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# Crystallographic and Magnetic Studies of an Unusual $Mo_3O_{13}$ Cluster Compound, $Na_2In_2Mo_5O_{16}$

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Highly reflective, black, hexagonal platelike crystals of $Na_2In_2Mo_5O_{16}$ were prepared by fused-salt electrolysis at 600 °C of a melt containing $Na_2MoO_4$, $MoO_3$, and $In_2O_3$. The compound crystallizes in the trigonal space group $P3m1$ with $a = 5.7856$ (8) Å, $c = 11.266$ (1) Å, $V = 326.6$ (2) Å$^3$, $Z = 1$, $R_F = 3.5\%$, and $R_{wF} = 3.7\%$ for 1111 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The structure of $Na_2In_2Mo_5O_{16}$ can be described as "layers" of indium and molybdenum oxygen polyhedra (in the *ab* plane) located at different values along the *c* axis. Planes of edge-sharing triangular $Mo_3O_{13}$ cluster units with intra- and intercluster Mo–Mo distances of 2.6164 (5) and 3.1691 (5) Å, respectively, are separated by individual layers of $InO_6$ octahedra and $MoO_4$ tetrahedra. Each $InO_6$ octahedral and $MoO_4$ tetrahedral layer contains a trigonal array of the respective polyhedra. The stacking sequence (at different values of *z*) of the individual layers is $Mo_3O_{13}$ cluster, $InO_6$, $MoO_4$, $MoO_4$, $InO_6$, and $Mo_3O_{13}$ cluster. The sodium ions are in large cavities created by the In–Mo–O network. One sodium ion has trigonal-antiprismatic coordination and lies on a fully occupied site, whereas the two other Na ions are 10-coordinate and are situated on sites with occupancies of 42 (2) and 62 (2)%, respectively. Magnetic susceptibility measurements indicate temperature-independent paramagnetic behavior.

## Introduction

Reduced molybdenum oxides with the general formula $A^{II}_2Mo_3O_8$ (A = Mg, Mn, Fe, Co, Ni, Zn, and Cd) were first prepared over 30 years ago.[1] These Mo(IV) oxides contain a $Mo_3O_{13}$ cluster unit, which is made up of three edge-sharing molybdenum $MoO_6$ octahedra.[2] All these compounds have low electrical conductivity and are weakly paramagnetic. A molecular orbital calculation[3] on an idealized, isolated $Mo_3O_{13}$ cluster accounted for the observed properties and the strong bonding by showing that the six d electrons per cluster are paired to fill three bonding orbitals. A recent report[4] has described the structural relationships in phases of the type $LiR^{III}Mo_3O_8$ (R = Sc, Y, In, Sm, Gd, Yb, Lu, Tb, Dy, Ho, and Er), which also contain the $Mo_3O_{13}$ cluster.

The preparation of $LiZn_2Mo_3O_8$ and $Zn_3Mo_3O_8$, which have seven and eight electrons, respectively, available for Mo–Mo bonding in the trigonal cluster,[5] has led to renewed interest in the $Mo_3O_{13}$-type cluster compounds. Addition of the seventh and eighth d electrons to the cluster dramatically affects the Mo–Mo intracluster distance and the magnetic behavior.

In addition, an unusual cluster compound, $La_3Mo_4SiO_{14}$, has recently been prepared by fused-salt electrolysis.[6] This compound contains both Mo triangular clusters and infinite chains of $MoO_6$ edge-sharing octahedra. The d-electron count in the $Mo_3O_{13}$ cluster in paramagnetic $La_3Mo_4SiO_{14}$ is difficult to determine due to the presence of the molybdenum octahedral chains.

This paper reports the preparation of a new $Mo_3O_{13}$-cluster-containing compound, $Na_2In_2Mo_5O_{16}$, by fused-salt electrolysis. This compound contains both $Mo^{4+}$ ($Mo_3O_{13}$ cluster) and $Mo^{6+}$ ($MoO_4$ tetrahedra) isolated from each other by $InO_6$ octahedra. The crystal structure and magnetic susceptibility are reported and compared with other compounds containing the $Mo_3O_{13}$ cluster unit.

## Experimental Section

**Synthesis.** The starting materials used were $Na_2MoO_4$ (Aesar, 46.28% Mo), $MoO_3$ (J. T. Baker, reagent grade), and $In_2O_3$ (Aldrich, 99.99%). $MoO_3$ was ignited at 475 °C in air before use. $NaMoO_4$ was dried at 140 °C in air. Single crystals of $Na_2In_2Mo_5O_{16}$ were prepared by the electrolysis of a melt formed at 600 ± 5 °C from a mixture of sodium molybdate, molybdenum(VI) oxide, and indium(III) oxide. A charge of approximately 35 g, weighed to the nearest 0.01 g, was mixed thoroughly and placed in a Coors 30-mL porcelain crucible. Platinum sheets of 1-cm$^2$ area served as the electrodes. The title compound and $MoO_2$ formed over the entire range of molar ratios studied ($Na_2MoO_4$:$MoO_3$:$In_2O_3$ = (2.00–0.80):1.00:(0.42–0.10)). The optimum composition of 1.20:1.00:0.20 produced clusters of small, black, hexagonal platelets of $Na_2In_2Mo_5O_{16}$ and a small amount of copper-colored $MoO_2$. Stoichiometries far from the optimum produced increasing amounts of $MoO_2$. Well-formed crystals were obtained by application of a constant current of 15 mA for 24 h. The electrolysis was carried out in air and was stopped by removing the electrodes from the melt and allowing the electrodes to cool to room temperature. Crystals of $Na_2In_2Mo_5O_{16}$ were found adhering to the cathode. The product was purified by dissolving the reduced molybdate matrix with alternate washings of hot 2 M HCl and hot 5% $NaH_2PO_4 \cdot 2H_2O$.

**Table I.** X-ray Powder Diffraction Data for $Na_2In_2Mo_5O_{16}$

| *d*(obs), Å | *d*(calc), Å | *I*/*I*(0) | *hkl* |
|---|---|---|---|
| 11.25 | 11.27 | 96 | 001 |
| 5.63 | 5.63 | 21 | 002 |
| 4.58 | 4.58 | 14 | 101 |
| 3.749 | 3.755, 3.744 | 100 | 003, 102 |
| 3.004 | 3.005 | 82 | 103 |
| 2.893 | 2.893 | 17 | 110 |
| 2.815 | 2.816 | 7 | 004 |
| 2.802 | 2.802 | 7 | 111 |
| 2.573 | 2.573 | 9 | 112 |
| 2.505 | 2.505 | 4 | 200 |
| 2.446 | 2.446 | 21 | 201 |
| 2.293 | 2.292 | 8 | 113 |
| 2.253 | 2.253 | 41 | 005 |
| 2.085 | 2.084 | 5 | 203 |
| 2.055 | 2.055 | 8 | 105 |
| 1.878 | 1.878 | 22 | 006 |
| 1.872 | 1.872 | 32 | 204 |
| 1.796 | 1.795 | 13 | 212 |
| 1.778 | 1.778 | 6 | 115 |
| 1.758 | 1.758 | 13 | 106 |
| 1.692 | 1.691 | 13 | 213 |
| 1.676 | 1.675 | 14 | 205 |
| 1.653 | 1.652 | 3 | 301 |
| 1.610 | 1.609 | 3 | 007 |
| 1.603 | 1.601 | 2 | 302 |
| 1.533 | 1.532 | 13 | 107 |
| 1.503 | 1.502 | 9 | 206 |
| 1.447 | 1.446 | 5 | 220 |

Polycrystalline $Na_2In_2Mo_5O_{16}$ was prepared by reacting stoichiometric quantities of $Na_2MoO_4$, $In_2O_3$, $MoO_3$, and Mo metal (Atomergic, 99.95%) in an evacuated sealed quartz tube at 550 °C for 48 h. Trace amounts of $MoO_2$ impurity were removed by soaking the product in 3 N $HNO_3$ at room temperature. The X-ray powder diffraction data for $Na_2In_2Mo_5O_{16}$, indexed by using the single-crystal cell parameters, are found in Table I.

**Physical Measurements and Properties.** Magnetic susceptibility data for $Na_2In_2Mo_5O_{16}$ were collected on a purified powder sample with a

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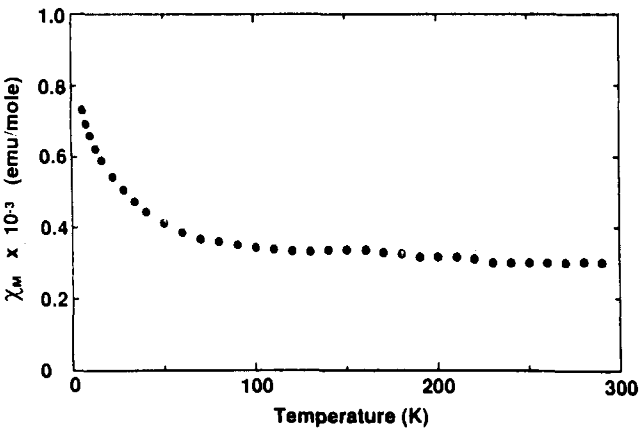

**Figure 1.** Molar susceptibility versus temperature for $Na_2In_2Mo_5O_{16}$.

**Table II.** Crystallographic Data for $Na_2In_2Mo_5O_{16}$

| | |
|---|---|
| $Na_2In_2Mo_5O_{16}$ | $T = 23$ °C |
| $a = 5.7856$ (8) Å | $\lambda = 0.71073$ Å |
| $c = 11.266$ (1) Å | $\rho_{obs} = 5.12$ (6) g/cm$^3$, $\rho_{calc} = 5.14$ g/cm$^3$ |
| $V = 326.6$ (2) Å$^3$ | $\mu = 81.2$ cm$^{-1}$ |
| $Z = 1$ | transmission coeff = 0.79–1.00 |
| fw = 1011.31 | $R(F_o) = 0.035$ |
| space group $P3m1$ (No. 156) | $R_w(F_o) = 0.037$ |

Quantum Design SQUID magnetometer using a field of 2 T between 2 and 300 K. The data are illustrated in Figure 1. Core diamagnetic corrections have been made. $\chi_M(300\text{ K}) = 2.58 \times 10^{-4}$ emu/mol. Temperature-independent paramagnetism was observed from room temperature to ~90 K. Below ~30 K the data were fit to a Curie–Weiss equation with $C = 0.007$ emu/mol K and $\Theta = -9$ K.

An electrical resistivity measurement at room temperature using two ultrasonically soldered indium contacts attached to a small hexagonal platelet of $Na_2In_2Mo_5O_{16}$ gave a value of $5 \times 10^4$ Ω cm.

**Structure Determination.** A single crystal of $Na_2In_2Mo_5O_{16}$ was mounted on a glass fiber. Crystal data, data collection, and refinement details are given in Table II. The program MULTAN 82[7] and the "Enraf-Nonius Structure Determination Package"[8] were used for data collection, data processing, and structure solution. Intensity data were corrected for decay, Lp, and absorption (empirical, $\psi$ scan) effects. A secondary extinction parameter (final $g = 8.1$ (3) $\times 10^{-7}$) was also refined in the final cycles.

Some difficulty was encountered in solving and refining the structure. Examination of the reciprocal lattice by precession photography and with an Enraf-Nonius CAD-4 diffractometer suggested a trigonal crystal system with no systematic absences. However, some reflections that must be equivalent in a trigonal system showed differences in intensity greater than $3\sigma$, possibly as a result of uncompensated absorption for this thin, platelike crystal or perhaps because the crystal lacked a 3-fold axis and was monoclinic. We assumed the latter possibility initially and solved the structure in the monoclinic space group *Cm*. Refinement in *Cm* ($R_F = 0.037$) gave a structure with trigonal symmetry, which, within experimental error, is the same as that reported below. Detailed examination of the *Cm* structure revealed the presence of 3-fold axes and possibly centers of symmetry arranged in a way consistent with space groups $P3m1$ and $P\bar{3}m1$.

To determine the correct space group, the structure was solved independently in $P3m1$ and $P\bar{3}m1$. Initial *E* maps in each space group revealed all the heavy atoms (Mo and In). Refinement of these heavy atoms led to considerably lower *R* factors for $P3m1$. Also, the temperature factor for Mo(3), which is constrained to lie at ($^1/_2$, $^1/_2$, $^1/_2$) in $P\bar{3}m1$, was unusually high in that space group. Light atoms were located and added to both structures. Sodium atom Na(1) was located on a fully occupied site. However, two partially occupied sites (Na(2) and Na(3)) were observed for the remaining sodium atom. In $P3m1$, these sites are not related by symmetry and the atom multipliers were refined independently. The Na(2) and Na(3) sites were found to be 62 (2) and 42 (2)% occupied, respectively, confirming, within experimental error, the stoichiometry obtained from plasma emission spectroscopy and ceric sulfate titrations.

**Table III.** Positional and Thermal Parameters for $Na_2In_2Mo_5O_{16}$

| atom | *x* | *y* | *z* | *B* or $B_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| In(1) | 0.000 | 0.000 | 0.292 | 0.439 (9) |
| In(2) | 0.000 | 0.000 | −0.29369 (9) | 0.469 (9) |
| Mo(1) | 0.667 | 0.333 | 0.1257 (1) | 0.47 (1) |
| Mo(2) | 0.333 | 0.667 | −0.1274 (1) | 0.46 (1) |
| Mo(3) | 0.51592 (7) | −0.516 | −0.50791 (8) | 0.622 (7) |
| Na(1) | 0.000 | 0.000 | −0.001 (1) | 1.8 (1)* |
| Na(2)[b] | 0.333 | 0.667 | 0.227 (1) | 1.5 (2)* |
| Na(3)[b] | 0.667 | 0.333 | 0.771 (2) | 1.8 (3)* |
| O(1) | 0.342 (1) | 0.171 | 0.5988 (5) | 0.45 (7)* |
| O(2) | 0.1619 (8) | 0.324 | 0.8289 (6) | 1.3 (1)* |
| O(3) | 0.667 | 0.333 | 0.972 (1) | 1.1 (2)* |
| O(4) | 0.333 | 0.667 | 0.5789 (9) | 0.3 (1)* |
| O(5) | 0.1753 (7) | 0.351 | 0.3967 (5) | 0.61 (8)* |
| O(6) | 0.324 (2) | 0.162 | 0.1660 (6) | 1.2 (1)* |
| O(7) | 0.333 | 0.667 | 0.022 (1) | 1.4 (2)* |
| O(8) | 0.667 | 0.333 | 0.365 (1) | 0.6 (1)* |

[a] Starred values are for refined isotropically. Thermal parameters for anisotropically refined atom are given in the form of the isotropic equivalent displacement parameters defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] The refined atom multiplicities for Na(2) and Na(3) are 0.103 (4) and 0.070 (4), respectively.

**Table IV.** Selected Interatomic Distances (Å) for $Na_2In_2Mo_5O_{16}$

| | | | |
|---|---|---|---|
| Mo(3)–Mo(3) | 2.6164 (5) | In(2)–O(1) | 2.097 (6) |
| Mo(3)–Mo(3) | 3.1691 (5) | In(2)–O(2) | 2.131 (5) |
| Mo(1)–O(3) | 1.73 (1) | Na(1)–O(2) | 2.51 (1) |
| Mo(1)–O(6) | 1.774 (7) | Na(1)–O(3) | 3.353 (2) |
| Mo(2)–O(2) | 1.787 (2) | Na(1)–O(6) | 2.49 (1) |
| Mo(2)–O(7) | 1.68 (1) | Na(1)–O(7) | 3.350 (1) |
| Mo(3)–O(1) | 1.979 (4) | Na(2)–O(5) | 2.48 (1) |
| Mo(3)–O(4) | 2.075 (4) | Na(2)–O(6) | 2.973 (5) |
| Mo(3)–O(5) | 2.028 (4) | Na(2)–O(7) | 2.31 (2) |
| Mo(3)–O(8) | 2.085 (6) | Na(3)–O(1) | 2.53 (2) |
| In(1)–O(5) | 2.113 (3) | Na(3)–O(2) | 2.966 (6) |
| In(1)–O(6) | 2.161 (7) | Na(3)–O(3) | 2.27 (2) |

**Table V.** Selected Bond Angles (deg) for $Na_2In_2Mo_5O_{16}$

| | | | |
|---|---|---|---|
| O(5)–In(1)–O(5) | 92.1 (2) | O(2)–Mo(2)–O(7) | 106.0 (2) |
| O(5)–In(1)–O(6) | 93.1 (2) | O(1)–Mo(3)–O(1) | 90.8 (3) |
| O(5)–In(1)–O(6) | 172.5 (2) | O(1)–Mo(3)–O(4) | 91.4 (2) |
| O(6)–In(1)–O(6) | 81.3 (3) | O(1)–Mo(3)–O(5) | 91.2 (2) |
| O(1)–In(2)–O(1) | 90.0 (2) | O(1)–Mo(3)–O(5) | 169.6 (2) |
| O(1)–In(2)–O(2) | 93.6 (2) | O(1)–Mo(3)–O(8) | 99.4 (1) |
| O(1)–In(2)–O(2) | 174.9 (2) | O(4)–Mo(3)–O(5) | 78.4 (2) |
| O(2)–In(2)–O(2) | 82.5 (2) | O(4)–Mo(3)–O(8) | 164.6 (2) |
| O(3)–Mo(1)–O(6) | 104.8 (2) | O(5)–Mo(3)–O(5) | 85.1 (1) |
| O(6)–Mo(1)–O(6) | 113.7 (2) | O(5)–Mo(3)–O(8) | 90.3 (2) |
| O(2)–Mo(2)–O(2) | 112.7 (2) | | |

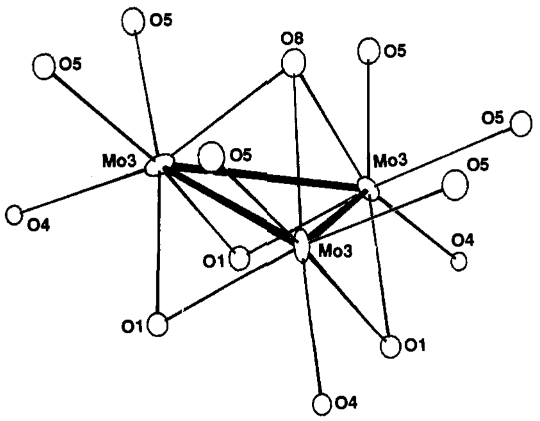

**Figure 2.** View of the $Mo_3O_{13}$ cluster found in $Na_2In_2Mo_5O_{16}$.

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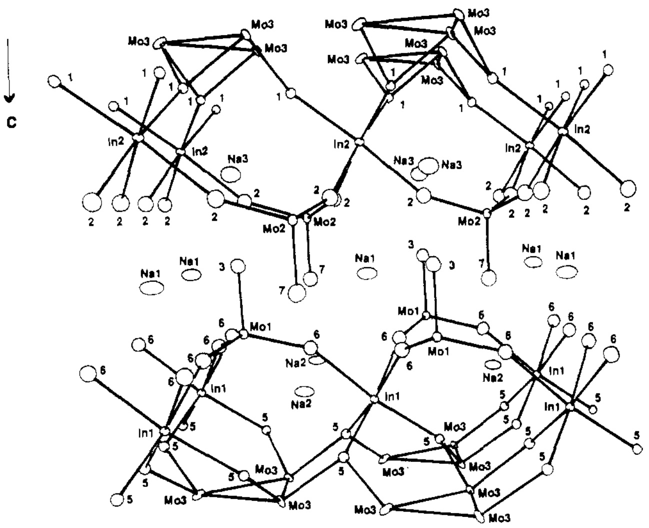

**Figure 3.** View of the atomic arrangement in the *ab* plane, showing the stacking perpendicualr to *c* for $Na_2In_2Mo_5O_{16}$ (numbered atoms are oxygens). Na–O bonds are omitted for clarity.

Refinement of the In and Mo (anisotropic) and Na and O (isotropic) positional and thermal parameters reduced $R_F$ to 0.035 for $P3m1$ and 0.106 for the centrosymmetric space group $P\bar{3}m1$. The noncentrosymmetric space group is clearly much more consistent with the diffraction data. However, as seen from the coordinates in Table III, the structure does not deviate greatly from being centrosymmetric. A final difference map showed no significant features. The highest positive peak (3.7 e/Å$^3$) was located 1.25 Å from Na(1) and was smaller than the largest negative peak (−4.1 e/Å$^3$). These relatively large positive and negative excursions may be the result of uncompensated absorption for this thin plate crystal.

## Results

**Crystal Structure of $Na_2In_2Mo_5O_{16}$.** Final positional parameters for $Na_2In_2Mo_5O_{16}$ are listed in Table III. Selected interatomic bond distances and angles are found in Tables IV and V, respectively.

The basic structural unit in $Na_2In_2Mo_5O_{16}$ is the $Mo_3O_{13}$ cluster unit (Figure 2). The Mo(3) atoms form equilateral triangles with a Mo(3)–Mo(3) distance of 2.6164 (5) Å (Table IV). The cluster contains three oxygens O(1), which are doubly bridging to two Mo atoms along the three edges of the triangle. The Mo(3)–O(1) distance is 1.979 (4) Å. One oxygen atom, O(8), triply bridges the Mo atoms to form a trigonal pyramid. The Mo(3)–O(8) distance is 2.085 (6) Å. Each molybdenum has three terminally bonded (or *intercluster*-bridging) oxygens: O(4) and O(5) (two) (Figure 2). The Mo–O (intercluster-bridging) distances are 2.028 (4) and 2.075 (4) Å for Mo(3)–O(5) and Mo(3)–O(4), respectively (Table IV). The $Mo_3O_{13}$ clusters share two of the intercluster bridging oxygens to form infinite sheets of edge-sharing clusters perpendicular to the *c* axis. The intercluster Mo(3)–Mo(3) distance is 3.1691 (5) Å.

The $Mo_3O_{13}$ cluster layers are oriented along the *ab* plane and are separated from each other by ~11.27 Å along the crystallographic *c* direction. These sheets are connected by a network of $InO_6$ octahedra and $MoO_4$ tetrahedra with Na atoms occupying large cavities created by this connectivity. The In(1)–O distances, 2.113 (3) and 2.161 (7) Å, are slightly longer than the In(2)–O distances, 2.097 (6)–2.131 (5) Å. The $In(1)O_6$ octahedra are located above the centroid (along the *c* direction) of three adjacent $Mo_3O_{13}$ clusters. Each $In(1)O_6$ octahedron corner-shares one of its octahedral triangular faces with three different intercluster-bridging O(5) oxygens (Figure 3). Similarly, the $In(2)O_6$ octahedra are located below the centroid (along the *c* direction) of three adjacent $Mo_3O_{13}$ clusters. However, each $In(2)O_6$ octahedron corner-shares one of its triangular faces with three doubly bridging intracluster O(1) oxygens from three adjacent $Mo_3O_{13}$ clusters. Each type of In octahedron forms a planar-trigonal array of isolated octahedra; i.e., there are no In–O–In interactions in the *ab* plane. In(1) and In(2) are aligned along the crystallographic *c* axis ~6.6 Å apart.

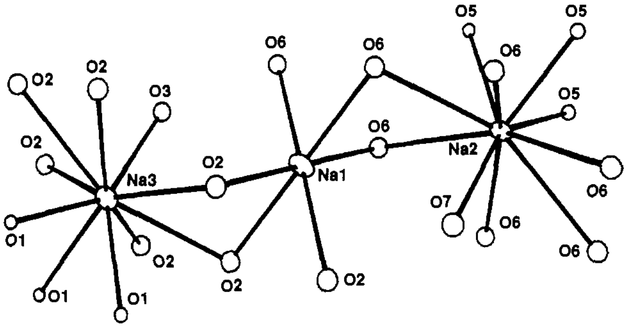

**Figure 4.** View of the Na–O connectivity in $Na_2In_2Mo_5O_{16}$ (horizontal axis in approximately the *c* direction from right to left).

Both $MoO_4$ tetrahedra in $Na_2In_2Mo_5O_{16}$ have one relatively short Mo–O bond: 1.73 (1) and 1.68 (1) Å for Mo(1)–O(3) and Mo(2)–O(7), respectively (Table IV). The remaining two Mo–O bond distances in the $MoO_4$ tetrahedra, Mo(2)–O(2), 1.787 (2), and Mo(1)–O(6), 1.774 (7) Å, are equivalent within experimental error. The Mo(1) and Mo(2) $MoO_4$ tetrahedra each corner-share three oxygens with $In(1)O_6$ and $In(2)O_6$ octahedra, respectively. Specifically, each Mo(1) tetrahedron corner-shares three O(6) oxygens with three adjacent $In(1)O_6$ octahedra. Likewise, each Mo(2) tetrahedron corner-shares three O(2) oxygens with three adjacent $In(2)O_6$ octahedra (Figure 3). The $Mo(1)O_4$ tetrahedra are located above the centroid (along the *c* direction) of the three adjacent $In(1)O_6$ octahedra with which they corner-share oxygens. Similarly, the $Mo(2)O_4$ tetrahedra are located below the centroid (along the *c* direction) of the three adjacent $In(2)O_6$ octahedra with which they corner-share oxygen (Figure 3). Both the $Mo(1)O_4$ and $Mo(2)O_4$ tetrahedra form a planar-trigonal array of isolated tetrahedra (reminiscent of the $InO_6$ geometry); i.e., there are no Mo–O–Mo interactions in the *ab* plane.

The sodium atoms occupy the cavities created by the $Mo_3O_{13}$ cluster, the $InO_6$ octahedra, and the $MoO_4$ tetrahedra framework (Figure 3). Na(1) is collinearly located halfway between the In(1) and In(2) octahedra along the crystallographic *c* direction (Figure 3). Na(1) exhibits trigonal-antiprismatic coordination formed by the oxygens of two octahedral triangular faces, one from an $In(1)O_6$ and one from an $In(2)O_6$ octahedron (Figures 3 and 4). Na(1)–O distances of 2.51 (1) and 2.49 (1) Å are found for O(2) (three) and O(6) (three), respectively (Table IV). Additionally, three O(3) and three O(7) atoms are located 3.353 (2) and 3.350 (1) Å from Na(1). Therefore, Na(1) sits in a 12-coordinate oxygen "cage"; however, the Na(1)–O(3) and Na(1)–O(7) distances are very long.

Na(2) and Na(3) are both found in ten-coordinate cavities. Na(2) and Na(3) are collinear with Mo(2) and Mo(1), respectively, along the crystallographic *c* direction. This atomic arrangement results in relatively short Na(2)–O(7) and Na(3)–O(3) distances of 2.31 (2) and 2.27 (2) Å, respectively (Table IV, Figure 3). Na(2) is located approximately in the center of an oxygen hexagon formed by the trigonal array of three adjacent $In(1)O_6$ octahedra. The Na(2)–O(6) (six) distance is 2.973 (5) Å (Figure 4). Na(2) is also bound to three $Mo_3O_{13}$ intercluster bridging oxygens from three adjacent clusters (Figure 4). The Na(2)–O(5) (three) distance is 2.48 (1) Å.

The oxygen environment of Na(3) is comparable to that observed for Na(2). The oxygen hexagon formed by the trigonal array of three adjacent $In(2)O_6$ octahedra has a Na(3)–O(2) (six) distance of 2.966 (6) Å. Na(3) is bound to three $Mo_3O_{13}$ doubly bridging intracluster oxygens from three adjacent clusters (Figure 4). The Na(3)–O(1) (three) distance is 2.53 (2) Å.

## Discussion

**Crystal Structure and Magnetic Properties of $Na_2In_2Mo_5O_{16}$.** $Zn_2Mo_3O_8$, $LiZn_2Mo_3O_8$, and $Zn_3Mo_3O_8$ constitute an important series of compounds because they contain six, seven, and eight electrons, respectively, per Mo trinuclear cluster. Torardi and McCarley[5] have shown that as the $Mo_3O_{13}$ cluster is reduced the Mo–Mo intracluster distances increase. For example, the 6 e/

**Table VI.** Mo–Mo and Mo–O Distances in $Na_2In_2Mo_5O_{16}$ Compared with Those in Other $Mo_3O_{13}$ Cluster Compounds

| compd | e/ cluster | Mo–Mo, Å[c] | Mo–Mo, Å[d] | Mo–O, Å[e] | Mo–O, Å[f] |
|---|---|---|---|---|---|
| $Zn_2Mo_3O_8$[a] | 6 | 2.524 (2) | 3.235 (2) | 1.928 (20) | 2.002 (30) |
| $Na_2In_2Mo_5O_{16}$ | 6 | 2.6164 (5) | 3.1691 (5) | 1.979 (4) | 2.085 (6) |
| $LiZn_2Mo_3O_8$[b] | 7 | 2.578 (1) | 3.234 (1) | 2.003 (8) | 2.079 (7) |
| $Zn_3Mo_3O_8$[b] | 8 | 2.580 (2) | 3.282 (2) | 2.056 (13) | 2.054 (11) |

[a] Reference 2. [b] Reference 5. [c] Intracluster bond distance. [d] Intercluster distance. [e] Doubly bridging oxygen. [f] Triply bridging oxygen.

cluster compound, $Zn_2Mo_3O_8$, has an intracluster Mo–Mo distance of 2.524 (2) Å whereas the 7 e/cluster compound, $LiZn_2Mo_3O_8$, has an intracluster distance of 2.578 (1) Å (Table VI). However, there is no additional lengthening of the Mo–Mo bonds for the eight-electron cluster. The Mo–O doubly bridging intracluster distances also change substantially in going from six to seven electrons, while the change upon addition of the eighth electron is smaller (Table VI).

The structure of $Na_2In_2Mo_5O_{16}$ is related to the aforementioned compounds in that it also contains the $Mo_3O_{13}$ cluster unit. However, in $Na_2In_2Mo_5O_{16}$, the triply bridging oxygen, O(8) is bound only to the three Mo atoms in the $Mo_3O_{13}$ cluster (Figure 2). In $Zn_2Mo_3O_8$, $LiZn_2Mo_3O_8$, and $Zn_3Mo_3O_8$[2,5] the triply bridging oxygen is also bound to a tetrahedrally coordinated Li and/or Zn ion. In $Na_2In_2Mo_5O_{16}$, tetrahedrally coordinated Mo(1) is located above O(8); however, instead of bonding to O(8) (Mo(1)–O(8) distance ~2.7 Å), Mo(1) is bound to O(3) (1.73 (1) Å), which is collinear with Na(3) in the crystallographic *c* direction. Given these differences, it is not surprising that the Mo–Mo and Mo–O distances in $Na_2In_2Mo_5O_{16}$ appear to be anomalous when compared with those of the remaining $Mo_3O_{13}$ cluster compounds in Table VI.

Valences of +6 and +4 have been calculated for the tetrahedral and cluster molybdenums, respectively, by bond length–bond strength calculations.[11] Also, these calculations suggest that indium is in the trivalent state. Although two sodium positions, Na(2) and Na(3), are partially occupied, the stoichiometry appears fixed near $Na_2In_2Mo_5O_{16}$ (on the basis of chemical analysis of several samples and the single-crystal X-ray results). Therefore, the $Mo_3O_{13}$ cluster in $Na_2In_2Mo_5O_{16}$ should contain six d electrons. Examination of Table VI reveals several differences between $Na_2In_2Mo_5O_{16}$ and $Zn_2Mo_3O_8$. Although both compounds have six d electrons per $Mo_3O_{13}$ cluster, the Mo–Mo intracluster distance in $Na_2In_2Mo_5O_{16}$ (2.6164 (5) Å) is significantly longer than that found for $Zn_2Mo_3O_8$ (2.524 (2) Å). In fact, the Mo–Mo intracluster distance for $Na_2In_2Mo_5O_{16}$ is longer than those in $LiZn_2Mo_3O_8$ (2.578 (1) Å) and $Zn_3Mo_3O_8$ (2.580 (2) Å), which have seven and eight d electrons per $Mo_3O_{13}$ cluster, respectively. Furthermore, the Mo–O doubly bridging distance in $Na_2In_2Mo_5O_{16}$ (1.979 (4) Å) is considerably longer than that for $Zn_2Mo_3O_8$ (1.928 (20) Å). Also, the triply bridging oxygen distance of 2.085 (6) Å for $Na_2In_2Mo_5O_{16}$ is greater than that for $Zn_2Mo_3O_8$ (2.002 (30) Å). Finally, the Mo–Mo intercluster distance in $Na_2In_2Mo_5O_{16}$ (3.1691 (5) Å) is shorter than that for $Zn_2Mo_3O_8$ (3.235 (2) Å).

Recent molecular orbital calculations on $[Mo_3O_4]^{4+}$ and $[Mo_3O_4(OH)_6(H_2O)_3]^{2-}$ as models for six d-electron $Mo_3O_{13}$ cluster units[10,12] suggest that the Mo–Mo interactions are strongly influenced by the doubly bridging and triply bridging atoms of the $[Mo_3O_4]^{4+}$ core. One possible reason for the increased Mo–Mo intracluster distance in $Na_2In_2Mo_5O_{16}$ compared to $Zn_2Mo_3O_8$ could be the lack of a fourth bond to the triply bridging oxygen in $Na_2In_2Mo_5O_{16}$. However, it may be that the overall structure of $Na_2In_2Mo_5O_{16}$, which is quite different from that of $Zn_2Mo_3O_8$, is affecting the Mo–Mo intracluster interactions.

Magnetically, $Zn_2Mo_3O_8$ and $Na_2In_2Mo_5O_{16}$ have similar temperature dependence. The molar susceptibilities at room temperature, $\chi_M$(300 K), are $2.58 \times 10^{-4}$ and $1.4 \times 10^{-4}$ emu/mol for $Na_2In_2Mo_5O_{16}$ and $Zn_2Mo_3O_8$,[5] respectively. The weak paramagnetic signal and temperature-independent behavior between 300 and ~90 K for $Na_2In_2Mo_5O_{16}$ (Figure 1) are consistent with the data reported for $Zn_2Mo_3O_8$. We attribute no significance to the extremely weak, poorly defined feature between 130 and 210 K, which presumably arises from experimental errors at the limit of detectability of the magnetometer. Molecular orbital calculations suggest that the six d electrons per cluster in both $Na_2In_2Mo_5O_{16}$ and $Zn_2Mo_3O_8$ are paired to fill three bonding orbitals.[3]

The low-temperature upturn seen in the $\chi$ vs $T$ plot (Figure 1) of $Na_2In_2Mo_5O_{16}$ may be attributed to the presence of paramagnetic impurities, which begin to order antiferromagnetically with $\Theta = -9$ K. Judging from the value of the molar Curie constant ($C = 0.007$ emu/mol K), the amount of these impurities is very small (~0.075 atom %) with an apparent moment of 0.23 $\mu_B$. The small negative value of $\Theta$ (~−9 K) is indicative of a weak coupling between the moments of the impurities, and thus, one can exclude any significant contribution of the impurities to the total susceptibility of $Na_2In_2Mo_5O_{16}$ at ambient temperature.

In conclusion, $Na_2In_2Mo_5O_{16}$ is a new and complex structure type containing the familiar $Mo_3O_{13}$ cluster unit. Studies are currently in progress to prepare a series of related compounds, with (1) different mono- and trivalent cations and (2) greater than six d electrons per cluster, to better understand the Mo–Mo and Mo–O bonding observed in these compounds.

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**Supplementary Material Available:** Tables SI–SIII, listing crystal and refinement data, anisotropic temperature factors, and nonessential bond angles (3 pages); Table SIV, listing calculated and observed factors (6 pages). Ordering information is given on any current masthead page.

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