planation must be sought which will presumably involve specific ion pairing or chemical reactions between TMA^+ and $COT\cdot^-$.

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Solvent Regulation of the Photoredox Behavior of Bromopentaamminecobalt(III) and Consequent Restrictions on the Possible Inferences from "Sensitized" Photoredox Reactions[1]

Sir:

Studies of "sensitized" photoredox reactions of coordination complexes have proved to be equivocal and controversial, being potentially complicated by radical reactions[2] and excited state electron transfer[3] reactions in addition to the more customary problems of donor instability. Thus, compelling evidence for excited state electron transfer from $Ru(bipy)_3^{2+}$ has been obtained with cobalt(III) complexes,[4] $Ru(NH_3)_6^{3+}$,[4,5] Fe^{3+} [5] among the relevant acceptors. The original impetus for study of "sensitized" photoredox reactions was the premise, borrowed in large part from mechanistic photochemical studies of organic systems,[6] that sensitized photoreactions could provide definitive information about excited state reactivity. For example, comparison of "sensitized" and direct photolysis photoredox yields has been the basis for determination of the efficiency of intersystem crossing between excited states of different spin multiplicity in $Co(NH_3)_6^{3+}$ [7] and $Co(HEDTA)X^-$ [2c] ($X =$ Cl, Br, NO_2). More fundamentally, this mechanistic approach assumes that well-defined "molecular" excited states generated in an energy transfer process can be simply related to "molecular" excited states populated by direct excitation. We have now found that the environmental influence on the photoredox chemistry of $Co^{III}(NH_3)_5X$ complexes is so great that we must question the assumed "molecularity" of charge transfer to metal excited states; as a result it is in principle unlikely that sensitized and direct photolyses can be simply related.

Consideration of the implications of proposed photoredox models[8-10] has very recently led to investigations of photoredox processes of cobalt complexes in other than aqueous media.[11,12] The results of such investigations indicate that quantum yields for these photoredox processes are strongly medium dependent, often in varying with composition of the medium in very complex ways.[13] Of more specific significance to attempts to study sensitized photoredox reactions, the results now available for $Co(NH_3)_5NO_2^{2+}$,[11] for $Co(NH_3)_5NCS^{2+}$, [12] and reported here for $Co(NH_3)_5Br^{2+}$ (Figure 1) demonstrate that it is not possible to identify experimentally a quantum yield which can be uniquely associated with the redox decompositions of charge transfer excited states of these systems. At one extreme, the behavior of $Co(NH_3)_5NO_2^{2+}$ seems to approach expectation for limiting photodissociative charge transfer processes,[8-10] with the observed product yields a complex function of the dynamics of radical recombination and dissociation processes.[14] The behavior of other $Co(NH_3)_5X^{2+}$ (at least for X = NCS, N_3, Cl, and Br) is far more complicated and none of these four complexes appears to exhibit limiting photodissociative behavior in aqueous solution.[10b] Very striking qualitative variations in photoredox behavior have been found for $Co(NH_3)_5Br^{2+}$. This complex appears to approach photodissociative behavior in 80% acetonitrile-water solutions[15] and to be nearly photoinert in 87% phosphoric acid solutions (Figure 1). Furthermore, while a well-defined maximum photoredox yield can be established experimentally in aqueous and phosphoric acid media, photolyses in several other media have not been found to approach a defined maximum limiting value at high excitation energies. The major points with regard to the possibility of a meaningful study of sensitized photoredox reactions are (1) the qualitative nature of the photoredox process (*i.e.*, whether excited states can be regarded as "dossociative" or "bound") apparently depends on the solvent environment and (2) it is not possible to associate an intrinsic molecular quantum yield with the photoredox processes stimulated by direct CT excitation. Since the proximity of an excited state donor must constitute a major change in the nature of the solvent environment of an acceptor cobalt complex, we can see no hope of relating a sensitized photoredox quantum yield to

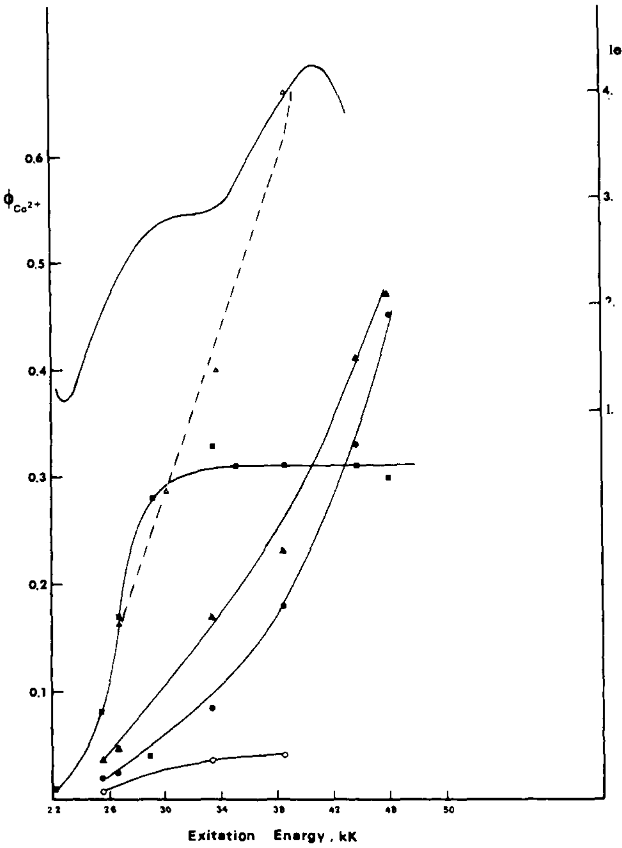

Figure 1. Absorption spectrum (upper curve, in water) and variations in the quantum yields of Co^{2+} (lower curves) with excitation energy and solvent medium obtained for irradiations of $Co(NH_3)_5Br^{2+}$. Aqueous solvent media employed: H_2O, ■; 80% CH_3CN, △; 50% glycerol, ▲; 75% glycerol, ●; 87% phosphoric acid, ○. Except for studies in phosphoric acid, all solutions were 10^{-3} *M* in $HClO_4$.

any specific yield resulting from direct excitation; furthermore, we would definitely expect that use of different kinds of sensitizers (*e.g.*, neutral aromatic, cationic, etc.) would necessarily result in different sensitized quantum yields. We therefore conclude that, while the study of excited state quenching by energy or electron transfer may be intrinsically interesting, and while study of energy transfer processes may aid in the resolution of some of the problems of ligand field photochemistry, there is no clear way to relate intermolecular energy transfer studies to intrinsic processes within "molecular" charge transfer states of coordination complexes.

References and Notes

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Synthesis and Structure of Dinuclear Niobium and Tantalum Complexes Containing an Unusual Bridging Ligand Derived from Acetonitrile

Sir:

In earlier work in this laboratory[1] it was found that the tantalum(IV) halides, $TaCl_4$ and $TaBr_4$, undergo unexpectedly complicated reactions when dissolved in acetonitrile. These reactions provided a red, soluble fraction containing 80–100% of the tantalum as unidentified products. In addition an insoluble fraction containing 0–20% of the tantalum was obtained as a green crystalline powder. Although the composition of the green products was somewhat variable, it always was close to that expected for the tantalum(III) adducts $TaX_3\,(CH_3CN)_3$, X = Cl or Br.

Subsequent work showed that these green compounds were diamagnetic, did not reduce Fe(III) when treated with aqueous iron(III) sulfate, and hydrolyzed instantly in water to produce tantalum(V) oxide. Such behavior was inconsistent with that expected for compounds containing tantalum in a reduced oxidation state.[2] By contrast the niobium(IV) halides NbX_4 (X = Cl, Br, I) react under the same conditions to provide the simple adducts $NbX_4(NCCH_3)_2$.[3]

In the unusual reactions leading to the green products some evidence indicated that Ta(III) might play an intermediate role, as in the scheme

$$2\mathrm{Ta(IV)} \longrightarrow [\mathrm{Ta(III)}] + \mathrm{Ta(V)}$$

$$[\mathrm{Ta(III)}] + \mathrm{CH_3CN} \longrightarrow \text{green products}$$

As predicted from this scheme, addition of zinc to the initial TaX_4–acetonitrile mixtures at room temperature afforded much improved yields of the green products (20–50% of the initial tantalum). Similarly analogous products were obtained when solutions of $NbCl_4$ in acetonitrile were reduced with zinc.

In a typical reaction 5.0 g (0.021 mol) of $NbCl_4$ and 0.69 g (0.011 mol) of granular zinc were treated with 30–50 ml of acetonitrile in an evacuated flask with stirring for 4–7 days. After removing acetonitrile by vacuum distillation, the powdered mixture was transferred to the fritted glass filter of an extractor adapted for high vacuum work and subsequently extracted with dry acetonitrile until the red soluble material was completely removed. The less soluble green powder then was dried under high vacuum and analyzed. *Anal.* Calcd for $NbCl_3(CH_3CN)_3$: Nb, 28.83; Cl, 33.00; C, 22.34; H, 2.82; N, 13.03. Found: Nb, 28.86; Cl, 32.74; C, 23.97; H, 3.44; N, 11.95. The corresponding product from the reaction of $TaCl_4$ and acetonitrile was obtained in exactly the same way. *Anal.* Calcd for $TaCl_3(CH_3CN)_3$: Ta, 44.10; Cl, 25.92; C, 17.56; H, 2.21; N, 10.24. Found: Ta, 44.36; Cl, 26.51; C, 17.99; H, 2.55; N, 9.96.

The infrared spectra of these products indicate that both acetonitrile and a new ligand (L) derived from acetonitrile are coordinated to the metal. In acetonitrile, reaction of these compounds with LiCl or bis(triphenylphosphine)iminium chloride, $[(C_6H_5)_3P]_2N^+Cl^-$, leads to substitution of 1 mol of CH_3CN/mole of metal, and with CsCl to 2 mol of CH_3CN/mole of metal. (As shown below, the structure of the $[(C_6H_5)_3P]_2N^+$ salt containing niobium has been determined, and, taken together with the infrared spectra, the data indicate all of the compounds are correctly formulated as dimers.) Thus the substitution reactions provide salts containing the anions $[M_2Cl_8(NCCH_3)_2L]^{2-}$ and $[M_2Cl_{10}L]^{4-}$, where L = $C_4H_6N_2$. A comparison of the infrared spectra of $[M_2Cl_6(NCCH_3)_4L]$ with those of $Cs_4[M_2Cl_{10}L]$ clearly reveal the bands of *L* at 2920–2930 (w), 2850–2860 (w), 1430–1433 (w), 1370–1382 (m),

Table I. Bond Distances (Å) and Angles (deg) in the Anion $[Nb_2Cl_8(CH_3CN)_2(C_4H_6N_2)]^{2-}$

Nb–Cl(1)	2.410 (2)	N(L1)–C(N1)	1.378 (8)
Na–Cl(2)	2.408 (2)	N(L2)–C(N2)	1.144 (8)
Nb–Cl(3)	2.425 (2)	C(N1)–C′(N1)	1.35 (1)
Nb–Cl(4)	2.399 (2)	C(N1)–C(M1)	1.48 (1)
Nb–N(L1)	1.752 (6)	C(N2)–C(M2)	1.47 (1)
Nb–N(L2)	2.411 (6)		
N(L2)–Nb–N(L1)	176.9 (3)	C′(N1)–C(N1)–C(M1)	120.9 (9)
Nb–N(L1)–C(N1)	178.1 (6)	N(L2)–C(N2)–C(M2)	178.9 (10)
N(L1)–C(N1)–C(M1)	114.4 (9)	Nb–N(L2)–C(N2)	172.5 (7)
N(L1)–C(N1)–C′(N1)	124.7 (9)		