The cluster compound In₄Ti₁.₅Mo₀.₅Mo₁₄O₂₆ containing Mo₁₄ clusters and the new mono- and bi-capped trioctahedral Mo₁₅ and Mo₁₆ clusters: Synthesis, crystal structure, and electrical and magnetic properties.

Philippe Gall, Thierry Guizouarn, Patrick Gougeon

To cite this version:

Philippe Gall, Thierry Guizouarn, Patrick Gougeon. The cluster compound In₄Ti₁.₅Mo₀.₅Mo₁₄O₂₆ containing Mo₁₄ clusters and the new mono- and bi-capped trioctahedral Mo₁₅ and Mo₁₆ clusters: Synthesis, crystal structure, and electrical and magnetic properties.. Journal of Solid State Chemistry, Elsevier, 2015, 227, pp.98–103. 10.1016/j.jssc.2015.03.030. hal-01153431

HAL Id: hal-01153431
https://hal-univ-rennes1.archives-ouvertes.fr/hal-01153431
Submitted on 4 Nov 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
The cluster compound In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ containing Mo$_{14}$ clusters and the new mono- and bi-capped trioctahedral Mo$_{15}$ and Mo$_{16}$ clusters: synthesis, crystal structure, and electrical and magnetic properties.

Philippe Gall, Thierry Guizouarn and Patrick Gougeon*

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6226 - INSA, Université de Rennes 1, Avenue du Général Leclerc, 35042 Rennes-Cedex, France.

Corresponding Author
Fax: Int. Code +2 23 23 67 99; E-mail: Patrick.Gougeon@univ-rennes1.fr

Abstract

Single crystals of the new quaternary compound In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ were obtained by solid state reaction. The crystal structure was determined by single-crystal X-ray diffraction. In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ crystallizes in the orthorhombic space group Pnma with unit-cell parameters a = 9.4432(14) Å, b = 11.4828(12) Å, c = 20.299(4) Å and Z = 4. Full-matrix least-squares refinement on $F^2$ using 3807 independent reflections for 219 refinable parameters resulted in $R_1 = 0.0259$ and $wR_2 = 0.0591$. The crystal structure contains in addition to Mo$_{14}$ clusters the first examples of mono- and bi-capped trioctahedral Mo$_{15}$ i.e. Mo$_{15}$ and Mo$_{16}$ clusters. The oxygen framework derives from a stacking along the a direction of close-packed layers with sequence (...ABAC...). The Mo-Mo distances range between 2.6938(5) and 2.8420(6) Å and the Mo-O distances between 1.879(5) and 2.250(3) Å, as usually observed in molybdenum oxide clusters. The indium atoms form In$_4^{6+}$ bent chains with In-In distances of 2.6682(5) and 2.6622(8) Å and the Ti atoms are in highly distorted octahedral sites of oxygen atoms with Ti-O distances ranging between 1.865(4) and 2.161(4) Å. Magnetic susceptibility measurements confirm the presence of Ti$^{4+}$ cations and the absence
of localized moments on the Mo network. Electrical resistivity measurements on a single crystal of In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ show a semimetallic behavior.

Keywords
Reduced molybdenum oxide, molybdenum clusters, disordered crystal structure, magnetic susceptibility, resistivity measurement.

INTRODUCTION

In solid state chemistry, the octahedral M$_6$ cluster constitutes the main structural feature of numerous ternary or quaternary chalcogenide, chalcohalide or halide compounds containing transition metals such as Nb, Mo, Ta, W or Re in low oxidation states. Larger clusters which are principally observed with the molybdenum, result either from the uniaxial face- or edge-sharing of Mo$_6$ octahedra. The former process is observed when the Mo$_6$ clusters are face-bridged by the ligands such as S, Se and Te and is exemplified by the series of compounds M$_{n-2}$Mo$_{3n}$X$_{3n+2}$ (M = Rb, Cs; X = S, Se or Te; n = 3, 4, 5, 6, 7, 8 and 10) containing Mo$_9$, Mo$_{12}$, Mo$_{15}$, Mo$_{18}$, Mo$_{21}$, Mo$_{24}$, Mo$_{30}$ and Mo$_{36}$ clusters [1]. The final stage of this face-sharing condensation is the infinite $\text{Mo}_6^{2+}$/ chain found in the quasi-one-dimensional compounds M$_2$Mo$_3$X$_6$ (M = Na, K, Rb, Cs; X = S, Se or Te) [2] and AgMo$_6$Te$_6$ [3]. The edge-sharing condensation of Mo$_6$ octahedra is observed in the reduced molybdenum oxides where the Mo$_6$ clusters are edge-bridged by the oxygens. This process leads to columnar bi [4], tri [5], tetra [6] and penta-octahedral [7] oligomers that are observed for example in the series M$_{n-3}$Mo$_{4n+2}$O$_{6n+4}$ (n = 2, 3, 4 and 5). The ultimate step of the edge-sharing-condensation process corresponds to the infinite $\text{Mo}_2^{2+}$/ chain of trans-edge-sharing Mo$_6$ octahedra that was first observed in NaMo$_4$O$_6$ [8] and subsequently in the isostructural M$_2$Mo$_4$O$_6$ (M = K [9], Ba [10], In [11], Sn [12] or Pb) compounds and in the four other structure-types Sc$_{0.75}$Zn$_{1.25}$Mo$_4$O$_7$ [13], Mn$_{1.5}$Mo$_8$O$_{11}$ [14], MMo$_6$O$_{10}$ (M = Li, Zn) [15] and R$_4$Mo$_4$O$_{11}$ [16].
In reduced molybdenum oxides, related clusters to Mo$_6$ and Mo$_{10}$ were also obtained by capping some faces. For example, the existence of mono- and bi-capped Mo$_6$ clusters, i.e. Mo$_7$ and Mo$_8$, was first mentioned by Leligny et al. in the compound LaMo$_{7.7}$O$_{14}$ [17] in which both clusters coexist randomly. Subsequently, the Mo$_7$ and Mo$_8$ clusters were found in well-ordered structures. The monocapped octahedral Mo$_7$ unit has been observed up to now either forming infinite chains with bioctahedral Mo$_{10}$ unit or quasi-isolated in the series of compounds $M_4M’_3Mo_{26}O_{48}$ ($M = Sr$, Eu, $M’= Al$, Ga, Fe) [18]. The bi-capped octahedral Mo$_8$ cluster was encountered in the two isomeric cis and trans forms in the series of polymorphic compounds $RMo_8O_{14}$ ($R = La$, Ce, Pr, Nd, Sm) [19]. In addition, the Mo$_9$ and Mo$_{10}$ clusters formed by capping three or four faces of the octahedral Mo$_6$ were observed in the modulated compound EuMo$_{7.96}$O$_{14}$ [20]. More recently, the Mo$_{11}$ and Mo$_{12}$ clusters resulting from the capping of one and two faces of the bioctahedral Mo$_{10}$ cluster were observed in the quaternary reduced molybdenum oxides $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ ($M = Sr$, Eu) [21]. In the latter compounds, the Mo network is dominated by bioctahedral Mo$_{10}$ clusters, which coexist statically with Mo$_{11}$ and Mo$_{12}$ clusters. In this work, we show how the face-capping principle can be extended to trioctahedral Mo$_{14}$ units formed by fusing three Mo$_6$ clusters with the synthesis, crystal structure, and physical properties of the new compound In$_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$. This latter compound contains in addition to Mo$_{14}$ clusters the first examples of mono- and bi-capped trioctahedral Mo$_{14}$ clusters i.e. Mo$_{15}$ and Mo$_{16}$ clusters.
EXPERIMENTAL

Synthesis

\(\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}\) was obtained as single crystals by heating a mixture of \(\text{In}_2\text{O}_3, \text{TiO}_2, \text{MoO}_3\) and \(\text{Mo}\) with the overall composition “\(\text{In}_2\text{Ti}_4\text{Mo}_{4}\text{O}_{8}\)” at 1400°C for 96H in a sealed molybdenum crucible. The latter was previously cleaned by heating at about 1500 °C for 15 mn under a dynamic vacuum of about \(10^{-5}\) Torr. The mixture of the starting materials was pressed into a pellet and loaded into a molybdenum crucible which was sealed under a low argon pressure using an arc welding system. The composition of the thus obtained crystals was proved to form single-crystal X-ray diffraction data (see below). Attempts made to prepare a single-phase powder of \(\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}\) were unsuccessful (only approximate yields of 15 to 25 % were obtained).

Single Crystal X-ray Study

A black crystal of approximate dimensions 0.196x0.037x0.025 mm\(^3\) was employed in the intensity data collection conducted with a Nonius KappaCCD diffractometer. The COLLECT program package [22] was used to establish the angular scan conditions (\(\phi\) and \(\omega\) scans) used in the data collection. A total of 317 frames were collected with a frame width of 1.10° and an exposure time of 66 s. Reflection indexing, Lorentz-polarization correction, peak integration, and background determination were performed by using the EvalCCD program [23]. An absorption correction (min/max transmission=0.5744/0.6063) was applied using the description of the crystal faces [24]. Of 54877 reflections collected in the 3.56–36.2 \(\theta\) range, 5281 were independent (\(R_{int}=0.0502\)). Analysis of the data revealed that the systematic absences (\(0kl\) \(k = 2n + 1\), (\(h0l\) \(l = 2n + 1\), and (\(hk0\) \(h = 2n + 1\) were consistent with the orthorhombic space group \(\text{Pbca}\). The initial positions for 7 molybdenum atoms forming a \(\text{Mo}_{14}\) cluster and some of the oxygen atoms as well as for the indium atom were determined with the direct methods program SIR-97 [25] in the \(\text{Pbca}\) space group. A subsequent difference Fourier synthesis revealed the remaining oxygen atoms and two peaks at 0.42 Å from each other. As this situation was similar to that encountered in the \(\text{M}_2\text{Ti}_{1.4}\text{Mo}_{0.6}\text{Mo}_{10}\text{O}_{20}\) (\(\text{M} = \text{Sr, Eu}\)) compounds, the peak the closest to the \(\text{Mo}_{14}\) cluster was assigned to a \(\text{Mo}\) atom (Mo8) and the peak farthest to a Ti atom. Subsequent refinements of this model included the...
atomic position and anisotropic displacement parameters for all atoms as well as the site occupancy factors for the Mo8 and Ti atoms. The later ones which were first refined freely converged to 0.25(2) and 0.74(3), respectively. Consequently, in the final refinement the sum the site occupancy factors of the Mo8 and Ti atoms was fixed to unity. A calculation of the two Mo8 and Ti probability density functions shows that they do not overlap and that for both atoms the position of the density maximum coincides with the refined position. The final full-matrix least squares refinement on $F^2$ which was based on a model including the positional and anisotropic displacement parameters for all atoms and site occupancy factors for Ti and Mo8 led to the values of $R = 0.0259$ and $wR = 0.0591$ for 3807 reflections with $I > 2\sigma(I)$ and to the stoichiometry $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}$. All structure refinements and Fourier syntheses were carried out using SHELXL-97 [26]. Reconstructed reciprocal space sections did not show any superlattice reflections or diffuse lines that preclude a possible ordering of the different clusters. Crystallographic data and X-ray structural analysis for the $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}$ compound are summarized in Table 1. The final atomic coordinates, and the equivalent isotropic displacement parameters are gathered in Table S1, and selected interatomic distances are listed in Table S2 in the Supporting information. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-428999.

Electrical Resistivity Measurements

The study of the temperature dependence of the electrical resistivity was carried out on a single crystal of $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}$ using a conventional ac four-probe method with a current amplitude of 0.1 mA. Contacts were ultrasonically made with molten indium on the single crystal. The ohmic behavior and the invariance of the phase were checked during the different measurements at low and room temperature.

Magnetic susceptibility measurements.

Susceptibility data were collected on a batch of single crystals (ca. 40 mg) using a Quantum Design SQUID magnetometer between 2 K and 400 K and at an applied field of 0.1 T.
RESULT AND DISCUSSION

Figure 1 shows the projections of the crystal structures of In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ and M$_2$Ti$_{1.4}$Mo$_{0.6}$Mo$_{10}$O$_{20}$ (M = Sr, Eu) on the (b, c) plane. From these figures, the structural relationship between the two structure types, which are both described in the space group Pbca, is evident.

The main structural feature of In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ is the presence of trioctahedral edge-sharing Mo$_{14}$, and mono- and bi-capped Mo$_{15}$ and Mo$_{16}$ clusters which coexist statistically due to the partial occupancy of the capping site Mo8 shown in light blue in Figure 2a. The Fig. 3 shows a perspective view of the crystal structure of In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ along the b axis. As in the M$_2$Ti$_{1.4}$Mo$_{0.6}$Mo$_{10}$O$_{20}$ compounds, the oxygen framework derives from a stacking along the a direction of close-packed layers with sequence (...ABAC...). Projections of the four layers onto the (100) plane are given in Fig. 4. While the B (y ~ 0.25) and C (y ~ 0.75) layers are entirely occupied by oxygen atoms (Figures 4b and 4d, respectively) and have the composition [O32], in the A layers (y ~ 0.0 and 0.5) one fourth of the oxygen atoms are substituted by the In ions and one eighth are missing in an ordered way (Figures 4a and 4c, respectively). Consequently, the latter layers can be formulated [O20In8□4] where □ stands for the oxygen vacancies. Within the O network, 7/13 of the octahedral interstices are occupied by the Mo1 to Mo7 atoms which form trioctahedral Mo$_{14}$ clusters and one thirteenth statistically by the capping Mo8 and Ti atoms. The trioctahedral Mo$_{14}$ cluster which results from the metal-edge condensation of three octahedral Mo$_6$-type clusters is similar to those previously observed in the compounds T1$_{1.6}$Sn$_{1.2}$Mo$_{14}$O$_{22}$ [5a and b], K$_3$Mo$_{14}$O$_{22}$, K$_{1.66}$Pb$_{1.34}$Mo$_{14}$O$_{22}$, and K$_{1.29}$Sn$_{1.71}$Mo$_{14}$O$_{22}$ [5c]. It is also interesting to note that the vacancies in the A layers correspond to the center of the octahedra forming the Mo$_{14}$ clusters. In the latter, the Mo-Mo distances range between 2.6938(5) and 2.8420(6) Å and the Mo-O distances between 1.879(5) and 2.250(3) Å, as usually observed in molybdenum oxide...
clusters. The shortest distances between the Mo\textsubscript{14} cluster and the capping Mo\textsubscript{8} atom agree well with the existence of metallic bonds: 2.798(10) Å for Mo\textsubscript{8}-Mo\textsubscript{1}, 2.864(10) Å for Mo\textsubscript{8}-Mo\textsubscript{2} and 2.802(10) Å for Mo\textsubscript{8}-Mo\textsubscript{3} (see Fig. 2a), leading thus to the formation of monocapped and bicapped biocathedral Mo\textsubscript{15} and Mo\textsubscript{16} clusters (Fig. 2b and 2c). The latter clusters which are new to solid-state chemistry coexist thus randomly with the Mo\textsubscript{14} clusters in In\textsubscript{4}Ti\textsubscript{1.5}Mo\textsubscript{0.5}Mo\textsubscript{14}O\textsubscript{26}. Moreover, it should be noted that the distances between the Mo\textsubscript{14} clusters and the Ti atoms which are greater than 3.15 Å preclude the presence of heteronuclear clusters such as Mo\textsubscript{14}Ti or Mo\textsubscript{14}Ti\textsubscript{2} as previously mentioned for the M\textsubscript{2}Ti\textsubscript{1.4}Mo\textsubscript{0.6}Mo\textsubscript{10}O\textsubscript{20} (M = Sr, Eu) compounds. The Ti atoms are surrounded by six oxygen atoms forming a highly distorted octahedron (Figure 6). The Ti-O distances range between 1.865(4) and 2.161(4) Å with a mean value of 2.01 Å closed to the value of 2.00 Å calculated from the sum of the ionic radii of O\textsuperscript{2-} and Ti\textsuperscript{4+} in octahedral coordination according to Shannon and Prewitt [27]. From the Ti-O bond lengths, the valence of the Ti atoms calculated by using the relationship of Brown and Wu \[\text{valence} = \left(\frac{d \text{Ti-O}}{1.806}\right)^{5.2}\] [28] is +3.7, suggesting a number of oxidation of +4. This confirms the tetrivalence of the titanium that was already proved by XPS measurements in Eu\textsubscript{3}Ti\textsubscript{1.4}Mo\textsubscript{0.6}Mo\textsubscript{10}O\textsubscript{20}. Another interesting structural feature in In\textsubscript{4}Ti\textsubscript{1.5}Mo\textsubscript{0.5}Mo\textsubscript{14}O\textsubscript{26} is the presence of indium forming an In\textsubscript{6}\textsuperscript{6+} bent chain shown in Fig. 5. The two indium distances In1-In2 and In2-In2 are quite comparable, 2.6682(5) and 2.6622(8) Å, respectively. These distances are also of the same order as those observed for the In\textsubscript{5}\textsuperscript{7+} chains found in In\textsubscript{8}Mo\textsubscript{18}O\textsubscript{28} [29] and In\textsubscript{11}Mo\textsubscript{40}O\textsubscript{62} [30] which are comprised between 2.616 and 2.665 Å and for the In\textsubscript{6}\textsuperscript{8+} chains in In\textsubscript{3}Mo\textsubscript{11}O\textsubscript{17} and In\textsubscript{11}Mo\textsubscript{40}O\textsubscript{62} which range from 2.645 to 2.689 Å.

An astonishing fact is the very close stoichiometry of the Ti and Mo capping atoms found in the M\textsubscript{2}Ti\textsubscript{1.4}Mo\textsubscript{0.6}Mo\textsubscript{10}O\textsubscript{20} (M = Sr, Eu) compounds and In\textsubscript{4}Ti\textsubscript{1.5}Mo\textsubscript{0.5}Mo\textsubscript{14}O\textsubscript{26} which is not
understood to date. An intriguing question is also why any variation in the ratio Mo/Ti led to multiphasic products in the case of the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ ($M = \text{Sr, Eu}$) compounds?

Magnetic Properties. The temperature dependence of the molar magnetic susceptibility of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ is shown in Figure 6. The susceptibility is nearly temperature-independent in the range 100-300 K with $\chi_{RT} = 3.4 \times 10^{-3}$ emu/mol. This indicates clearly the absence of localized moments on the different Mo clusters as well as on the Ti atoms reflecting their tetravalence as previously observed in the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ ($M = \text{Sr, Eu}$) series. The low-temperature upturn results probably from small amounts of paramagnetic impurities often present in the starting reactants.

The electrical resistivity of a single-crystal of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ as a function of the temperature is shown in Figure 7. $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ presents a poorly metallic behavior with a transition to a semiconducting state below 50 K and a room temperature resistivity value of $5 \times 10^{-3}$ $\Omega$cm. The poor metallic character of this compound probably results from the positional disorder of the clusters as previously observed for the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ ($M = \text{Sr, Eu}$) compounds.

CONCLUSION

In summary, the novel reduced molybdenum oxide $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ has been synthesized by solid-state reaction at 1400°C for 96h in sealed molybdenum crucibles. Its crystal structure contains in addition to $Mo_{14}$ clusters the first examples of mono- and bi-capped trioctahedral $Mo_{14}$ that is $Mo_{15}$ and $Mo_{16}$ clusters. Magnetic susceptibility measurements confirm the presence of $Ti^{4+}$ cations. Electrical resistivity measurements on a single crystal of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ show a semimetallic behavior. The existence of $Mo_{18}$ and $Mo_{22}$ clusters in $Ba_3Mo_{18}O_{28}$ [6] and $In_6Mo_{22}O_{34}$ [7], respectively, lets us to envisage that
the mono and bicapped principle can be extended to the latter two clusters leading thus to Mo$_{19}$, Mo$_{20}$, Mo$_{23}$ and Mo$_{24}$ clusters in compounds in which the Mo-Ti-O networks would have the compositions (Ti$_{1.5}$Mo$_{0.5}$)Mo$_{18}$O$_{32}$ and (Ti$_{1.5}$Mo$_{0.5}$)Mo$_{22}$O$_{38}$, respectively.

**References**


(c) Gougeon, P.; Potel, M.; Sergent, M. Acta Cryst. 1990, C46, 1188.

(b) Dronskowski, R; Simon, A. Acta Chem. Scand. 1991, 45, 850.


Table 1. X-ray Crystallographic and Experimental data for $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$\text{In}<em>4\text{Ti}</em>{1.5}\text{Mo}<em>{0.5}\text{Mo}</em>{14}\text{O}_{26}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>2339.22</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71069 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>orthorhombic, Pbc</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 9.4432(14)$ Å, $b = 11.4828(12)$ Å, $c = 20.299(4)$ Å</td>
</tr>
<tr>
<td>Volume</td>
<td>2201.1(6) Å$^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 7.059 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>12.662 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>4186</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.050 x 0.058 x 0.093 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.55 to 31.99 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-14 $\leq h \leq$ 14, -17 $\leq k \leq$ 15, -30 $\leq l \leq$ 28</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>43390 / 3807 $[R(\text{int}) = 0.0465]$</td>
</tr>
<tr>
<td>Completeness to theta = 31.99</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3807 / 0 / 219</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.140</td>
</tr>
<tr>
<td>Final R indices [$I &gt; 2\sigma(I)$]</td>
<td>$R_1 = 0.0259$, $wR_2 = 0.0591$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0316$, $wR_2 = 0.0620$</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.00044(2)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.829 and -2.241 e.Å$^{-3}$</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Figure 1. Projections of the crystal structures of (a) In₄Ti₁.₅Mo₀.₅Mo₁₄O₂₆ and (b) M₂Ti₁.₄Mo₀.₆Mo₁₀O₂₀ (M = Sr, Eu) compounds on the (b, c) plane.

Figure 2. The (a) Mo₁₄, (b) Mo₁₅, and (c) Mo₁₆ clusters with their oxygen and titanium environments.

Figure 3. Perspective view of the crystal structure of In₄Ti₁.₅Mo₀.₅Mo₁₄O₂₆ along the b axis.

Figure 4. Arrangement of the oxygen and indium atoms within the ABAC layers.

Figure 5. The tetrameric cation In₄⁶⁺ with its oxygen environment.

Figure 6. The temperature dependence of the molar magnetic susceptibility of In₄Ti₁.₅Mo₀.₅Mo₁₄O₂₆.

Figure 7. Temperature dependence of the electrical resistivity for In₄Ti₁.₅Mo₀.₅Mo₁₄O₂₆.

TABLE CAPTIONS

Table 1. X-ray Crystallographic and Experimental data for In₄Ti₁.₅Mo₀.₅Mo₁₄O₂₆.
Figure 1. Projections of the crystal structures of (a) $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{1.5}\text{O}_{26}$ and (b) $\text{M}_2\text{Ti}_{1.4}\text{Mo}_{0.6}\text{Mo}_{10}\text{O}_{20}$ ($\text{M} = \text{Sr, Eu}$) compounds on the (b, c) plane.
Figure 2. The (a) Mo$_{14}$, (b) Mo$_{15}$, and (c) Mo$_{16}$ clusters with their oxygen and titanium environments.
Figure 3. Perspective view of the crystal structure of $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}$ along the $b$ axis.
Figure 4. Arrangement of the oxygen and indium atoms within the $ABAC$ layers.
Figure 5. The tetrameric cation $\text{In}_4^{6+}$ with its oxygen environment.
Figure 6. The temperature dependence of the molar magnetic susceptibility of $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{1.4}\text{O}_{26}$.
Figure 7. Temperature dependence of the electrical resistivity for In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$.
Synopsis

The novel reduced molybdenum oxide In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ has been synthesized by solid-state reaction at 1400°C for 96h in sealed molybdenum crucibles. Its crystal structure contains in addition to Mo$_{14}$ clusters the first examples of mono- and bi-capped trioctahedral Mo$_{14}$ i.e. is the Mo$_{15}$ and Mo$_{16}$ clusters. Magnetic susceptibility measurements confirm the presence of Ti$^{4+}$ cations and the absence of localized moments on the Mo network. Electrical resistivity measurements on a single crystal of In$_4$Ti$_{1.5}$Mo$_{0.5}$Mo$_{14}$O$_{26}$ show a semimetallic behavior.
The cluster compound $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}$ containing $\text{Mo}_{14}$ clusters and the new mono- and bi-capped trioctahedral $\text{Mo}_{15}$ and $\text{Mo}_{16}$ clusters: synthesis, crystal structure, and electrical and magnetic properties.

Philippe Gall, Thierry Guizouarn and Patrick Gougeon*

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6226 - INSA, Université de Rennes 1, Avenue du Général Leclerc, 35042 Rennes-Cedex, France.

We present here the synthesis, the crystal structure, and the electrical and magnetic properties of the new compound $\text{In}_4\text{Ti}_{1.5}\text{Mo}_{0.5}\text{Mo}_{14}\text{O}_{26}$ in which $\text{Mo}_{14}$ clusters coexist statistically with mono- and bi-capped trioctahedral $\text{Mo}_{14}$ that is $\text{Mo}_{15}$ and $\text{Mo}_{16}$ clusters.
Highlights

- Single crystals of In₄Ti₁.₅Mo₀.₅Mo₁₄O₂₆ were obtained by solid state reaction.
- The crystal structure contains Mo₁₄, Mo₁₅ and Mo₁₆ clusters.
  - The indium atoms form In⁴⁺ bent chains.
- Poorly metallic behavior.
- Absence of localized moments on the Mo network as well as on the Ti atoms.

