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Contrasting Reactivities of Ligand-to-Metal Charge-Transfer Excited States in Ammine and Methylamine Complexes of Cobalt(III)

Many of the prevailing ideas about the reactivities of ligand-to-metal charge-transfer (LMCT) excited states in coordination compounds evolved from early studies of a relatively small number of $Co(NH_3)_5X^{2+}$ complexes (X is a uninegative ligand such as Cl^-, Br^-, or NO_2^-).[1-4] A general observation in these systems is that irradiation (typically ≥254 nm) into the X → Co CT (charge-transfer) absorption band causes efficient redox decomposition accompanied, in most cases, by ligand substitution or linkage isomerization. Such behavior has been interpreted in terms of a model in which homolytic fission of the Co–X bond is the primary photochemical act. This process affords a solvent-caged radical pair, which, in subsequent steps, either recombines or reacts further to yield the final products. Interestingly, prompt reaction has not been observed to follow population of the higher lying N → Co CT state. Instead this state undergoes efficient radiationless deactivation to the X → Co CT state[3] or crosses to a dissociative CT state arising from transfer of an electron from a solvent molecule to the complex.[5]

We have begun to examine the LMCT photochemistry of a broader selection of cobalt(III) systems and report here the first study of complexes containing a monodentate primary alkylamine. Our results reveal several interesting contrasts between the excited-state reactivities of these complexes and those of their ammine analogues. Particularly noteworthy is the finding that members of the $Co(NMeH_2)_5X^{2+}$ family can undergo intramolecular redox reactions from *both* the X → Co and N → Co CT excited states. Moreover, replacement of NH_3 by $NMeH_2$ in the first coordination sphere appears to diminish the chemical involvement of solvent in the photoredox process.

Analytically pure samples of several methylamine complexes were prepared by literature procedures.[6] Table I summarizes the salient ultraviolet absorption features measured in aqueous solution. Assignment of the intense bands as LMCT in character follows from the agreement between the observed ν_{max} values and those calculated from the Jørgensen relationship in eq 1; χ_L and χ_M denote the optical electronegativities of the ligand and metal, respectively, Dq is the ligand field strength parameter, and δSP represents the difference in spin-pairing energy between the ground and excited states involved in the transition.[3]

$$\nu_{max} = 30(\chi_L - \chi_M) + 10Dq + \delta SP \tag{1}$$

In general, the methylamine complexes undergo N → Co CT transitions at energies $\sim 5 \times 10^3\ cm^{-1}$ below those found for the corresponding ammine complexes owing to the smaller χ_L and Dq values of $NMeH_2$ vs NH_3.

Ultraviolet irradiation of the methylamine complexes in acidified water causes bleaching of the LMCT band(s) with concomitant production of Co^{2+} and free $NMeH_2$. Quantum yield ($\phi_{Co^{2+}}$) data compiled in Table II reveal that this photoredox process occurs with high efficiency. In particular, these complexes are uniformly more photosensitive than their ammine analogues. To cite one example, we find that $\phi_{Co^{2+}}$ for 254-nm photolysis of $Co(NMeH_2)_6^{3+}$ in deoxygenated solution is about 3 times larger than the value measured for $Co(NH_3)_6^{3+}$ under similar conditions.[2] This unexpectedly high photosensitivity of cobalt(III) methylamine complexes is especially significant in view of the recent interest in base-generating photoinitiators for deep-UV lithographic applications.[7]

Photolysis of $Co(NMeH_2)_5Br^{2+}$ at 254 nm obeys the stoichiometric relationship (mol of $NMeH_2$) = 5 (mol of Co^{2+}), independent of oxygen concentration in solution. Furthermore, flash photolysis experiments confirm the production of $Br^\bullet$ (identified as $Br_2^{\bullet -}$). These results are diagnostic of reaction (eq 2) from the Br → Co CT excited state.

$$Co(NMeH_2)_5Br^{2+} \xrightarrow[H_3O^+]{h\nu\ (254\ nm)} Co^{2+}(aq) + 5NMeH_3^+ + Br^\bullet \tag{2}$$

More complicated behavior obtains for $Co(NMeH_2)_6^{3+}$ and $Co(NMeH_2)_5Cl^{2+}$ upon 254-nm irradiation in that $\phi_{Co^{2+}}$ and the $NMeH_2/Co^{2+}$ ratio depend upon the oxygen content of the solution. We attribute such behavior to the photochemical production of the $^{\bullet +}NMeH_2$ cation radical (eq 3) from the higher lying N → Co CT excited state (Table I).

$$Co(NMeH_2)_6^{3+} \xrightarrow[H_3O^+]{h\nu\ (254\ nm)} Co^{2+}(aq) + 5NMeH_3^+ + {}^{\bullet +}NMeH_2 \tag{3}$$

In the absence of oxygen, this reactive species (or, more likely, some descendant[8]) causes thermal reduction of the parent Co(III) complex with an accompanying increase of $\phi_{Co^{2+}}$. Scavenging of nitrogenous radicals by O_2 inhibits this thermal process and results in a $\phi_{Co^{2+}}$ value more representative of the primary photoreaction (eq 3). The larger relative amount

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Table I. Charge-Transfer Spectral Assignments for (Methylamine)cobalt(III) Complexes[a]

complex	$10^{-3}\nu_{max}$(calc), cm^{-1}	$10^{-3}\nu_{max}$(obs), cm^{-1} ($10^{-3}\epsilon$, M^{-1} cm^{-1})	assgnt
$Co(NMeH_2)_6^{3+}$	45.12	44.44 (31.0)	N → Co
$Co(NMeH_2)_5Cl^{2+}$	43.55	42.28[b] (26.6)	N → Co
	41.15		Cl(σ) → Co[c]
$Co(NMeH_2)_5Br^{2+}$	43.07	44.51 (18.1)	N → Co
	36.77	37.85 (18.0)	Br(σ) → Co[c]

[a] Measured in 10 °C acidic (pH ~ 3.2) solution. [b] Overlapping of N → Co and Cl → Co absorption bands occurs. [c] σ refers to an electron in an orbital having σ-symmetry with respect to the metal-ligand bond.

Table II. Quantum Yields and Product Ratios for Photoredox Reactions of (Methylamine)cobalt(III) Complexes

complex	λ_{excit}, nm	$\phi_{Co^{2+}}$[a] ($NMeH_2/Co^{2+}$)[b] Ar purged	air-saturated
$Co(NMeH_2)_6^{3+}$	254	0.70 ± 0.03 (5.89 ± 0.13)	0.45 ± 0.03 (5.20 ± 0.07)
$Co(NMeH_2)_5Cl^{2+}$	254	0.54 ± 0.02 (4.91 ± 0.07)	0.40 ± 0.02 (4.30 ± 0.20)
	313	0.29 ± 0.01	0.29 ± 0.01
$Co(NMeH_2)_5Br^{2+}$	229	0.59 ± 0.03	0.49 ± 0.01
	254	0.43 ± 0.01 (5.02 ± 0.40)	0.38 ± 0.03 (5.02 ± 0.35)
	313	0.32 ± 0.02	0.31 ± 0.01

[a] Quantum yield of Co^{2+} production measured in acidic (pH ~ 3.2) aqueous solution at 10 °C. [b] Ratio of (mol $NMeH_2$) to (mol Co^{2+}) in photolyte. Co^{2+} analysis: Vydra, F.; Pribil, R. *Talanta* **1960**, *4*, 44. $NMeH_2$ analysis: DeBernardo, S.; Weigele, M.; Toome, V.; Manhart, K.; Leimgruber, W.; Böhlen, P.; Stein, S.; Udenfriend, S. *Arch. Biochem. Biophys.* **1974**, *163*, 390.

of free $NMeH_2$ observed in deoxygenated solution presumably arises from radical disproportionation processes that regenerate the amine.[2,8]

Special note should be taken of the wavelength-dependent effect of oxygen on the photochemical behavior of the haloamine complexes. In both cases, O_2 decreases $\phi_{Co^{2+}}$ at shorter excitation wavelengths but causes little or no change at longer wavelengths (Table II). This behavior reflects the contributions of two photoactive LMCT excited states that undergo imperfect communication with one another. Thus preferential population of the N → Co state at shorter wavelengths leads to the production of radicals that can be scavenged by O_2 (vide supra), whereas longer wavelength irradiation favors population of the lower energy Cl → Co or Br → Co CT state, which undergoes redox chemistry (e.g., eq 2) unaffected by O_2. Very different behavior has been reported for the corresponding $Co(NH_3)_5X^{2+}$ complexes in that internal conversion from the N → Co CT state to the lower-lying X → Co CT state occurs with nearly unit efficiency.[3] Evidently, replacement of NH_3 by $NMeH_2$ alters the kinetic parameters of the N → Co state such that chemical reaction increases in importance relative to other relaxation processes. At least two plausible explanations for this ligand effect deserve consideration: (1) the N → Co excited states in the methylamine complexes intrinsically are more dissociative, that is, they possess weaker Co-N bonds, and (2) the hydrophobic methyl groups situated on the periphery of the charged complex reduce interaction with the solvent; one consequence of this decreased solvation is a lowering of the reorganizational barrier that must be surmounted during dissociation of the solvent-caged primary radical pair. Experimental tests of these explanations are underway in our laboratory.

Finally, the photoredox behavior of $Co(NMeH_2)_5Br^{2+}$ in a 1:1 (v/v) glycerol-water mixture was investigated at several excitation wavelengths. In striking contrast to the results obtained for $Co(NH_3)_5Br^{2+}$ under similar conditions,[5] we find smaller $\phi_{Co^{2+}}$ values in this mixed solvent than in aqueous solution at *all* wavelengths in the interval 313-229 nm. Consequently, primary photooxidation of the solvent plays an unimportant role in the LMCT photochemistry of the methylamine complexes at very high excitation energy. This result again suggests that the methyl groups on the coordinated nitrogen atoms shield the complex from the solvent. More generally, we propose that LMCT excited states in alkylamine complexes of the type considered here approach "molecular" behavior[9] more closely than their ammine counterparts.

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Department of Chemistry
University of Georgia
Athens, Georgia 30602

Scott K. Weit
Charles Kutal*

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Synthesis and Structural Characterization of a Polyoxovanadate Coordination Complex with a Hexametalate Core: $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{O_2NC(CH_2O)_3\}_2]$

The coordination chemistry of polyoxometalates has received considerable attention by virtue of the structural analogy of these species to metal oxide surfaces.[1-3] Although polyoxomolybdate coordination chemistry has witnessed a remarkable development in the past decade,[4] the chemistry of analogous covalent polyoxovanadate derivatives remains unexplored. By exploitation of the solubility of polyvanadate tetra-*n*-butylammonium salts soluble in aprotic, polar solvents,[5-7] the polyoxoalkoxyvanadate-oxalate complex $[(n\text{-}C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$[8] was recently prepared, suggesting that simple organic subunits may be incorporated into polyoxovanadate frameworks. Our efforts have been directed toward the synthesis of simple coordination com-

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