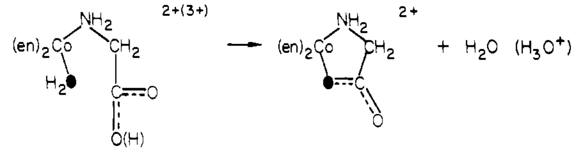
Table II. ^{18}O-Tracer Results for the Chelation of Glycine in the *trans*-$[Co(en)_2(OH_2/OH)(glyO/H)]^{3+/2+/+}$ Ions (25.0 °C, variable μ)

expt	complex (conditions)	R^a	atom % enrichment^b	% retention^c
1	glyOMe	0.01713	0.627	
2	*cis*-$[Co(en)_2Br(glyOH)]Br_2$	0.01546	0.545	100
3	$[Co(en)_2(glyO)]^{2+}$	0.01532	0.538	98.7
4	$[Co(en)_2(glyO)]^{2+}$ (0.01 $HClO_4$)	0.01471	0.508	93.2
5	$[Co(en)_2(glyO)]^{2+}$ (pH 3.7)	0.01507	0.527	96.7
6	$[Co(en)_2(glyO)]^{2+}$ (pH 8.0)	0.01493	0.519	95.2
7	$[Co(en)_2(glyO)]^{2+}$ (pH 10.0)	0.01485	0.515	94.5
8	$[Co(en)_2(glyO)]^{2+}$	0.00448	0.002	0.4
9	CO_2 (blank)	0.00444		

^{a} Observed R values; $R = [46]/([44] + [46])$ (for CO_2). ^{b} Atom % enrichment = $100R/(2 + R) - 100R'(2 + R')$ where R is as given and R' is for the CO_2 blank (experiment 9). ^{c} Percent retention per O atom on comparison with experiment 2.

complex in 10^{-2} mol dm^{-3} $HClO_4$ (experiment 4, 10 days) appears to result in some exchange into the reactant and/or product, but this is minor and is in agreement with results obtained previously on the chelate.[9] Clearly close to complete retention of the oxygens of the carboxylate group occurs under all conditions. Thus loss of bound water or hydroxide ion is required in forming the chelate.

The results clearly eliminate any prior isomerization to, or equilibration with, the cis-aqua ions (Scheme I). For these species tracer results[1] require subsequent cyclization to occur intramolecularly with incorporation of the coordinated water oxygen into the chelate (eq 5). This would halve the retention



(5)

results found here. For the trans-hydroxo ion the result is not as clear since the corresponding tracer experiment was not done for the cis species. However the kinetic analysis given above appears to eliminate involvement of the cis ion as an intermediate.

A distinction between paths a and b in Scheme II is not clear-cut. However, two independent pieces of information seem to support a concerted process. First, no N_3^- was incorporated during the cyclization process at pH 8. It is known that this anion competes favorably with solvent and the glycinate moiety in the corresponding base hydrolysis reaction of *cis*-$[Co(en)_2Br(glyO)]^+$[4] and that the *cis*- and *trans*-$[Co(en)_2N_3(glyO)]^+$ ions are stable under the reaction conditions.[4] We feel that if an intermediate of reduced coordination number were formed (Scheme II, path b), it would compete favorably for N_3^- as well as for the carboxylate moiety. Second, the rates found here are appreciably faster than those for isomerization in the closely related *trans*-$[Co(en)_2(H_2O/OH)(NH_3)]^{3+/2+}$ ions [$k_{H_2O} \simeq 10^{-8}$ s^{-1} (extrapolated data), $k_{OH} \simeq 1 \times 10^{-5}$ s^{-1}].[10] In these latter species there is no additional involvement of an attached ligand, and for the hydroxo complex at least the isomerization appears to occur without hydroxide exchange.[10] Thus we support a process involving the synergic displacement of coordinated water, or hydroxide, by the trans carboxylic acid or carboxylate anion (Scheme II, path a).

Registry No. *trans*-$[Co(en)_2(OH)(gly\text{-}O)]^+$, 70050-74-7; *trans*-$[Co(en)_2(OH_2)(gly\text{-}O)]^{2+}$, 77881-59-5; *trans*-$[Co(en)_2(OH_2)(gly\text{-}OH)]^{3+}$, 77881-60-8; $[Co(en)_2(gly\text{-}O)]^{2+}$, 16070-98-7.

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Molybdenum(IV) Compounds for Mediation of Electron Transfer. 1. Synthesis, Characterization, and Reactions of Compounds Containing Molybdenum(IV) Coordinated to Trihalostannate(II) Ions

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The presence of molybdenum in various enzymes such as nitrogenase, nitrate reductase, and sulfite oxidase, which catalyze the oxidation or reduction of small molecules, has stimulated interest in interactions of molybdenum and small molecules in general. The evidence[1] indicates that for nitrate reductase and sulfite oxidase, at least, the substrate binds directly to molybdenum atoms.

Molybdenum has been shown to catalyze the reduction of nitrate at mercury electrodes,[2] by Zn metal,[2] and by tin(II).[3,4] The latter system was also used to reduce nitrous acid, although nitrite is more labile to reduction than nitrate and can be reduced by Sn(II) alone. The perchlorate ion, although potentially a strong oxidant, is very inert in dilute aqueous acid at room temperature. However, its reduction, both at mercury electrodes[2] and by Sn(II)[5] is catalyzed by molybdenum. The chlorate ion in aqueous acid is so activated by molybdenum that it may be titrated to Cl^- by Sn(II) solutions in the presence of low concentrations of molybdenum.[6] Mechanisms derived from kinetic studies[5] indicate that the catalytically active species of molybdenum is Mo(IV).

In view of the importance of molybdenum in the biological reduction of oxyanions and the results that implicate Mo(IV) as the catalytically active species in the Sn(II) reductions, synthesis of a Mo(IV) complex compound containing $SnCl_3^-$ ligands has been attempted. Such a complex should allow Mo(IV), bound to a source of electrons in the form of Sn(II) ligands, also to bind to substrates such as NO_3^-, ClO_4^-, ClO_3^-, and N_2. Molybdenum would then act as a template and a pathway for electrons to effect rapid reduction of substrate.

Complexes containing Sn(II) as a ligand in the form of the $SnCl_3^-$ ion are well-known,[7] including the trigonal-bipyramidal $[Pt(SnCl_3)_5]^{3-}$, characterized by X-ray crystallography.[8] However, all compounds previously isolated have been of group 8 or 1B metals; this is, to our knowledge, the first report of a molybdenum compound containing a trihalostannate ligand.

Experimental Section

All manipulations were performed under nitrogen with use of standard Schlenk-type glassware. Solvents were dried with use of standard techniques and stored under nitrogen. Aqueous solutions were degassed by bubbling with nitrogen. Microanalyses were performed by the microanalytical laboratory at the University of Illinois. Infrared spectra were recorded as Nujol mulls with use of NaCl or CsBr windows on a Perkin Elmer 467 or 599B spectrometer. Electronic spectra were recorded on a Cary 14 spectrophotometer. Cuvettes were fitted with serum caps and preflushed with N_2, and the spectrum was recorded immediately after the solution was injected. Magnetic susceptibility measurements were made with use of the Guoy method.

NMe_4SnCl_3. The preparation of this salt has been previously reported,[9] and the method used here is similar except that it was

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performed under a nitrogen atmosphere.

$NMe_4Cl{\cdot}H_2O$ (6.0 g, 47 mmol) in 20 cm^3 of degassed 3 M HCl was added dropwise to a solution of $SnCl_2{\cdot}2H_2O$ (10.1 g, 45 mmol) in 30 cm^3 degassed 3 M HCl with vigorous stirring. [In 3 M HCl, the average ligand number n in $SnCl_n^{2-n}$ is 3.0.[9]] A white precipitate developed immediately. After refrigeration, the compound was filtered off, washed with 2-propanol and diethyl ether, and dried in vacuo. The yield was 10.8 g (80%e.

Anal. Calcd for $C_4H_{12}Cl_3NSn$: C, 16.06; H, 4.04; Cl, 35.5; N, 4.68; Sn, 39.7. Found: C, 16.28; H, 4.56; Cl, 35.4; N, 4.56; Sn, 39.4.

The other trichlorostannate salts were prepared in an analogous manner but were more soluble in 3 M HCl and required refrigeration to induce precipitation. The ammonium salt, on the basis of its infrared spectrum and analytical data, is formulated as being a hydrated double salt.

NEt_4SnCl_3. Anal. Calcd for $C_8H_{20}Cl_3NSn$: C, 27.04; H, 5.64; Cl, 29.9; N, 3.94; Sn, 33.4. Found: C, 27.00; H, 5.74; Cl, 30.0; N, 3.97; Sn, 33.1.

$NH_4SnCl_3{\cdot}NH_4Cl{\cdot}1.5H_2O$ or $(NH_4)_2SnCl_4{\cdot}1.5H_2O$. Anal. Calcd for $H_{11}Cl_4N_2O_{1.5}Sn$: H, 3.43; Cl, 43.8; N, 8.66; Sn, 36.7. Found: H, 3.46; Cl, 44.5; N, 8.66; Sn, 36.6.

NEt_4SnBr_3. Tetraethylammonium tribromostannate was prepared in a manner similar to the above by dissolving $SnCl_2{\cdot}2H_2O$ in 3 M HBr and generating the $SnBr_3^-$ ion. Anal. Calcd for $C_8H_{20}Br_3NSn$: C, 19.66; H, 4.13; Br, 49.1; N, 2.87; Sn, 24.3. Found: C, 20.08; H, 4.26; Br, 48.6; N, 2.78; Sn, 23.1.

$[NEt_4]_2[MoCl_4(SnCl_3)_2]$. A dichloromethane solution of NEt_4SnCl_3 (4.5 g, 12.6 mmol) was added to a suspension of $MoCl_4$ (1.5 g, 6.3 mmol) in CH_2Cl_2. The mixture was stirred vigorously for a few days, and the mauve-pink solid was filtered off, washed with CH_2Cl_2, and dried in vacuo. The yield was 5.8 g (98%). Anal. Calcd for $C_{16}H_{40}Cl_{10}MoN_2Sn_2$: C, 20.26; H, 4.25; Cl, 37.4; Mo, 10.1; N, 2.95; Sn, 25.0. Found: C, 20.97; H, 4.36; Cl, 36.7; Mo, 9.9; N, 2.87, Sn, 24.0.

The other compounds listed below were prepared analogously. The ammonium salt is again formulated as a double salt.

$[NMe_4]_2[MoCl_4(SnCl_3)_2]$. Anal. Calcd for $C_8H_{24}Cl_{10}MoN_2Sn_2$: C, 11.49; H, 2.89; Cl, 42.4; N, 3.35; Sn, 28.4. Found: C, 11.50; H, 2.99; Cl, 42.1; N, 3.15; Sn, 27.0.

$[NEt_4]_2[MoCl_4(SnBr_3)_2]$. Anal. Calcd for $C_{16}H_{20}Cl_{10}MoN_2Sn_2$: C, 15.82; H, 3.32; Cl, 11.7; N, 2.31; Sn, 19.5. Found: C, 16.46; H, 3.36; Cl, 12.9; N, 2.02; Sn, 20.3.

$[NH_4]_2[MoCl_4(SnCl_3)_2]{\cdot}2NH_4Cl$. Anal. Calcd for $H_{16}Cl_{12}MoN_4Sn_2$: H, 1.94; Cl, 51.2; Mo, 11.6; N, 6.74; Sn, 28.6. Found: H, 2.14; Cl, 48.8; Mo, 12.3; N, 6.58; Sn, 28.0.

$[NMe_4]_6[MoCl_4(SnCl_3)_6]$. A dichloromethane solution of NMe_4SnCl_3 (18 g, 60 mmol) was added to a suspension of $MoCl_4$ (2.38 g, 10 mmol) and stirred for 2 months in the absence of air. The compound is insoluble in all the organic solvents tested. It is highly air sensitive, precluding simple physical measurements for this preliminary report. Anal. Calcd for $C_{24}H_{72}Cl_{22}MoN_6Sn_6$: C, 14.15; H, 3.54; Cl, 38.38; Mo, 4.72; N, 4.13; Sn, 35.09. Found: C, 14.37; H, 14.37; Cl, 37.89; Mo, 4.67; N, 4.05; Sn, 34.85.

Results and Discussion

Synthesis. The synthetic method used for the preparation of the molybdenum complexes containing trihalostannate ligands described in this report is somewhat different from that used for other metals. In the latter method, an aqueous solution of a suitable metal starting material is reacted with an HCl solution of $SnCl_2{\cdot}2H_2O$. Under these conditions, tin is present primarily as $SnCl_3^-$. This method is unsuitable for the preparation of mononuclear complexes of Mo(IV) because of the reactivity of suitable Mo starting materials with water, so the ammonium salts of $SnCl_3^-$ were isolated and used as a source of the ligands. The method of prepraration is typical[1] of that used for Mo complexes of the type $MoCl_4{\cdot}2L$, where $MoCl_4$ is reacted directly with the ligand. However, the synthesis requires some time because of the insolubility of $MoCl_4$ in nonreactive solvents, unlike most other complexes of this type where $MoCl_4$ is dissolved in the ligand itself. Attempts to prepare the compound from $MoCl_4(CH_3CN)_2$ were not successful, due to incomplete replacement of the acetonitrile ligands by trihalostannate.

Table I. Electronic Spectral, Infrared, and Magnetic Susceptibility Data for $B_2[MoCl_4(SnX_3)_2]$

	IR abs below 350 cm^{-1}	electronic spectrum, nm	magnetic susceptibility, μ_B
B = NEt_4 X = Cl	345, 334 307, 295	782 (500)[a] 515 br (2600) 393 sh (4100)	1.17
B = NEt_4 X = Br	342, 333	787 (1500)[a] 530 br (2800) 410 sh (4200)	1.04
B = NMe_4 X = Cl	345 300	783 (1500)[a] 517 br (3500) 397 sh (4000)	1.23
B = NH_4 X = Cl	345, 330 310	759 (600)[b] 520 (2800) 412 (2600)	

[a] In MeCN. [b] In MeOH.

Characterization. The mauve-pink solids show typical properties of six-coordinate mononuclear tetrachloro Mo(IV) complexes. They are insoluble in most organic solvents, except strongly coordinating solvents such as DMF, Me_2SO, and pyridine, which replace the $SnCl_3^-$ ligands, but are sparingly soluble in MeOH. They are moderately air sensitive in the solid state but very air sensitive in solution. The electronic spectral, infrared, and magnetic susceptibility data are listed in Table I.

The electronic spectra are characterized by absorptions around 780, 520, and 400 nm. The absorptions obey Beer's Law within the limited concentration range (4×10^{-5} to 2×10^{-4} M) allowed by solubility, indicating the presence of a single species in solution. Tetrachloromolybdenum(IV) alkyl cyanides have been shown[19] to exhibit a low-intensity d–d absorption around 500 nm and charge-transfer absorption at around 400 nm. Compounds of the general formula $MoCl_4{\cdot}2L$, where L is a variety of O, P, N, or As donor ligands, all exhibit bands around 500 and 400 nm. The origin of these bands is uncertain, but the absorptions observed in the compounds prepared in this study in the 500- and 400-nm regions appear, on the basis of their intensity, to arise from charge transfer.

The infrared spectra are uninformative except for the bands below 350 cm^{-1}. For $MoCl_4{\cdot}2L$,[10] ν(Mo–Cl) has been observed as two bands between 310 and 350 cm^{-1}. A trans configuration has been considered[11-13] to be characterized by two bands around 340 and 330 cm^{-1} and a cis configuration characterized by bands at 340 and 310 cm^{-1}. The bands observed around 345 and 330 cm^{-1} in the compounds in this work can also be assigned to ν(Mo–Cl) but give no information concerning cis–trans configurations.

For the SnX_3^- group, the infrared assignments[14,15] are for X = Cl $\nu_1(A_1)$ at 297 cm^{-1} and for X = Br $\nu_1(A_1)$ at 211 cm^{-1}. The tetraalkylammonium salts were found to exhibit this band around 280 cm^{-1} for X = Cl. When SnX_3^- coordinates to a metal, the band shifts to a higher wavenumber. Lindsey et al.[16] observed for X = Cl a doublet around 330 cm^{-1}, but Kingston and Scollary,[17] for a series of Pt, Pd, and Rh com-

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plexes, suggested that the Sn–Cl stretch is around 285–315 cm^{-1}, somewhat lower than the Mo–Cl vibration. In the compounds prepared in this study, the Sn–Cl stretching vibration is shifted to higher wavenumber due to the coordination of the stannate group, and either a doublet or a broad singlet is observed in the 300–310-cm^{-1} region. The Sn–Br stretching moment was below the range of the instrument.

Except for the NH_4^+ salt, the magnetic moments of the compounds are somewhat lower than the range of 1.9–2.8 μ_B observed[2] for other compounds of this type. The counterion has been shown[18,19] to influence the value of the magnetic moment, or perhaps some spin–spin interaction is taking place in the alkylammonium salts. The ammonium salt shows an expected value for a d^2 octahedral system ($\sim$2.8 μ_B).

Exploratory cyclic voltammograms obtained for $Sn_2MoCl_{10}^{2-}$ in acetonitrile gave separate and irreversible reduction and oxidation waves, probably Mo(IV) → Mo(III) and Sn(II) → Sn(IV). Reduction waves are diffusion controlled and may be interpreted as a reduction followed by another reaction before reoxidation. An irreversible oxidation of Sn(II) to Sn(IV) is observed. No Mo oxidations are observed in the absence of available oxygen to stabilize Mo(V) or Mo(VI). Oxomolybdenum(V) complexes are not oxidized to Mo(VI) in this medium because additional oxygen is not available.

For determination of the number of electrons by which the compounds could be oxidized and for confirmation of the presence of one Mo(IV) and two Sn(II), the compounds were treated with an excess of acidified $KMnO_4$ and titrated with ferrous ammonium sulfate. The result of 5.8 electron equivalents confirmed the presence of Mo(IV) being oxidized to Mo(VI) and two Sn(II) being oxidized to Sn(IV). A solution of $[NEt_4]_2[MoCl_4(SnCl_3)_2]$ in 3 M degassed H_2SO_4, which was used for all subsequent experiments, was also titrated to both a $KMnO_4$ and a $K_2Cr_2O_7$ endpoint. Both gave the same result of 6.0 electron equivalents. These titrations were the basis of the analysis discussed in the next section. It was found that the reducing equivalents of solutions of the complex remained constant for at least 4 h, which was longer than the time taken for any subsequent experiments.

Reactions. Nitrate. The addition of an excess of either sodium nitrate or nitric acid to a solution of $[NEt_4]_2[MoCl_4(SnCl_3)_2]$, hereafter abbreviated "$MoSn_2$", in 3 M H_2SO_4 produced an immediate decoloration corresponding to the oxidation of $MoSn_2$. The resultant solution was then titrated with MnO_4^- or $Cr_2O_7^{2-}$ to determine the number of oxidizable equivalents remaining and thus the corresponding extent of oxidation of $MoSn_2$.

Titrations with MnO_4^- indicated 0.5–0.9 reducing equivalents remaining per mole of $MoSn_2$ oxidized, but those with $Cr_2O_7^{2-}$ indicated no oxidizable material remained. Hydroxylamine, which is the primary reduction product when Sn(II) reduces nitric acid[3,4] in the presence of Mo(VI), is oxidized fairly rapidly by MnO_4^- and very slowly by $Cr_2O_7^{2-}$. The stoichiometry of the reaction of $MoSn_2$ with nitric acid is concluded to be

$$Mo^{4+} + 2Sn^{2+} \rightarrow Mo^{6+} + 2Sn^{4+} + 6e^- \tag{1}$$

$$NO_3^- + 6e^- + 8H^+ \rightarrow NH_3OH^+ + 2H_2O \tag{2}$$

It has previously been observed that the primary product of reduction of HNO_3 by Sn(II) using molybdenum (as MoO_4^{2-}) catalyst is NH_3OH^+.[4] This system containing Mo(IV) initially bound to $SnCl_3^-$ reacts very fast indeed, consistent with the hypothesis that $[Cl_3Sn–Mo(IV)–ONO_2]$ constitutes the activated state for Mo-catalyzed reduction of NO_3^- by Sn(II).

Perchlorate. The addition of excess $HClO_4$ to a solution of $MoSn_2$ in 3 M H_2SO_4 produces a rapid yellowing of the solution followed by a slower fading of the yellow color to a pale yellow. Titrations of aliquots with both MnO_4^- and $Cr_2O_7^{2-}$ indicate a fast (10–15 min) oxidation of $MoSn_2$ in solution by 4 equiv, followed by a slower oxidation which still leaves $\sim$1.5 reducing equivalents. Probably the initial oxidation of the $MoSn_2$ is that of Sn(II) to Sn(IV). The remaining oxidation, as evidenced by color changes, is partial oxidation of Mo(IV) to Mo(V), both of which can be oxidized by MnO_4^- or $Cr_2O_7^{2-}$. Alternatively, Mo(IV) may be oxidized slowly to Mo(VI). The final yellow color of the solution appears to be a form of Mo(V). Mo-catalyzed Sn(II) reductions of ClO_4^- produce[2,5] chloride ion. Reduced oxochloro species are labile oxidants, and their presence would be incompatible with oxidizable Mo(V). More detailed study of reaction products is required to characterize this system completely, but results are consistent with previous postulates that Mo(IV) mediates electron transfer from Sn(II) to ClO_4^- and is not itself an active reducing agent in the catalytic process. Molybdenum-catalyzed reductions of ClO_4^- by $SnCl_3^-$ give the same kinetics whether Mo catalyst is added as Na_2MoO_4 or as $Sn_2MoCl_{10}^{2-}$, indicating that $SnCl_3^-$ dissociates from $MoCl_4$ in aqueous solution as expected.

Chlorate. The reduction of ClO_3^- can be effected by many chemical species, but its reduction by $MoSn_2$ produces rather unexpected initial products. Upon addition of an excess of $NaClO_3$ to a solution of $MoSn_2$ in 3 M H_2SO_4, the solution immediately turns yellow with the evolution of a yellow gas. The solution was swept with dinitrogen gas which passed into a series of flasks containing a KI solution where the gas was reduced to chloride ion with the production of I_3^-. I_3^- was then titrated with thiosulfate to determine the oxidizing equivalents present in the yellow gas. The evolution of the yellow gas is initially rapid until the resulting solution is colorless but then continues quite slowly for a few days. Initially, 12 equiv of thiosulfate are required per mole of $MoSn_2$. After 3 days, 18 equiv of thiosulfate are required. If the yellow gas were Cl_2, reaction 3 would account for the fast initial reaction which

$$Mo(IV) + 2Sn(II) + 2ClO_3^- + 10Cl^- \rightarrow Mo(VI) + 2Sn(IV) + 6Cl_2 \tag{3}$$

would leave no Cl^- to continue slow reduction of ClO_3^- to Cl_2, so this process is ruled out. $ClO_2\cdot$, a common product of one-electron reduction of ClO_3^- and of disproportionation of ClO_2^-, must be a primary product. Equations 4 and 5 are consistent with analyses described above.

$$Mo(IV) + 2Sn(II) + Cl^- + 3ClO_3^- \xrightarrow{\text{fast}} 2ClO_2 + Cl_2 + Mo(VI) + Sn(IV) + 9Cl^- \tag{4}$$

$$5Cl^- + ClO_3^- + 6H^+ \xrightarrow{\text{slow}} 3Cl_2 + 3H_2O \tag{5}$$

After the yellow gas had been purged from the reaction solution, no reducing material was left, indicating the presence of Mo(VI) and Sn(IV) products. The appearance of ClO_2 suggests either rapid one-electron reductions of ClO_3^- by Mo(IV) and Mo(V) or disproportionation of ClO_2^-, as observed by G. Gordon. Two plausible mechanisms for producing 12 equiv of oxidizing gas are suggested (Schemes I and II). Scheme I is consistent with previously observed rapid

Scheme I

$$MoSn_2 + 3ClO_3^- \rightarrow 3ClO_2^- + Mo(VI) + 2Sn(IV)$$

$$3ClO_2^- \rightarrow 2ClO_2\uparrow + ClO^-$$

$$ClO^- + Cl^- + 2H^+ \rightarrow Cl_2\uparrow + H_2O$$

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catalytic oxidation of Sn(II) by ClO_3^- in the presence of Mo and rapid oxidation of Mo(IV) by intermediate oxidation states of chlorine.[5]

Scheme II

$$Mo(IV) + 2Sn(II) + ClO_3^- \rightarrow ClO^- + 2Sn(IV) + Mo(IV)$$

$$Mo(IV) + ClO_3^- \rightarrow ClO_2 + Mo(V)$$

$$Mo(V) + ClO_3^- \rightarrow ClO_2 + Mo(VI)$$

$$2H^+ + ClO^- + Cl^- \rightarrow Cl_2 + H_2O$$

It seems unlikely that two Sn^{2+} would reduce ClO_3^- by 4 equiv leaving Mo(IV) unreacted in the presence of the very reactive OCl^- and that Mo(IV) should prefer two 1-e processes to one 2-e process in reacting with ClO_3^-. This complicated reaction system requires further investigation of stoichiometry and kinetics as functions of reactant concentrations, order of mixing, etc., before it can be completely understood. If ClO_2 is the product of successive one-electron oxidation of Mo(IV) → Mo(V) → Mo(VI), acid ClO_3^- will be established as a good reagent for discriminating between one- and two-electron donors among reducing agents. If Mo(IV) is oxidized preferentially by two one-electron steps, it is interesting to note one-step two-electron reductions of Mo(VI) occur as well. Adding $2e^-$ to an empty d orbital—Mo(VI) → Mo(IV)—should not provide mechanistic difficulty as great as removing two electrons simultaneously from different orbitals (Mo(IV) → Mo(VI)).

$[NMe_4]_6[MoCl_4(SnCl_3)_6]$ is too air (oxygen) sensitive for immediate qualitative study. This is consistent with the hypothesis that the activated state for molybdenum-catalyzed reductions of inert oxidized species contains Mo(IV) bound to an electron source ($SnCl_3^-$) while still accessible to oxidant (O_2 in this case).

Conclusion

The compounds $B_2[MoCl_4(SnX_3)_2]$ are the first example of molybdenum complexes containing SnX_3^- ligands. $[NEt_4]_2[MoCl_4(SnCl_3)_2]$ (and presumably the other compounds in this series) is an effective reducing agent for small oxoanions such as perchlorate, chlorate, nitrate, and nitrite. The reduction and oxidation products are only easily interpreted in the case where nitrate is used, but, with both nitrate and perchlorate, the reductions (that is, the oxidation of $MoSn_2$) occur rapidly, consistent with previously observed Mo-catalyzed reductions by Sn(II). A tentative conclusion is that Mo(IV) is a particularly effective site at which oxoanions or other oxidized nonmetals can bind and that it allows rapid transfer of electrons from electron donor to substrate. Reactivity of these complexes with N_2 at 1 atm over aqueous acid takes place very slowly if at all, since we were able to make the preliminary studies under N_2 without apparent interference. $[N_2]$ in water is $\sim 10^{-4}$ M at 1 atm and 298 K. Substrates in kinetic studies have generally been >0.1 M and exhibited reaction orders >1. The concentration effect above could involve a factor of 10^{-5} on the rate of reduction of N_2 vs. NO_3^-, to which should be added the decreased ligating ability of N_2 vs. the oxoions studied. Reactions lasting 1 month with N_2 at 1 atm and reactions with N_2 under high pressure have so far yielded no evidence for nitrogen reduction by systems containing Sn(II) and Mo(IV) in acid solution.

Registry No. $[NEt_4]_2[MoCl_4(SnCl_3)_2]$, 78004-09-8; $[NMe_4]_2[MoCl_4(SnCl_3)_2]$, 78004-10-1; $[NEt_4]_2[MoCl_4(SnBr_3)_2]$, 78004-12-3; $[NH_4]_2[MoCl_4(SnCl_3)_2]\cdot 2NH_4Cl$, 78004-13-4; NMe_4SnCl_3, 14877-00-0; NEt_4SnCl_3, 7781-71-7; $NH_4SnCl_3\cdot NH_4Cl$, 53149-60-3; NEt_4SnBr_3, 29920-61-4; HNO_3, 7697-37-2; $HClO_4$, 7601-90-3; $HClO_3$, 7790-93-4.

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Evolving Cation Coordination in Aqueous Solutions Prepared from Iron(III) Chloride Hexahydrate

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Our 10.4 *m* aqueous solution prepared from iron(III) chloride hexahydrate, $FeCl_3\cdot 6H_2O$, in which the initial solute species were identified as hexaaquoiron(III) and solvent separated Fe–Cl ion pairs,[1] has been reexamined by X-ray diffraction in an attempt to determine if this solute species is the thermodynamic as well as the kinetic product.

Shown in Table I are the pair correlation functions obtained via X-ray diffraction examination of the aqueous 10.4 *m* $FeCl_3\cdot 6H_2O$ solution two 2 weeks[1] (10.4-A) and 14 months (10.4-B) after preparation. The $D(r)$'s are shown in Figure 1.

The ARDF obtained from 10.4-B is somewhat different from that obtained from 10.4-A, particularly in the vicinity of the first peak. Since this first peak describes the nearest-neighbor Fe–ligand atom pairs,[1-6] the difference in the ARDF's indicates that the average coordination of Fe^{3+} in 10.4-B is different than that found in 10.4-A. The first peak in the ARDF of 10.4-A is centered at 2.04 (±0.01) Å, and the area under this peak is ca. 64 e^2. The location of P1 is consistent with Fe–O[1-4] but not Fe–Cl[4-6] nearest neighbors. The peak area is consistent with an average of 6.0 (±0.3) oxygen (water) neighbors/Fe, i.e., hexaaquoiron(III) as previously reported.

In 10.4-B the first peak is centered at 2.16 (±0.01) Å, and the area under the peak is 86 (±5) e^2. The increase in peak area and the shift in the maximum are both consistent with Fe–Cl and Fe–O nearest-neighbor interactions in 10.4-B and can be explained in no other plausible manner. Because the tetrahedral ligand···ligand peak, found a 3.6–3.7 Å in the ARDF's of the aqueous[1,5] and nonaqueous solutions[6] prepared from anhydrous $FeCl_3$, is not present in the ARDF of 10.4-B, it appears that Fe^{3+} is predominantly, if not exclusively, octahedrally coordinated in 10.4-B as well as in 10.4-A.

An *average* solute species of ca. $FeCl_{1.5}(H_2O)_{4.5}{}^{1.5+}$ is consistent with both the primary peak area and its location in the ARDF obtained for 10.4-B. The uncertainty[7] in the primary peak area, ±5 e^2, is principally due to uncertainty in the resolution of the primary peak from the remainder of the ARDF and causes an uncertainty of ±0.3 in the values of n_{Fe-Cl} and n_{Fe-O}. The existence of this mean species is supported by the shoulder at 2.9–3.0 Å, which is attributed to cis Cl···O atom-pairs. Because of its comparatively small scattering power the cis O···O atom pairs make only minimal contributions to the peak at 2.9–3.0 Å, and the ARDF of 10.4-A does not indicate a cis O···O peak.

The peak at 3.2 Å is due primarily, if not exclusively, to H-bonded Cl–O atom pairs.[8-10] The peak at 4.1–4.3 Å in each ARDF is attributed to solvent separated Fe···Cl atom pairs, with the trans O···Cl pairs of 10.4-B possibly causing the increase in magnitude and the shift to larger *r* for this peak.

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