bicarbonate complexes given by Bauman.[6]

Ion-pair formation constants according to eq 1 are recovered from eq 4 by subtracting equilibrium constants for the ionization of H_2CO_3 (eq 3). In this way, we have fit log K_f values to eq 5 to obtain the thermodynamic data given in Table IV.

We then calculate A, B, and C coefficients for a three-parameter equation, in which now the heat capacity change for eq 1 is not negligible. Table V compares our results with those published by Bauman.[6]

It is concluded that use of the balanced-like-charges approach permits linearization of the temperature dependence of formation constants for selected metal–bicarbonate reactions. The resulting two-parameter equation facilitates extrapolation of log K values to high temperatures and should simplify computer-assisted and other calculations for these reactions.

Acknowledgment. This work was supported by the Director, Office of Basic Research, Office of Basic Energy Sciences, Division of Engineering, Mathematical and Geosciences, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098. Thanks are given to J. E. Bauman, University of Missouri, and David Garvin, National Bureau of Standards, for their review and comments.

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Intramolecular Energy Transfer between Ligand Field Excited States in a Bimetallic System

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Received March 22, 1983

The bimetallic complex $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ (I) has been synthesized via the reaction of $Cr(NH_3)_5H_2O^{3+}$ with $Co(CN)_6{}^{3-}$ in 0.02 M $HClO_4$ solution (55 °C, 9 h). The UV–visible absorption spectrum of I reveals ligand field (LF) band maxima at 310 and 468 nm characteristic of the $Co–C_6$ and $Cr–N_6$ chromophores, respectively. Selective excitation of the $Co–C_6$ chromophore in 0.02 M $HClO_4$ solution using 313-nm irradiation results in bridging-cyanide labilization and the formation of $Co(CN)_5H_2O^{2-}$ ($\phi_{CN} = 0.08$). This cyanide quantum yield corresponds to a fourfold reduction in yield relative to that of the corresponding monometallic anion $Co(CN)_6{}^{3-}$, which is consistent with but not conclusive evidence for intramolecular $Co–C_6 \rightsquigarrow Cr–N_6$ energy transfer. More compelling evidence for such transfer is obtained from $Cr–N_6$ sensitization data. When absorbance-matched solutions of I are excited at 313 and 436 nm, the former wavelength yields a $Cr–N_6$ emission signal 76% as intense as that for 436-nm excitation. Furthermore, $Co–C_6$ irradiation is accompanied by a sensitized NH_3 ligand release yield of $\phi_{NH_3} = 0.16$, which is 73% of that obtained on direct $Cr–N_6$ excitation. The actual pathway for intramolecular energy transfer in I has not as yet been established, but the present data and possible symmetry requirements favor ${}^1T_{1g} \rightsquigarrow {}^4T_{2g}$ or ${}^3T_{1g} \rightsquigarrow {}^4T_{2g}$ transfer over a ${}^3T_{1g} \rightsquigarrow {}^2E_g$ pathway.

Introduction

Excitation energy transfer involving transition-metal (TM) complexes is presently an area of active theoretical and practical interest.[1-9] However, the energy-transfer systems studied so far have been primarily intermolecular in nature. Such processes generally occur via an exchange mechanism and necessitate collisional approach of donor and acceptor. In contrast, for the corresponding case of *intramolecular* energy transfer, the donor and acceptor species are in perpetual encounter and the probability of efficient transfer may therefore be significantly enhanced. This report describes the results of a study of intramolecular energy transfer between spectroscopically independent TM centers, where the chromophores are exclusively ligand field (LF) in character. The compound investigated was the bimetallic species $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ (I), which has been examined under conditions of normal photochemical interest, i.e., room-temperature aqueous solution.

Under ideal circumstances, energy-transfer efficiencies may be evaluated for bimetallic systems by selective excitation of one metal center (the donor) and by monitoring the extent of (1) quenching of donor emission and photoreaction and (2) sensitization of emission and photoreaction characteristic of the other metal center (the acceptor). It is important to note that although donor excited-state quenching (emission or reaction) may reveal which donor state is actually involved in energy transfer, it is not in itself definitive evidence for electronic energy transfer.[1] The observation of sensitized acceptor reaction is also inconclusive since it is possible the reaction is due to a chemical reaction between the excited donor and ground-state acceptor wherein no acceptor excited states are generated.[1] Unambiguous evidence for energy transfer is obtained, however, with the observation of *sensitized acceptor emission*, provided the donor and acceptor chromophores are

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spectroscopically independent.

The photobehavior of a bimetallic system closely related to the title compound, $(NC)_5Co(\mu\text{-}CN)Co(NH_3)_5$ (II), was recently reported by Nishizawa and Ford.[9,10] The electronic spectrum of II in aqueous solution over the LF region is of particular interest,[9,11] being virtually superimposable upon that of an equimolar mixture of $Co(CN)_6^{3-}$ and $Co(NH_3)_5NCCH_3^{3+}$. This observation is indicative of the spectroscopic independence of the Co(III) chromophores in II, designated as $Co\text{-}C_6$ and $Co\text{-}N_6$, and meets the requirements for energy transfer involving a very weak interaction coupling the initial and final states.[12] Furthermore, since little spectral overlap occurs between the spin-allowed LF absorption bands of the two metal centers, it was possible to selectively excite either chromophore by an appropriate choice of irradiation wavelength. However, the photoinertness of the $Co\text{-}N_6$ chromophore and the general absence of room temperature emission for Co(III) complexes seriously restricted the number of experimental probes of intramolecular energy transfer. For II the dramatic quenching of $Co\text{-}C_6$ chromophore photoreactivity relative to that of $Co(CN)_6^{3-}$ on selective $Co\text{-}C_6$ excitation served as the sole energy-transfer probe. Their results are consistent with, but do not conclusively establish, efficient intramolecular energy transfer between the $Co\text{-}C_6$ and $Co\text{-}N_6$ chromophores.

The preparation and characterization of the title compound, $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$, have not previously been described and are reported herein. The compound exhibits the same desirable spectral characteristics noted for II (vide infra). Of special importance, the presence of the Cr(III) chromophore also permits sensitized Cr(III) emission and photoreaction to be employed as critical determinants of Co(III) $\rightsquigarrow$ Cr(III) energy transfer. We believe our data for I constitute the most convincing evidence so far presented for intramolecular energy transfer between LF-centered excited states. Petersen and co-workers[13] have recently described an interesting Ru(II),-Rh(III) mixed bimetallic system that is also believed to display this phenomenon, but alternative electron-transfer or energy-transfer mechanisms involving metal-to-ligand charge-transfer excited states could not be excluded.

Experimental Section

Synthesis of $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$. $[Cr(NH_3)_5H_2O](ClO_4)_3$ (1.5 g, 0.0033 mol) and $K_3[Co(CN)_6]$ (1.1 g, 0.0033 mol) were separately dissolved in 75 mL of 0.02 M $HClO_4$ and heated to 80 °C. The two solutions were then combined in a stoppered flask, and the flask was placed in a water bath at 55 °C for 9 h. Some orange crystals, presumably $[Cr(NH_3)_5H_2O][Co(CN)_6]$, formed during this period and were filtered off after the solution cooled to room temperature. The solution was then run through H^+ (Dowex 50W-X8, 20–50 mesh) and ClO_4^- (Dowex 2-X8, 20–50 mesh) ion-exchange resins to remove charged impurities. The product was precipitated from the eluate (200 mL) by the stepwise addition with scratching of 800 mL of distilled acetone. The light orange solid was filtered, transferred to a beaker, stirred with 75 mL of absolute ethanol, refiltered, washed with absolute ethanol and ether, and sucked dry (yield 0.50 g, 0.0014 mol, 43%). Anal. Calcd for $CoCrC_6H_{15}N_{11}\cdot H_2O$: C, 19.26; H, 4.46; N, 41.56. Found: C, 19.47; N, 4.63; N, 41.63.

Photolysis Procedures. The light source employed for 313- or 436-nm irradiations was an Oriel 1000-W mercury–xenon lamp. The lamp output, after passage through an infrared water filter, was focused onto the inlet slit (2 mm) of a J-Y Optics H-10V monochromator. The light emerging from the outlet slit (usually 1 mm, ~5.5-nm band-pass) was then passed through a thermostated cell compartment that accepts 1-cm square cells and 1-, 5-, or 10-cm cylindrical cells. Photolyses were generally carried out in 0.02 M $HClO_4$ solution, at complex concentrations providing essentially total light absorption. For quantum yield calculations, photolyses were not carried out past 10% reaction. The light finally impinged on a photomultiplier tube (Hamamatsu 1 P28) via a pinhole inlet. This arrangement allowed variations in the lamp intensity to be readily monitored. Another source of radiation for photolyses was the 488.0-nm line of a Coherent Radiation argon ion laser (Model 52). Absolute light intensities were determined by ferrioxalate actinometry (≤436 nm).

Emission Procedures. A modified Aminco-Bowman spectrofluorimeter (Model 48203-D) with a red-sensitive R446S potted phototube was utilized for steady-state emission studies.[14] A 5.5-nm band-pass for excitation and emission was normally employed, and second-order grating phenomena were eliminated by using a Corning CS 3-71 cutoff filter just prior to the photomultiplier tube. Emission spectra were recorded on a Houston 2000 X-Y recorder. Variations in lamp intensity (125 W Hg–Xe) were regularly monitored by observing the emission intensity of a standard aqueous solution of $[Ru(bpy)_3]Cl_2$.

In order to compare the relative Cr(III) emission intensities of I upon irradiation into its $Co\text{-}C_6$ (313 nm) and $Cr\text{-}N_6$ (436 nm) chromophores, absorbance-matched aqueous solutions at 313 and 436 nm, respectively, were prepared. Correction for differing lamp intensities at these two wavelengths were carried out by using absorbance-matched aqueous solutions of $[Ru(bpy)_3]Cl_2$ via a procedure described earlier.[15]

The excitation source for determination of excited-state emission lifetimes was a Molectron UV-12 N_2 laser (250 kW). An Aminco dewar (Model B28-62140) was used for measurements at 77 K. All other associated equipment and lifetime analysis procedures have been described elsewhere.[14]

Analysis Procedures. Ammonia quantum yields, ϕ_{NH_3}, were determined by electrochemical analysis of photolyzed solutions. The corresponding cyanide quantum yields, ϕ_{CN}, were obtained from spectral analysis of photolytes.[9] The photolysis data were corrected for very minor dark-reaction changes. All UV–visible absorption spectra before and after photolysis were obtained on a Cary 118C spectrophotometer. A Markson Electromark analyzer (Model 4403) was used to measure conductance while NH_3 concentrations were determined by using an Orion ammonia-sensing combination electrode (Model 95-10).

Results and Discussion

Preparation of $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$. The synthesis of I was initially attempted, without success, by using an approach analogous to that employed by Haim and co-workers[11] for compound II. This method involved isolating a sample of $[Cr(NH_3)_5H_2O][Co(CN)_6]$ and then heating the solid to promote loss of coordinated water and attack at the vacant Cr(III) coordination site by a cyanide N lone pair. Irrespective of the temperature and heating time involved, a water-insoluble orange product was obtained. This product has very recently been shown by Jepsen and House[16] to result from the dehydration step being accompanied by the loss of 1.5 mol of HCN/mol of complex. Our synthetic goal was finally achieved by the reaction of the same two reagents, $Cr(NH_3)_5H_2O^{3+}$ and $Co(CN)_6^{3-}$, *in solution* rather than in the solid state. Precipitation of the undesired double-complex salt $[Cr(NH_3)_5H_2O][Co(CN)_6]$ is largely prevented by performing the initial reagent mixing at high temperature (75–80 °C). Our overall synthetic strategy is modeled after that employed successfully by Gaswick and Haim[17] for the in situ preparation of the

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(10) We have also examined this system, our results being presented in part at the 169th National Meeting of the American Chemical Society, Philadelphia, PA, 1975. Our data and conclusions are in essential agreement with that of Nishizawa and Ford.[9]

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Table I. UV-Visible Spectral Data for $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ and Related Monometallic Compounds in Aqueous Solution

complex	λ_{max}[a]				ref
$Co(CN)_6{}^{3-}$			311 (196)	258 (138)	c
$Cr(NH_3)_6{}^{3+}$	463 (39)	351 (33)			d
$(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$	468 (45)		310 (232)[b]		this work
$Cr(NH_3)_5H_2O^{3+}$	480 (36)	359 (31)			e

[a] Absorption wavelengths in nm. Values in parentheses are the molar absorptivities. [b] The corresponding minima for $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ are at 405 nm (18) and 278 nm (103). [c] Reference 11. [d] Wong, C. F. C.; Kirk, A. D. *Inorg. Chem.* **1978**, *17*, 1672. [e] Riccieri, P.; Zinato, E. *Ibid.* **1980**, *19*, 853.

Table II. Photochemical and Photophysical Data for $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ and Related Monometallic Compounds[a]

complex	λ_{irr},[b] nm	ϕ_{CN}[c]	ϕ_{NH_3}[d]	ϕ_P	τ_P, μs
$(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$	313	0.08 ± 0.01	0.16 ± 0.02[e]	0.76[h]	1.9 ± 0.2,[j] 46 ± 3[k]
	436	$<1 \times 10^{-5}$	0.21 ± 0.02[e]	1.0[h]	
	488	$<1 \times 10^{-5}$	0.23 ± 0.03[f]		
$K_3[Co(CN)_6]$	313	0.31 ± 0.02			
$[Cr(NH_3)_6](ClO_4)_3$	488		0.47[g]	1.5[i]	2.2 ± 0.2,[j] 35 ± 2[k]

[a] Photolyses carried out in 0.02 M $HClO_4$ solution at 20 °C, unless otherwise stated. [b] Irradiation wavelength for cyanide and NH_3 quantum yield studies. [c] Calculated from spectral changes at 379 nm. The value for $Co(CN)_6{}^{3-}$ is in good agreement with that reported.[9] [d] Ammonia release monitored with an NH_3-selective electrode. [e] Employing ferrioxalate actinometry. [f] Calculated from photolysis data for absorbance-matched solutions of I and $[Cr(NH_3)_6](ClO_4)_3$, assuming $\phi_{NH_3} = 0.47$. [g] Literature value for 436-nm irradiation (Angermann, K.; Schmidt, R.; van Eldik, R.; Kelm, H.; Wasgestian, F. *Inorg. Chem.* **1982**, *21*, 1175 and references therein). [h] Relative $Cr\text{-}N_6$ $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence yields. [i] Phosphorescence yield of $Cr(NH_3)_6{}^{3+}$ relative to that of I on 436-nm excitation. [j] Emission lifetime in 0.02 M $HClO_4$ solution at 20 °C. [k] Solid-state lifetime 77 K.

cyanide-bridged species $(NC)_5Co(\mu\text{-}CN)Cr(H_2O)_5$. We find acidic solutions of I to be indefinitely stable in the absence of light. In interesting contrast, solid samples of I undergo slow thermal decomposition in the dark to a water-insoluble product. For this reason, solid samples of I were stored in a freezer, and fresh samples were prepared after 3–4 weeks.

Characterization of $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$. Microanalysis (C, H, N) and conductance measurements support the proposed formulation for I. A 1.0×10^{-3} M aqueous solution of I yields a molar conductance of 5 Ω^{-1} cm^2 mol^{-1} consistent with its nonelectrolyte status. Molecular neutrality is also in accord with the nonretention of I on a cation or anion resin (see synthesis). The IR spectrum (KBr disk) shows several intense bands in the C≡N stretching region—2165, 2144 (sh), 2131, and 2122 cm^{-1} (sh). In keeping with earlier assignments for II,[11] the less intense peak at 2165 cm^{-1} may be attributed to the bridging C≡N group. Strong evidence for spectroscopically independent $Co\text{-}C_6$ and $Cr\text{-}N_6$ chromophores is provided by the UV-visible spectrum of I in aqueous solution. The observed absorption maxima and associated molar absorptivities match closely those for $Co(CN)_6{}^{3-}$ and $Cr(NH_3)_6{}^{3+}$, which serve as convenient monometallic model compounds (Table I). Irrespective of the wavelength of excitation (vide infra), I displays a relatively strong steady-state emission signal centered at 685 nm, which is assigned to $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence associated with the $Cr\text{-}N_6$ chromophore.[18] Emission is totally quenched in basic solution and regenerated on reacidification, in accord with prior observations on Cr(III) amine systems containing N-H protons.[15,19] A doublet excited-state lifetime for I of 1.9 μs in 0.02 M $HClO_4$ solution was obtained at 20 °C from pulsed-emission studies.

It should be noted that the microanalysis data do not exclude $[Cr(NH_3)_5H_2O][Co(CN)_6]$ as an alternative formulation for I. However, this latter structure is difficult to reconcile with the very low molar conductance recorded, and more importantly, a genuine sample of this double complex salt is very insoluble in water. Furthermore, the position of the longest wavelength LF absorption band of I is inconsistent with the presence of a $Cr\text{-}N_5O$ chromophore (Table I). In addition, water-soluble salts of $Cr(NH_3)_5H_2O^{3+}$ are extremely poor emitters in room-temperature solution and have reported lifetimes of <5 ns.[20] In contrast, the aqueous solution lifetime noted above for I is 3 orders of magnitude longer (1.9 μs, 20 °C) and matches closely that reported for $Cr(NH_3)_6{}^{3+}$ (Table II).

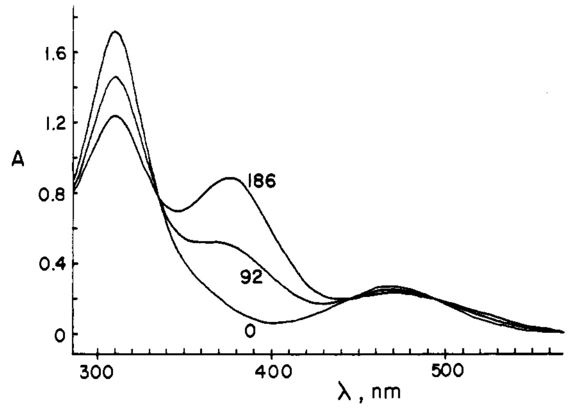

Figure 1. Ligand field absorption spectrum of $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ in 0.02 M $HClO_4$ solution (1.4×10^{-3} M, 5-cm cell) after 0-, 92-, and 186-min photolyses at 313 nm and 20 °C.

Photobehavior of $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$. In the present study, evidence for energy transfer has been sought by comparing the photobehavior of I with that of the constituent monometallic units or related model compounds. The constituent monometallic anion $Co(CN)_6{}^{3-}$ is well-known and photoaquates on 313-nm irradiation, reacting via its $^3T_{1g}$ level to form $Co(CN)_5H_2O^{2-}$ with a quantum yield of 0.31.[9] The corresponding cationic monomer $Cr(NH_3)_5NC^{2+}$ is unknown. However, the ligand donor atom environment is similar to that of $Cr(NH_3)_6{}^{3+}$, and on that basis, the $Cr\text{-}N_6$ chromophore should be reactive under LF excitation, resulting in NH_3 and/or CN^- ligand loss. In addition, by analogy with $Cr(NH_3)_6{}^{3+}$, the $Cr\text{-}N_6$ chromophore is expected to exhibit detectable emission in fluid solution at ambient temperatures. As noted below, the photobehavior observed for I is critically

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[18] For convenience, symmetry labels associated with the O_h point group are employed, although the $Co\text{-}C_6$ and $Cr\text{-}N_6$ chromophores in I more strictly possess C_{4v} symmetry (see Figure 2).

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dependent on the excitation locus.

A. Co–C_6 Excitation. Selective excitation of the Co–C_6 chromophore associated with the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ LF transition[18] was achieved with 313-nm irradiation. The title compound has a molar absorptivity of 227 at this wavelength compared with a value of 8 for the Cr–N_6 model compound, $Cr(NH_3)_6^{3+}$. On these grounds it is assumed approximately 96% of 313-nm light is absorbed by the Co–C_6 chromophore. Photolysis of a solution of I in 0.02 M $HClO_4$ at 313 nm produced a growth in photolyte absorption at 379 nm (Figure 1), in agreement with $Co(CN)_5H_2O^{2-}$ generation (i.e., bridging-cyanide labilization). Alternatively, this observation may be associated with formation of $(H_2O)(NC)_4Co(\mu\text{-}CN)Cr(NH_3)_5^+$ (i.e., terminal-cyanide labilization) since this bimetallic product also contains a Co–C_5O chromophore. The former path (bridge labilization) is confirmed from ion-exchange studies where the 379-nm absorbing species remained in the eluate after passage through a cation resin but was retained on an anion-exchange column. From the absorbance rise at 379 nm, a value of $\phi_{CN} = 0.08$ has been calculated (Table II).[9] This result corresponds to an approximate fourfold reduction in yield relative to that of the constituent monometallic anion $Co(CN)_6^{3-}$. Although cyanide reaction quenching is consistent with intramolecular Co–C_6 $\rightsquigarrow$ Cr–N_6 energy transfer, it does not provide conclusive proof since I and $Co(CN)_6^{3-}$ are different species that may have different rate constants for their radiationless decay processes. For example, ϕ_{CN} quenching may be associated simply with an enhanced rate constant in I for the Co–C_6 radiationless processes ${}^3T_{1g} \rightsquigarrow {}^1A_{1g}$ and/or ${}^1T_{1g} \rightsquigarrow {}^1A_{1g}$ (Figure 2).

However, compelling evidence for Co–C_6 $\rightsquigarrow$ Cr–N_6 energy transfer was obtained from a combination of sensitized Cr–N_6 emission and photochemical reaction data. When absorbance-matched 0.02 M $HClO_4$ solutions of I were excited at 313 and 436 nm, the former excitation yielded a 685-nm emission signal 76% as intense as that for 436-nm excitation (Table II). This observation contrasts sharply with an anticipated 313-nm excitation signal only 4% as intense in the absence of energy transfer, which would result from the small amount of direct Cr–N_6 excitation. Furthermore, Co–C_6 irradiation is accompanied by sensitized NH_3 ligand release with $\phi_{NH_3} = 0.16$ for 313-nm photolysis. This NH_3 release yield is approximately 73% of that obtained on direct Cr–N_6 excitation: $\phi_{NH_3}(436\text{ nm}) = 0.21$; $\phi_{NH_3}(488\text{ nm}) = 0.23$ (vide infra).

To our knowledge these data constitute the first reported example of energy transfer from a Co(III) to a Cr(III) complex center in room-temperature solution.[21-23] We assume an exchange mechanism is responsible for the *intramolecular* Co–C_6 $\rightsquigarrow$ Cr–N_6 energy transfer observed in this bimetallic system, since the following factors argue strongly against the presence of an efficient long-range dipole–dipole-transfer pathway:[12] (1) the small oscillator strengths of potential donor and acceptor LF bands (including spin-allowed absorptions); (2) the very close approach of metal donor and acceptor sites (~4.5 Å, a distance well within the range required for efficient exchange transfer). Significantly, selective excitation of $Co(CN)_6^{3-}$ in the presence of $Cr(en)_3^{3+}$ in aqueous solution[24] yields no corresponding evidence for *intermolecular* energy transfer between these Co(III) and Cr(III) centers. The latter observation is consistent with the very short excited-state lifetime of $Co(CN)_6^{3-}$ in room-temperature solution (<10 ns),[25] which markedly reduces the probability of a collisional exchange interaction between donor and acceptor during the donor lifetime. These present results clearly demonstrate the advantage inherent in the permanent donor/acceptor encounter condition provided by bimetallic systems such as I.

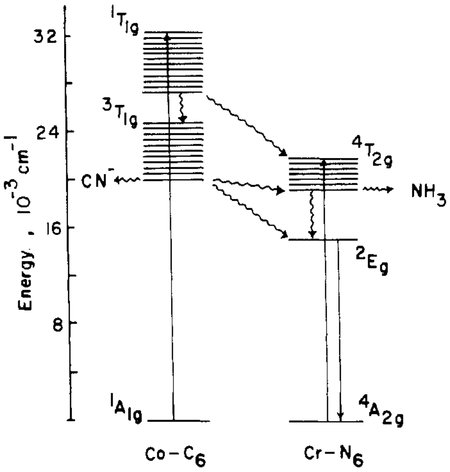

Figure 2. Energy level diagram for $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5$ depicting possible excited-state relaxation processes following selective Co–C_6 or Cr–N_6 excitation. For clarity of presentation of the various energy-transfer options, radiationless decay to the ${}^1A_{1g}$ and ${}^4A_{2g}$ ground states have not been depicted. The ${}^4T_{2g}$ state for the Cr–N_6 chromophore is distorted from ground-state geometry, as indicated by absorption to upper vibrational levels. The position of the vibrationally equilibrated ${}^4T_{2g}$ state, $({}^4T_{2g})^0$, has been estimated with use of an empirical procedure suggested by Adamson and co-workers.[33] To a reasonable approximation, the ${}^2E_g$ state is undistorted and its energy is provided directly from the ${}^2E_g \rightarrow {}^4A_{2g}$ emission spectrum. Although the ${}^2E_g$ level is depicted as unreactive, some NH_3 release may occur directly out of this level.[14,20] For the Co–C_6 chromophore, the ${}^1T_{1g}$ and ${}^3T_{1g}$ excited states are both shown as distorted. The energy of the $({}^3T_{1g})^0$ level was calculated from absorption and emission data for $Co(CN)_6^{3-}$.[25,34] An estimate for the corresponding $({}^1T_{1g})^0$ state has been made on the assumption of a comparable Stoke shift to that for the ${}^3T_{1g}$ level.

B. Cr–N_6 Excitation. Selective excitation of the Cr–N_6 chromophore associated with the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ LF transition[18] was possible by using either 436- or 488-nm irradiation. The Cr–N_6 chromophore in I has C_{4v} symmetry under which the ${}^4T_{2g}$ excited state splits into ${}^4B_2$ and ${}^4E$ components. Although π-acceptor ligand character is greater along the z axis due to the bridging isocyano group, the first LF absorption band is observed at a longer wavelength than that for $Cr(NH_3)_6^{3+}$ (Table I), implying weaker σ-donor ligand character along the same axis. It is therefore not readily apparent whether the ${}^4B_2$ or ${}^4E$ component lies lower in energy, and no theoretical predictions concerning preferential axis labilization are possible.[26] However, photolysis studies in 0.02 M $HClO_4$ solution on 436- and 488-nm irradiation establish NH_3 ligand loss as a major reaction pathway. Tests of the photolyte using an

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(21) Another indication of energy transfer would be the observation of a risetime for the population of the Cr(III) ${}^2E_g$ level.[22] Provided energy transfer were slow enough, this population process would be detected in emission lifetime decay traces obtained upon exclusive Co–C_6 excitation. We have observed no risetime for Cr–N_6 emission for an RC time constant as low as 20 ns in our detection circuit, consistent with an energy-transfer rate constant in excess of 10^7 s^{-1}. However, energy transfer may have been partially masked in these pulse experiments, since at the 337-nm N_2 excitation line employed, approximately 25% of the laser output is directly absorbed by the Cr–N_6 chromophore.

(22) Castelli, F.; Forster, L. S. *Chem. Phys. Lett.* **1975**, *30*, 465.

(23) *Intermolecular* energy transfer between a Co(III) and Cr(III) center has been reported under *solid-state* conditions for the complex salt $[Cr(NH_3)_6][Co(CN)_6]$: Kataoka, H. *Bull. Chem. Soc. Jpn.* **1976**, *46*, 2078.

(24) Emission measurements on this solution mixture were performed quickly prior to double-complex salt precipitation. For $Cr(en)_3^{3+}$ as acceptor, crystallization does not occur for several minutes in the presence of a high-backing electrolyte concentration. Similar experiments employing $Cr(NH_3)_6^{3+}$ were not possible due to very rapid double-salt precipitation.

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(26) Kirk, A. D. *Coord. Chem. Rev.* **1981**, *39*, 225.

ammonia-selective electrode gave NH_3 quantum yields of 0.21 and 0.23 for 436- and 488-nm excitation, respectively. Extended photolysis resulted in a shift in the position of the first LF band to lower energy, consistent with $Cr-N_5O$ chromophore formation. This latter spectrum was essentially unaffected by passage of the photolyte through cation- and anion-exchange resins, which provides further support for the reaction proceeding predominantly via NH_3 loss and formation of the neutral bimetallic product $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_4(H_2O)$.

It is noteworthy that these $Cr-N_6$ chromophore irradiations revealed no spectral evidence for formation of $Co(CN)_5H_2O^{2-}$ even on extensive photolysis. This observation constitutes very strong evidence against $^4T_{2g}(Cr-N_6) \rightsquigarrow {}^3T_{1g}(Co-C_6)$ energy transfer, since direct excitation of the $Co-C_6$ chromophore produces $Co(CN)_5H_2O^{2-}$ in readily detectable yield (Figure 1).[27] Although such transfer is in accord with the Wigner spin rules,[29] transfer from the $(^4T_{2g})^0$ level is probably slightly endothermic (Figure 2). The absence of this pathway is also reasonable in view of the exceptionally large rate constant for $^4T_{2g} \rightsquigarrow {}^2E_g$ intersystem crossing in Cr(III) systems.[30,31]

It is also of interest that ϕ_{NH_3} and $^2E_g \rightarrow {}^4A_{2g}$ emission for I are only 50% and 66% as great, respectively, as the corresponding values for $Cr(NH_3)_6^{3+}$ (Table II). However, the two compounds have similar ^2E_g lifetimes in 0.02 M $HClO_4$ solution at 20 °C: 1.9 μs for I; 2.2 μs for $Cr(NH_3)_6^{3+}$.[14] The two species also have similar apparent activation energies for their emission intensities in aqueous solution: 9.7 kcal mol^{-1} for I; 10.4 kcal mol^{-1} for $Cr(NH_3)_6^{3+}$.[31] These similarities indicate that the deactivation processes for the ^2E_g state have comparable rate constants for the two complexes. Thus, the decrease in NH_3 and phosphorescence yields for I most probably result from variations in radiationless decay rates from the $^4T_{2g}$ level.

Pathways for $Co-C_6 \rightsquigarrow Cr-N_6$ Intramolecular Energy Transfer. As noted earlier the photobehavior of I on $Co-C_6$ excitation provides convincing evidence for $Co-C_6 \rightsquigarrow Cr-N_6$ energy transfer. However, the question as to what transfer pathway is operative has not as yet been addressed. On the basis of energy criteria (Figure 2) and the Wigner spin rules,[29] three candidates require consideration—namely $^1T_{1g} \rightsquigarrow {}^4T_{2g}$, $^3T_{1g} \rightsquigarrow {}^4T_{2g}$, and $^3T_{1g} \rightsquigarrow {}^2E_g$ intramolecular transfer.[35] At present no clearcut distinction between these three alternative routes is possible. However, the observation that sensitized emission and sensitized NH_3 release yields are 76% and 73%, respectively, of the corresponding values for direct $Cr-N_6$ excitation (Table II) is more readily rationalized in terms of $^1T_{1g} \rightsquigarrow {}^4T_{2g}$ or $^3T_{1g} \rightsquigarrow {}^4T_{2g}$ transfer. Since the $^4T_{2g}$ state is also the level initially produced upon direct $Cr-N_6$ irradiation, one may then assign a $^1T_{1g} \rightsquigarrow {}^4T_{2g}$ or $^3T_{1g} \rightsquigarrow {}^4T_{2g}$ transfer efficiency of approximately 75% to accommodate the experimental data.

In addition, possible symmetry requirements[9] also favor these pathways over $^3T_{1g} \rightsquigarrow {}^2E_g$ transfer. For compound I each metal chromophore possesses C_{4v} symmetry. As a result the singlet and triplet T_{1g} excited states of the Co(III) center are split into A_2 and E components, with the latter lying lower in energy.[9] Thus, on the basis of relative population densities $Co-C_6 \rightsquigarrow Cr-N_6$ energy transfer should occur preferentially from a donor level of E symmetry. The potential Cr(III) acceptor levels, $^4T_{2g}$ and ^2E_g, are correspondingly split into components of $B_2 + E$ and $A_1 + B_1$ symmetry, respectively. Only in the case of transfer to the $^4T_{2g}$ level is it possible for the donor and acceptor surfaces to be of the same symmetry type (both E), and such transfer might then be especially rapid due to the presence of an avoided crossing, which will allow transfer to proceed adiabatically.[31,36]

Acknowledgment. The authors gratefully acknowledge the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The financial support of the Camille and Henry Dreyfus Foundation is also gratefully acknowledged.

Registry No. I, 87279-44-5; $(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_4(H_2O)$, 87279-45-6; $Co(CN)_5H_2O^{2-}$, 14842-83-2; $[Cr(NH_3)_5H_2O](ClO_4)_3$, 32700-25-7; $K_3[Co(CN)_6]$, 13963-58-1.

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(27) This conclusion is valid provided cyanide loss in I is associated with the $^3T_{1g}$ level as previously established for the monometallic species $Co(CN)_6^{3-}$.[28,34]

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(35) Although $^1T_{1g} \rightsquigarrow {}^2E_g$ transfer is energetically feasible, it is disallowed by the Wigner spin rules. The possibility of $^1T_{1g} \rightsquigarrow {}^4T_{1g}(Cr-N_6)$ transfer cannot be excluded but would presumably be followed by very efficient $^4T_{1g} \rightsquigarrow {}^4T_{2g}$ internal conversion.

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