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 ($\rho_{290°K}/\rho_{4.2°K}$) in the single crystal of $WO_{2.59}F_{0.41}$ 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 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.

Acknowledgments.—The method of preparation utilized in this paper was suggested by T. E. Gier. The electrical data were obtained by J. L. Gillson, the single-crystal X-ray data by C. M. Foris, and the reflectance data by E. Wallace. Discussions with J. R. Barkley concerning the reflectance data are gratefully acknowledged.

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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 $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ is the starting compound, the product depends upon the reaction conditions. At room temperature the cluster $Mo_6(OCH_3)_8{}^{4+}$ remains virtually untouched and the derivative $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$ 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 $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$ 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 paper[1] 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 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

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reactions of phenol with both $Na_2[(Mo_6Cl_8)(OCH_3)_6]$ and $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ is here reported, with particular emphasis on the behavior of the methoxy groups of the $Mo_6(OCH_3)_8{}^{4+}$ cluster.

Experimental Section

Materials.—The molybdenum(II) cluster alkoxides were prepared as previously reported.[1] Reagent grade phenol was dried by distillation from a benzene solution. After removal of the water–benzene azeotrope and the excess benzene, the phenol was distilled at reduced pressure under nitrogen. Methanol was dried by distillation over magnesium methoxide in a stream of nitrogen. Ether and toluene were dried over sodium and distilled under nitrogen. Acetonitrile was distilled over phosphorus pentoxide in a stream of nitrogen.

$Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$.—A solution of 12.62 g (134.1 mmol) of phenol in 200 ml of toluene was added to a solution of 14.64 g (13.41 mmol) of $Na_2[(Mo_6Cl_8)(OCH_3)_6]$ in 50 ml of methanol. The reaction flask was then placed in an oil bath and all of the methanol was distilled off as an azeotrope under a slow stream of nitrogen. The oil bath temperature ultimately reached 155°. The reddish brown oil which precipitated eventually solidified into a yellow crystalline product. After the mixture was cooled, the precipitate was removed by filtration and washed several times with toluene and then with ether. All operations were performed under nitrogen. The product weighed 19.4 g (98.8%) after it was dried at 100° under vacuum. *Anal.* Calcd for $C_{36}H_{30}Cl_8Mo_6Na_2O_6$: C, 29.54; H, 2.07; Cl, 19.37; Mo, 39.32; Na, 3.14. Found: C, 29.70; H, 2.25; Cl, 19.4; Mo, 39.2; Na, 3.18.

$Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$.—A solution of 7.5 g (79.69 mmol) of phenol in 150 ml of toluene was added to a solution of 8.7 g (8.24 mmol) of $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ in 30 ml of methanol. This and subsequent operations were performed under dry, oxygen-free nitrogen. The reaction flask, equipped with a stopcock adapter, was then evacuated by means of an oil pump, and the volatiles were collected in a pair of traps cooled with liquid nitrogen, while the reaction mixture was being stirred with a magnetic stirrer. No attempt was made to heat the solution, which, because of the rapid rate of evaporation, cooled considerably below room temperature. When about half of the solvent had been removed, fresh toluene was added to restore the original volume and pumping was resumed. The process was repeated two times. Eventually the reaction mixture consisted of a yellow-brown crystalline precipitate suspended in a dark brown solution. The precipitate was filtered, washed several times with toluene and then with ether, and dried under vacuum at 110°. It then weighed 7.2 g (61.2%). *This derivative, like the starting methoxide, is pyrophoric and should be handled and stored under nitrogen.* *Anal.* Calcd for $C_{44}H_{54}Mo_6Na_2O_{14}$: C, 37.00; H, 3.81; Mo, 40.30; Na, 3.22. Found: C, 37.62; H, 3.75; Mo, 39.4; Na, 3.14.

$Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$.—(a) A solution of 7.85 g of $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ in 64 g of phenol was heated at 100° by means of an oil bath for 1 hr under a slow stream of nitrogen. All subsequent operations were also performed under nitrogen. The phenol was distilled off by heating at 80° (oil bath temperature) under vacuum (0.1 mm). The dark brown residue was then heated at 120° under vacuum to constant weight. The yield was quantitative. Upon exposure to atmospheric oxygen the compound undergoes an exothermic reaction and turns black. *Anal.* Calcd for $C_{64}H_{62}Mo_6Na_2O_{14}$: C, 45.84; H, 3.73; Mo, 34.33; Na, 2.74. Found: C, 45.11; H, 3.80; Mo, 33.6; Na, 2.63.

(b) A solution of 8 g (85 mmol) of phenol in 150 ml of toluene was added to a solution of 5 g (4.73 mmol) of $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ in 20 ml of methanol. Again all operations were performed under nitrogen. The reaction flask was placed in an oil bath, and the methanol was distilled off as an azeotrope by heating the bath to 170°. A brown oily product, which solidified on cooling, formed. It was ground with a spatula, filtered, washed several times with toluene, and dried under vacuum at 120°; yield 5.1 g (64.2%). Its physical and chemical properties and infrared spectra are identical with those of the compound obtained by method a. *Anal.* Found: C, 45.08; H, 3.97.

Analytical Procedures.—Molybdenum was determined as the trioxide after wet oxidation with sulfuric and nitric acids, precipitation as sulfide, and ignition to the oxide. Halogens were determined by Volhard titration after fusion with sodium carbonate in platinum. Sodium was determined by flame photometry after wet oxidation of the sample with sulfuric and nitric acids. Carbon and hydrogen were determined by standard procedures. Some of the cluster compounds reported could not be completely freed from possible impurities. This fact coupled with difficulties in handling the compounds probably accounts for the deviation of the analytical values from the calculated values.

Spectra.—Infrared spectra between 500 and 3500 cm^{-1} were recorded with a Perkin-Elmer 337 grating spectrophotometer for either Nujol or hexachlorobutadiene mulls between KBr disks. The spectra in the 200–600-cm^{-1} region were recorded with a Perkin-Elmer 621 grating spectrophotometer for Nujol mulls between polyethylene disks 0.8 mm thick. The mulls were prepared and placed between the disks in a bag filled with dry nitrogen, and the spectra were then immediately recorded.

Proton magnetic resonance spectra were recorded at 56.4 Mc/sec at 32° with a Varian DP-60 instrument. Samples were prepared and sealed under nitrogen. Tetramethylsilane was used as an internal standard.

Magnetic Measurements.—Magnetic susceptibilities were measured by the Gouy method with a magnetic balance made from a Varian magnet and a modified Mettler H16 balance. Samples were prepared and sealed under nitrogen. The sample tube was calibrated with $Hg[Co(NCS)_4]$ and freshly distilled water.

Results and Discussion

General Data.—The reaction of $Na_2[(Mo_6Cl_8)(OCH_3)_6]$ with excess phenol in toluene–methanol solution yields the phenoxy derivative $Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$ as a yellow crystalline precipitate upon removal of the methanol. Its diamagnetism and its spectral properties (described later) indicate that this derivative probably has a structure analogous to that of the starting methoxide.

Reaction between $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ and phenol gives compounds which appear to have retained the basic hexamolybdenum(II) cluster structure but with part of the methoxy groups replaced by phenoxy groups. The extent of the replacement appears to depend on the reaction conditions. When the starting methoxide is treated with phenol (about 1:10 molar ratio) in toluene–methanol solution, a compound with a composition corresponding to $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$ is isolated in good yield upon removal of most of the methanol under vacuum at or below room temperature. Because of the presence of phenoxy groups in the molecule, the oxidation number of molybdenum could not be determined by the usual method.[1] Modifications of the procedure also gave erratic results. However, the compound is both very sensitive to oxygen and diamagnetic, facts strongly indicating that the molybdenum(II) cluster is retained. It appears that, at room temperature, the six ligand methoxy groups of the starting $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ are readily replaced by phenoxy groups, whereas the $\{Mo_6(OCH_3)_8\}^{4+}$ cluster remains largely untouched. Such a difference in reactivity between the ligand and cluster methoxy groups in

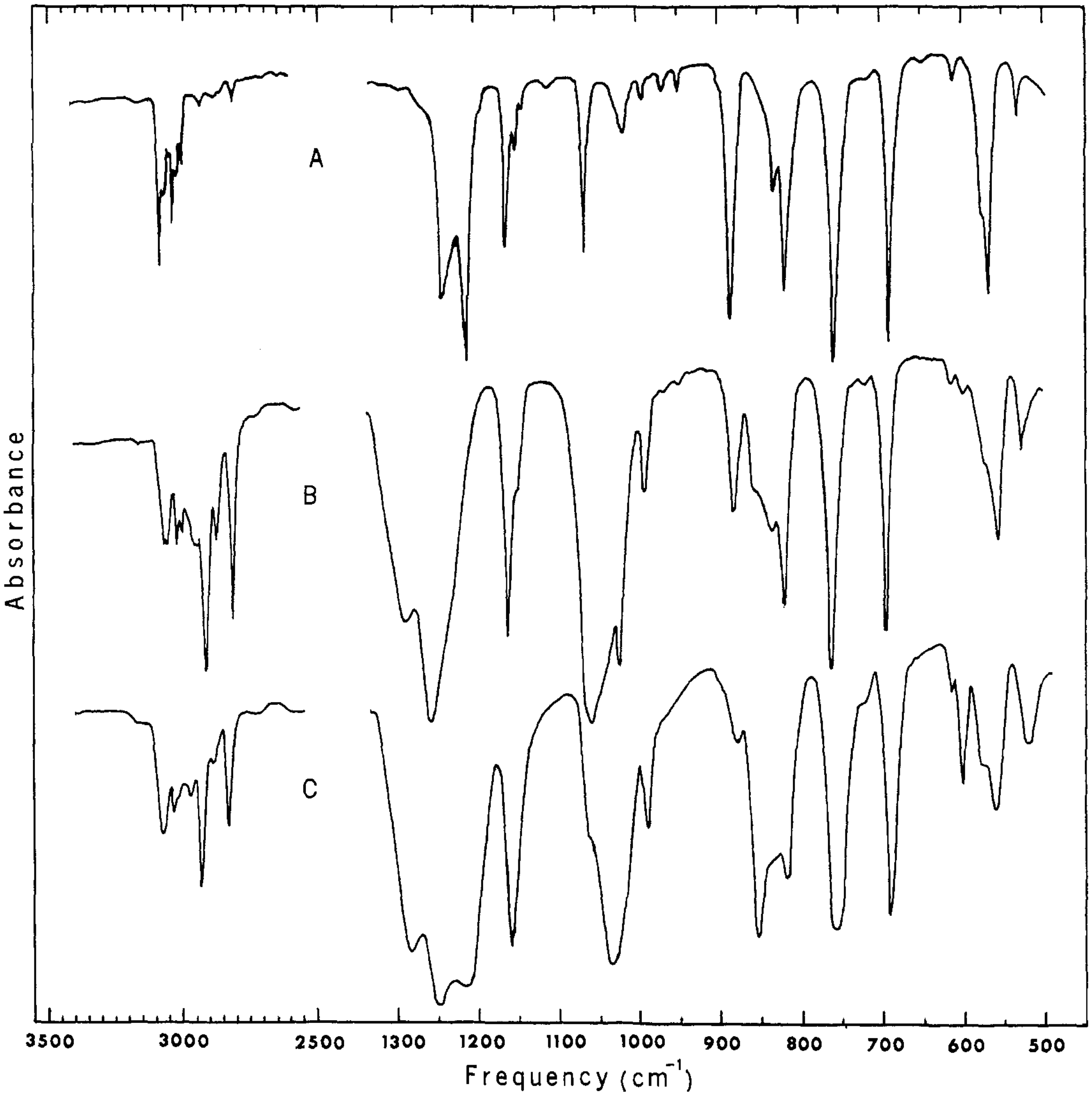

Figure 1.—Infrared spectra in Nujol mull (500–1300 cm^{-1}) and hexachlorobutadiene mull (2500–3500 cm^{-1}) of: A, $Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$; B, $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$; C, $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$.

the starting compound is not unexpected. However, this difference does not seem to be as striking as in the case for ligand and cluster halogen ions in molybdenum(II) halides. Attempts have been made to measure both conductivity and molecular weight of this phenoxy derivative dissolved in various solvents. Unfortunately the solutions, on handling, decompose too rapidly in spite of all precautions. Decomposition is indicated by considerable darkening and, in some cases, separation of a solid. No problems were encountered in recording the infrared and pmr spectra presented later.

When $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ is heated in phenol at 100° or, alternatively, methanol is stripped from a boiling toluene–methanol solution of the reagents, a compound of composition corresponding to $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$ is formed. Like $Na_2[Mo_6(OCH_3)_8](OC_6H_5)_6$ this compound is oxygen sensitive and diamagnetic. The same difficulties mentioned with regard to working with $Na_2[Mo_6(OCH_3)_8](OC_6H_5)_6$ are also encountered when trying to determine the oxidation number of molybdenum, conductivity, and molecular weight for this derivative. However, the infrared and pmr spectra presented later are in agreement with the proposed formulation, in which half of the cluster methoxy groups are replaced by phenoxy groups. It is interesting to note that, under the above experimental conditions, no more than four methoxy groups per cluster appear to be susceptible to replacement b phenoxy groups. Perhaps steric problems are involve If, as seems likely, replacement occurs *via* an S$_N$2 mechanism, once four phenoxy groups have become incorporated into the cluster, additional nucleophilic attack could be made difficult by crowding around the molybdenum atoms. The possibility that the product with four methoxy groups per cluster is a mixture of compounds with different numbers of methoxy groups per cluster appears to be ruled out by the fact that products of the same composition with identical chemical, physical, and spectral properties are obtained by heatin $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ with varying excesses of phenol under different reaction conditions.

Infrared Spectra.—Figure 1 shows portions of the infrared spectra of the three phenoxy derivatives in the

500–3500-cm^{-1} range. The spectrum of $Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$ (curve A) shows only absorptions associated with the phenoxy groups. In the spectrum of $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$ (curve B) the CH stretchings of the methyl groups show up as a series of bands between 2800 and 3000 cm^{-1}, and the CO stretching of the methoxy groups[1] appears as a very strong absorption at about 1060 cm^{-1}. The rest of the spectrum remains substantially unchanged except for minor features, like the weak peak at about 610 cm^{-1} and the shoulder at about 860 cm^{-1}, which become much more intense in the spectrum of $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$ (curve C). Both weak absorptions may be due to the presence, in $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$, of impurities of higher substituted derivatives. The spectrum of $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$ (curve C) shows the same characteristics, with the exception of the two more intense peaks mentioned before and the presence of three strong absorptions in the 1200–1300-cm^{-1} region, instead of two. These absorptions are probably associated with the CO stretching of the phenoxy groups. The appearance of these new features in the spectrum of $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$ supports the idea that there are two types of phenoxy groups in the molecule, namely, ligand and cluster phenoxy groups.

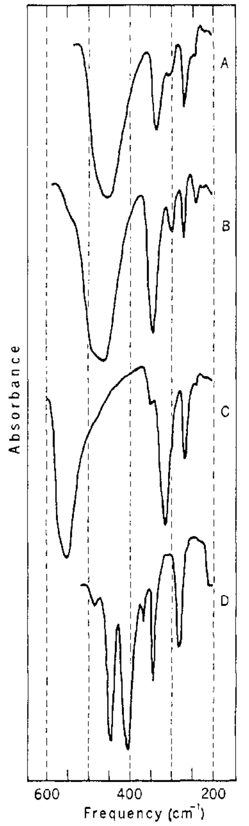

Figure 2.—Infrared spectra in Nujol mull of: A, $Na_2[(Mo_6Br_8)(OCH_3)_6]$; B, $Na_2[(Mo_6Cl_8)(OCH_3)_6]$; C, $Na_2[(Mo_6Cl_8)(OC_2H_5)_6]$; D, $Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$.

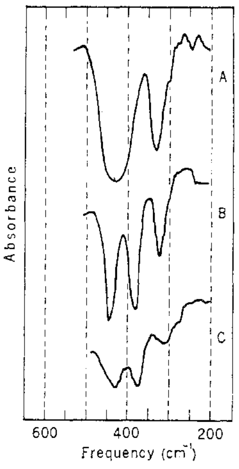

Figure 3.—Infrared spectra in Nujol mull of: A, $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$; B, $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$; C, $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$.

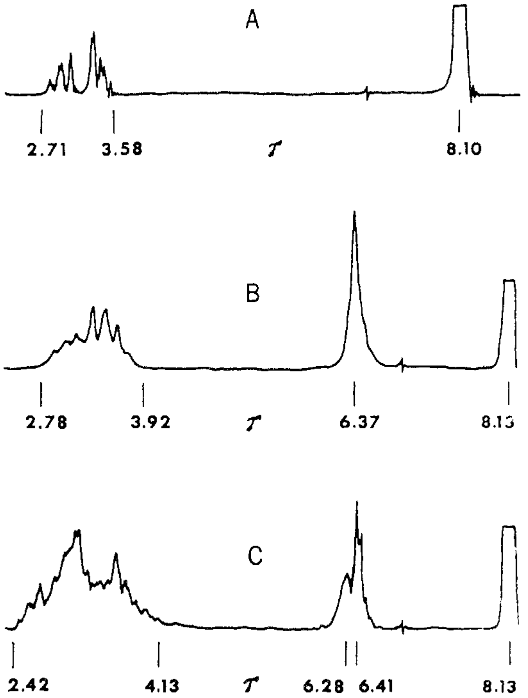

Figure 4.—Proton magnetic resonance spectra of: A, $Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$, 28.2% solution in acetonitrile; B, $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$, 38.2% solution in acetonitrile; C, $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$, 30.0% solution in acetonitrile.

Figures 2 and 3 show spectra in the 200–600-cm^{-1} range for the phenoxy derivatives and also for all of the other molybdenum(II) cluster alkoxides prepared so far.[1] In a number of transition metal alkoxides the metal–oxygen stretchings are reported to absorb in the upper part of this region,[3–5] and some of the absorptions associated with the $Mo_6X_8^{4+}$ cage can be found in the 200–350-cm^{-1} range.[6–9] The changes in the spectra with changes in ligand and cluster ions give some indica-

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tion of the origin of some absorptions. However, without infrared absorptions to even lower frequencies and Raman spectra, no conclusive assignments can be made.

Proton Magnetic Resonance Spectra.—The pmr spectra of the three phenoxides in acetonitrile solution are shown in Figure 4. The spectrum of $Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$ (curve A) shows, between 2.71 and 3.58 ppm, the peaks of the phenyl protons, in addition to the signal of the solvent protons at 8.10 ppm. In the case of $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$ (curve B), in addition to the phenyl protons between 2.78 and 3.92 ppm, the signal of the methyl protons appears as a fairly sharp peak at 6.37 ppm. The peak at 8.13 ppm is due to the solvent. The ratio between the area of the methyl signal and that of the phenyl is appropriate for $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$. All these characteristics strongly support the cluster formulation used. In the spectrum of $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$ (curve C) the signal of the methyl protons collapses to a multiplet with two main peaks at 6.28 and 6.41 ppm. This splitting may be due to the fact that, upon introduction of some phenoxy groups in the cluster, the remaining methoxy groups become magnetically nonequivalent. An even more complicated situation exists in the case of the phenyl protons. In addition to ligand phenoxide ions, there are now magnetically nonequivalent cluster phenoxy groups. Indeed, the pattern of their pmr signal, between 2.42 and 4.13 ppm, is considerably more complex than in the other two derivatives. Again, the ratio between the total area of the phenyl signal and that of the methyl is exactly as required for $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$.

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Notes

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The Tin-119m Mössbauer Isomer Shift and the Valence State of Tin in Transition Metal Compounds

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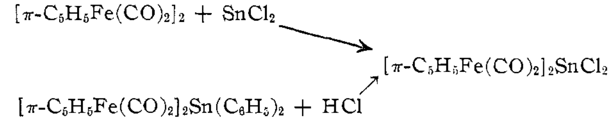
The reaction of tin(II) halides with transition metal halides has been extensively investigated,[2] and the products have been variously described as containing tin(II) donor groups or tin(IV)–metal bonds. The anionic products from platinum metal halides have been described as derivatives of tin(II) where the trihalostannate(II) ion acts as a donor ligand toward the platinum metal.[3] The infrared spectra of these compounds have been interpreted in terms of a σ-donating trichlorostannate(II) group,[3c, 4] and the high *trans* effect,[3b] as well as infrared[5] and F^{19} nmr[6] data, has been used as evidence that the trichlorostannate(II) ion is a weak σ donor and a strong π acceptor. Two modes of reaction are suggested: reduction of the platinum metal halide by tin(II) followed by complexation with the remaining excess tin(II) species or ligand replacement of chloride by trichlorostannate(II). The replacement of the trichlorostannate(II) group as tin(II) from the anions by pyridine, *p*-toluidine, triphenylphosphine, and carbon monoxide[3a] is taken as evidence for the nature of tin in the anionic species.

Several reactions of tin(II) materials give products with tin formally in the IV oxidation state,[7] identical with those prepared from tin(IV) sources,[8] for example



$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 + SnCl_2 \rightarrow [\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2 \leftarrow [\pi\text{-}C_5H_5Fe(CO)_2]_2Sn(C_6H_5)_2 + HCl$$

π-$C_5H_5Fe(CO)_2I$ produces π-$C_5H_5Fe(CO)_2SnCl_2I$ in an analogous reaction which may proceed through an intermediate tin(II) chloride coordination with the metal followed by iodine migration.[9] The possibility of a tin(II) carbeneoid species whose insertion would result in a tin(IV) product has also been raised.[7,10]

We sought by the use of ^{119m}Sn Mössbauer spectroscopy to test the valence state of the tin atom in a typical series of tin–transition metal derivatives prepared from tin(II) chloride. It is the practice of inorganic chemists to distinguish the formal oxidation states of tin(II) and tin(IV) and further to write electronic con-

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