{14} , Ta_6X_{15} and TaX_4 .^{5,11–15}

Beyond these well-established binary systems, the range of cluster compounds and structural diversity expands significantly in heteroanionic halides of niobium and tantalum. Among the most common examples are chalcogenides, which include M_3 clusters, such as Ta_3SBr_7 and ANb_3SBr_7 ($A = Rb, Cs$),^{16–18} as well as M_4 clusters exhibiting planar, butterfly or tetrahedral geometries (e.g. Nb_4OI_{10} ; $Ta_4S_9Br_8$; Ta_4SBr_{11} ; $Nb_4Se_4I_4$).^{19–26} Octahedral M_6 clusters are also observed, as in Nb_6I_9S .²⁷ A notable characteristic of these compounds is the presence of bridging halides along with the interstitial or capping atoms, which are most often chalcogenides, and rarely pnictides (Nb_4PnX_{11} , $Pn = N, P$; $X = Cl, Br, I$).²⁵

Occasionally, molecular MX_5 units are found to be incorporated into a cluster network. A notable example is $Nb_7S_2I_{19}$ which can be represented as $(Nb_3SI_7)_2(NbI_5)$, emphasising the stabilisation of thermodynamically unstable NbI_5 monomers within the inorganic framework of Nb_3SI_7 . This structure exemplifies a form of structural synergism, where the enclosed molecule influences the topology of the surrounding cluster framework.²⁸ Similarly, space-filling $[ZrCl_5]^-$ units are observed in the compound described as $Cs_3Zr_7Cl_{20}Mn$ and $[TaBr_6]^-$ units in $(Ta_6Br_{12})Br_3(TaBr_6)_{0.86}$.^{29,30}

Less common is the occurrence of pentanuclear M_5 clusters. Reported examples generally fall into two categories: those composed of two different metals, which give rise to a

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variety of geometries, and metal halide clusters that typically adopt a square-pyramidal cluster core. The latter is commonly observed in compounds with the general formula $[M_5X_{13}]^{n-}$ ($M = \text{Mo, W, Tc}; X = \text{Cl, Br, I}; n = 0, 1, 2, 3$).^{31–33}

Oxyiodides of niobium and tantalum are reported as MO_2I , MOI_2 and NbOI_3 .^{34–36} More recently there has been some progress in the development of metal-rich oxyiodides.^{19,37} In the course of this progress, we present a new class of metal-rich oxyiodides based on a distinctive M_5 cluster motif, observed for both niobium and tantalum.

These clusters, of the general formula $M_5\text{O}_4\text{I}_{11}$ with $M = \text{Nb}$ and Ta , are shown to exist in two polymorphic forms for tantalum (*o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$, *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$), as well as in the compound $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$, containing molecular $[\text{TaI}_5]$ in its structure. The syntheses and crystal structures of the compounds are reported, and their electrical conductivities and electronic structures are analysed through a combination of experimental measurements and theoretical calculations.

Experimental

Preparations

Manipulations of starting materials, such as charging the silica ampoules (estimated volume 5 cm³) with starting materials were performed in an argon-filled glovebox (MBraun, labmaster 130, O₂ < 1 ppm, H₂O < 1 ppm).

o- $\text{Ta}_5\text{O}_4\text{I}_{11}$, *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ and $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$

A mixture of TaI_5 (144.8 mg, 0.178 mmol), Ta (6.1 mg, 0.03 mmol, Merck, 99.9%), Li_2O (5.1 mg, 0.169 mmol, ABCR, 96%) and Li_2CN_2 (4.6 mg, 0.085 mmol) was fused into an evacuated silica tube and heated with 0.5 K min^{−1} to 500 °C in a Simon–Müller furnace. After heating at 500 °C for 48 hours, *o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ and *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ were obtained as black, plate-like (*o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$) and rod-shaped (*m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$) crystals, which are sensitive to moisture (estimated yield: ~30% (*o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$); ~10% (*m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$); a powder X-ray diffraction pattern is shown in Fig. S1, top). Reactions at 500 °C with a shorter reaction time of 12 hours resulted in a few black crystals of $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$. Additional side phases were red TaO_2I and black, fibrous TaOI_2 , as well as $\text{Ta}_2\text{O}_3\text{I}_4$ and $\text{LiTa}_3\text{O}_2\text{I}_{12}$ which are reported in this study.

$\text{Nb}_5\text{O}_4\text{I}_{11}$

NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol) and $\text{Li}_2(\text{CN}_2)$ (7.2 mg, 0.135 mmol) were fused into a silica ampoule and heated to 400 °C with a rate of 0.1 K min^{−1}. The holding time was 24 hours before the reaction was cooled down to room temperature with a rate of 0.1 K min^{−1}. Black, plate-like crystals of $\text{Nb}_5\text{O}_4\text{I}_{11}$ were obtained at the walls of the ampoule (yield: ~10%); NbOI_2 and NbI_5 were sublimed to the cooler part of the ampoule, while LiI , $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ ³⁸ and an amorphous phase were found in the hotter part at the bottom. Crystals behave sensitive in moist air. A powder X-ray diffraction pattern is shown in Fig. S1, bottom.

NbI_4 and TaI_5 were synthesised according to literature by reacting appropriate amounts of niobium or tantalum (Merck, 99.9%) with resublimed iodine (Merck, 99.999%) at 400–450 °C in evacuated quartz ampoules.³⁹

$\text{Li}_2(\text{CN}_2)$ was synthesised as described before,⁴⁰ by reacting LiH (99.4%, Alfa Aesar) with melamine (≥99%) in a 6 : 1 molar ratio under argon.

Powder X-ray diffraction

All reaction products were investigated by powder X-ray diffraction (PXRD) using a StadiP diffractometer (Stoe, Darmstadt) with Ge-monochromated $\text{Cu-K}\alpha_1$ radiation, and a Mythen1 Detector.

Single-crystal X-ray diffraction

Data collections were performed on a Rigaku XtaLAB Synergy-S single-crystal X-ray diffractometer equipped with HyPix-6000HE detector and monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 150 K. X-ray intensities were corrected for absorption with a numerical method (crystal faces) using CrysAlisPro 1.171.43.121a (Rigaku Oxford Diffraction, 2024). The structures were solved by direct methods (SHELXT) and refined by full-matrix least-squares methods performed with SHELXL–2019/3 as implemented in Olex2 1.5.

EDX and SEM

Energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were performed on a HITACHI SU8030 scanning electron microscope with a Bruker QUANTAX 6G EDX-detector. Single crystals of *o*- and *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ were mounted onto carbon tape under an argon atmosphere during sample preparation. For inert transfer, a vacuum transfer device, similar to the one reported by Yao *et al.*, was used.⁴¹ In our adapted design, it consists of a steel lid with an O-ring seal (Fig. S2a). The lid is placed on top of the sample holder and evacuated within the glovebox airlock. It is then rapidly flooded with argon to create a reduced-pressure environment, ensuring an airtight seal *via* the O-ring (Fig. S2b and c). Once inserted into the SEM transfer chamber and evacuated, the internal pressure becomes equal to, or slightly higher than, the external pressure. This allows the magnetic lid to be lifted using neodymium magnets from outside the chamber (Fig. S2d).

Electrical conductivity

Conductivity measurements were performed in a Lake Shore Cryotronics CRX-6.5K probe station with a Keithley 2636B source meter unit. Rod-shaped crystals of *o*- and *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ were contacted on a silicon substrate with 770 nm oxide layer using silver paste (Fig. S3, right) and transferred into the measuring chamber under protective gas. The conductive silver pads at each end of the crystals were connected to the circuit with gold coated tungsten tips. The chamber was kept under vacuum ($<5 \times 10^{-5}$ mbar) and the temperature was varied between 140 K and 350 K. Before each measurement,



sufficient time was allowed for the sample to reach the chosen temperature. Two-point conductivity measurements were performed by varying the applied source-drain voltage from -2 V to 2 V while detecting the current. For time-resolved photo-current measurements, using a picosecond pulsed laser driver (Taiko PDL M1, PicoQuant) together with a laser head 779 nm (pulse length < 500 ps) the crystals were illuminated at ~ 55 mW cm $^{-2}$ laser output power using the continuous wave mode under a constant bias of 1 V. The electrical measurements shown in this work had crystal dimensions (length L ; width W ; height H) of o -Ta $_5$ O $_4$ I $_{11}$: $L = 205$ μ m; $W = 124$ μ m; $H = 75$ μ m and m -Ta $_5$ O $_4$ I $_{11}$: $L = 119.4$ μ m; $W = 32.4$ μ m; $H = 27.3$ μ m.

DRIFT (diffuse reflectance infrared fourier transformation) spectroscopy

Samples were measured at room temperature under inert conditions in diffuse reflectance with a Harrick Praying Mantis attachment using a Bruker Vertex 70 infrared spectrophotometer with a deuterated triglycine sulfate (DTGS) detector and KBr beamsplitter. The background spectra were collected using pure dried KBr in powder form.

TXRF (total internal reflection X-ray fluorescence) spectroscopy

TXRF studies were performed using a S2 Picofox (Bruker AXS Microanalysis, Berlin, Germany) equipped with a Mo X-ray tube, which was operated at 50 kV and 600 μ A. The measurement period for each sample was 1000 s (live time). Fitting of the resulting spectra was done using the Spectra software (Bruker Nano GmbH) in the super bias mode (maximum stripping cycles of 2000).

XPS (X-ray photoelectron spectroscopy)

XPS measurements were performed under ultra-high vacuum (UHV) conditions (8×10^{-10} mbar) using an XR50 Al-K $_{\alpha}$ standard source equipped with a PHOIBOS 100 hemispherical analyser (SPECS GmbH, Berlin, Germany). Since o -Ta $_5$ O $_4$ I $_{11}$ represents the major phase of the synthesis, the crystals used for XPS measurements were carefully selected under the optical microscope. To avoid exposure to air and prevent oxidation, the synthesised samples were mounted on a double-sided conductive carbon tape under argon atmosphere. For inert transfer into the spectrometer, a custom-built vacuum transfer device (an enlarged version of the design used for SEM/EDX) was employed. This device consists of an aluminium lid with an O-ring that seals the sample holder under reduced pressure within the glovebox airlock (Fig. S4, SI). Upon evacuation of the XPS transfer chamber, the external pressure drops below the internal pressure, causing the lid to detach and fall off, thereby revealing the sample without contact to air. The chamber is then further evacuated to UHV before transferring the sample into the measurement chamber (see Fig. S5, SI for details).

The binding energy scale was calibrated to the signal positions of Au 4f $_{7/2}$ (84.0 eV), Ag 3d $_{5/2}$ (368.2 eV) and Cu 2p $_{3/2}$ (932.6 eV). To take charging effects into account, the acquired

Ta 4f spectrum was referenced by setting the I 3d $_{5/2}$ peak to a binding energy of 619 eV. Peak fitting of XPS spectra was performed using the software Unifit 2018 (Unifit Scientific Software GmbH, Leipzig, Germany).

DFT (Density functional theory)

DFT calculations were performed in the software package Abinit (v. 10).⁴² The Perdew–Burke–Ernzerhof exchange–correlation functional was used with the dispersion correction of Grimme.^{43,44} Calculations were performed using a plane wave basis set and the PAW formalism,⁴⁵ with an energy cut-off of 100 Ha inside the PAW spheres and 24 Ha outside. A $4 \times 2 \times 2$ (o -Ta $_5$ O $_4$ I $_{11}$) or $3 \times 2 \times 2$ (m -Ta $_5$ O $_4$ I $_{11}$) Monkhorst–Pack grid⁴⁶ of k -points was used to sample reciprocal space. These quantities were chosen following convergence studies. Methfessel–Paxton smearing was used to determine band occupation.⁴⁷ PAW data files were used as received from the Abinit library. The structures were relaxed to an internal pressure of 2 MPa prior to calculations of the electronic band structure.

Results and discussion

Synthesis and crystal structure

The two most stable compounds reported in the Ta–O–I system appear to be TaO $_2$ I and TaOI $_2$, both of which were synthesised *via* transport reactions involving Ta, I $_2$ and Ta $_2$ O $_5$ in temperature gradients of 450 – 550 $^{\circ}$ C.^{34,35,48} In our study, we aimed to access more metal-rich compounds in this system by further reducing tantalum below the Ta(IV) oxidation state in TaOI $_2$. For this purpose we have explored Li $_2$ CN $_2$ as an unconventional reduction agent, which has previously been shown its reducing nature, as demonstrated in metathesis reactions of NiCl $_2$ with Li $_2$ CN $_2$, yielding elemental Ni, along with LiCl, C $_3$ N $_4$ and N $_2$.⁴⁹

The employment of Li $_2$ CN $_2$ into the Ta–O–I system triggers reduction reactions likely above 300 $^{\circ}$ C, marked by the emergence of a violet gas phase. As the temperature exceeded 400 $^{\circ}$ C, this gas phase darkened significantly. Upon cooling, crystalline iodine was found deposited on the cooler part of the ampoule, indicating that molecular iodine is present in the gas phase, likely along with reactive precursors that contribute to the observed cluster formation.

Additionally, slightly increased pressure was observed in the ampoules, indicating the formation of N $_2$. Amorphous C $_3$ N $_4$ was identified as a side product *via* infrared spectroscopy (see Fig. S6, SI). These findings further confirm that Li $_2$ CN $_2$ acts as a reducing agent in our system, consistent with its previously reported behaviour in the reduction of NiCl $_2$ to elemental Ni.

Thermal analysis of reactions aimed to investigate the impact of Li $_2$ CN $_2$ on the Ta–O–I system proved to be complex, as the reaction pathways are intricate. In addition to the observed cluster compounds (discussed in detail in this study), various crystalline and amorphous by-products were detected.



Each experiment resulted in the formation of multiple products, indicating that several reactions occurred simultaneously. The spatial distributions of these products within the reaction container suggests the occurrence of partial transport reactions along a narrow temperature gradient.

Among the consistently identified side products were LiI , TaOI_2 and TaO_2I , as well as two previously unreported compounds: $\text{LiTa}_3\text{O}_2\text{I}_{12}$ and $\text{Ta}_2\text{O}_3\text{I}_4$. While these compounds are not the focus of this study, their structures have been characterised by us and are briefly described as follows. Both compounds feature Ta^{5+} ions in distorted octahedral coordination environments. The structure of $\text{LiTa}_3\text{O}_2\text{I}_{12}$ forms kinked strands of $[\text{Ta}_3\text{O}_2\text{I}_{10/4/2}]^-$ units which are separated by disordered lithium ions (Fig. 1 left). In $\text{Ta}_2\text{O}_3\text{I}_4$, each Ta^{5+} ion is coordinated by three oxygen and three iodide ions, forming octahedra that connect *via* corner-sharing oxygen atoms and edge-sharing iodides, with one terminal iodide per octahedra. This connectivity results in zig-zag layers (Fig. 1 right).

Efforts to minimise the amount of these side products by adjusting reactant ratios frequently resulted in lower yields of the desired cluster compounds. Likewise, prolonging the reaction duration to steer the system toward thermodynamic equilibrium did not improve reaction selectivity or reproducibility. This suggests that the cluster formation may proceed under kinetic control, potentially influenced by the side phases. Notably, the cluster compounds were consistently found in close proximity to TaO_2I , implying that this phase could serve as a precursor in the cluster-forming process.

Comparable unconventional reduction methods with Li_2CN_2 were recently reported in the Nb-O-I system, resulting in several novel niobium oxyiodides, such as the oxygen centred $\text{Nb}_4\text{OI}_{12-x}$ clusters with $x = 0, 1, 2$.^{19,37}

In extension of these findings, analogous reactions were also performed in the Ta-O-I system, yielding distinct cluster networks, referred to as $o\text{-}M_5\text{O}_4\text{I}_{11}$ ($M = \text{Nb}, \text{Ta}$), $m\text{-}M_5\text{O}_4\text{I}_{11}$,

and $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$, where o and m denote the orthorhombic and monoclinic polymorphs, respectively.

The crystal structure of $o\text{-}M_5\text{O}_4\text{I}_{11}$ was solved and refined from single-crystal X-ray diffraction data in the orthorhombic space group $Pmc2_1$ (No. 26). The characteristic motif of $o\text{-}M_5\text{O}_4\text{I}_{11}$ is depicted in Fig. 2: The Ta_5 cluster core adopts the motif of a distorted square pyramid. At the base of the pyramid, four μ_3 -oxygen atoms bridge the edges between the metal atoms. Each of the four outer metal atoms exhibits distorted octahedral coordination by oxygen and iodide atoms with additional metal-to-metal bonding with the central metal atom on top of the pyramid (Fig. 2) with intermetallic distances given in Table 1.

The connectivity within and between clusters can be described using the notation $[(\text{Ta}_5\text{O}_4)\text{I}_{12}^{\text{I}}\text{I}_{10/2}^{\text{a-a}}]$ where two inner (i) iodide ligands cap the edges at the apex of the distorted square-pyramidal cluster core, and four outer (a) iodides are terminally coordinated, one positioned above and three below the base of the pyramid. Additionally, ten iodide ligands are shared (10/2) between adjacent clusters, referred to as bridging outer (a-a) iodides. This notation follows the convention originally developed for describing octahedral cluster compounds.^{1,7,50}

Each cluster is connected to four neighbouring clusters at its corners through bridging iodide ligands, forming extended layers expanding into the ac -plane. Along the a -axis, the $\text{Ta}(2)$

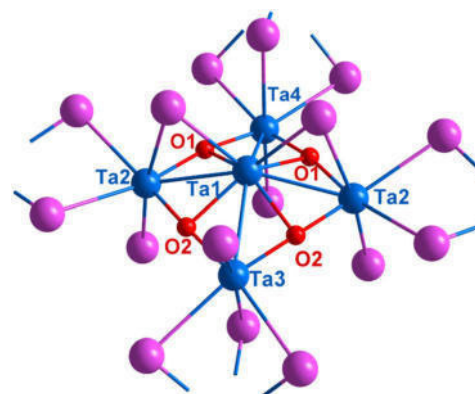


Fig. 2 Building block of isotopic $M_5\text{O}_4\text{I}_{11}$ structures ($M = \text{Nb}, \text{Ta}$), with the $[M_5\text{O}_4]$ cluster core displayed for $M = \text{Ta}$, corresponding to $o\text{-}M_5\text{O}_4\text{I}_{11}$ (iodide atoms are shown in pink).

Table 1 Comparison of selected interatomic distances and bond angles in $o\text{-}M_5\text{O}_4\text{I}_{11}$ and $\text{Nb}_5\text{O}_4\text{I}_{11}$. For atom labelling, see Fig. 2

Distance/pm; $\angle^\circ$	$o\text{-}M_5\text{O}_4\text{I}_{11}$	$\text{Nb}_5\text{O}_4\text{I}_{11}$
Intra cluster		
$M(1)-M(2)$	283.2(1)	285.2(1)
$M(1)-M(3)$	288.7(1)	287.8(4)
$M(1)-M(4)$	290.7(1)	290.4(4)
$\angle M(2)-M(1)-M(2)$	149.3(1)	148.9(1)
$\angle M(3)-M(1)-M(4)$	136.9(1)	131.3(1)
Inter cluster		
$M(2)-M(2)$	435.7(1)	430.1(3)
$M(3)-M(4)$	388.4(1)	377.5(4)

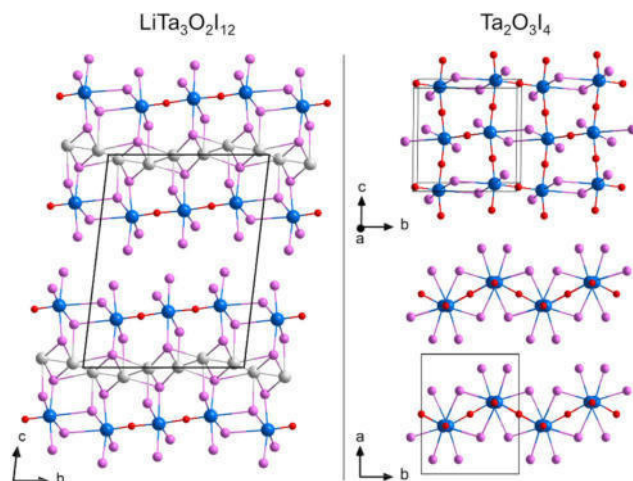


Fig. 1 Sections of the crystal structures of $\text{LiTa}_3\text{O}_2\text{I}_{12}$ (left) and $\text{Ta}_2\text{O}_3\text{I}_4$ (right). Tantalum atoms are depicted in blue, iodine pink, oxygen red and lithium grey.



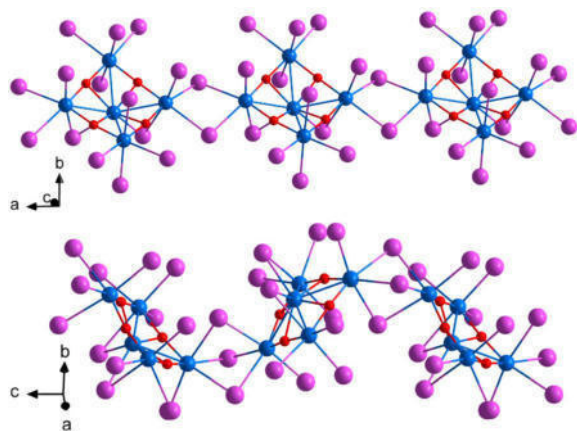


Fig. 3 Cluster connectivities in the structure of $M_5O_4I_{11}$ along a (top) and c (bottom), corresponding to o - $Ta_5O_4I_{11}$. M atoms are depicted in blue, oxygen in red and iodine in pink.

atoms are linked by two bridging iodides positioned perpendicular to an (m_x) mirror plane (Fig. 3 top). Ta(3) and Ta(4) are connected by three iodide bridges along a (2_1) screw axis that runs parallel to the c -axis, creating a tilted arrangement of clusters, as illustrated in Fig. 3, bottom. In the extended crystal structure, this leads to the formation of undulating layers which are separated by a van der Waals gap (Fig. 4).

A comparison of selected interatomic distances and bond angles in o - $Ta_5O_4I_{11}$ and the isostructural $Nb_5O_4I_{11}$ is given in Table 1. As expected, given the similarity of ionic radii of niobium and tantalum,⁵¹ the shortest M - M bond lengths for both compounds fall within the same range. However, the $\angle M(3)-M(1)-M(4)$ bond angle, which traces the undulation of the layers along the c -axis, differs by around 6° . Furthermore, the inter cluster $M(3)-M'(4)$ distance in this direction is 11 pm shorter in $Nb_5O_4I_{11}$, resulting in a slightly more pronounced corrugation of the layers.

The crystal structure of the monoclinic m - $Ta_5O_4I_{11}$ contains a $[Ta_5O_4]$ cluster core similar to that found in o - $Ta_5O_4I_{11}$. However, the core in m - $Ta_5O_4I_{11}$ is less distorted due to a

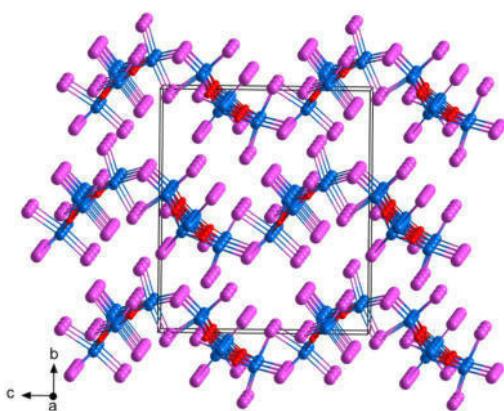


Fig. 4 Waved layer structure of $M_5O_4I_{11}$, corresponding to o - $Ta_5O_4I_{11}$. M atoms are depicted in blue, oxygen in red and iodine in pink.

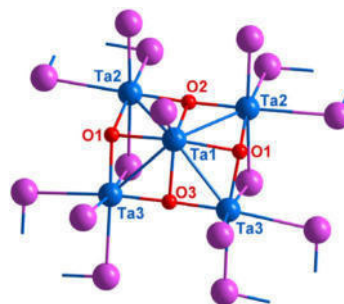


Fig. 5 Building block of the m - $Ta_5O_4I_{11}$ structure. Tantalum atoms are depicted in blue, oxygen atoms in red and iodine atoms in pink.

different spatial arrangement of the iodine atoms, leading to variations in how the cluster interconnect (Fig. 5). Each $[(Ta_5O_4)I_2]^{11-}$ cluster includes two inner (i) μ_2 -bridging iodides located at the base of the pyramid, five terminal outer (a) iodides each bonded to one of the five tantalum atoms towards the pyramid's apex, and eight outer (a-a) iodides that are shared between two clusters ($8/2$) (see Table S1 in SI for comparison of interatomic distances).

Each cluster is interconnected with four neighbouring clusters at all four corners through two iodide bridges, forming an extended layered network. In this structure, the surrounding cluster pyramids are oriented oppositely to the central one: when the central cluster points upwards, the adjacent clusters point downwards, and *vice versa* (Fig. 6); this alternating orientation results in a sinusoidal layering pattern. These undulating layers are further separated by a van der Waals gap (Fig. 7).

The cluster network of $Ta_5O_4I_{11}(TaI_5)$ is closely related to that of m - $Ta_5O_4I_{11}$, but with the additional incorporation of molecular $[TaI_5]$ units. This leads to a significant transformation of the overall structural architecture. Fig. 8 shows a section of the $Ta_5O_4I_{11}(TaI_5)$ structure (top) along with the arrangement of $[Ta_5O_4I_{11}]$ layers (bottom left) and $[TaI_5]$ units (bottom right). A closer comparison of the layer formation and

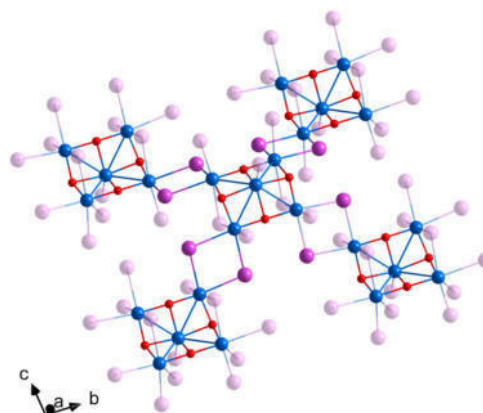


Fig. 6 Section of the m - $Ta_5O_4I_{11}$ structure depicting the inter-cluster connectivity within one layer. Tantalum atoms are depicted in blue, oxygen in red and iodine in pink.

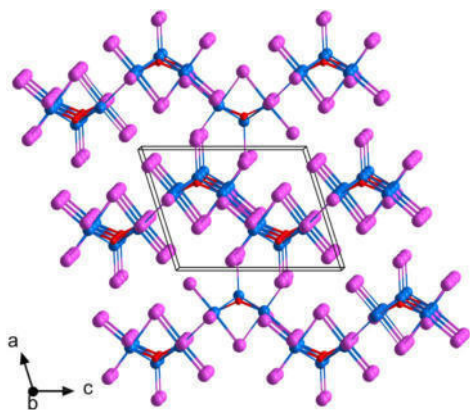


Fig. 7 Sinusoidal connectivity of clusters in the layered structure of $m\text{-Ta}_5\text{O}_4\text{I}_{11}$. Note that there is no connectivity between adjacent layers. Tantalum atoms are depicted in blue, oxygen in red and iodine in pink.

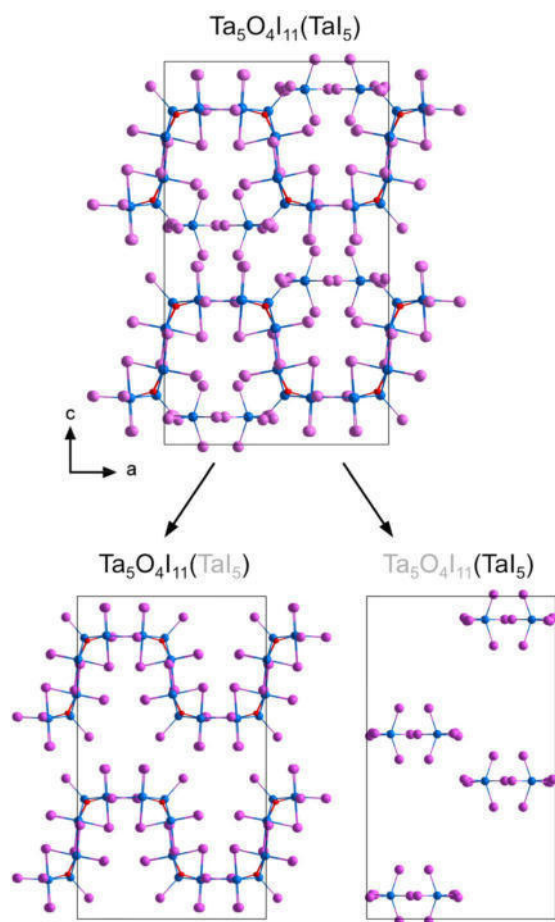


Fig. 8 Projected crystal structure of $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$ (top) and segmentation of the structure into $[\text{Ta}_5\text{O}_4\text{I}_{11}]$ (left) and $[\text{TaI}_5]$, appearing as two superimposed TaI_5 units (right).

organisation in $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$ (Fig. 8) and $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ (Fig. 7) reveals clear structural differences, even though the cluster connectivity pattern $[(\text{Ta}_5\text{O}_4)\text{I}_{11}]_2\text{I}_5^{\text{a-a}}$ remains the same in both structures.

Notable differences between both structures are observed in the amplitude of the sinusoidal waves of the layers and by the directional shift of these waves relative to one another. In $m\text{-Ta}_5\text{O}_4\text{I}_{11}$, the clusters alternate in an up-and-down fashion, whereas in $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$, for each directional shift of the wave, two of the four adjacent clusters point in the same direction as the central cluster and two are inverted and point the other direction (compare Fig. 7 and Fig. 8). This more pronounced corrugation creates voids that accommodate $[\text{TaI}_5]$ molecules, which contribute to the stabilisation of the structure of $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$.

This finding aligns with the observations made for the compound $\text{Nb}_7\text{S}_2\text{I}_{19} \triangleq (\text{Nb}_3\text{SI}_7)_2(\text{NbI}_5)$, which Miller and Lin described as exhibiting a synergistic relationship between the extended framework and the enclosed $[\text{NbI}_5]$ molecule.²⁸ In this structure, $[\text{NbI}_5]$ molecules are packed within hexagonal channels formed between the $[\text{Nb}_3\text{SI}_7]$. In contrast, when $[\text{NbI}_5]$ molecules are absent, Nb_3SI_7 adopts a van der Waals layered structure that lacks these hexagonal voids.¹⁷

As with the $[\text{NbI}_5]$ units in $\text{Nb}_7\text{S}_2\text{I}_{19}$, the $[\text{TaI}_5]$ molecules in $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$ are incorporated as trigonal bipyramidal monomers (see Fig. 9) similar to the geometries reported for TaCl_5 and TaBr_5 in the vapour phase.^{52,53} However, in the solid state, TaI_5 typically crystallises as $(\text{TaI}_5)_2$ dimers composed of edge-sharing bioctahedra.⁵⁴

The Ta–I bond lengths of molecular $[\text{TaI}_5]$ in the structure of $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$ range from 260(1) pm to 271(1) pm, with an average of 266(1) pm. This closely matches the average Nb–I distance of 267(1) pm of the NbI_5 monomers in $\text{Nb}_7\text{S}_2\text{I}_{19}$, as well as the average Ta–I distance of 267(1) pm in Ta_2I_{10} , not considering edge-sharing iodides.⁵⁴

Although all $M_5\text{O}_4\text{I}_{11}$ -based compounds share a similar penta-nuclear cluster core, they display distinct structural frameworks. These differences arise from variations in the inner (i) and outer (a) iodine ligand environments, the presence of incorporated $[\text{TaI}_5]$ molecules, as well as the cluster connectivity (a–a).

In particular, $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ features clusters interconnected by two and three μ_2 -bridging iodides at the corners (Fig. 3), resulting in shorter inter cluster Ta–Ta distances and potentially stronger electronic interactions, since $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ clusters are only connected by two iodide bridges at all four corners (Fig. 6). This difference is expected to influence the electronic properties of the material, particularly electrical conductivity, which is discussed later in this study.

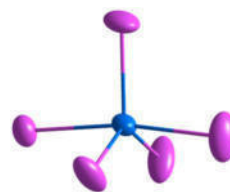


Fig. 9 Molecular $[\text{TaI}_5]$ in the structure of $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$ with 80% displacement ellipsoids. Blue: Ta, pink: I.



The $[\text{Ta}_5\text{O}_4]$ cluster motive demonstrates both structural stability and geometric flexibility, as it persists across different environments and tolerates considerable distortions. However, despite these characteristics, the *o*- and *m*-modifications of $\text{Ta}_5\text{O}_4\text{I}_{11}$ are not interconvertible by thermal treatment. Heating beyond 650 °C results in decomposition and the formation of TaOI_2 , rather than phase transition between the two forms.

For *o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$, the structures with niobium and tantalum are isotypic. However, no analogues of *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ or $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$ could be observed for niobium. Instead, niobium forms distinct cluster types such as $\text{Nb}_4\text{OI}_{12-x}$, reflecting differences in cluster stability and connectivity between the two elements.^{19,37}

$\text{Ta}_5\text{O}_4\text{I}_{11}$ carries six cluster electrons, but their distribution across the four short Ta–Ta bonds is not straightforward. From a formal oxidation state perspective, the four basal tantalum atoms can be assigned to Ta^{4+} , while the apical atom is considered more reduced, with an oxidation state of Ta^{3+} . To further probe this, XPS measurements are employed in the next section.

Analysis of Ta–Ta distances provide additional insights into the presence of metal–metal bonding in *o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$. The average Ta–Ta bond length is approximately 286 pm, which is slightly shorter than in other tantalum halide clusters such as Ta_6I_{14} (~292 pm), Ta_3SeI_7 (~295 pm) or $\text{Ta}_4\text{SBr}_{11}$ (~305 pm). This comparison supports the presence of bonding interactions between the tantalum atoms. Additional insight into electron distribution and bonding can be gained through ELF (Electron Localisation Function) analysis.

Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and total reflection X-ray fluorescence (TXRF)

When in contact with moist air, samples of $\text{Ta}_5\text{O}_4\text{I}_{11}$ show pronounced surface degradation and partial delamination (Fig. S7 in SI). To prevent this, a custom-designed vacuum transfer device was developed, enabling inert handling and transfer of samples. Details of the vessel design and operation are provided in the Experimental section and illustrated in Fig. S2 of the SI.

The scanning electron micrographs in Fig. 10 were obtained from samples transferred under inert conditions. Fig. 10 shows crystal agglomerates and surfaces morphologies of *o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ (Fig. 10a–c) and *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ (Fig. 10d–f). The two compounds clearly exhibit different morphologies: *o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ frequently shows well defined individual layers (Fig. 10c), suggesting weaker interlayer interactions. In contrast, *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ displays more compact, block-like surface features (Fig. 10f), indicating stronger interactions between adjacent layers.

To verify the composition, determined by X-ray diffraction, EDX measurements of multiple crystals were performed, resulting in an average Ta : O : I ratio of 5 : 4.3(5) : 10.9(3). TXRF measurements verified the Ta : I ratio to be 5 : 11.3(2).

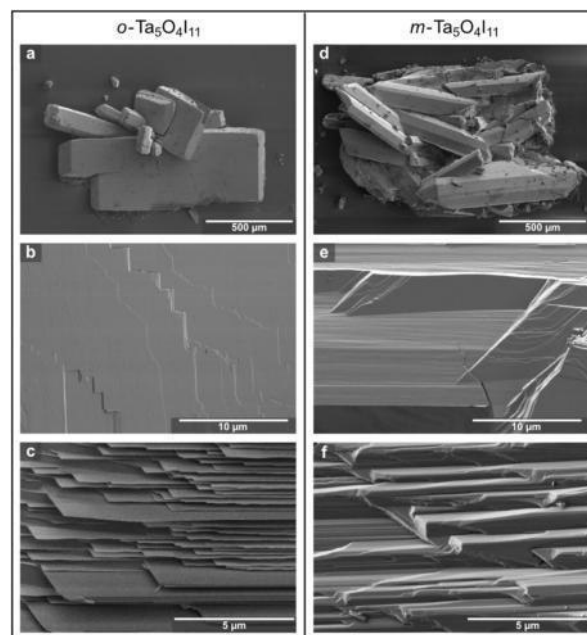


Fig. 10 Scanning electron micrographs of *o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ crystals (a–c) and *m*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ crystals (d–f), showing a layered morphology.

X-ray photoelectron spectroscopy (XPS)

Further insights on the oxidation state of tantalum in *o*- $\text{Ta}_5\text{O}_4\text{I}_{11}$ were achieved using X-ray photoelectron spectroscopy (XPS).

The Ta 4f spectrum shown in Fig. 11 can be described by two doublets (Ta 4f_{7/2} and Ta 4f_{5/2}), which are assigned to the oxidation states of Ta^{4+} and Ta^{3+} .^{55,56} The fit parameters are summarised in Table S2 (SI). The intensity ratio of Ta^{4+} and Ta^{3+} components of 4.14 : 1 is in good agreement with the proposition of a Ta^{3+} at the central position on top of the dis-

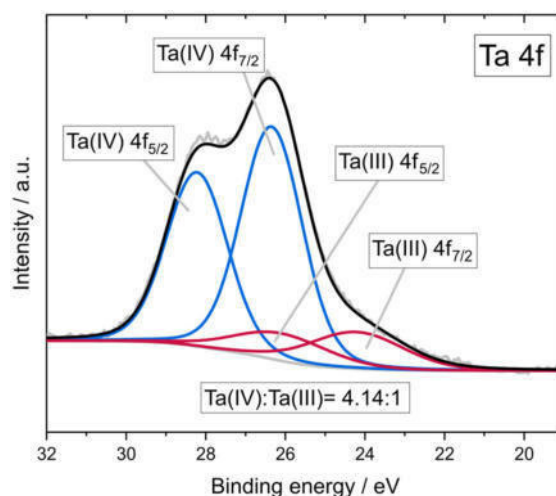


Fig. 11 XPS spectrum of Ta 4f depicting Ta(IV) and Ta(III) oxidation states in a ratio of 4.14 : 1.



torted pyramid and four Ta⁴⁺ at the corners of the pyramid base.

The survey spectrum in Fig. S8 (SI) reveals the presence of iodine and oxygen (notably, the additional carbon and silicon signals can be attributed to the carbon tape substrate) giving further evidence for the proposed structure.

Optical band gap determination from DRIFTS (Diffuse reflectance infrared fourier transform spectroscopy)

The absorption coefficient F was obtained using Kubelka-Munk analysis following:

$$F(R_{\infty}) = \frac{\alpha}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}},$$

where

$$R_{\infty} = \frac{R_{\text{sample}}}{R_{\text{standard}}}$$

is the reflectance of an infinitely thick specimen, α is the absorption and S is the scattering coefficient. For particle sizes greater than the light wavelengths measured, the scattering coefficient is understood to be approximately independent of frequency ($F(R_{\infty}) \sim \alpha$) and therefore $F(R_{\infty})$ could be understood as a “pseudo-absorbance” coefficient.^{57–63}

The band gap determination was performed on the DRIFTS data according to Zanata *et al.*⁶⁴ The energy is plotted against the absorption coefficient α and fitted with a sigmoid-Boltzmann function:

$$\alpha(E) = \alpha_{\text{max}} + \frac{\alpha_{\text{min}} - \alpha_{\text{max}}}{1 + \exp\left(\frac{E - E_0^{\text{Boltz}}}{\delta E}\right)}$$

where α_{min} (α_{max}) stands for the minimum (maximum) absorption coefficient; E_0^{Boltz} is the energy coordinate at which the absorption coefficient is halfway between α_{min} and α_{max} ; and δE is associated with the slope of the sigmoid, indicating the energy range over which most optical transitions occur.⁶⁴

The band gap can then be calculated by following equation with $n_{\text{dir}}^{\text{Boltz}} = 0.3$ and $n_{\text{indir}}^{\text{Boltz}} = 4.3$:

$$E_g^{\text{Boltz}} = E_0^{\text{Boltz}} - n_{\text{dir}/\text{indir}}^{\text{Boltz}} \cdot \delta E$$

The optical band gaps of *o*-Ta₅O₄I₁₁ were determined to be 0.241 eV (direct) and 0.226 eV (indirect) indicating semiconducting behaviour (see Fig. S9, SI). The band gap of *m*-Ta₅O₄I₁₁ could not be measured within the detectable range of the DRIFTS setup. To further assess the electronic properties, conductivity measurement were subsequently performed.

Electrical properties

We reasoned that the structural differences in *o*-Ta₅O₄I₁₁ vs. *m*-Ta₅O₄I₁₁ as well as their distinct ligand environments should manifest in different electrical properties. Hence, two-point current-voltage scans of both modifications (*o* and *m*) were carried out at varying temperatures. Exemplarily results, obtained at 300 K are displayed in Fig. S3 (SI).^{19,65} The measurements revealed that *o*-Ta₅O₄I₁₁ is roughly one order of

magnitude more conductive than *m*-Ta₅O₄I₁₁ with typical values of $5 \times 10^{-5} \text{ S m}^{-1}$ to $2 \times 10^{-4} \text{ S m}^{-1}$ for *o*-Ta₅O₄I₁₁ vs. $4 \times 10^{-6} \text{ S m}^{-1}$ to $2 \times 10^{-5} \text{ S m}^{-1}$ for *m*-Ta₅O₄I₁₁.

Using the two-point conductivities obtained at different temperatures, we arrive at the Arrhenius plot in Fig. 12, indicating temperature-activated, Arrhenius type transport for both phases, which is typical for semiconductors.^{66,67} From the slopes of both plots, we calculate activation energies of $E_A = 0.10 \text{ eV}$ for *o*-Ta₅O₄I₁₁ and $E_A = 0.40 \text{ eV}$ for *m*-Ta₅O₄I₁₁, respectively. Due to the poor signal strength from *m*-Ta₅O₄I₁₁ at temperatures below 240 K, additional conductivities were measured above 300 K up to 350 K to improve the fit confidence. *o*-Ta₅O₄I₁₁ was measured between 140 K–300 K.

To a first order approximation, the electrical band gap of an intrinsic semiconductor can be gauged as two times the activation energy, hence 0.2 eV for *o*-Ta₅O₄I₁₁ and 0.8 eV for *m*-Ta₅O₄I₁₁, respectively.

Both crystal species exhibit low photocurrents toward optical excitation at 779 nm illuminated with 40 mW output power. *o*-Ta₅O₄I₁₁ showed higher photocurrents around 1 nA while *m*-Ta₅O₄I₁₁ exhibited around 15 pA at 300 K (Fig. S10, SI). At lower temperatures, the photocurrent decreases gradually until it is below the noise level at ~0.1 pA.

Band structure

The spin-unpolarised electronic band structures of *o*-Ta₅O₄I₁₁ and *m*-Ta₅O₄I₁₁ were calculated using density functional theory (DFT). At the DFT level, *o*-Ta₅O₄I₁₁ is a band metal (Fig. 13), unlike the small-gap semiconductor observed in our optical and electrical measurements. Since the experimental gap of *o*-Ta₅O₄I₁₁ is small, the DFT calculations were performed with spin orbit coupling, as this could plausibly open a small gap, however this was not observed. The opening of the gap could therefore be due to electronic correlations and magnetic interactions between Ta atoms, as was determined in the related Mott insulating material Ta₄SBr₁₁.²² However, due to the large size of the unit cell of *o*-Ta₅O₄I₁₁, computational

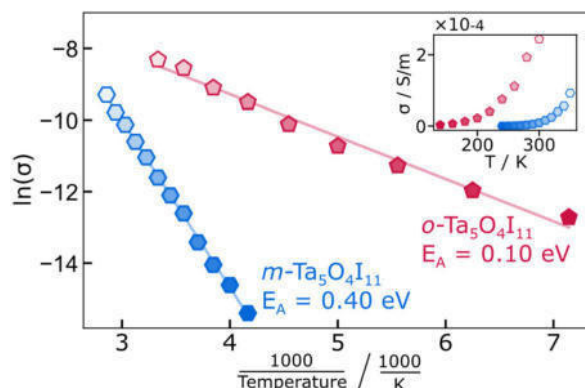


Fig. 12 Arrhenius-plot of the temperature-dependent conductivity between 140 K–300 K for *o*-Ta₅O₄I₁₁ (red) and 240 K–350 K for *m*-Ta₅O₄I₁₁ (blue). The inset shows the linear plot of conductivity versus temperature.



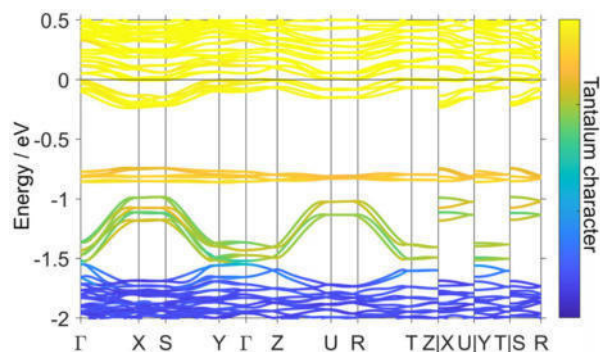


Fig. 13 Calculated electronic band structure of $o\text{-Ta}_5\text{O}_4\text{I}_{11}$, with bands coloured by their Ta character. Spin–orbit coupling was included in the calculation. Special points in and paths through reciprocal space were chosen following the literature.⁶⁸

exploration of potential Mott behaviour was not possible in this case.

In contrast, DFT calculations showed $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ to be a semiconductor with a gap of 0.4 eV (Fig. 14), in accordance with experiments. The existence of a band gap in $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ is therefore most likely not due to magnetic interactions or spin–orbit coupling. Significant differences in the electronic structure and chemical bonding between $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ and $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ can be seen. In $o\text{-Ta}_5\text{O}_4\text{I}_{11}$, the states near the Fermi energy have predominantly Ta d character, with several distinct band manifolds being visible. The upper manifolds are nearly flat, indicating localised electrons. In $m\text{-Ta}_5\text{O}_4\text{I}_{11}$, a much greater degree of hybridisation can be seen near the Fermi level, with the valence electrons having some O and I character in addition to Ta character (see Fig. S11–S14 in the SI for details). The formation of a band gap in $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ could then be ascribed to the formation of covalent bonds between Ta and other cluster atoms, whereas Ta atoms in $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ are more ionic. In $o\text{-Ta}_5\text{O}_4\text{I}_{11}$, the Ta atoms would therefore be expected to behave closer to idealised Ta^{3+} and Ta^{4+} , which contain unpaired d electrons, leading to partially filled bands at the DFT level.

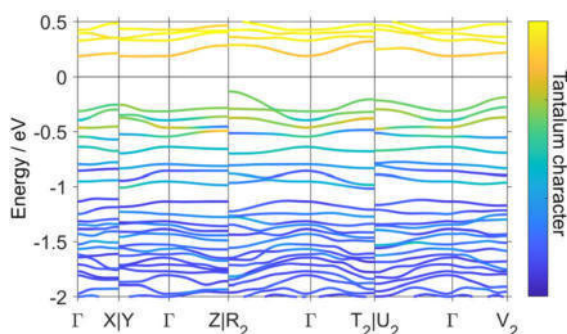


Fig. 14 Calculated electronic band structure of $m\text{-Ta}_5\text{O}_4\text{I}_{11}$, with bands coloured by their Ta character. Spin–orbit coupling was not included in the calculation. Special points in and paths through reciprocal space were chosen following the literature.⁶⁸

Electron localisation function (ELF)

We have also calculated from DFT the electron localisation function (ELF) of $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ and $m\text{-Ta}_5\text{O}_4\text{I}_{11}$, further elucidating the electronic structure and chemical bonding in these materials.^{69,70} Like the band structures, the ELF of the two polymorphs are strikingly different. The ELF of the Ta and O atoms in $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ are largely spherical, indicating ionic bonding (Fig. 15). The monoclinic modification shows

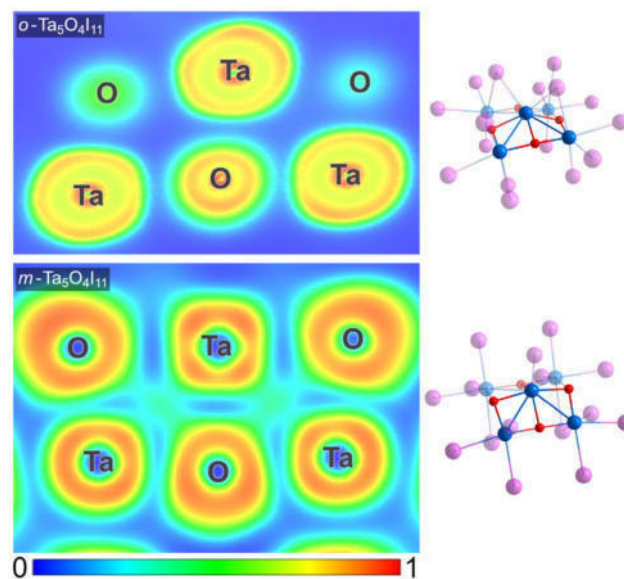


Fig. 15 Calculated ELF of $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ (top) and $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ (bottom), showing the presence of increased covalent bonding between Ta and O in the monoclinic phase, as demonstrated by the deviation of the shapes of the ELF from idealised ionic spheres.

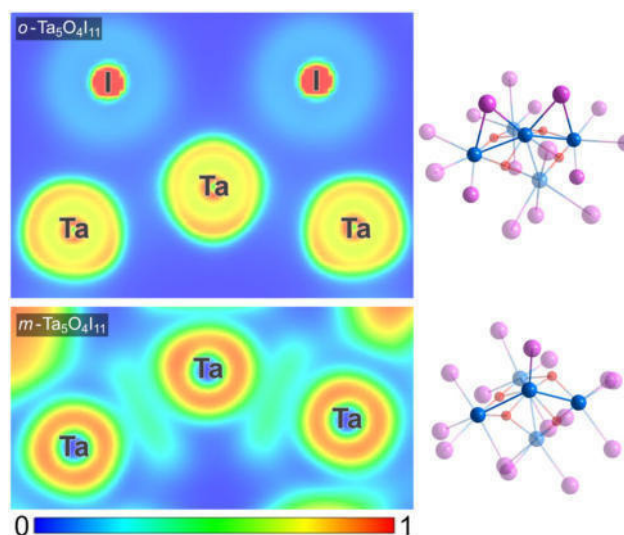


Fig. 16 Calculated ELF of $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ (top) and $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ (bottom), showing the presence of interstitial localised electrons in the monoclinic phase, corresponding to Ta–Ta bonds. No similar feature can be seen in the orthorhombic phase.



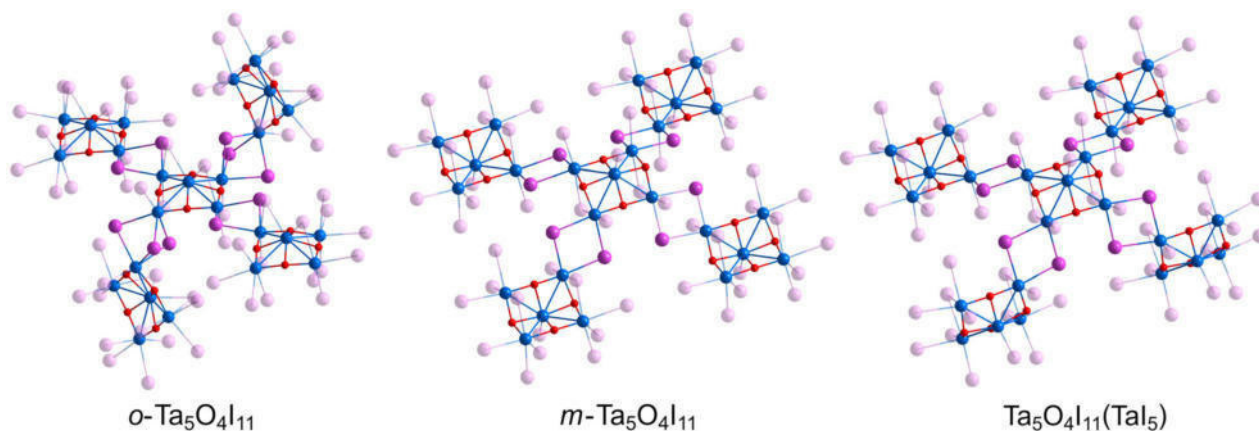


Fig. 17 Comparison of the inter cluster connectivity of o -Ta₅O₄I₁₁, m -Ta₅O₄I₁₁ and Ta₅O₄I₁₁(TaI₅).

the ELF of the atoms to be more distorted, as well as the presence of some interstitial electron density, which are indicators of covalent bonding. As Fig. 16 shows, this extra electron density lies in the planes between pairs of Ta atoms, corresponding to the formation of Ta–Ta bonds. This feature is absent in o -Ta₅O₄I₁₁, where there are instead nodal planes between the Ta atoms, again indicative of ionic interactions (compare Fig. S15 in SI).

Charge-disproportionated Ta³⁺ and Ta⁴⁺ ions, as seen in the XPS measurements of o -Ta₅O₄I₁₁ (Fig. 11), do not appear in our DFT calculations, where the ELF and electron counts around the Ta atoms are nearly identical at each site. Therefore, this disproportionation could be driven by whichever factors which lead to the opening of the band gap and are not accounted for in our DFT calculations.⁷¹

Conclusions

Heterogeneous solid-state reactions involving an unidentified gas phase have led to the formation of the compounds Nb₅O₄I₁₁, o -Ta₅O₄I₁₁, m -Ta₅O₄I₁₁, and Ta₅O₄I₁₁(TaI₅), all featuring an [M₅O₄] cluster core. In these structures, each cluster is connected to four neighbouring clusters at the corners *via* two or three bridging iodide ligands, creating distinct extended layered networks. These connectivity patterns are summarised in Fig. 17. A common structural characteristic among these compounds is a sinusoidal layering pattern within the crystal lattice, with layers separated by van der Waals gaps. The presence of bridging outer ligands spatially separates adjacent clusters, resulting in semiconducting behaviour with low electrical conductivity primarily confined to the layers, particularly evident in both forms of Ta₅O₄I₁₁.

In all compounds, the [Ta₅O₄] cluster core possesses six cluster electrons involved in metal–metal bonding, that could likely be localised along the four shorter metal–metal contacts between the pyramidal base and apex. According to a localised bonding model, the metal atoms in the basal plane may be assigned to Ta⁴⁺, while the apical metal atom

corresponds to Ta³⁺ in o -Ta₅O₄I₁₁, ensuring charge neutrality. This interpretation is supported by XPS, and it is partially consistent with charge distribution predicted by DFT calculations.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data are available within the article.

The data that support the findings of this study are available on request from the corresponding author, H.-J. Meyer. Computational data are available from DOI: [10.5281/zenodo.17424860](https://doi.org/10.5281/zenodo.17424860).

Supplementary information (SI): See DOI: <https://doi.org/10.1039/d5dt02097b>.

CCDC 2351105 (Ta₅O₄I₁₁(TaI₅)), 2380271 (o -Ta₅O₄I₁₁), 2389419 (Ta₂O₃I₄), 2390289 (LiTa₃O₂I₁₂), 2400835 (Nb₅O₄I₁₁) and 2424946 (m -Ta₅O₄I₁₁) and contain the supplementary crystallographic data for this paper.^{72a–f}

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(b) CCDC 2380271: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2kwy8](https://doi.org/10.5517/ccdc.csd.cc2kwy8);
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Supporting Information

Structural Modifications of $M_5O_4I_{11}$ ($M = \text{Nb}, \text{Ta}$) Cluster Networks from Heterogeneous Solid-State Reactions

Fabian Grahlow, Jan Beitzberger, Mario Martin, Eric Juriatti, Heiko Peisert, Marcus Scheele, Markus Ströbele, Carl P. Romao, and Hans-Jürgen Meyer

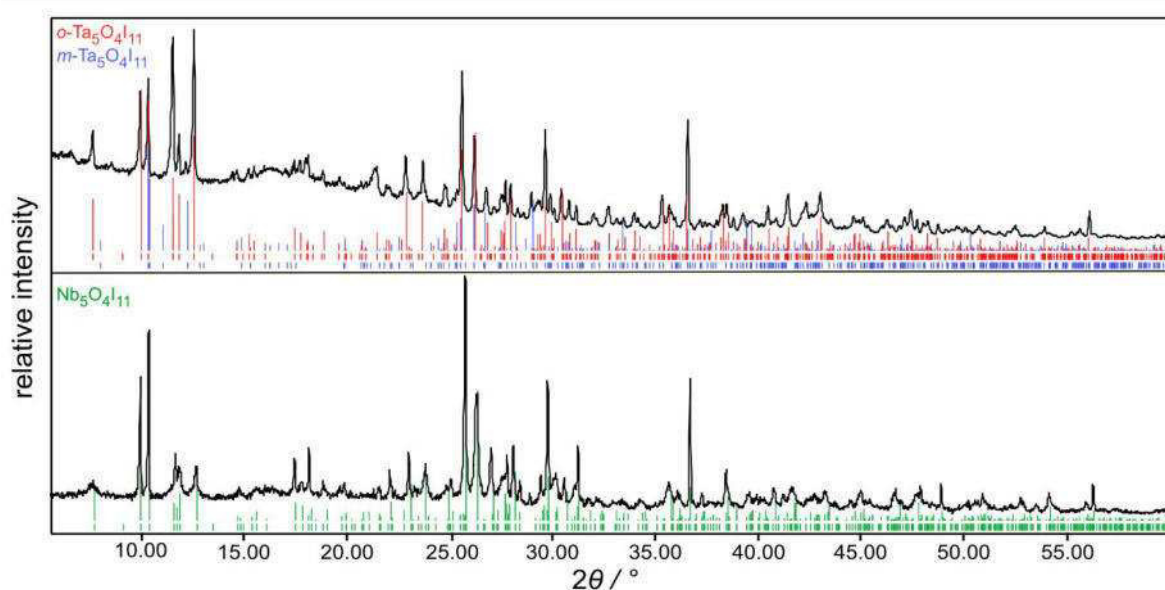


Figure S1. Powder X-ray diffraction patterns of $\text{Ta}_5\text{O}_4\text{I}_{11}$ (orthorhombic and monoclinic) and $\text{Nb}_5\text{O}_4\text{I}_{11}$ with the corresponding Bragg positions, calculated from the single-crystal X-ray diffraction measurements.

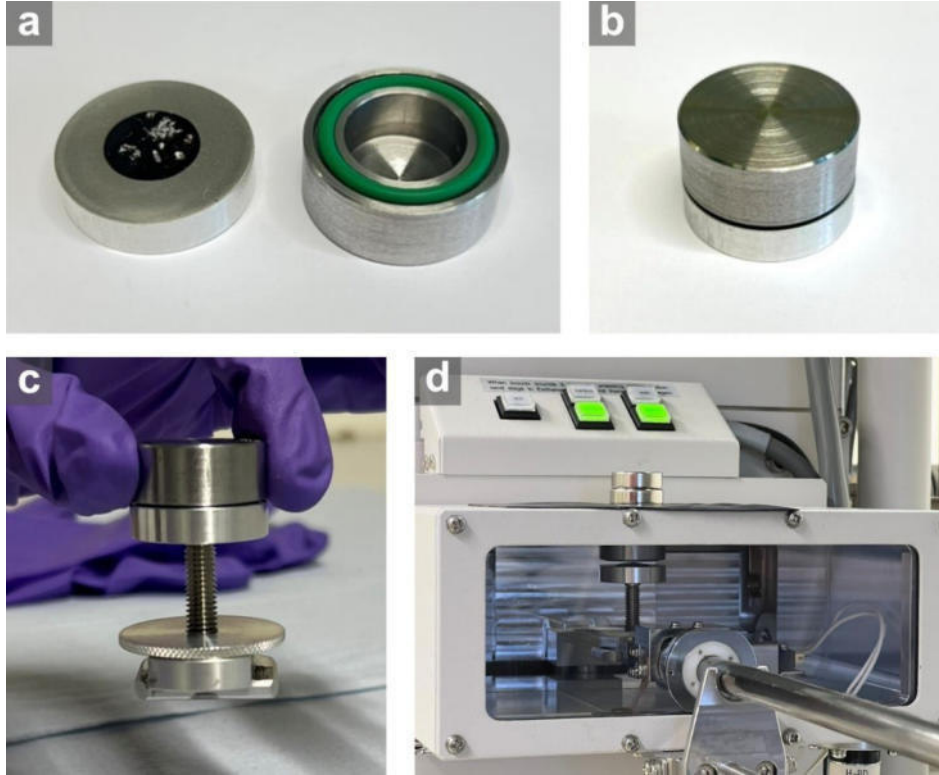


Figure S2. Procedure for inert transfer of samples into the scanning electron microscope. (a) The sample is fixed onto the sample holder using carbon tape. (b) The lid is placed on top of the sample holder, evacuated within the glovebox airlock, and then rapidly flooded with argon to ensure airtight seal. (c) The sealed sample is screwed on the transfer holder and transferred into the SEM airlock, while the reduced-pressure environment maintains the seal. (d) Once the SEM chamber is evacuated, the transfer chamber lid can be lifted using an external magnet.

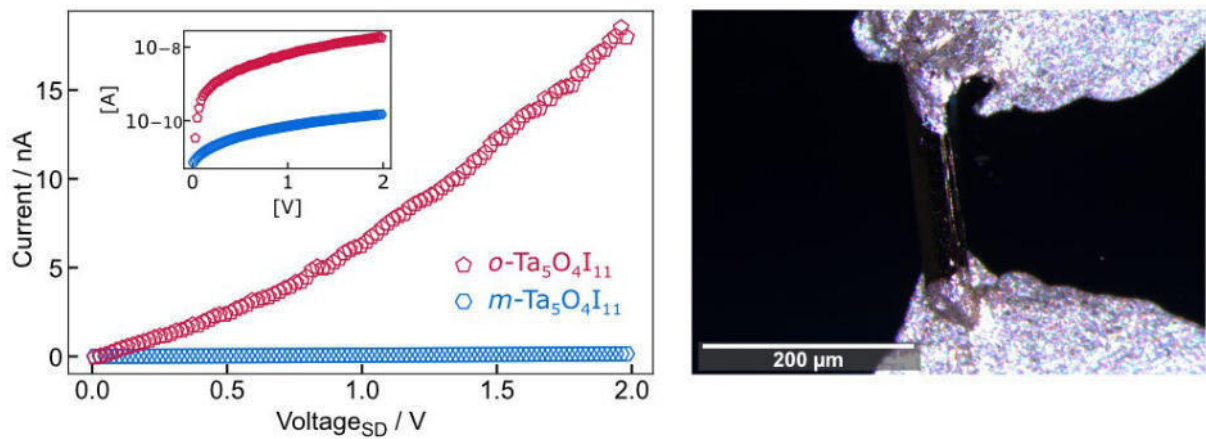


Figure S3. I - U -sweeps of an o - $\text{Ta}_5\text{O}_4\text{I}_{11}$ crystal (red) and a m - $\text{Ta}_5\text{O}_4\text{I}_{11}$ crystal (blue) at a temperature of 300 K (left). The inset shows the same data on a logarithmic scale to see the increase of current of m - $\text{Ta}_5\text{O}_4\text{I}_{11}$ (left). Single crystals are fixed onto Si/SiO_2 using conductive silver paste (right).



Figure S4. Sample holder and lid for inert transfer for XPS measurements. The sample is fixed onto the sample holder using carbon tape (left). The lid is placed on top of the sample holder, evacuated within the glovebox airlock, and then rapidly flooded with argon to ensure airtight seal (right).

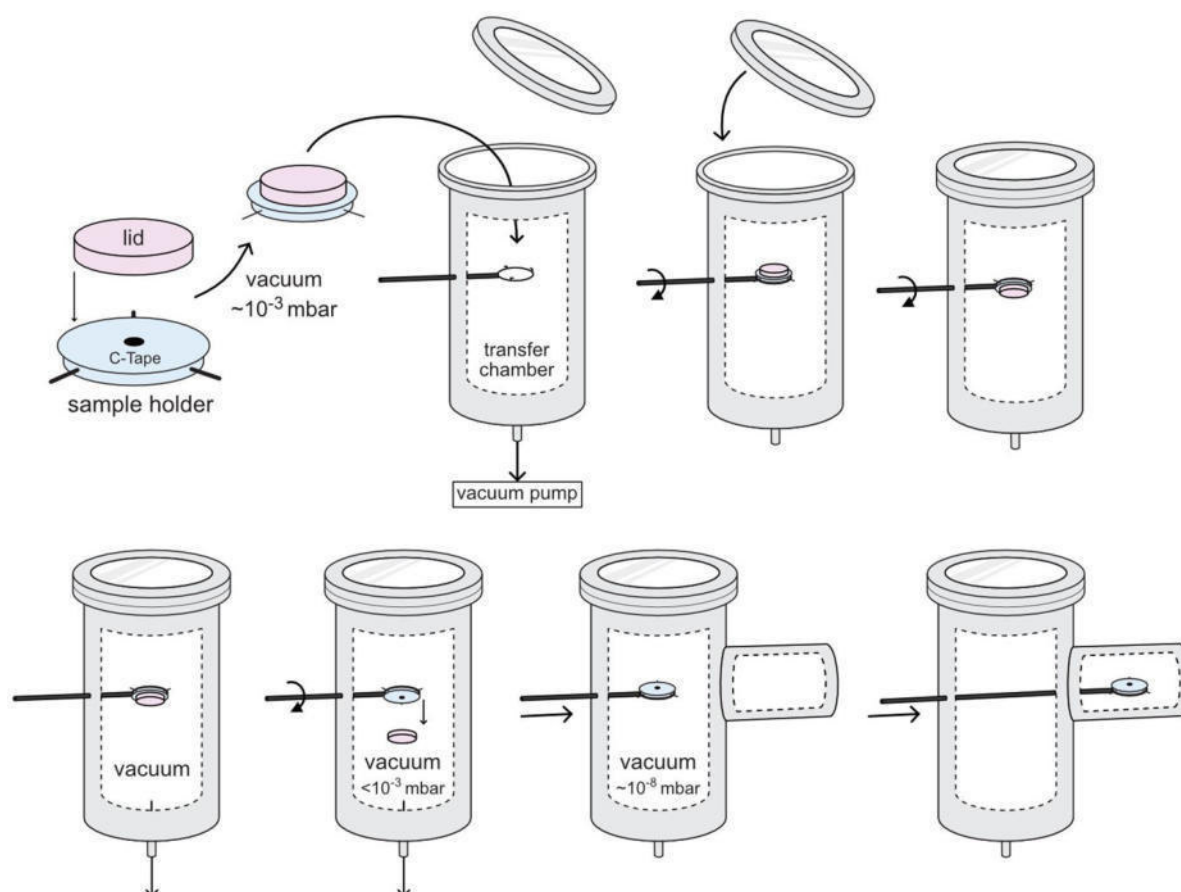


Figure S5. Schematic illustration of the inert transfer procedure for XPS measurements. The sample is mounted on a holder using carbon tape and sealed with a lid under reduced pressure ($\sim 10^{-3}$ mbar) inside a glovebox airlock (compare Figure S4). The sealed holder is then placed into the XPS transfer chamber, which is subsequently closed. From outside the chamber, the sample holder is inverted. As the chamber is evacuated, the internal pressure of the sealed holder becomes higher than the chamber pressure ($< 10^{-3}$ mbar), causing the lid to detach and fall to the bottom of the chamber. The pressure is further reduced to $\sim 10^{-8}$ mbar before the sample is transferred into the XPS measurement chamber.

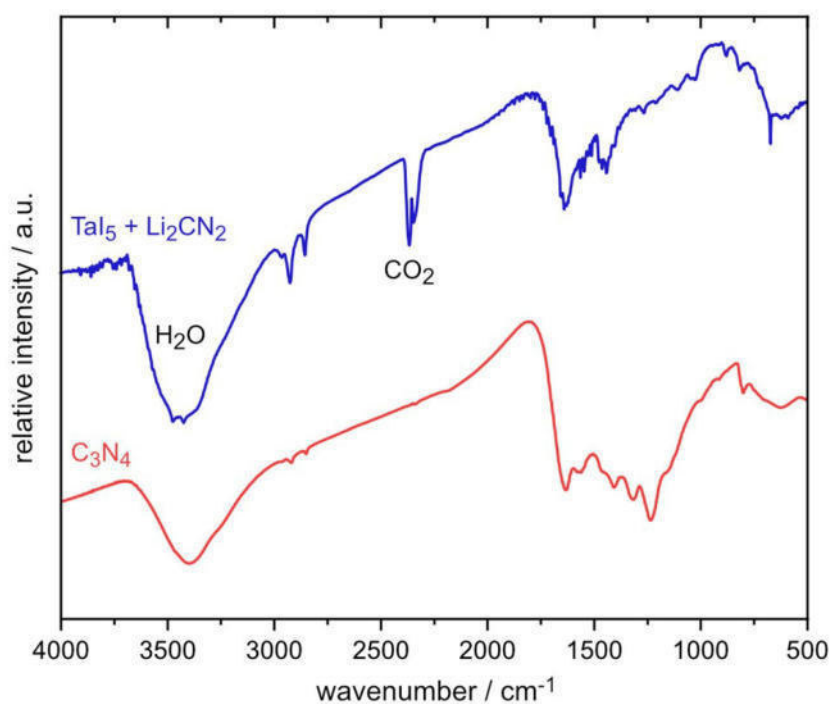


Figure S6. IR spectrum of the product from the reaction of Ta_5 and Li_2CN_2 (blue, top) compared to the IR spectrum of amorphous C_3N_4 , synthesized according to literature procedure (red, bottom).¹

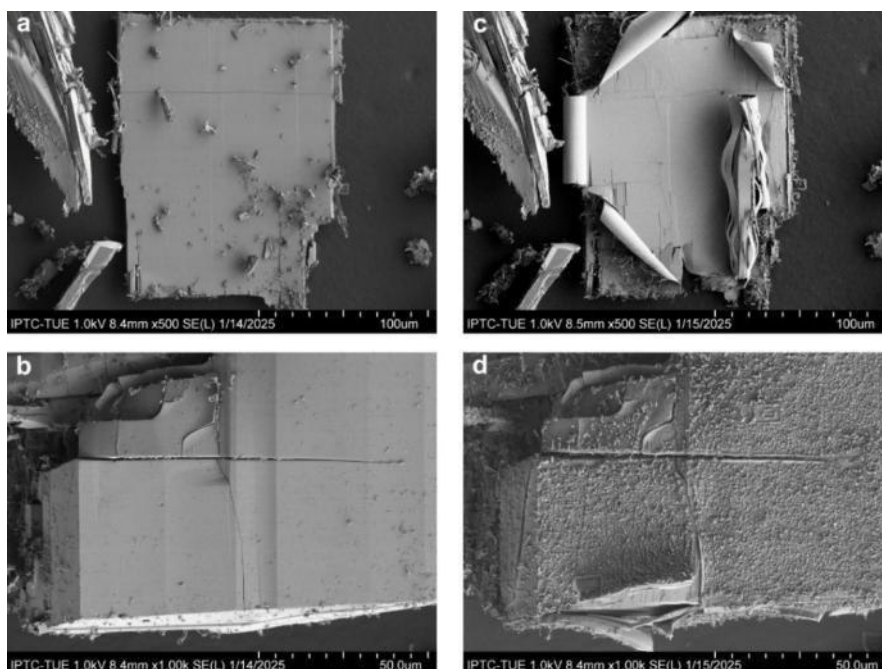


Figure S7. SEM images of two $\text{Ta}_5\text{O}_4\text{I}_{11}$ crystals after inert transfer into the device (a, b), and the corresponding crystals after being exposed to air for five minutes before being re-examined in the SEM (c, d).

¹ H. Zhao, X. Chen, C. Jia, T. Zhou, X. Qu, J. Jian, Y. Xu, T. Zhou, *Materials Science and Engineering: B* **2005**, 122, 90-93.

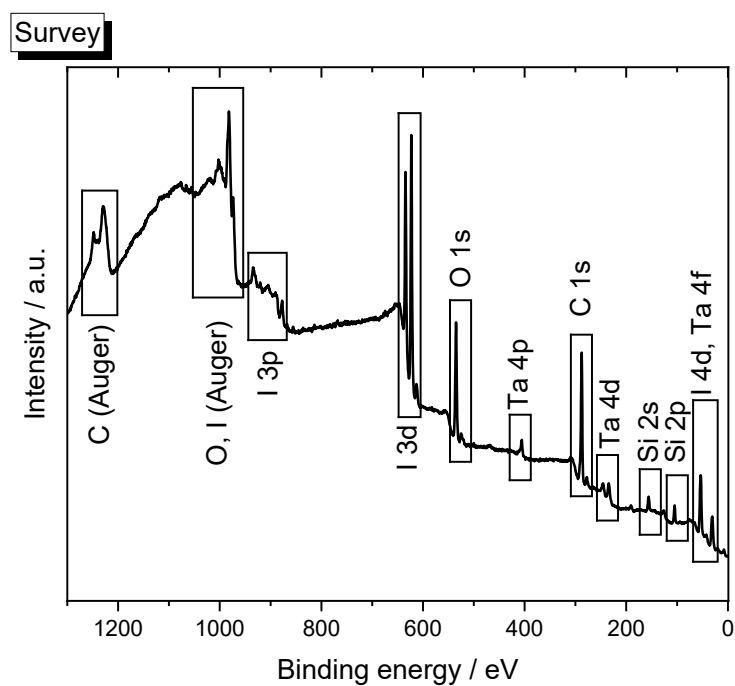


Figure S8. XPS survey spectrum for binding energies of 1300-0 eV showing Ta, I and O signals from the sample and C, Si and O signals from the conductive carbon tape.

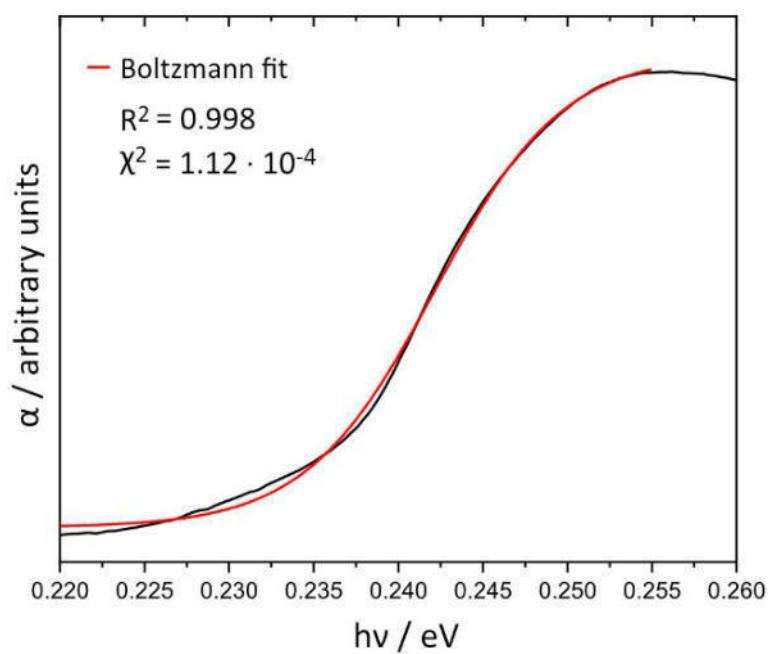


Figure S9. Optical absorption spectrum of $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ with the Boltzmann function used to fit α .

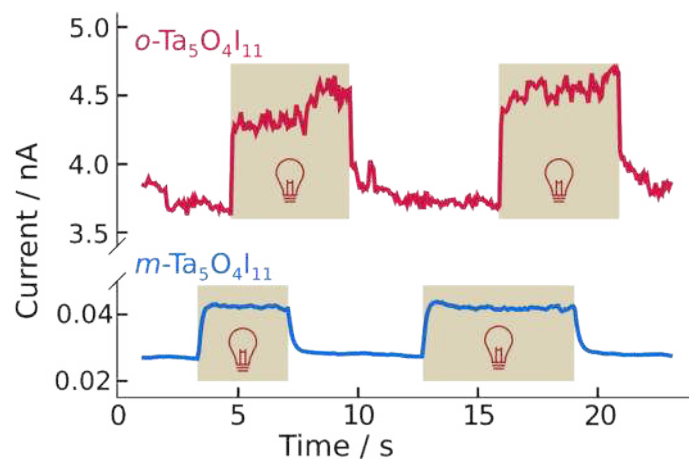


Figure S10. Photoresponse of an $o\text{-Ta}_5\text{O}_4\text{I}_{11}$ crystal (top, red) and a $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ crystal (bottom, blue) toward a 779 nm laser at 300 K.

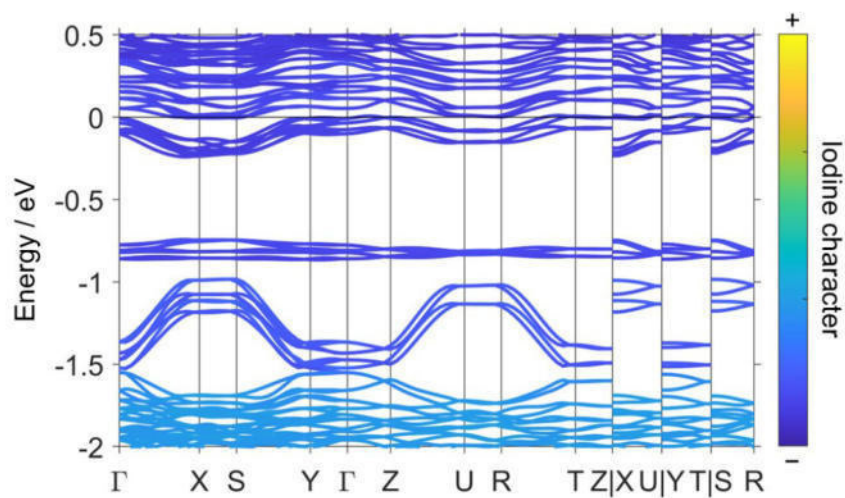


Figure S11. Calculated electronic band structure of $o\text{-Ta}_5\text{O}_4\text{I}_{11}$, with bands coloured by their I character. Spin-orbit coupling was included in the calculation. Special points in and paths through reciprocal space were chosen following the literature.¹

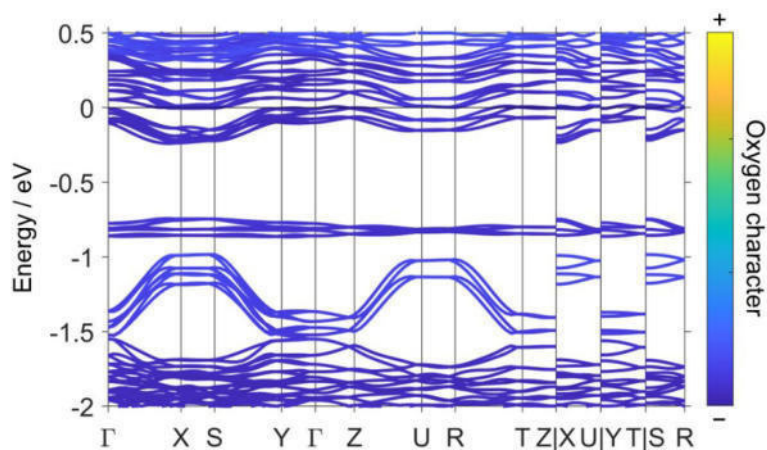


Figure S12. Calculated electronic band structure of $o\text{-Ta}_5\text{O}_4\text{I}_{11}$, with bands coloured by their O character. Spin-orbit coupling was included in the calculation. Special points in and paths through reciprocal space were chosen following the literature.¹

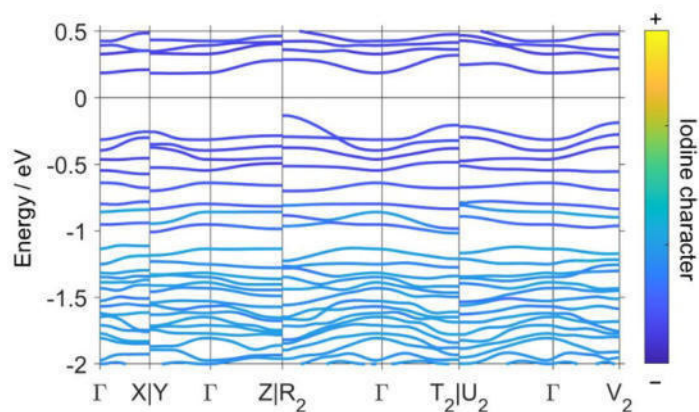


Figure S13. Calculated electronic band structure of $m\text{-Ta}_5\text{O}_4\text{I}_{11}$, with bands coloured by their I character. Spin-orbit coupling was included in the calculation. Special points in and paths through reciprocal space were chosen following the literature.¹

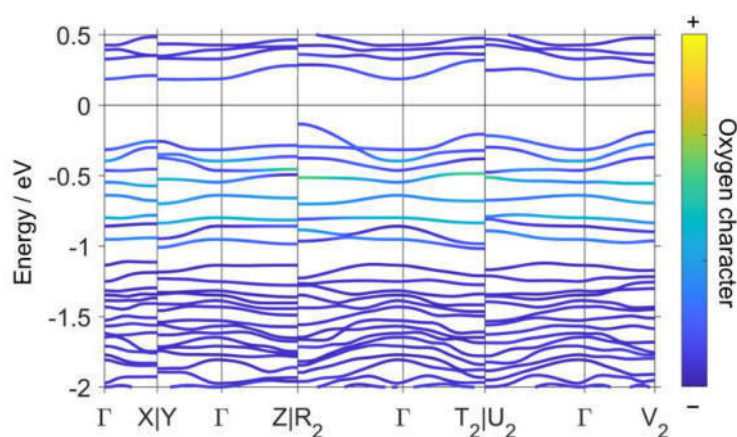


Figure S14. Calculated electronic band structure of $m\text{-Ta}_5\text{O}_4\text{I}_{11}$, with bands coloured by their O character. Spin-orbit coupling was included in the calculation. Special points in and paths through reciprocal space were chosen following the literature.¹

1. Y. Hinuma; G. Pizzi; Y. Kumagai; F. Oba; I. Tanaka. Band structure diagram paths based on crystallography. *Comput. Mater. Sci.* **2017**, 128, 140-184.

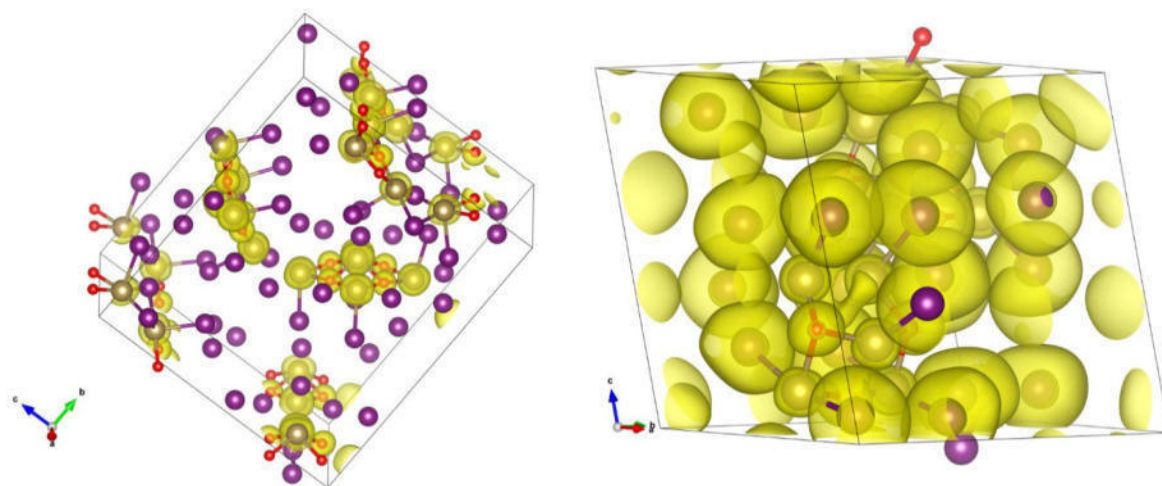


Figure S15. Three-dimensional ELF images of orthorhombic (left) and monoclinic (right) $\text{Ta}_5\text{O}_4\text{I}_{11}$ with isosurfaces at the 0.65 level.

Table S1. Comparison of selected interatomic distances (pm) and bond angles ($^\circ$) in $m\text{-Ta}_5\text{O}_4\text{I}_{11}$ and $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{Ta}_5)$.

distance / pm ; $\angle / ^\circ$	$m\text{-Ta}_5\text{O}_4\text{I}_{11}$	distance / pm ; $\angle / ^\circ$	$\text{Ta}_5\text{O}_4\text{I}_{11}(\text{Ta}_5)$
intra cluster		intra cluster	
Ta(1) – Ta(2)	286.34(3)	Ta(1) – Ta(5)	286.91(4)
Ta(1) – Ta(3)	286.97(3)	Ta(1) – Ta(2)	287.66(4)
		Ta(1) – Ta(3)	287.17(4)
		Ta(1) – Ta(4)	287.57(4)
$\angle \text{Ta}(2) - \text{Ta}(1) - \text{Ta}(3)$	132.21(1)	$\angle \text{Ta}(3) - \text{Ta}(1) - \text{Ta}(5)$	131.33(1)
		$\angle \text{Ta}(2) - \text{Ta}(1) - \text{Ta}(4)$	130.57(1)
inter cluster		inter cluster	
Ta(2) – Ta(3)	443.17(4)	Ta(2) – Ta(3)	439.06(5)
Ta(4) – Ta(5)	434.12(3)	Ta(4) – Ta(5)	433.71(7)

Table S2. XPS-fit parameters for the Ta 4f spectrum depicted in Figure 11.

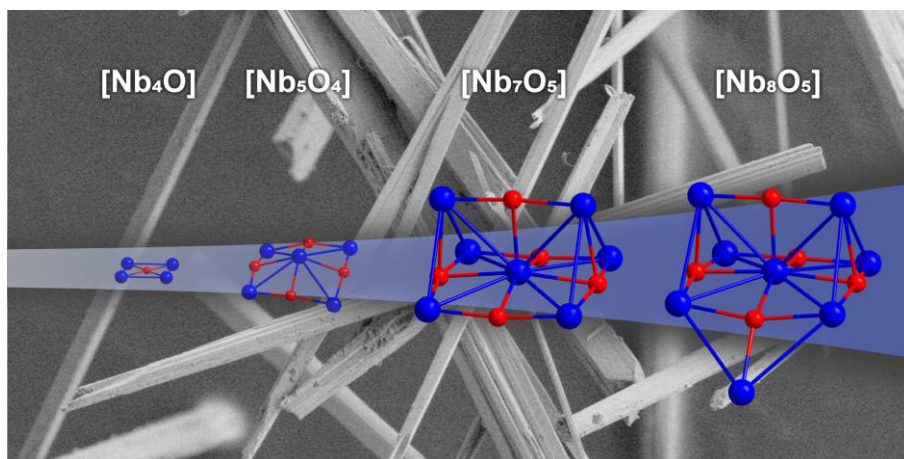
	Position (eV)	Gaussian width (eV)	Lorentzian width (eV)	rel. area (%)
$\text{Ta}^{4+} 4f_{7/2}$	26.35	1.65	0.30	46.1
$\text{Ta}^{4+} 4f_{5/2}$	28.23	1.65	0.30	34.5
$\text{Ta}^{3+} 4f_{7/2}$	24.23	2.50	0.50	11.1
$\text{Ta}^{3+} 4f_{5/2}$	26.10	2.50	0.50	8.3

Table S3. Crystallographic data of $M_5O_4I_{11}$ ($M = \text{Nb, Ta}$) cluster compounds.

	$\text{Nb}_5\text{O}_4\text{I}_{11}$	$o\text{-Ta}_5\text{O}_4\text{I}_{11}$	$m\text{-Ta}_5\text{O}_4\text{I}_{11}$	$\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$
CCDC Identification code	2400835	2380271	2424946	2351105
Formula weight	1924.45	2364.65	2364.65	3180.10
Radiation type	Cu K_α	Mo K_α	Mo K_α	Mo K_α
Wavelength / pm	154.184	71.073	71.073	71.073
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	$Pmc2_1$	$Pmc2_1$	$P2_1/m$	$Pbca$
Unit cell dimensions / Å	$a = 9.7963(2)$	$a = 9.8198(1)$	$a = 8.9594(1)$	$a = 17.7586(3)$
	$b = 17.8082(3)$	$b = 17.8539(1)$	$b = 13.6077(1)$	$b = 13.4107(4)$
	$c = 15.2052(2)$	$c = 15.3672(1)$	$c = 15.3672(1)$	$c = 30.4660(6)$
			$\beta = 107.500(2)$	
Volume / Å ³	2652.61(8)	2694.20(4)	1351.20(3)	7255.6(3)
Z	4	4	2	8
Density (calculated) / g cm ⁻³	4.819	5.830	5.812	5.822
Absorption coefficient / mm ⁻¹	117.683	32.835	32.735	31.645
Crystal size / mm ³	0.09×0.05×0.01	0.36×0.04×0.04	0.18×0.09×0.03	0.14×0.02×0.01
Theta range for data collection	3.823° to	2.074° to	2.370° to	2.017° to
	68.216°	30.507°	25.344°	25.350°
Reflections collected	10180	128478	39410	53383
Independent reflections	4407	8650	2583	6642
R_{int}	0.0339	0.0403	0.0303	0.0507
restraints / parameters	1 / 208	1 / 206	0 / 98	0 / 245
Goodness-of-fit on F^2	1.025	1.102	1.479	1.015
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0485$	$R_1 = 0.0215$	$R_1 = 0.0154$	$R_1 = 0.0226$
	$wR_2 = 0.1254$	$wR_2 = 0.0560$	$wR_2 = 0.0342$	$wR_2 = 0.0443$
R indices (all data)	$R_1 = 0.0515$	$R_1 = 0.0218$	$R_1 = 0.0154$	$R_1 = 0.0305$
	$wR_2 = 0.1270$	$wR_2 = 0.0561$	$wR_2 = 0.0343$	$wR_2 = 0.0464$
Largest diff. peak and hole	1.205 and	1.509 and	0.759 and	1.946 and
	-0.493 e·Å ⁻³	-1.157 e·Å ⁻³	-0.731 e·Å ⁻³	-1.789 e·Å ⁻³

Publication 4

Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicenter Nb–Nb bonding



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14376**Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicentre Nb–Nb bonding**Jan Beittlberger,^a Markus Ströbele,^a Patrick Schmidt,^a Carl P. Romao^b and
H.-Jürgen Meyer^{a*}

A series of niobium oxyiodide compounds has recently been identified using a non-conventional reduction method. The continuation of these studies of heterogeneous solid-state reactions in a closed system has led to the crystallization and structural analysis of two novel compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. Both crystal structures are derived from the pentanuclear $[\text{Nb}_5\text{O}_4]$ cluster core and are expanded through the incorporation of additional niobium atoms, forming new $[\text{Nb}_7\text{O}_5]$ and $[\text{Nb}_8\text{O}_5]$ cluster cores. Furthermore, it is shown that oxyiodide clusters containing between four and eight niobium atoms can form from the same mixture of reactants by simply adjusting the composition and temperature. A comprehensive assembly model for these clusters is presented, and electronic structure calculations provide insight into the nature of niobium–niobium bonding within the $[\text{Nb}_7\text{O}_5]$ core.

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rsc.li/dalton**Introduction**

Metal-rich halide cluster compounds of group 5 and 6 transition metals are well known from the research initiated by the groups of Schäfer, von Schnering and Simon.¹ Preparations of these compounds are typically performed by metallothermic reduction, in which a metal halide (MX_n) is reacted with metal (M), which can be the same metal (M) or an electropositive alkali metal or Al.² Attempts to employ non-conventional reduction agents have been demonstrated to provide insights into the reduction pathway (namely through metal intercalation followed by metal halide elimination) by using non-conventional reduction agents, such as Cr, Fe, Co, or Ni, *etc.*, assisted by thermal scanning.³ Recently, we have successfully employed lithium carbodiimide as a reduction agent, as will be explained subsequently.⁴

The vast majority of transition metal cluster compounds is based on an octahedral cluster core of metal (M) atoms which most commonly appear with $[\text{M}_6\text{X}_8]$ with eight face-capping X or $[\text{M}_6\text{X}_{12}]$ with twelve edge-capping X halide (X) environments.⁵ In addition, interstitially (Z) stabilized octahedral clusters of the type $[\text{M}_6\text{ZX}_{12}]$ are reported for *electron-poor* group 4 metals.⁶

More than twenty binary tungsten iodide compounds have been discovered and structurally characterized; most of them are based on the $[\text{M}_6\text{X}_8]$ type cluster.⁷ In contrast, binary niobium iodide compounds involve only Nb_6I_{11} , Nb_3I_8 , NbI_3 , and NbI_4 .⁸ An interesting extension of the niobium halide chemistry has been achieved by the employment of an extra non-metal element, leading to heteroanionic cluster compounds, which may provide similar or completely distinct cluster architectures. Thus, heteroanionic clusters can be envisioned to constitute anion replacements in given architectures and to induce a modified structure or connectivity pattern of clusters, as exemplified for $\text{Nb}_6\text{I}_9\text{S}$ (derived from Nb_6I_{11}), $\text{Nb}_3\text{X}_7\text{S}$ (X = Cl, Br, I), and $\text{ANb}_3\text{Br}_7\text{S}$ with A = Rb, Cs (both derived from Nb_3X_8).⁹ Different cluster architectures are obtained in compounds with chalcogenides, such as Nb_3TeI_7 , $\text{Nb}_4\text{Se}_4\text{I}_4$, $\text{Nb}_7\text{S}_2\text{I}_{19}$, and with pnictide anions in $\text{Nb}_4\text{PnX}_{11}$ with Pn = N, P, X = Cl, Br, I.^{9b,10} Beside the difference in the number of Nb atoms forming the cluster core, the cluster design and connectivity are showing a great variety and so do the properties.

Niobium oxyiodide compounds are reported for NbOI_3 , NbO_2I , and the metal-rich example NbOI_2 .¹¹ Condensed metal–oxide–halides volatilize easily and can be crystallized only within a specific equilibrium window. This observation highlights the sensitivity of these systems to changes in conditions, such as temperature and composition, which can significantly impact the formation of different niobium oxyiodide phases.

The Nb–O–I system was recently a subject of investigations with a focus on metal-rich compounds by employing $\text{Li}_2(\text{CN}_2)$

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as a reducing agent. The reaction, *i.e.* the reduction, involves the decomposition of the $(\text{NCN})^{2-}$ ion into C_3N_4 , as evidenced by IR spectroscopy.^{4b} Previous reactions have shown, that the interplay between NbI_4 , $\text{Li}_2(\text{CN}_2)$ and Li_2O can form a heterogeneous system in which local temperatures have an important impact on the phase formation. As a result, we have already reported the compounds $\text{Nb}_4\text{OI}_{12}$, $\text{Nb}_4\text{OI}_{11}$, and $\text{Nb}_4\text{OI}_{10}$ with their crystal structures, all based on the rectangular $[\text{Nb}_4\text{O}]$ core.^{4a} With decreasing iodide content, the series of $\text{Nb}_4\text{OI}_{12-x}$ compounds is showing structures with increasing connectivity between clusters, increasing electrical conductivities, and an increasing number of electrons from six ($x = 2$) to eight electrons ($x = 0$) per cluster. Furthermore, we have conducted a detailed analysis of the properties of oxyiodides of the type $\text{M}_5\text{O}_4\text{I}_{11}$, where $\text{M} = \text{Nb}$ or Ta .¹²

In continuation of this research, we now present two additional niobium oxyiodides, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, featuring $[\text{Nb}_7\text{O}_5]$ and $[\text{Nb}_8\text{O}_5]$ cluster cores, each accommodating 13 electrons available for niobium–niobium bonding.

Results and discussion

Synthesis and crystal structure

In our synthesis, NbI_4 was reacted with $\text{Li}_2(\text{CN}_2)$ and Li_2O . The specific combination of these reactants (see Experimental section) constitutes a heterogeneous reaction system governed by temperature-dependent equilibria, leading to the formation of various solid and gaseous phases. Within this system, $\text{Li}_2(\text{CN}_2)$ is proposed to function as an unconventional reducing agent for NbI_4 , thereby undergoing decomposition of the $(\text{CN}_2)^{2-}$ anion to form C_3N_4 .

To gain insight into the reaction mechanism, we performed a series of reactions at different temperatures and durations. Heating the mixture to 300 °C yielded an unknown crystalline phase, along with LiI , NbOI_2 , and an amorphous powder, as determined by powder X-ray diffraction (PXRD) (see Fig. S1, SI). Upon heating at 400 °C for 1 hour, the unidentified phase disappeared, and the compound $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was formed, accompanied by NbOI_2 and NbI_5 . Prolonged heating at 400 °C for 24 hours resulted in the crystallization of the known $\text{Nb}_5\text{O}_4\text{I}_{11}$, which contains the $[\text{Nb}_5\text{O}_4]$ cluster core.¹²

Further heating at 500 °C for 1 hour produced crystals characterized as $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, which were found on the walls of the ampoule. Extending the heating time at 500 °C to 24 hours led to the formation of $\text{Nb}_4\text{OI}_{10}$, a previously reported compound featuring a $[\text{Nb}_4\text{O}]$ cluster core.^{4a}

These results, while focused on solid-state products, do not account for the role of gaseous species that significantly influence the formation pathways of the observed materials. A quenching experiment of the gas phase from 400 °C to room temperature revealed the presence of a black fluid that appeared as small droplets on the ampoule walls (Fig. S2a). After 48 hours at ambient temperature, these droplets transformed into dark red, filamentous crystallites (Fig. S2b), which subsequently decomposed over time (Fig. S2c).

The two new compounds presented in this study, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, were structurally characterized by single-crystal X-ray diffraction (see Table 1). $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ crystallizes as rod-like crystals, whereas $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$ forms plate-like crystals. Several single crystals of the latter were refined, and in each case, the iodide content of the enclosed NbI_5 molecules were found to have slightly more than five iodide atoms, associated with the presence of some polyiodide. For clarity and simplicity, this compound will hereafter be referred to as $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$.

The crystal structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ features an oxygen-stabilized Nb_7 cluster arrangement, in which a central niobium atom (Nb2) is surrounded by six additional niobium atoms (Nb1 and Nb3), forming a trigonal prismatic coordination environment around Nb2 (Fig. 1).

Cluster cores composed of seven metal atoms are relatively rare and often adopt significantly different geometries compared to the $[\text{Nb}_7\text{O}_5]$ cluster core observed in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. For instance, in $[\text{N}(\text{PPh}_3)_2][\text{Os}_6\text{Au}(\text{CO})_{20}\text{H}_2]$, the $[\text{Os}_6\text{Au}]$ cluster is described as two butterfly-shaped units sharing a wing tip.¹³ Another example is the asymmetric $[\text{MoFe}_6]$ cluster core in

Table 1 Crystallographic and refinement data of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$

	$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$	$\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$
CCDC	2311571	2428720
Space group	<i>Cmcm</i>	<i>Pnma</i>
Temperature/K	230	200
Unit cell dimensions/Å	<i>a</i> = 14.5783(3) <i>b</i> = 17.6445(3) <i>c</i> = 13.5823(2)	<i>a</i> = 11.4282(4) <i>b</i> = 13.4336(6) <i>c</i> = 31.479(1)
Volume/Å ³	3493.7(1)	4848.1(3)
Z	4	4
Wavelength/Å	1.54184	1.54184
μ/mm^{-1}	122.292	128.729
2 θ range for data collection	7.866 to 136.454	5.598 to 133.306
Total number of reflections	17 730	47 074
Independent reflections	1742	4437
Refined parameters	85	240
<i>R</i> _{int}	0.0316	0.0589
<i>R</i> ₁	0.0197	0.0274
<i>wR</i> ₂	0.0534	0.0516
Goodness-of-fit on <i>F</i> ²	1.060	1.036

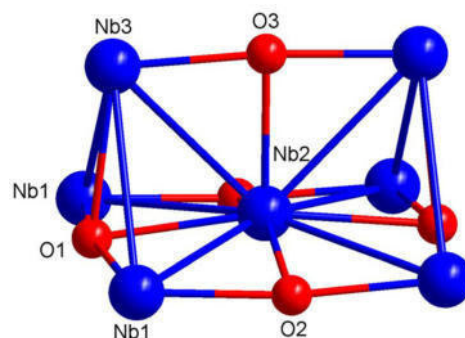


Fig. 1 Structure of the $[\text{Nb}_7\text{O}_5]$ cluster core inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.



$[\text{Ph}_4\text{As}]_2[\text{MoFe}_6\text{S}_6(\text{CO})_{16}]$.¹⁴ Octahedral M_6 clusters containing a central transition-metal atom are also known, particularly among rare-earth and zirconium-based compounds.¹⁵

In contrast, the $[\text{Nb}_7\text{O}_5]$ cluster core can be regarded as an extension to the $[\text{M}_5\text{O}_4]$ cluster core found in the $\text{M}_5\text{O}_4\text{I}_{11}$ compounds ($\text{M} = \text{Nb}, \text{Ta}$) through addition of three more atoms, namely two Nb3 atoms and the O3 ion depicted in Fig. 1. The $[\text{Nb}_7\text{O}_5]$ cluster core represents six short Nb–Nb distances between the central Nb2 with the surrounding six niobium atoms measuring 2.7883(7) Å (Nb2–Nb3) and 2.8050(4) Å (Nb1–Nb2). These distances are significantly shorter than the Nb1 and Nb3 separation, which measure 3.0667(6) Å. The cluster is surrounded by iodide ligands, including four edge-capping ligands, four terminal ligands, and twelve iodide ligands that bridge between adjacent cluster cores in a 12/2 fashion, as illustrated in Fig. 2. Using the notation originally developed for octahedral cluster compounds, distinguishing between inner (i), outer (a), and outer-bridging (a–a) ligand functionalities, the connectivity pattern of the cluster can be described as $(\text{Nb}_7\text{O}_5\text{I}_4^{\text{i}})\text{I}_4^{\text{a}}\text{I}_{12/2}^{\text{a-a}}$.

This cluster fragment is further stabilized by three lithium ions and one additional iodide ion, completing the overall formula $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$. Four outer iodide ligands from the cluster, along with the additional iodide ion (I5), surround each lithium ion (Li1 and Li2) in a square-pyramidal fashion (see Fig. 3). The less flexible cluster-bound iodide ligands (I2 and I3) form the base of the square pyramid, with Li–I distances ranging from 2.904(6) to 3.17(1) Å, while the more flexible additional iodide ion (I5) occupies the apical position, showing Li–I distances of 2.64(2) Å and 2.76(1) Å.

The complete structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ is constructed by linking each $[\text{Nb}_7\text{O}_5]$ cluster to six neighbouring clusters, forming a three-dimensional framework. As illustrated in Fig. 4, a view along the c -axis of the structure reveals an alternating orientation of the adjacent clusters, highlighting the spatial arrangement and connectivity within the extended structure.

The second cluster compound obtained from the same basic reaction is $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. The $[\text{Nb}_8\text{O}_5]$ cluster core con-

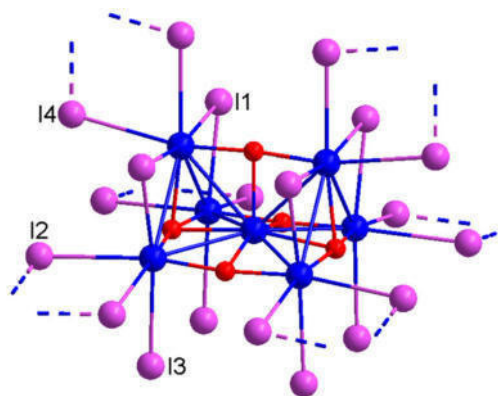


Fig. 2 Iodide coordination of the $[\text{Nb}_7\text{O}_5]$ cluster core, with twelve iodide atoms having bridging functionality (indicated by dashed lines). Niobium atoms are coloured in blue, oxygen in red and iodine in pink.

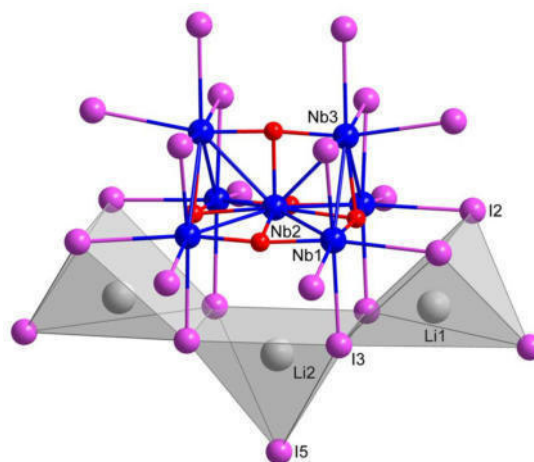


Fig. 3 Square-pyramidal lithium (grey) coordination in the structure with the additional iodide atom (I5).

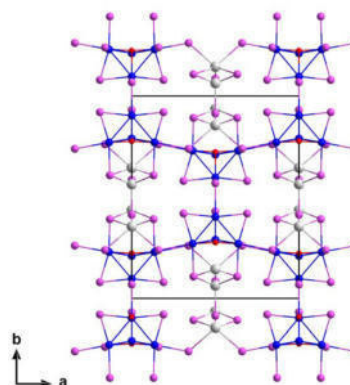


Fig. 4 Projection of the crystal structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, looking along the c -axis. Niobium atoms are shown in blue, oxygen in red, iodine in pink and lithium in grey.

tained within this compound can be viewed as an extension of the $[\text{Nb}_7\text{O}_5]$ core found in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, incorporating just one additional niobium atom. As shown in Fig. 5, this extension occurs through the addition of a niobium atom (Nb5) positioned at one edge of the $[\text{M}_5\text{O}_4]$ base, effectively expanding the cluster architecture.

As observed for the previously discussed $[\text{Nb}_7\text{O}_5]$ cluster core, the Nb–Nb distances between the central Nb2 atom and the six surrounding niobium atoms (Nb1, Nb3, Nb4) in $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ are relatively short, ranging from 2.7911(3) to 2.8600(7) Å. In contrast, the Nb–Nb distances between Nb3–Nb1 and Nb3–Nb4 are notably longer, falling in the range of 2.9981(6) to 3.1812(7) Å. The Nb–Nb distance involving the additional Nb5 atom is with 3.1418(7) Å in the same range. A comprehensive comparison of Nb–O bond lengths for both compounds is provided in Table 2. This comparison shows a good overall agreement between the structural metrics observed in the two cluster compounds.



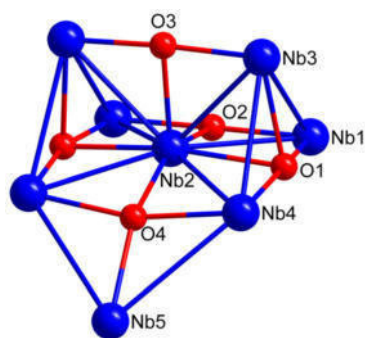


Fig. 5 The $[\text{Nb}_8\text{O}_5]$ cluster core of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$.

Table 2 Nb–O distances in the cluster cores of the two compounds and the average Nb–O distances with the corresponding coordination number (CN) of the oxygen

Compound distance/Å	$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$	$\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$
Nb1–O1	2.0005(9)	1.958(5)
Nb1–O2	1.9568(5)	1.9564(6)
Nb2–O1	2.197(6)	2.205(6)
Nb2–O2	2.097(6)	2.093(8)
Nb2–O3	2.080(8)	2.079(7)
Nb2–O4		2.084(7)
Nb3–O1	2.247(6)	2.233(5)
Nb3–O3	1.9464(6)	1.9415(7)
Nb4–O1		2.010(5)
Nb4–O4		2.122(1)
Nb5–O4		2.073(7)
$\bar{\text{O}} \text{ Nb-O1 (CN = 4)}$	2.11(1)	2.10(1)
$\bar{\text{O}} \text{ Nb-O2 (CN = 3)}$	2.00(1)	2.00(1)
$\bar{\text{O}} \text{ Nb-O3 (CN = 3)}$	1.99(1)	1.99(1)
$\bar{\text{O}} \text{ Nb-O4 (CN = 4)}$		2.10(1)

The presence of the additional niobium atom in the structure $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ alters, both the local environment and the connectivity pattern of the cluster. The connectivity changes from $(\text{Nb}_7\text{O}_5\text{I}_4)^{\text{I}}\text{I}_4^{\text{a}}\text{I}_{12/2}^{\text{a-a}}$ in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ to $(\text{Nb}_8\text{O}_5\text{I}_8)^{\text{I}}\text{I}_5^{\text{a}}\text{I}_{8/2}^{\text{a-a}}$ in $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ (Fig. 6). As a result, the number of connec-

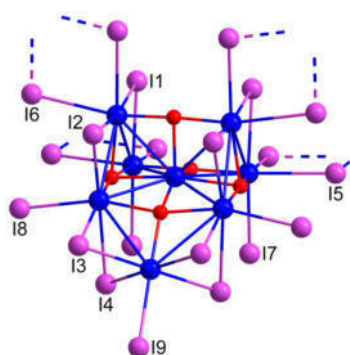


Fig. 6 Iodide coordination of the $[\text{Nb}_8\text{O}_5]$ cluster core with eight iodide atoms with bridging functionality (indicated by dashed lines) connecting to four adjacent clusters. Niobium atoms are coloured in blue, oxygen in red and iodine in pink.

tions to neighboring clusters is reduced to just four, leading to a dimensional reduction in the overall connectivity, from a three-dimensional framework in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ to a layered arrangement in $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with zig-zag layers extending along the *ab*-plane (Fig. 7).

Between the layers of the $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ structure, channels are formed that accommodate NbI_5 units (Fig. S3). The observed disorder in these regions arises from the partial incorporation of excess iodine, likely in the form of coordinated polyiodide species such as I_2^- or I_3^- . These species preferentially align along the crystallographic *a*-axis, contributing to the structural complexity and variability of the interlayer region.

The intercalation of molecular species within a solid-state framework is relatively uncommon but well-documented in the literature. Such molecules can reside in interlayer spaces or structural channels when the host framework provides cavities large enough to accommodate them. A notable example is the crystal structure of $\text{Nb}_7\text{S}_2\text{I}_{19}$, which can be described as $(\text{Nb}_3\text{SI}_7)_2(\text{NbI}_5)$.^{10d} In this compound, six $[\text{Nb}_3\text{S}]$ units form iodide-bridged ring arrangements that create central channels occupied by NbI_5 molecules. Another example is $\text{Ta}_5\text{O}_4\text{I}_{11}(\text{TaI}_5)$, where TaI_5 molecules are intercalated between corrugated layers.¹² In this case, TaI_5 acts as a structural template for layer formation, as a similar cluster connectivity is observed in $\text{m-Ta}_5\text{O}_4\text{I}_{11}$. A comparable template effect is reported in $[\text{K}_5(\text{Ti}_2\text{Cl}_9)][(\text{Nb}_6\text{Cl}_{12}\text{O}_4)_3(\text{Ti}_3\text{Cl}_4)_2]$,¹⁶ where the complex anion $[(\text{Nb}_6\text{Cl}_{12}\text{O}_4)_3(\text{Ti}_3\text{Cl}_4)_2]^{2-}$ forms a layered framework with large channels, which are filled by $[\text{K}_5(\text{Ti}_2\text{Cl}_9)]^{2+}$ units. A related scenario is found in $\text{Cs}_3(\text{ZrCl}_5)\text{ZrCl}_{15}\text{Mn}$,

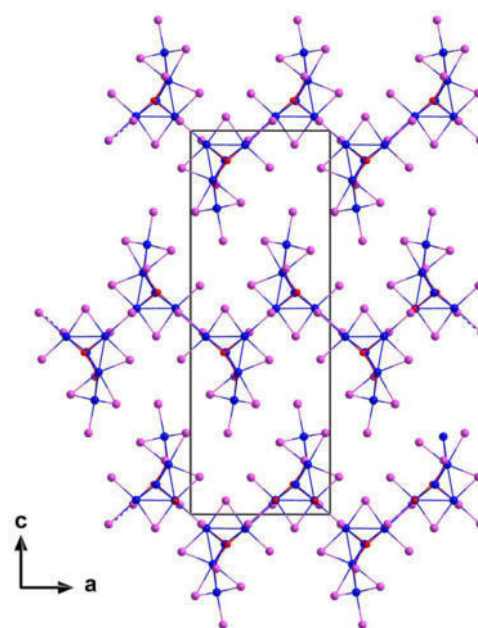


Fig. 7 Projected structure with the $\text{Nb}_8\text{O}_5\text{I}_{17}$ section of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$. The NbI_5 molecules between the layers are omitted for clarity. Niobium atoms are shown in blue, oxygen in red and iodine in pink.



where ZrCl_5^- units are incorporated into a three-dimensional framework constructed from $[\text{Zr}_6(\text{Mn})\text{Cl}_{12}]^{1-}\text{Cl}_{6/2}^{a-15a}$. Such a monoanionic molecule can also be intercalated into a simple metal halide, as demonstrated by the compound $(\text{Ta}_6\text{Br}_{15})$ $(\text{TaBr}_6)_{0.86}$.¹⁷ These examples show how molecular species can be stabilized within solid-state matrices by occupying voids or acting as templates that influence framework formation.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Scanning electron microscopy was performed with the aid of a custom-designed vacuum transfer device to transfer the samples under inert conditions. Fig. 8 shows some crystals of $\text{Li}_3\text{Nb}_7\text{O}_{515}$, having a rod-like morphology with right-angled edges and a rough surface.

To confirm the composition determined by X-ray diffraction of $\text{Li}_3\text{Nb}_7\text{O}_{515}$, EDX measurements on multiple crystals were performed. These measurements result in an average Nb:I ratio of 7 : 15.2(6).

Electronic band structure and ELF calculations

The electronic structure of $\text{Li}_3\text{Nb}_7\text{O}_{515}$ was investigated using density functional theory (DFT). The calculated band structure, shown in Fig. 9, reveals seven metal-centred energy bands located below the Fermi level. Among these, the highest-energy band intersects the Fermi level at multiple points in the Brillouin zone. These seven bands correspond to one formula unit of $\text{Li}_3\text{Nb}_7\text{O}_{515}$ and primarily arise from niobium–niobium bonding interactions within the $[\text{Nb}_7\text{O}_5]$ cluster, rather than in between clusters. In total, they accommodate 13 electrons per cluster. However, this number of electrons cannot be straightforwardly assigned to specific niobium–niobium contacts within the cluster core, especially when considering a notably large number of relatively short Nb–Nb distances within the cluster, discussed previously. The presence of a high density of bands at and above the Fermi level indi-

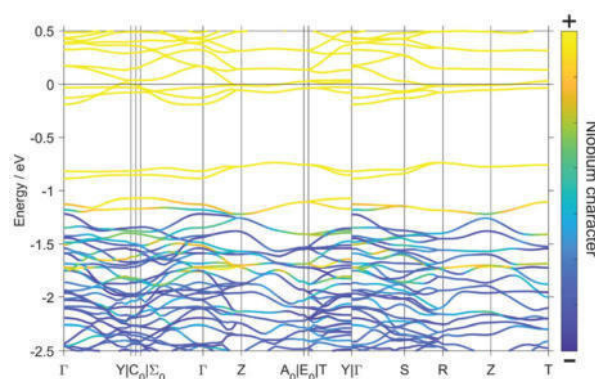


Fig. 9 DFT-calculated electronic band structure of $\text{Li}_3\text{Nb}_7\text{O}_{515}$ with bands coloured by their niobium character. Special points in and paths through the Brillouin zone were chosen following the literature.¹⁸

cates delocalization of electrons across these bands. This suggests a more delocalized distribution of bonding interactions across the cluster core.

Beside the reasonably high niobium content of the bands, there is also some content arising from oxygen orbitals in bands below the Fermi energy (Fig. S4). Hence, there seems to be oxygen states hybridizing with niobium states which leads to some covalent character of some Nb–O bonds. Electron localization function (ELF) calculations of the cluster core support this interpretation. As shown in (Fig. 10, left), there is notable electron density extending from the O1 atom into the Nb1–Nb3 bonding region, indicating participation of oxygen in metal–metal bonding. Furthermore, a pronounced region of electron density is observed between Nb1, Nb2, and Nb3 (Fig. 10, right), consistent with the presence of a three-centred

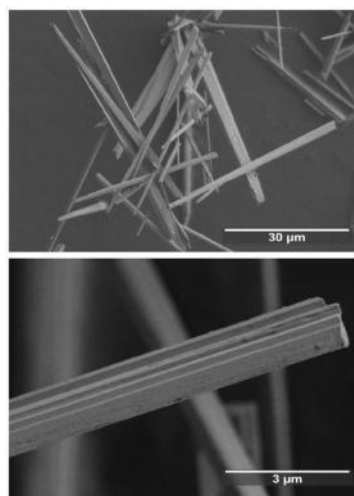


Fig. 8 Scanning electron micrographs of $\text{Li}_3\text{Nb}_7\text{O}_{515}$.

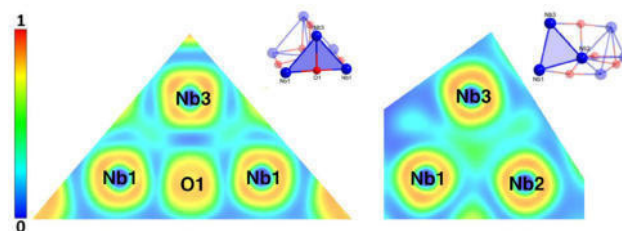


Fig. 10 Electron localisation functions of the $[\text{Nb}_7\text{O}_5]$ cluster core in $\text{Li}_3\text{Nb}_7\text{O}_{515}$.

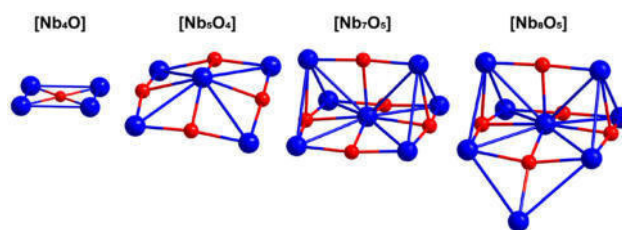


Fig. 11 The expansion of cluster architectures of niobium oxide cluster cores in various niobium oxyiodides.



bond. The ELF analysis suggests the presence of four such three-centred bonds, in addition to four Nb–Nb bonds with an admixture of electron density coming from oxygen within the cluster. These bonding interactions highlight the significant role of orbital mixing between niobium d-orbitals and oxygen p-orbitals in stabilizing the cluster core and the cluster framework.

Conclusion

With the discovery of the niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$, the family of cluster architectures featuring $[\text{Nb}_x\text{O}_y]$ cores is expanded by two new members. The smallest cluster in this series is the $[\text{Nb}_4\text{O}]$ core in $\text{Nb}_4\text{OI}_{12-x}$, followed by the $[\text{Nb}_5\text{O}_4]$ core in $\text{Nb}_5\text{O}_4\text{I}_{11}$, and now the $[\text{Nb}_7\text{O}_5]$ and $[\text{Nb}_8\text{O}_5]$ cores reported in the present work. These clusters are illustrated in Fig. 11.

All compounds were synthesized *via* heterogeneous solid-state reactions between NbI_4 and $\text{Li}_2(\text{CN}_2)$, which served as an unconventional reducing agent, in the presence of an oxide. The formation of the reported compounds occurs *via* temperature-dependent equilibria, influenced by slight variations in composition and the generation of various solid and gaseous phases (Fig. S5). Importantly, the gas phase and the specific gaseous species involved is thought to play a key role in guiding the formation pathways of the resulting cluster compounds.

Experimental section

Materials and methods

All manipulations of starting materials and products were performed in a glovebox under dry argon with moisture and oxygen levels below 1 ppm. Li_2O (ABCR, 95%) was used as purchased. NbI_4 and $\text{Li}_2(\text{CN}_2)$ were synthesized as described in the literature.¹⁹

Synthesis

$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was synthesized from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol), and $\text{Li}_2(\text{CN}_2)$ (7.2 mg, 0.135 mmol) were encapsulated into a fused silica ampoule with 3 cm length and a volume of about 1.5 cm³. The ampoule was heated in a box furnace from room temperature to 500 °C with a rate of 0.1 °C min^{−1}. The holding time was 24 h before the reaction was cooled down to room temperature with a rate of 2 °C min^{−1}. Rod-like crystals of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ were found at the bottom of the ampoule in the powder, beside LiI and an amorphous phase, produced by the decomposition of $\text{Li}_2(\text{CN}_2)$. The product was washed with dried ethanol to get rid of the LiI . A powder pattern of pure product was recorded (Fig. S6). The estimated yield of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ was about 80%; crystals appear black and decompose in air due to moisture after some time.

$\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ was synthesized from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol) and $\text{Li}_2(\text{CN}_2)$ (7.2 mg, 0.135 mmol) were encapsulated into a fused silica ampoule with 3 cm length and a volume of about 1.5 cm³. The ampoule was heated in a Simon-Müller furnace from room temperature to 500 °C with a rate of 0.1 °C. The holding time was 1 h before the reaction was cooled down to room temperature with a rate of 2 °C min^{−1}. Plate-like crystals of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ were found at the wall in the middle of the ampoule with NbOI_2 and NbI_5 at the top of the ampoule and LiI , $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and amorphous C_3N_4 in the powder. An X-ray powder pattern of pure product was recorded (Fig. S7). Crystals appear black and decompose in air due to moisture quite fast.

Crystallography

A rod-like $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and a plate-like $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ single-crystal were mounted on a Rigaku XtaLab Synergy-S X-ray diffractometer using $\text{Cu-K}\alpha$ ($\lambda = 1.54184$ Å) radiation. The single crystal was kept under N_2 cooling at 230 K during the data collection. Corrections for absorption effects were applied with CrysAlisPro 1.171.42.70a (Rigaku Oxford Diffraction, 2022). The crystal structure was solved by the integrated space group and crystal-structure determination routine of SHELXT²⁰ and full-matrix least-squares refinement with SHELXL-2018/3²⁰ implemented in Olex2 1.5.²¹

Reaction products were investigated by powder X-ray diffraction (PXRD) using a StadiP diffractometer (Stoe, Darmstadt) with $\text{Ge}[111]$ -monochromated $\text{Cu-K}\alpha_1$ radiation and a Mythen1 detector.

Density functional theory

Density functional theory (DFT) calculations were performed using the Abinit software package (v. 9).²² The Perdew–Burke–Ernzerhof exchange–correlation functional²³ was used with the vdW-DFT–D3(BJ) dispersion correction of Grimme.²⁴ A Monkhorst–Pack grid of k -points with real-space basis vectors (3 3 0) (−2 2 0) and (0 0 3) was used to construct the electronic structure of crystalline $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.²⁵ Plane-wave calculations were performed using an energy cutoff of 40 Ha outside of the PAW spheres and a 120 Ha cutoff inside them. Pseudopotentials sets were used as received from the Abinit library.²² These computational parameters were chosen following convergence studies.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data that support the findings of this study are available on request from the corresponding author, H.-J. Meyer. Computational data are available at <https://doi.org/10.5281/zenodo.15366543>.



Supplementary information is available. See DOI: <https://doi.org/10.1039/d5dt01819f>.

CCDC 2311571 ($\text{Li}_3\text{Nb}_7\text{O}_{15}\text{I}_{15}$) and 2428720 ($\text{Nb}_8\text{O}_{51}\text{I}_{17}(\text{NbI}_{5,37})$) contains the supplementary crystallographic data for this paper.^{26a,b}

Acknowledgements

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Supporting Information

Niobium oxyiodide cluster compounds $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with expanding cluster architectures and multicenter Nb–Nb bonding

Jan Beitzberger,^a Markus Ströbele,^a Patrick Schmidt,^a Carl P. Romao,^b and H.-Jürgen Meyer^{*a}

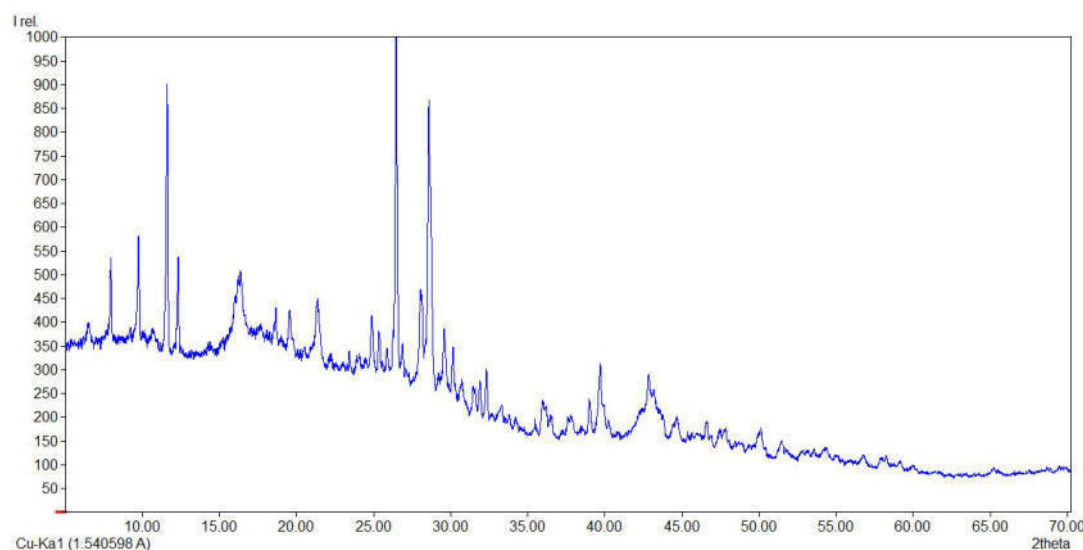


Figure S 1. Measured powder X-ray diffraction pattern of the unknown phase after the reaction of NbI_4 with Li_2CN_2 and Li_2O at 300 °C for 24 h.

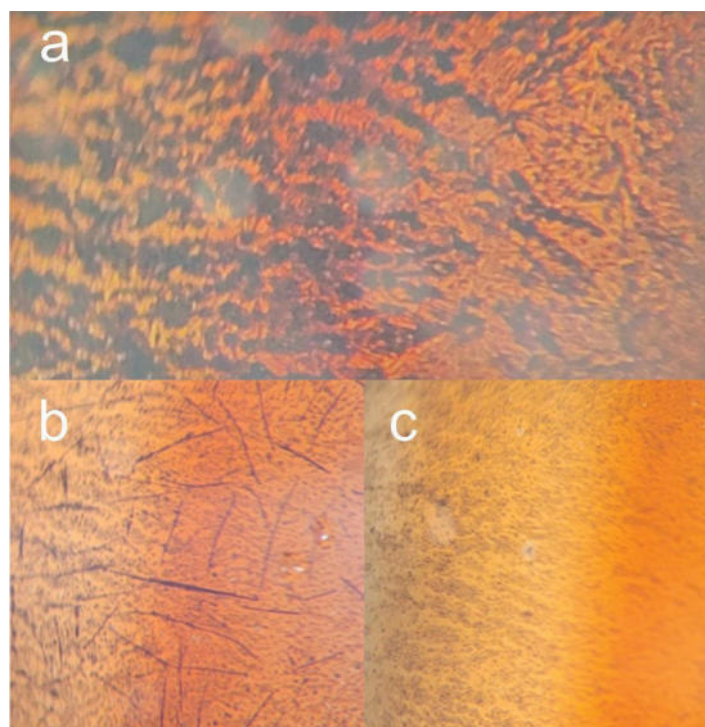


Figure S 2. Substance on the wall after quenching the reaction from 400 °C to room temperature. The product forms black droplets (a) which transform at room temperature into dark red, string-like crystallites (b). These crystallites decompose after some time at room temperature.

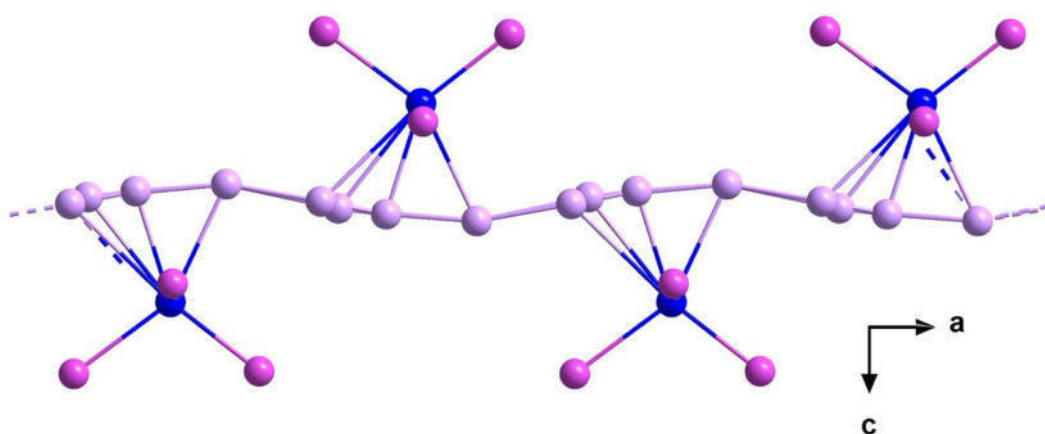


Figure S 3. " $\text{NbI}_{5.37}$ " between the layers inside the structure of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$, looking at the ac -plane.

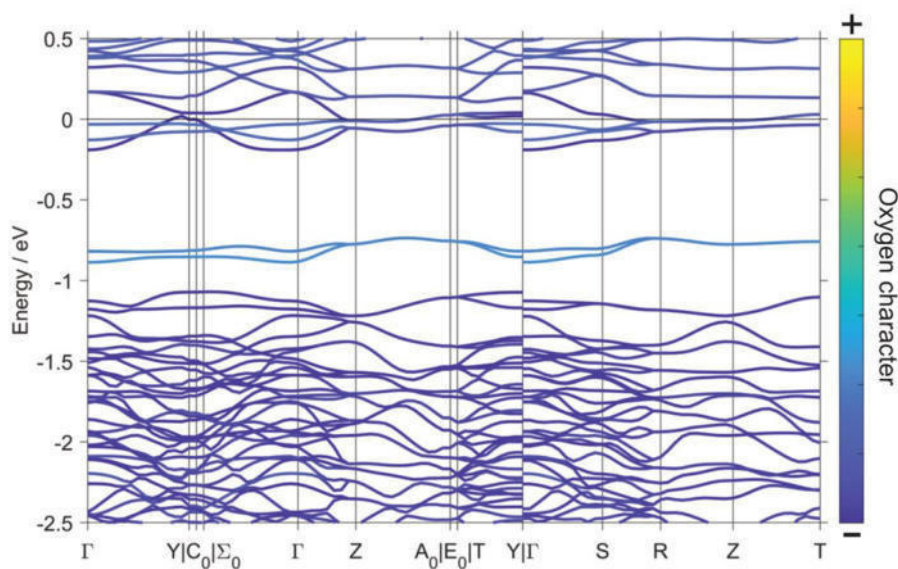


Figure S 4. DFT-calculated electronic band structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ with bands coloured by their oxygen character. Special points in and paths through the Brillouin zone were chosen following the literature.^[1]

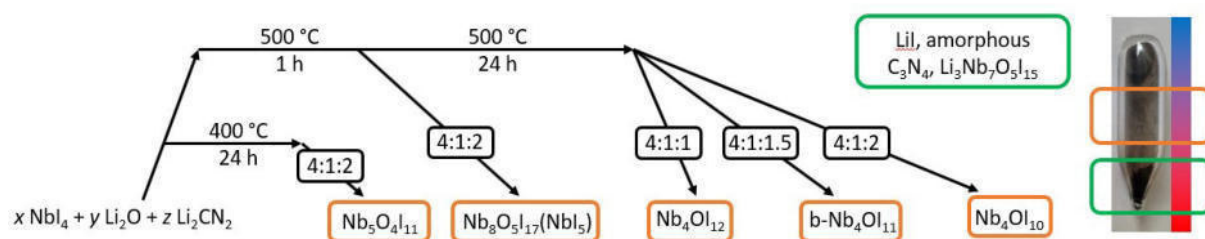


Figure S 5. Reaction conditions for the various cluster compounds, synthesized through the reaction of NbI_4 with $\text{Li}_2(\text{CN}_2)$ and Li_2O .

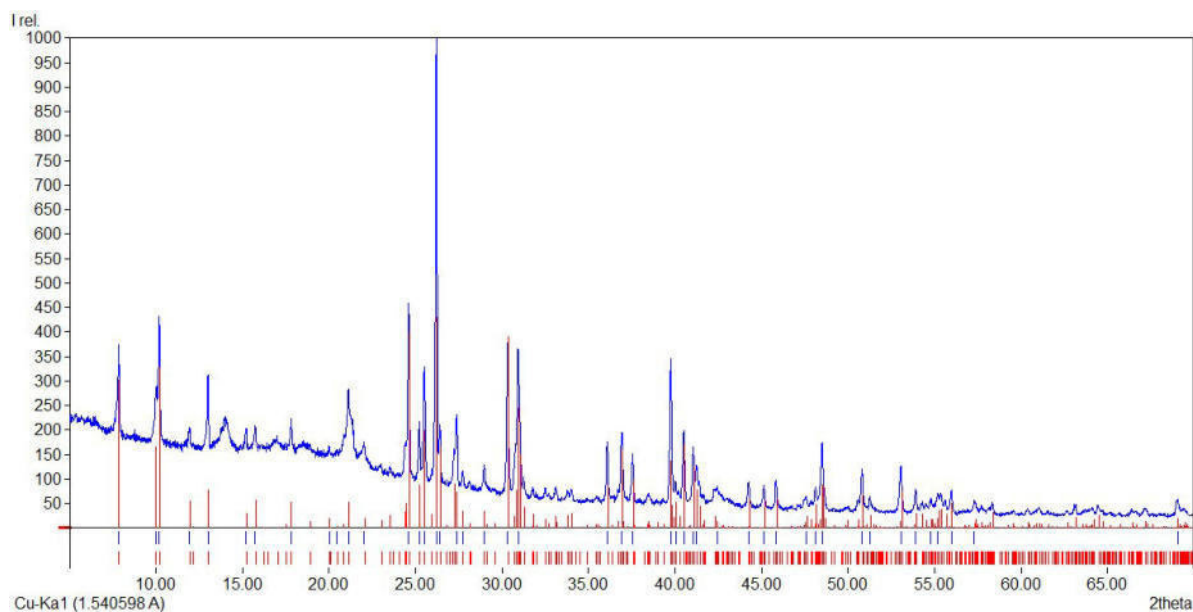


Figure S 6. Measured powder X-ray diffraction pattern of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ with $\text{Cu-K}\alpha_1$ radiation. In blue is the measured powder pattern, red correspond to the single-crystal X-ray measurement of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$.

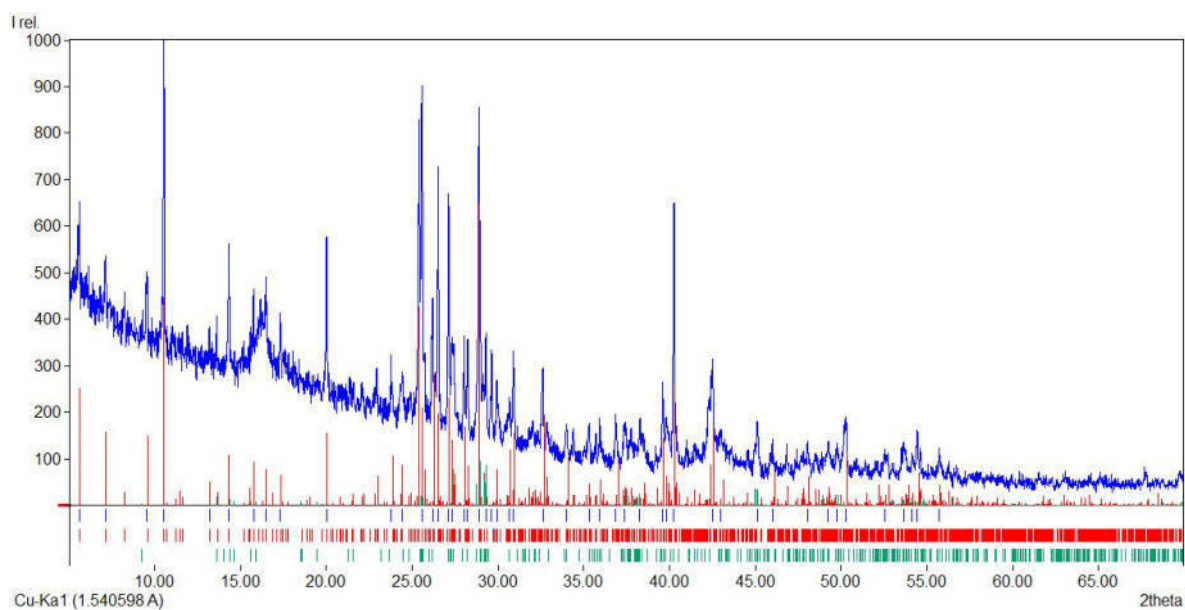
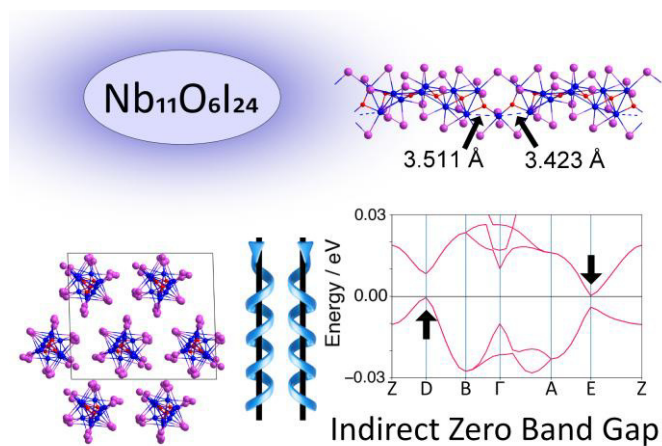


Figure S 7. Measured powder X-ray diffraction pattern of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$ with $\text{Cu-K}\alpha_1$ radiation. In blue is the measured powder pattern, red correspond to the single-crystal X-ray measurement of $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_{5.37})$ and green are Bragg positions of coproduced NbI_5 ^[2].

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Publication 5

Zero Indirect Band Gap and Flat Bands in a Niobium Oxyiodide Cluster Material



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Zero Indirect Band Gap and Flat Bands in a Niobium Oxyiodide Cluster Material

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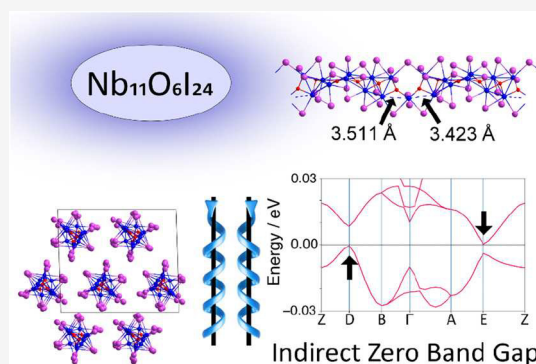


Article Recommendations



Supporting Information

ABSTRACT: Explorative chemistry in a reaction system composed of NbI_4 , $\text{Li}_2(\text{CN}_2)$, and Li_2O has led to the discovery of a number of niobium oxyiodide cluster compounds. During this reaction, the formation of solid phases was detected alongside gaseous phases, resulting in a range of products with cluster cores of varying shapes. After several niobium oxyiodide cluster compounds have already been identified within this reaction system, two additional compounds, $\text{Nb}_6\text{O}_3\text{I}_{15}$ and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, are discovered and structurally characterized by single-crystal X-ray diffraction. Both structures are based on the butterfly-shaped, oxygen-capped niobium cluster $[\text{Nb}_4\text{O}]$, which is extended to larger cluster fragments. The $[\text{Nb}_4\text{O}]$ cluster core in $\text{Nb}_6\text{O}_3\text{I}_{15}$ is extended by two $[\text{NbO}]$ units to form a three-dimensional framework, and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ contains two connected $[\text{Nb}_4\text{O}]$ units, which form chiral units within an antiferrochiral hexagonal packing of strings. The striking string-like character of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ was investigated in terms of its electronic structure and properties. DFT calculations showed $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ to possess a zero indirect band gap, with a pair of 3-dimensional flat bands surrounding the Fermi level. These unusual features of the electronic band structure suggest the presence of strongly correlated intercluster singlet electron states, arising from the helical shape of the clusters, the hexagonal packing of the strings, and the delocalized nature of cluster electron wave functions.



1. INTRODUCTION

Transition metal clusters can exhibit a variety of structural arrangements in which the metal atoms can have multiple oxidation states. The arrangement of metal–metal bonds present in such clusters can give rise to many exotic electronic properties, which depend on the geometric arrangement of atoms within the clusters as well as the arrangement of the clusters relative to each other. Clusters can be used as optic,¹ superconducting,² electronic,³ magnetic,⁴ sensor,¹ and catalytic⁵ materials due to the localization of their electrons and consequent strong electron correlation effects.⁶

One of the most prominent cluster types is the octahedral M_6 cluster, which commonly appears in $[M_6X_{12}]$ - and $[M_6X_8]$ -type architectures (M = metal, X = halide).⁷ Therein, the octahedral metal cluster core is surrounded by 12 edge-capping X atoms in $[M_6X_{12}]$, and eight face-capping X atoms in $[M_6X_8]$. As a result of the relative sizes of M and X , the $[M_6X_{12}]$ -type is obtained for a combination of large metal atoms and small halides and vice versa for the $[M_6X_8]$ -type, with small metal atoms and large halides. $[M_6X_8]$ -type clusters can form Chevrel phases (for X = chalcogenides), which are well-known for their robust type-II superconductivity.²

Niobium halides include both cluster types, exemplified by $\text{Nb}_6\text{Cl}_{14}$ ($[M_6X_{12}]$) and Nb_6I_{11} ($[M_6X_8]$).^{8,9} These compounds

are typically prepared at comparatively high temperatures (700–950 °C), indicating their thermodynamic stability. A preferred synthesis route involves the metallothermic reduction of more highly oxidized niobium halides with niobium metal. Variation of the oxidation state of these clusters can give rise to magnetic properties depending on the number of unpaired electrons.¹⁰

Binary niobium halides involve the compounds Nb_3X_8 (X = Cl, Br, I),^{11,12} NbX_3 (X = F, I),^{13,14} NbX_4 (X = F, Cl, Br, I)^{15–18} and NbX_5 (X = F, Cl, Br, I).^{19–22} In all these compounds, the niobium centers are octahedrally coordinated by halide atoms; however, the overall structural connectivity depends strongly on the halide. For example, NbF_5 forms tetrameric units composed of corner-sharing $[\text{NbF}_4\text{F}_{2/2}]$ octahedra,¹⁹ whereas the chloride and bromide analogues crystallize as dimeric, edge-sharing octahedral units.^{20,21} In niobium pentafluoride, either dimeric structures analogous to

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those of the chloride and bromide compounds are observed, or chains of corner-sharing $[\text{NbI}_4\text{I}_{2/2}]$ octahedra are formed, arranged in a hexagonal packing arrangement.^{22,23}

Metal-rich niobium halide compounds, such as the Peierls-distorted NbX_4 ($X = \text{Cl}, \text{Br}, \text{I}$) and NbI_3 , exhibit string-like connectivities.^{14,16–18} In contrast, the Nb_3X_8 compounds feature layered structures based on triangular Nb_3 clusters.^{11,12} The electronic properties of the Nb_3X_8 compounds have been extensively studied due to the presence of flat electronic bands in single-layer Nb_3Cl_8 , and a complex interplay between Mott insulating behavior and singlet formation in the bulk.^{4,24,25}

The introduction of another anion, alongside the halide, leads into the field of heteroanionic compounds, which significantly expands the structural and chemical diversity of these compounds. In many instances, the heteroanion substitutes for a halide within an existing framework, thereby modifying the connectivity within the crystal structure. Examples include $\text{Nb}_6\text{I}_9\text{S}$,²⁶ derived from Nb_6I_{11} , as well as Nb_3SX_7 ($X = \text{Cl}, \text{Br}, \text{I}$)^{27–29} and ANb_3SBr_7 ($A = \text{Rb}, \text{Cs}$)^{30,31} whose central clusters can be derived from Nb_3Br_8 .¹² The one-dimensional chains of clusters in ANb_3SBr_7 lead to the formation of an electronic Luttinger liquid, a type of quantum metal.³¹

Alternatively, the incorporation of heteroatoms can lead to the formation of clusters with distinct shapes. Especially Nb_4 clusters have shown to adopt various shapes such as square, rectangular, rhombohedral, tetrahedral, and butterfly type cluster core geometries.^{32–36} The introduction of $4f$ heteroatoms to $3d$ organometallic butterfly clusters has been used to synthesize many single-molecule magnets.³⁷

Butterfly shaped metal clusters can be related to an octahedral $[\text{M}_6\text{X}_{12}]$ -type cluster with two missing metal edges. This type of cluster is usually (μ_4 -) capped by a heteroatom, as can also be derived from the $[\text{M}_6\text{ZX}_{12}]$ -type cluster,^{38–42} possessing an interstitial Z heteroatom, by removing two metal corners. Butterfly clusters of this type are well-established; most of them were prepared by means of solution chemistry.

A first example was reported by Manassero et al., who characterized the compound $[\text{Me}_3\text{NCH}_2\text{Ph}][\text{Fe}_4(\text{CO})_{13}\text{H}]$ ($\text{Me} = \text{methyl group}$; $\text{Ph} = \text{phenyl group}$).⁴³ It features a Fe_4 core arranged in a butterfly geometry, capped by a carbonyl ligand. The cluster possesses a total number of 12 electrons available for metal–metal bonding. Further synthetic developments have expanded the chemistry of these clusters. For instance, oxidative reactions of the carbon-centered cluster $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$ have yielded compounds such as $(\text{Et}_4\text{N})\text{-}[\text{Fe}_4\text{C}(\text{CO})_{12}\text{CO}_2\text{CH}_3]^{44}$ ($\text{Et} = \text{ethyl group}$) and $\text{Fe}_4\text{C}(\text{CO})_{13}$.⁴⁵

The butterfly motif is not limited to iron-based systems; analogous clusters have been identified for various transition metals. One notable example is $\text{W}_4\text{C}(\text{O}^i\text{Pr})_{12}(\text{NMe})$ ($^i\text{Pr} = \text{isopropyl group}$), a tungsten cluster that contains only six electrons for metal–metal bonding.⁴⁶ This low electron count results in relatively long $\text{W}–\text{W}$ distances, averaging at 2.78 Å. In contrast, the molybdenum cluster $\text{Mo}_4\text{Br}_4(\text{O}^i\text{Pr})_8$ adopts a related butterfly structure, but with 12 electrons for $\text{Mo}–\text{Mo}$ bonding, leading to significantly shorter average $\text{Mo}–\text{Mo}$ bond lengths of approximately 2.50 Å.⁴⁷

Compounds containing butterfly clusters were also obtained by means of solid-state reactions under moderate heating conditions (as low as 400 °C). The series of compounds $\text{Nb}_4\text{PnX}_{11}$ ($\text{Pn} = \text{N}, \text{P}$; $X = \text{Cl}, \text{Br}, \text{I}$)³⁶ features μ_4 -pnictogen-

capped butterfly cores, where the central pnictide atom bridges all four niobium atoms. A Ta_4 based butterfly cluster with a μ_4 -capping sulfur atom has been observed in the tantalum compound $\text{Ta}_4\text{SBr}_{11}$; magnetic correlations between these clusters create a Mott insulating state.⁴⁸

Flexibility in the number of electrons available for metal–metal bonding interactions is widespread in cluster compounds, especially for niobium. An example is the octahedral $[\text{Nb}_6\text{Cl}_{18}]^{x-}$ cluster ($x = 2, 3, 4$), where the successive reduction of cluster electrons leads to an elongation of the $\text{Nb}–\text{Nb}$ bonds.⁴⁹ Another cluster system with variable electron counting is reported for triangular Nb_3 clusters. The valence electron concentration (VEC) varies, with 6 (Nb_3SX_7 with $X = \text{Cl}, \text{Br}, \text{I}$;^{27–29} $(\text{PEt}_3\text{H})[\text{Nb}_3\text{Cl}_{10}(\text{PEt}_3)_3]^{50}$), 7 (Nb_3X_8 with $X = \text{Cl}, \text{Br}, \text{I}$;^{11,12} ANb_3SBr_7 with $A = \text{Rb}, \text{Cs}$ ^{30,31}), 7.5 ($\text{AVNb}_3\text{Cl}_{11}$ with $A = \text{K}, \text{Rb}, \text{Cs}, \text{TI}^{51}$), and 8 cluster electrons ($\text{Nb}_3\text{Cl}_7(\text{PMe}_2\text{Ph})_6^{50}$ and $\text{NaNb}_3\text{Cl}_8^{52}$) having been reported. Also, a variable halide content can lead to different numbers of cluster electrons, as demonstrated by the $\text{Nb}_4\text{OI}_{12-x}$ series, which includes the members $\text{Nb}_4\text{OI}_{12}$ (VEC = 6), a - and b - $\text{Nb}_4\text{OI}_{11}$ (VEC = 7), and $\text{Nb}_4\text{OI}_{10}$ (VEC = 8).⁵³

Heteroanionic cluster compounds are generally more thermally labile than their octahedral counterparts based on $[\text{M}_6\text{X}_{12}]$ and $[\text{M}_6\text{X}_8]$ clusters. Therefore, their synthesis requires carefully controlled reduction conditions, using a suitable reduction agent and reaction temperatures. Recently, a series of niobium oxyiodide clusters was obtained by reducing NbI_4 with $\text{Li}_2(\text{CN})_2$, in the presence of Li_2O as an oxide source under closely related temperature conditions near 500 °C, yielding compounds like $\text{Nb}_4\text{OI}_{12}$, $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$, and others.^{54–56}

These compounds appear to be metastable products, which decompose at elevated temperatures. We report the synthesis and characterization of two more compounds in this system, $\text{Nb}_6\text{O}_3\text{I}_{15}$ and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$. These compounds contain a previously unreported structural feature: oxygen-capped $[\text{NbO}_4]$ butterfly cluster units, which, in conjunction with $[\text{NbO}]$, form extended, asymmetric clusters. Analysis of the electronic structure and properties of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ reveals that the cluster shape and packing lead to flat electronic bands, which are perturbed to create an indirect band gap with zero magnitude.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Crystal Structure

The reaction between NbI_4 , $\text{Li}_2(\text{CN})_2$ and Li_2O involves both solid and gaseous phases, and is governed by temperature-dependent equilibria. On heating, the mixture generates a sequence of intermediate solid and vapor phases. The collective experimental observations have led to an assumption of a process that is close to a non-equilibrium system.⁵⁷ The product formation is highly sensitive to the reaction temperature, duration, and heating and cooling rates, which determine the temporal exposure of reactants and intermediates to local thermal and chemical environments. Slight changes in these parameters lead to the crystallization of different niobium oxyiodide clusters with the rectangular $[\text{Nb}_4\text{O}]$, $[\text{Nb}_5\text{O}_4]$, and $[\text{Nb}_8\text{O}_5]$ cores known from earlier work,^{53–56} to the newly discovered butterfly-based $[\text{Nb}_6\text{O}_3]$ and $[\text{Nb}_{10}\text{O}_4]$ architectures. Such temperature-dependent selectivity indicates kinetic control of the product formation, with multiple competing reaction pathways accessible within a narrow thermal window.

Moreover, several products are metastable, decomposing upon extended heating or exposure to higher temperatures. Such metastable phases can only be stabilized under specific kinetic conditions or by rapid cooling. The persistence of these phases is governed not by thermodynamic stability, but by kinetic barriers that hinder transformation into more stable forms. Thereby, the product formation is a result of competing kinetic processes, occurring under a continuous interplay between solid-state reactions and gas-phase transport.

The newly isolated compounds $\text{Nb}_6\text{O}_3\text{I}_{15}$ and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ require sensitive reaction conditions, close to those obtained for $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$.⁵⁶ Both compounds were obtained from a reaction of NbI_4 with Li_2O and $\text{Li}_2(\text{CN}_2)$ in 2:1:1 molar ratio. The reaction mixture was heated to 500 °C for 1 h, followed by a controlled cooling to 450 °C with a rate of 1 °C/min, and then further cooled to room temperature with a rate of 0.1 °C/min. Both compounds crystallize as black solids. $\text{Nb}_6\text{O}_3\text{I}_{15}$ forms block-shaped crystals (Figure S1, top), while $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ crystallizes as elongated platelets (Figure S1, bottom).

The structures of both compounds were determined by single-crystal X-ray diffraction, with corresponding crystallographic data and refinement parameters summarized in Table 1.

Table 1. Crystallographic Data from X-ray Single-Crystal Refinement on $\text{Nb}_6\text{O}_3\text{I}_{15}$ and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$

	$\text{Nb}_6\text{O}_3\text{I}_{15}$	$\text{Nb}_{11}\text{O}_6\text{I}_{24}$
CCDC No.	2401147	2380623
sum formula	$\text{Nb}_6\text{O}_3\text{I}_{15}$	$\text{Nb}_{11}\text{O}_6\text{I}_{24}$
Space group	$C2/c$	$P2_1/c$
Temperature (K)	150	150
Unit cell dimensions (Å)	$a = 26.9643(4)$ $b = 14.3399(2)$ $c = 24.8587(4)$	$a = 16.4086(1)$ $b = 16.2749(2)$ $c = 18.8946(2)$
Monoclinic angle (°)	$\beta = 95.744(1)$	$\beta = 91.713(1)$
Volume (Å ³)	9563.7(2)	5043.52(9)
Z	4 ($Z' = 12$)	4
Wavelength (Å)	0.71073	1.54184
μ (mm ⁻¹)	16.616	135.138
Calculated density (g/cm ³)	5.228	5.483
2 θ range for data collection	4.25 to 60.062	5.388 to 127.596
Total number of reflections	58082	44314
Independent reflections	13984	8139
Refined parameters	431	370
R_{int}	0.0192	0.0236
R_1 ($I \geq 2\sigma(I)$ /all)	0.0236/0.0286	0.0292
wR_2 ($I \geq 2\sigma(I)$ /all)	0.0551/0.0565	0.0745
Goodness-of-fit on F^2	1.031	1.020

2.1.1. The Crystal Structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$. The compound $\text{Nb}_6\text{O}_3\text{I}_{15}$ features the presence of two slightly different $[\text{Nb}_4\text{O}]$ cluster cores, which can be described as oxygen-capped butterfly clusters. Both butterfly clusters are extended by two $[\text{NbO}]$ units each, to yield $[\text{Nb}_4\text{O}(\text{NbO})_2]$ fragments. The shapes of these two clusters are shown in Figure 1 and interatomic distances are collected in Table 2.

The Nb–Nb backbone, connecting the wings of the butterfly (Nb2 – Nb5 and Nb8 – $\text{Nb8}'$), is slightly longer (2.9552(7) Å and 2.968(1) Å, respectively) than the other Nb–Nb bonds (2.8850(7)–2.9184(7) Å) in the structure. A related cluster can be found in the structures of $\text{Nb}_4\text{PnX}_{11}$ ($\text{Pn} = \text{N}, \text{P}; \text{X} = \text{Cl}, \text{Br}, \text{I}$),³⁶ where the butterfly clusters are capped

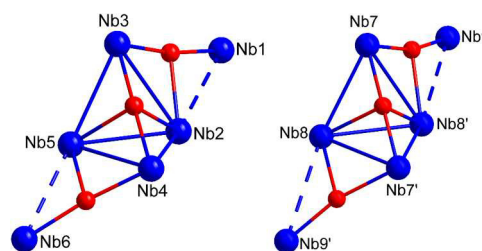


Figure 1. Two crystallographically distinct $[\text{Nb}_4\text{O}]$ clusters extended by two $[\text{NbO}]$ units in the structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$.

Table 2. Comparison of Corresponding Nb–Nb Distances of Two Distinct $[\text{Nb}_4\text{O}(\text{NbO})_2]$ Cluster Cores of $\text{Nb}_6\text{O}_3\text{I}_{15}$ Compared in the Left and Right Column

Atoms	Distance/Å	Atoms	Distance/Å
Nb3–Nb5	2.9184(7)	Nb7–Nb8	2.8867(7)
Nb3–Nb2	2.9081(7)	Nb7–Nb8'	2.8880(7)
Nb2–Nb4	2.8850(7)	Nb7'–Nb8'	2.8867(7)
Nb4–Nb5	2.8945(7)	Nb7'–Nb8	2.8880(7)
Nb2–Nb5	2.9552(7)	Nb8–Nb8'	2.968(1)
Extensions of $[\text{Nb}_4\text{O}]$ -fragments			
Nb1–Nb2	3.1017(7)	Nb8'–Nb9	3.2720(7)
Nb5–Nb6	3.1027(7)	Nb8–Nb9	3.2720(7)

by a pnictide atom, as $[\text{Nb}_4\text{Pn}]$. Here, a contrary situation appears, as the backbone linkage is the shortest Nb–Nb bond. For example, in $\text{Nb}_4\text{NBr}_{11}$, the Nb–Nb backbone bond (2.928(3) Å) is slightly shorter than the other Nb–Nb distances (3.003(2) Å). A similar situation can be found in the μ_4 -S-capped Ta_4 cluster in the structure of $\text{Ta}_4\text{SBr}_{11}$.⁴⁸ A direct comparison of these clusters is, however, limited, as the connectivity pattern varies and their valence electron counts, from a classical point of view, differ with $\text{VEC} = 9$ for $\text{Nb}_6\text{O}_3\text{I}_{15}$, $\text{VEC} = 7$ for $\text{Ta}_4\text{SBr}_{11}$, and $\text{VEC} = 6$ for $\text{Nb}_4\text{PnX}_{11}$.

The Nb–Nb distances in both crystallographically independent $[\text{Nb}_4\text{O}]$ butterfly clusters of $\text{Nb}_6\text{O}_3\text{I}_{15}$ are almost the same (Table 2). The Nb–Nb distances with the additional $[\text{NbO}]$ extensions are somewhat longer and show some surprising differences when comparing both $[\text{Nb}_4\text{O}(\text{NbO})_2]$ cluster cores. The distances Nb1–Nb2 and Nb5–Nb6 are nearly the same, but notably shorter than the Nb8–Nb9 contacts in the parent cluster. This disparity could reflect differences in the electronic distribution, assuming that the cluster exhibiting the shorter Nb–Nb contacts to the $[\text{NbO}]$ units possesses higher electron density than the one with the longer connection. An intramolecular charge separation has recently been discussed for the low-temperature polymorph of the van der Waals layered compound Nb_3Cl_8 , exhibiting alternating layers of $[\text{Nb}_3]^{7+}$ and $[\text{Nb}_3]^{9+}$ clusters.⁵⁸ Another explanation could be attributed to matrix effects, influencing the Nb–Nb distances.

A butterfly type niobium cluster with a capping oxygen atom has not been reported previously. The closest known analogue is found in $\text{Nb}_4\text{OTe}_9\text{I}_4$, which contains a flattened, oxygen-centered tetrahedral Nb_4 cluster.⁵⁹ Due to the availability of only four cluster electrons for Nb–Nb bonding, the Nb–Nb distances therein are relatively long (3.050(3)–3.057(4) Å).

The overall crystal structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$ features a $[\text{Nb}_4\text{O}(\text{NbO})_2]$ cluster core that is interconnected with four neighboring clusters via pairs of μ_2 -iodide bridges (Figure 2). Two of these bridging connectivities occur at the “wingtips” of

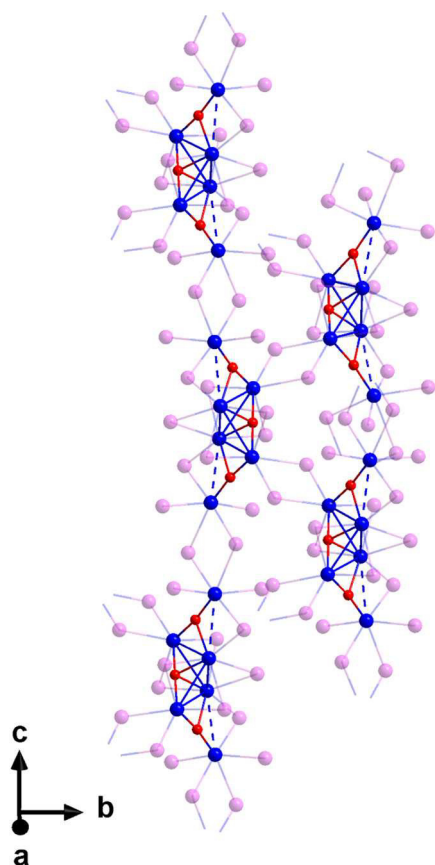


Figure 2. Connectivity of the $[\text{Nb}_4\text{O}(\text{NbO})_2]$ cluster in the structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$ with μ_2 -iodide bridges. Niobium atoms are colored in blue, oxygen in red and iodine in light pink.

the butterfly cluster, connecting along the *a*- and *b*-axis directions, and two are at the $[\text{NbO}]$ elongation, connecting along the *c*-axis. This connectivity of clusters results in the formation of a three-dimensional framework, displayed in Figure 3.

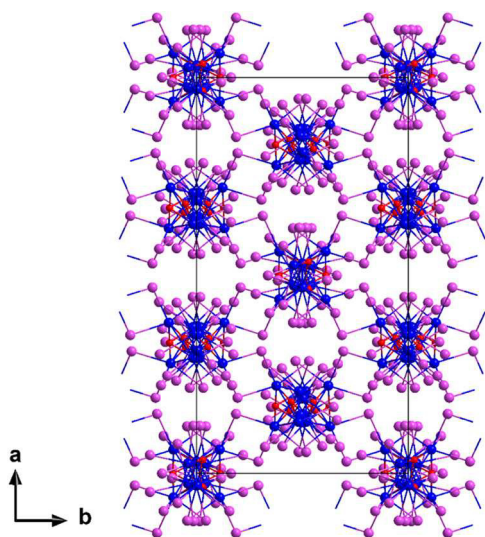


Figure 3. Section of the crystal structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$, showing the formation of a three-dimensional network.

2.1.2. The Crystal Structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$. The crystal structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ is based on a $[\text{Nb}_{10}\text{O}_4]$ core built from two independent butterfly $[\text{Nb}_4\text{O}]$ clusters of the same type as the previous structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$. A comparison of the extended butterfly cluster $[\text{Nb}_4\text{O}(\text{NbO})_2]$ in $\text{Nb}_6\text{O}_3\text{I}_{15}$ with the $[\text{Nb}_{10}\text{O}_4]$ core in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ is shown in Figure 4. Two

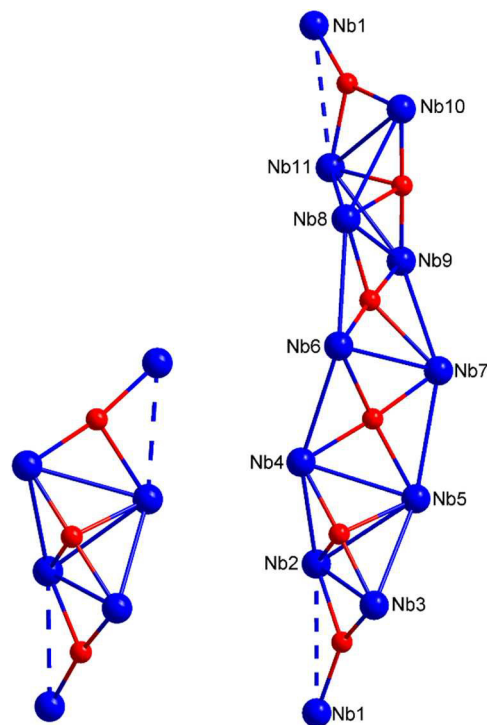


Figure 4. Comparison of cluster fragments in structures of $\text{Nb}_6\text{O}_3\text{I}_{15}$ (left) and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ (right). Corresponding Nb–Nb bond lengths of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ are summarized in Table 3.

$[\text{Nb}_4\text{O}]$ clusters in the structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ are interconnected by a pair of niobium atoms (Nb6 and Nb7) as (ONb_2O) to form the $[(\text{Nb}_4\text{O})(\text{ONb}_2\text{O})(\text{Nb}_4\text{O})]$ fragment, which is interconnected with two adjacent clusters by one niobium atom (Nb1) as $[\text{ONbO}]$ to yield the infinite chain structure ${}^\infty[(\text{Nb}_4\text{O})(\text{ONb}_2\text{O})(\text{Nb}_4\text{O})(\text{ONbO})]$, displayed in Figure 5. The two $[\text{Nb}_4\text{O}]$ units are mirrored relative to each other, leading to a twist of the overall $[(\text{Nb}_4\text{O})_2(\text{Nb}_2\text{O}_2)]$ unit,

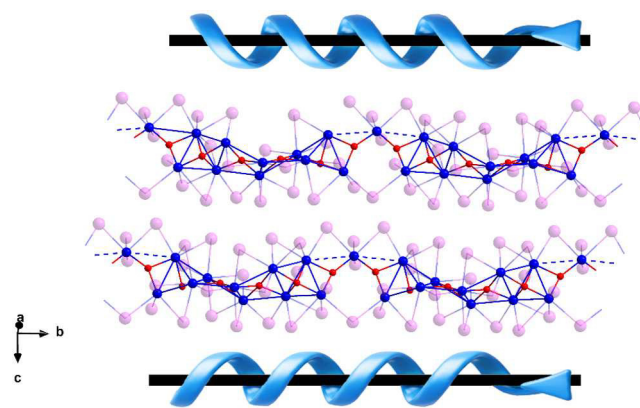


Figure 5. Helical-shaped and string-like connectivity of the clusters in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$. Niobium atoms are colored in blue, oxygen in red and iodine in light pink.

giving it a helical shape. An analysis of interatomic Nb–Nb distances is of particular interest, as they reflect the electronic interaction of 19 cluster electrons within and between butterfly clusters of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$. These distances show notable variations, as summarized in Table 3.

Table 3. Nb–Nb Bond Distances Inside the $[(\text{Nb}_4\text{O})_2(\text{Nb}_2\text{O}_2)]$ Core of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$

Atoms	Distance/Å	Atoms	Distance/Å
[Nb ₄ O]-fragments			
Nb2–Nb4	2.7941(9)	Nb8–Nb10	3.0032(9)
Nb4–Nb5	2.8632(9)	Nb10–Nb11	2.8995(9)
Nb3–Nb5	3.0128(9)	Nb9–Nb11	2.7913(9)
Nb2–Nb3	2.9176(9)	Nb8–Nb9	2.8697(9)
Nb2–Nb5	2.9951(9)	Nb8–Nb11	2.9961(9)
Interconnection between [Nb ₄ O]-fragments			
Nb4–Nb6	3.0759(9)	Nb6–Nb8	3.082(1)
Nb5–Nb7	3.071(1)	Nb7–Nb9	3.072(1)
Nb6–Nb7	2.9230(9)		
Interconnection of [Nb ₁₀ O ₄] clusters			
Nb1–Nb2	3.5110(9)	Nb1–Nb11	3.4230(9)

The Nb–Nb distances of the [Nb₄O]-fragments (2.7913(9)–3.0128(9) Å) show a somewhat wider distribution of distances than those in $\text{Nb}_6\text{O}_3\text{I}_{15}$ (2.8850(7)–2.968(1) Å, see Table 2). This may be caused by the interconnection of the butterfly clusters via Nb6/Nb7 atoms within the [Nb₁₀O₄] fragments, with Nb–Nb contacts ranging between 3.071(1)–3.082(1) Å. The [Nb₁₀O₄] fragment is interconnected with two adjacent clusters through another niobium atom (Nb1) at longer distances (Nb1–Nb2 = 3.5110(9) Å and Nb1–Nb11 = 3.4230(9) Å) shown in Figure 5.

The overall crystal structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ is composed of cluster strings running parallel to the *b*-axis, following a hexagonal stick packing motif (Figure 6). Each single string is separated by a van der Waals gap. This type of one-dimensional chain structure is also found in other cluster based compounds, such as $\text{Nb}_6\text{I}_3\text{S}^{26}$ whose structure consists

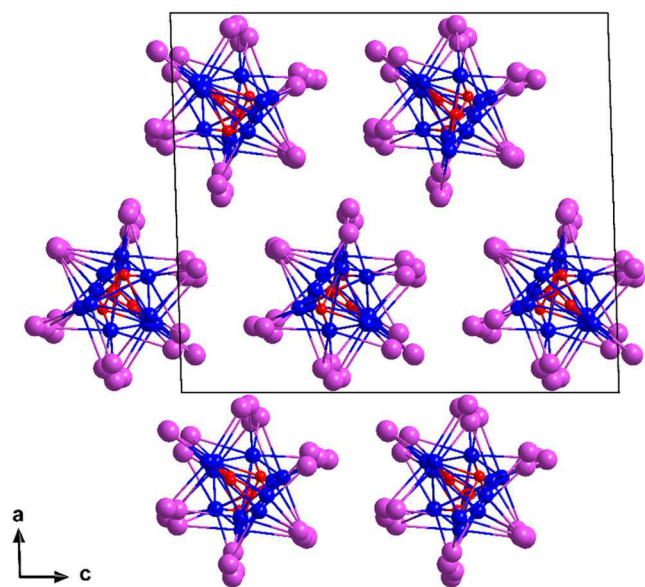


Figure 6. Section of the crystal structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ along the *b*-axis, illustrating the hexagonal packing of the strings.

of sulfur-bridged $[\text{M}_6\text{X}_8]$ -type octahedra, as well as *a*- and *b*- $\text{Nb}_4\text{OI}_{11}$,⁵³ where rectangular $[\text{Nb}_4\text{O}]$ clusters are interconnected into a one-dimensional chain structure. These anion-bridged compounds show semiconducting behavior with small band gaps. In contrast, the one-dimensional chains in the structure of $\text{ANb}_3\text{Br}_7\text{S}$ (*A* = Cs, Rb) are separated by alkali ions and the material exhibits semimetallic behavior with characteristics of a Luttinger liquid.³¹

To gain insights into the electronic structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, its electrical conductivity and the electronic band structure were investigated.

2.2. Electronic Structure

The electronic band structures of $\text{Nb}_6\text{O}_3\text{I}_{15}$ (Figure 7) and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ (Figure 8) were calculated using density functional

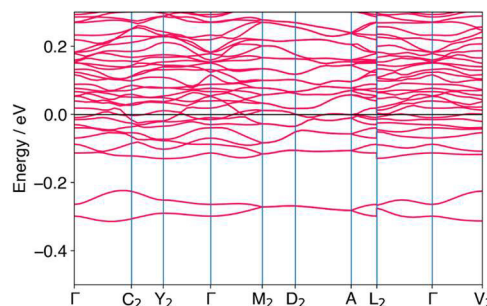


Figure 7. Electronic band structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$, showing metallic bands formed from Nb 4*d* orbitals. Special points in and paths through the Brillouin zone were chosen following the literature.⁶⁸

theory (DFT). In both cases, the bands near the Fermi energy correspond to Nb 4*d* orbitals; I 5*p* orbitals appear at lower energies (see Supporting Information, Figures S1–S3). $\text{Nb}_6\text{O}_3\text{I}_{15}$ is found to be a metal, whereas $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ has an indirect zero band gap between the valence band maximum

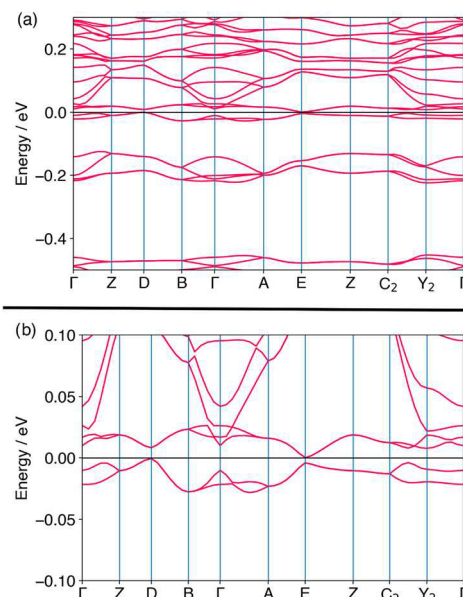


Figure 8. Electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, showing the band manifolds near the Fermi energy (a), and a closeup of the flat bands surrounding the Fermi energy and the indirect zero gap between D (0 1/2 1/2) and E (−1/2 1/2 1/2) (b). Special points in and paths through the Brillouin zone were chosen following the literature.⁶⁸

(VBM) at D ($0\ 1/2\ 1/2$) and the conduction band minimum (CBM) at E ($-1/2\ 1/2\ 1/2$).

This finding of an indirect zero band gap is highly unusual. Many zero-gap materials are known, including doped semiconductors, Dirac materials, and topological insulators; however, in these experimentally realized materials, the zero gap is direct.⁶⁰ The study of systems with indirect zero band gaps has largely been limited to theoretical proposals based on model Hamiltonians,^{61–66} with the exception of a recent experimental realization in a photonic metamaterial.⁶⁷ Therefore, the DFT calculations suggest that $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ holds a unique status as an atomic crystal with an inherent zero indirect band gap.

Additionally, the electronic bands near the Fermi energy are nearly flat, corresponding to spatially localized wave functions. Such localized states can enhance electronic correlation effects, which have been associated with phenomena such as unconventional superconductivity⁶⁹ and the fractional quantum Hall effect.⁷⁰ Flat bands have been studied extensively in the 2-dimensional cluster compound Nb_3Cl_8 ^{4,24} and related materials.^{25,71} The strongly correlated flat bands in Nb_3Cl_8 do not lead to superconductivity, which allows the material to be used as a field-free Josephson diode.^{72,73}

The effective dimensionality of the electronic structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ is therefore of interest, because zero-dimensional flat bands, corresponding to the atomic limit, would fail to produce the quantum effects commonly associated with flatbands.⁷⁴ The bands near the Fermi energy are flat in all directions in reciprocal space (Figure 8), indicating either zero or three-dimensional character. However, since each $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ structural unit possesses an odd number of electrons, the absence of a metallic state is a clear indication that the clusters do not behave like isolated atoms. The formation of a singlet state indicates intercluster interactions along the *a* and *c* directions, since each unit cell contains only one repetition of the $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ unit along each string along *b*.

The dimensionality and localization of the wave function can be seen through the maximally localized Wannier functions (MLWFs),⁷⁵ which are shown for the valence band maximum in Figure 9a,c and for the conduction band minimum in Figure 9b,d, based on Wannierization of the band manifold between -0.05 and 0.35 eV (see Supporting Information, Figure S6). The MLWFs show that the electronic states are delocalized over the $[(\text{Nb}_4\text{O})_2(\text{Nb}_2\text{O}_2)]$ clusters and into the interstitial space, with some reach into neighboring clusters. The delocalization thereby allows adjacent clusters to interact, forming a quantum singlet state.

The nature of the states near the Fermi energy, as well as the stability of the singlet state, were analyzed further through calculation of the crystal orbital Hamilton populations (COHP).^{76,77} The COHP decomposes the electronic states into bonding and antibonding orbitals, showing the states near the Fermi level to be comprised of Nb–O and Nb–I antibonding orbitals and Nb–Nb bonding orbitals, a situation which persists up to about -2 eV, where Nb–I bonding orbitals become predominant (Figure S7). At the Fermi energy, the COHP of the bonding and antibonding orbitals are essentially balanced, indicating that the quantum singlet state is energetically stable at the DFT level. The covalent bond strengths (as represented by the integrated COHP) of the Nb–O, Nb–I, and Nb–Nb bonds all ranged from -2 to -3 eV, showing that all three bond types play a role in the

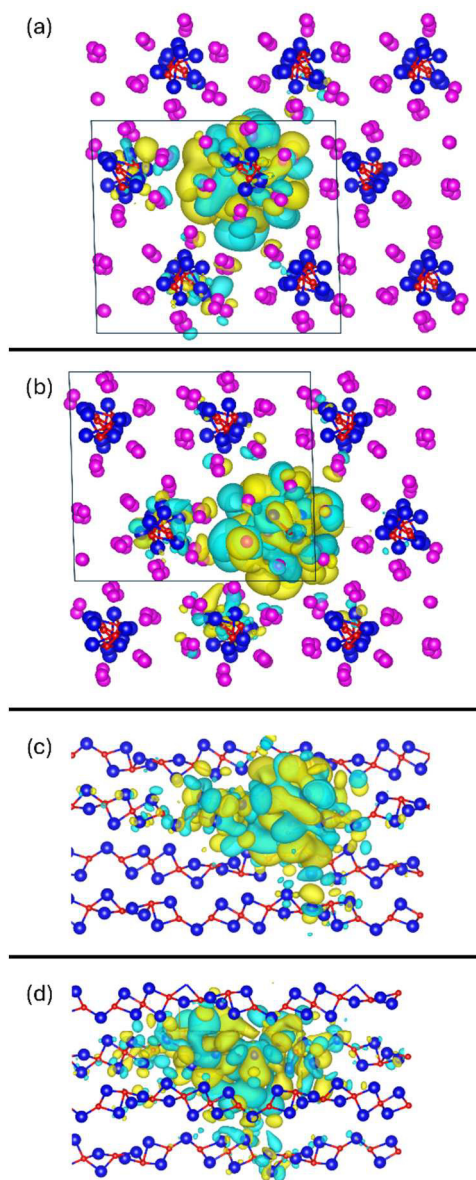


Figure 9. Maximally localized Wannier functions of the highest occupied (a, c) and lowest unoccupied (b, d) bands in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, shown along *b* (a, b) and along *a* (c, d). Iodine atoms are omitted from (c, d) for clarity. The MLWFs are delocalized over $[(\text{Nb}_4\text{O})_2(\text{Nb}_2\text{O}_2)]$ clusters and into the interstitial space, allowing electron–electron interactions that lead to the formation of a singlet state.

formation of the complex $[(\text{Nb}_4\text{O})_2(\text{Nb}_2\text{O}_2)]$ cluster structure.

We have also investigated the topology of the flat bands as another potential origin of the zero indirect gap.^{61,62} Topological flat bands can show the fractional quantum Hall effect and quantum spin Hall effect, in addition to having topological protection of the band gap.^{78–80} Calculation of the $\mathbb{Z}_2$ topological invariant using the Wilson loop method⁸¹ revealed nontrivial topology in the $k_a k_c$ plane, corresponding to a weak topological insulator with $\mathbb{Z}_2 = (0; 010)$.⁸² This finding indicates that $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ behaves like a series of stacked 2D topological insulators,^{80,83} each of which has the hexagonal structural motif typical of 2D topological flatband materials.^{74,84}

At this point, we can connect the electronic properties of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ to its structure. Once we have established the three-dimensional nature of the electronic structure, the destructive interference of the wave function, which creates flat bands in the *ac* plane, can be assumed to arise from the hexagonal structural motif, as is seen in Kagome materials and twisted bilayer graphene.^{74,84} In the vicinity of D and E in Figure 8, we find the flat band picture to be perturbed, creating the indirect zero band gap. The origin of this unusual gap can be related to the helical shape of the clusters (Figure 4), as chirality and helicity are known to play an important role in the formation of such gaps in model systems and photonic crystals.^{61,66,67}

Specifically, in these model systems local symmetry breaking appears in the form of terms in the Hamiltonian which move the VBM and CBM to different points in momentum space.^{61,66,67} Meanwhile, the retention of global symmetry prevents the opening of a topologically trivial gap and thereby the system acquires a zero indirect gap.^{61,66,67} We can identify these features in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, which contains two pairs of chiral clusters with opposite helicity within each unit cell, leading to an overall antiferrochiral⁸⁵ arrangement which retains global inversion symmetry. In contrast, other Nb cluster compounds which lack the helical motif do not show indirect band gaps, including examples such as $\text{Nb}_4\text{OI}_{10}$ and $\text{CsNb}_3\text{Br}_7\text{S}$, which also possess flat bands.^{31,54–56} $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ is distinguished from the model systems by the preservation of time reversal symmetry (TRS); in the models TRS is broken, creating a zero indirect gap between TRS-related points at $\pm\mathbf{k}$.^{61,66,67}

Inclusion of spin–orbit coupling (SOC) in the DFT calculations causes only minor changes to the bands near the Fermi level (Figure S8), as the spin–orbit interaction is weak in the Nb 4d states. However, these changes are nevertheless instructive regarding the origins of the indirect zero band gap. With SOC, the band gap takes a very small negative value (*ca.* -3 meV). Such band inversion due to SOC is well-known in direct zero gap materials, where it can cause the opening of a positive gap, because crossing of the inverted bands becomes forbidden.^{86,87} In $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, band inversion can create a negative gap as the bands are separated in momentum space. Band inversion is allowed because SOC breaks electronic symmetry (specifically, SU(2) spin rotation symmetry),^{86,87} demonstrating how a combination of symmetries enforces the formation of a zero gap. Because SOC is weak in the bands near the Fermi level, this symmetry is almost preserved, and the zero indirect gap is robust.

We summarize the relevant structural features of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ in Figure 10a, and compare them to those of monolayer Nb_3Cl_8 in Figure 10b. Both materials contain 2D layers of hexagonally packed Nb clusters, creating topological flatbands.⁸⁸ The Nb_3 clusters in Nb_3Cl_8 are identical and achiral, while the $[(\text{Nb}_4\text{O})_2(\text{Nb}_2\text{O}_2)]$ clusters in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ are chiral. However, monolayer Nb_3Cl_8 is noncentrosymmetric (space group $P3m1$), whereas $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ is centrosymmetric due to the antiferrochiral arrangement of clusters. The breaking of global inversion symmetry in Nb_3Cl_8 opens a gap at the Dirac cones,⁸⁸ whereas local symmetry breaking in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ shifts the VBM and CBM in momentum space while the global symmetries protect their degeneracy.

2.3. Electrical Conductivity of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$

The two-point probe electrical conductivity, σ , of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ single crystals at 300 K are shown in Figure S10. Exemplifying measurements of two samples are displayed, from which σ is

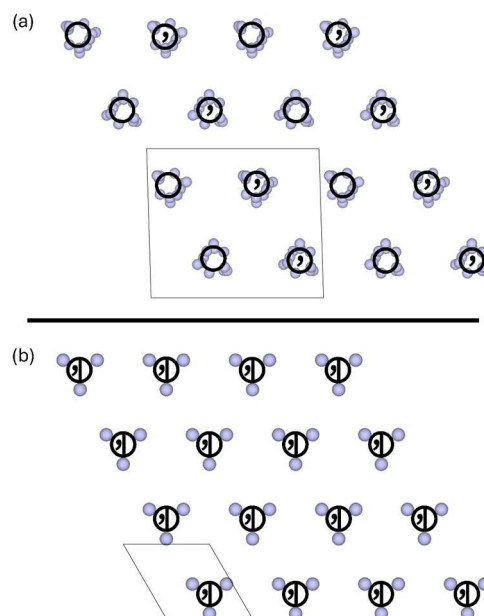


Figure 10. Cluster packing and enantiomorphism of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ (a) and monolayer Nb_3Cl_8 (b). Nb atoms are shown as lilac spheres, with the enantiomorphism of the clusters indicated using open circles/circles with commas. Both materials contain a hexagonal packing of clusters; a geometry associated with topological flatbands.⁸⁸ The clusters in Nb_3Cl_8 are achiral, whereas those in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ are chiral, providing a local symmetry breaking which removes the momentum-space coincidence of the VBM and CBM. Global inversion symmetry is broken in the breathing Kagome lattice of Nb_3Cl_8 , creating a direct band gap,⁸⁸ and unbroken in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ by antiferrochirality, preserving its zero gap.

calculated as 0.22 S/m for crystal 1 (light blue) and 0.27 S/m for crystal 2 (dark blue). These values are similar to those obtained for $\text{Nb}_4\text{OI}_{10}$ crystals (0.8–1.2 S/m).⁵⁴

In Figure 11, temperature-dependent two-point probe transport measurements of crystal 1 and 2 in the range of 60 K–300 K are displayed and an Arrhenius-like behavior is observed.^{53,89}

Via linear fitting, activation energies of 0.06 eV for crystal 1 (light blue) and 0.07 eV for crystal 2 (dark blue) were obtained. These results are close to those of $\text{Nb}_6\text{I}_9\text{S}$, having activation energies of 0.048–0.07 eV.²⁶ We note that the

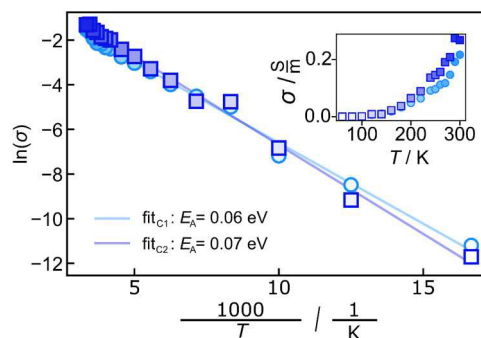


Figure 11. Arrhenius plot of the electrical conductivity (σ in S/m) from two $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ crystals between 60 K–300 K (in 20 K steps between 60 K–240 and 240 K–300 K in 10 K steps). The two lines represent linear fits, revealing activation energies of around 0.07 eV (light blue = crystal 1, dark blue = crystal 2). The inset shows the linear plot of conductivity against temperature.

crystals did not exhibit a notable photocurrent under 779 nm excitation, consistent with a small or vanishing band gap.

The measured electrical conductivity (Figure 10) cannot by itself confirm the predicted indirect band gap and flat bands, however it is consistent with the DFT calculations. The absence of metallic conduction follows from the DFT-predicted formation of a quantum singlet state, although other consequences of strongly correlated electronic states would require different experimental probes. Direct zero-gap materials often display a non-Arrhenius relationship between conductivity and temperature, with a positive $d\sigma/dT$ gradient at low temperature and a negative gradient at higher temperature.^{90,91} However, the indirect gap predicted in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ would require momentum transfer from the phononic system for electrical conduction, which would be enhanced upon increasing temperature. Additionally, the flat band structure around the Fermi energy results in a large range of potential transitions with direct and indirect gaps ≤ 0.1 eV. The DFT-predicted electronic properties therefore require further investigation and verification. For example, angle-resolved photoemission spectroscopy (ARPES) or magneto-resistance measurements could confirm the unusual features of the band structure. Electronic structure calculations using hybrid exchange–correlation functionals or post-DFT methods, could also be used to corroborate or improve the predicted band gap, however these are highly computationally intensive in such a large system.

3. CONCLUSION

Recently, a number of cluster compounds have been discovered in the field of niobium oxyiodides. Two new niobium oxyiodides are now presented, based on the $[\text{Nb}_4\text{O}]$ butterfly cluster with $[\text{NbO}]$ elongations. A butterfly cluster with two elongations is represented by the $[\text{Nb}_4\text{O}(\text{NbO})_2]$ -fragment in the structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$, in which the connectivity of cluster generates a three-dimensional network. Two butterfly clusters are connected by a pair of (NbO) units and a bridging (ONbO) unit, leading to the infinite chain structure $^{1}_{\infty}[(\text{Nb}_4\text{O})(\text{ONb}_2\text{O})(\text{Nb}_4\text{O})(\text{ONbO})]$ in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$.

Electronic structure calculations suggest that $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ has a zero indirect band gap, a highly unusual property not previously reported in an atomic crystal. The zero gap closes a small (0.02 eV) gap between a pair of three-dimensional flatbands which otherwise surround the Fermi energy. The flatbands are shown by examination of the Wannier functions to arise from electron delocalization over $[(\text{Nb}_4\text{O})_2(\text{ONb}_2\text{O})]$ clusters and into the interstitial spaces, where interactions between adjacent clusters lead to quantum interference effects and the formation of a singlet state. Comparison to model systems allows us to suggest that the chirality of the twisted clusters in the overall antiferrochiral crystal leads to the formation of the zero indirect gap.

Electrical conductivity measurements suggest that $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ behaves as a semiconductor with a very small gap, consistent with the flatband picture from DFT.

The sensitive thermal behavior of compounds formed in this heterogeneous reaction of NbI_4 , Li_2O , and $\text{Li}_2(\text{CN}_2)$ implies metastability and kinetic control of the product formation. While in classical chemical thermodynamics the product formation occurs in or near thermodynamic equilibrium, nonequilibrium systems are characterized by time-dependence, spatial gradients, and fluxes of matter and energy. These features can explain the formation of several metastable

compounds⁵⁷ and arises when the product formation strongly depends on reaction conditions, particularly on the temperature, the duration at that temperature, and the applied heating and cooling rates. The formation of the compound $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ under such conditions, with its complex crystallographic structure and unusual electronic properties, emphasizes the importance of considering products from such (near) non-equilibrium reaction conditions.

4. EXPERIMENTAL SECTION

All manipulations of starting materials and products were performed in a glovebox under dry argon with moisture and oxygen levels below 1 ppm. Li_2O (ABCR, 95%) was used as purchased. NbI_4 was synthesized as described in the literature.⁹² $\text{Li}_2(\text{CN}_2)$ was synthesized as described previously.⁹³

4.1. Synthesis

$\text{Nb}_6\text{O}_3\text{I}_{15}$ and $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ were synthesized from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol) and $\text{Li}_2(\text{CN}_2)$ (7.2 mg, 0.135 mmol) were encapsulated into a fused silica ampule with 3 cm length and a volume of about 1.5 cm^3 . The ampule was heated in a box furnace from room temperature to 500 $^{\circ}\text{C}$ with a rate of 0.1 $^{\circ}\text{C}/\text{min}$. The holding time was 1 h before the reaction was cooled down to 450 $^{\circ}\text{C}$ with a rate of 1 $^{\circ}\text{C}/\text{min}$ and afterward to room temperature with a rate of 0.1 $^{\circ}\text{C}/\text{min}$. Block-like crystals of $\text{Nb}_6\text{O}_3\text{I}_{15}$ and elongated, plate-like crystals of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ were found on the wall of the ampule below the side phases NbOI_2 and NbI_5 and beside the side phases $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ and $\text{b-Nb}_4\text{OI}_{11}$. At the bottom of the ampule, LiI , $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and amorphous powder can be found. The products are black and quickly decompose in air due to moisture.

4.2. Crystallography

A block-like $\text{Nb}_6\text{O}_3\text{I}_{15}$ and a plate-like $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ single-crystal were mounted on a Rigaku XtaLab Synergy-S X-ray diffractometer using $\text{Mo-K}\alpha$ ($\lambda = 0.71073$ Å) radiation for $\text{Nb}_6\text{O}_3\text{I}_{15}$ and $\text{Cu-K}\alpha$ ($\lambda = 1.54184$ Å) radiation for $\text{Nb}_{11}\text{O}_6\text{I}_{24}$. The single crystals were kept under N_2 cooling at 150 K during the data collection. Corrections for absorption effects were applied with CrysAlisPro 1.171.43.121a (Rigaku Oxford Diffraction, 2022). The crystal structures were solved by the integrated space group and crystal-structure determination routine of SHELXT⁹⁴ and full-matrix least-squares refinement with SHELXL-2019/3⁹⁴ implemented in Olex2 1.5.⁹⁵

4.3. Electrical Conductivity

Conductivity measurements were performed on a Lake Shore Cryotronics CRX-6.5 K probe station with a Keithley 2636B source meter unit. Plate-like crystals of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ were contacted with silver paste on a silicon substrate with a 770 nm oxide layer and transferred into the measurement chamber under an argon atmosphere. The conductive silver pads at each end of the crystals were connected to the circuit with gold-coated tungsten tips. The chamber was kept under vacuum ($<5 \cdot 10^{-5}$ mbar) while the temperature was decreased in 10 K steps between 300 and 240 K and in 20 K steps between 240 and 60 K during the measurements. Two-point conductivity measurements were performed by varying the applied source-drain voltage from -200 mV to 200 mV while detecting the current. The dimensions (length (L), width (W), height (H)) of the used crystals are for crystal 1: $L = 67.2$ μm ; $W = 18.4$ μm ; $H = 16.2$ μm and for crystal 2: $L = 90.4$ μm ; $W = 16.6$ μm ; $H = 14.4$ μm .

4.4. Density Functional Theory

Density functional theory (DFT) calculations of the electronic structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ were performed using the Abinit (v. 10)⁹⁶ and Quantum Espresso (QE, v. 6.4.1)⁹⁷ software packages. The calculation without SOC was repeated with the same DFT input parameters in each software to ensure reproducibility; the calculation including SOC was performed using Abinit. The Perdew–Burke–Ernzerhof exchange–correlation functional⁹⁸ was used with the vdW–DFT–D3(BJ) dispersion correction of Grimme.⁹⁹ Methfessel–

Paxton smearing¹⁰⁰ was used to determine band occupation. Pseudopotentials were used as received from Pseudo Dojo.¹⁰¹ A $2 \times 2 \times 2$ Monkhorst–Pack grid¹⁰² of k-points was used to sample reciprocal space. Plane-wave calculations were performed using the projector augmented wave (PAW) formalism,¹⁰³ using an energy cutoff of 20 Ha outside of the PAW spheres and a 100 Ha cutoff inside them. These computational parameters were chosen following convergence studies. Structural relaxation was performed prior to the calculation of the band structure. MLWFs were constructed using Wannier90¹⁰⁴ from QE wave functions. Topological analysis of the resulting tight-binding band structure was performed using WannierTools.¹⁰⁵ COHP analysis was performed using LOBSTER.¹⁰⁶

The electronic structure of Nb₆O₃I₁₅ was calculated in QE using the same DFT parameters as for Nb₁₁O₆I₂₄.

A secondary calculation of the electronic structure of Nb₁₁O₆I₂₄ using the LDA¹⁰⁷ exchange–correlation functional was performed in Abinit with a 25 Ha energy cutoff outside of the PAW spheres and a 125 Ha cutoff inside. This calculation showed an essentially identical electronic band structure (see Figure S9), demonstrating that the zero indirect band gap is not an artifact of the choice of functional or pseudopotential.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c03891>.

Photographs of synthesized crystals, electronic band structure of Nb₆O₃I₁₅, niobium, oxygen, and iodine character of the band structure of Nb₁₁O₆I₂₄, band structure of Nb₁₁O₆I₂₄ with tight-binding model, band structure of Nb₁₁O₆I₂₄ calculated including SOC, band structure of Nb₁₁O₆I₂₄ calculated using LDA, and *I*–*U* curves of Nb₁₁O₆I₂₄ (PDF)

Accession Codes

Deposition Numbers 2380623 and 2401147 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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Zero Indirect Band Gap and Flat Bands in a Niobium Oxyiodide Cluster Material – Supporting Information

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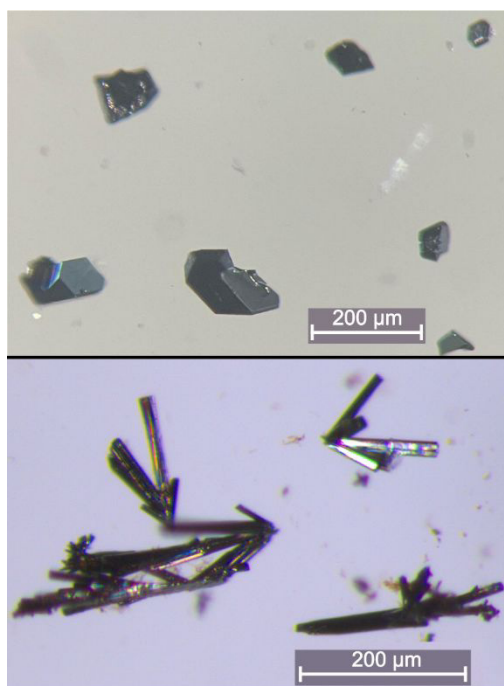


Fig. S1: Examples of block-shaped Nb₆O₃I₁₅ (top) and columnar Nb₁₁O₆I₂₄ (bottom) crystals

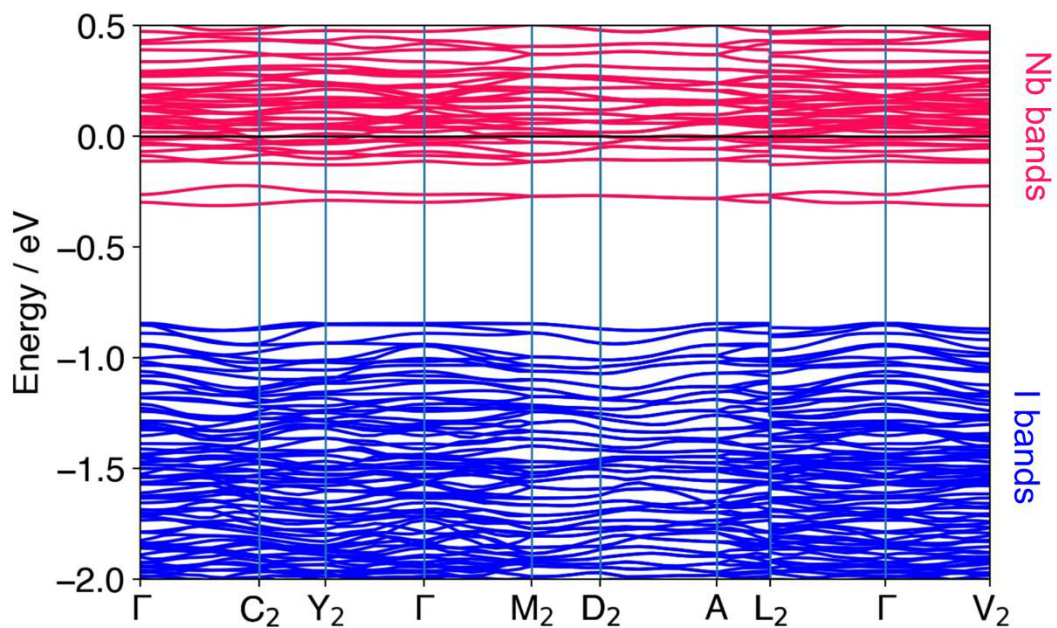


Fig. S2: Electronic band structure of $\text{Nb}_6\text{O}_3\text{I}_{15}$, with bands colored according to their main Nb or I character.

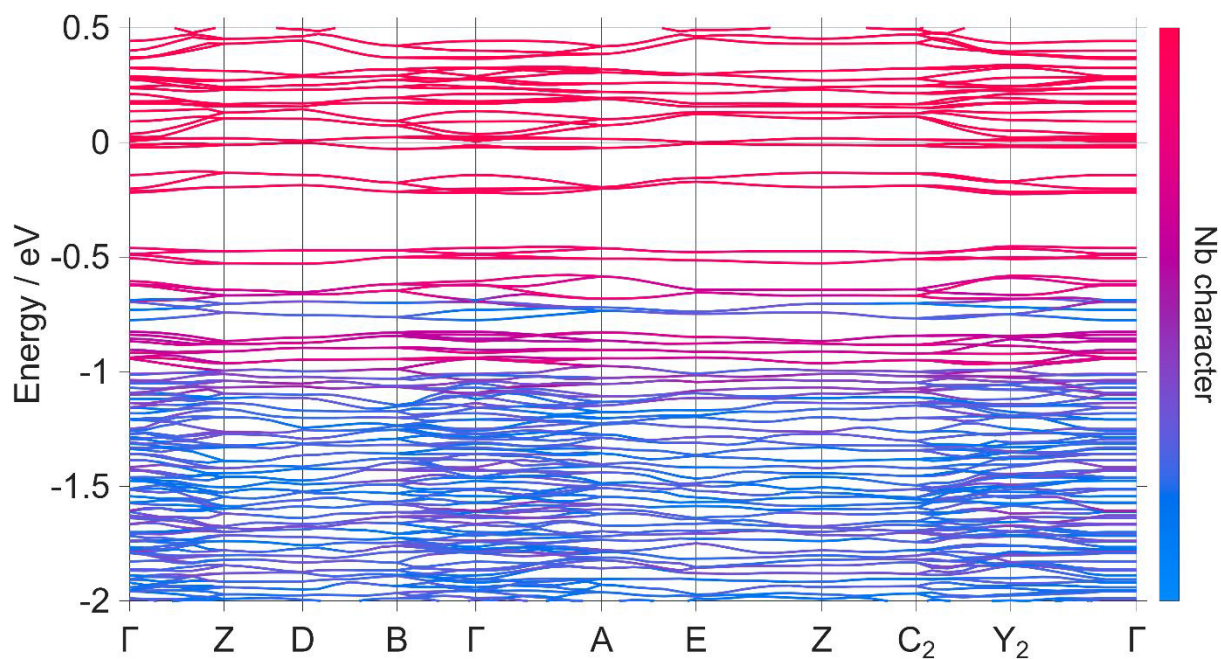


Fig. S3: Electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, with bands colored according to their Nb character.

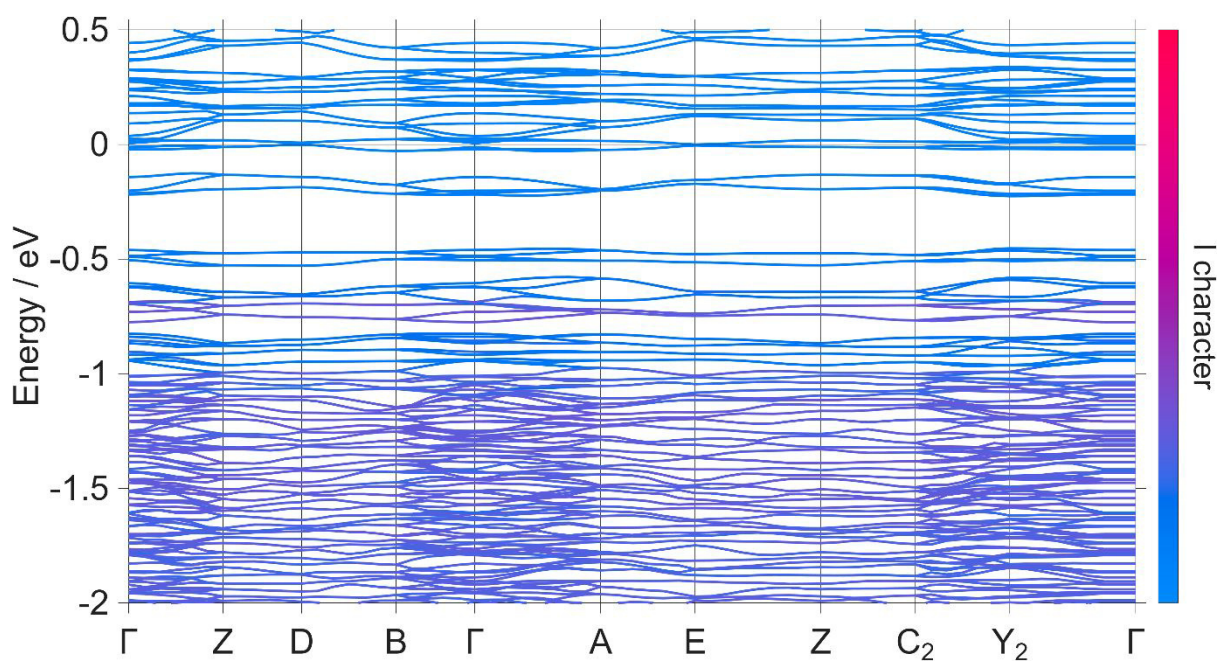


Fig. S4: Electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, with bands colored according to their I character.

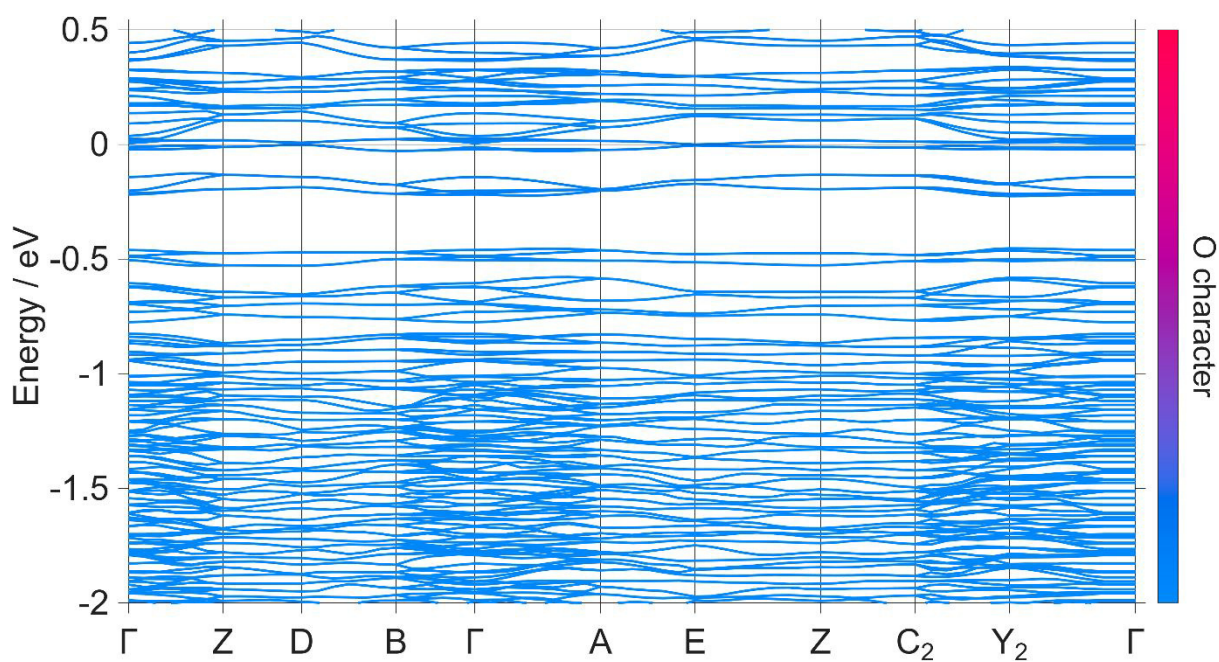


Fig. S5: Electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, with bands colored according to their O character.

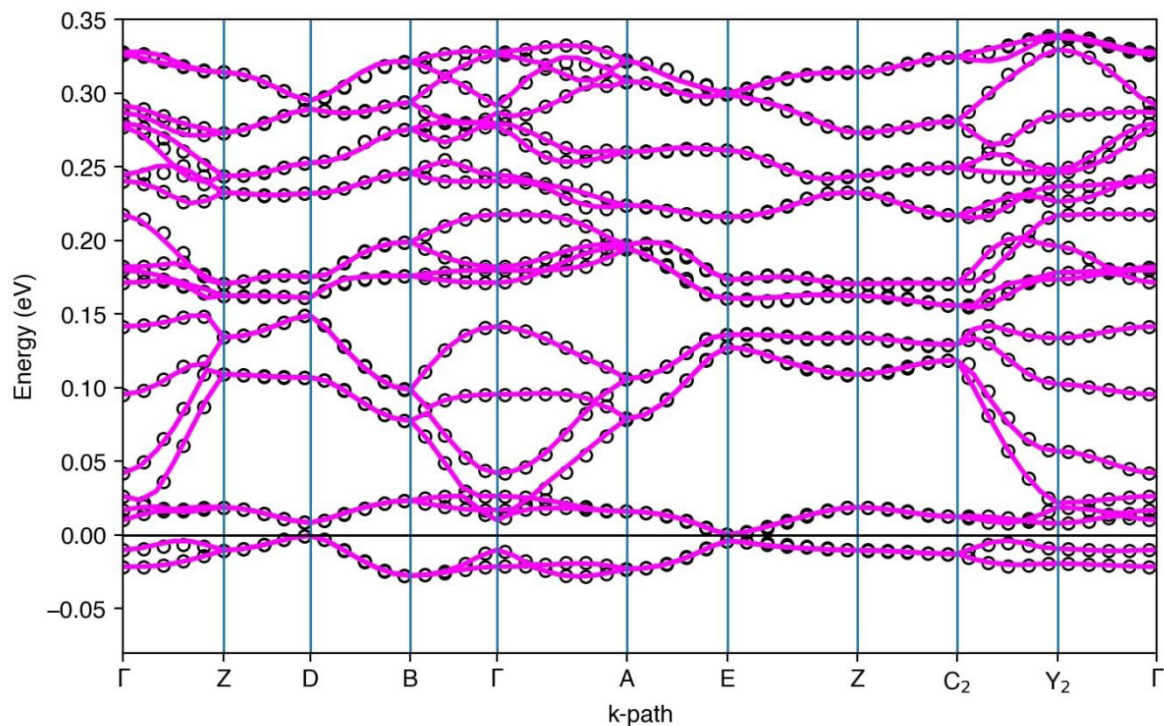


Fig. S6: Electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, with magenta lines showing the DFT-calculated bands and open circles showing the bands from the tight-binding model corresponding to the Wannier functions.

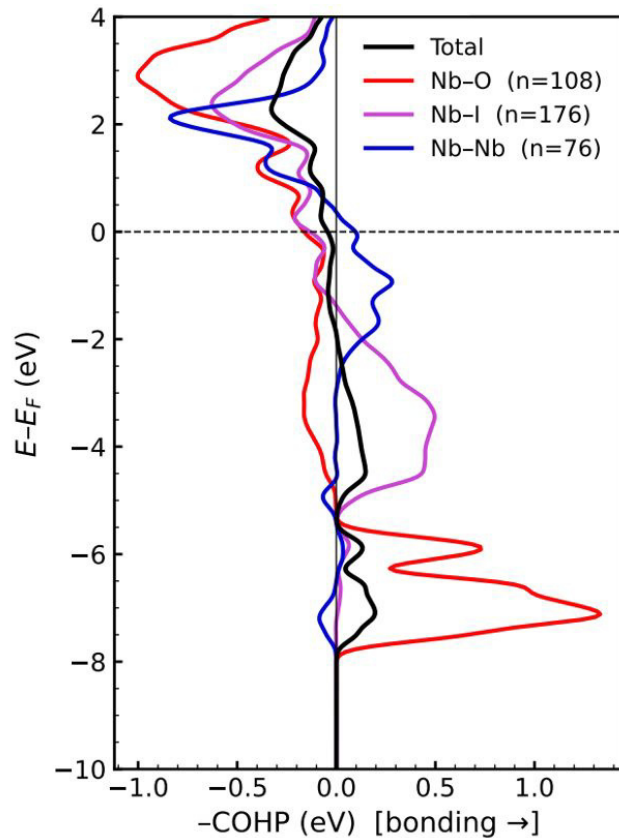


Fig. S7: Crystal orbital Hamilton populations (COHP) in $\text{Nb}_{11}\text{O}_6\text{I}_{24}$.

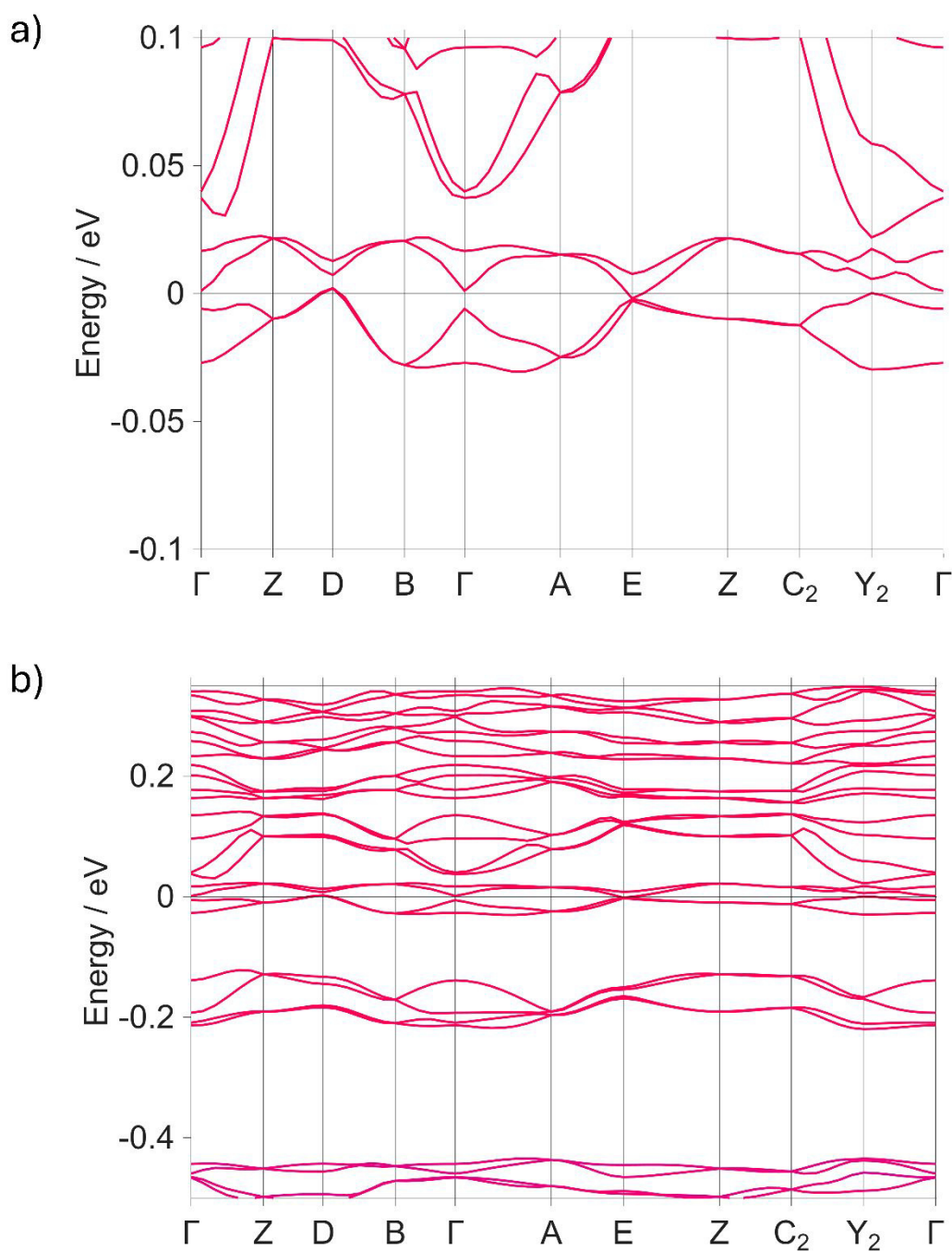


Fig. S8: Electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, calculated with spin-orbit coupling. A close-up of the bands near the Fermi energy is shown in (a), whereas a wider view is shown in (b).

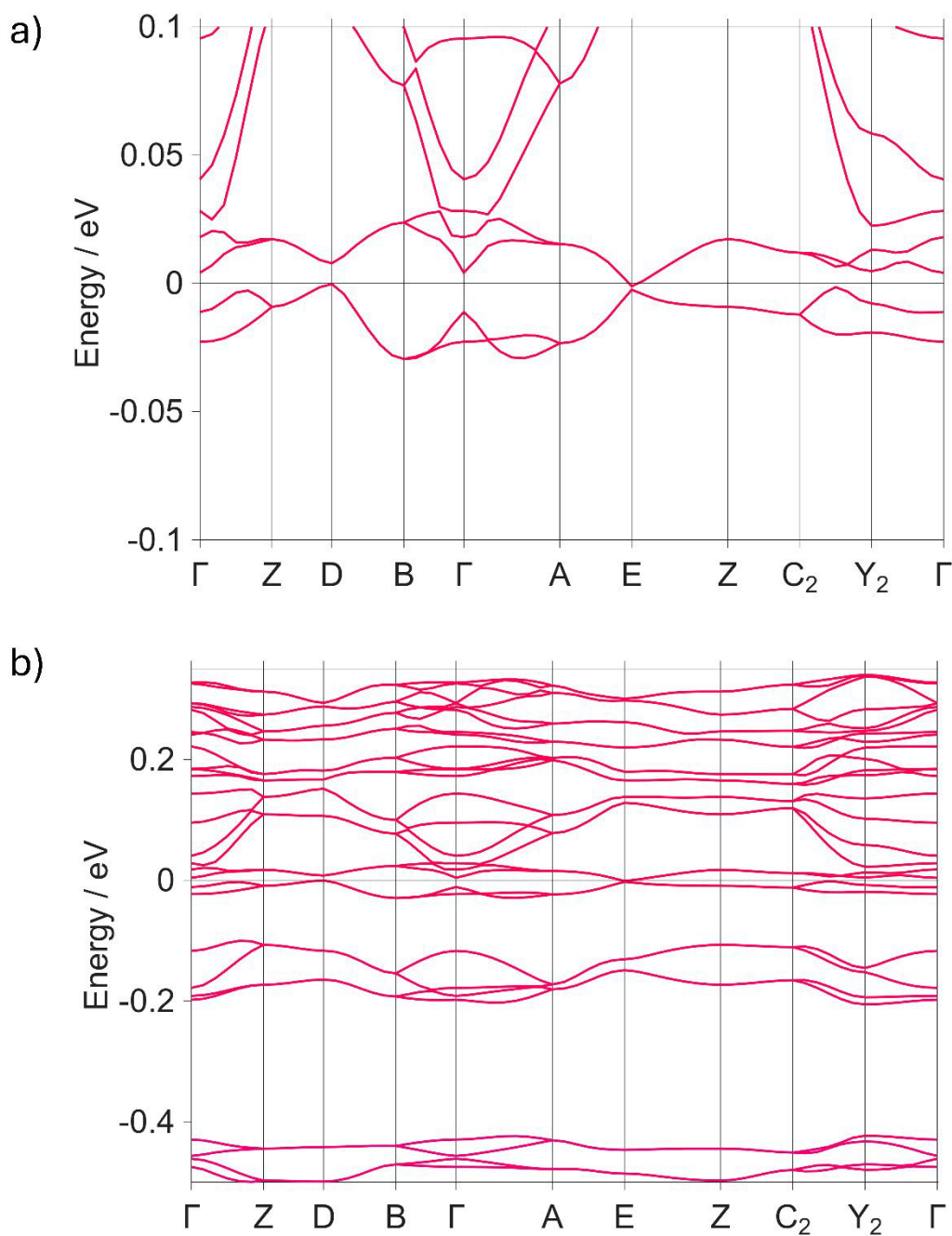


Fig. S9: Electronic band structure of $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, calculated using the LDA exchange–correlation functional. A close-up of the bands near the Fermi energy is shown in (a), whereas a wider view is shown in (b).

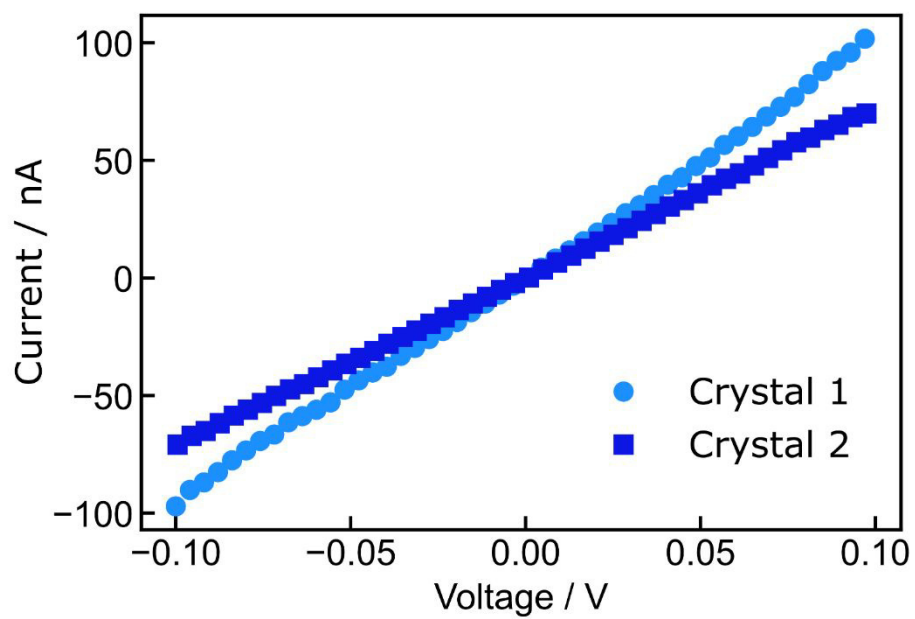
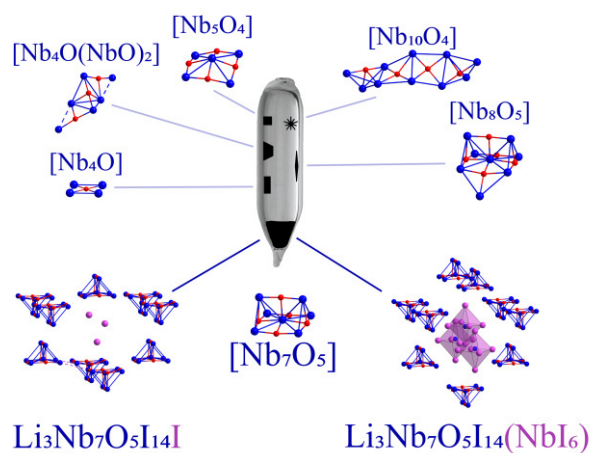


Fig. S10: I - U curves of two individual $\text{Nb}_{11}\text{O}_6\text{I}_{24}$ -crystals at 300 K without illumination, showing Ohmic behavior.

Publication 6

Niobium Oxyiodide Clusters from Heterogeneous Solid-State Reactions: The Example of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$



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Niobium oxyiodide clusters from heterogeneous solid-state reactions: the example of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{Nbl}_6)$

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No fewer than nine niobium oxyiodide phases have been synthesised and characterised from the reaction between Nbl_4 and Li_2O in the presence of $\text{Li}_2(\text{CN})_2$ under closed-system conditions at temperatures between 400 °C and 500 °C. Reactions in this system proceed through diffusion-controlled solid–solid pathways as well as gas-phase reactions that extend beyond equilibrium, which enables the concurrent formation of multiple niobium oxyiodide compounds. The crystal structures of these products display a range of architectures based on different niobium oxide clusters, including the $[\text{Nb}_7\text{O}_5]$ core, which is a characteristic structural motif in the structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{Nbl}_6)$, the compound examined in this report.

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Introduction

Metal-rich halide cluster compounds of group 5 and 6 transition metals are well known. Among binary niobium iodides, well known representatives are Nb_6I_{11} , Nb_3I_8 , NbI_3 , and NbI_4 .^{1–3} These compounds are typically synthesised through metallothermic reactions involving binary metal halides. For example, Nb_6I_{11} is commonly prepared from Nb_3I_8 and metallic niobium at elevated temperatures,¹ whereas Nb_3I_8 itself is obtained from reactions between niobium powder and niobium pentaiodide.²

The extension of the metal-rich systems with chalcogenide or pnictide anions has greatly broadened this chemistry, leading to the formation of numerous heteroanionic cluster compounds. These compounds can be regarded as architectures in which anions are either substituted or structurally integrated, often necessitating distinct coordination environments. Variations in connectivity and structural motifs are evident, for example, in the structures of one-dimensional compounds such as $\text{Nb}_6\text{I}_9\text{S}$ and $\text{ANb}_3\text{Br}_7\text{S}$ ($A = \text{Rb}$ and Cs).⁴ Further structural diversity is observed in chalcogenide-containing compounds such as Nb_3TeI_7 ,⁵ $\text{Nb}_4\text{Se}_4\text{I}_4$,⁶ and $\text{Nb}_7\text{S}_2\text{I}_9$,⁷ as well as in layered pnictide analogues like $\text{Nb}_4\text{PnX}_{11}$ ($\text{Pn} = \text{N}$ and P ; $X = \text{Cl}$, Br , and I).⁸ Beyond differences in the number of Nb atoms constituting the cluster cores, these compounds display pronounced variations in their electronic structures and properties.

Niobium oxyiodides such as NbOI_3 , NbO_2I , and the metal-rich NbOI_2 have been known for a long time and studied intensively.⁹ Condensed niobium oxide iodides are highly volatile and can be crystallised only within narrow equilibrium conditions. This highlights the sensitivity of these systems to parameters such as temperature, pressure, and composition, all of which profoundly influence the formation of distinct niobium oxyiodide phases.

The semiconducting compounds NbOX_2 ($X = \text{Cl}$, Br , and I) can be synthesised from Nb powder, Nb_2O_5 , and NbX_5 and have been studied for applications such as photocatalytic water splitting,¹⁰ 2D dielectric capacitors,¹¹ and ferroelectric materials.^{11,12} Metallothermic reduction remains a conventional and efficient route for preparing NbOX_2 and related metal-rich metal halides. An alternative approach, introduced by L. Messerle *et al.*, uses bismuth as a “non-conventional” reducing agent.¹³ Additional soft reduction pathways have been reported using transition metals $M = \text{Cr}$, Mn , Fe , Co , or Ni .^{14,15} Owing to their lower electropositivity, these reduction agents facilitate the formation of multiple intermediate compounds with progressively decreasing oxidation states, as has been exemplified by the reduction cascade from WCl_6 to WCl_2 , which illustrates a distinctive reduction mechanism.¹⁵ Following this mechanism, the reductant metal (M) is first incorporated and then released as MCl_x .

Lithium carbodiimide is known to serve as a reactant delivering $(\text{NCN})^{2-}$ ions in solid-state metathesis (SSM) reactions with metal halides, yielding metal carbodiimides.¹⁶ However, when it is reacted with more electropositive metal halides, $\text{Li}_2(\text{CN})_2$ instead acts as a reducing agent. This has been demonstrated by its reaction with NiCl_2 , which produces

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metallic nickel along with C_3N_4 .¹⁷ In other combinations, $Li_2(CN_2)$ exhibits only a weaker reducing effect.

Transferring these findings, we explored the Nb–O–I system by reacting NbI_4 with Li_2O in the presence of $Li_2(CN_2)$. Our previous results demonstrated that interactions among NbI_4 , Li_2O , and $Li_2(CN_2)$ generate a heterogeneous system in which local temperature and pressure variations strongly affect the phase formation.¹⁸ As a result of these investigations, we have already identified a family of Nb_4O_{12-x} compounds, namely Nb_4OI_{12} , two modifications of Nb_4OI_{11} , and Nb_4OI_{10} , all featuring rectangular $[Nb_4O]$ cluster cores.¹⁹ From the same reaction system, we also obtained $Nb_5O_4I_{11}$ featuring a $[Nb_5O_4]$ cluster core.²⁰ Subsequent reactions produced $Li_3Nb_7O_5I_{15}$ and $Nb_8O_5I_{17}(NbI_5)$, which contain $[Nb_7O_5]$ and $[Nb_8O_5]$ cluster cores, respectively; the latter is extended by an additional niobium atom.¹⁸ More recently, we reported two new compounds $Nb_6O_3I_{15}$ and $Nb_{11}O_6I_{24}$, forming three-dimensional and one-dimensional assemblies of their crystal structures.²¹ The compound presented in this work, $Li_3Nb_7O_5I_{14}(NbI_6)$, is proposed as the competing phase to the formation of $Li_3Nb_7O_5I_{15}$.

Results and discussion

The Nb–O–I system was investigated by reacting NbI_4 with Li_2O in the presence of $Li_2(CN_2)$, loaded into fused silica ampoules. Both the previously reported reactions and the one described here were conducted with minor adjustments to the relative amounts of starting materials. The temperature programs applied to the silica ampoules were varied within narrow limits, while the overall reaction volume was kept constant. A natural temperature gradient along the ampoule was consistently evidenced by the occurrence of small amounts of volatile $NbOI_2$ as a side-phase, which was typically found at the cooler end of the ampoule.

Essentially all niobium oxyiodide compounds discussed in the Introduction section are formed close to 500 °C, appearing in the reaction vessel in different combinations with each other. These compounds occur as crystalline materials, including well-formed single-crystals, distributed across several regions in the silica ampoule. Their spatial distribution highlights the crucial role of gas-phase species in transporting both, reactants and products throughout the system.

Only two compounds, the previously reported $Li_3Nb_7O_5I_{15}$ ¹⁸ and the new $Li_3Nb_7O_5I_{14}(NbI_6)$, were obtained at the bottom of the silica ampoule. These compounds are likely formed without the involvement of a gas-phase transport process. In addition, $Li_3Nb_7O_5I_{14}(NbI_6)$ is produced at significantly lower temperatures and appears consistently in all reactions, although in varying quantities. At 450 °C, it is observed as a black, poorly crystalline powder. Unfortunately, the crystallinity and the crystal size of this compound were insufficient to fully characterise the compound by single-crystal X-ray analysis with acceptable refinement values. Therefore, the crystalline powder of $Li_3Nb_7O_5I_{14}(NbI_6)$ was analysed by powder X-ray

diffraction, and the crystal structure was refined by Rietveld analysis. The corresponding diffraction pattern showing the final structure refinement is presented in Fig. 1, and relevant refinement parameters are summarised in Table 1.

Overall, this system generates a range of niobium oxyiodides, but these phases are thermally metastable, as evidenced by their transformation into $NbOI_2$ at temperatures exceeding 500 °C.

The structural refinement of the crystalline powder of $Li_3Nb_7O_5I_{14}(NbI_6)$ by means of Rietveld refinement reveals a close relationship with the structure of $Li_3Nb_7O_5I_{15}$. $Li_3Nb_7O_5I_{14}(NbI_6)$ was found to crystallise orthorhombically in the space group *Imma*, featuring four crystallographically distinct niobium sites and three distinct oxygen sites in the structure. The localisation and refinement of lithium ions in the structure was fostered by their presence in special Wyckoff positions 4*e* of Li1 and Li2, and 4*f* of Li3.

The crystal structure of $Li_3Nb_7O_5I_{14}(NbI_6)$ is based on a $[Nb_7O_5]$ cluster core (Fig. 2) that has been previously reported as a basic building block in other crystal structures of niobium oxyiodides, obtained in the same reaction system.¹⁸ The niobium-to-niobium distances within the $[Nb_7O_5]$ cluster core of $Li_3Nb_7O_5I_{14}(NbI_6)$ range between 2.71(1) Å and 3.097(9) Å, which are in good accordance with the corresponding distances in $Li_3Nb_7O_5I_{15}$ (Table 2). This type of cluster core is surrounded by iodine atoms, which can be assigned as inner (i), outer (a), and outer–outer bridging (a–a) ligands when following the nomenclature that has been originally introduced for octahedral cluster compounds.²²

The surrounding of the cluster core with iodine atoms (Fig. 3) coincides with the pattern obtained in $Li_3Nb_7O_5I_{15}$,¹⁸ with relevant distances summarised in Table 2. Besides four inner I^i and outer I^a , there are twelve surrounding I^{a-a} iodine atoms making up a $[Nb_7O_5I_4^aI_{12/2}^{a-a}]$ cluster (Fig. 3) in the structure of $Li_3Nb_7O_5I_{14}(NbI_6)$. The connectivity between adjacent clusters is established by six pairs of I^{a-a} bridges departing from each of the six corners of niobium atoms of the $[Nb_7O_5]$ core, to build up a three-dimensional network, indicated by broken-off bonds in Fig. 3. The connectivity pattern

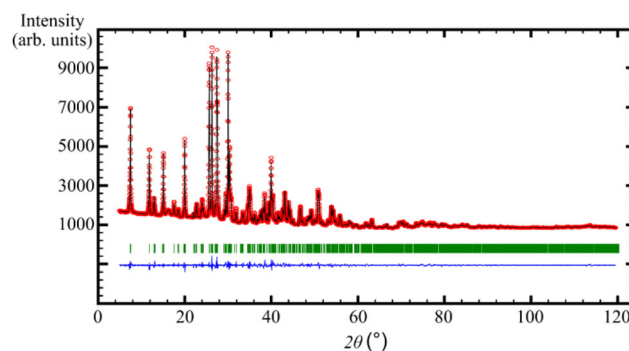
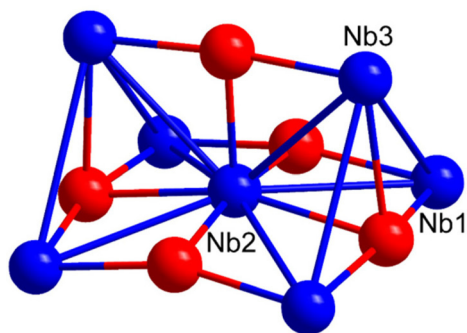


Fig. 1 Powder X-ray diffraction pattern subjected to Rietveld refinement for the crystal structure of $Li_3Nb_7O_5I_{14}(NbI_6)$ at 298 K, with the experimental (red) and calculated (black) intensities, Bragg positions (green), and the difference curve (blue) shown.

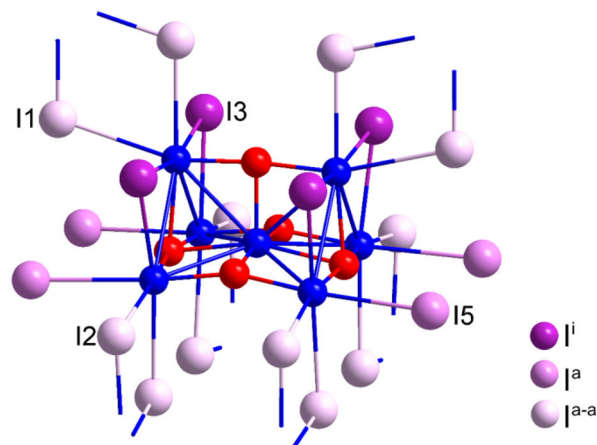
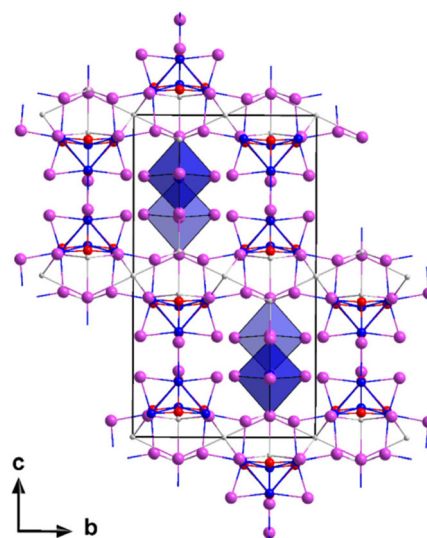
Table 1 Selected crystallographic data and Rietveld refinement values of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$

	$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$
CCDC	2493985
Crystal system	Orthorhombic
Space group	<i>Imma</i>
Temperature (K)	298
Unit cell dimensions (Å)	$a = 13.5176(1)$ $b = 13.4466(2)$ $c = 23.7811(3)$
Volume (Å ³)	4322.56(9)
Z	4
Wavelength, Cu-K α , (Å)	1.54060
μ (mm ⁻¹)	128.992
Reflections collected	1856
Parameters	261
R_{Bragg}	2.734
R_p/R_{wp}	3.143/4.2119
χ^2	1.3461

**Fig. 2** Structure of the $[\text{Nb}_7\text{O}_5]$ cluster core inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$, with labelled niobium atoms.**Table 2** Selected interatomic distances in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$

Distances/Å	$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$	$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ ¹⁸
Nb1–Nb2	2.821(7)	2.8050(4)
Nb1–Nb3	3.097(9)	3.0667(6)
Nb2–Nb3	2.71(1)	2.7883(7)
Nb–O	1.902(6)–2.254(9)	1.9464(6)–2.247(6)
Nb–I ⁱ	2.825(9)–2.842(5)	2.7528(5)–2.7908(3)
Nb–I ^a	2.934(9)	2.8761(5)
Nb–I ^{a-a}	2.92(1)–2.994(8)	2.9105(7)–3.0224(5)
Nb–I of $[\text{NbI}_6]^-$	Nb4–I4: 2.57(1); Nb4–I6: 2.598(7); Nb4–I7: 2.756(6); Nb4–I8: 3.09(2)	—
Li–I ^a	2.722(5)–2.95(2)	2.904(6)–2.97(1)
Li–I ^{a-a}	2.750(6)	3.17(1)
Li–I to other iodides	Li1–I4: 2.83(1); Li2–I8: 2.9(3); Li3–I8: 3.218(5)	Li–I5: 2.64(2)–2.76(2)

in this network creates open channels to host molecular $(\text{NbI}_6)^-$ units with average Nb–I distances of ~ 2.73 Å, displayed as a blue polyhedron in Fig. 4. The incorporation of (NbI_5)

**Fig. 3** Iodide coordination of the $[\text{Nb}_7\text{O}_5]$ cluster core with the connectivity implied by the broken bonds. Niobium atoms are coloured in blue, oxygen in red and iodide in pink.**Fig. 4** Section of the crystal structure viewed along the *a*-direction, with $(\text{NbI}_6)^-$ units shown as blue octahedra.

molecules has been previously reported in $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$ with an average Nb–I distance of ~ 2.66 Å.¹⁸ An example of a $(\text{TaBr}_6)^-$ ion is represented in the structure of the octahedral cluster compound $(\text{Ta}_6\text{Br}_{15})(\text{TaBr}_6)_{0.86}$ with an average Ta–Br distance of ~ 2.53 Å.²³

Lithium ions in the crystal structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ are refined in nearly square-pyramidal (Li1 and Li2) and distorted octahedral (Li3) iodide environments (Fig. 5). A similar square-pyramidal environment of lithium ions was also observed in the structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, here with an average Li–I distance of 2.85 Å. The octahedrally surrounded Li3 atom shows an average Li–I distance of 3.05 Å.

The crystal structure of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ displays a close resemblance to that of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ when substituting the $(\text{NbI}_6)^-$ with one I^- ion. This incorporation of $(\text{NbI}_6)^-$ as an

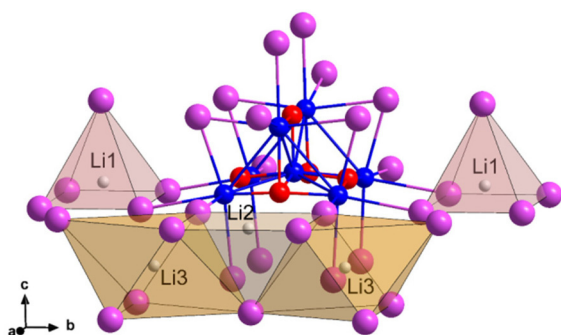


Fig. 5 Iodide coordination of the lithium atoms inside $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$.

anion clarifies that $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ can also be described as a double salt, which leads to the formula $\text{Li}_2[\text{Nb}_7\text{O}_5\text{I}_{14}]\cdot\text{Li}[\text{NbI}_6]$. In this respect, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ could be as well depicted as $\text{Li}_2\text{Nb}_7\text{O}_5\text{I}_{14}\cdot\text{LiI}$.

In spite of the similarity of local structures and bridging iodine atoms in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ there are clear differences in the connectivity patterns between clusters in both structures (Fig. 6).

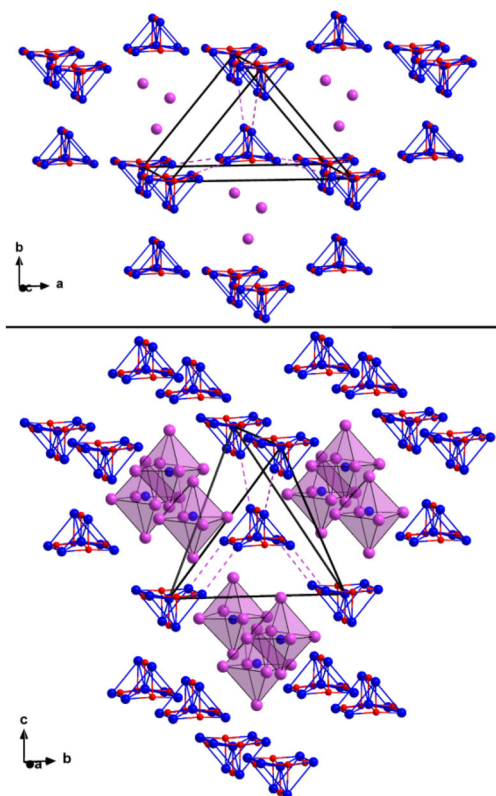


Fig. 6 Comparison of the cluster arrangement in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ (top) and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ (bottom) with the created cavities for I^- (violet balls) and $(\text{NbI}_6)^-$ ions (violet polyhedra). Two iodide bridges, which connect the central cluster with six and four adjacent clusters, respectively, are illustrated with pink dashed lines.

For $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, this results in a structural arrangement where each $[\text{Nb}_7\text{O}_5]$ cluster is surrounded by six adjacent clusters *via* iodine bridges. In contrast, in $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$, the $[\text{Nb}_7\text{O}_5]$ cluster core connects only to four adjacent clusters *via* iodine bridges.

Conclusion

The series of previously known metal-rich niobium oxyiodides is complemented by the basic compound $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$, which appears as a major phase at 450 °C, but is transformed at slightly higher temperatures into other newly discovered niobium oxyiodide compounds. The crystal structures of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$ show a close structural relationship to each other, and both phases appear as bottom phases in the reaction vessel, compared to other compounds in this system.

The discovery of the large series of compounds and crystal structures arises from the heterogeneous reaction between NbI_4 and Li_2O , with $\text{Li}_2(\text{CN}_2)$ serving as a mild reduction agent. These reaction conditions permit niobium, oxygen, and iodine to coexist as gas phase species (*e.g.* as NbI_x , NbOI_2 , I_2 , *etc.*). The composition of the gas phase is thought to be decisive for the formation of multiple compounds in one and the same reaction, allowing formation conditions for several phases, possibly under locally marginal temperature and pressure gradients, or cooling rates, as would be likely expected for non-equilibrium conditions. This finding and recent developments in the field of niobium oxyiodides expand the knowledge beyond the previously reported compounds NbOI_3 , NbO_2I and NbOI_2 by the newly reported examples $\text{Nb}_4\text{OI}_{10}$, $\text{Nb}_4\text{OI}_{11}$ (two modifications), $\text{Nb}_4\text{OI}_{12}$, $\text{Nb}_5\text{O}_4\text{I}_{11}$, $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{15}$, $\text{Nb}_6\text{O}_3\text{I}_{15}$, $\text{Nb}_8\text{O}_5\text{I}_{17}(\text{NbI}_5)$, $\text{Nb}_{11}\text{O}_6\text{I}_{24}$, and $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$. Some of these metal-rich compounds have been reported to exhibit semiconducting behaviour, although in practice their applications are limited by their moisture sensitivity, which is characteristic for all reported niobium oxyiodides.

Experimental section

All manipulations of starting materials and products were performed in a glovebox under dry argon with moisture and oxygen levels below 1 ppm. Li_2O (ABCR, 95%) was used as purchased. NbI_4 was synthesised as described in the literature.²⁴ $\text{Li}_2(\text{CN}_2)$ was synthesised as described before.¹⁶

Synthesis of $\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$

$\text{Li}_3\text{Nb}_7\text{O}_5\text{I}_{14}(\text{NbI}_6)$ was synthesised from NbI_4 , Li_2O and $\text{Li}_2(\text{CN}_2)$. For this purpose, NbI_4 (160.8 mg, 0.268 mmol), Li_2O (2 mg, 0.067 mmol) and $\text{Li}_2(\text{CN}_2)$ (7.2 mg, 0.135 mmol) were encapsulated into a fused and evacuated silica ampoule with a length of 3 cm and a volume of about 1.5 cm³. The ampoule was heated in a box furnace from room temperature to 450 °C

at a rate of $0.1\text{ }^{\circ}\text{C min}^{-1}$. The holding time was 24 h before the reaction mixture was cooled to room temperature at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. A block like, polycrystalline material of $\text{Li}_3\text{Nb}_7\text{O}_{514}(\text{NbI}_6)$ was obtained at the bottom of the ampoule in the powder form, besides LiI and an amorphous phase, produced by the decomposition of $\text{Li}_2(\text{CN}_2)$. The product was washed with dry acetonitrile to remove coproduced LiI. The estimated yield of $\text{Li}_3\text{Nb}_7\text{O}_{514}(\text{NbI}_6)$ was about 70%, intermingled with finely divided niobium powder, which is inappropriate for compositional chemical analysis. The crystalline powder appears black and decomposes in moist air.

Powder X-ray diffraction

PXRD patterns of products were obtained using a Stadi-P (STOE, Darmstadt) powder diffractometer with germanium monochromated $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.5406\text{ \AA}$) and a Mythen 1K detector.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

Crystallographic data have been deposited at the CCDC under 2493985.²⁵ The data that support the findings of this study are available on request from the corresponding author, H.-J. Meyer.

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