Table I. Rate Constants for the Reduction of BrO_3^- by $IrCl_6^{3-}$ at 25.0 °C and $I = 0.500$ M[a]

$10^3[BrO_3^-]$, M	$[H^+]$, M	$10^4[BrO_3^-]\cdot[H^+]^2$, M^3	10^2k_1, s^{-1} Obsd[b]	10^2k_1, s^{-1} Calcd[c]
3.00	0.500	7.50	3.86 ± 0.09 (4)	3.93
1.00	0.500	2.50	1.51 ± 0.05 (5)	1.39
0.800	0.500	2.00	1.12 ± 0.06 (8)	1.14
0.500	0.500	1.25	0.744 ± 0.036 (4)	0.756
0.300	0.500	0.750	0.510 ± 0.020 (2)	0.502
5.00	0.497	12.4	6.54	6.42
10.0	0.490	24.0	12.4	12.3
20.0	0.480	46.1	27.7	23.5
0.800	0.450	1.62	1.03 ± 0.08 (2)	0.944
0.500	0.450	1.01	0.66 ± 0.08 (2)	0.634
20.0	0.402	32.2	17.0 ± 0.2 (2)	16.5
5.00	0.402	8.08	4.36	4.23
3.00	0.397	4.73	2.44 ± 0.05 (3)	2.52
1.00	0.397	1.58	0.995 ± 0.005 (2)	0.924
0.800	0.397	1.26	0.780 ± 0.005 (4)	0.761
0.750	0.397	1.18	0.844 (2)	0.720
0.500	0.397	0.788	0.552 ± 0.023 (3)	0.521
20.0	0.301	18.1	9.00 ± 0.16 (2)	9.32
5.00	0.301	4.50	2.60	2.41
3.00	0.301	2.72	1.59 ± 0.07 (3)	1.50
0.800	0.301	0.752	0.489 ± 0.037 (4)	0.489
0.500	0.301	0.453	0.363	0.351
3.00	0.250	1.88	1.10 ± 0.02 (2)	1.08
2.50	0.250	1.56	1.06 (2)	0.913
40.0	0.198	15.7	7.28	8.10
30.0	0.198	11.8	5.87	6.12
20.0	0.198	7.84	3.85 ± 0.16 (2)	4.10
10.0	0.198	3.92	2.16 ± 0.06 (2)	2.11
5.00	0.198	1.96	1.19	1.12
4.00	0.198	1.57	0.984 ± 0.055 (2)	0.919
3.00	0.198	1.18	0.728 ± 0.011 (4)	0.720
2.00	0.198	0.784	0.465	0.519
1.00	0.198	0.392	0.249	0.320
10.0	0.150	2.25	1.43	1.26
7.50	0.150	1.69	1.17 ± 0.03 (2)	0.980
10.0	0.102	1.04	0.622 ± 0.009 (2)	0.649
5.00	0.102	0.520	0.354	0.385
20.0	0.100	2.00	1.13 ± 0.02 (3)	1.14
17.0	0.100	1.70	1.01 ± 0.01 (2)	0.985
3.00	0.100	0.300	0.225 ± 0.001 (2)	0.273
0.800	0.100	0.0800	0.160	0.161
20.0	0.051	0.520	0.310 ± 0.015 (2)	0.385
5.00	0.051	0.130	0.194	0.187

[a] $[IrCl_6^{3-}]_0 = (0.4-8.0) \times 10^{-4}$ M. [b] The uncertainties given are average deviations for a number (given in parentheses) of different determinations under the same conditions but with various $[IrCl_6^{3-}]_0$. [c] Calculated from $k_1 = 0.00121 + 50.8\cdot[BrO_3^-][H^+]^2$.

suggested that both terms in the rate law are probably due to outer-sphere mechanisms for the Fe(II) complexes listed as the first four entries in Table II. The consistency of the k_H values, which vary by only a factor of about 60 while the k values vary by 4 orders of magnitude, is certainly suggestive of a common feature in all these mechanisms. This again supports the possbility of an inner-sphere mechanism for the k_H path with rate-limiting displacement of water. However, the oxygen-exchange rate, if expressed in terms of eq 7 with $M^{n+} = H_2O$, gives $k_H \approx 8 \times 10^{-5}$ M^{-3} s^{-1} as a limiting rate of substitution.[27] Another possibility is that the species $H_2BrO_3^+$ is so reactive with respect to reduction that its reactions are essentially diffusion-controlled outer-sphere processes, thus requiring that K be about 10^{-9}–10^{-11} M^{-2}, which is quite reasonable. In fact, if one uses the rule of thumb that an oxy acid of formula $XO_2(OH)$ has a first dissociation constant of about 10^3 M and that successive dissociation constants decrease by about a factor of 10^{-5}, then the formation constant of $H_2BrO_3^+$ would be estimated to be 10^{-3} $M^{-1} \times 10^{-8}$ $M^{-1} = 10^{-11}$ M^{-2}, in good agreement with the value required for diffusion-controlled redox reactions of $H_2BrO_3^+$ with metal ions.

Table II. Values of k and k_H for the Reduction of BrO_3^- by Metal Ions at 25 °C[a]

Metal ion	k, M^{-1} s^{-1}	k_H, M^{-3} s^{-1}	Ionic strength, M	Ref
$Fe(CN)_6^{4-}$	0.00125	0.193	0.5 M	8
$Fe(bpy)(CN)_4^{2-}$	0.0062	0.227	0.5	9
$Fe(bpy)_2(CN)_2$	0.0295	0.755	0.5	9
$Fe(bpy)_3^{2+}$	≤0.0042[b]	≤0.15[b]	0.5	9
Fe^{2+}	0.372	[c]	0.5	7
VO^{2+}	4.93		2.0	4
U^{4+}	12.5	3.2	2.0	12
Hg^0	3.7[d]	2.0[d]	1.0	11
$IrCl_6^{3-}$		10.2	0.5	This work

[a] The parameters k and k_H are defined in eq 7. [b] Estimated values; the reaction follows a different rate law. [c] Another term with a complex $[H^+]$ dependence was also observed. [d] Corrected for disproportionation of Hg_2^{2+}.

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Registry No. BrO_3^-, 15541-45-4; $IrCl_6^{3-}$, 14648-50-1.

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Synthesis and Characterization of Some New Complexes of the Mo_2^{4+} Ion

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Complexes of the quadruply bonded Mo_2^{4+} ion often undergo ligand substitution without disruption of the metal–metal

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bond. This fact has led to the synthesis of many new complexes and shows that, with some restrictions, the Mo_2^{4+} unit may be treated synthetically as though it were a mononuclear metal ion.[1] The Mo_2^{4+} unit is always coordinated at eight sites. These may be considered to be at the corners of eclipsed squares whose centers are occupied by the metal ions. Additionally, two sites coaxial to the metal–metal bond are available and are sometimes coordinated.[2]

Mo_2^{4+} binuclear units have a different coordination chemistry from mononuclear ions. It has been shown that molecules with weak donor sites close to one another become good bidentate ligands spanning the binuclear unit. New types of geometrical isomerism are also possible and have been demonstrated. These considerations raise interesting reactive and catalytic possibilities. Herein, we report the preparation and characterization of a new group of complexes containing the Mo_2^{4+} unit.

Experimental Section

Materials. Methanesulfonic acid was dried by azeotropic distillation. Diglyme and dimethoxyethane were refluxed with CaH_2 and distilled from it. Dimethylformamide was dried over molecular sieves and distilled at reduced pressure. Acetonitrile was dried over molecular sieves and distilled. The butyrolactone was dried over $CaSO_4$ and distilled at reduced pressure. Tetramethylammonium chloride was recrystallized from anhydrous ethanol. Sodium methanesulfonate was prepared by neutralization of the acid with NaOH. It was recrystallized from water and dried for several hours at 110 °C. Other reagents were of the highest purity readily available and were used without further purification.

Instrumentation. Magnetic measurements were done by the Gouy technique. Conductance measurements were performed with an LKB type 3216 conductivity bridge at 25 °C. Electronic spectra were recorded on a Cary 14 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer as Nujol and hexachlorobutadiene mulls between KCl plates. Far-infrared spectra below 450 cm^{-1} were recorded as Nujol mulls as polyethylene plates with a Digilab Model 296 interferometer. Raman spectra were recorded on a SPEX Model 1401 double-monochromator spectrophotometer with a laser operating at 5145 Å. Because this line falls within the electronic absorption bands of the complexes, a spinning-sample technique was necessary to prevent thermal decomposition. Even so, spectra could be obtained for only the more stable compounds. For these compounds KBr pellets were prepared and mounted with double-stick tape on the shaft of a mechanical stirring motor which spun the sample.

Syntheses. All the compounds reported here are air sensitive and were prepared under nitrogen in a commercial Schlenk-type apparatus using standard anaerobic techniques.[3]

Tetrakis(μ-methanesulfonato)-dimolybdenum(II), $Mo_2(MS)_4$. A degassed solution of 5 mL of methanesulfonic acid in 20 mL of diglyme was added to 2 g of tetrakis(μ-acetato)-dimolybdenum(II). The mixture was heated under N_2 to 100 °C for 10 min by which time complete dissolution had taken place. The volume was reduced to 10 mL by distillation under vacuum. Upon cooling to room temperature, a pink solid formed. It was filtered off and washed with anhydrous ether. The yield is nearly quantitative (about 2.6 g) for a noncrystalline, diamagnetic, pink powder. Anal. Calcd for $C_4H_{12}S_4O_{12}Mo_2$: C, 8.39; H, 2.09; Mo, 33.56. Found: C, 8.47; H, 2.20; Mo, 33.10.

Tetrakis(μ-methanesulfonato)-bis(γ-butyrolactone)dimolybdenum(II). Thirty milliliters of degassed γ-butyrolactone was added to 0.6 g of $Mo_2(MS)_4$ and this suspension was heated with stirring to 70 °C. After all of the solid dissolved, half of the solvent was distilled off under vacuum. Upon cooling, a highly air-sensitive, pink solid formed. It was filtered off and washed with anhydrous ether. The product is a highly air-sensitive, pink, diamagnetic, noncrystalline solid. Anal. Calcd for $C_{12}H_{24}S_4O_{16}Mo_2$: C, 19.22; H, 3.22; Mo, 25.80. Found: C, 19.59; H, 3.50; Mo, 25.59.

Tetrakis(μ-methanesulfonato)-bis(*N*,*N*-dimethylformamide)dimolybdenum(II). Ten milliliters of degassed DMF was added to 0.3 g of $Mo_2(MS)_4$. A red solution formed upon stirring. Addition of 10 mL of degassed dimethoxyethane and cooling to 0 °C precipitated a pink solid. This was filtered off and washed with anhydrous ether. The product is a highly air-sensitive, pink, diamagnetic, noncrystalline solid. Anal. Calcd for $C_{10}H_{26}N_2S_4O_{14}Mo_2$: C, 16.71; H, 3.62; N, 3.90; Mo, 26.74. Found: C, 16.49; H, 3.67; N, 3.71; Mo, 26.97.

Tetramethylammonium Tetrachlorobis(μ-methanesulfonato)-dimolybdate(II). To 0.44 g of $Mo_2(MS)_4$ was added a degassed solution of 0.84 g of $(CH_3)_4NCl$ in 20 mL of anhydrous methanol. The resulting suspension immediately became red-purple. It was stirred for 15 min and filtered. The red-purple solid was washed with anhydrous ether and dried under nitrogen. The product is rather air stable and can be handled in air when dry without discoloration. It is diamagnetic. Attempts to recrystallize it from methanol, however, repeatedly failed. Regardless of precautions, it was observed that the mother liquor was always badly discolored within 24 h. Anal. Calcd for $C_{10}H_{30}N_2Mo_2Cl_4S_2O_6$: C, 17.85; H, 4.45; N, 4.17; Mo, 28.57; Cl, 21.13. Found (for the product of the initial reaction): C, 17.86; H, 4.70; N, 4.09; Mo, 28.71; Cl, 21.11.

Tetra-*n*-butylammonium Tetrabromobis(μ-methanesulfonato)-dimolybdate(II). Attempts to prepare a bromide or an iodide complex in methanol solvent failed. The products obtained appeared homogeneous and resembled the chloride product but upon elemental analysis proved to be of variable composition. Attempts to recrystallize from methanol resulted in the same type of discolored solutions as noted for the chloride compound. For the bromide complex the following synthetic procedure was finally adopted. To 0.4 g of $Mo_2(MS)_4$ and 0.8 g of $(C_4H_9)_4NBr$ was added 300 mL of benzene. The suspension was refluxed with stirring under nitrogen for 2 h. After the solution was cooled, the red-purple solid which formed was filtered off, stirred with 10 mL of benzene, filtered again, washed with small portions of cold methanol, and finally washed with anhydrous ether. The solid was dried in a stream of nitrogen. It is a red-purple, noncrystalline, air-stable, diamagnetic solid. Anal. Calcd for $C_{34}H_{78}N_2Mo_2Br_4S_2O_6$: C, 34.40; H, 6.58; N, 2.36; Mo, 16.19; Br, 26.89. Found: C, 34.63; H, 6.74; N, 2.54; Mo, 16.02; Br, 26.99. By way of comparison, a typical attempt to prepare the compound in methanol resulted in a compound which was also diamagnetic and identical in appearance but with the following analysis: C, 34.01; H, 6.66; N, 2.38; Mo, 16.22; Br, 22.48. Different preparations using methanol as a solvent resulted in fluctuation of up to 10% in these figures.

Tetra-*n*-butylammonium Tetraiodobis(μ-methanesulfonato)-dimolybdate(II). The procedure used was identical with that for the bromide except that 0.9 g of $(C_4H_9)_4NI$ was used and the solvent was toluene. It was observed that the reaction with iodide ion in benzene was slower than with bromide ion. This necessitated the use of a higher boiling solvent. Anal. Calcd for $C_{34}H_{78}N_2Mo_2I_4S_2O_6$: C, 29.69; H, 5.67; N, 2.04; Mo, 13.95; I, 36.97. Found: C, 30.56; H, 5.99; N, 1.94; Mo, 13.89; I, 36.12.

Ammonium Octakis(isothiocyanato)dimolybdate(II)–Tetrakis(dimethoxyethane). To 0.52 g of $Mo_2(MS)_4$ was added a degassed solution of 0.55 g of NH_4NCS in 40 mL of dimethoxyethane. The suspension immediately became blue-green. After the suspension was stirred for 15 min, it was filtered. The residue was a white solid, which infrared spectroscopy showed to be $NH_4CH_3SO_3$. The filtrate was a blue-green solution. Precipitation of the thiocyanate complex can be effected either by adding an equal volume of hexane or by cooling. The product can be recrystallized from dimethoxyethane, filtered, and washed with hexane. The product is highly air-sensitive and exists as diamagnetic green needlelike crystals. The only bands observed above 400 cm^{-1} in the infrared spectrum are those of NH_4^+, coordinated SCN^-, and DME. In deuterioacetone the proton spectrum consists solely of DME and NH_4^+. Anal. Calcd for $C_{24}H_{56}N_{12}Mo_2S_8O_8$: C, 26.46; H, 5.15; N, 15.45; Mo, 17.64. Found: C, 26.88; H, 5.22; N, 15.87; Mo, 17.56.

Attempted Preparation of a Fluoride Complex. Addition of $(C_2H_5)_4NF$ to suspensions of $Mo_2(MS)_4$ in various solvents resulted in the immediate formation of black paramagnetic suspensions, an indication of oxidation. No diamagnetic compounds could be obtained from these suspensions and this synthesis was abandoned.

Attempted Preparation of an Acetonitrile Complex. $Mo_2(MS)_4$ is slightly soluble in boiling acetonitrile, giving a blue color. It also dissolved in a methanolic solution of acetonitrile to give a bright blue solution. However, attempts to isolate the species in solution failed. Adding nonsolvents or reducing the volume yielded only the starting material.

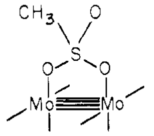
Table I. Infrared Spectra of Tetrakis-(μ-methanesulfonato)-dimolybdenum(II) and Sodium Methanesulfonate below 1300 cm^{-1}

$Mo_2(CH_3SO_3)_4$ freq, cm^{-1}	Assign	$NaCH_3SO_3$ freq, cm^{-1}	Mode	Assign[a]
1265 vs	ν(SO)			
1220 vs	ν(SO)	1246 s	E	$\nu_{as}(SO_3)$
1100 sh	ν(SO)	1190 vs		
1083 vs	ν(SO)			
1056 m	ν(SO)			
1015 vs	ν(SO)	1059 s	A	$\nu_s(SO_3)$
985 m				
964 m	$\varphi_r(CH_3)$	961 vw	E	$\varphi_r(CH_3)$
773 s	ν(CS)	786 s	A	ν(CS)
560 vs	$\delta_s(SO_3)$	779 w		
527 s	$\delta_d(SO_3)$	561 s	E	$\delta_s(SO_3)$
395 s	ν(MoO)[b]	536 s	E	$\delta_d(SO_3)$
		344 w	E	$\varphi_r(SO_3)$
295 s	ν(MoO)[b]			
265 s	ν(MoO)[b]			
157 m				
136 m				
100 m	OMoO bend[b]			

[a] Assignments for $NaCH_3SO_3$ are from M. G. Miles, G. Doyle, R. P. Cooney, and R. S. Tobias, *Spectrochim. Acta, Part A*, **25a**, 1515 (1969). [b] Assignments for MoO stretching and bending modes are from comparison with the sulfate complex: A. Loewenschuss, J. Shamir, and M. Ardon, *Inorg. Chem.*, **15**, 238 (1976).

Results and Discussion

Tetrakis(μ-methanesulfonato)-dimolybdenum(II), $Mo_2(MS)_4$. This compound was prepared in the hope that it would prove to be a useful intermediate for the synthesis of Mo_2^{4+} complexes with delicate ligands. We thought that the methanesulfonate ligand would be particularly easy to replace because of its low basicity. The ease with which $Mo_2(MS)_4$ can be prepared in high purity and its relative air stability appeared to be favorable portents for this notion. Table I compares the infrared spectrum of $Mo_2(MS)_4$ with that of sodium methanesulfonate. Assignments can be made by analogy to those of sodium methanesulfonate. The anticipated structure for $Mo_2(MS)_4$ is analogous to the carboxylate[4] or trifluoromethanesulfonate[5] complexes with the anions as bidentate bridging ligands and local C_s symmetry, as in I.



I

Inspection of Table I shows that the sulfur–oxygen stretching modes are split beyond what is anticipated for a reduction from C_{3v} to C_s symmetry upon coordination. $Mo_2(MS)_4$ has six widely separated S–O stretching frequencies from 1265 to 1015 cm^{-1}. Even in the lowest symmetry only three are expected. There are several possible explanations. These include interligand interactions, splitting of S–O modes by the local crystal symmetry, and the binding of some of the free oxygen atoms of one complex to the axial sites of an adjacent complex. This type of polymerization has been observed in the crystal structure of the sulfate complex[6] and its S–O stretching region is complex.[7] For $Mo_2(MS)_4$ it is noteworthy that three of the six ν(SO) bands are quite close to those of the tetrahalobis(methanesulfonato)molybdenum(II) complexes discussed below (1265, 1083, 1015 cm^{-1}).

$[NH_4]_4Mo_2(NCS)_8 \cdot 4C_2H_4(OCH_3)_2$. Ammonium thiocyanate reacts rapidly with $Mo_2(MS)_4$ in dimethoxyethane to form a green, diamagnetic, crystalline thiocyanate complex. The infrared spectrum of this complex indicates N bonding for the thiocyanate ligands. Strong bands at 1920 and 2095 cm^{-1} are consistent with C–N stretching modes of known complexes having N-bonded thiocyanate as reviewed recently by Bailey et al.[8] Further support for this structure comes from the observation of a C–S stretching mode at 820 cm^{-1} and an N–C–S bending mode at 471 cm^{-1}. A strong band at 295 cm^{-1} is assigned to Mo–N stretching and compares closely to the value of 303 cm^{-1} observed for $Cs_3Mo(NCS)_6$, which is also N bonded.[9]

Table II. Vibrational Spectra of $(NR_4)_2Mo_2(MS)_2X_4$ Compounds below 450 cm^{-1}

	Cl freq, cm^{-1}		Br freq, cm^{-1}		I freq, cm^{-1}	
	IR	Raman	IR	Raman	IR	Raman
ν(Mo–O)				440 w		447 w
	375 m		374 m		377 m	
ν(M–M)		372 vs		364 vs		362 vs
		343 s				
ν(M–Cl)	317 s					
ν(Mo–O)	270 s		275 s		265 s	
ν(Mo–Br)			245 s			
				233 w		241 w
ν(Mo–I)					212 s	
	160 m		183 m		145 m	
	132 w		138 w		138 w	
	115 w					

Table III. Electronic Spectra of the Tetrahalobis(μ-methanesulfonato)-dimolybdate(II) Anions as Nujol Mulls

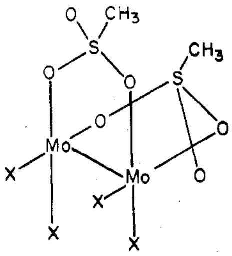
Wavelength, nm				
Cl anion	Br anion	I anion	$K_4Mo_2Cl_8 \cdot 2H_2O$[a]	Assign
525	542	563	532	$\delta \rightarrow \delta^*$
405 vw	420 vw	420 vw	417 w	$\pi \rightarrow \delta^*$
300	310	302	318	$\pi \rightarrow \delta_{x^2-y^2}$
267	272	270	294	$\pi \rightarrow \pi^*$
218	235	252		

[a] Assignments for $K_4Mo_2Cl_8 \cdot 2H_2O$ from J. G. Norman, Jr., and H. J. Kolari, *J. Am. Chem. Soc.*, 97, 33 (1975).

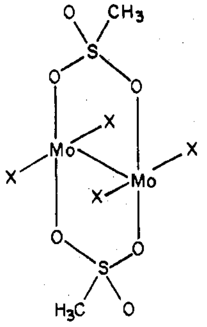
Halide Complexes from $Mo_2(MS)_4$. Tetraalkylammonium halides, except for fluorides, react with $Mo_2(MS)_4$ to form mixed-ligand complexes of the formula $(NR_4)_2Mo_2(MS)_2X_4$. The infrared spectra, exclusive of cation bands, are quite similar above 450 cm^{-1}. The S–O stretching regions contain only three bands, in contrast to $Mo_2(MS)_4$. Comparison to sodium methanesulfonate shows that ν_{sym} is reduced by 45 cm^{-1} and one of the ν_{asym} is reduced by 120 cm^{-1}. The other ν_{asym} is increased by ca. 35 cm^{-1}. These changes are fully consistent with simple bridging bidentate coordination of the methanesulfonate ions.

The vibrational spectra below 450 cm^{-1} are instructive. Table II presents these data. The intense Raman band between 372 and 362 cm^{-1} is clearly assignable to the metal–metal stretching mode. A second intense Raman band at 343 cm^{-1} in the chloride complex but absent from the other halide complexes is observed in other binuclear Mo_2^{4+} chloride complexes and has been assigned to strong mixing of the Mo–Cl and Mo–Mo A_1 mode stretching frequencies.[10] Two intense infrared bands are observed at nearly the same frequency in all compounds, one at 377–374 cm^{-1} and the other at 275–265 cm^{-1}. These bands are assigned to Mo–O stretching frequencies. This leaves a single intense band in the spectra of each of the halide complexes and it is assigned to metal–halide stretching. Though it is not expected to be a pure mode, the calculation of force constants based simply on the reduced mass of the metal–halide system gives values which are remarkably constant.

The presence of two bidentate methanesulfonate ligands and four monodentate halides restricts the choice of structures for these compounds to a choice between a cis idealized C_{2v} geometry and a trans idealized D_{2h} configuration, IIa and IIb.



IIa



IIb

In D_{2h} symmetry the infrared- and Raman-active bands are expected to be mutually exclusive. In C_{2v} symmetry all infrared modes are expected to be Raman active and all Raman modes except A_2 modes are expected to be infrared active. As Table II shows, the Raman and infrared spectra for the basic skeleton of the $Mo_2(MS)_2X_4^{2-}$ anions are mutually exclusive, indicative of D_{2h} symmetry.

The electronic spectra of this series of compounds were recorded in methanol and as Nujol mulls. The data from Nujol mulls appear in Table III. Band positions correlate well with those of $K_4Mo_2Cl_8{\cdot}2H_2O$. It can be seen from the table that two bands are affected by the change in halides. The $\delta \rightarrow \delta^*$ band is affected, as well as a band Norman and Kolari assigned to $X \rightarrow \delta^*$.[11] This assignment seems to be supported by our data.

In methanol solution, the bromide and iodide complexes give a single visible peak at 522 and 536 nm, respectively. The chloride peak is broadened and appears to be an overlapping of two peaks centered at 510 and 533 nm, respectively. The latter splitting is not observed in Nujol mull spectra and may be indicative of either solvolysis or, possibly, isomerization to form a mixture of cis and trans species.

Complexes of $Mo_2(MS)_4$ with DMF and γ-Butyrolactone. The first Mo_2^{4+} complexes discovered were those with bidentate bridging carboxylate ligands. The synthesis of an ethyl acetate complex showed that even very weak donors can also bind this way and that the Mo_2^{4+} strongly favors such coordination.[5] γ-Butyrolactone and DMF might be expected to displace methanesulfonate from $Mo_2(MS)_4$ and coordinate as bidentate ligands analogously to ethyl acetate. On the other hand, it is known that the sites coaxial to the metal–metal bond can accommodate monodentate ligands. Pyridine and tetrahydrofuran are ligands for which axial bonding has been proven by x-ray crystallography.[2] DMF has been shown to coordinate axially to dirhodium tetraacetate, another binuclear complex.[15] Furthermore, the possibility that two monodentate ligands can displace a methanesulfonate ligand must be considered. Evidence has been presented for monodentate DMF complexes of Mo_2^{4+}.[10]

In order to distinguish among these possibilities, an extensive comparative analysis was made of the infrared spectra of the free ligands, the complexes, and related compounds. The results of the work are lengthy[12] and in the interest of brevity are not presented here. However, the data indicate that the methanesulfonate ions are not displaced from bridging the Mo_2^{4+} ion and that DMF and butyrolactone coordinate the molybdenum ions in a monodentate fashion via their most polar oxygen atoms, probably coaxial to the metal–metal bond. Four particularly important spectral observations support this conclusion.

1. Three S–O stretching modes are observed in each compound. Their frequencies are very close to those arising from bridging methanesulfonate in the compounds discussed above. No bands assignable to ionic methanesulfonate S–O stretches are observed in either compound. For example, the frequencies are 1260, 1073, and 1010 cm^{-1} for the butyrolactone complex and 1260, 1073, and 1010 cm^{-1} for the DMF complex. In $Mo_2Cl_4(MS)_2^{2-}$ these values are 1272, 1069, and 1013 cm^{-1} while in CH_3SO_3Na they are 1246, 1190, and 1059 cm^{-1}.

2. The band corresponding to C═O stretching in both DMF and butyrolactone is shifted to substantially lower energy, indicative of coordination via the carbonyl oxygen.[13] For DMF the shift is from 1672 to 1659 cm^{-1} on coordination while for the lactone the shift is from 1770 to 1728 cm^{-1}.

3. For butyrolactone the C–O single bond stretching frequency appears at 1166 cm^{-1}; this band is shifted to 1191 cm^{-1} in the complex. Such a shift is consistent with monodentate coordination via C═O.[14] Bidentate coordination in which C–O also binds lowers the C–O stretching frequency.[5]

4. The far-infrared spectra of the $Mo_2(MS)_4$, γ-butyrolactone, and DMF complexes in the region 450–200 cm^{-1} exclusive of ligand bands are virtually identical. This is the region for metal–ligand stretching which implies the same $Mo_2O_8O'_2$ skeleton for all these complexes.

Four bidentate methanesulfonate ligands and two monodentate auxiliary ligands per complex are strongly suggestive of a structure in which $Mo_2(MS)_4$ has simply added the auxiliary ligands to the sites coaxial to the metal–metal bond.

Summary

The complex tetrakis(μ-methanesulfonato)-dimolybdenum(II) has been synthesized and used to prepare a series of other complexes containing the Mo_2^{4+} unit. Complexes with such weak ligands as dimethylformamide and γ-butyrolactone are formed without displacement of the methanesulfonate ligands. Infrared spectroscopy indicates that they bind as monodentate ligands, probably at sites coaxial to the metal–metal bond. Chloride, bromide, and iodide complexes have been prepared in which two methanesulfonate ligands are displaced. These species are probably trans isomers with idealized D_{2h} symmetry. Full replacement of the methanesulfonate ligands was achieved by displacement with thiocyanate ion. Infrared spectroscopy shows this ligand to be N bonded.

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Registry No. $Mo_2(MS)_4$, 64784-67-4; $Mo_2(MS)_4{\cdot}2$(γ-butyrolactone), 64784-65-2; $Mo_2(MS)_4{\cdot}2$(*N*,*N*-dimethylformamide), 64813-92-9; $(NMe_4)_2Mo_2(MS)_2Cl_4$, 64784-69-6; $[(n\text{-Bu})_4N]_2Mo_2(MS)_2Br_4$, 64784-71-0; $[(n\text{-Bu})_4N]_2Mo_2(MS)_2I_4$, 64784-73-2; $[NH_4]_4Mo_2(NCS)_8$, 64784-74-3; tetrakis(μ-acetato)-dimolybdenum(II), 14221-06-8; $MeSO_3H$, molybdenum(II) salt, 64784-75-4; thiocyanic acid, ammonium molybdenum(II) salt, 64784-76-5.

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Isolation and Characterization of Isothiocyanato Complexes of Molybdenum(II) Containing Strong Metal–Metal Bonds

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Although salts of the octaisothiocyanatodirhenate(III) anion, $Re_2(NCS)_8^{2-}$, have been isolated,[1,2] their reactions with tertiary phosphines do not yield metal–metal bonded complexes of the types $Re_2(NCS)_6(PR_3)_2$ and $Re_2(NCS)_4(PR_3)_4$. Instead, the magnetically dilute thiocyanate bridged dimers $(Bu_4N)_2Re_2(NCS)_8(PR_3)_2$ are formed.[2] This behavior is in marked contrast to the ease with which salts of the octahalodirhenate(III) anions, $Re_2X_8^{2-}$ (X = Cl, Br, or I), afford the complexes $Re_2X_6(PR_3)_2$ and/or $Re_2X_4(PR_3)_4$.[3,4] The mild conditions under which the Re–Re quadruple bond of $Re_2(NCS)_8^{2-}$ is cleaved led us to suggest[2] that in this anion the metal–metal bond is weaker than that in the related octahalodirhenate(III) anions, a conclusion which was supported by differences in the electronic absorption spectra of these species.[2]

In order to understand more fully those factors which favor this reaction course, we felt it was important to establish whether those metal–metal bonded dimers which are electronically related to $Re_2(NCS)_8^{2-}$ are inherently unstable or whether this behavior is restricted to the rhenium(III) dimer and is therefore a property of the Re–Re bond. Accordingly, we have investigated the possibility of isolating metal–metal bonded molybdenum(II) dimers containing coordinated thiocyanate ligands.

During the last 10 years or so, many complexes containing the binuclear metal–metal bonded species Mo_2^{4+} have been synthesized.[5-13] There is ample evidence to show that the Mo_2^{4+} unit, which contains a quadruple metal–metal bond,[14] can survive substitution reactions, representative examples being the preparations of $Mo_2Cl_8^{4-}$ from $Mo_2(O_2CCH_3)_4$[8] and $Mo_2Cl_4(PR_3)_4$ from $Mo_2Cl_8^{4-}$.[12] Prior to the present investigation, there have been no reports dealing with thiocyanate complexes of Mo_2^{4+}.

Experimental Section

Starting Material. The preparation of the complex $Mo_2Cl_4(PEt_3)_4$ was achieved using the previously described procedure.[12] All solvents and other starting materials were obtained from commercial sources.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere, and solvents were deoxygenated by purging with N_2 gas for several hours.

A. Reactions of $Mo_2Cl_4(PEt_3)_4$ with Potassium Thiocyanate. (i) $Mo_2(NCS)_4(PEt_3)_4$ (I). A mixture of $Mo_2Cl_4(PEt_3)_4$ (1.0 g) and KSCN (0.8 g) in 40 mL of methanol was refluxed for at least 15 h. The green reaction mixture was then allowed to cool to room temperature. The resulting dark green crystalline solid was filtered off, washed with water and small portions of methanol and petroleum ether, and then dried in vacuo for several hours. A second crop of I was collected when the volume of the filtrate was reduced to ~10 mL by rotary evaporation; yield 0.60 g; mp 195–200 °C (dec). Anal. Calcd for $C_{28}H_{60}Mo_2N_4P_4S_4$: C, 37.52; H, 6.69; N, 6.25; S, 14.31; mol wt, 896. Found: C, 37.22; H, 6.54; N, 6.41; S, 14.50; mol wt (acetone), 910. Compound I is very soluble in toluene, acetone, acetonitrile, and tetrahydrofuran and slightly soluble in methanol and ether.

(ii) $(Bu_4N)_2Mo_2(NCS)_6(PEt_3)_2$ (II). The green filtrate obtained in (i) was placed in a 50 mL round bottom flask equipped with a magnetic stirrer. The flask was capped with a rubber serum cap and then flushed with nitrogen. A solution of Bu_4NBr (0.8 g) in 10 mL of methanol was added to the contents of the flask by means of a syringe. After stirring this mixture for 4 h at room temperature, the resulting solution was concentrated by rotary evaporation. The royal blue solid II which precipitated was filtered off and washed with water to remove undissolved KSCN, with toluene to remove any contamination from I, and finally with small portions of methanol and petroleum ether before being dried in vacuo; yield 0.23 g; mp 140 °C (dec). This complex can be recrystallized from acetone and ether. Anal. Calcd for $C_{50}H_{102}Mo_2N_8P_2S_6$: C, 47.62; H, 8.09; N, 8.89; S, 15.24. Found: C, 47.58; H, 8.03; N, 8.87; S, 15.22. This salt is very soluble in acetone, acetonitrile, and tetrahydrofuran but is insoluble in toluene.

An alternative procedure which may be used for the isolation of II is as follows. The reaction mixture from (ii) was evaporated to dryness and the resulting solid dissolved in a small volume of acetone. It was then filtered to remove any insoluble KSCN, and petroleum ether was added slowly to the clear filtrate until it became cloudy. Crystals of II appeared upon keeping this mixture under an atmosphere of nitrogen at 0 °C overnight.

(iii) The Interconversion of I and II. A mixture of I (0.08 g) and KSCN (0.05 g) in 8 mL of methanol was refluxed for 2 h followed by stirring the resulting solution with Bu_4NBr (0.15 g) for an additional hour. The royal blue complex II separated upon concentrating the reaction solution. It was filtered off and washed with toluene and petroleum ether. Similarly, the dark green complex I was isolated upon refluxing II (0.05 g) with PEt_3 (0.2 mL) in 7 mL of methanol for 12 h.

B. Reactions of $Mo_2(NCS)_4(PEt_3)_4$ with 1,2-Bis(diphenylphosphino)ethane, Bis(diphenylphosphino)methane, 2,2′-Bipyridyl, and 1,10-Phenanthroline. The compounds $Mo_2(NCS)_4(L\text{–}L)_2$ (where L–L is a bidentate ligand) were generally prepared by refluxing $Mo_2(NCS)_4(PEt_3)_4$ with an excess of ligand in methanol or absolute ethanol for at least 20 h. The resulting precipitates were collected and washed with toluene to remove any unreacted molybdenum starting material, then with methanol or ethanol, and finally with diethyl ether. The products were allowed to dry in vacuo for 5 h prior to analysis.

(i) $Mo_2(NCS)_4(dppe)_2$ (III). A mixture of 0.1 g of I and 0.13 g of 1,2-bis(diphenylphosphino)ethane (dppe) in 13 mL of methanol or ethanol was refluxed for 24 h. The yellow crystalline solid was filtered off and treated as above; yield 0.09 g. Recrystallization can be accomplished by dissolution in a small volume of dichloromethane followed by the addition of ethanol. Anal. Calcd for $C_{56}H_{48}Mo_2N_4P_4S_4$: C, 55.09; H, 3.96; N, 4.59. Found: C, 54.86; H, 4.01; N, 4.42. This complex is soluble in dichloromethane, slightly soluble in acetone, but insoluble in most other organic solvents.

Compound III can also be obtained from the reaction of II with dppe. However, attempts to synthesize it by reacting KSCN with α-$Mo_2Cl_4(dppe)_2$[13] were unsuccessful. The reaction of III with excess PEt_3 in refluxing methanol failed to give I.

(ii) $Mo_2(NCS)_4(dppm)_2$ (IV). This complex was obtained as a crop of dark green crystals, greenish yellow when powdered, when I (0.09 g) and bis(diphenylphosphino)methane (dppm) (0.13 g) were reacted in 15 mL of ethanol under reflux conditions for 30 h; yield 0.06 g. Anal. Calcd for $C_{54}H_{44}Mo_2N_4P_4S_4$: C, 54.37; H, 3.72; N, 4.70; mol wt, 1193. Found: C, 53.25; H, 4.00; N, 4.78; mol wt, 1150 (acetone). The solubility of IV is noticeably different from that of III. Thus, in addition to being soluble in dichloromethane, it also dissolves readily in acetone and acetonitrile, and it is slightly soluble in methanol.

(iii) $Mo_2(NCS)_4(bpy)_2$ (V). Refluxing I (0.11 g) with 2,2′-bipyridyl (bpy) (0.12 g) in 15 mL of methanol afforded the insoluble aqua green complex V; yield 0.07 g. Anal. Calcd for $C_{24}H_{16}Mo_2N_8S_4$: C, 39.14; H, 2.17; N, 15.21. Found: C, 38.88; H, 2.34; N, 14.91. This complex is insoluble in most organic solvents.

(iv) $Mo_2(NCS)_4(phen)_2$ (VI). The reaction of I (0.11 g) with 1,10-phenanthroline (phen) (0.12 g) in 15 mL of ethanol yielded the dark green complex; yield 0.10 g. Anal. Calcd for $C_{28}H_{16}Mo_2N_8S_4$: C, 42.86; H, 2.06; N, 14.28. Found: C, 43.28; H, 1.88; N, 13.71. This complex exhibits the same lack of solubility as V.

C. Stability of the Molybdenum(II) Thiocyanate Complexes. The molybdenum thiocyanate complexes reported herein appear to be

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