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The synthesis of $LiMo_4O_6$, $Zn_{0.5}Li_xMo_4O_6$ and $Li_xMo_4O_6$ ($x \approx 0.1$) from $InMo_4O_6$

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Abstract

Ion exchange and intercalation chemistry of $InMo_4O_6$ were found to be possible due to the open channels in this structure (approximately 1.95 Å across at narrowest constriction). The In^+ cation could be replaced with Li^+ via ion exchange, with little change in the lattice parameters of the structure ($InMo_4O_6$ $a = 9.665(1)$ Å, $c = 2.864(1)$ Å; $LiMo_4O_6$ $a = 9.698(1)$ Å, $c = 2.855(1)$ Å) due to the rigidity of the bonds holding the Mo_4O_6 structural framework together. Most of the Li^+ could then be removed by reaction with an iodine solution in acetonitrile. Zinc or indium cations could then be intercalated into the "empty" structure at relatively low temperatures (500 °C).

Keywords: Intercalation; Ion exchange chemistry; Cluster compounds; Transition metal oxides

1. Introduction

Inorganic polymer structures that contain metal–metal bonds hold considerable interest in fields such as materials research and condensed matter physics. Our previous work has largely centered on $LiMo_3Q_3$ ($Q = S$, Se) compounds [1], which are soluble in highly polar solvents and can be blended with organic polymers to produce novel "nanocomposites". In this compound, Mo_6 octahedra share trans faces to form an infinite linear chain. The Se atoms bridge the edges of the shared faces, forming a condensed Chevrel-like structure [2]. The extensive Mo–Mo bonding imparts considerable resistance to bending of the chain, unlike the large degree of flexibility in typical organic polymers. The incorporation of these conducting inorganic "rigid rod polymers" into an organic polymer matrix affects both the mechanical and the electrical properties of the composite and could provide for improved materials applications such as anti-static coatings. The study of conduction in the inorganic "molecular wires" (~6 Å in diameter) could provide interesting experimental media for studying localization effects and conduction in truly one-dimensional systems. However, since the chalcogenides in these systems may pose environmental problems, and the compounds slowly hydrolyze in air, we have started looking for new materials with more environmentally friendly components.

Important structural features of such new compounds include not only the infinite one-dimensional chains, suitable for solvation and incorporation into organic polymers, but also an open structure, suitable for ion exchange and intercalation chemistry. The $Mo_3Se_3^-$ chains, while most easily synthesized with In^+ between the chains, are only soluble when the counter ion is Li^+, which can be inserted via ion exchange [1]. It is believed that the solubility is driven by the high solvation energy of Li^+ in polar solvents. We were therefore also interested in the ion exchange chemistry of new "molecular wire" precursors. Solid-state structures incorporating open channels or layer-type structures are well known to exhibit ion exchange and intercalation chemistry [3]. Thus we are studying these types of structures.

The compound $NaMo_4O_6$, first reported by McCarley et al. [4], looked to be a possible starting point. Its structure contains infinite anion chains of edge-shared Mo_6 octahedra, with all non-shared edges capped by oxygen. This builds up an infinite chain of Mo_4O_6 building blocks. In the solid, the infinite chains are aligned parallel to one another and cross-linked by oxygen bridges to form open channels in which the Na^+ cation resides (see Fig. 1). A variety of similar phases, including $Ba_{0.62}Mo_4O_6$ [5], $InMo_4O_6$ [6], KMo_4O_6 [7], and $Pb_3(Mo_4O_6)_4$ [8], have all been synthesized by standard high-temperature solid-state meth-

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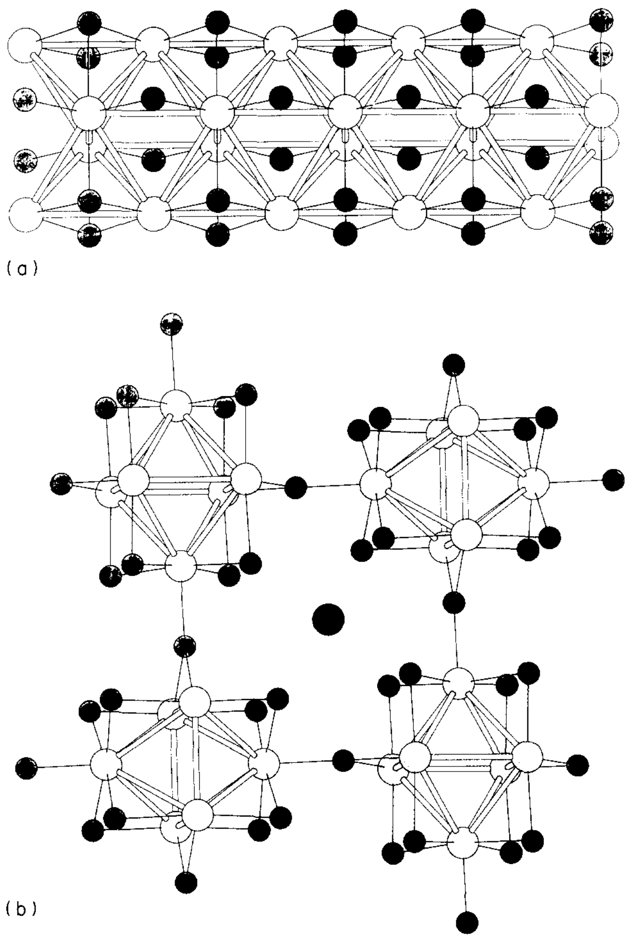

Fig. 1. (a) A single polymeric chain of Mo_4O_6 building blocks, viewed perpendicular to the *c* axis. The small circles represent oxygen atoms, and the light circles molybdenum. (b) The $NaMo_4O_6$ structure viewed down the chain axis. Note the strong interaction between the edge-capping oxygen in one chain and a Mo in the adjacent chain. The large dark circle is sodium.

ods. Here we show that In^+ can be easily removed and replaced through ion exchange with Li^+, and the Li^+ can subsequently be removed by oxidation with I_2. Indium can then be reinserted into the empty "Mo_4O_6" structure, by oxidative intercalation; similarly zinc can also be intercalated into the compound. We report here the formation of three new compounds: $LiMo_4O_6$, $Li_xMo_4O_6$, and $Zn_{0.5}Li_xMo_4O_6$ ($x \approx 0.1$).

2. Experimental and results

$InMo_4O_6$ powder (0.250 g, 0.420 mmol), prepared according to the reported synthesis [6], was mixed with LiI (0.1126 g, 0.821 mmol), and pressed into a pellet under an argon atmosphere. The pellet was sealed in a 36 cm long, 1.5 cm diameter, evacuated quartz tube. The end of the tube containing the pellet was placed in a furnace with about 5 cm of the other end sticking out of the furnace, at about room temperature. The furnace was then quickly heated (1 °C min^{-1}) to 340 °C, and then very slowly (3 °C h^{-1}) brought up to about 460 °C (melting point of LiI = 449 °C) and held continuously at that temperature. After a day, yellow crystals (shown by X-ray powder diffraction to be InI_3) began collecting at the cool end of the tube. Considerable amounts of red InI were collected later, and in all reactions some excess LiI also sublimed towards the cool end of the tube. We presume that InI_3 forms as a side reaction as moisture, associated with LiI, reacts with the LiI at elevated temperatures to form I_2, which then reacts with the InI to form InI_3. The tube was slowly pulled out, over a period of days, until no more deposits were noticed. In most cases complete reaction was accomplished in 5–6 days. The sintered pellet was ground up and washed well with acetonitrile, to remove excess LiI, and allowed to dry overnight under vacuum. Analysis by electron microprobe indicated that the indium had been completely removed and presumably replaced by Li, at least to the sensitivity of the instrument (Fig. 2). The X-ray patterns show a marked difference in the intensities of major lines (Fig. 3). However, due to the rigidity of this structure the lattice constants do not show much variation. For $InMo_4O_6$ $a = 9.665(1)$ Å, $c = 2.864(1)$ Å (these experimental values are in good agreement with those previously determined,

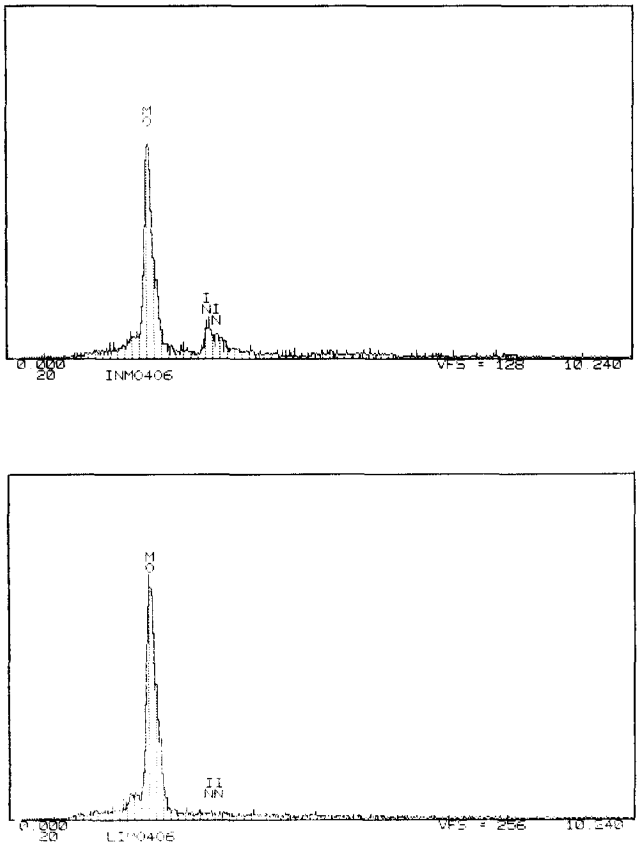

Fig. 2. Electron microprobe results for $InMo_4O_6$ (top) and $LiMo_4O_6$ (bottom) taken on a JEOL 733 Superprobe.

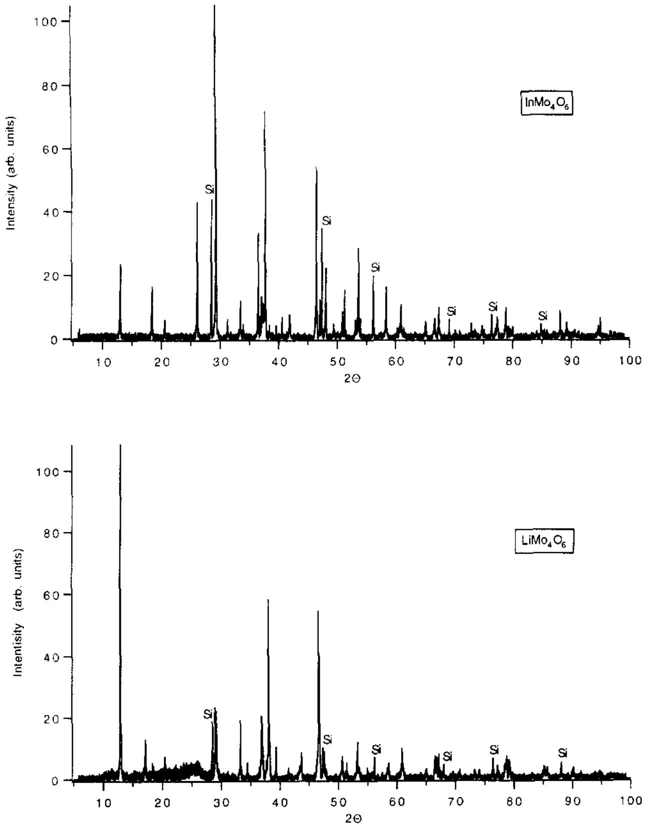

Fig. 3. X-ray powder diffraction patterns for $InMo_4O_6$ (top) and $LiMo_4O_6$ (bottom), taken on a Scintag diffractometer with Cu Kα radiation. Note the difference in the intensities of the major peaks.

$a = 9.6650(5)$ Å, $c = 2.8633(3)$ Å [9]), and for $LiMo_4O_6$ $a = 9.698(1)$ Å, $c = 2.855(1)$ Å. Subsequent reactions showed that this preparation is also successful on a much larger scale (2 g of $InMo_4O_6$).

The $LiMo_4O_6$ thus formed could be deintercalated by reaction with iodine in an acetonitrile solution [3]. A heavy-walled Pyrex tube approximately 30 cm in length was loaded with 0.200 g of $LiMo_4O_6$ (0.411 mmol) and a one-half equivalent (plus 10%) of I_2 dissolved in acetonitrile; the molarity of this solution was determined by titration with a 0.0990N standard solution of $Na_2S_2O_3$ in water from Aldrich. The redox potential of $LiMo_4O_6$ is low enough to react with water, resulting in the deintercalation of Li^+ to form LiOH. This is expected, since the redox potential (vs. Li/Li^+) of Mo(VI) in MoO_3 is around 2.0–2.8 V, and of Mo(IV) in MoO_2 is about 1.1–1.6 V. Since the Mo in Mo_4O_6 is formally Mo(III), we expect the redox potential to be less than 2 V vs. Li, a value low enough to expect reaction with water [10]. Consequently, $LiMo_4O_6$ is always handled in an argon-filled glove box. The tube was placed in liquid nitrogen to freeze the acetonitrile, evacuated and then sealed. It was then placed in a furnace and heated slowly to 85 °C. After 3–4 days the tube was removed from the furnace and the solid filtered and washed with more acetonitrile, again in an argon-filled dry box to prevent air exposure. The filtrate was titrated with a 0.0990N solution of $Na_2S_2O_3$ in water. This titration indicated that approximately 80% of the iodine had reacted, presumably to form $Li_xMo_4O_6$ ($x \approx 0.2$) and LiI. Powder X-ray and electron microprobe are not sensitive enough to show the loss of the lithium cation, nor are we certain the product is homogeneous in Li concentration. Re-reaction of this compound with more of the iodine solution showed that another 10% of the original lithium concentration could be deintercalated after two weeks at 100 °C, making (nominally) $Li_{0.1}Mo_4O_6$. This compound does not react, at room temperature, with water to form a basic solution. The change in the lattice parameters upon the deintercalation of Li, as determined from the X-ray powder diffraction pattern, was minor, $a = 9.706(1)$ Å, $c = 2.867(1)$ Å, but no other phases were detectable (Fig. 4). It has also been determined that the product compound ($Li_xMo_4O_6$ ($x \approx 0.1$)) is thermally unstable at 900 °C, decomposing to form Mo and MoO_2.

To reintercalate the indium cation, 0.500 g of $Li_xMo_4O_6$ ($x \approx 0.1$) was mixed with a molar equivalent of indium powder, and pressed into a pellet under argon. This pellet was sealed in an evacuated quartz tube and heated to 500 °C for 5 days. The resulting powder pattern shows a combination of the $InMo_4O_6$ and $Li_xMo_4O_6$ phases, indicating some indium has been reinserted into the structure. In a similar reaction, the $Li_xMo_4O_6$ was mixed with a half-molar equivalent of zinc powder, pressed into a pellet and sealed in an evacuated quartz tube. The reaction was also heated to 500 °C and held for 5 days. The X-ray powder diffraction pattern shows only the expected phase ($Li_xZn_{0.5}Mo_4O_6$ ($x \approx 0.1$)), neither zinc nor ZnO being present. Electron microprobe analysis showed a fairly even distribution of zinc throughout the sample, with a mean ratio of Mo:Zn of 90:10 (deviation and error of approximately 5%), as expected. Heating a small sample of the product in a Perkin-Elmer Series 7 DSC showed no endotherm up to 500 °C; if any elemental

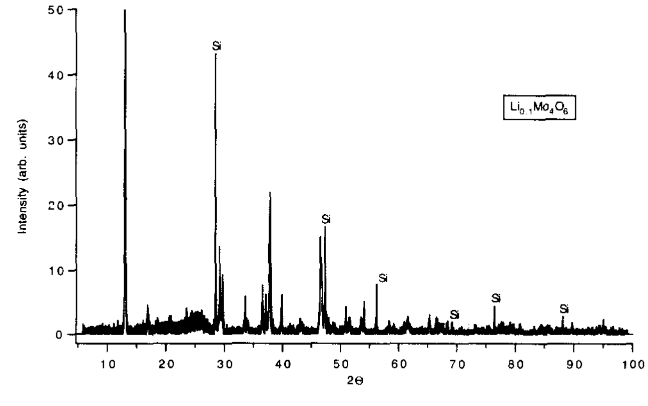

Fig. 4. X-ray powder pattern of $Li_xMo_4O_6$ ($x \approx 0.10$) (blown up to show less intense peaks). There is essentially no change from the $LiMo_4O_6$ pattern.

zinc was still present a melting point around 419.5 °C would be expected. We have found that the direct intercalation of zinc into $InMo_4O_6$, using ZnI_2 in a reaction similar to that used for Li exchange, does not occur at 460 °C. We have also attempted to intercalate other metals, such as Cu and K, under similar conditions without success. Due to the high electronegativity of Cu, it is expected that it would not intercalate since the reduction potential for Mo_4O_6 is probably rather low, as previously discussed. The inactivity of potassium we attribute to its rather large size.

Attempts to dissolve these compounds have so far been unsuccessful. Any attempts to break the strong oxygen bridges holding the chains together, either thermally or chemically, have resulted in either no reaction, or complete decomposition of the structure. Work aimed at synthesizing a material with this structure without bridging bonds in place (i.e. by replacing the oxygen with fluorine) has so far failed to produce the desired compounds.

3. Conclusions

We have shown that the $NaMo_4O_6$-type compounds undergo intercalation and ion exchange chemistry. The open channels are suitable for insertion and removal of assorted cations. These reactions are all accomplished at relatively low temperatures, significantly below the temperatures required for the synthesis of the parent compound. Complete, and quantitative, intercalation of zinc and indium into $Li_xMo_4O_6$ ($x \approx 0.1$) is limited by the presence of this remaining lithium. We have not determined the maximum zinc content in $Li_xMo_4O_6$, but expect that $Li_xZn_{0.5}Mo_4O_6$ may not be the limiting composition, since the Mo_4O_6 host lattice can be reduced by more than one electron per formula unit (as in $Ba_{0.62}Mo_4O_6$ [5] and $Pb_{0.75}Mo_4O_6$ [8]). We have shown that this compound has a rigid open structure extremely well suited for ion exchange chemistry; it has, however, so far proved to be unsuitable for "molecular wire" applications.

Acknowledgments

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