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

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

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

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

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

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; $[NMe_4]_2[MoCl_4(SnCl_2)_2]$, 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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Table I. Comparison of the ARDF's of the Aqueous ICHH Solutions 10.4-A and 10.4-B

	$g(r)$			$g(r)$	
r, Å	10.4-A	10.4-B	r, Å	10.4-A	10.4-B
0.1	0.01	0.01	2.6	0.57	0.62
0.2	0.04	0.00	2.7	0.68	0.81
0.3	0.08	−0.05	2.8	0.81	0.99
0.4	0.06	−0.07	2.9	0.97	1.13
0.5	−0.01	−0.08	3.0	1.13	1.14
0.6	−0.03	−0.05	3.1	1.19	1.20
0.7	−0.04	−0.03	3.2	1.09	1.14
0.8	−0.01	0.03	3.3	0.89	1.02
0.9	0.03	0.06	3.4	0.84	0.90
1.0	0.01	0.03	3.5	0.80	0.86
1.1	−0.05	−0.01	3.6	0.86	0.84
1.2	−0.09	−0.03	3.7	0.96	0.87
1.3	−0.06	−0.04	3.8	1.19	0.93
1.4	−0.03	0.02	3.9	1.41	1.07
1.5	0.04	0.05	4.0	1.44	1.27
1.6	0.19	−0.02	4.1	1.30	1.44
1.7	0.37	−0.04	4.2	1.08	1.47
1.8	0.70	0.30	4.3	0.87	1.38
1.9	1.09	0.97	4.4	0.74	1.11
2.0	1.31	1.62	4.5	0.71	0.80
2.1	1.24	2.03	4.6	0.79	0.60
2.2	0.98	1.83	4.7	0.87	0.58
2.3	0.69	1.27	4.8	0.97	0.71
2.4	0.52	0.69	4.9	1.07	0.87
2.5	0.50	0.45	5.0	1.15	0.99

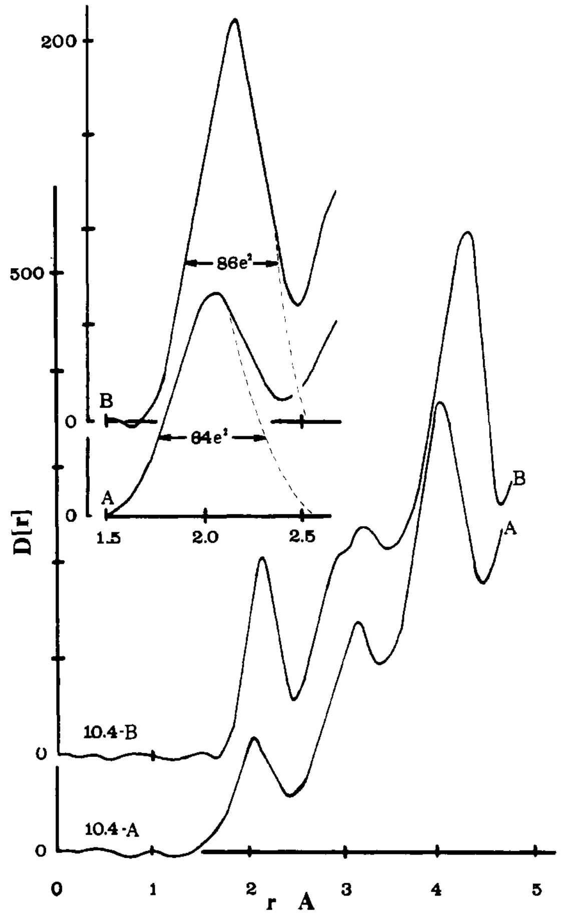

Figure 1. ARDF's calculated with a dampening factor of $\exp(-0.01s^2)$ for the 10.4 *m* aqueous solution prepared from $FeCl_3·6H_2O$ obtained 2–6 weeks (10.4–A) and 14–15 months (10.4–B) after solution preparation. In the insert the resolution of and the area under the primary peak in each $D(r)$ are shown.

Although the average specie found in this solution is somewhat similar to that reported by Magini and Radnai[4] to exist in one of their solutions, our findings should *not* be taken as evidence to support the existence of any of the several solute species they propose. Rather, this reinvestigation establishes that hexaaquoiron(III) is the initial product formed when $FeCl_3·6H_2O$ is dissolved into water and that Fe^{3+} appears to be, on the average, octahedrally coordinated in this solution even though, after 14 months, some of the inner-sphere waters have been replaced by chlorides.

Registry No. $FeCl_3·6H_2O$, 10025-77-1; $[Fe(OH_2)_6]Cl_3$, 57533-67-2.

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Formation of a Complex with a Carbide Bridge between Two Iron Atoms from the Reaction of (Tetraphenylporphyrin)iron(II) with Carbon Tetraiodide

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Dihalogenocarbene complexes of iron porphyrins, Fe(porphyrin)(CXX′) with X = X′ = F, Cl, or Br, have recently been obtained from reaction of tetrahalomethanes with iron porphyrins in the presence of an excess of reducing agent[1-3] (eq 1). These complexes could be good precursors of other organometallic species such as other carbene or carbyne complexes, if it were possible to use the leaving-group properties of the halogen substituents of their carbenic carbon. Effectively, the $Fe(TPP)(CBr_2)$ complex is more reactive toward nucleophiles than the $Fe(TPP)(CCl_2)$ complex.[3,4] Therefore we have attempted to prepare the $Fe(TPP)(CI_2)$ complex from the reaction between CI_4 and Fe(TPP) in the presence of a reducing agent in excess. This note reports that this reaction does not afford the expected complex but leads to a new complex which exhibits characteristics corresponding to a heme dimer structure with two iron atoms bridged by a formally dicarbenic carbon. Quite independently of our work, it has been very recently predicted[5] from calculations that the complex $[Fe(TPP)]_2C$ should be a stable diamagnetic molecule with a linear M–C–M spine.

$$\mathrm{Fe^{II}(P)} + \mathrm{CX_3X'} \xrightarrow[-2X^-]{+2e^-} [\mathrm{(P)Fe^{II}} \leftarrow \mathrm{CXX'}] \qquad (1)$$

Experimental Section

Preparation of $[Fe(TPP)]_2C$ (1). $Fe^{III}(TPP)(Cl)$ (500 mg, 6.9×10^{-4} mol) was dissolved in 25 mL of an anaerobic (argon) 9:1(v:v) CH_2Cl_2–CH_3OH solution, in the presence of 100 mg of iron powder, in a tube stoppered with a serum cap. CI_4 (360 mg, 6.9×10^{-4} mol) was then added under argon and the solution vigorously stirred at 20 °C. Formation of **1** is complete within about 1 h under these conditions, as shown by visible spectroscopy (λ_m = 400 and 530 nm). After filtration of the solution, washing with water, drying over Na_2SO_4, and evaporation, the solid residue was dissolved in a 1:9 (v:v) CH_2Cl_2–CH_3OH (or C_2H_5OH) solution. Complex **1** was then ob-

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