

(aca)<sub>2</sub> were determined by the Gouy method.<sup>4b</sup> Sample tubes were calibrated with Hg[Co(SCN)<sub>4</sub>].

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(4b) Chap. 6 in "Modern Coordination Chemistry," by B. N. Figgis and J. Lewis, edited by J. Lewis and R. G. Wilkins, Interscience Publishers, Inc., New York, N. Y., 1960.

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## The Reactions of Some Oxygen Donors with Molybdenum Pentachloride: Coordination Compounds of Molybdenum(V) Oxotrichloride and Molybdenum(VI) Dioxodichloride

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The reactions of the donor molecules triphenylarsine oxide, triphenylphosphine oxide, and dimethylsulfoxide with molybdenum pentachloride have been investigated. The new compound MoCl<sub>5</sub>·(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsO has been prepared, but analogous compounds using triphenylphosphine oxide and dimethylsulfoxide could not be prepared. Some complexes of the oxychlorides of molybdenum have been prepared by two routes: the reaction of the donor molecules with solutions of molybdenum pentachloride or with solutions of the oxychlorides themselves. The new compounds MoOCl<sub>3</sub>·2(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PO, MoO<sub>2</sub>Cl<sub>2</sub>·2(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PO, MoOCl<sub>3</sub>·2(CH<sub>3</sub>)<sub>2</sub>SO, MoO<sub>2</sub>Cl<sub>2</sub>·2(CH<sub>3</sub>)<sub>2</sub>SO, MoOCl<sub>3</sub>·2(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsO, MoO<sub>2</sub>Cl<sub>2</sub>·2(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsO, MoOCl<sub>3</sub>·(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsO·(CH<sub>3</sub>)<sub>2</sub>CO, and MoO<sub>2</sub>Cl<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>NO have been prepared. The compounds have been characterized by magnetic moment measurements, melting points, and infrared spectra.

### Introduction

In recent years, considerable attention has been focused upon the donor behavior of various oxygen-type donor molecules toward metal salt acceptor species. Several decades ago the syntheses of triphenylphosphine oxide-metal complexes were reported.<sup>1</sup> Recently the behavior of phosphine oxides as ligands has been elucidated more fully.<sup>2,3</sup> Lindqvist<sup>4</sup> has reported complete structure determinations for a few crystalline complexes of phosphine oxides with metal halides. Cotton<sup>5</sup> has published a complete analysis of the infrared spectra of triphenylphosphine oxide complexes. A study of the donor properties of triphenylarsine oxide has been carried out in this Laboratory,<sup>6</sup>

while compounds of triphenylarsine oxide with some metal carbonyls have been reported from Hieber's laboratory.<sup>7,8</sup>

The preparation and properties of compounds using dimethylsulfoxide as the donor group have been reported<sup>9-11</sup> and Drago<sup>12</sup> has prepared and studied the infrared spectra of some similar complexes. Complexes of pyridine N-oxide have been reported by Quagliano and workers in our own Laboratory,<sup>13</sup> along with a complete study of their infrared spectra.<sup>14</sup> Other compounds of pyridine-N-oxide have been synthesized by Carlin,<sup>15</sup> and some visible spectra measurements reported.

We wished to extend the study of oxygen donor

- (1) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 262 (1906).
- (2) J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **80**, 4775 (1958).
- (3) (a) F. A. Cotton, E. Bannister, R. Barnes, and R. H. Holm, *Proc. Chem. Soc. (London)*, 158 (1959); (b) F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1873, 1878, 2276 (1960).
- (4) (a) I. Lindqvist and C.-I. Branden, *Acta Cryst.*, **12**, 642 (1959); (b) C.-I. Branden and I. Lindqvist, *Acta Chem. Scand.*, **14**, 726 (1960); (c) I. Lindqvist, private communication.
- (5) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).
- (6) D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961).

- (7) W. Hieber and A. Lipp, *Chem. Ber.*, **92**, 2075 (1959).
- (8) G. Franz, dissertation, Technischen Hochschule, München, 1959.
- (9) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).
- (10) I. Lindqvist and P. Einarsson, *Acta Chem. Scand.*, **13**, 420 (1959).
- (11) D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 8013 (1960).
- (12) R. S. Drago and Devon Meek, *J. Phys. Chem.*, **65**, 1446 (1961).
- (13) J. V. Quagliano, T. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 3770 (1961).
- (14) J. V. Quagliano, *et al.*, to be published.
- (15) R. L. Carlin, *J. Am. Chem. Soc.*, **83**, 3773 (1961).

compounds with metal halides by preparing complexes of  $\text{MoCl}_5$  with various oxygen donors. The compound  $\text{MoCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$  was prepared fairly readily early in the research by the reaction of its two components in a  $\text{CCl}_4\text{-CH}_2\text{Cl}_2$  solution.

The attempted synthesis of the analogous triphenylphosphine oxide complex gave products which obviously were mixtures of two substances, one green and one orange. The mole ratio in which the reactants were mixed influenced the color of the product, but analyses showed that no product retained a Cl/Mo ratio greater than 3 and that some were as low as 2. The physical properties of the products differed sharply from the properties of the  $\text{MoCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$  complex. Analyses and infrared spectra indicated that the products were mixtures of the complexes  $\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$  and  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ . The latter complexes were prepared independently starting with the appropriate molybdenum oxychlorides. After these compounds had been prepared other complexes of  $\text{MoOCl}_3$  and  $\text{MoO}_2\text{Cl}_2$  were prepared in a straightforward manner, using various other oxygen donors as ligands.

### Experimental

**Reagents.**—Reagent grade chemicals were used without further purification except in the cases noted.

Carbon tetrachloride and methylene chloride, used as solvents in some preparations, were dried over calcium chloride and saturated with dry nitrogen. Triphenylarsine oxide was prepared from Eastman "White Label" triphenylarsine<sup>16</sup>; observed m.p.: 192–194°, 193–195°. Phillips and Tyree observed a m.p. of 194.5–196°.

Triphenylphosphine oxide was prepared from Eastman "White Label" triphenylphosphine, using the foregoing procedure.

Pyridine N-oxide, obtained from the K and K Chemical Company, was purified by vacuum distillation,<sup>17</sup> and stored in a moisture-free container.

Molybdenum(VI) dioxodichloride was prepared by the chlorination of  $\text{MoO}_3$ ,<sup>18</sup> obtained from S. W. Shattuck Chemical Company. The reaction was carried out in a heavy-walled Pyrex tube at 550°, and the pale yellow  $\text{MoO}_2\text{Cl}_2$  sublimed into a receiving tube. Calcd. for  $\text{MoO}_2\text{Cl}_2$ : Mo, 48.25. Found on two different preparations: Mo, 47.5, 48.5.

Molybdenum(V) oxotrichloride solutions were prepared by dissolving  $\text{MoCl}_5$  obtained from Climax Molybdenum Company in either acetone or ethanol<sup>19</sup> in a nitrogen atmosphere. More nitrogen was bubbled through the green solution to expel the hydrogen chloride evolved.

**Analyses.**—The complexes were decomposed for molybdenum analyses by digestion with concentrated  $\text{H}_2\text{SO}_4$  and

$\text{HNO}_3$  in the usual fashion. For those complexes which did not contain arsenic, the digested sample was diluted, put through a Jones Reductor<sup>20</sup> into Fe(III) solution, and titrated with ceric solution.<sup>21</sup> Since arsenic interferes with the Jones Reductor method, a mercury reduction technique<sup>22</sup> was used on the digested samples containing arsenic. The resulting solution of Mo(V) was titrated with ceric solution.

All chloride analyses were performed gravimetrically, first mixing the solid sample with solid  $\text{AgNO}_3$ , then digesting with fuming  $\text{HNO}_3$ . Interference from the slightly soluble silver molybdate was eliminated by dissolving the filtered precipitate in aqueous ammonia, and reprecipitating with  $\text{HNO}_3$ . The molybdate precipitate did not reform under these conditions.

Carbon and hydrogen analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

**Magnetic Moment Measurements.**—Magnetic susceptibility measurements were performed on finely powdered samples using a conventional Gouy apparatus. The magnet was a Variflux<sup>23</sup> permanent magnet. All measurements were performed using 5-cm. pole faces and a 1-cm. pole gap, giving a field strength of approximately 3000 gauss. The standard used was  $\text{Hg}[\text{Co}(\text{CNS})_4]$ , with an assumed gram susceptibility of  $16.44 \times 10^6$  at 20°. In calculating  $\mu_{\text{eff}}$ , a Curie temperature of 0°K. was assumed. Separate determinations were within 0.02 Bohr magneton of each other.

**Infrared Spectra.**—A Baird Associates recording spectrophotometer, serial No. AB2-193, was used. The spectra were measured on mineral oil mulls of the samples between NaCl plates. Duplicate spectra were taken on several independent preparations of each compound.

**Preparation of Complexes.**—All operations were performed in a nitrogen atmosphere. Most of the complexes were prepared several times. The analyses given are the mean of the results on different preparations.

$\text{MoCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$ .—A red solution of 1.3 g.  $\text{MoCl}_5$  in 100 ml.  $\text{CCl}_4$  was added to 1.6 g. of  $(\text{C}_6\text{H}_5)_3\text{AsO}$  dissolved in 50 ml.  $\text{CH}_2\text{Cl}_2$ . The resulting green solution was evaporated until clouding occurred. It was stoppered and stored at  $-10^\circ$  for several days. At the end of this period, bright green crystals had formed. The product was washed with  $\text{CCl}_4$ , in which it is insoluble, and dried. Attempts to prepare the product in  $\text{CCl}_4$  solvent resulted in the precipitation of a bright green oil, very difficult to crystallize. Removal of too much  $\text{CH}_2\text{Cl}_2$  by evaporation from the mixed solvent system also caused formation of the green oil. Both the oil and the crystals are extremely sensitive to air or moisture, turning blue and evolving HCl. Both are soluble in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , but insoluble in benzene and  $\text{CCl}_4$ ; m.p. 78–81°. *Anal.* Calcd. for  $\text{MoCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$ :

(20) W. W. Scott, "Standard Methods of Chemical Analysis," N. H. Furman, ed., Vol. 1, D. Van Nostrand Company, Inc., New York, N. Y., 1925, p. 595.

(21) G. F. Smith and W. H. Fly, *Anal. Chem.*, **21**, 1233 (1949).

(22) I. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. 3, "Titration Methods," Interscience Publishers, Inc., New York, N. Y., 1957, p. 153.

(23) Changing the position of shunt rings, size of pole faces, and pole gap makes it possible to vary the field intensity of this magnet, produced by the Laboratory for Science, Oakland, California.

(24) B. N. Figgis and J. Lewis, in J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, pp. 415–416.

(16) R. L. Shriner and C. N. Wolf, *Organic Syntheses*, **30**, 97 (1950).

(17) Performed by Mr. D. L. Venezky.

(18) I. Nordenskjöld, *Ber.*, **34**, 1575 (1901).

(19) William Wardlaw and H. Webb, *J. Chem. Soc.*, 2100 (1930).

Cl, 29.77; Mo, 16.12; C, 36.31; H, 2.54. Found: Cl, 28.37; Mo, 16.09; C, 35.72; H, 3.17.

**Attempt to Prepare  $\text{MoCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{PO}$ .**—A red solution of  $\text{MoCl}_5$  in  $\text{CCl}_4$  was added slowly to a solution of  $(\text{C}_6\text{H}_5)_3\text{PO}$  in  $\text{CH}_2\text{Cl}_2$ . The red color faded to light green and, on swirling, to bright yellow. The bright yellow color was observed when the mole ratio of  $(\text{C}_6\text{H}_5)_3\text{PO}$  to  $\text{MoCl}_5$  was 4:1 or greater. As more  $\text{MoCl}_5$  solution was added, the red color faded more slowly and the mixed solution remained green instead of turning yellow. The experiment was performed several times, stopping the addition of  $\text{MoCl}_5$  at various stages of solution colors ranging from orange-yellow to green. Evaporation of the solutions resulted in the formation of crystals of corresponding colors. Solutions which contained a very large excess of  $(\text{C}_6\text{H}_5)_3\text{PO}$  yielded orange-yellow crystals. Green solutions which contained only about a 2:1 mole ratio of  $(\text{C}_6\text{H}_5)_3\text{PO}$  to  $\text{MoCl}_5$  yielded green crystals. Other products were varying shades of greenish-yellow. When  $\text{CH}_2\text{Cl}_2$  was employed as the solvent for both starting materials, the same type of results was obtained. Use of excess  $\text{CCl}_4$  in the solvent system precipitated a green oil. The oil dissolved in acetone and green crystals were obtained from the resulting solution.

Both green and yellow products were soluble in  $\text{CH}_2\text{Cl}_2$  and insoluble in  $\text{CCl}_4$  and cyclohexane. Both types of crystals were unaffected by air and moisture. Analytical results on the orange crystals correspond most nearly to the formula  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ , while determinations on the green products approached values corresponding to the formula  $\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ .

**$\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ .**—A colorless solution of 1.7 g.  $\text{MoO}_2\text{Cl}_2$  dissolved in 100 ml.  $\text{CH}_2\text{Cl}_2$  and about 5 ml. ethanol was added to 4.7 g.  $(\text{C}_6\text{H}_5)_3\text{PO}$  dissolved in 50 ml.  $\text{CH}_2\text{Cl}_2$ . The combined solution was bright orange. Warming and evaporation caused bright orange-yellow crystals to form. When filtered, washed with  $\text{CCl}_4$ , and dried the crystals were insensitive to air or water. They are soluble in  $\text{CH}_2\text{Cl}_2$ , less soluble in acetone, and insoluble in  $\text{CCl}_4$  and cyclohexane; m.p. 216–218°. Their color slowly turned from orange to colorless at 175–185°. *Anal.* Calcd. for  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ : Cl, 9.39; Mo, 12.70; C, 57.24; H, 4.00. Found: Cl, 9.34; Mo, 12.66; C, 56.47; H, 3.95.

**$\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ .**—To a green solution of 2.2 g. of  $\text{MoCl}_5$  dissolved in 50 ml. absolute ethanol was added 2.2 g. of  $(\text{C}_6\text{H}_5)_3\text{PO}$  in 25 ml. of ethanol. The mixture was evaporated to a smaller volume, yielding a crop of light green crystals. The crystals were washed with ethanol and dried. Only after many days exposure to moist air did they darken and turn blue. The product is soluble in acetone, ethanol, and  $\text{CH}_2\text{Cl}_2$ , but insoluble in  $\text{CCl}_4$ ; m.p. 221–224°. *Anal.* Calcd. for  $\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ : Cl, 13.73; Mo, 12.38; C, 55.80; H, 3.90. Found: Cl, 13.63; Mo, 12.48; C, 55.45; H, 4.09.

**$\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$ .**—A colorless solution of 1.2 g.  $\text{MoO}_2\text{Cl}_2$  in 100 ml.  $\text{CH}_2\text{Cl}_2$  and 5 ml. ethanol was added to a solution of 3.9 g.  $(\text{C}_6\text{H}_5)_3\text{AsO}$  in 50 ml.  $\text{CH}_2\text{Cl}_2$ . Addition of small quantities of  $\text{CCl}_4$  and evaporation caused the precipitation of a greenish-white powder, which was filtered, washed with  $\text{CCl}_4$ , and dried. The product is insoluble in  $\text{CCl}_4$  and only slightly soluble in  $\text{CH}_2\text{Cl}_2$ , acetone, and ethanol. It apparently is unaffected by moist air; m.p. 243–244°. *Anal.* Calcd. for  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$ : Cl,

8.41; Mo, 11.38; C, 51.27; H, 3.59. Found: Cl, 8.21; Mo, 11.79; C, 51.52; H, 3.67.

**$\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$ .**—To a green solution of 2.1 g.  $\text{MoCl}_5$  in 50 ml. ethanol was added a solution of 5.1 g.  $(\text{C}_6\text{H}_5)_3\text{AsO}$  in 50 ml. ethanol. A brown tar precipitate formed. Warming caused the tar to dissolve and further evaporation produced light green crystals. The crystals were filtered, washed with ethanol, and dried. Prolonged exposure to moist air causes the product to darken and turn blue. The crystals are soluble in ethanol, soluble with decomposition in warm  $\text{CH}_2\text{Cl}_2$ , and insoluble in acetone and  $\text{CCl}_4$ ; m.p. 218–220°. *Anal.* Calcd. for  $\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$ : Cl, 12.33; Mo, 11.12; C, 50.12; H, 3.51. Found: Cl, 12.32; Mo, 11.35; C, 49.16; H, 3.43.

**$\text{MoOCl}_3 \cdot (\text{C}_6\text{H}_5)_3\text{AsO} \cdot (\text{CH}_3)_2\text{CO}$ .**—To a green solution of 3.4 g.  $\text{MoCl}_5$  in 50 ml. acetone was added a solution of 3.3 g.  $(\text{C}_6\text{H}_5)_3\text{AsO}$  in 50 ml. acetone. Evaporation and freezing of the solution resulted in the formation of oily green crystals. Washing with cold acetone and drying yielded finely divided light green crystals, only slowly attacked by moist air. The product is soluble in acetone,  $\text{CH}_2\text{Cl}_2$ , and soluble with decomposition in ethanol. It is insoluble in  $\text{CCl}_4$ ; m.p. 95–97°. *Anal.* Calcd. for  $\text{MoOCl}_3 \cdot (\text{C}_6\text{H}_5)_3\text{AsO} \cdot (\text{CH}_3)_2\text{CO}$ : Cl, 17.77; Mo, 16.03; C, 40.13; H, 3.54. Found: Cl, 17.39; Mo, 16.01; C, 41.08; H, 4.00.

**Attempt to Prepare  $\text{MoCl}_5 \cdot (\text{CH}_3)_2\text{SO}$ .**—A red solution of 2.5 g.  $\text{MoCl}_5$  in 100 ml.  $\text{CCl}_4$  was added to a solution of 2 ml. of  $(\text{CH}_3)_2\text{SO}$  in 50 ml.  $\text{CCl}_4$ . A green oil formed which solidified on scratching. As addition of the  $\text{MoCl}_5$  solution was continued, more green solid precipitated. A strong odor of mercaptans was observed. After washing with  $\text{CCl}_4$  and drying, the resulting green powder still smelled strongly of mercaptans. The product was highly sensitive to air and moisture, turning blue upon exposure. It is insoluble in  $\text{CCl}_4$ , and slightly soluble in  $\text{CH}_2\text{Cl}_2$  and acetone. Repetitions of the experiment gave essentially the same results. Analytical determinations on the product corresponded most nearly to the formula  $\text{MoOCl}_3 \cdot 2(\text{CH}_3)_2\text{SO}$ .

**$\text{MoOCl}_3 \cdot 2(\text{CH}_3)_2\text{SO}$ .**—To a green solution of 3.4 g.  $\text{MoCl}_5$  in 50 ml. ethanol was added a solution of 1 ml.  $(\text{CH}_3)_2\text{SO}$  in 25 ml. ethanol. The solution was evaporated to a smaller volume, and stored for two days at  $-10^\circ$ . At the end of this time green crystals had formed. The crystals were washed with cold ethanol, filtered, and dried. The product is soluble in acetone with decomposition, slightly soluble in ethanol and  $\text{CH}_2\text{Cl}_2$ , and insoluble in  $\text{CCl}_4$ . The product is quite sensitive, turning blue on brief exposure to moist air; m.p. 140–142°. *Anal.* Calcd. for  $\text{MoOCl}_3 \cdot 2(\text{CH}_3)_2\text{SO}$ : Cl, 28.40; Mo, 25.62; C, 12.83; H, 3.23. Found: Cl, 28.68; Mo, 25.68; C, 13.96; H, 3.40.

**$\text{MoO}_2\text{Cl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$ .**—Two g. of  $\text{MoO}_2\text{Cl}_2$  was dissolved in 100 ml.  $\text{CH}_2\text{Cl}_2$  containing a few ml. ethanol. One ml. of  $(\text{CH}_3)_2\text{SO}$  was added dropwise to the solution. White finely divided crystals formed. Precipitation of more crystals was effected by adding an excess of  $\text{CCl}_4$ . The product was filtered, washed with  $\text{CCl}_4$ , and dried. The white crystals apparently are unaffected by brief exposure to moist air, but on standing for a few weeks, even under nitrogen, turn blue. The crystals are slightly soluble in acetone, ethanol, and  $\text{CH}_2\text{Cl}_2$ , and insoluble in  $\text{CCl}_4$ ; m.p. 172–173°. *Anal.* Calcd. for  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$ : Cl, 19.98; Mo, 27.03; C, 13.53; H, 3.41. Found: Cl, 20.01; Mo, 26.80; C, 13.76; H, 3.44.

TABLE I

Compound	M-O frequency (M = N, P, As, S) ( $\text{cm.}^{-1}$ )	Shift due to coördination ( $\text{cm.}^{-1}$ )	$\mu_{\text{eff}}$ , Bohr Magneton
$(\text{C}_6\text{H}_5)_3\text{AsO}$	878		
$\text{MoCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$	750	-128	1.61
$\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$	877, 841	-37	1.74
$\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$	878, 848	-30	Diamagnetic
$\text{MoOCl}_3 \cdot (\text{C}_6\text{H}_5)_3\text{AsO} \cdot (\text{CH}_3)_2\text{CO}$	858	-20	1.73
$(\text{CH}_3)_2\text{CO}$	1718 <sup>26</sup> (M = C)		
$\text{MoOCl}_3 \cdot (\text{C}_6\text{H}_5)_3\text{AsO} \cdot (\text{CH}_3)_2\text{CO}$	1670 (M = C)	-48	
$(\text{C}_6\text{H}_5)_3\text{PO}$	1182		
$\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$	1160, 1145	-37	1.70
$\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$	1162, 1140	-42	0.32
$(\text{CH}_3)_2\text{SO}$	1050		
$\text{MoOCl}_3 \cdot 2(\text{CH}_3)_2\text{SO}$	1032, 999	-18, -51	1.64
$\text{MoO}_2\text{Cl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$	1030, 986	-20, -64	Diamagnetic
$\text{C}_6\text{H}_5\text{NO}$	1243 <sup>14</sup>		
$\text{MoO}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_5\text{NO}$	1205, 1173, 1153	-38	Diamagnetic

$\text{MoO}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_5\text{NO}$ .—A solution of 0.7 g.  $\text{MoO}_2\text{Cl}_2$  in 100 ml.  $\text{CH}_2\text{Cl}_2$  to which 1 or 2 ml. of ethanol had been added was added to a solution of 0.8 g. of  $\text{C}_6\text{H}_5\text{NO}$  in 50 ml.  $\text{CH}_2\text{Cl}_2$ . Evaporation and addition of  $\text{CCl}_4$  precipitated a finely divided white crystalline powder, which was washed with  $\text{CCl}_4$ , filtered, and dried. The product is apparently unaffected by moist air, slightly soluble in ethanol and  $\text{CH}_2\text{Cl}_2$ , but insoluble in acetone and  $\text{CCl}_4$ ; m.p. 180–182°. *Anal.* Calcd. for  $\text{MoO}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_5\text{NO}$ : Cl, 18.23; Mo, 24.66; C, 30.87; H, 2.59. Found: Cl, 17.85; Mo, 24.11; C, 31.13; H, 2.72.

### Results

The complexes are listed in Table I, together with the values of the magnetic moments and the results of study of the infrared spectra. In the infrared spectra of the donor molecules, other workers have assigned M–O stretching frequencies as follows: As–O<sup>6</sup>, 879  $\text{cm.}^{-1}$ ; P–O, 1190,<sup>25</sup> 1180,<sup>2</sup> and 1195<sup>5</sup>  $\text{cm.}^{-1}$ ; S–O,<sup>12</sup> 1045  $\text{cm.}^{-1}$ ; and N–O,<sup>13</sup> 1243  $\text{cm.}^{-1}$ . Our assumptions of stretching frequencies in the free donor molecules do not differ substantially from those listed above. Table I lists the observed M–O stretching frequencies (M = N, P, As, or S) for the free donor molecules and for the complexes prepared. In the complex containing acetone, it is noted that a shift was observed in the carbonyl frequency from the value of 1718  $\text{cm.}^{-1}$ <sup>26</sup> assigned for an uncoördinated C=O group to the lower value of approximately 1670  $\text{cm.}^{-1}$ .

### Discussion

The discrepancy between the donor properties of triphenylphosphine oxide and triphenylarsine

(25) L. W. Daasch and D. C. Smith, "Infrared Spectra of Phosphorus Compounds," NRL Report 3657, Naval Research Laboratory, Washington, D. C., 1950.

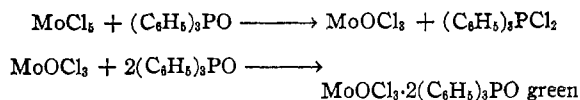
(26) E. J. Hartwell, R. E. Richards, and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

oxide was noted in the difference of the products of their reaction with  $\text{MoCl}_5$ . The reaction of triphenylphosphine oxide with  $\text{MoCl}_5$  produced both a green and an orange product, neither corresponding to the formula  $\text{MoCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{PO}$ . Since analyses indicated the formation of oxychloride complexes, the appropriate oxychlorides of molybdenum were treated with triphenylphosphine oxide. The latter method produced pure  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ , which is orange, and identical in properties to the orange product of the reaction of  $\text{MoCl}_5$  with a large excess of  $(\text{C}_6\text{H}_5)_3\text{PO}$ . Pure  $\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ , which is green, also was produced, and its properties corresponded to the green product of the reaction with  $\text{MoCl}_5$ . The properties which were compared in each case were infrared spectra, melting point, magnetic moment, appearance, and solubility.

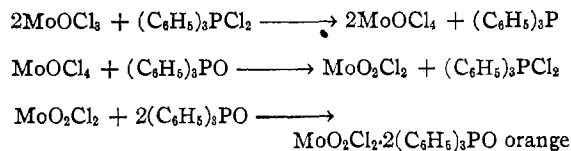
It seems apparent that  $\text{MoCl}_5$  is capable of abstracting the oxygen of  $(\text{C}_6\text{H}_5)_3\text{PO}$  to form  $\text{MoOCl}_3$ , which then forms a complex with the remaining  $(\text{C}_6\text{H}_5)_3\text{PO}$ . Under conditions of a large excess of  $(\text{C}_6\text{H}_5)_3\text{PO}$ , oxidation to  $\text{MoO}_2\text{Cl}_2$  occurs, and the product is the almost pure complex of  $\text{MoO}_2\text{Cl}_2$ . It has been shown previously<sup>27</sup> that  $\text{PCl}_5$  will abstract an oxygen from triethylphosphine oxide, yielding  $(\text{C}_2\text{H}_5)_3\text{PCl}_2$ , which is easily reduced to  $(\text{C}_2\text{H}_5)_3\text{P}$ . It seems likely that some sort of similar reaction occurs in the present case.  $\text{MoOCl}_3$  apparently is formed first, and with excess  $(\text{C}_6\text{H}_5)_3\text{PO}$  the end products are probably  $\text{MoO}_2\text{Cl}_2$  and  $(\text{C}_6\text{H}_5)_3\text{P}$ .

The following sequence of reactions seems reasonable in view of the products obtained

(27) J. N. Collie and F. Reynolds, *ibid.*, 107, 367 (1915).



In a large excess of  $(\text{C}_6\text{H}_5)_3\text{PO}$ , the  $\text{MoOCl}_3$  appears to react further.



It should be noted that the stoichiometry of the reaction producing the orange product requires at least a four-fold excess of  $(\text{C}_6\text{H}_5)_3\text{PO}$ . It was observed that when the mole ratio of  $(\text{C}_6\text{H}_5)_3\text{PO}$  to  $\text{MoCl}_5$  was four or larger, products were obtained which were nearly pure  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ .

Triphenylarsine oxide was the only donor molecule of those tested with which it was possible to prepare a simple addition compound with  $\text{MoCl}_5$ . Even in this case, consistently low results on Cl analyses indicate some tendency toward formation of oxychloride complexes. Preparation of complexes using oxychlorides as starting materials proved quite straightforward.

When acetone was used as the solvent for  $\text{MoCl}_5$ , producing  $\text{MoOCl}_3$ , one  $(\text{CH}_3)_2\text{CO}$  molecule was found to coordinate to the  $\text{MoOCl}_3$  when reacting with  $(\text{C}_6\text{H}_5)_3\text{AsO}$ . When  $\text{MoOCl}_3$  solutions reacted with  $(\text{C}_6\text{H}_5)_3\text{PO}$ , the infrared spectra of the product showed only a very small peak near the carbonyl stretching frequency and analytical methods did not detect any acetone coordination. Under the conditions of the reaction with  $\text{MoOCl}_3$  acetone apparently is comparable in donor properties to  $(\text{C}_6\text{H}_5)_3\text{AsO}$ , but not as good as  $(\text{C}_6\text{H}_5)_3\text{PO}$ .

The reaction of  $\text{MoCl}_5$  with  $(\text{CH}_3)_2\text{SO}$  yielded a product corresponding approximately in properties and analyses to  $\text{MoOCl}_3 \cdot 2(\text{CH}_3)_2\text{SO}$ . There apparently was considerable decomposition as evidenced by the strong odor of mercaptans both in the solution during reaction and in the dried product. The evidence indicates some reaction similar to the case of  $(\text{C}_6\text{H}_5)_3\text{PO}$ , with abstraction of the oxygen to form  $\text{MoOCl}_3$ , and probably also oxidation to  $\text{MoO}_2\text{Cl}_2$  with formation of  $(\text{CH}_3)_2\text{S}$ . When pure oxychlorides of molybdenum were used as the starting materials, the formation of oxychloride complexes of  $(\text{CH}_3)_2\text{SO}$  went forward quite smoothly.

We were not able to prepare a complex corresponding to  $\text{MoOCl}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}$ . Infrared shifts in the N-O frequency of the green product indi-

cated complexing, and reproducible analyses showed approximately a 4:1 Cl to Mo mole ratio. However, no reasonable formula could be proposed to fit the data. The reaction with  $\text{MoO}_2\text{Cl}_2$  to form  $\text{MoO}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_5\text{NO}$  took place readily.

The magnetic moments for all the complexes studied are close to the spin-only value for the molybdenum ion considered. It is interesting to note that the orange  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ , the only colored Mo(VI) complex, has a slight paramagnetism. Although the value of  $\mu_{\text{eff}}$  varied with the purity of the complex, in no case was this complex found to be diamagnetic, as were all other Mo(VI) complexes.

A study of the infrared spectra of the compounds prepared shows that the stretching frequency of the M-O bond (M = N, P, As, or S) is lowered in each case upon coordination. This lowering in frequency is attributed to weakening of the bond by reduction of electron density in the M-O bond when the O coordinates to the Mo atom. An examination of Table I shows that the As-O stretching frequency has undergone an unusually large shift upon the formation of the complex  $\text{MoCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$ . It seems, in view of this large shift, that the As-O bond is weakened almost to the point of the oxygen being entirely lost. We recently have been informed<sup>28</sup> that preliminary results of determinations of the crystal structure of  $\text{SbCl}_5 \cdot (\text{C}_6\text{H}_5)_3\text{AsO}$  show that the length of the As-O bond actually is greater than that of the Sb-O bond. The latter fact seems an interesting analogy to our  $\text{MoCl}_5$  case. Also, it should be remembered that in the reactions of  $\text{MoCl}_5$  with  $(\text{C}_6\text{H}_5)_3\text{PO}$  and  $(\text{CH}_3)_2\text{SO}$ , the oxygen was lost entirely to the  $\text{MoCl}_5$  molecule, forming  $\text{MoOCl}_3$ .

It has been noted before<sup>6</sup> that in complexes containing two or more  $(\text{C}_6\text{H}_5)_3\text{AsO}$  groups per molecule, the As-O peak is split, with one peak appearing at the frequency of the uncoordinated molecule and another at a lower frequency. This splitting was observed in the case of  $\text{MoOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$  and  $\text{MoO}_2\text{Cl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$ . Only a single peak was observed in the spectra of  $\text{MoOCl}_3 \cdot (\text{C}_6\text{H}_5)_3\text{AsO} \cdot (\text{CH}_3)_2\text{CO}$ , which contained only one arsine oxide donor group per molecule.

A value of  $967 \text{ cm.}^{-1}$  has been assigned<sup>29</sup> for the Mo(V)-O stretching frequency. This peak was observed in all  $\text{MoOCl}_3$  complexes and not in Mo-

(28) I. Lindqvist, private communication.

(29) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

$O_2Cl_2$  complexes. The latter fact also was evidence for two separate products in the reaction of  $MoCl_5$  with  $(C_6H_5)_3PO$ , since the green products exhibited a peak at  $967\text{ cm.}^{-1}$ , the orange ones did not, and

obvious mixtures had a small peak in this region.

The visible spectra of several of the complexes reported here have been studied, and will be the subject of a later communication.

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## Synthesis of Fluorometallates in Methanol. Some Structure Relationships. II. Uranium and Group V Metals<sup>1a</sup>

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The complexes  $(NH_4)_3UO_2F_5$ ,  $K_3UO_2F_5$ ,  $(NH_4)_3VOF_5$ ,  $K_3VOF_5$ ,  $(NH_4)_3NbOF_6$ ,  $K_3NbOF_6$ ,  $(NH_4)_3TaOF_6$ , and  $K_3TaOF_6$  were prepared by bromination of the metal in methanol and subsequent precipitation of the fluorometallate by addition of the bromination solution to a solution of the alkali fluoride in methanol. A study of the bromination of uranium in methanol showed that the uranium bromides formed react with methanol to give hydrogen bromide, which further reacts with the metal, hydrogen being evolved. Cell constants of the complexes were determined from X-ray powder data and densities were measured. The uranium complexes were isostructural, as were the vanadium complexes. These complexes appear to be tetragonal and contain eight formula units per unit cell. The niobium and tantalum complexes were isostructural, were face-centered cubic, and contained four formula units per unit cell. Magnetic susceptibility measurements showed that the vanadium complexes contain one unpaired electron per vanadium atom. Infrared studies suggest hydrogen bonding in  $(NH_4)_3UO_2F_5$ .

### Introduction

In previous work,<sup>2,3</sup> alkali fluorometallates of some transition and post-transition metals were prepared from methanol solution. The method of preparation consisted of bromination of the metal in methanol and subsequent addition of the bromination solution to a solution of the alkali fluoride in methanol. The fluorometallates usually precipitate immediately. The present study extends the method to the preparation of some ammonium and potassium oxyfluorometallates of niobium, tantalum, vanadium, and uranium and reports on the structures, magnetic susceptibilities and, in the case of the ammonium complexes, the hydrogen bonding of these complexes.

A study of the bromination of uranium in methanol was carried out to aid in the determination of the optimum conditions for bromination of the metal. Uranium was chosen for this

study because it brominates readily at room temperature, in contrast to the other metals. Since structural data were not available for several of the fluorometallates prepared here, powder diffraction data were used to determine the cell constants of these compounds. Density measurements were made to determine the number of formula units per unit cell. Magnetic measurements and infrared spectra were used to aid in the characterization of the complexes.

### I. The Bromination of the Metals in Methanol Experimental

The metal bromides were prepared by the addition of a small excess of bromine to 0.02 mole of the metal suspended in 100 ml. of dry methanol under a dry atmosphere of nitrogen or air. In each case, the reaction mixture was refluxed until the distillate was colorless. Any residue was removed by filtration. The solutions were used immediately for the precipitation of the fluorometallates. It should be noted that the bromination reactions of uranium and vanadium are rapid and exothermic and may require chilling.

### Discussion of the Bromination Reaction

Ducelliez and Raynaud<sup>4</sup> have brominated manganese in ether solution. Raynaud<sup>5</sup> has

(1) (a) This work was supported in part by the Atomic Energy Commission; (b) From a thesis submitted to the University of New Hampshire by A. E. Baker in partial fulfillment of the requirements for the degree of Doctor of Philosophy; (c) To whom communications should be addressed.

(2) D. S. Crockett and H. M. Haendler, *J. Am. Chem. Soc.*, **82**, 4158 (1960).

(3) H. M. Haendler, F. A. Johnson, and D. S. Crockett, *ibid.*, **80**, 2662 (1958).

(4) F. Ducelliez and A. Raynaud, *Compt. rend.*, **156**, 576 (1914).