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Articles

Sol–Gel Approach to Synthesis of Mo_2O_3. MoO(OH) and Other Intermediates from Hydrolysis of Molybdenum(III) Alkoxides and $Mo_2(NMe_2)_6$

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The products of hydrolysis of $Mo_2(NMe_2)_6$, $Mo_4(OEt)_{12}$, $Mo_2(O\text{-}i\text{-}Pr)_6$, and $Mo_2(O\text{-}t\text{-}Bu)_6$ in hydrocarbon solvents have been studied. The latter two result in extensive oxidation of the molybdenum and cannot be used for preparation of Mo(III) compounds. Hydrolysis of $Mo_2(NMe_2)_6$ provides a black crystalline precipitate that yields an amorphous red-brown material, $Mo_3(OH)_9(NMe_2)\cdot{}^1/_2HNMe_2$, upon filtration and drying. A brown compound of Mo(III), $Mo_2(OH)_5(OEt)$, is obtained upon hydrolysis of $Mo_4(OEt)_{12}$. Thermolysis of $Mo_3(OH)_9(NMe_2)\cdot{}^1/_2HNMe_2$ ultimately yields a material that retains nitrogen tenaciously. Thermolysis of $Mo_2(OH)_5(OEt)$ *in vacuo* at 240 °C leads to evolution of ethene and ethane as major gaseous products and oxidation of the molybdenum from an average oxidation state 3.0 to 3.4. Upon reaction of $Mo_2(OH)_5(OEt)$ with H_2 at 250 °C, the new compound MoO(OH) is produced. Conversion of the latter to Mo_2O_3 was not successful, giving the material Mo_3O_5 instead. The reactive MoO(OH) converted cleanly to the crystalline layered compound $LiMoO_2$ upon reaction with Li_2CO_3 at 600 °C *in vacuo*. Magnetic susceptibilities and Mo 3d XPS data are reported for $Mo_2(OH)_5(OEt)$ and MoO(OH).

Introduction

Sol–gel chemistry has been one of several approaches to formation of compounds that must be formed at lower temperatures because of metastability or that otherwise require very high temperatures to overcome slow solid-state diffusion processes.[1–3] We were interested in the possible synthesis of Mo_2O_3, for which there is only one previous reference[4] and which is expected to be unstable toward disproportionation into the metal and MoO_2. Hydrolysis of appropriate alkoxide or dialkylamidomolybdenum(III) compounds, as in sol–gel processes, was considered as a likely route to oxide–hydroxide or oxide–alkoxide precursors. Conversion of these at sufficiently low temperature could avoid the thermodynamic result and provide Mo_2O_3. Oxidation by water or by the ligands also must be avoided.

Chisholm and his group have recently considered the use of $Mo_2(OR)_6$ as single-source precursors for oxides MoO_x. Thermal decomposition of $Mo_2(OR)_6$ may yield MoO_2 or Mo_2C, the latter by way of $Mo_2C_4O_4$, an oxy carbide.[5] Thus, removal of all of the alkoxide (or dialkylamide) ligands by hydrolysis is desirable in order to avoid formation of materials containing carbon (or nitrogen). In this study the latter circumstance was not easily attained. The compounds $Mo_3(OH)_9(NMe_2)\cdot{}^1/_2HNMe_2$, $Mo_2(OH)_5(OEt)$, and MoO(OH) were obtained, all in amorphous form, and conversion to Mo_2O_3 proved to be possible only with simultaneous formation of Mo and MoO_2.

Experimental Section

Materials. All handling and manipulation of materials was conducted in a drybox under N_2 or Ar, on the Schlenk line under N_2, or on the high-vacuum manifold. Solvents were dried over appropriate reagents, distilled, and stored under N_2 or under vacuum. The compounds $Mo_2(NMe_2)_6$,[6] $Mo_4(OEt)_{12}$,[7] $Mo_2(O\text{-}i\text{-}Pr)_6$,[7] and $Mo_2(O\text{-}t\text{-}Bu)_6$[7] were prepared by the literature methods. All other reagents were dried by appropriate procedures and used without further purification.

Hydrolysis Experiments. All reactions were performed with addition of deoxygenated water via syringe to solutions of the starting compounds in hexane (for $Mo_2(NMe_2)_6$) or toluene (for all others), under N_2 or Ar atmosphere with rapid stirring. Sufficient solvent was used to effect complete solution of the material. Typically samples in amounts ranging from 2 to 10 g were used in order to recover sufficient material for elemental analyses, determination of oxidation state of molybdenum, IR and XPS spectra, magnetic susceptibility data, and subsequent chemical conversions. Dark brown (for $Mo_2(O\text{-}t\text{-}Bu)_6$ and $Mo_4(OEt)_{12}$) or black (for $Mo_2(NMe_2)_6$ and $Mo_2(O\text{-}i\text{-}Pr)_6$) precipitates formed immediately, leaving essentially colorless supernatant solutions in all cases after only a few minutes. Stirring was

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(1) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: New York, 1989.

(2) Mehrotra, R. C. *Struct. Bonding* **1992**, *77*, 1.

(3) Rao, C. N. R.; Gopalakrishnan, J. *Acc. Chem. Res.* **1987**, *20*, 228.

(4) Babenko, V. I.; Grigon'ev, S. M.; Utenkova, O. V.; Brazhevskii, V. P. Patent SU 1469402A1, 1989; CA111(6): 49601W.

(5) Baxter, D. V.; Chisholm, M. H.; DiStasi, V. F.; Klang, J. A. *Chem. Mater.* **1991**, *3*, 221.

(6) Chisholm, M. H.; Haitko, D. A.; Murillo, C. A. *Inorg. Synth.* **1982**, *21*, 51.

(7) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichart, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

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continued usually for 1 h and the precipitate was filtered, washed with the same solvent in several portions and dried *in vacuo*. The dried products had brown to red-brown colors. Analytical, IR and XRD data for these hydrolysis products (listed in Table I) are given below.

$Mo_3(OH)_9[N(CH_3)_2]\cdot{}^1/_2HN(CH_3)_2$. Anal. Obsd (calcd): Mo, 57.3 (56.7); C, 8.94 (7.10); H, 3.01 (3.67); N, 4.06 (4.14); oxidation state of Mo, 3.33 (3.33). IR (Nujol mull) cm^{-1}: 3153 (sh), 1734 (vw), 1304 (w), 1169 (w), 1155 (w), 1124 (vw), 903 (w), 620 (m), 496 (s), 320 (w). The freshly precipitated, glistening hydrolysis product, when transferred while still in contact with the liquid reaction medium into sealed glass capillaries, gave Guinier XRD patterns with the following *d* spacings (Å): 4.60, 4.20, 3.90, 3.60, 3.40, 3.30, 2.70, 2.65, 2.55, 2.50, 2.23, 1.82.

$Mo_2O_2(OH)_5$. Anal. Obsd (calcd): Mo, 63.2 (62.1); oxidation state of Mo, 4.7 (4.5). IR (Nujol mull) cm^{-1}: 1086, 1018, 972, 480.

$Mo_3(OH)_{11}(OC_3H_7)$. Anal. Obsd (calcd): Mo, 54.4 (57.8); oxidation state of Mo, 3.80 (4.0). IR (Nujol mull) cm^{-1}: 3242 (w, b), 1570 (w), 1300 (vw), 1165 (vw), 1101 (m), 1020 (vw), 937 (vw), 920 (m), 804 (m), 499 (m).

$Mo_2(OH)_5(OC_2H_5)$. Anal. Obsd (calcd): Mo, 58.2 (59.6); C, 8.7 (7.5); H, 3.0 (3.1); oxidation state of Mo, 3.0 (3.0). IR (Nujol mull) cm^{-1}: 1261 (w), 1094 (w), 1043 (m), 897 (w), 557 (vw), 482 (m).

Thermal Decomposition of $Mo_3(OH)_9(NMe_2)\cdot{}^1/_2HNMe_2$. Preliminary experiments established that temperatures in excess of 300 °C *in vacuo* had to be achieved before appreciable loss of amine ligand occurred from these samples. To assess the effects of heating this material on its composition and structure, two samples, *ca.* 1 g each, were utilized. The samples were transferred to a fused silica tube equipped with Teflon high-vacuum needle valve and ground joint for attachment to the vacuum system. The tube was then coupled to the vacuum system and pumped down to a pressure of 1×10^{-5} Torr. A tube furnace was then mounted so that the sample was located near the center of its heated zone. The temperature was then increased in increments of 50 °C and maintained at each step until the resulting increase in pressure was again reduced below 1×10^{-4} Torr. One sample (**A**) was thus heated to 350 °C and held there for 29 h. The other sample (**B**) was taken up to 600 °C and held for 11 h. Anal. Found for **A**: Mo, 74.9; C, 3.54; H, 0.44; N, 2.21. Found for **B**: Mo, 77.6; C, 0.65; H, 0.08; N, 2.26. In the XRD film for **A** only one line at d = 3.33 Å was observed. For **B** a weak diffraction pattern (24-h exposure) was obtained with *d* spacings (Å) at 4.75, 4.25, 3.91, 3.70, 3.58, 3.48, 3.40, 3.30, 3.00, 2.95, 2.85, 2.70, 2.62, 2.55, 2.50, and 2.22.

A sample of **B** sealed in a fused silica ampule and held at 600 °C for 1 week showed an XRD pattern corresponding to that of MoO_2 plus six additional lines of an unknown compound with *d* spacings of 4.90, 2.28, 2.15, 1.39, 1.31, and 1.20 Å. Another sample treated similar to **B** but ultimately held for 24 h at 800 °C showed lines in the XRD of Mo, MoO_2 and a set arising from an unidentified compound at 4.86, 2.26, 2.10, 2.00, 1.48, and 1.45 Å.

Thermal Decomposition of $Mo_2(OH)_5(OEt)$. Following a procedure like that described in the preceding section, a sample of $Mo_2(OH)_5(OEt)$ derived from hydrolysis of $Mo_4(OEt)_{12}$ was heated *in vacuo*. The temperature was raised slowly to 240 °C and held there for 1 day. The initial brown solid turned black and was amorphous to X-rays. Anal. Found: Mo, 69.0; oxidation state of Mo, 3.4. In a separate experiment the gases evolved during thermolysis of $Mo_2(OH)_5(OEt)$ were analyzed by GC-MS. Major constituents of the evolved gases were ethene and ethane, with minor amounts of propene, propane, and butane also detected.

Preparation of MoO(OH) from $Mo_2(OH)_5(OEt)$. Studies of the reaction of the hydrolysis product $Mo(OH)_5(OEt)$ with H_2 at various temperatures established that the ethoxide ligand was not removed below 200 °C and that reduction to Mo metal occurred at greater than 300 °C. Samples held in a stream of H_2 at 250 °C for 48 h provided the black pyrophoric material of composition MoO(OH). Anal. Calcd for MoO_2H: Mo, 74.4; H, 0.8; oxidation state of Mo, 3.0. Found: Mo, 74.3; H, 0.6; oxidation state of Mo, 3.0. Only two broad bands at 650 (m) and 500 (w) cm^{-1}, probably from Mo–O stretching modes, appear in the IR spectrum (Nujol mull).

Thermal Decomposition of MoO(OH). Following the procedure described for thermal decomposition of $Mo_3(OH)_9(NMe_2)\cdot{}^1/_2HNMe_2$, a sample of MoO(OH) was held in a working vacuum and slowly heated to 300 °C where it was held for 24 h. In the temperature interval 200–300 °C the evolution of gases not condensable at −196 °C was noted. A pyrophoric black solid was recovered upon cooling. Anal. Found: Mo, 77.2; oxidation state of Mo, 3.34. This corresponds to a material with the composition Mo_3O_5.

Preparation of $LiMoO_2$ from MoO(OH) and Li_2CO_3. MoO(OH) (0.30 g, 2.3 mmol), and Li_2CO_3 (0.087 g, 1.2 mmol) were ground together with a mortar and pestle and loaded into a fused silica tube fitted with joints and Teflon needle-valve stopcock for connection to the vacuum manifold. The reaction tube was maintained under working vacuum throughout the subsequent heating. The temperature of the reaction mixture was then raised to 600 °C and held there for 2 days. After cooling, the product was removed from the reaction vessel and transferred to a copper tube which was sealed by the cold-weld vacuum pinch-off technique.[8] The product was then annealed at 900 °C for 2 days. XRD *d* spacings (Å): 5.209 (s), 2.607 (w), 2.445 (ms), 2.358 (m), 2.092 (ms), 1.9385 (w), 1.6590 (mw), 1.5327 (mw), 1.4330 (mw), 1.3814 (mw), 1.2338 (w). These lines agree very well with those reported for hexagonal (rhombohedral) $LiMoO_2$ with the α-$NaFeO_2$ structure.[9]

Attempted Preparation of $NaMoO_2$ from MoO(OH). The reaction between Na_2CO_3 and MoO(OH) was conducted as described for the previous reaction. In this case the products recovered after reaction at 600 °C were further annealed for 4 days at 500 °C in a sealed copper tube. Lines in the XRD pattern corresponded to the strongest lines of Na_2MoO_4 (5.26, 3.22, and 2.746 Å) and $Na_{0.66}MoO_2$ (5.99 and 2.996 Å).[10]

Following similar procedures other attempts to prepare $NaMoO_2$ from MoO(OH) were made using $NaNH_2$ and Na metal as sources of the sodium. These reactions, at 200 °C followed by annealing at 400 °C for the former, and at 550 °C for the latter, did not give the desired results. Only lines of Mo and Na_2MoO_4 could be identified in the XRD patterns of the poorly crystalline products.

Elemental Analyses. Mo was determined by conversion of samples to MoO_4^{2-} in basic solution followed by acidification and precipitation of the 8-hydroxyquinolate, $MoO_2(ONC_9H_6)_2$.[11] Analyses for C, H and N were performed by Oneida Research Services (Whitesboro, NY) or Schwarzkopf Microanalytical Laboratory (Woodside, NY).

Determination of Oxidation State for Mo. Weighed samples for which the percentage Mo had been previously determined were treated with standardized 0.1 M Ce(IV) solution in 1 M sulfuric acid. A known volume of the Ce(IV) solution containing an excess of the reagent was added to the sample under N_2 or Ar. After complete reaction had taken place, sometimes requiring warming of the solution, and all molybdenum was oxidized to Mo(VI), an aliquot of freshly standardized Fe(II) sulfate solution was added to react with the excess Ce(IV). Titration of the excess Fe(II) was then performed with the standard Ce(IV) solution, with potentiometric detection of the endpoint. The net volume of standard Ce(IV) solution required to oxidize all Mo to Mo(VI) was then used to calculate the average oxidation state of Mo in the sample.

Physical Methods. X-ray diffraction powder patterns were recorded on an Enraf-Nonius Delft FR-552 Guinier camera. All diffraction lines were indexed with reference to NBS powdered silicon as an internal standard. Cu Kα radiation was used in all cases. Exposure times were from 4 to 24 h depending on the degree of crystallinity of samples. The most air-sensitive samples were sealed in X-ray capillary tubes; less air-sensitive samples were sealed between pieces of cellophane tape in the slotted sample holders of the Guinier camera.

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(8) Kayser, F. X.; Stowe, G. L. *J. Vac. Sci. Technol.* **1977**, *14*, 747. The cold-weld pinch-off device was purchased from CHA Industries, Menlo Park, CA.

(9) Aleandri, L. E.; McCarley, R. E. *Inorg. Chem.* **1988**, *27*, 1041.

(10) Aleandri, L. E.; McCarley, R. E., unpublished research.

(11) Elwell, W. R.; Wood, D. F. *Analytical Chemistry of Molybdenum and Tungsten*; Pergamon Press: New York, 1971.

Table I. Summary of Results for Hydrolysis Experiments

starting compound	H_2O/s.c.[a] ratio	product composition[b]	no. of expts.	av oxid.[c] state (Mo)
$Mo_2(NMe_2)_6$	6	$Mo_3(OH)_9(NMe_2)\cdot{}^1/_2HNMe_2$[d]	7	3.33
$Mo_2(O\text{-}t\text{-}Bu)_6$	6	$Mo_2O_2(OH)_5$	1	4.7
$Mo_2(O\text{-}i\text{-}Pr)_6$	6	$Mo_3(OH)_{11}(O\text{-}i\text{-}Pr)$	5	3.8
$Mo_4(OEt)_{12}$	12–14	$Mo_2(OH)_5(OEt)$	many	3.0

[a] Molar ratio of added H_2O to starting compound. [b] Simplest formula based on analytical data in text. [c] Average oxidation state of Mo determined by reaction with standard Ce(IV) sulfate. [d] Initial product is precipitated as a black microcrystalline material of undetermined composition. Final product after vacuum drying is amorphous.

Infrared spectra were recorded using an IBM IR/90 Fourier transform infrared spectrometer. Samples were prepared in a Nujol mull and pressed between CsI plates. Spectra were recorded over the range 200–3500 cm^{-1}. X-ray photoelectron spectra (XPS) were obtained using an AEI ES 200B spectrometer on powders freshly ground under argon and transferred to the spectrometer in a sealed sample holder. Nonmonochromatized Al $K\alpha$ X-rays (1486.6 eV) were used to generate the photoelectrons. Binding energies of all peaks were referenced to the C(1s) peak (BE = 285.0 eV) of adventitious or inherent carbon in the sample.

Magnetic susceptibility measurements were made on a SQUID susceptometer at a magnetic field of 1 T over the range 2–350 K. The susceptibilities were fit to the Curie-Weiss equation $\chi_M = C(T - \theta)^{-1} + \chi_0$, according to a nonlinear least-squares refinement, where $C = (N\mu_B^2/3k)\mu^2$. The small moments μ derived for all of the materials measured here are indicative of magnetic impurities or isolated metal ions with unpaired electrons contained in a host matrix which is basically diamagnetic or Pauli paramagnetic.

A GC mass spectrum was obtained for the gases evolved during vacuum thermal decomposition of $Mo_2(OH)_5(OEt)$ on a Finnegan 4000 GC-MS. Volatile materials (excluding H_2 and CH_4) that were evolved during decomposition as described above were collected in a 100-mL flask at −196 °C. The gases were then transferred to a detachable septum vial through a Teflon needle-valve connection to the vacuum manifold. A gas-tight syringe was then used to withdraw the gases from the vial and inject them into the GC-MS where they were initially frozen in a U-tube before entering the GC column. The U-tube was then slowly warmed to 100 °C to allow the gases to bleed into the column. This procedure gave better resolution of the eluted peaks.

Results and Discussion

Hydrolysis Reactions. In this work the main objective was to obtain a material that could be converted to Mo_2O_3 at sufficiently low temperatures that its decomposition into Mo(s) and MoO_2(s) could be avoided. An essential element of the procedure was that the precursor materials must contain Mo in the +3 oxidation state. Thus it was necessary to find starting molybdenum(III) alkoxides or dialkylamides for which hydrolysis did not result in oxidation or reduction of the metal. Examination of the results summarized in Table I shows that only $Mo_4(OEt)_{12}$ satisfied this condition. In each of the other cases either limited ($Mo_2(NMe_2)_6$) or extensive ($Mo_2(O\text{-}t\text{-}Bu)_6$ and $Mo_2(O\text{-}i\text{-}Pr)_6$) oxidation of the molybdenum accompanied the hydrolysis. Because of the extensive oxidation, further study of the hydrolysis products in the latter two cases was not pursued. We assume but have not established that this oxidation occurs by reaction of hydrolysis products or intermediates with either added water, or alcohol formed during hydrolysis, as in the processes

$$M(OR)_3 + xH_2O \rightarrow M(OH)_x(OR)_{3-x} + xROH \quad (1)$$

$$M(OH)_x(OR)_{3-x} + H_2O \rightarrow M(OH)_{1+x}(OR)_{3-x} + {}^1/_2H_2(g) \quad (2)$$

$$M(OH)_x(OR)_{3-x} + ROH \rightarrow M(OH)_x(OR)_{4-x} + {}^1/_2H_2(g) \quad (3)$$

For this reason the use of water or the parent alcohol of the alkoxide as solvents was avoided, and addition of excess water beyond that required for complete hydrolysis had to be examined for its effects.

In no case did complete hydrolysis result from reactions conducted with addition of the stoichiometrically required amount of water. In each of the two cases studied most extensively an insoluble product containing unremoved organic ligands was obtained. On the basis of analytical data, oxidation state determinations, and IR spectra, the materials isolated upon hydrolysis of $Mo_2(NMe_2)_6$ and $Mo_4(OEt)_{12}$ are formulated as $Mo_3(OH)_9(NMe_2)\cdot{}^1/_2HNMe_2$ and $Mo_2(OH)_5(OEt)$, respectively. These formulas do not imply any knowledge about the true molecularity or structure of the compounds. However the tenacious retention of the organic ligands under high vacuum, even at temperatures up to 350 °C, shows that they are bound predominantly as Mo–NMe_2 and Mo–OEt groups. The protonated donors $HNMe_2$ and HOEt should be more loosely bound and probably would be lost at these elevated temperatures or perhaps converted to the amido or alkoxo ligands by elimination of H_2 or proton transfer to an oxide ligand.

It was established that the black solid that precipitated during hydrolysis of $Mo_2(NMe_2)_6$ was indeed crystalline. Attempts to grow larger crystals of this product by performing the hydrolysis in unstirred solutions with very slow vapor-phase transfer of water into the solution over the course of many hours did not succeed. Also it was not possible to isolate this material under conditions where its true composition could be determined. After its initial isolation from the mother solution, loss of solvent or incorporated dimethylamine caused the black crystalline material to change color and become noncrystalline according to XRD. Since it is known that hydrolysis or ammonolysis of metal alkoxides or dialkylamides can lead to polynuclear oxoalkoxides[12,13] and nitrido/imido amides,[14] respectively, the black crystalline hydrolysis product most likely is a polynuclear oxo/hydroxo dimethylamido species containing additional coordinated dimethylamine. Partial oxidation during hydrolysis gives Mo in the +3.33 average oxidation state, which was determined for the final red-brown material that resulted from facile loss of volatile components of the black compound at room temperature.

Hydrolysis of $Mo_4(OEt)_{12}$ with stoichiometric addition of water results in quantitative precipitation of $Mo_2(OH)_5(OEt)$. This material might well be a polynuclear compound consisting of discrete cluster units interconnected through Mo–O–Mo intercluster linkages, or it might possess an extended structure. Indeed it is conceivable that the tetranuclear cluster of unknown structure present in $Mo_4(OEt)_{12}$ might be retained in the hydrolysis product with –OH replacing 10 of the 12 –OEt ligands. However,

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(12) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.

(13) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, *11*, 663.

(14) (a) Banazak Holl, M. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1992**, *114*, 3854. (b) Banazak Holl, M. M.; Kersting, M.; Pendley, B. D.; Wolczanski, P. T. *Inorg. Chem.* **1990**, *29*, 1518. (c) Banazak Holl, M. M.; Wolczanski, P. T.; Van Duyne, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 7989.

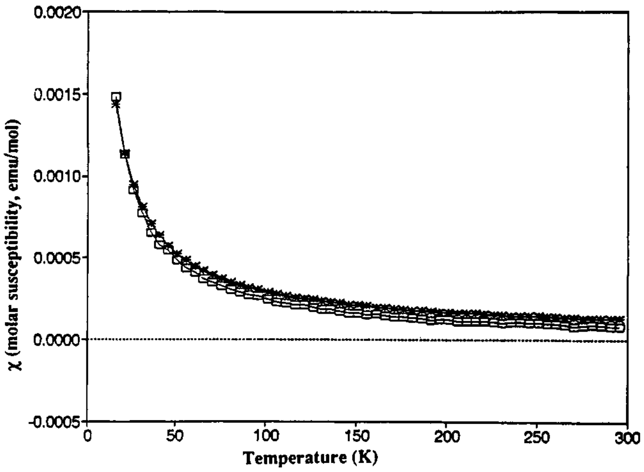

Figure 1. Molar magnetic susceptibility vs temperature at 1 T for $Mo_2(OH)_5(OEt)$. Open squares represent observed data and asterisks represent a least-squares fit of the data to the Curie–Weiss equation.

the actual process that occurs during hydrolysis must be very complicated because, if a slight excess of water is added (14 mol/mol of tetramer), a small amount of soluble product is generated. A few crystals of the new hexanuclear cluster compound $Mo_6O(OEt)_{18}$ can be obtained from the filtrate containing this soluble product.[15] The procedure is entirely reproducible but always provides only minuscule yields of the hexanuclear product. It is especially difficult to envision the process whereby addition of excess water leads to a product that retains the same OEt/Mo ratio as that in the starting material. Efforts to prepare $Mo_6O(OEt)_{18}$ by other, more rational approaches will be the subject of a separate report.

The magnetic susceptibilities shown in Figure 1 for $Mo_2(OH)_5(OEt)$ show that this material is only weakly paramagnetic with a very small apparent moment of $0.45\mu_B$ per formula unit. This is consistent with the material basically having a small temperature-independent susceptibility, $\chi_0 = 42 \times 10^{-6}$ emu/mol, and an impurity or isolated, trapped atoms with unpaired spins giving rise to the small apparent moment and rapid increase of χ_M at low temperatures. We interpret this as the result of pairing of the three 4d electrons available to each Mo(III) atom through metal–metal bond formation, as it is in most Mo(III) alkoxide dimers and tetramers.[16] The trapping of some Mo atoms in local environments where metal–metal bonding is incomplete, or where some cluster units may actually exist with unpaired spins because of an odd electron count, is understandable in an amorphous material of this type.

The Mo 3d XPS for $Mo_2(OH)_5(OEt)$ is depicted in Figure 2. From this spectrum the $3d_{5/2}$ and $3d_{3/2}$ binding energies (B.E.) taken from the peak maxima are 230.4 and 233.2 eV, respectively. The $3d_{5/2}$ B.E. of 230.4 eV can be compared with the average of several values taken from the literature[17,18] for each of Mo, 227.8 eV; MoO_2, 229.0 eV; and MoO_3, 232.5 eV. In this comparison it is apparent that either the value for $Mo_2(OH)_5(OEt)$ is too high or the value for MoO_2 is too low, since we should expect B.E.(Mo(III)) < B.E.(Mo(IV)). The latter is the likely explanation because the B.E. of MoO_2 is only 1.2 eV greater that that of Mo metal. Because MoO_2 is metallic, the delocalized conduction electrons may screen the core hole during the photoionization process and give an anomalously low B.E.[19] From a different perspective we might expect the B.E. for Mo(III) in a nonconducting oxide system to be about midway between that of Mo(VI) in MoO_3 and Mo(0) in the metal, viz., at about 230.2 eV. In this light the B.E. for $Mo_2(OH)_5(OEt)$ is about right.

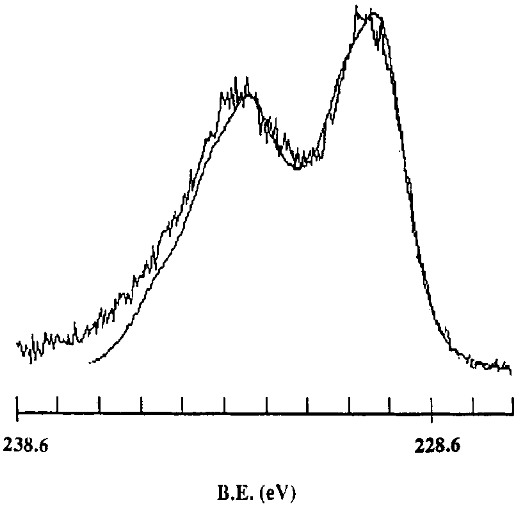

Figure 2. Mo 3d XPS spectrum of $Mo_2(OH)_5(OEt)$. Binding energies are referenced to C 1s band at 285.0 eV. A least-squares fitting of the spectrum gives a major component with 3 $d_{5/2}$ at 230.4 eV.

Thermal Decomposition of Hydrolysis Products. Vacuum thermolysis of $Mo_3(OH)_9(NMe_2)\cdot{}^1/_2HNMe_2$ at 350 °C for 29 h resulted in only partial loss of the amine and amido ligands, and formation of a material with the approximate composition $Mo_2O_3N_{0.4}C_{0.76}H_{1.12}$. It is obvious from the composition that some fragmentation of the dimethylamido ligand takes place at this temperature. At 600 °C vacuum thermolysis provides a material of approximate composition $Mo_2O_3N_{0.40}C_{0.13}H_{0.20}$ containing less carbon and hydrogen but nearly the same amount of nitrogen as that for the product obtained at 350 °C. Continued loss of carbon and hydrogen at higher temperatures may result from formation of CO_2 and H_2O. In any case, thermolysis leaves much of the nitrogen in the residue, combined probably as nitride in an oxide lattice. The material is thus unsuited as a precursor for Mo_2O_3.

Thermolysis of $Mo_2(OH)_5(OEt)$, even at the low temperature of 240 °C, resulted in partial oxidation of the molybdenum from oxidation state 3.0–3.4. GC-MS determination of the gases evolved found mainly ethene and ethane, with minor amounts of propene, propane, and butane. This behavior is consistent with homolytic cleavage of the C–O bond of the ethoxide ligand and subsequent reactions of the ethyl radical. Such a process would result in an increase in the average oxidation number of the molybdenum from 3.0 to 3.5 if it were the only process to occur. However some loss of ethene could also

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[15] Hollingshead, J. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 7402.

[16] Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 432.

[17] Sasaki, T. A.; Kiuchi, K. *Chem. Phys. Lett.* **1981**, *84*, 356.

[18] Werfel, F.; Minni, E. *J. Phys. C: Solid State Phys.* **1983**, *16*, 6091.

[19] Such an effect has been found in the Zr 3d XPS of zirconium halides over the range of oxidation states from 0 to 4. Compounds having metallic or delocalized bonding character were found to have 3d B.E.'s lower than expected by ca. 1.0 eV, when compared to compounds with localized bonding and nonmetallic character: Corbett, J. D. *Inorg. Chem.* **1983**, *22*, 2669.

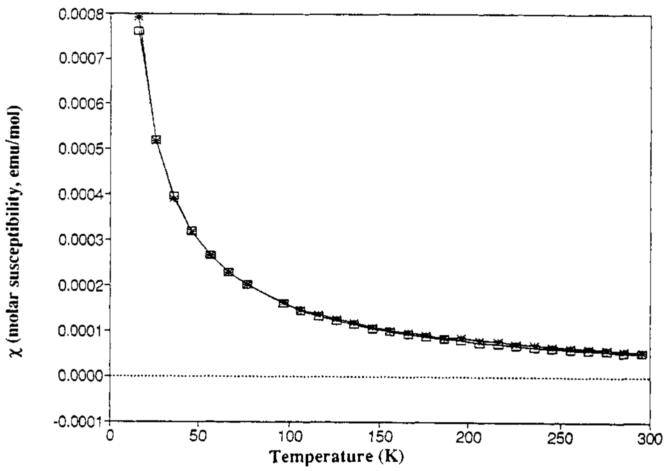

Figure 3. Molar magnetic susceptibility vs temperature at 1 T for MoO(OH). Open squares represent observed data and asterisks represent least-squares fit to Curie–Weiss equation.

occur by transfer of a H atom from the ethyl radical to an O atom to generate an OH group (subsequently lost as H_2O); this process would thus involve no change in the oxidation number. These results are similar to those found for thermolysis of $Mo_2(OR)_6$ and $W_2(OR)_6$ compounds.[5]

Preparation of MoO(OH). Because of the oxidation which accompanied vacuum thermolysis of $Mo_2(OH)_5(OEt)$, its decomposition in flowing H_2 was examined. The results depended upon temperature of the reaction; at 130 °C incomplete removal of ethoxide ligand was found, while at temperatures above 300 °C reduction to Mo metal occurred. At the intermediate temperature of 250 °C the new compound MoO(OH) was generated. The absence of any bands in the IR spectra between 800 and 1100 cm^{-1} showed that all ethoxide ligands had been removed. The compound is amorphous and pyrophoric. Bands in the Mo 3d XPS are somewhat broader than those in the XPS of $Mo_2(OH)_5(OEt)$ and give a somewhat lower Mo $3d_{5/2}$ B.E. of 229.7eV. Magnetic susceptibility data for MoO(OH) are also quite similar to those for $Mo_2(OH)_2(OEt)$, as shown in Figure 3. Here the apparent moment was even smaller, $0.37\mu_B$. Again this may be attributed to some impurity with unpaired spins or to a low population of paramagnetic centers arising from trapped metal ions or clusters with unpaired electron spins. Basically it appears that MoO(OH) is extensively metal–metal bonded, pairwise as in MoO_2, or in more extended form as in $LiMoO_2$.[9]

Reactions of MoO(OH). Of prime interest in this investigation was the preparation of the unknown oxide Mo_2O_3. It was hoped that simple heating of MoO(OH) would cause loss of H_2O and conversion to Mo_2O_3. Unfortunately, heating *in vacuo* to 300 °C resulted in loss of noncondensable gas (H_2) as well as H_2O. Thus simultaneous reactions occurred, eqs 4–6, that resulted in partial oxidation of the molybdenum:

$$MoO(OH)(s) = MoO_2(s) + {}^1/_2H_2(g) \tag{4}$$

$$2MoO(OH)(s) = Mo_2O_3(s) + H_2O(g) \tag{5}$$

or

$$3MoO(OH)(s) = Mo_3O_5(s) + H_2O(g) + {}^1/_2H_2(g) \tag{6}$$

The product of the reaction at 300 °C was a black, pyrophoric solid that was amorphous by XRD. After annealing this material at 400 °C for 25 h the lines of MoO_2 became prominent in the XRD. Thus the oxide produced at 300 °C might consist of the amorphous compound Mo_3O_5, or an amorphous mixture of Mo_2O_3 and MoO_2. In an attempt to avoid oxidation during thermolysis of MoO(OH), the latter was performed at 300 °C under flowing H_2, with the result that Mo metal was formed. We conclude that formation of crystalline Mo_2O_3 is not feasible by these approaches.

The high reactivity of MoO(OH) suggested that it could be useful in the preparation of ternary oxides of Mo(III). Although several reactions were conducted, the most successful one was that between MoO(OH) and Li_2CO_3. This reaction, when conducted at 600 °C *in vacuo*, leads cleanly to the layered compound $LiMoO_2$, as shown in eq 7:

$$2MoO(OH)(s) + Li_2CO_3(s) = 2LiMoO_2(s) + CO_2(g) + H_2O(g) \tag{7}$$

Previously $LiMoO_2$ was prepared via the reaction between Mo metal and excess Li_2MoO_4 at 900 °C for 21 days.[9] In addition to being slow, a problem with the latter method was that it also required removal of excess Li_2MoO_4 by washing the product extensively with water. To prevent oxidation of $LiMoO_2$ by water, the washing procedure must be conducted at ≤25 °C, and complete removal of Li_2MoO_4 is then difficult. Similar approaches designed to produce $NaMoO_2$ by reaction of MoO(OH) with Na_2CO_3, Na metal, or $NaNH_2$ were not successful.

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