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Synthesis of Reduced Complex Oxides of Molybdenum by Fused Salt Electrolysis

WILLIAM H. McCARROLL,* CYNTHIA DARLING,
AND GARY JAKUBICKI

Chemistry Department, Rider College, P.O. Box 6400,
Lawrenceville, New Jersey 08648

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Fused salt electrolysis has been used to prepare a number of reduced oxides of molybdenum with lanthanum, neodymium, and yttrium in single crystal or oriented polycrystalline form. The average valence of molybdenum in the various compounds ranged from 5.67 to 3.50. Previously unreported compounds include $La_5Mo_4O_{16}$ (triclinic a = 5.64 Å, b = 20.70 Å, c = 5.64 Å, α = 86.55°, β = 90.0°, γ = 93.45°); $La_2Mo_2O_7$ (orthorhombic, a = 12.19 Å, b = 6.05 Å, c = 3.87 Å); $LaMo_2O_5$ (hexagonal, a = 8.378 Å, c = 19.26 Å). In addition, single crystal specimens have been prepared of Y_2MoO_5, $Ln_5Mo_3O_{16}$ (Ln = La, Nd) and metal atom cluster compounds of the $A_2Mo_3O_8$ type (A = Mg, Co, Ni, Zn).

Fused salt electrolysis is a well-established technique for the synthesis of solids which are thermodynamically unstable or display otherwise unusual valence states (*1*). However, its application to the preparation of transition metal oxides other than binary systems and the well-known alkali metal oxide bronzes of tungsten and molybdenum has been relatively limited but interesting examples include some spinel phases and some reduced titanates and vanadates (*2–6*). An attractive feature of the method is that it is often possible to prepare single crystal or oriented polycrystal specimens which are suitable for structural and other physical characterizations. This paper describes the preparation of a number of complex oxides of molybdenum, most of which either have not been prepared before or were found previously only in polycrystalline form. These include the well-established metal atom cluster compounds of the type $A_2Mo_3O_8$ (A = Mg, Co, Ni, Zn) and several ternary compounds with the rare earths.

Experimental

All chemicals used in the electrolyses were of reagent grade or better. MoO_3 was ignited in air at 475°C before use while the rare earth oxides, MgO and ZnO, were treated similarly at 1000°C. The reactants were weighed to the nearest 0.01 g and mixed carefully before heating. The source of molybdenum was always a mixture of sodium molybdate and molybdenum trioxide. A typical charge weighed from 25 to 35 g and was contained in either a Coors porcelain or a McDanel high density alumina crucible. Smooth platinum foil electrodes with a nominal surface area of 2 cm^2 were used. A wire wound crucible furnace capa-

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* Author to whom correspondence should be addressed

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ble of operation to about 1100° was used to heat the charge. The melt was allowed to equilibrate for 1 hr after operating temperature was reached and constant currents between 20 and 200 mA were used for 30 to 40 min. Normally the electrolysis was terminated by removing the electrodes from the melt and allowing them to cool rapidly to room temperature in air.

The products of interest are found adhering to the cathode and are separated from the matrix by appropriate chemical and mechanical means which are described subsequently. Quantitative analyses for principal metallic constituents were carried out using standard classical volumetric methods. The oxidation number of molybdenum was determined using a cerimetric technique (*7*) in which the sample is dissolved in hot standardized ceric sulfate which is about 2 *M* in sulfuric acid and the remaining ceric ion determined by back titration. Because attack of the crucibles, particularly the porcelain ones, is always a problem, a semiquantitative emission spectrographic analysis of all new phases was carried out. Products were routinely identified by X-ray powder diffraction photography using a 114.6-mm diameter Philips camera. Single crystal studies were carried out using a Charles Supper Model II Weissenberg camera and an Enraf-Nonius precession camera. Filtered copper radiation was used throughout. Order of magnitude estimates of room temperature resistivities were made by two probe measurements.

Results

The optimum synthesis conditions and results for the preparation of several rare earth compounds are summarized in Table I. Of these Y_2MoO_5, $La_5Mo_3O_{16}$, and $Nd_5Mo_3O_{16}$ have been reported previously but only in the form of polycrystalline powders (*8, 9*). The formation of metal atom cluster compounds of the type $A_2Mo_3O_8$ (*10–13*) was confirmed by X-ray diffraction examination only. The results for the various phases are given below.

Y_2MoO_5

This compound grows out from the cathode as a cluster of thin black needles or laminates up to 5 mm long. It can be separated successfully from the matrix by washing with hot 3 *M* HCl which slowly attacks the product but rapidly dissolves the matrix. The unit cell parameters, as determined by Weissenberg photography and given in Table I, are in good agreement with those determined by Kerner-Czeskleba and Tourne (*13*) from polycrystalline material. The compound appears to be isomorphous with Y_2ReO_5 (*14*). The structure is not known. Anal. Calcd for Y_2MoO_5: Y, 50.27; Mo, 27.12. Found: Y, 49.85; Mo, 27.40.

$La_5Mo_3O_{16}$ and $Nd_5Mo_3O_{16}$

These compounds both grow at the cathode in the form of clusters of cubes or truncated cubes. The lanthanum compound is black in the massive form but is dark green when pulverized while the neodymium compound is very dark violet. The lattice constants found in this work are slightly larger than the values of 11.215 and 10.99 Å obtained by Hubert (*15, 16*) for polycrystalline samples of the La and Nd compounds. Both compounds dissolve slowly in hot 3 *M* hydrochloric acid while the attack by 3 *M* nitric acid is even more sluggish. HCl is the more effective reagent in separating these phases from the matrix. Anal. Calc. for $La_5Mo_3O_{16}$: La, 56.09; Mo, 23.24. Found: La, 55.92; Mo, 23.12. Calc. for $Nd_5Mo_3O_{16}$: Nd, 57.00; Mo, 22.76. Found: Nd, 56.72; Mo, 22.45.

$La_5Mo_4O_{16}$

This compound grows on the cathode near the top of the melt in the form of very thin black plates. It is invariably mixed with $La_5Mo_{13}O_{16}$ and sometimes $La_2Mo_2O_7$. It is

TABLE I

PRODUCTS FROM FUSED SALT ELECTROLYSIS CONTAINING Y, La, AND Nd

Starting mole ratios of oxides	T (°C)	I (mA)	V (volts)	Nature of cathode product	Formula	Unit cell data
$Na_2MoO_4 : MoO_3 : Y_2O_3$ 2.00 : 3.00 : 2.00	1090	200	2.0	Black laminar prisms 0.05 × 1 × 4 mm. $\rho \simeq 10^5$ ohm-cm[a]	Y_2MoO_5	Monoclinic. $a = 7.48 \pm 0.01$ Å, $b = 5.72 \pm .01$ Å, $c = 12.23 \pm 0.02$ Å, $\beta = 107.7 \pm 0.1$.
$Na_2MoO_4 : MoO_3 : La_2O_3$ 2.00 : 2.00 : 1.00	1075	50	1.1	Dark green-black cubes 1–1.5 mm on edge. $\rho > 10^7$ ohm-cm[a]	$La_5Mo_3O_{16}$	Cubic. $a = 11.2268 \pm .0007$ Å. *Pn*3*n* Fluorite variant. May be pseudo-cell.
$Na_2MoO_4 : MoO_3 : Nd_2O_3$ 2.00 : 2.00 : 0.90	1085	50	1.1	Dark violet-black cubes 1–2 mm on edge. $\rho > 10^7$ ohm-cm[a]	$Nd_5Mo_3O_{16}$	Cubic. $a = 11.005 \pm 0.001$ Å. Similar to $La_5Mo_3O_{16}$. May be pseudo-cell.
$Na_2MoO_4 : MoO_3 : La_2O_3$ 2.50 : 2.00 : 1.00	1070	100	1.3	Very thin black plates 2–3 mm long. $\rho \simeq 1$ ohm-cm[a]	$La_5Mo_4O_{16}$	Triclinic. $a = 5.64 \pm 0.01$ Å, $b = 20.70 \pm 0.04$ Å, $c = 5.64 \pm 0.01$ Å, $\alpha = 86.55 \pm .1°$, $\beta = 90.0 \pm .1°$ $\gamma = 93.45 \pm .1°$.
$Na_2MoO_4 : MoO_3 : La_2O_3$ 2.30 : 2.40 : 1.00	1075	100	1.3	Purple prismatic agglomerates 1 × 1 × 3–10 mm. $\rho \simeq .1$ ohm-cm[a]	$La_2Mo_2O_7$	Orthorhombic. *Pnn*2 or *Pnnm* $a = 12.19 \pm .03$ Å, $b = 6.05 \pm 0.02$ Å, $c = 3.87 \pm 0.01$ Å.
$Na_2MoO_4 : MoO_3 : La_2O_3$ 3.00 : 3.00 : 1.00	1100	200	1.1	Black hexagonal plates 0.2 × 2 mm. $\rho \simeq 10$ ohm-cm[a]	$LaMo_2O_5$	Hexagonal. $a = 8.378 \pm 0.003$ Å, $c = 19.26 \pm 0.01$ Å. $P6_3mc$, $P\bar{6}2c$ or $P6/mcc$.
$Na_2MoO_5 : MoO_3 : La_2O_3$ 3.75 : 3.50 : 1.00	1080	100	1.1	Purple-brown needles and denrites. $\rho < 0.1$ ohm-cm[a]	MoO_2	—

[a] Resistivities are order of magnitude estimates only.

highly susceptible to attack by both dilute hydrochloric and nitric acid. However, it can be separated from both the molybdate matrix and the other reduced phases by a combination of prolonged washings in hot 5% K_2CO_3, quick washes in 1M HCl and a combination of sieving, rolling, and culling. This compound has not been reported previously and does not appear to isostructural with any known compound. Anal. Calc. for $La_5Mo_4O_{16}$: La, 52.05; Mo, 28.76. Found: La, 71.74; Mo, 28.45. Average oxidation number of Mo: Calc., 4.25; found, 4.24. Spectrographic analysis: the only minor constituent found in significant quantities was Al at a level of 0.05–0.5% by weight.

Oscillation, Weissenberg, and precession photographs of a crystal rotated about an axis parallel to one edge of the crystal are superficially indicative of a pseudo-tetragonal cell but closer examination of the photographs shows a distinct lack of symmetry. The cell actually appears to be triclinic with the plate axis (001). Although one angle is 90° and $a = c$ (See Table I), no cell of higher symmetry could be found which was compatible with the observed diffraction pattern.

$La_2Mo_2O_7$

This compound grows out from the cathode as highly reflecting red-violet prismatic needles up to one centimeter in length which are severely twinned. However single crystal fragments can be separated and single crystal X-ray studies show that the unit cell is orthorhombic, possible space groups *Pnn2* or *Pnnm*. The unit cell parameters are given in Table I. Its bright color and high electrical conductivity are reminiscent of oxide bronzes but in contrast to these phases no variation in cell size or chemical composition is apparent. It dissolves slowly in hot 3 *M* HCl and is rapidly decomposed by dilute HNO_3.

$La_2Mo_2O_7$ is always found co-deposited with $La_5Mo_3O_{16}$ and inclusions of the latter are not uncommon, particularly if the amount of La_2O_3 in the melt is increased over the optimum value given in Table I. However, mechanical separation is relatively easy and this, combined a brief wash in hot 1 *M* HCl is effective in yielding small amounts (i.e., 15–30 mg/run) of a pure product. Anal. Calc. for $La_2Mo_2O_7$: La, 47.76; Mo, 32.99. Found: La, 47.46; Mo, 32.65. Average oxidation number of Mo: Calc., 4.00; found, 4.01 ± 0.03. Spectrographic analysis shows no other metallic constituents present in excess of 0.05% by weight.

$LaMo_2O_5$

This compound is found on the cathode as well-formed, reflecting, black hexagonal plates up to 1 mm in largest dimension as single crystals and up to 2.5 mm as oriented crystal aggregates. The compound is completely inert to hot, constant boiling HCl or 6M H_2SO_4. Hot, 3 *M* HNO_3 very slowly attacks the crystals and will dissolve about 0.1 gm of finely pulverized material in about 10 min. The compound is hexagonal with the systematic absence hhl odd limiting the space groups to $P6_3mc$, $P\bar{6}mc$, or $P6_3/mmc$. If the preparation is carried out in an alumina crucible, $LaMo_2O_5$ is the exclusive product. However, if a previously used alumina crucible is employed the product is contaminated with $La_3Mo_4AlO_{14}$. If a porcelain crucible is used the principal product is $La_3Mo_4SiO_{14}$ (*17*). The chemical inertness of this compound is similar to that of $Zn_2Mo_3O_8$. Anal. Calc. for $LaMo_2O_5$: La, 33.81; Mo, 46.71. Found: La 33.41; Mo 46.80. Average oxidation number of Mo: Calc., 3.50; found, 3.48 ± 0.02. Emission spectrographic analysis shows the only minor constituent present at a level of 0.05% by weight or greater is aluminum which is in the 0.05–0.05% range.

$A_2Mo_3O_8$ ($A = Mg, Co, Ni, Zn$)

All of these compounds were prepared

by the electrolysis of melts prepared from mixtures of sodium molybdate, molybdenum trioxide, and the appropriate divalent metal oxide in the molar ratios of 1.00: 1.00: 1.50 at 1100°C. The magnesium and zinc compounds grow in the form of thin black hexagonal plates up to 1 mm in largest dimension while the cobalt and nickel compounds are found as truncated octahedra about 1 mm long. In general the crystals of the Ni compound were larger than those of the Co analog. Their resistivities are in accord with those observed previously for polycrystalline samples (*10*). In all instances no other reduced compound was obtained. However, in the case of the cobalt containing preparation, Co_3O_4 was produced at the anode.

Discussion

Fused salt electrolysis has been used to prepare a variety of reduced oxides of molybdenum. No particular effort was made to optimize the growth conditions for the $A_2Mo_3O_8$ type compounds since the main effort was directed towards the preparation of the rare earth compounds. However, their relative ease of preparation clearly demonstrates the versatility of the method and it should prove to be a viable means of preparing single crystal specimens of these compounds suitable for electrical and magnetic measurements. In this respect, it should be noted that Stroebel and coworkers have recently prepared high quality single crystals of $Fe_2Mo_3O_8$ by a vapor transport method (*18*) and this technique may be applicable to other members of this series also.

In the region Na_2MoO_4: MoO_3: R_2O_3 = 2.50–3.00: 2.50–3.00: 1.00 (R = La or Nd) the solidified matrix from the electrolysis is dominated by scheelite-type phases whose intense colors (black in the case of the La compound and deep purple in the case of the Nd analog) give clear evidence that they contain molybdenum in a reduced state. However, their lattice constants are essentially identical with the fully oxidized phases $NaLaMo_2O_8$ and $NaNdMo_2O_8$ indicating that the level of reduction is probably very small. Both materials are insulators. Curiously, these were the only compounds produced in this study that contained sodium and although they were not found adhering to the cathode they were found concentrated in the vicinity of it. It appears therefore that these materials crystallize out of a melt which contains molybdenum in a reduced state.

Hubert (*16*) determined the crystal structure of $La_5Mo_3O_{16}$ using powder data and found that it is an ordered variant of the fluorite structure in which all of the molybdenums are crystallographically equivalent. This is noteworthy since mixed valence oxides in which the atoms are crystallographically equivalent usually show high electrical conductance unless they are present as discrete ions. Our Weissenberg photographs confirm Hubert's choice of unit cell except for a very few extremely weak reflections indicating that the true cell is probably larger and of lower symmetry. The structure of the lanthanum compound is now being reinvestigated by A. K. Cheetham at Oxford.

Kerner-Czeskleba and Cros (*19*) and Kerner-Czeskleba *et al.* (*20*) have recently reported the preparation of $La_{12}Mo_6O_{35}$ and $Nd_{12}Mo_6O_{35}$ by reacting stoichiometric quantities of the rare earth oxide and molybdenum metal in carefully controlled atmospheres with partial pressures of oxygen of 10^{-7} to 10^{-12} atm and temperatures between 725 and 1200°C. The final percentage of oxygen present was determined gravimetrically. They succeeded in isolating single crystals of $La_{12}Mo_6O_{35}$ and find that it has an orthorhombic unit cell but with a cubic pseudo-cell identical that found for $La_5Mo_3O_{16}$. Indeed, the powder patterns of $Nd_5Mo_3O_{16}$ (*15*) and $Nd_{12}Mo_6O_{35}$ (*20*) appear to be substantially identical. Although this observation led Kerner-Czeskleba and co-workers to question the existence of compounds of the type $R_5Mo_3O_{16}$ our analytical results (q.v.) are wholly consistent with this formulation. It is also interesting to note that the preparation of $Nd_{14}Mo_8O_{45}$ by a solid state reaction in air has been reported (*21*). The compound is cubic with a lattice constant which is slightly larger (5.521 Å) than one half the value found for $Nd_5Mo_3O_{16}$. Thus the rather peculiar situation prevails where three different compounds with significantly different ratios of Nd and Mo can be prepared which have unit cells or pseudo-cells with virtually identical dimensions. Clearly, a complete structural analysis is required to answer this apparent anomaly.

$La_2Mo_2O_7$ seems difficult if not impossible to prepare by a solid state reaction (*22–24*). Manthiram and Gopalakrishnan (*25*) report the preparation of phases with the formula $Ln_2Mo_2O_7$ where Ln = Ce, Pr, Nd, and Sm, which have X-ray powder diffraction patterns similar to $La_{12}Mo_6O_{35}$ but can be indexed on the basis of a different orthorhombic unit cell. The $La_2Mo_2O_7$ composition was reported to have a more complex, nonindexable X-ray diffraction pattern. Attempts to prepare $La_2Mo_2O_7$ in our laboratory by similar state reactions at 1150°C for 2 days resulted in a mixture, as identified by X-ray diffraction, which is primarily $La_5Mo_3O_{16}$ (or $La_{12}Mo_6O_{35}$) and $LaMo_2O_5$.

The chemical inertness of $LaMo_2O_5$, coupled with an average oxidation number of 3.5 and an unusually high density (d_{pyc} = 7.00 ± 0.04 gm/cm^3; $d_{X\text{-ray}}$ = 6.98 gm/cm^3) are strongly suggestive of a metal atom cluster compound. Indeed all oxides of molybdenum with an average valence less than four whose crystal structures have been determined are found to contain one or more type of cluster interaction (*17, 26–28*). A crystal structure study of this compound is now in progress. Although aluminum is present at significant levels in the electrolytic preparations of $LaMo_2O_5$, it appears to be an impurity since the compound also can be prepared by a solid state reaction of stoichiometric quantities of La_2O_3, Mo, and MoO_2 at 1225°C.

The effect of the container on the product obtained may be an important consideration. The type of crucible used does not seem to affect the nature of the product obtained in the syntheses of $Ln_5Mo_3O_{16}$, $La_5Mo_4O_{16}$, or $La_2Mo_2O_7$. However, as mentioned previously, multiple reduced products are obtained in $LaMo_2O_5$ preparations unless a new alumina crucible is used under the conditions indicated in Table I. If, however, low current densities and long electrolysis periods are used (e.g., 5 ma/cm^2 and 48 hr at 1075°C) with a new alumina crucible the principal product is $La_3Mo_4AlO_{14}$. However, the presence of aluminum (or silicon) in the melt may affect the nature of the cathode product formed. Reid and Watts (*6*) found that the presence of small amounts of Al_2O_3 preferentially causes the deposition of reduced sodium titanates from Na_2TiO_3–TiO_2 melts ostensibly by lowering the activity of sodium ion in the melt and allowing the preferential reduction of titanium. Similar considerations may apply here also.

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