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Dichlorodinitrosylmolybdenum, Dichlorodinitrosyltungsten, and Some of Their Derivatives[1]

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The compounds $Mo(NO)_2Cl_2$ and $W(NO)_2Cl_2$ have been prepared by reaction of ClNO with $Mo(CO)_6$ and $W(CO)_6$ in dichloromethane at room temperature. They are reactive, dark green solids which readily combine with additional ligands to give compounds of the type $M(NO)_2Cl_2L_2$, where L = an amine, phosphine, or arsine. They also combine with $[As(C_6H_5)_4]Cl$ to give tetraphenylarsonium salts of the complex anions $[M(NO)_2Cl_4]^{2-}$. The infrared spectra indicate that in all of the compounds prepared, the NO groups occupy *cis* positions in the octahedral group of ligands.

Introduction

Nitrosyl (NO) complexes of the transition elements already form an exceedingly numerous class of compounds, within which there is considerable diversity of chemical, physical, and structural properties.[2] Nonetheless, it appears likely that a great many more remain to be prepared and studied, and this paper constitutes the first report of efforts directed to the systematic preparation of nitrosyl complexes of the group VI (Cr, Mo, W) elements.

Relatively few nitrosyl complexes of the group VI elements have been prepared heretofore. These belong to only a few general groups. First, there are those containing π-cyclopentadienyl groups, represented by the π-cyclopentadienyl metal dicarbonyl nitrosyls, $(\pi\text{-}C_5H_5)Cr(CO)_2NO$,[3,4] $(\pi\text{-}C_5H_5)Mo(CO)_2NO$,[4] $(\pi\text{-}C_5H_5)W(CO)_2NO$,[4] and $(\pi\text{-}CH_3COC_5H_4)Cr(CO)_2NO$,[5] by the series of cyclopentadienylchromium dinitrosyl compounds,[3,6] $(\pi\text{-}C_5H_5)Cr(NO)_2X$, in which X may be CH_3, CH_2Cl, C_2H_5, C_6H_5, $\sigma\text{-}C_5H_5$, Cl, Br, I, SCN, CN, or NO_2, and, most recently, by the binuclear compound[7] $[(\pi\text{-}C_5H_5)Cr(NO)_2]_2$. Second, there are two cyano complexes, $K_4[Mo(CN)_5NO]\cdot 2H_2O$,[8] for which the formula $K_4[Mo(OH)_2(CN)_5NO]$ has more recently been proposed,[9] and $K_3[Cr(CN)_5(NO)]\cdot H_2O$.[9] Finally, there are $[Cr(H_2O)_5NO]SO_4$[10] and the N,N-dialkyldithiocarbamate complexes,[11,12] $Cr(R_2NCS_2)_2(NO)_2$.

It may also be noted that the employment of nitrosyl chloride as a preparative reagent for metal nitrosyl compounds has also been quite limited. Among the very few instances of its successful utilization are in the preparation of some platinum complexes, *viz.*, $K_2[Pt(NO)Cl_5]$, $K_2[Pt(NO)(NO_2)_4Cl]$, and $K_2[Pt(NO)(en)_2Cl]Cl_2$, by reaction of ClNO with four-coordinate Pt(II) compounds,[13] in the preparation of the well-known $Fe(NO)_2(CO)_2$ by action of ClNO upon $Fe(CO)_5$,[14] and in the reaction of ClNO with $Ni(CO)_4$ in the gas phase[15] to give $Ni(NO)Cl_2$.

It has now been found that ClNO reacts readily with $Mo(CO)_6$ and $W(CO)_6$ to produce in good yields $Mo(NO)_2Cl_2$ and $W(NO)_2Cl_2$, which constitute excellent starting materials for the preparation of a host of $Mo(NO)_2$ and $W(NO)_2$ containing compounds. It appears that a diverse and reasonably systematic synthetic chemistry can thus be built up.

Discussion

$Mo(NO)_2Cl_2$ and $W(NO)_2Cl_2$ are obtained as dark green powders which are very hygroscopic. While they decompose rapidly in air, losing nitric oxide, they can be kept without decomposition under vacuum or in an atmosphere of dry nitrogen. The compounds dissolve in water with the evolution of nitric oxide, but dissolve in degassed abolute alcohol, acetone, or acetonitrile without gas evolution. Both compounds are insoluble in nondonor solvents such as benzene, carbon tetrachloride, chloroform, dichloromethane, and alkanes. $Mo(NO)_2Cl_2$ and $W(NO)_2Cl_2$ are thermally stable and do not decompose until >100°. $Cr(CO)_6$ failed to react with ClNO under conditions similar to those used for preparing the molybdenum and tungsten compounds.

The structures of the $M(NO)_2Cl_2$ compounds may be discussed on the basis of their chemical properties and their infrared spectra. Since the compounds are not volatile and dissolve only in solvents with coordinating ability, it seems fairly certain that they must be polymeric. In the individual $Mo(NO)_2Cl_2$ units, the metal atoms could have, at most, 14 electrons in valence shell orbitals, assuming that the metal atoms are zerovalent and the nitric oxide molecules are then to be considered as coordinated NO^+ groups. The frequencies of the NO stretching bands in the parent compounds and in all their derivatives (1600–1805

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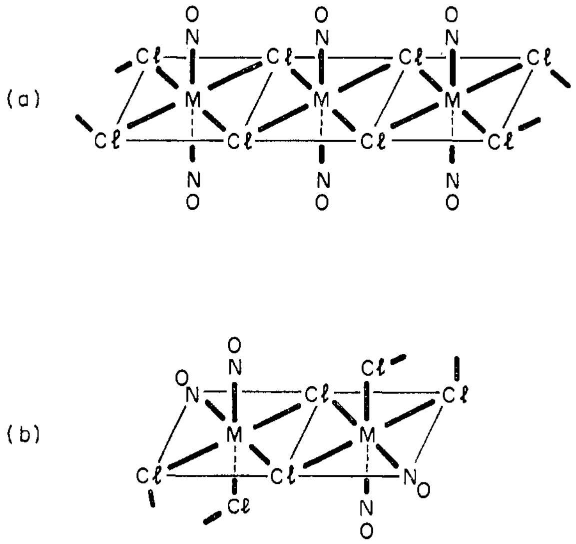

Fig. 1.—The two possible polymeric structures for M(NO)$_2$Cl$_2$.

cm.$^{-1}$) suggest that the NO$^+$ formalism[16] is appropriate here. If valence shell electron populations of 18 are to be achieved, polymerization must occur so that each chlorine atom forms a bridge between two metal atoms, and this might occur in either of the two ways shown in Fig. 1. In (a) the chains are straight, each pair of NO groups occupying *trans* positions in the octahedron about M, whereas (b) represents one of several possible kinked chain structures in which each pair of NO groups occupies *cis* positions in the octahedron. The appearance of two NO stretching frequencies (Fig. 2) in the M(NO)$_2$Cl$_2$ compounds indicates a kinked chain, as in Fig. 1 (b).

The M(NO)$_2$Cl$_2$ compounds are isoelectronic with Ru(CO)$_2$I$_2$, and the latter resembles the nitrosyl compounds closely in being nonvolatile, dissolving only in coordinating solvents, giving adducts with two molecules of various ligands, and in having two CO stretching bands in the infrared spectrum. Irving[17] in his study of Ru(CO)$_2$I$_2$ also concluded that the structure must be polymeric, with all iodine atoms serving as bridges. He appeared, however, to favor a straight chain structure like that in Fig. 1 (a) for Ru(CO)$_2$I$_2$, whereas, here also, the infrared spectrum indicates a kinked chain.

Another compound isoelectronic with the dichlorodinitrosyl compounds reported here is Fe(CO)$_2$I$_2$, first reported by Hieber and Legally.[18] We have found[19] that this compound also has two infrared active CO stretching modes and believe it to be structurally analogous to the M(NO)$_2$Cl$_2$ compounds and Ru(CO)$_2$I$_2$.

Mo(NO)$_2$Cl$_2$ and W(NO)$_2$Cl$_2$ readily form octahedral complexes of the type M(NO)$_2$Cl$_2$L$_2$ and we report here the preparation and properties of several such complexes in which the ligands L are triphenylphosphine, triphenylarsine, pyridine, *p*-toluidine, and cyclohexylamine; these complexes are listed in Table I. They vary considerably in their stabilities. The triphenylphosphine, triphenylarsine, and pyridine complexes are stable for a period of several weeks in air at room temperature. The *p*-toluidine and cyclohexylamine derivatives are stable under vacuum or in an inert atmosphere, but decompose within a few hours in the presence of air. Solutions of the triphenylphosphine, triphenylarsine, and pyridine complexes are stable in air; those of *p*-toluidine and cyclohexylamine are very unstable under such conditions.

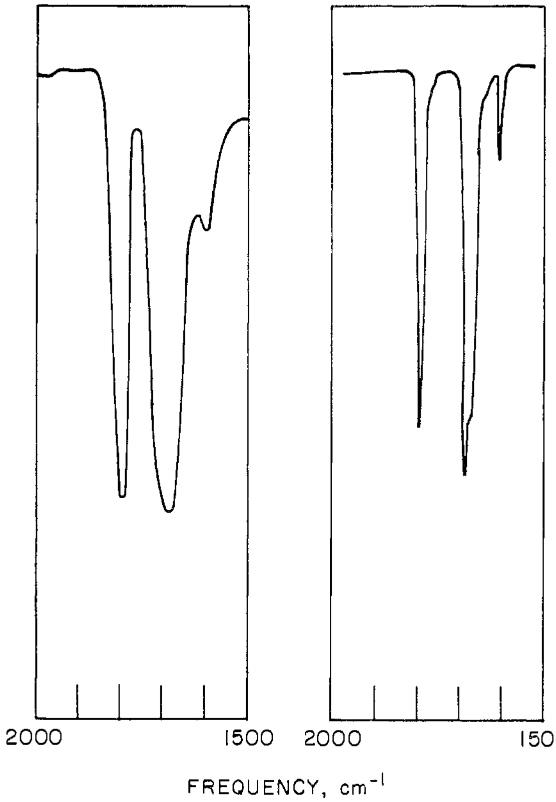

Fig. 2.—The infrared spectra in the NO stretching region of (left) Mo(NO)$_2$Cl$_2$ in Nujol and (right) Mo(NO)$_2$Cl$_2$(C$_5$H$_5$N)$_2$ in CH$_2$Cl$_2$. The small peak at 1608 cm.$^{-1}$ in right spectrum is due to pyridine.

The reaction of the M(NO)$_2$Cl$_2$ compounds with tetraphenylarsonium chloride in acetonitrile gives compounds of the type [M(NO)$_2$Cl$_4$]$^{2-}$[(C$_6$H$_5$)$_4$As]$^+_2$.

The infrared spectra of all the derivatives of the M(NO)$_2$Cl$_2$ compounds have been recorded in the 400–4000 cm.$^{-1}$ range. The NO stretching frequencies are listed in Table II. The most obvious implication of the infrared spectra is that in all of the derivatives, which are presumably octahedral complexes, the NO groups are in *cis* positions. Thus, for the M(NO)$_2$Cl$_2$L$_2$ compounds, three geometrical isomers, Fig. 3 (a–c), are possible, one (b) existing in optical antimers, while for the [M(NO)$_2$Cl$_4$]$^{2-}$ anions the structure must be that shown in Fig. 3 (d).

It is noteworthy that the variation in NO stretching frequencies as the additional ligands are changed is not, perhaps, entirely what would have been expected from the existing data on the effects of these ligands in sub-

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TABLE I

ANALYTICAL AND OTHER DATA OF NEW COMPOUNDS

Compound	Color	M.p., °C.	Mo or W		C		H		N		Cl	
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Mo(NO)_2Cl_2[(C_6H_5)_3P]_2$	Yellow-green	247			57.41	57.49	4.12	3.99	3.48	3.73	8.98	9.44
$Mo(NO)_2Cl_2[(C_6H_5)_3As]_2$	Green	220			52.26	51.56	3.86	3.58	2.90	3.34	...	...
$Mo(NO)_2Cl_2(C_5H_5N)_2$	Green	~150 dec.			31.61	31.19	2.64	2.60	13.84	14.58	18.73	18.45
$Mo(NO)_2Cl_2(CH_3C_6H_4NH_2)_2$	Golden yellow	~94 dec.			37.86	38.06	4.43	4.53	...	...	15.69	16.03
$Mo(NO)_2Cl_2(C_6H_{11}NH_2)_2$	Yellow-green	~100 dec.			33.30	33.88	6.86	6.12	...	...	...	...
$[Mo(NO)_2Cl_4][(C_6H_5)_4As]_2$	Yellow-green	213			53.55	54.12	3.80	3.77	2.56	2.63	13.57	13.34
$W(NO)_2Cl_2[(C_6H_5)_3P]_2$	Green	236			52.10	51.46	3.58	3.57	3.02	3.34	8.10	8.45
$W(NO)_2Cl_2[(C_6H_5)_3As]_2$	Green	278			43.71	43.76	3.30	3.23	2.80	2.84	7.32	7.19
$W(NO)_2Cl_2(CH_3C_6H_4NH_2)_2$	Green	~93 dec.			32.30	31.80	4.22	3.40	...	...	13.99	13.42
$[W(NO)_2Cl_4][(C_6H_5)_4As]_2$	Yellow-green	261			49.35	49.99	3.80	3.47	2.41	2.43	12.23	12.33
$Mo(NO)_2Cl_2$	Dark green		41.1	42.3	...	...	...	...	12.7	12.4	32.2	31.3
$W(NO)_2Cl_2$	Dark green		58.4	58.9	...	...	...	...	...	...	21.6	21.8

TABLE II

NO STRETCHING FREQUENCIES[a] OF COMPLEXES OF $Mo(NO)_2Cl_2$ AND $W(NO)_2Cl_2$

Compound	Medium	NO stretching frequency, cm.$^{-1}$		
$Mo(NO)_2Cl_2$	Nujol	1805 s	1690 s	1600 w
$Mo(NO)_2Cl_2[(C_6H_5)_3P]_2$	CH_2Cl_2	1790 s	1670 s	
$Mo(NO)_2Cl_2[(C_6H_5)_3As]_2$	CH_2Cl_2	1765 s	1645 s	
$Mo(NO)_2Cl_2(C_5H_5N)_2$	CH_2Cl_2	1790 s	1680 s	1675 sh
$Mo(NO)_2Cl_2(CH_3C_6H_4NH_2)_2$	CH_2Cl_2	1785 s	1665 s	
$Mo(NO)_2Cl_2(C_6H_{11}NH_2)_2$	CH_2Cl_2	1775 s	1655 s	
$[Mo(NO)_2Cl_4][(C_6H_5)_4As]_2$	Nujol	1720 s	1600 s	
$W(NO)_2Cl_2$	Nujol	1800 s	1680 s	1600 w
$W(NO)_2Cl_2[(C_6H_5)_3P]_2$	CH_2Cl_2	1790 s	1670 s	
$W(NO)_2Cl_2[(C_6H_5)_3As]_2$	CH_2Cl_2	1765 s	1645 s	
$W(NO)_2Cl_2(CH_3C_6H_4NH_2)_2$	CH_2Cl_2	1755 s	1640 s	
$[W(NO)_2Cl_4][(C_6H_5)_4As]_2$	Nujol	1720 s	1600 s	
$Fe(CO)_2I_2$[b]	Nujol	2100 s	2050 s	
$Ru(CO)_2I_2$[c]	Not specified	2050 s	1995 s	

[a] Spectra recorded with a Perkin-Elmer Model 337 spectrophotometer (grating optics). [b] Determined in these laboratories.[19] [c] Reference 17.

stituted metal carbonyls.[20-22] If it be assumed that the NO frequencies will vary directly with the ability of the additional ligands to accept metal $d\pi$ electrons, a decidedly anomalous order of ligands is obtained, *i.e.*, Cl (bridging) > $(C_6H_5)_3P \approx C_5H_5N$ > arylamine > alkylamine > $(C_6H_5)As \gg Cl^-$.

To some extent, purely electrostatic effects can be invoked to explain this order. Thus, the great difference between $[M(NO)_2Cl_2]_x$ and $[M(NO)_2Cl_4]^{2-}$ must be due principally to the fact that in the latter a great deal more negative charge accumulates on the metal atom, thus enhancing its tendency to release electrons to NO. Similarly, the order of NO stretching frequencies, arylamine compound > alkylamine compound, accords with the greater basicity of the latter ligand, which again will tend to make the metal atom more negative.

The order of NO frequencies for the compounds containing $(C_6H_5)_3P$, $(C_6H_5)_3As$, and C_5H_5N, however, appears to defy simple explanation; especially the great difference between the phosphine and arsine complexes.

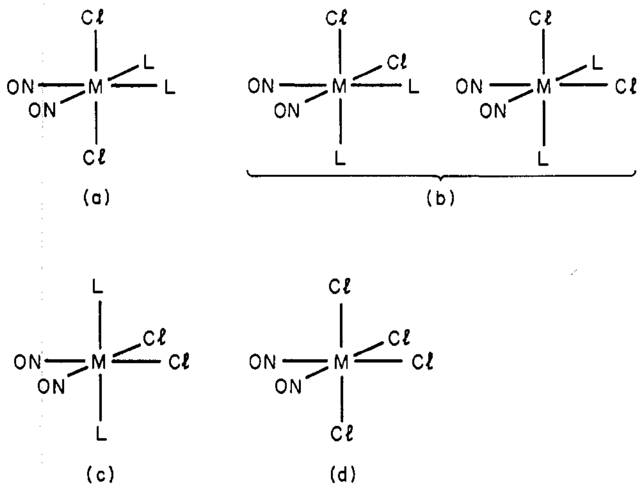

Fig. 3.—The possible isomers for $M(NO)_2Cl_2L_2$ compounds, (a)-(c), and the structure of $[M(NO)_2Cl_4]^{2-}$, (d), assuming *cis* NO groups.

At present, we do not propose to discuss hypotheses to account for this. It is hoped that work now in progress, using a more extensive series of ligands, will lead to more certain conclusions.

Experimental

Molybdenum and tungsten carbonyls, purchased from Climax Molybdenum Company, were used as received. Triphenylphosphine and triphenylarsine were used as received from Distillation Products. Pyridine was refluxed over and then distilled from barium oxide. Cyclohexylamine was dried over KOH and distilled. *p*-Toluidine was recrystallized from acetone before use. All solvents were degassed before use.

Melting and decomposition points are uncorrected. Most analytical data are the results of microanalyses by S. M. Nagy, M.I.T., or Galbraith Laboratories, Knoxville, Tenn. In a few cases, nitrogen was determined by the authors using a semimicro Kjeldahl method. All colors, melting or decomposition temperatures, and analytical data are collected in Table I.

$M(NO)_2Cl_2$ (M = Mo or W).—The methods used for $Mo(NO)_2Cl_2$ and $W(NO)_2Cl_2$ were identical. The reaction was carried out in a single-neck 200-ml. round-bottom flask, which was swept with dry nitrogen, and the metal carbonyl (5 g.) and dichloromethane (50 ml.) were then introduced. After nitrosyl chloride had been passed into the suspension for several minutes, a vigorous reaction commenced, carbon monoxide was evolved rapidly, and a dark green solid precipitated. After standing for 1 hr., the solvent was removed under vacuum and a small quantity of unreacted carbonyl sublimed into a trap at −196°. The product, a dark green powder, was kept under vacuum or in nitrogen.

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Yields (based on carbonyl): 3.9 g. of $Mo(NO)_2Cl_2$, 91%; 4.3 g. of $W(NO)_2Cl_2$, 96%.

$Mo(NO)_2Cl_2(P(C_6H_5)_3)_2$.—$Mo(NO)_2Cl_2$ (1.15 g., 0.005 mole) and triphenylphosphine (3.95 g., 0.015 mole) in benzene were heated under nitrogen for 15 min. at refluxing temperature. The dark green $Mo(NO)_2Cl_2$ completely dissolved to give a clear green solution. The solvent was partially removed under vacuum, pentane added, and the solution cooled. On standing for 30 min., small yellow-green crystals separated. The product was separated by filtration, washed with pentane, and dried under vacuum. The compound was recrystallized from benzene–pentane (2:1); yield 2.1 g., 70%.

$Mo(NO)_2Cl_2((C_6H_5)_3As)_2$, $W(NO)_2Cl_2((C_6H_5)_3P)_2$, and $W(NO_2)Cl_2((C_6H_5)_3As)_2$.—These complexes were obtained following essentially the same procedure as that used for $Mo(NO)_2Cl_2(P(C_6H_5)_3)_2$.

$Mo(NO)_2Cl_2(p\text{-}CH_3C_6H_4NH_2)_2$ and $W(NO)_2Cl_2(p\text{-}CH_3C_6H_4NH_2)_2$.—*p*-Toluidine (1.07 g., 0.010 mole) in acetone (15 ml.) was added, under nitrogen, to a solution of $Mo(NO)_2Cl_2$ (1.15 g., 0.005 mole) or $W(NO)_2Cl_2$ (1.60 g., 0.005 mole) in the same solvent (25 ml.). After a few minutes, the solution became yellow-green in color. The solvent was then removed under vacuum. The residual golden yellow solid was washed with pentane and dried under vacuum. The compound decomposes rapidly in solution and was not recrystallized. Yields: 2.10 g. of $Mo(NO)_2Cl_2(C_7H_9N)_2$, 94%; 2.55 g. of $W(NO)_2Cl_2(C_7H_9N)_2$, 96%.

$Mo(NO)_2Cl_2(C_5H_5N)_2$.—$Mo(NO)_2Cl_2$ (1.15 g., 0.050 mole) was dissolved in pyridine (15 ml.) under nitrogen, at room temperature without effervescence. Pentane was added and the solution cooled. On standing, small green crystals were precipitated; yield 1.37 g., 71%.

$[Mo(NO)_2Cl_4][(C_6H_5)_4As]_2$ and $[W(NO)_2Cl_4][(C_6H_5)_4As]_2$.—A solution of tetraphenylarsonium chloride (4.2 g., 0.01 mole) in acetonitrile (10 ml.) was added, under nitrogen, to a solution of $Mo(NO)_2Cl_2$ (1.15 g., 0.005 mole) or $W(NO)_2Cl_2$ (1.60 g., 0.005 mole) in the same solvent (20 ml.). The solution immediately became lighter in color. The solvent was removed under vacuum. The yellow-green residual solid was recrystallized from an acetone–alcohol mixture. Yields: 3.96 g. of Mo compound, 74%; 4.95 g. of W compound, 86%.

$Mo(NO)_2Cl_2(C_6H_{11}NH_2)_2$.—Cyclohexylamine (1.0 g., 0.01 mole) was added to a solution of $Mo(NO)_2Cl_2$ (1.15 g., 0.005 mole) in acetone (20 ml.). The solvent was removed under vacuum, leaving a yellow-green residue of $Mo(NO)_2Cl_2(C_6H_{11}NH_2)_2$. Attempts to recrystallize the product from a variety of solvents always resulted in some decomposition and were therefore abandoned.

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A Spectrophotometric Study of Molybdenum(V) and Molybdenum(VI) in Hydrobromic Acid[1]

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Ultraviolet spectrophotometry was used to study the species of Mo(V) and Mo(VI) present in hydrobromic acid solutions. An investigation of the equilibrium between Mo(VI), Mo(V), and Br_3^- in 8.6 *M* HBr led to the conclusion that both the Mo(V) and Mo(VI) species are dimeric. Each of the following compounds of Mo(V) was prepared and its characteristic spectrum determined in inert solvents: $(NH_4)_2MoOBr_5$, $(C_9H_8N)MoOBr_4$, and $MoO(OH)_2Br_2 \cdot 4H_2O$. The spectra of solutions of Mo(V) in aqueous HBr, 1.0–8.6 *M* in concentration, can be interpreted in terms of the presence of four Mo(V) species, all of which are dimeric. In the highest HBr concentration $(MoOBr_4^-)_2$ is the predominant form, with no spectral evidence for the presence of $MoOBr_5^{2-}$.

A number of workers have made investigations of the species of Mo(V) existing in hydrochloric acid solution. Among the variety of methods employed in these studies have been spectrophotometric,[3–6] magnetic,[7–9] and potentiometric[3] measurements. The general conclusions to be reached from these studies are: (1) monomeric $MoOCl_5^{2-}$ is the predominant species in high (>10 *M*) concentration; (2) at intermediate HCl concentrations (2–7 *M*) two or more dimeric forms exist in equilibrium; (3) at low HCl concentrations the situation is less clear, and tetramers are possibly present.

Investigations of solutions of Mo(V) in hydrobromic acid have been few, although several oxybromo compounds of Mo(V) have been isolated from such solutions.[10–13] No work has been reported on the nature of solutions of Mo(VI) in hydrobromic acid.

In the present work a spectrophotometric investigation of the species of Mo(V) existing in hydrobromic acid is reported. Known compounds of molybdenum(V) and bromine were prepared and their spectra determined in inert solvents. A comparison of these spectra with the spectra of solutions of Mo(V) in aqueous HBr made it possible to identify some of the species in solution. In preliminary experiments it was observed that Mo(VI) reacts with moderately concentrated solutions of HBr to form an equilibrium mixture of Mo(V), Mo(VI), and Br_3^-. Certain features of this equilibrium were also investigated.

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