Photoredox Behavior of Coordination Complexes of *nd*^{6} Metals. Contrasting Redox Modes in Azidopentacyanocobaltate(III) and Azidopentaamminerhodium(III)[1]

Sir:

It is commonly believed that acidopentacyanocobaltate(III) complexes differ profoundly in their photochemical behavior from their pentaammine analogs.[2-7] These differences are believed to manifest themselves principally in a lack of photoredox behavior and relatively high quantum yields for photoaquation of the cyano complexes. This behavior might imply a very efficient electronic relaxation from higher (charge transfer) to lower (ligand field) excited states, uncharacteristic of low spin d^6 metallo complexes;[8-10] however, it has been pointed out that some bulk solution recombination reactions might be expected in these cases, and that these complexes have been rarely irradiated in their charge transfer to metal absorption (CTTM) bands.[8] These two points seem to be of some particular significance since the respective ligand field splitting energies are such that the $Co^{III}(CN)_5X$ and $Rh^{III}(NH_3)_5X$ complexes have very similar absorption spectra, with the former red shifted with respect to the latter (for example see Figure 1); photoredox behavior and bulk solution recombination reactions have been observed with the rhodium(III) analogs.[9] A new dimension has recently been added to this puzzle with the discovery that nitrene intermediates are produced on irradiating the nominally CTTM bands of rhodium(III) and iridium(III) azide complexes.[11]

We have very recently performed an extensive flash photolysis study of $Rh(NH_3)_5N_3^{2+}$.[12] In this study we have found that the nitrene intermediates may form absorbing dimers (eq 1) or react with I^- in a series of

$$2(NH_3)_5RhNH^{3+} \rightleftharpoons [(NH_3)_5RhN]_2H^{5+} + H^+ \qquad (1)$$

steps which generate a different absorbing intermediate; the latter reactions result eventually in the formation of I_3^- without the observable intermediacy of I_2^-. The similarity of the absorption spectra of $Rh(NH_3)_5N_3^{2+}$ and $Co(CN)_5N_3^{3-}$ and the similarity of the assignment of the respective electronic transitions[13,14] intrigued us and we have undertaken a careful comparative investigation of the photoredox behavior of the pentacyano complex.

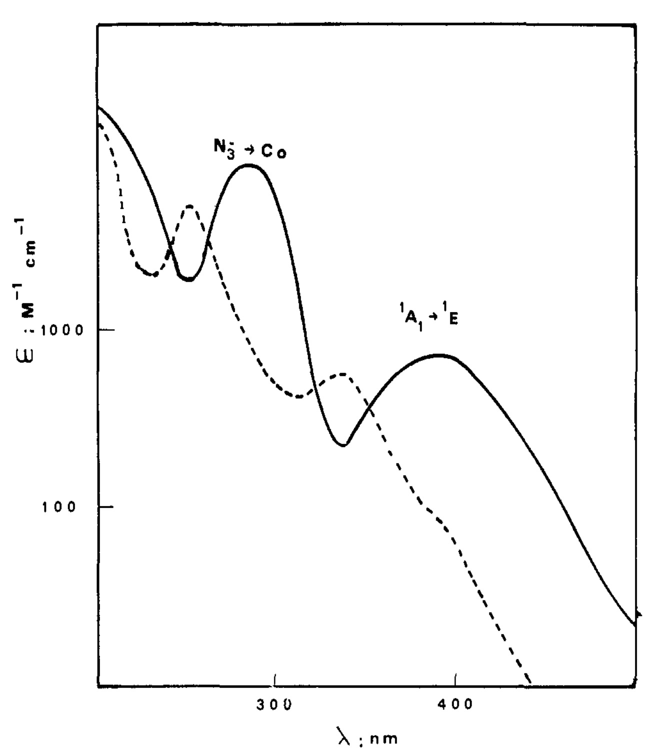

Figure 1. Absorption spectra of $Co(CN)_5N_3^{3-}$ (solid line) and $Rh(NH_3)_5N_3^{2+}$ (dashed line). Band assignments for $Co(CN)_5N_3^{3-}$ are based on ref 13.

We have searched the 380–900-nm spectral region for transient absorbances in flash photolysis experiments using carefully deaerated solutions varying in $[Co(CN)_5N_3^{3-}]$ from 1.0×10^{-3} to 1.0×10^{-6} *M* and varying in pH, $1.0 \leqslant pH \leqslant 8.0$. For the pentacyanocobaltate, and in contrast to $Rh(NH_3)_5N_3^{2+}$, no transient was observed in the absence of scavenging species (*e.g.*, I^-), thus in this case flash photolysis provides no evidence for the transient formation of absorbing dimers or nitrene intermediates. On the other hand we observed the formation of the I_2^- transient during the flash pulse (~40 μsec) when iodide was present in solution. A very efficient reaction with I^- (eq 2) is char-

$$N_3\cdot + I^- \longrightarrow N_3^- + I\cdot \qquad (2)$$

acteristic of the azide radical, $N_3\cdot$;[15,16] the $I\cdot$ produced in (2) would be rapidly and efficiently complexed by I^- (eq 3; $K_3 = 8 \times 10^4\ M^{-1}$, $k_3 \sim 10^{10}\ M^{-1}\ sec^{-1}$ [17])

$$I^- + I\cdot \rightleftharpoons I_2^- \qquad (3)$$

to form the strongly absorbing I_2^- radical anion.[17,18] By using cutoff[9,10] and band pass[19] filters in the flash experiments, we have been able to show that the radical responsible for the production of I_2^- is generated from the irradiation of the CTTM absorption band of $Co(CN)_5N_3^{3-}$ (λ_{max} 281 nm). Only azide aquation was observed to result from irradiation of the lower energy

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ligand field absorption band (λ_{max} 360 nm). By comparing the change of absorbance of $Co(CN)_5N_3{}^{3-}$ to the yield of $I_2{}^-$ in flash photolysis experiments, we estimate that $\phi_{aq}/\phi_{redox} \simeq 2$[20] for irradiation of the 281-nm CTTM band and $\phi_{aq}/\phi_{redox} > 1.7 \times 10^2$ for irradiation of the ligand field band (no $I_2{}^-$ was detected). In the continuous irradiation of the 281-nm CTTM band we found that nitrogen (and no hydrogen; $3 \leqslant pH \leqslant 9$) was produced, permitting us to estimate $\phi_{redox} = (7.4 \pm 1) \times 10^{-3}$. Most of the N_2 could be quenched by radical scavengers; *e.g.*, irradiation of $Co(CN)_5N_3{}^{3-}$ in 10^{-3} *M* I^- reduced the yield of N_2 by 75%. The photoredox behavior in the deeper ultraviolet ($\lambda \leqslant 254$ nm) is far more complex with $\phi_{redox} \sim 7 \times 10^{-3}$ at 254 nm and $\phi_{redox} \sim 7 \times 10^{-2}$ at 214 nm. However, for irradiations at $\lambda \leqslant 254$ nm not all the nitrogen can be scavenged by I^- (*e.g.*, only 50% of the N_2 is scavengeable at 254 nm), indicating that irradiations at these wavelengths produce both $Co(CN)_5NH^{2-}$ and $(Co(CN)_5{}^{2-} + \cdot N_3)$ intermediates. For those experiments in which I^- was in the solution during irradiation, $Co(CN)_5I^{3-}$ was found among the products.

The photochemical behavior of $Rh(NH_3)_5N_3{}^{2+}$ contrasts to that of $Co(CN)_5N_3{}^-$ in its simplicity; I^- scavenging experiments indicate that less than 10% of product nitrogen is scavengeable at any wavelength, so the simple photoredox process must be formation of $Rh(NH_3)_5NH^{3+}$ intermediates. However, this system is also very remarkable in that this product is associated *only* with irradiation of the 251-nm absorption band (*i.e.*, for excitations at 250 ± 30 nm); at 254 nm $\phi = 0.2$.

We find further that photoredox behavior seems to be a reasonably common feature of the photochemistry of acidopentacyanocobaltates. Thus flash irradiation of the ligand field absorption band of $Co(CN)_5I^{3+}$ in 10^{-3} *M* I^- did not produce $I_2{}^-$ while irradiation of the 254–360-nm region of this complex resulted in the formation of appreciable $I_2{}^-$. Flash photolysis of $Co(CN)_5NCS^{3-}$ or of $Co(CN)_5SCN^{3-}$ in the presence of NCS^- resulted in the formation of $(NCS)_2{}^-$ (λ_{max} 475 nm[21]).

We infer that previous investigations have failed to find evidence for photoredox behavior in $Co^{III}(CN)_5X$ complexes either because they did not irradiate CTTM absorption bands or because they did not attempt to detect, possibly transient, redox products. It is evident that these complexes exhibit the general pattern of photochemical behavior characteristic of most complexes of d^6 metals: (1) low energy irradiation results predominantly in aquation of coordinated ligands; (2) irradiation of CTTM bands results in oxidation–reduction and in aquation processes, and (3) product yields are strongly wavelength dependent.

The photoredox chemistry of $Co(CN)_5N_3{}^-$ qualitatively appears to combine some features of the behavior of $Rh(NH_3)_5N_3{}^{2+}$ with those reported for $Co(NH_3)_5N_3{}^{2+}$.[15] However, the photochemical behavior of $Co(NH_3)_5N_3{}^{2+}$ has not been examined with care in the deep ultraviolet and the differences between the pentaammine- and pentacyanocobaltates may be more apparent than real. More specifically, we cannot rule out the possibility that nitrene production is characteristic of the population of a ligand-centered state which does not communicate efficiently with other states in the molecules. Nevertheless the azido complexes of rhodium(III) (and probably iridium(III)) appear to be unique in that there is no appreciable formation of azide radicals on irradiating any CTTM band (*i.e.*, with $\lambda \leqslant 214$ nm). A very likely source of this difference in behavior is the difference in radial extension of the metal-centered nonbonding 3d and 4d electrons; the back-bonding interaction, possible in the latter cases but not for cobalt,[13] could sufficiently stabilize the CTTM excited states that N–N cleavage becomes the preferred mode of excited-state reactive decomposition.

Guillermo Ferraudi, John F. Endicott*
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

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[20] α_{aq} = quantum yield for aquation = decomposition yield of $Co(CN)_5N_3{}^{3-}$ less the yield of $I_2{}^-$ and corrected for the yield resulting from irradiation of the ligand field band only.

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Theoretical Analysis of Long-Range Hyperfine Interactions in Aliphatic Free Radicals. Origin of the W and Anti-W Rules

Sir:

We wish to report the main results of an *ab initio* investigation of long-range interactions in the *n*-propyl radical, the simplest compound in which hyperfine splittings have been observed for α, β, and γ protons separated from the paramagnetic site by one, two, and three bonds, respectively.[1,2]

The spin-restricted SCF equations of the doublet ground state have been solved by the open-shell IBMOL program[3] based on Roothaan's method.[4] A (9s,5p/4s) Gaussian basis set reduced to a double-ζ form by the usual contraction technique[5] has been chosen.

Two contributions to hyperfine splitting have been considered. The direct or delocalization contribution (a_{dir}) is given by the restricted SCF ground-state wave function ψ_0. The indirect or spin-polarization contribution (a_{ind}) arises from a configuration interaction which has been limited to monoexcited states and computed by a first-order perturbation treatment.[6]

For protons, the resulting coupling constants are

$$a_H = a_{dir} + a_{ind} = (8\pi/3)(g_e/g_0)g_H\beta_H(\rho_{dir} + \rho_{ind}) \quad (1)$$

with

$$\rho_{dir} = |\phi_u(\mathbf{r}_H)|^2 \quad (2)$$

$$\rho_{ind} = -2\sum_{d}\sum_{v^*}\rho_{d\rightarrow v^*} \quad (3)$$

$$\rho_{d\rightarrow v^*} = \frac{\langle\phi_d\phi_u|\phi_u\phi_{v^*}\rangle}{E_0 - E_{d\rightarrow v^*}}\phi_d(\mathbf{r}_H)\phi_v(\mathbf{r}_H) \quad (4)$$

where ϕ_d and ϕ_{v^*} are doubly occupied and virtual orbitals and ϕ_u is the orbital containing the unpaired

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