nearest neighbors of HF molecules in the hydrogen-bonded lattice. The cages have cubic symmetry only on space averaging. At temperatures near 0 °C, the rapid diffusion and interchange of water and HF molecules produces time averaging to cubic symmetry on the NMR time scale.

The bond lengths in the hexafluoride ions of the hydrates are not known. If one assumes P–F, As–F, and Sb–F bond lengths similar to those measured[11-13] for K salts of these ions,

1.58, 1.72, and 1.77 Å, respectively, the corresponding van der Waals ionic diameters are 5.86, 6.14, and 6.24 Å. These values are only slightly in excess of the cage "free diameters", which, with the unit cell parameters in Table III and 2.8 Å for the van der Waals diameter of water, are 5.78, 5.83, and 5.92 Å, respectively.

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Photochemistry of the Dinuclear Cobalt(III) Complexes (CN)₅Co(μ-CN)Co(NH₃)₅ and (CN)₅Co(μ-NC)Co(NH₃)₅. Intramolecular Energy Transfer between Metal Centers

MASATO NISHIZAWA and PETER C. FORD*

Irradiation of aqueous $(NC)_5Co(\mu\text{-NC})Co(NH_3)_5$ in the wavelength region 254–365 nm leads to photoaquation of the pentacyanocobaltate(III) center, giving $Co(CN)_5H_2O^{2-}$ and $Co(NH_3)_5CN^{2+}$ as products with large quantum yields (0.2–0.3 mol/einstein). These wavelengths represent ligand field (LF) excitation of the pentacyanocobaltate(III) chromophore; hence, efficient photoreaction of that center indicates that in this case energy transfer to the lower LF states of the pentaamminecobalt(III) chromophore is at best competitive with ligand labilization. In contrast, LF excitation of the former chromophore in the linkage isomer dinuclear complex $(NC)_5Co(\mu\text{-CN})Co(NH_3)_5$ leads to very little reaction at that site. Since $Co(CN)_6^{3-}$ is quite photoactive under these conditions, this result implies that coordination of the $Co(NH_3)_5^{2+}$ moiety to one CN provides a new pathway for rapid deactivation of the $Co(CN)_6^{3-}$ LF states. The differences between the two dinuclear complexes' photochemical behaviors are rationalized in terms of symmetry restrictions and larger Franck–Condon terms inhibiting energy transfer between the two cobalt(III) centers of $(NC)_5Co(\mu\text{-NC})Co(NH_3)_5$ relative to the linkage isomer. For comparison the complex ion $Co(CN)_5(CH_3CN)^{2-}$ has been synthesized. Ligand field excitation of this species leads to highly efficient photoaquation of CH_3CN exclusively ($\phi \sim 0.4$).

Introduction

In recent years there has been considerable interest in sensitization (energy-transfer) and redox (electron-transfer) processes involving metal complex excited states.[1] Much of this interest has derived from schemes proposing to utilize such reactions for the conversion of radiant energy to chemical potential energy, i.e., for solar energy storage. Most studies have focused on bimolecular processes, and a number of these have been demonstrated where both chromophores in the energy or electron transfer are metal complexes. However, the diffusion terms in bimolecular rate laws and the uncertain relative configurations of the interacting centers make comparison of quantitative data a rather challenging exercise. Clearly, to understand in detail the principles governing energy or electron transfer, one must elucidate the dominating structural or spatial parameters. The ideal situation would be to have two chromophores in fixed positions relative to each other, a situation best approximated by placing both the acceptor and donor metal centers in the same complex. A limited number of photochemical studies have been done on such systems; however, in each of these examples a key excited state of at least one center is charge transfer in character.[2-5] Ligand

field excited states play important roles in the photoreactions of transition-metal complexes especially with regard to photodegradation of complexes by ligand labilization. As a consequence, it is of interest to examine energy transfer between two metal centers, both having lowest energy ligand field (LF) states. Examples are the dicobalt complexes $(CN)_5Co(\mu\text{-CN})Co(NH_3)_5$("$C_6N_6$") and $(CN)_5Co(\mu\text{-NC})Co(NH_3)_5$("$C_5NCN_5$"),[6] each possessing a pentacyanocobalt(III) chromophore linked to a pentaamminecobalt(III) center, the sole difference being the configuration of the bridging cyanide ligand.

The spectra of C_6N_6 and C_5NCN_5 in aqueous solution are shown in Figure 1 and the spectra of comparison mononuclear complexes in Figures 2 and 3. The spectra of the mononuclear species show the two spin-allowed, Lapporte-forbidden LF bands expected for a diamagnetic d^6 complex with an approximately octahedral field ($^1T_1 \leftarrow {}^1A_1$ and $^1T_2 \leftarrow {}^1A_1$ in O_h symmetry). Notably the LF bands for the pentaammine species occur at considerably longer wavelengths than in the pentacyano series, owing to the greater ligand field strength of the CN^- ion. The dinuclear ions' LF spectra appear to be the sum of the two types of spectra (Figures 2 and 3) although the onset of charge-transfer absorption occurs at somewhat

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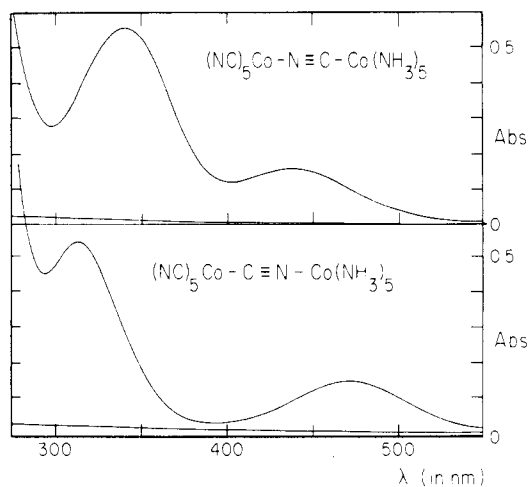
Figure 1. UV–vis spectra in aqueous solution of $(CN)_5Co(\mu\text{-CN})\text{-}CoNH_3)_5$ (bottom, 1.06×10^{-3} M, 2-cm cell) and $(CN)_5Co(\mu\text{-}NC)Co(NH_3)_5$ (top, 1.09×10^{-3} M, 2-cm cell).
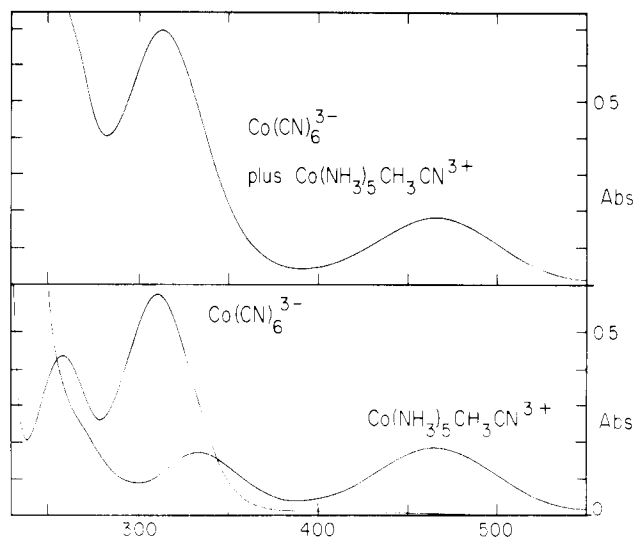
Figure 2. Bottom: Spectra in aqueous solution of $[Co(NH_3)_5CH_3\text{-}CN](ClO_4)_3$ (1.5×10^{-3} M, 2-cm cell) and $K_3Co(CN)_6$ (1.5×10^{-3} M, 2-cm cell). Top: Sum of these two spectra taken by placing both cells (in series) in the spectrometer sample-cell compartment.

lower energy for the dinuclear ions than for the mononuclear analogues.

As mononuclear complexes, the pentacyano- and pentaaminecobalt(III) derivatives $Co(CN)_5L^{(2+n)-}$ and $Co(NH_3)_5L^{(3-n)+}$ demonstrate very different photochemical behaviors.[7] Irradiation of the pentacyano derivatives in the wavelength region of the LF bands generally results in ligand photosubstitution, most commonly the replacement of L^{n-} or of CN^- by solvent. Quantum yields are moderately large (~ 0.1–0.4 mol/einstein) and appear to be independent of λ_{irr}. For example aqueous $Co(CN)_6^{3-}$ undergoes CN^- photoaquation with a wavelength-independent $\Phi_{CN} = 0.31$. Similarly, $Co(CH)_5NH_3^{2-}$ loses NH_3 with $\Phi_{NH_3} = 0.35$, and $Co(CN)_5H_2O^{2-}$ exchanges H_2O with $\Phi_{ex} \simeq 0.15$ but photoaquates some CN^- with $\Phi_{CN} = 0.001$.[7,8] In contrast, while LF excitation of the pentaammine derivatives leads principally to photosolvation of coordinated ligands, quantum yields are much smaller and are sharply λ_{irr} dependent. For example,
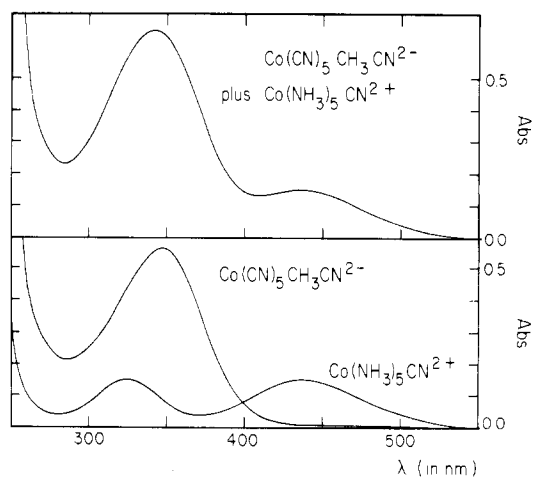

Figure 3. Bottom: Spectra in aqueous solution of $[Co(NH_3)_5C\text{-}N](ClO_4)_2$ (1.5×10^{-3} M, 2-cm cell) and $K_2[Co(CN)_5CH_3CN]$ (1.5×10^{-3} M, 2-cm cell). Top: Sum of these two spectra taken by placing both cells (in series) in the spectrophotometer sample-cell compartment.

photoaquation of NH_3 from $Co(NH_3)_6^{3+}$ occurs with $\Phi_{NH_3} = 5.4 \times 10^{-3}$ and 3.1×10^{-4} at $\lambda_{irr} = 365$ and 472 nm, respectively.[7] Several rationalizations have been offered for these photoreactivity differences,[9,10] an attractive one being the interpretation drawn from spectral data that the lowest excited state (ES) of the pentacyano complexes has triplet character while that of the pentaammine series has quintet character.[10] Such an argument is consistent with the greater ligand field strength of CN^- and with certain parallels in the LF photoreactivity patterns of the pentacyanocobalt(III) species with other strong-field d^6 complexes.[11,12]

With regard to the dinuclear cobalt(III) complexes, the additive nature of their spectra suggests the interactions between LF states of the two Co(III) centers to be relatively weak (vide infra). Thus the goal of the present study is to examine whether photoreaction patterns will show the two cobalt centers to be acting independently or acting in some strongly coupled manner. Comparisons are made to the photochemistries of the acetonitrile complexes $Co(NH_3)_5(CH_3CN)^{3+}$[11] and $Co(CN)_5(CH_3CN)^{2-}$, which serve as models for the respective Co(III) chromophores in the dimers when N-coordinated to the bridging CN^-.

Experimental Section

Materials. The complexes $(CN)_5Co(\mu\text{-CN})Co(NH_3)_5$ and $(CN)_5Co(\mu\text{-NC})Co(NH_3)_5$ were prepared by the published methods.[6] The spectral properties (UV–vis, IR) of the compounds prepared were identical with those reported.

Photolysis Procedures. Photolyses were carried out in aqueous $HClO_4$ solutions (pH 2–4) at 25 °C. Experiments at the irradiation wavelength (λ_{irr}) 254 nm were carried out on an apparatus utilizing an Oriel low-pressure mercury pen lamp equipped with a long-wavelength filter.[11] Photolyses at $\lambda_{irr} = 313$, 365, and 436 nm were carried out with an Oriel 200-W high-pressure mercury short-arc lamp equipped with interference filters to isolate the desired wavelength.[13] An Oriel 150-W xenon short-arc lamp combined with an interference filter was used for 430-nm photolysis.[14] Light intensities were determined by ferrioxalate actinometry (254, 313, 365, and 436 nm) and Reinecke salt actinometry (460 nm).

Spectral changes of photolysis solutions were monitored by the periodic recording of electronic spectra on a Cary 118C recording

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Table I. Quantum Yields (mol/einstein) for the Photolysis of Pentacyanocobaltate(III) Mononuclear and Dinuclear Complexes

complex	$\lambda_{irr}{}^a$	$\Phi_{spec}{}^{b,c}$	$\Phi_{Co^{2+}}{}^d$	$\Phi_{H^+}{}^e$
$(NC)_5Co(\mu\text{-}CN)Co(NH_3)_5$	254		$(1.6 \pm 0.4) \times 10^{-2}$	$(6.0 \pm 0.9) \times 10^{-2}$
	313	$(3.2 \pm 0.5) \times 10^{-3}$	$(9 \pm 2) \times 10^{-4}$	$(3.8 \pm 0.8) \times 10^{-3}$
	365	$(1.6 \pm 0.3) \times 10^{-3}$	$(3 \pm 1) \times 10^{-4}$	$(1.2 \pm 0.3) \times 10^{-3}$
	460	$<1 \times 10^{-5}\,f$	$<1 \times 10^{-4}\,f$	$<1 \times 10^{-4}\,f$
$(NC)_5Co(\mu\text{-}NC)Co(NH_3)_5$	254	0.20 ± 0.03	$(3.9 \pm 0.5) \times 10^{-3}$	$(2.2 \pm 0.2) \times 10^{-2}$
	313	0.21 ± 0.02	$(7 \pm 1) \times 10^{-4}$	$(4.1 \pm 0.3) \times 10^{-3}$
	366	0.28 ± 0.01	$(6 \pm 2) \times 10^{-4}$	$(3.7 \pm 0.6) \times 10^{-3}$
	436	$(3 \pm 1) \times 10^{-3}$	$\leqslant 2 \times 10^{-4}\,f$	$\leqslant 1 \times 10^{-3}\,f$
$Co(CN)_6{}^{3-}$	254	0.31^g		
	313	0.31^g		
	365	0.31^g		
	405	0.29 ± 0.02^h		
	436	0.34 ± 0.05^h		
$Co(CN)_5(NCCH_3)^{2-}$	313	0.37 ± 0.02		$<4 \times 10^{-3}$
	366	0.40 ± 0.02		
	436	0.2 ± 0.1		

^{a} Photolysis carried out in pH 2–4 aqueous $HClO_4$ with an initial concentration of $\sim 10^{-3}$ M (25 °C); λ_{irr} given in nm. ^{b} Calculated from spectral changes at 380 nm (see text). ^{c} Quantum yields based on spectral changes with the assumption of the products described in text. ^{d} Co(II) yields based on the thiocyanate analysis method. ^{e} Quantum yields for consumption of acid based upon pH changes. ^{f} See text. ^{g} Reference 7. ^{h} Nishizawa, M.; Ford, P. C. *Inorg. Chem.*, in press.

spectrophotometer equipped with a thermostated cell compartment. Dark reactions were monitored spectrally, and all photolysis data were corrected for the minor dark reaction changes. Quantum yields were plotted incrementally against percent reaction and extrapolated back to 0% reaction to correct for any inner filter effects.[15] No differences in quantum yields were found for deaerated solutions. Yields for the generation of Co(II) were determined by the thiocyanate analysis method[16] at the conclusion of each photolysis experiment. The consumption of hydronium ion was estimated from the pH change measured in the course of the photolysis by using a Sargent-Welch Model NX pH meter. Products were also evaluated by ion-exchange chromatography using both cationic (Dowex 50W-X4, 200–400 mesh) and anionic (Dowex 1-X10, 50–100 mesh) resin in separate experiments. Eluants were aqueous $HClO_4$ and aqueous NaCl solutions, respectively. Product yields were calculated from the spectra of elution aliquots collected quantitatively.

Results

Photolysis of $(NC)_5Co(\mu\text{-}CN)Co(NH_3)_5$. Irradiation of the C_6N_6 species at 365 or 313 nm leads to slow spectral changes, including some absorbance increase at ~ 380 nm and decreases in the intensities of the band maxima at 474 and 313 nm. Analysis of the photolysis solution shows some cobalt(II) formation and consumption of acid, the quantum yields for both being smaller for 366-nm than for 313-nm photolysis and immeasurable for 460-nm photolysis. The optical density decreases at the 474-nm λ_{max} of the pentammine chromophore as well as the pH changes can be entirely accounted for by the minor photoreduction of that chromophore. In contrast the absorbance increases at 380 nm must represent a different photochemical event. Since $Co(CN)_5H_2O^{2-}$ displays a λ_{max} ($\epsilon = 260$) at 380 nm, spectral quantum yields Φ_{spec} were calculated by assuming this species to be the absorbing product. Quantum yields for the C_6N_6 complex are summarized in Table I. Notably, Φ_{spec}, $\Phi_{Co^{2+}}$, and Φ_{H^+} are all relatively small and are markedly sensitive to λ_{max}.

Irradiation at 254 nm corresponds to the onset of the charge-transfer absorptions of the pentaamine center. At this wavelength the compound is much more photoactive as evidenced by the larger spectral changes and the formation of a pale brown precipitate upon prolonged photolysis. This precipitate displayed IR bands at 2130 and 2170 cm^{-1} and turned blue reversibly when heated at 120 °C. A similar precipitate formed when authentic samples of $CoCl_2 \cdot 6H_2O$ and $K_3[Co(CN)6]$ were mixed in aqueous solution. No precipi-

tation was observed when the photoreaction was carried out in the presence of added $Na_4(EDTA)$. These observations support the view that the precipitate is a salt containing both Co^{2+} and $Co(CN)_6{}^{3-}$. Cobalt(II) analysis of the solutions that were photolyzed for shorter times (before the onset of precipitation) demonstrated a $\Phi_{Co^{2+}}$ value (0.02) much larger than those measured at longer λ_{irr}.

Photoreactions of $(NC)_5Co(\mu\text{-}NC)Co(NH_3)_5$. An entirely different behavior is seen for the C_5NCN_5 species. Irradiation at 254, 313, or 365 nm leads to rapid changes in the spectrum with optical density decreases at each peak maximum of the starting material, optical density increases at 380 nm, and isosbestic points at 259, 358, and 440 nm maintained for high precentage conversion to products. Analysis of the solution for Co(II) formation and for H$^+$ uptake show very small values of $\Phi_{Co^{2+}}$ and Φ_{H^+} at these λ_{irr}. Ion-exchange analysis of the photolysis solution showed but two significant photoproducts, $Co(NH_3)_5CN^{2+}$ and $Co(CN)_5H_2O^{2-}$, as identified from their elution behavior and electronic spectra. Spectral quantum yields Φ_{spec} were thus calculated from the absorbance increase at 380 nm on the basis of the approximation that these two species are the only products (eq 1). Notably these values

$$(NC)_5Co(\mu\text{-}NC)Co(NH_3)_5 + H_2O \xrightarrow{h\nu}$$
$$Co(CN)_5H_2O^{2-} + Co(NH_3)_5CN^{2+} \quad (1)$$
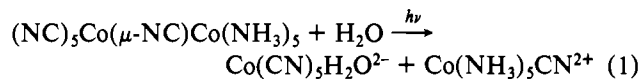
(Table I) are large and only moderately λ_{irr}-sensitive for λ_{irr} = 365, 313, or 254 nm. In marked contrast, Φ_{spec} is 2 orders of magnitude smaller at λ_{irr} = 436 nm.
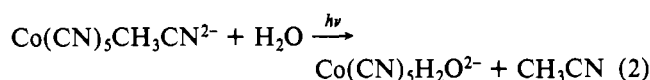
Photosynthesis of and Photoaquation Quantum Yields for $Co(CN)_5CH_3CN^{2-}$. Exhaustive photolysis of $K_3Co(CN)_6$ dissolved in 3/1 acetonitrile/water solution led to the conversion of the initial spectrum ($\lambda_{max} = 311$ nm) to a new species with $\lambda_{max} = 345$ nm. Addition of acetone to this solution precipitated a pale yellow microcrystalline solid, which was recrystallized from aqueous acetonitrile and acetone. The IR spectrum of this material in a KBr pellet gave bands at 2936 (m), 2322 (m), 2298 (w), 2160 (m), 2148 (w, sh), and 2134 (vs) cm^{-1}, the first three characteristic of coordinated acetonitrile[17] and the last three of coordinated cyanide. This species in aqueous solution displayed an electronic spectrum with a λ_{max} at 348 nm ($\epsilon = 189$ M^{-1} cm^{-1}) (Figure 2). Exhaustive photolysis of this solution leads to a new spectrum with λ_{max} = 380 nm ($\epsilon = 250$ M^{-1} cm^{-1}), which corresponds closely to that of $Co(CN)_5H_2O^{2-}$ ($\lambda_{max} = 380$ nm, $\epsilon = 260$ M^{-1} cm^{-1}).

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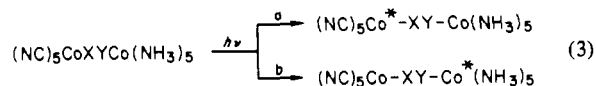(17) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 227.

Thus we may conclude that the photolysis product in acetonitrile solution is almost exclusively the $Co(CN)_5CH_3CN^{2-}$ ion and that eq 2 is the photoreaciton observed in aqueous

$$Co(CN)_5CH_3CN^{2-} + H_2O \xrightarrow{h\nu}$$
$$Co(CN)_5H_2O^{2-} + CH_3CN \quad (2)$$

solution. Quantum yields for this process are large (Table I), and the absence of significant pH changes in the reaction solution indicates that both photoreduction to Co(II) and photoaquation of CN^- play at most very minor roles at longer irradiation wavelengths.

Discussion

The key observations reported here are the dramatic differences in the aqueous solution photoreactivities of the two binuclear complexes. Given the similarity of the C_6N_6 spectrum to a composite spectrum obtained by adding the spectra of $Co(CN)_6^{3-}$ and $Co(NH_3)_5(CH_3CN)^{3+}$ (Figure 2) and of the C_5NCN_5 spectrum to the composite spectrum of $Co(CN)_5(CH_3CN)^{2-}$ plus $Co(NH_3)_5CN^{2+}$ (Figure 3), we conclude that, at least for the LF states, there is little first-order interaction between the two chromophoric centers. Thus, it can be argued that initial excitation of individual molecules is largely localized at one Co(III) center or the other (eq 3),
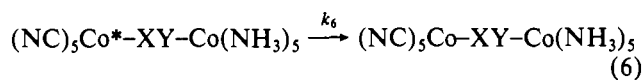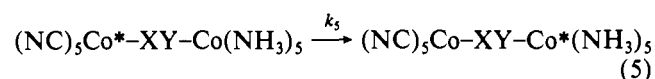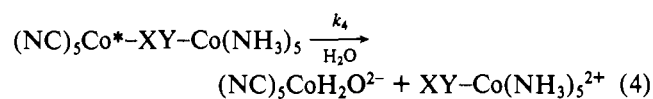
$$(NC)_5CoXYCo(NH_3)_5 \xrightarrow{h\nu} \begin{array}{l} \xrightarrow{a} (NC)_5Co^*-XY-Co(NH_3)_5 \\ \xrightarrow{b} (NC)_5Co-XY-Co^*(NH_3)_5 \end{array} \quad (3)$$

the relative proportions of excitation at $Co(CN)_5X$ or $Co(NH_3)_5Y$ centers being a function of the specific absorbances of the respective chromophores at each λ_{irr}. If there were no energy or electron transfer between the centers and if there were no major perturbations of the excited-state lifetimes from those of the mononuclear complexes, then the photochemistry at each λ_{irr} would be the sum of that expected for the individual chromophores weighted according to the extent of light absorption by each. In other words, each metal center would act as an inner filter of the other's photochemistry. While such is certainly not the case for C_6N_6 (vide infra), the behavior does not depart far from this type of model for C_5NCN_5.

For C_5NCN_5 the LF absorption of the $Co(CN)_5X$ chromophore dominates the spectral region 254–365 nm, where eq 1 is the predominant photoreaction (Figure 3). An analogy can be drawn to $Co(CN)_5(CH_3CN)^{2-}$, which undergoes efficient photoaquation of CH_3CN (eq 2), and with $Co(CN)_6^{3-}$, which loses CN^- under LF excitation. In both cases Φ_{subst} values are essentially λ_{irr}-independent (Table I), suggesting that initial excitation is followed by deactivation to a common ES of the $Co(CN)_5S$ chromophore. Similar behavior is seen for the LF photochemistries of rhodium(III) and iridium(III) pentaammine complexes,[11,12,18] and for these cases the common ES is concluded to be the lowest energy triplet LF state, the lowest state of the ES manifold.

For C_5NCN_5 the Φ_{spec} values measured at 254, 313, and 365 nm (Table I) can be corrected (approximately) for the inner-filter effect of $Co(NH_3)_5Y$ by assuing this to have the same spectrum as $Co(NH_3)_5CN^{2+}$ and attributing the balance of the light absorbed to the other center. When this is done, the corrected quantum yields for eq 1 are 0.22, 0.28, and 0.30 mol/einstein, respectively. (Note, this correction is inherently poor at 254 nm, the CT region where the composite and dinuclear spectra differ significantly.) These values support the view that for C_5NCN_5 LF excitation of the $Co(CN)_5X$ chromophore leads to reactions reasonably unperturbed by the other metal center. The small $\Phi_{Co^{2+}}$ values at 254 nm can be

attributed to minor absorption into the CT state(s) of the $Co(NH_3)_5Y$ center and subsequent photoreduction. Furthermore, the dramatically different behavior at 436 nm can be attributed to the strong absorption of $Co(NH_3)_5Y$ and the weak absorption of $Co(CN)_5X$ at this λ_{irr}. The $Co(NH_3)_5CN^{2+}$ photochemistry has been reported, and both CN^- and NH_3 aquations were observed with small quantum yields at comparable λ_{irr}. However, the low Φ_{H^+} value (10^{-3}) for C_5NCN_5 indicates that eq 1 is the major photoreaction at this wavelength, and, if one uses the spectrum of $Co(CN)_5-(CH_3CN)^{2-}$ to estimate the light absorbed by the $Co(CN)_5X$ chromophore at 436 nm, the residual absorption by the center is sufficient to account for the observed quantum yields for eq 1.

For C_6N_6 an entirely different pattern is seen, and the photochemistry of this species in aqueous solution in no way parallels that of its mononuclear analogue $Co(CN)_6^{3-}$ even at the λ_{irr} where the $Co(CN)_5X$ chromophore is strongly absorbing. Thus, in this case, the presence of the $Co(NH_3)_5Y$ center must enhance the deactivation of the $Co(CN)_5X$ LF excited states via nonreactive pathways. Equations 4–6 illustrate

$$(NC)_5Co^*-XY-Co(NH_3)_5 \xrightarrow[H_2O]{k_4}$$
$$(NC)_5CoH_2O^{2-} + XY-Co(NH_3)_5^{2+} \quad (4)$$

$$(NC)_5Co^*-XY-Co(NH_3)_5 \xrightarrow{k_5} (NC)_5Co-XY-Co^*(NH_3)_5 \quad (5)$$

$$(NC)_5Co^*-XY-Co(NH_3)_5 \xrightarrow{k_6} (NC)_5Co-XY-Co(NH_3)_5 \quad (6)$$

lustrate possible courses for deactivation of the $Co(CN)_5X$ center. Initial excitation (eq 3a) gives a localized LF state, which can undergo labilization (eq 4), energy transfer to $Co(NH_3)_5Y$ (eq 5), or nonradiative deactivation (eq 6). Given the very low reactivity of the $Co(NH_3)_5X$ LF states, eq 5 is tantamount to an added pathway for nonradiative deactivation. Thus the effective quantum yield for eq 4 will depend upon the extent of excitation that goes via eq 3a than upon the relative values of k_4, k_5, and k_6. For C_5NCN_5 the ratio $k_4/(k_5 + k_6)$ must be large (~ 0.5) in order to achieve the quantum yields seen for eq. 4. In contrast, for C_6N_6 this ratio must be several orders of magnitude smaller. The reason is unlikely to lie solely in the k_4 term, given the lability of CN^- from the LF state of $Co(CN)_6^{3-}$.

The key appears to lie in the relative values of k_5 for the two dinuclear complexes; that is, energy transfer from the $Co(CN)_5X$ to $Co(NH_3)_5Y$ is apparently much more rapid for C_6N_6 than for C_5NCN_5. From the standpoint of energetics, there is no clearcut reason for this differentiation. If initial excitation of $Co(CN)_5X$ (eq 3a) is followed by rapid internal conversion to give either the lowest singlet or triplet LF ES of this center, in either case this state is significantly higher in energy than the lowest LF state of the same multiplicity of the other chromophore. However, the symmetry of the relevant states must be taken into account. The lowest energy state of $Co(CN)_5X$ has ^3E symmetry (a one-electron configuration of $(d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1$) for either dimer while the lowest triplet of $Co(NH_3)_5X$ is $^3A_2$ $((d_{xy})^1(d_{xz},d_{yz})^3(d_{x^2-y^2})^1)$ for C_5NCN_5 and $^3E((d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1)$ for C_6N_6. If energy transfer involves only the lowest triplet states of the two centers (or the lowest singlets), the former case, $^3E \rightarrow {}^3A_2$, would be symmetry disallowed while the latter would be allowed. It is likely that energy transfer from the ^3E of $Co(CN)_5X$ to the other center could involve coupling to a higher state of that center (i.e., the ^3E) for which this restriction does not hold. That this must occur slowly for C_5NCN_5 relative to other deactivation processes may reflect greater Franck–Condon

(18) Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* 1979, *101*, 4549.

contributions relative to the situation for C_6N_6.

In the absence of quantitative rate data for the individual k_4, k_5, and k_6 steps, our discussion by necessity must be speculative. For example, despite the rationale that k_5 should be faster for C_6N_6 than for its linkage isomer, it can also be argued that k_4 should be faster for C_5NCN_5, owing to the Co–NCR bond linkage being weaker than that of Co–CN. Certainly the fact that $Co(CN)_5CH_3CN^{2-}$ photoaquates only CH_3CN suggests this possibility, although photosubstitution quantum yield differences between $Co(CN)_6^{3-}$ and $Co(CN)_5CH_3CN^{2-}$ are small. However, attempts in this laboratory to observe emission from the LF states of the $Co(CN)_5X$ chromophore of both dimers and of the double salt [Co(N-

$H_3)_5H_2O][Co(CN)_6]$ were unsuccessful[19] under conditions (77 K) where emission is easily seen from $K_3Co(CN)_6$, suggesting that the presence of a proximate pentaamminecobalt(III) center does accelerate nonradiative deactivation.

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Carbonyl Substitution Reactions of Cyclopentadienylbromodicarbonylruthenium(II) and (Ethyltetramethylcyclopentadienyl)bromodicarbonylruthenium(II). A Kinetic Study

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Reaction of $Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Br$ with phosphorus(III) ligands (L) in diethylene glycol dimethyl ether (diglyme) gives the monosubstituted derivative $Ru(\eta^5\text{-}C_5Me_4Et)(CO)LBr$ [L = $P(OPh)_3$, $P(OMe)_3$, or PPh_3]. Kinetic studies have shown that these reactions proceed via a dissociative mechanism. The corresponding carbonyl substitution reactions of $Ru(\eta^5\text{-}C_5H_5)(CO)_2Br$ with $P(OPh)_3$ or PPh_3 in diglyme also proceed via a dissociative mechanism although the previously reported reactions in di-*n*-butyl ether have been shown to involve free radicals. Comparison of the kinetic data for the two ruthenium compounds shows that the ethyltetramethylcyclopentadienyl compound is considerably more labile and that the $\eta^5\text{-}C_5Me_4Et$ ligand is able to stabilize the transition state and so promote ligand dissociation.

Substitution reactions of cyclopentadienylmetal compounds have been of special interest ever since Schuster-Woldan and Basolo studied the reactions of $[M(\eta^5\text{-}C_5H_5)(CO)_2]$ (M = Co, Rh, or Ir) and proposed that the cyclopentadienyl ligand promoted an associative pathway for carbonyl substitution reactions.[1] Since that time substitution reactions of one or more cyclopentadienyl transition-metal compounds from each group in the periodic table have been investigated,[2] including a report by one of us on the carbonyl substitution reactions of $[Mo(Cp')(CO)_3X]$ (I) $[Cp' = \eta^5\text{-}C_5H_5; X = Cl, Br, or I]$.[3] In this latter study it was shown that modifying the cyclopentadienyl ring with a fused benzene substituent [i.e., I, Cp' = η^5-indenyl] had a dramatic effect on both the rate and mechanism of the carbonyl substitution reaction[4] while modifying the cyclopentadienyl ligand with a fused cyclohexane substituent [i.e., I, Cp' = η^5-tetrahydroindenyl] had only a minor effect.[5] Similarly, the ease of carbonyl substitution in the complexes $[Fe(Cp')(CO)_2I]$ increases in the order Cp' = η^5-tetrahydroindenyl < η^5-cyclopentadienyl ≪ η^5-indenyl.[6]

Surprisingly, the only other systematic kinetic studies upon the effect of modifying the cyclopentadienyl ring appear to

have been restricted to comparing (methylcyclopentadienyl)metal compounds with the corresponding unsubstituted-cyclopentadienyl compound; as might be anticipated, no significant effects upon the rate or mechanism of ligand substitution have resulted from such a minor modification.[7] We therefore decided to investigate the kinetics and mechanism of substitution reactions of bromodicarbonyl(ethyltetramethylcyclopentadienyl)ruthenium(II) (reaction 1) and

$$Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Br + PR_3 \rightarrow$$
$$Ru(\eta^5\text{-}C_5Me_4Et)(CO)(PR_3)Br + CO \quad (1)$$
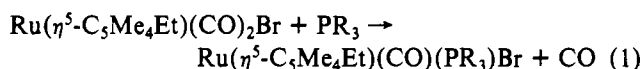
compare these results with those reported for analogous reactions of $[Ru(\eta^5\text{-}C_5H_5)(CO)_2Br]$.[8] Subsequent events led us to reinvestigate the reactions of the unsubstituted-cyclopentadienyl compound.

This study has additional significance in that (peralkylcyclopentadienyl)metal compounds are increasingly being used as homogeneous catalysts; for example, $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ catalyzes the hydrogenation of arenes,[9] $[Y(\eta^5\text{-}C_5Me_4Et)_2\text{-}n\text{-}Bu]$ catalyzes the polymerization of ethylene,[10] and $Ta(\eta^5\text{-}C_5Me_5)Cl_2(1\text{-octene})$ catalyzes the dimerization of α-olefins.[11]

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