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Tungsten and Molybdenum Oxyfluorides of the Type $\text{MO}_{3-x}\text{F}_x$

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Oxyfluorides of the type $\text{WO}_{3-x}\text{F}_x$ and $\text{MoO}_{3-x}\text{F}_x$ have been prepared at 700° and 3 kbars in either 48% aqueous HF or anhydrous HF. The cubic ReO_3 structure is found in the region $x = 0.17$ – 0.66 for $\text{WO}_{3-x}\text{F}_x$ and in the region $x = 0.74$ – 0.97 for $\text{MoO}_{3-x}\text{F}_x$. In these regions the tungsten phases are blue, red, or gold whereas the molybdenum phases are all gold. Low values of electrical resistivity and small negative values of the thermoelectric power found in both systems are indicative of metallic behavior. However, the resistivity of a crystal in the $\text{WO}_{3-x}\text{F}_x$ system increased only very slightly with temperature, and in the $\text{MoO}_{3-x}\text{F}_x$ system resistivities were found to decrease significantly with temperature. Optical reflectance data in the $\text{WO}_{3-x}\text{F}_x$ system can be correlated with x as in the Na_xWO_3 system. At low values of x light green and semiconducting $\text{WO}_{2.96}\text{F}_{0.04}$ with a WO_3 -like structure is found in the tungsten system. A unique compound $\text{Mo}_4\text{O}_{11}\text{F}$ ($x = 0.25$) is found in the molybdenum system. Blue needles of this compound are semiconducting and the structure of $\text{Mo}_4\text{O}_{11}\text{F}$ is closely related to that of MoO_3 and $\text{Mo}_4\text{O}_{10}(\text{OH})_2$.

Introduction

Oxyfluorides of the type $\text{MO}_{3-x}\text{F}_x$ with the rhenium trioxide structure are known where M is Ti, Nb, Ta, and Mo.^{1–4} When M is Ti, the only reported value of x is 2, *i.e.*, $\text{Ti}^{\text{IV}}\text{OF}_2$.² The compositions $\text{M}^{\text{V}}\text{O}_2\text{F}$ ($x = 1$) are well established in the Nb and Ta systems, and apparently x may vary continuously from 1 to nearly 3 in these systems.³ The range of x in the $\text{MoO}_{3-x}\text{F}_x$ system has not been well established.^{3,4} Distorted ReO_3 structures (VF_3 type) are found for TiF_3 and MoF_3 , and the existence of NbF_3 and TaF_3 has been questioned.¹ Since the structure of WO_3 is closely related to that of ReO_3 , it would seem that $\text{WO}_{3-x}\text{F}_x$ phases with ReO_3 -related structures might well exist; however, none has been reported.

Although WOF_4 is well established, the other proposed oxyfluorides of tungsten are not well characterized. Priest and Schumb⁵ reported WOF_2 , but no structural data were given. However, these authors also found a series of cubic phases which apparently were structurally related to the cubic tungsten bronzes and ReO_3 . They represented these phases as $a\text{WO}_2 \cdot b\text{WO}_3 \cdot c\text{HF}$ where the cubic cell edges varied from 3.77 to 3.84 Å and reported them to be "more or less hydrated." The existence of these cubic bronzelike phases has been confirmed by Buslaev and Bochkareva.⁶

This paper reports the preparation and characterization of compounds in the $\text{WO}_{3-x}\text{F}_x$ and $\text{MoO}_{3-x}\text{F}_x$ systems.

Experimental Section

The reactants were tungsten metal (99.99%), tungsten trioxide (99.98%), molybdenum metal (99.95%), molybdenum trioxide (99.99%), and reagent grade 48% hydrofluoric acid. Tungsten metal, molybdenum metal, and tungsten trioxide were obtained

(1) D. Bable in "Structure and Bonding," Vol. III, C. K. Jørgensen, Ed., Springer-Verlag, New York, N. Y., 1967, pp 37–39.

(2) K. Vorres and J. Donohue, *Acta Cryst.*, **8**, 25 (1955).

(3) H. Schafer, H. G. Schnering, K. J. Niehues, and H. G. Nieder-Vahrenholz, *J. Less-Common Metals*, **9**, 95 (1965).

(4) D. E. LaValle, R. M. Steele, M. K. Wilkinson, and H. L. Yakel, *J. Am. Chem. Soc.*, **82**, 2433 (1960).

(5) H. F. Priest and W. C. Schumb, *ibid.*, **70**, 3378 (1948).

(6) Y. A. Buslaev and V. A. Bochkareva, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **1**, 294 (1965).

from Electronic Space Products, Inc. Molybdenum trioxide was obtained from Johnson, Matthey & Co. Anhydrous HF was obtained from the Matheson Co.

Various ratios of reactants (Table I) were sealed in pressure-collapsible gold ampoules and heated at 700° for 8 hr under 3000 atm of supporting pressure. The products were washed well with water and dried in a vacuum oven at 120°.

Fluorine analyses were carried out essentially by a method given in ref 7. The sample was fused with sodium peroxide in a Parr bomb, acidified to a Ph of 3.3, and distilled as hydrofluoro-silicic acid. The distillate was titrated directly with thorium nitrate using alizarin red and methylene blue as indicators. The accuracy of this method is felt to be $\pm 5\%$ or better.

X-Ray powder patterns were obtained on a Hägg-Guinier camera at 25° using strictly monochromatic $\text{Cu K}\alpha_1$ radiation and an internal standard of high-purity KCl ($a = 6.2931$ Å). The cell dimensions were refined by least squares. Optical reflectance data were obtained on a Cary 14 using a Model 1411 diffuse reflectance accessory.

Where single crystals of sufficient size were available, four-probe electrical resistivity measurements were carried out from 4.2 to 298°K. Bars were cut from crystals except in the case of $\text{MoO}_{2.75}\text{F}_{0.25}$ which was needlelike in habit. Four probes of an indium alloy were ultrasonically soldered on with the aid of a micromanipulator. The thermoelectric power was determined at an average temperature of 45° with $\Delta T = 30^\circ$ and is referred to lead ($\alpha_{\text{Pb}} = 2.76 \mu\text{V}/\text{deg}$).

Results

All products which appeared to be single phase by X-ray and microscopic examination were analyzed in duplicate for fluorine. Some were also analyzed for oxygen, hydrogen, and tungsten or molybdenum. Representative average fluorine analyses are given in Table I. The several metal and oxygen analyses agreed well with the $\text{MO}_{3-x}\text{F}_x$ formulations. Hydrogen was not detected in any sample, and if present, it must have been less than 0.04% by weight. Furthermore, infrared data showed no evidence of hydroxyl groups or water.

$\text{WO}_{3-x}\text{F}_x$ System.—It was found that $\text{WO}_{3-x}\text{F}_x$ compositions could be prepared up to a maximum value of $x = 0.43$ in 48% aqueous HF and up to $x = 0.66$ in anhydrous HF. Cubic tungsten bronzelike X-ray patterns were obtained for $x = 0.17$ – 0.66 . The

(7) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol II, Interscience Publishers, Inc., New York, N. Y., 1947, pp 321–324.

TABLE I
 DATA FOR $\text{WO}_{3-x}\text{F}_x$ PHASES

ml of HF ^a	Reactants		Product		
	g of M	g of WO_3	% F	x	a , Å
3.0 ^b	0.30 (W)	2.00	5.39	0.66	3.836
1.5	0.30 (W)	0.75	3.17	0.39	3.820
3.0	0.15 (W)	2.00	2.64	0.32	3.816
3.0	0.06 (W)	2.00	2.35	0.29	3.807
3.0	0.03 (W)	2.00	1.47	0.18	3.789
3.0	0.00 (W)	2.00	0.30	0.04	3.755 ^c
3.0 ^b	0.14 (Mo)	3.00	9.67	0.74	3.833
3.0 ^b	0.16 (Mo)	4.00	10.60	0.82	3.836
3.0	0.12 (Mo)	3.00	12.58	0.97	3.844
3.0	0.02 (Mo)	3.00	3.31	0.25	3.702 ^c

^a Generally 48% HF–52% H_2O . ^b Anhydrous HF was used.
^c (Volume)^{1/3}/mol.

cell dimensions increased regularly with x over this range (Table I and Figure 1). The products were blue-black in the fluorine-poor region of this range and changed gradually to red and finally to gold in the fluorine-rich end. Attempts to extend the range of x to higher values by increasing the W: WO_3 reactant ratio led to the occurrence of WO_2 as a second phase in the 48% aqueous HF system or of W metal as a second phase in the anhydrous HF system.

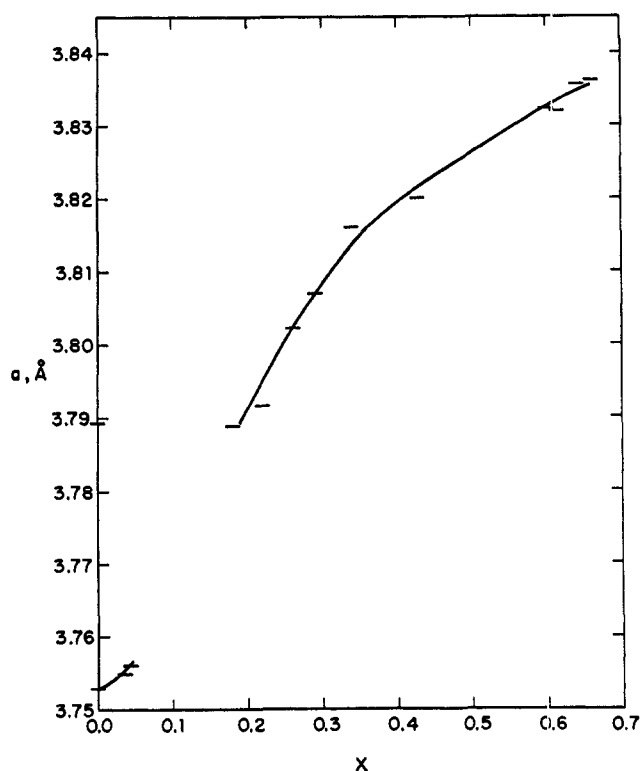


Figure 1.—Composition vs. cell edge for $\text{WO}_{3-x}\text{F}_x$ phases.

A two-phase region existed for $x = 0.17$ – 0.04 , and $\text{WO}_{2.96}\text{F}_{0.04}$ was light green and quite distorted from cubic symmetry. The orthorhombic cell for which $a = 7.3767$ (7), $b = 7.4691$ (7), and $c = 3.8462$ (3) Å was found to index the $\text{WO}_{2.96}\text{F}_{0.04}$ pattern very well (Table II). An X-ray powder pattern of WO_3 was indexed as monoclinic: $a = 7.3010$ (3), $b = 7.5380$ (3), $c = 3.8444$ (2) Å, and $\beta = 90.890$ (3)°. This cell is

 TABLE II
 X-RAY POWDER PATTERN FOR $\text{WO}_{3-x}\text{F}_x$

I/I_0	hkl	d_{obsd} , Å	d_{calcd} , Å
100	001	3.8454	3.8462
90	020	3.7338	3.7354
90	200	3.6882	3.6883
15	120	3.3318	3.3319
60	111	3.1023	1.1024
70	021	3.6791	2.6793
70	201	2.6618	2.6621
80	220	2.6241	2.6242
10	121	2.5189	2.5184
60	221	2.1677	2.1677
5	320	2.0538	2.0537
15	131	2.0110	2.0109
20	311	1.9963	1.9963
25	002	1.9237	1.9231
20	040	1.8676	1.8673
25	400	1.8450	1.8442
45	112	1.8061	1.8057
20	022	1.7093	1.7097
20	202	1.7052	1.7052

very similar to that reported by Magnéli.⁸ The equivalent of a cubic cell edge for WO_3 and $\text{WO}_{2.96}\text{F}_{0.04}$ was taken to be the cube root of the volume of one formula unit. Although the symmetries of WO_3 and $\text{WO}_{2.96}\text{F}_{0.04}$ appear to be different at room temperature, it is possible that $\text{WO}_{2.96}\text{F}_{0.04}$ is really monoclinic with the deviation of β from 90° being too small to detect. Furthermore, even if the symmetries of WO_3 and $\text{WO}_{2.96}\text{F}_{0.04}$ are different at room temperature, it is possible that they are the same at 700° so that complete solid solubility in the range of x from 0.0 to 0.04 is possible. No attempt was made, however, to produce $\text{WO}_{3-x}\text{F}_x$ phases within this range.

A single crystal large enough for four-probe electrical resistivity measurements was found in a preparation where x was 0.41. This crystal showed a room-temperature resistivity of 8.4×10^{-4} ohm cm decreasing regularly with temperature to 7.6×10^{-4} ohm cm at 4.2°K . The thermoelectric power of this crystal was $-5.5 \mu\text{V}/\text{deg}$.

Two-probe electrical resistivity measurements on pressed pellets were made at other compositions since single crystals were not available. At room temperature all phases in the cubic range ($x = 0.17$ – 0.66) showed resistivities of the order of 10^{-4} to 10^{-3} ohm cm. A pellet of $\text{WO}_{2.96}\text{F}_{0.04}$ had a room-temperature resistivity of about 10^4 ohm cm. Although measurements on powders reliably give only a lower limit of resistivity, this limit suffices to show that the entire cubic range is metallic whereas $\text{WO}_{2.96}\text{F}_{0.04}$ is almost certainly not metallic.

The reflectance spectra for the $\text{WO}_{3-x}\text{F}_x$ compositions were so similar to those found in the Na_xWO_3 ^{9,10} system that they are not reproduced here. In the cubic and metallic region ($x = 0.17$ – 0.66), the specular part of the reflectance dominates, and one peak is found which shifts to lower wavelengths with increasing x :

(8) ASTM X-Ray Powder Diffraction File Card 5-0363 (data supplied by A. Magnéli).

(9) B. W. Brown and E. Banks, *J. Am. Chem. Soc.*, **76**, 963 (1954).

(10) P. G. Dickens, R. M. P. Quilliam, and M. S. Whittingham, *Mater. Res. Bull.*, **3**, 941 (1968).

6750 Å for $x = 0.17$, 5800 Å for $x = 0.35$, and 5450 Å for $x = 0.41$. For WO_3 and $\text{WO}_{2.96}\text{F}_{0.04}$ the diffuse reflectance dominates, and an absorption edge is found at about 4400 Å for both phases. There is also a peak at 12,400 Å for $\text{WO}_{2.96}\text{F}_{0.04}$.

MoO_{3-x}F_x System.—An ReO_3 structure was found from $x = 0.74$ to $x = 0.97$ under the experimental conditions employed. As in the $\text{WO}_{3-x}\text{F}_x$ system, the unit cell edge increases with increasing x : $a = 3.833$ Å for $x = 0.74$ and $a = 3.844$ Å for $x = 0.97$. The color of the $\text{MoO}_{3-x}\text{F}_x$ products was gold throughout this range. Single-phase products were prepared only in the anhydrous HF system. Similar products could be obtained in the 48% aqueous system, but blue needles of $\text{Mo}_4\text{O}_{11}\text{F}$ (see below) were also always present. However, in the 48% aqueous system gold cubes up to 2 mm across were obtained whereas the products of the anhydrous HF system were all polycrystalline. Consequently, most analyses were performed on the products of the anhydrous HF system whereas crystals suitable for electrical resistivity measurements were taken from the products of the aqueous system.

Four-probe electrical resistivity measurements were made on single crystals at two different compositions (Figure 2). Although the resistivity of both crystals was low, the resistivity definitely decreased with increasing temperature. At the highest temperature an activation energy of about 0.01 eV is indicated. The thermoelectric power was found to be -14 $\mu\text{V}/\text{deg}$ for $x = 0.86$ and about -1 $\mu\text{V}/\text{deg}$ for $x = 0.97$. Both of these values are more typical of metals than semiconductors.

In attempting to lower the value of x in the $\text{MoO}_{3-x}\text{F}_x$ system, a unique compound was found at $x = 0.25$. This compound, $\text{Mo}_4\text{O}_{11}\text{F}$, crystallized as blue needles. The possible space groups (Cmc2₁, Cmc₂, or C2cm) were determined from single-crystal precession photographs. The orthorhombic cell has dimensions $a = 3.8791 \pm 6$ Å, $b = 14.057 \pm 2$ Å, and $c = 3.7225 \pm 6$ Å, where a is the needle axis. These cell dimensions are very similar to those of MoO_3 ¹¹ ($a = 3.963$ Å, $b = 13.855$ Å, and $c = 3.696$ Å) and even more similar to those given¹² for $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ ($a = 3.888$ Å, $b = 14.082$ Å, and $c = 3.734$ Å). Furthermore, whereas the space group for MoO_3 is Pbnm, Kihlberg, *et al.*,¹² have suggested Cmc₂ for $\text{Mo}_4\text{O}_{10}(\text{OH})_2$. Thus $\text{Mo}_4\text{O}_{11}\text{F}$ and $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ are probably isostructural having structures closely related to that of MoO_3 .

Four-probe electrical resistivity measurements on $\text{Mo}_4\text{O}_{11}\text{F}$ crystals were carried out parallel to the a axis. Semiconducting behavior was observed (Figure 2). An activation energy of 0.13 eV was indicated.

Discussion

Under the conditions of this work, cubic bronzelike phases with the formula $\text{WO}_{3-x}\text{F}_x$ were found to exist for $x = 0.17$ – 0.66 . It is likely that this range would vary significantly with temperature and pressure, but this

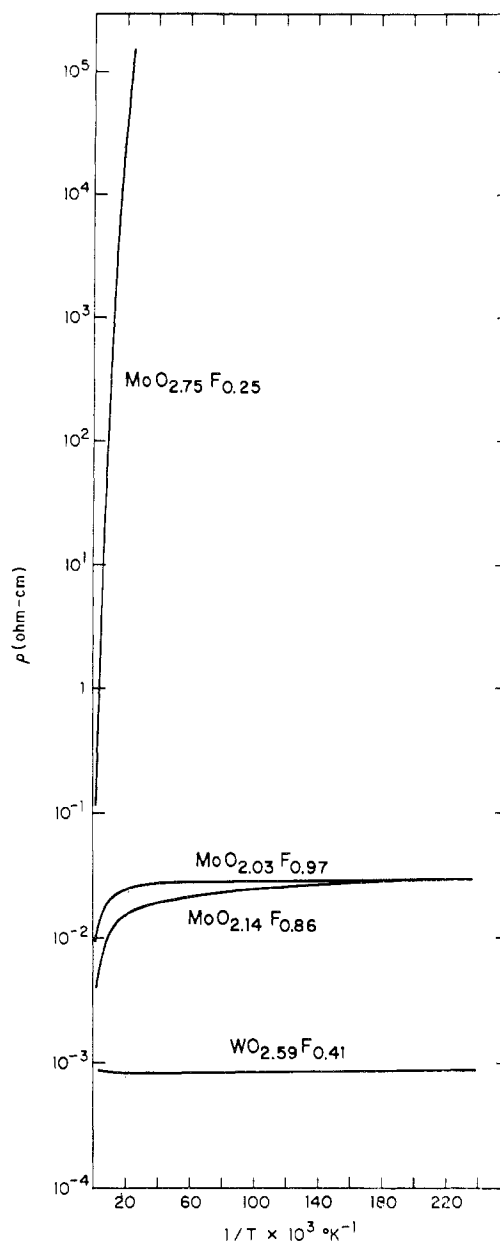


Figure 2.—Electrical resistivity vs. reciprocal temperature.

was not investigated. Tungsten bronzes are known in the system H_xWO_3 ($x = 0.1$ – 0.5),¹³ and earlier reports on the bronzelike oxyfluorides^{5,6} suggested that they also contained hydrogen. Consequently, the formula $\text{H}_y\text{WO}_{3-x}\text{F}_x$ was considered a possibility. However, the analyses did not detect hydrogen and indicated that y must be less than 0.1 at all values of x . This is not surprising since the preparative temperature of this work was considerably higher than those employed to prepare the H_xWO_3 and $a\text{WO}_2 \cdot b\text{WO}_3 \cdot c\text{HF}$ phases.

There are obvious similarities between the A_xWO_3 and $\text{W}_{1-x}\text{Re}_x\text{O}_3$ ¹⁴ systems and the $\text{WO}_{3-x}\text{F}_x$ system. In all three systems electrons are added with increasing x . This is done in three quite different ways, but the effects on structure and properties are very similar. At low

(11) S. Westman and A. Magnéli, *Acta Chem. Scand.*, **12**, 363 (1958).

(12) L. Kihlberg, G. Hägerström, and A. Rönquist, *ibid.*, **15**, 1187 (1961).

(13) O. Glemser and C. Naumann, *Z. Anorg. Allgem. Chem.*, **265**, 288 (1951).

(14) A. W. Sleight and J. L. Gillson, *Solid State Commun.*, **4**, 601 (1966).

values of x these phases are semiconductors and possess symmetries lower than cubic. However, when x is sufficiently high ($\sim 1/4$), the materials become cubic and metallic. The cubic phases exist over wide ranges of compositions with conductivities generally increasing with increasing x . The color variations are also very similar being blue-black for low values of x , changing to violet, red, and eventually gold with increasing x . (The gold color is not achieved at maximum values of x in the $W_{1-x}Re_xO_3$ system.)

The conduction band in the tungsten bronzes presumably results from a π^* -type interaction between the t_{2g} orbitals of tungsten and the appropriate p orbitals of oxygen.¹⁵ This band is not disrupted significantly by the A cation interstitials or by replacing tungsten by rhenium; however, the replacement of oxygen by fluorine might well be expected to be much more disruptive. Nonetheless, the cubic phases of the type $WO_{3-x}F_x$ are metals although the low-resistivity ratio ($\rho_{290^\circ K} / \rho_{4.2^\circ K}$) in the single crystal of $WO_{2.96}F_{0.41}$ might be caused by fluorine acting as a scatterer to the conduction electrons. That fluorine does not readily enter into the formation of the conduction band is also indicated by the fact that the $MoO_{3-x}F_x$ compositions, which contain more fluorine, have higher resistivities. However, since the d-orbital extension for molybdenum is not as great for tungsten, this may also contribute to the difference in properties between the two systems.

Reflectance measurements in the Na_xWO_3 system were first reported by Brown and Banks.⁹ For metallic samples ($x = 0.20-0.85$) they found that the region 3350–12,500 Å was dominated by one peak. The position of this peak decreased from about 6500 Å at $x = 0.3$ to about 4800 Å at $x = 0.85$. Dickens, *et al.*,¹⁰ have also

(15) J. B. Goodenough, *Bull. Soc. Chim. France*, 1200 (1965).

studied the reflectance of the sodium tungsten bronzes. They have shown that the specular reflectance generally dominates over diffuse reflectance, and they have proposed that a modified Drude-Zener free-electron theory can account qualitatively for the observed dependence of the peak position with x . However, in the semiconducting region of the Na_xWO_3 system (x less than about 0.25) the diffuse reflectance dominates over the specular reflectance. There is an absorption edge at about 4600 Å, and when x is greater than 0.0, there is a peak at about 12,000 Å.

The situation in the $WO_{3-x}F_x$ system appears to be directly analogous to that in the Na_xWO_3 system. In the metallic region the reflectance spectra are dominated by one peak which shifts to lower wavelengths with increasing electron concentration. On the other hand, $WO_{2.96}F_{0.04}$ does not show this peak. The peak caused by the specular reflectance is gone, and the spectra are presumably dominated by the diffuse reflectance. An absorption edge much like that in WO_3 is found for $WO_{2.96}F_{0.04}$ and a peak is found at 12,400 Å. This peak may result from an interband transition which does not occur in WO_3 . More quantitative interpretation of the data is difficult because all the reflectance data are a mixture of specular and diffuse components, and the peak in the specular reflectance is not completely resolved from the peak in the diffuse reflectance.

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The Reaction of Molybdenum(II) Cluster Alkoxides with Phenol

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By treatment of $Na_2[(Mo_6Cl_8)(OCH_3)_6]$ with excess phenol the ligand methoxide ions are displaced and the corresponding phenoxy derivative $Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$ is formed. When $Na_2[\{Mo_6(OCH_3)_3\}(OCH_3)_3]$ is the starting compound, the product depends upon the reaction conditions. At room temperature the cluster $Mo_6(OCH_3)_5^{4+}$ remains virtually untouched and the derivative $Na_2[\{Mo_6(OCH_3)_3\}(OC_6H_5)_3]$ is isolated in good yield. Under more vigorous conditions half of the cluster methoxy groups are replaced. The resulting compound appears to have retained the basic hexamolybdenum(II) cluster structure, and it is formulated as $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_2]$ on the basis of elemental analysis, magnetic properties, and infrared and pmr spectra. Low-frequency infrared spectra (200–600 cm^{-1}) of other molybdenum(II) cluster alkoxides, as well as of the phenoxy derivatives, are also shown.

Introduction

In a recent paper¹ new molybdenum(II) derivatives were described, in which either the ligand halogens or both ligand and cluster halogens in molybdenum(II) halides are replaced by alkoxy groups. The compounds

(1) P. Nannelli and B. P. Block, *Inorg. Chem.*, **7**, 2423 (1968).

have the general formula $Na_2[(Mo_6X_8)(OR)_6]$, where X is either a halogen or an alkoxy group and OR is a ligand alkoxide ion. These derivatives possess most of the chemical properties of typical metal alkoxides;² *e.g.*, they react with hydroxylic compounds. A study of the

(2) D. C. Bradley, *Progr. Inorg. Chem.*, **2**, 303 (1960).