must be born in mind however that it is difficult to compare the absolute values of equilibrium constants for different chloroaluminate melts because of the large cation effect on the solvent acid–base equilibria.[24] Thus, Gale and Osteryoung[3] postulated that the increased extent of $Al_2Cl_7^-$ ion formation in room-temperature chloroaluminates, as compared to the inorganic systems, results from the decreased polarizing power of the organic cation. By the same argument, the large size of the organic cation can be expected to enhance the formation of the $Al_3Cl_{10}^-$ anion, but a comparison with other systems is impossible for lack of experimental data.

Conclusion

In conclusion, the results of this paper show that the solvent equilibria in acidic $AlCl_3$–*N*-*n*-butylpyridinium chloride melts are adequately represented by the combination of two equilibria, (I) and (II). Obviously it would be interesting to confirm the conclusions of this work directly by Raman spectroscopic studies on very acidic melts (molar ratio of $AlCl_3$:BuPyCl > 2:1), where the mole fraction of $Al_3Cl_{10}^-$ becomes appreciable. The results obtained thus far by this technique in this laboratory are inconclusive because of the poor quality of the spectra in acidic melts (as was also noted earlier[8]). Finally, the results of this work allow a precise calculation of the pCl values over the whole composition range of acidic melts, at least on a relative scale: the absolute value of the pCl depends of course also on the value of K_I, which is not known with sufficient accuracy. Fortunately, for most practical applications, the variation of pCl with the melt composition is the more important factor.

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Appendix

The composition of the melt is defined by 1 mol of $BuPyAlCl_4$ + X mol of $AlCl_3$ (the mole fraction of aluminum chloride, more commonly used to represent the composition of these melts, is then given by $(1 + X)/(2 + X)$). The mass balances for aluminum and chlorine are given by

$$(AlCl_4^-) + 2(Al_2Cl_7^-) + 3(Al_3Cl_{10}^-) = 1 + X \qquad (1A)$$

$$4(AlCl_4^-) + 7(Al_2Cl_7^-) + 10(Al_3Cl_{10}^-) + (Cl^-) = 4 + 3X \qquad (2A)$$

where $(AlCl_4^-)$ is the number of moles of $BuPyAlCl_4$ in the system, etc. It follows at once that

$$(AlCl_4^-) = 1 - X + (Al_3Cl_{10}^-) - 2(Cl^-) \qquad (3A)$$

$$(Al_2Cl_7^-) = X - 2(Al_3Cl_{10}^-) + (Cl^-) \qquad (4A)$$

Furthermore, the total number of moles in the system is given by

$$T = (AlCl_4^-) + (Al_2Cl_7^-) + (Al_3Cl_{10}^-) + (Cl^-) = 1 \qquad (5A)$$

so that $[AlCl_4^-] = (AlCl_4^-)/T$, etc., where square brackets denote mole fractions. In acidic melts, the mole fraction of chloride ions can be neglected in the mass balances so that

$$[AlCl_4^-] = 1 - X + [Al_3Cl_{10}^-] \qquad (6A)$$

$$[Al_2Cl_7^-] = X - 2[Al_3Cl_{10}^-] \qquad (7A)$$

Substitution of these equations into the expression for the mole fraction equilibrium constant K_{II} yields a quadratic equation

$$(1 - 4K_{II})[Al_3Cl_{10}^-]^2 + [1 - X(1 - 4K_{II})][Al_3Cl_{10}^-] - K_{II}X^2 = 0 \qquad (8A)$$

which can be solved to give

$$[Al_3Cl_{10}^-] = \{-[1 - X(1 - 4K_{II})] + ([1 - X(1 - 4K_{II})]^2 + 4K_{II}X^2(1 - 4K_{II}))^{1/2}\}/2(1 - 4K_{II}) \qquad (9A)$$

(obviously, this equation can be further simplified if the condition $4K_{II} << 1$ is fulfilled). The potential of cell 1 can then be calculated by using eq 3 after substitution of eq 9A in eq 6A and 7A. The value of the equilibrium constant for reaction II was calculated by varying the K_{II} value to obtain a minimum standard deviation E_{SD} between the experimental and calculated potentials, where the standard deviation of the potential is given by

$$E_{SD} = \left(\left[\sum_{i=1}^{D}(E_{i,\text{theor}} - E_{i,\text{exptl}})^2\right]/(D - 1)\right)^{1/2} \qquad (10A)$$

where D is the number of data points. The values of the equilibrium constant given in Table I are the mean values obtained from at least three independent titrations for each temperature. The experimental potential values of the independent titration experiments were adjusted to one common reference electrode (aluminum in a melt with a 2:1 molar ratio of $AlCl_3$:BuPyCl composition) for the sake of clarity of the graphical representation of the data.

Registry No. BuPyCl, 1124-64-7; $AlCl_3$, 7446-70-0; $AlCl_4^-$, 17611-22-2; $Al_2Cl_7^-$, 27893-52-3; $Al_3Cl_{10}^-$, 37233-70-8.

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Mechanism of the Water-Mediated Reduction of Tris(2,2′-bipyridine-*N*,*N*′)iron(III), -ruthenium(III), and -osmium(III) Complexes

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A new mechanism is proposed for the reduction of $[M(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) ions by water. The initial step in the reaction is nucleophilic attack of a water molecule (or OH^-) at the metal center to form a seven-coordinate intermediate. This intermediate may undergo oxidation by another molecule of $[M(bpy)_3]^{3+}$ to give a seven-coordinate M(IV)–oxo species and $[M(bpy)_3]^{2+}$. Subsequent ligand loss and/or oxidation follows. Dioxygen evolution results from the formation of binuclear oxo complexes, which act as catalysts (in the presence of $[M(bpy)_3]^{3+}$) for the oxidation of water to dioxygen.

Dioxygen evolution from $[M(bpy)_3]^{3+}$ ions (bpy = 2,2′-bipyridine) is of particular interest in the area of solar energy research, since the Ru(III) complex is produced during the photoreduction of water to H_2 using $[Ru(bpy)_3]^{2+}$ as sensitizer.[1] The kinetics of the reduction of $[Fe(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{3+}$ by water have been studied in great detail,[2-7] but there is no

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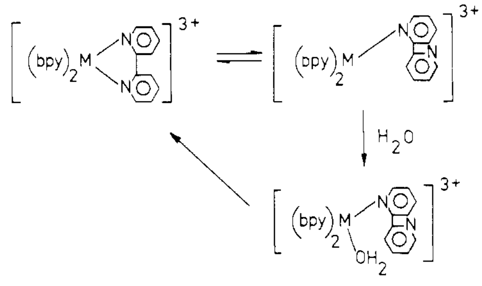
agreement on the mechanism of these reactions.[5-8] This paper attempts to rationalize the experimental observations in terms of a new mechanism that involves initial nucleophilic attack at the metal center by water or hydroxide ion.

The outer-sphere oxidation of water or hydroxide ion by $[M(bpy)_3]^{3+}$ (reaction 1) is not considered feasible on energetic grounds,[5,7,8] although it has been suggested to occur via an intimate ion pair.[8] The latter proposal is also unacceptable because it

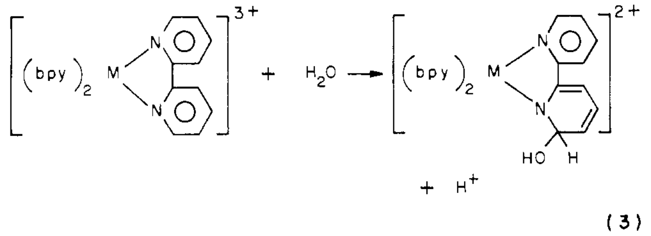
$$M(III) + OH^- \text{ (or } OH_2) \rightarrow M(II) + \cdot OH \text{ (or } OH_2^+) \quad (1)$$

requires that the more strongly oxidizing $[Ru(bpy)_3]^{3+}$ would produce more oxygen than $[Fe(bpy)_3]^{3+}$, contrary to the experimental evidence.[5,7]

An alternative initial reaction is ligand dissociation (reaction 2) to form a five-coordinate intermediate,[5,6] but the reaction rates Os < Fe < Ru do not follow the relative lability expected for a dissociative process (i.e. Os < Ru < Fe).[7] Furthermore, the reactions are strongly retarded in concentrated acid,[9] while dissociative processes involving $[M(bpy)_3]^{n+}$ ions are strongly catalyzed by acid.[10-13] The correlation of increased complex stability with decreasing water activity could, however, be accommodated by the formation of a pseudobase or by covalent hydration (reaction 3)[9,14] and was taken as evidence for such a rate-determining step.[7] However, the major products of ligand oxidation are *N*-oxides[5] (in the case of Fe(III)), which is not consistent with either pseudobase formation or covalent hydration.[5]



(2)



(3)

We now propose a mechanism in which the initial reaction is nucleophilic attack of water at the metal ion to form a seven-coordinate intermediate (reaction 4). Such a mechanism was

$$[M(bpy)_3]^{3+} + OH_2 \rightarrow [M(bpy)_3(OH_2)]^{3+} \rightleftarrows [M(bpy)_3(OH)]^{2+} + H^+ \rightarrow [M(bpy)_2(bpyH)(OH)]^{3+} \quad (4)$$

rejected by previous workers[7] without consideration of the evidence that we now present.

It has been shown that the rate law for substitution of ammine ligands in $[Ru(NH_3)_6]^{3+}$ depends of water activity[15,16] in a like manner as that for the reduction of the $[M(bpy)_3]^{3+}$ ions. Since pseudobase formation is impossible with $[Ru(NH_3)_6]^{3+}$, we suggest that the initial step, in both reactions, is nucleophilic attack of water at the metal ion to form a seven-coordinate intermediate.[15,16] This is also supported by mechanistic studies on the $[Ru(OH_2)_6]^{3+}$ water-exchange reaction, which apparently occurs via an associative-interchange (I_a) mechanism,[17] and the isolation and characterization of a seven-coordinate Fe(III) complex containing a coordinated aqua ligand, viz., $[Fe(edta)(OH_2)]^-$.[18] The above arguments lead us to propose that (4) is the most reasonable representation of the initial reactions.

The order of the M(III)/M(II) redox potentials (Ru > Fe > Os), which follows the susceptibility of the $[M(bpy)_3]^{3+}$ ions to reduction, has been used to support a pathway involving pseudobase formation or covalent hydration,[7] but the observed order of reactivity is also identical with that expected for the associative process proposed here (reaction 4).[20,21] Moreover, these redox potentials are a complex function of stabilization of both oxidation states (generally dominated by π back-bonding in the M(II) oxidation state[19] and the ionization potential of the M^{2+} ion). Thus the correlation of reaactivity with oxidation states used[7] to support covalent hydration is not meaningful.

The overall reaction scheme we propose is assocative water attack (reaction 4), followed by ligand oxidation (Scheme I) and formation of dioxygen (Scheme II). Scheme I accounts for the formation of *N*-oxides,[5] since the oxo-donor properties of $M^{IV}{=}O$ species are now well-established.[22-26] The first step in Scheme I is the base-catalyzed disproportionation of a M(III) species with $[M(bpy)_3]^{3+}$ to produce M(IV) and M(II) ions. Such processes have been encountered in a variety of reactions involving aqua, alcohol, and amine ligands coordinated to M(III) ions of the iron triad.[22-29] The postulated disproportionations are strongly favored

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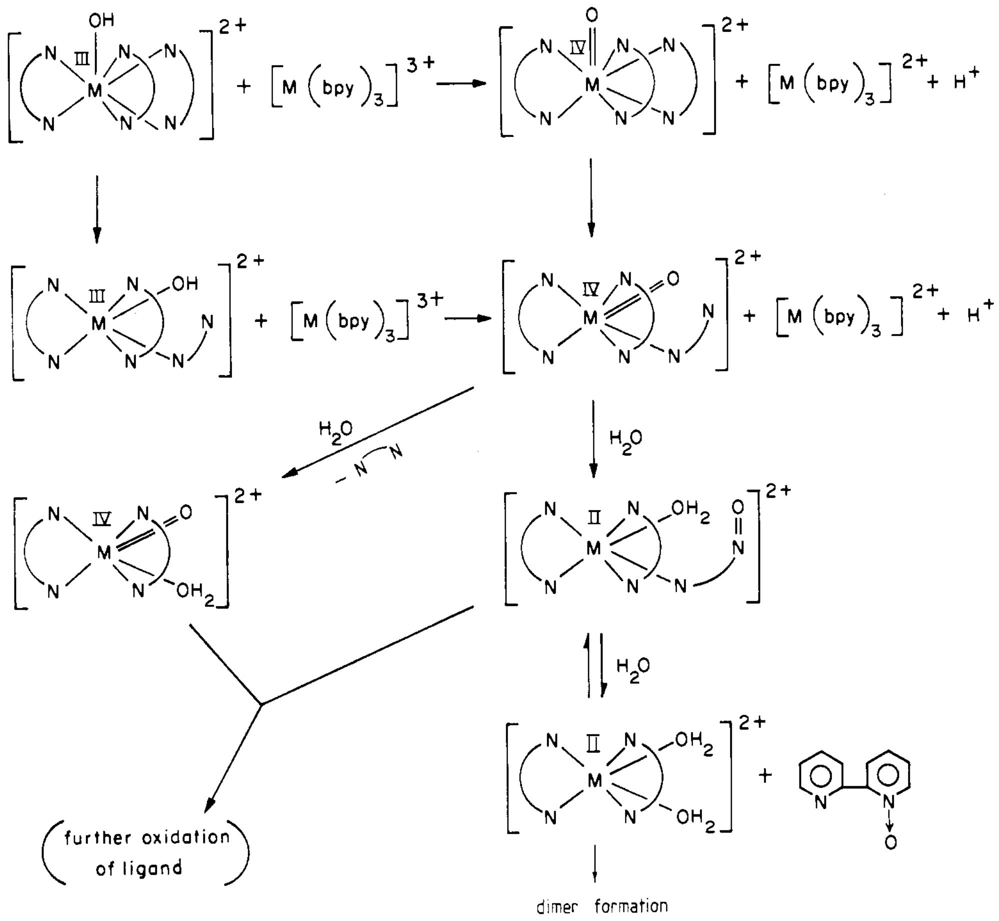
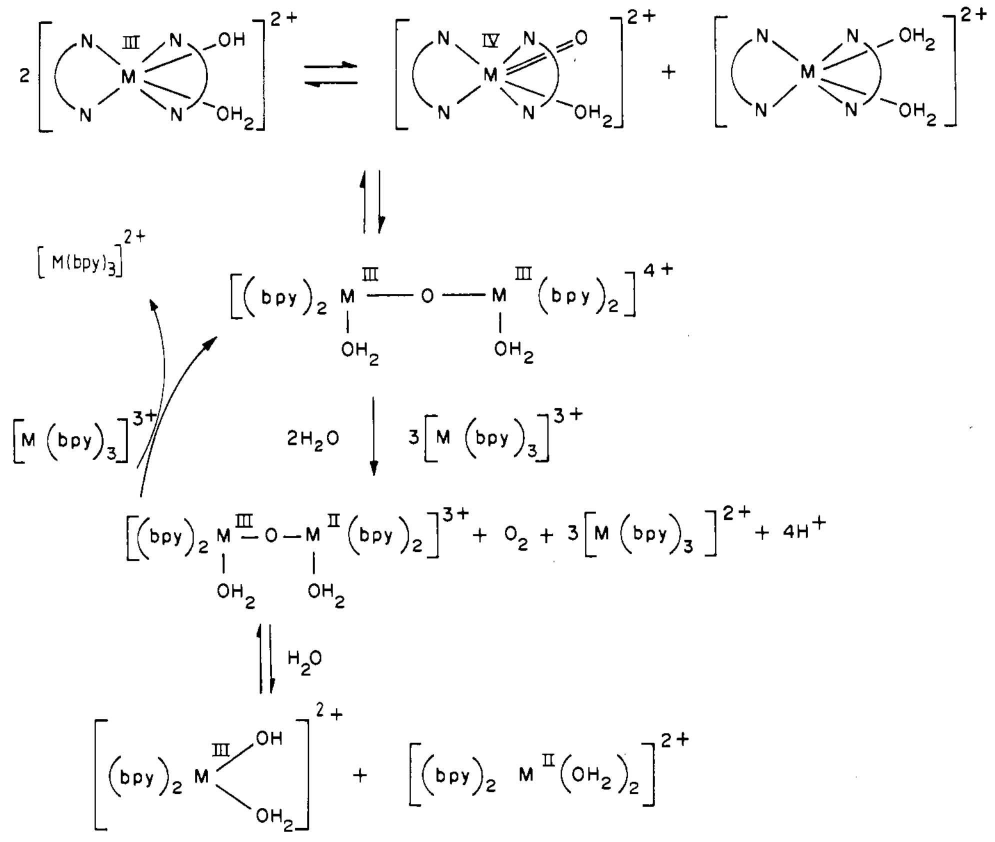
Scheme I



Scheme II

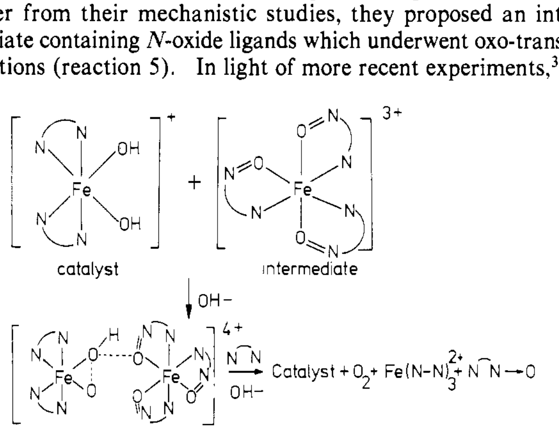


thermodynamically, because the redox potentials of $M^{III}L_5OH^{2+}/M^{IV}L_5O^{2+}$ (L_5 denotes polypyridine ligands)[22-26] are much less positive than the corresponding potentials of $[M(bpy)_3]^{3+/2+}$.[7] Moreover, the rates of disproportionation will greatly exceed the observed rates of production of $[M(bpy)_3]^{2+}$ and hence the disproportionations do not control the overall rates.[30,31] As the rate-determining reactions that precede disproportionation are all first-order in M(III), the proposed mechanism accommodates the observed kinetics.

Mononuclear Fe(IV) species have been proposed as intermediates in the reductions, but only for O_2 evolution[6] (where the binuclear ions are more efficient). A seven-coordinate M(IV) species, as proposed in Schemes I and II, is at least feasible since the existence of a seven-coordinate M(IV) complex containing an aqua ligand has been established by X-ray crystallography for $[Os^{IV}(edta)(OH_2)]$.[32]

The differences observed in the ligand oxidations of the Fe(III)[5] and Ru(III)[7] complexes most likely arise from the differences in relative lability of the metal–ligand bonds. For the ruthenium complex, once the *N*-oxide is formed, the dangling ligand may be further oxidized by the subsequent formation of new oxo complexes, especially since *N*-oxides are activated toward further nucleophilic attack.[33] For Fe(III), however, the oxidized bidentate ligand is readily lost before further reactions occur.[6,34]

The oxo-bridged diruthenium(III) complex of Scheme II has been prepared recently,[35] and the corresponding iron complex is well-known.[34] These complexes, and the osmium analogue, may be prepared directly from aqueous solutions of $[M(bpy)_2(OH_2)_2]^{n+}$,[34,36] and they are known to act as catalysts for dioxygen evolution from water.[34-36] Further, the iron dimer is one of the final products of the reduction of $[Fe(bpy)_3]^{3+}$.[6,34] Finally, the redox potentials of the $[M(bpy)_3]^{3+}$ ions are such that the monomers will oxidize the dimers at near-neutral or high pH[7,34-36] and we have found that $[Ru(bpy)_3]^{3+}$ reduces the Ru dimer under appropriate conditions. All these observations support Scheme II as the predominant mechanism for O_2 evolution, as does the observation that aged acidic aqueous solutions of $[Fe(bpy)_3]^{3+}$ (in which ligand loss and dimer formation[34] have occurred) produce more dioxygen, when treated with water at higher pH, than freshly prepared solutions. The formation of relatively small amounts of dioxygen from Ru(III), and even less by Os(III),[7] is also consistent with Scheme II, as only small quantities of products with two vacant coordination sites capable of forming the required oxo-bridged intermediate are present. Although Nord et al.[5] proposed that a binuclear ion was performing the oxidation of water from their mechanistic studies, they proposed an intermediate containing *N*-oxide ligands which underwent oxo-transfer reactions (reaction 5). In light of more recent experiments,[34-36] the complex is more likely to be the binuclear oxo-bridged complex proposed here.



(5)

In summary, we propose that the initial step in the reduction of the $[M(bpy)_3]^{3+}$ ions (M = Fe(III), Ru(III), Os(III)) is nucleophilic attack at the metal center to form a seven-coordinate intermediate. A sequence of reactions ensues that is dependent on the metal ion present. However, dioxygen is produced from μ-oxo species of the type shown in Scheme II, while ligand oxidations occur via $M^{IV}{=}O$ intermediates.

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Note Added in Proof. After this manuscript was accepted for publication, a paper appeared detailing the mechanism of oxidation of water by the ruthenium oxo-bridged dimer.[37] The overall mechanism is much more complex than detailed in Scheme II,[37] but the details have been omitted for simplicity because they do not affect the arguments presented here.

Registry No. $[Fe(bpy)_3]^{3+}$, 18661-69-3; $[Ru(bpy)_3]^{3+}$, 18955-01-6; $[Os(bpy)_3]^{3+}$, 30032-51-0; H_2O, 7732-18-5.

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(30) Since the rate constants for the self-exchange reactions of $[M(bpy)_3]^{3+/2+}$ are close to diffusion-controlled,[31] the cross reactions depicted are almost certainly diffusion-controlled, especially considering the large expected thermodynamic driving force (0.5–1 V). Further, the concentrations employed in the experiments were $>10^{-4}$ M in $[M(bpy)_3]^{3+}$; therefore, the initial pseudo-first-order disproportionation reactions would be $>10^6$ s^{-1}. By contrast the fastest observed rate constant for production of $[M(bpy)_3]^{2+}$ was 150 s^{-1} ($[Ru(bpy)_3]^{3+}$, 0.5 M OH^-), which is still much slower than the disproportionation reaction under the same conditions.

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