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Contrasting Photochemical Processes in Azido- and Isothiocyanatopentaamminecobalt(III) Complexes. Implications for Excited State Processes[1]

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Abstract: Contrasts in the photoreactivity of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$ have been explored in fluid solutions using irradiations in the range $580 \geq \lambda \geq 214$ nm. The predominant product of all irradiations of the azido complex has been established to be $Co(NH_3)_4OH_2N_3^{2+}$, but the ammonia aquation process was found to be much less important for $Co(NH_3)_5NCS^{2+}$. In a similar manner, the photoredox modes are less efficient in the isothiocyanato than the azido complex for irradiations with $\lambda \leq 254$ nm. This contrast is attributed to a "heavy atom effect", i.e., to relatively more rapid electronic relaxation and deactivating cascade of photoactive excited states in the isothiocyanato complex. For such ultraviolet irradiations, thermalization of the charge transfer excited states is the postulated mechanism for the observed plateaus in photoredox yield with excitation energy. For deep ultraviolet excitations ($\lambda \leq 254$ nm) a new photoredox process predominates; this new process, postulated to involve direct photooxidation of the solvent, has been found to be common to several pentaammine complexes.

Among the most fundamental concerns in photochemical studies of transition metal complexes are the elucidation of the interdependence of photoreaction mode and efficiency on the electronic structure of the central metal and the coordination environment of the central metal. For the photoredox reactions of prototypical cobalt(III) complexes, efforts to explore such dependencies have often been frustrated by the preponderate observation of a single significant photoreaction mode following excitation of charge transfer to metal (CTTM) absorption bands.[2] Some useful insights[2,3] have resulted from the discovery that CTTM bands of ruthenium(III) complexes have very small photoredox efficiencies;[4,5] similarly the discovery[6] of a nitrene pathway (eq 1)

$$M(NH_3)_5N_3^{2+} + h\nu \xrightarrow{H^+} M(NH_3)_5NH^{3+} + N_2 \qquad (1)$$

following charge transfer excitation of heavy metal azido complexes gives promise of providing an instructive contrast to the photoredox mode reported for first-row transition metal complexes.[2,7-10] With regard to this latter contrast in reactivities, the change of metal from cobalt to rhodium or iridium in the azidopentaammine complex represents a rather dramatic electronic perturbation. Since $Co(NH_3)_5N_3^{3+}$ actually seems to be one of the most photosensitive cobalt complexes, exhibiting two major photoreaction modes,[3,8,11] we have chosen to explore relatively small electronic perturbations of the system by contrasting the photoreactivity of azido and isothiocyanato complexes. This alteration in the acido ligand results in some small changes in the relative energies of metal centered excited states[12-15] but almost no differences in the energies of charge transfer excited states since the reduction potentials[2c,3,16] of N_3^- and NCS^- are very similar (see Figures 4 and 5, below). Even such a small alteration of the coordination environment and the electronic structure of the complex does dramatically alter the photoreactivity of the system, with $Co(NH_3)_5NCS^{2+}$ being relatively photoinsensitive for low energy excitations.

Experimental Section

Materials. The preparations of $[Co(NH_3)_5N_3](ClO_4)_2$[8,17] and $[Co(NH_3)_5NCS](ClO_4)_2$[18] were performed according to literature descriptions; $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5Cl^{2+}$ were available from earlier studies.[3,19] All complexes were recrystallized until no free NCS^-, N_3^-, etc. could be detected and absorption spectra agreed with literature reports.[7a,8,17,20]

Water was redistilled from alkaline permanganate in all-glass apparatus. Nitrogen streams were purged of oxygen using scrubbing towers filled with chromous solutions.

The Sephadex C-25 cation exchange resin was used in the sodium form. The Bio-Rad AG-50W-X4 (100-200 mesh) resins were used in the acid form.

Other materials used were reagent grade and used without purification. Spectralquality acetonitrile, glycerol, 2-propanol, and ethylene glycol were used without further purification. The neat alcohols exhibited no significant absorbance in the 200-400 nm region.

Photochemical Apparatuses. The various photochemical apparatuses used in this study have been described previously[4,8,9,21,22] and will be mentioned only briefly here. Irradiations at $\lambda \geq 285$ nm were performed using a Xenon Model 270 spectral irradiator (Xenon Corporation, Medford, Mass.). The instrument was operated in the monochromator mode with the output of the high intensity grating focused through 0.9×1.5 cm slits onto a sample in a standard cuvet. Irradiation wavelengths and band widths were determined by passing the irradiator output through a Bausch and Lomb high intensity monochromator equipped with a Charles M. Reeder and Co. (Detroit, Mich.) thermopile and microvoltmeter detection systems (band widths at half maximum intensity were ±20 nm in this system). Irradiations at 254 nm were performed using Ultraviolet Products, Inc., immersion and helical low pressure mercury lamps ($I_0 \simeq 8 \times 10^{-4}$ and 3.5×10^{-3} einstein $l.^{-1}$ min^{-1}, respectively) and a Phillips spectral lamp (low pressure mercury; $I_0 \simeq 10^{-5}$ einstein $l.^{-1}$ min^{-1}); band widths of the resonance irradiations were about ±2 nm. Irradiations at 229 and 214 nm were performed using resonance emission lines of zinc and cadmium Phillips spectral lamps. The Phillips lamps were arranged on an optical bench with a collimating lens system, slits, filters, and sample cells as appropriate to the experiment. For all these lamps we periodically checked the approximate intensity and distribution of resonance lines using the Bausch and Lomb monochrometer–thermopile setup. Every deep ultraviolet irradiation with the zinc and cadmium lamps (at 214 or 229 nm) was paired with a near-ultraviolet irradiation (using an acetic acid filter solution) of the same substrate, and corrections were made for near-ultraviolet photolyses as appropriate. Actinometric determinations were performed each time the lamps were used; this was especially critical for the zinc lamps since several of the lamps used in this study had a useful 214 nm output for only relatively short periods of operation.

Flash photolysis experiments were performed with the Xenon Model 720 flash photolysis apparatus (see also the more extensive flash photolysis study of the azido complexes in ref 9b).

Procedures. Uranyl oxalate,[23,24] ferrioxalate,[25] or Reineckate salt[26] were used as primary reference actinometers for far-ultraviolet (214 and 229 nm) and near-ultraviolet and visible irradiations, respectively. Frequent actinometric checks of the various light sources were made during each series of irradiation experiments using $Co(NH_3)_5Cl^{2+}$ [3,27] or $Rh(NH_3)_5Br^{2+}$ [21b,28] as secondary actinometric references.

Cobalt(II) was analyzed by the method of Kitson,[29] calibrated, and modified as described elsewhere.[8,27]

For the thiocyanate and ammonia analyses a 1-ml column of Bio-Rad AG 50W-X2 cation exchange resin was preconditioned by washing with 25 ml of a solution 1 *M* in $NaClO_4$ and 10^{-3} *M* in $HClO_4$.

Ammonium ion was determined using the method of Bollester et al.[30] in the initial effluents of cation exchange separated photolyte solutions; the method was calibrated with known aliquots of NH_4^+ treated by the identical cation exchange procedure.

All resins were washed thoroughly with acid and with distilled water before use.

The Sephadex C-25 resin was prepared by washing a 1 × 4 cm column in succession with: (1) 150 ml of a solution 0.1 *M* in $HClO_4$; (2) 150 ml of a solution 0.1 *M* in $NaClO_4$ (neutral); and finally (3) a 0.1 *M* solution of $NaClO_4$ which had been saturated with H_3BO_3 was passed through the column until the pH of the effluent solution was between 5 and 6. Aliquots of irradiated solutions ($3 \leqslant pH \leqslant 5$; $[HClO_4] + [NaClO_4] = 0.01$ *M*) were placed on the column and elutions of NH_4^+ were carried out with 0.01 *M* $NaClO_4$ solutions saturated with H_3BO_3. Elution times for NH_4^+ were generally about 5 min. A similar procedure was used for separations of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_4OH_2N_3^{2+}$ except that a 2–2.5-cm column was used, and elutions were accomplished with 0.03 *M* $NaClO_4$ saturated in H_3BO_3. For the separations of the cobalt complexes, contact time with the resin was less than 10 min. All these separations were carried out in a semidarkened room, and each procedure was checked with solutions containing known amounts of NH_4^+, N_3^-, $Co(NH_3)_5N_3^{2+}$, and $Co(NH_3)_4OH_2N_3^{2+}$.

For the separation of $Co(NH_4)_5NCS^{2+}$ and $Co(NH_3)_5OH_2^{3+}$ we used 1 ml of a Bio-Rad AG 50W-X2 resin prepared in the sodium form by the passing of 100 ml of a solution 1 *M* in $NaClO_4$ and washed with 50 ml of distilled water. Elution was performed with acidic (10^{-3} *M* $HClO_4$) NaCl solutions, of concentrations regularly increased from 10^{-3} to 0.1 *M*. Blank separations were accomplished with samples containing 5×10^{-3}, 10^{-3}, or 5×10^{-4} *M* $Co(NH_3)_5OH_2^{3+}$ in the presence of 5×10^{-3} *M* $Co(NH_3)_5NCS^{2+}$. Composition of 5-ml fractions of effluent solution was determined from the absorbance using a Cary 14; an expanded scale, 0–0.2 absorbance unit, slide wire was used for the most dilute solutions.

For analysis of NCS^-, a 3-ml aliquot of photolyte (or 3 ml of a blank solution) was added slowly to 1 ml of preconditioned resin. The column was washed with 4 ml of 10^{-3} *M* $HClO_4$, the effluent was collected in a 10-ml volumetric flask, 2 ml of a 0.5 *M* $Fe(NO_3)_3$ solution of 1 *M* in $HClO_4$ was added, and the resulting mixture was diluted to volume with distilled water. The solution absorbance was determined at 450 nm.[26]

We were unable to find evidence for $Co(NH_3)_4OH_2NCS^{2+}$ using a Sephadex C-25 resin in the sodium form and the procedures which effected separations of $Co(NH_3)_4OH_2N_3^{2+}$ from $Co(NH_3)_5N_3^{2+}$.

Photolysis Procedures. In general solutions to be photolyzed were prepared with a substrate absorbance of 2 or greater at the excitation wavelength. For $Co(NH_3)_5NCS^{2+}$, the solutions were prepared with an absorbance ⩾5 at the excitation wavelength. Unless otherwise specified all solutions were purged with Cr^{2+} scrubbed N_2 before and during irradiations. Solutions irradiated at other than ambient temperatures were allowed to stand in a thermostated cell holder until a constant temperature was achieved. Temperature fluctuations were about 0.2°.

Irradiations in deuterated solutions were performed per the usual procedures except that the N_2 purge gas was dried in a $CaCl_2$ tower following Cr^{2+} scrubbing.

Flash irradiations of $Co(NH_3)_5NCS^{2+}$ were performed with either $\lambda \geqslant 300$ nm (1.5 w/v% $CuSO_4 \cdot 5H_2O$ as a filter solution[23]) or $\lambda \geqslant 320$ nm (ethanol saturated with naphthalene as a filter solution[23]). While full arc flashing of NaSCN solutions produced a dispersion of sulfur, flash experiments with the filter solutions produced no detectable dispersion.

Results

The principal results of our quantum yield determination are summarized in Table I.[31] For the determinations cited in the table we have generally used solutions more than 10^{-3} *M* in substrate. Substrate concentrations were varied for some of the yield determinations for each complex; where the yields appeared to exhibit a dependence on substrate concentration (or radiation intensity), we have varied conditions in order to obtain well-defined, substrate independent and intensity independent yields for the table and figures. For excitation of a given compound at a specified wavelength, yield entries under different column headings represent independent determinations and often different series of photolyte solutions. Each of the complexes has presented us with a different set of experimental problems; therefore aspects of the experimental results for each complex are discussed separately below.

A. $Co(NH_3)_5N_3^{2+}$. 1. Stoichiometry of Photoreactions. The photochemistry of this complex is greatly complicated by secondary photolysis. Investigations and discussions of the problems connected with determination of product yields from CTTM excitations may be found in an earlier study.[8] The present work reports the irradiation of this complex in each of its principal absorption bands, definitive identifications of products, and complete mass balances. For all excitation ranges we have found that (1.05 ± 0.05) $\phi_{NH_3} = \phi_{Co(NH_3)_4OH_2N_3^{2+}} + 5\phi_{Co^{2+}} = (1.1 \pm 0.1)\ \phi_{H^+}$, and $\phi_{Co^{2+}} = (1.5 \pm 0.1)\ \phi_{N_2}$.

We have found three photochemically different excitation ranges for this complex.

2. Region I: Ligand Field Excitation ($\lambda \geqslant 450$ nm). These lower energy excitations resulted predominantly in photoaquation of coordinated ammonia. This previously unsuspected[7] reaction mode has been unequivocally established by the separation, identification, and quantitative determination of all the reaction products. We were able to achieve excellent separations of $Co(NH_3)_4OH_2N_3^{2+}$ from large excesses of unchanged $Co(NH_3)_5N_3^{2+}$ on the Sephadex C-25 cation exchange resin. However, the determination of yields in this system is not a simple matter; the difficulties encountered may be briefly summarized: (a) although Co^{2+} was not found to be a detectable primary photolysis product ($\phi_{Co^{2+}} + < 10^{-3}$) with excitation $\lambda \geqslant 520$ nm, irradiations beyond about 15% conversion to products did produce significant amounts of cobalt(II); (b) the amount of Co^{2+} in the analytical solutions increased slowly with time even in the dark; (c) irradiation caused greater changes in substrate absorbance at 520 nm than at 301 nm; (d) the magnitude of

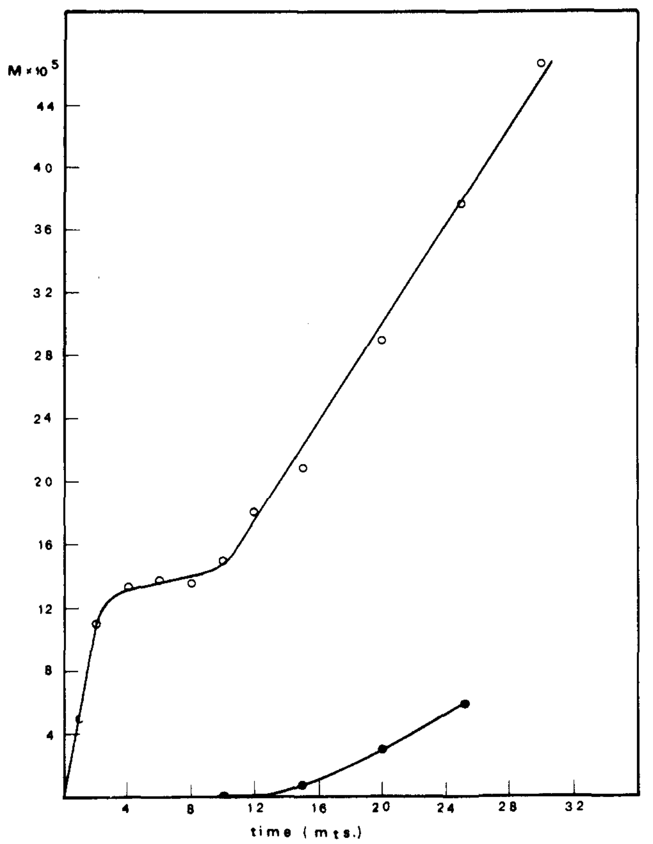


Figure 1. Effects of secondary photolysis in the 520-nm irradiation of $Co(NH_3)_5N_3^{2+}$: (○) $\Delta[H^+]$, (●) $[Co^{2+}]$ extrapolated to zero analytical time. The initial conditions were $[H^+] \simeq 10^{-3}$ *M* ($[HClO_4] + [NaClO_4] = 0.1$ *M*); $A_{520} \simeq 1.5$.

substrate absorbance change was a complex function of the ratio of dark time to exposure time, especially for more than 5% conversion to products. Furthermore we found that irradiated solutions were oxidizing toward I^-; measurement of absorbance changes in solutions treated with I^-, followed by extraction of I_2 into ether, demonstrated that the formation of I_2 was accompanied by a loss of cobalt(III) absorbance. Under similar conditions we found that solutions of $Co(NH_3)_4OH_2Cl^{2+}$ and $Co(NH_3)_4OH_2N_3^{2+}$ slowly oxidize I^-.

To minimize such difficulties, the yields cited in this paper have been determined in relatively concentrated solutions, $[Co(III)] > 10^{-3}$ *M*, and for small (<5%) conversions to products. All analytical determinations were performed immediately after termination of irradiation. For the cobalt(II) analyses we timed the period from the mixing of analytical solutions, observed the rate of change of cobalt(II) absorbance in the analytical thiocyanate solutions, and extrapolated the absorbance to zero time. Figure 1 demonstrates some of the variations in analytical parameters as a function of exposure time.

As noted above and in Table I, we have achieved a cation exchange separation of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_4OH_2N_3^{2+}$ (≤5% conversion) for irradiations at several energies in the visible and ultraviolet regions. The species we eluted and identified as $Co(NH_3)_4OH_2N_3^{2+}$ had absorption maxima at 308 nm (ϵ (8.8 ± 0.8) × 10^3 M^{-1} cm^{-1}) and ~530 nm; reported values for $Co(NH_3)_4OH_2N_3^{2+}$ [32] are λ_{max} 308 nm (ϵ 8.2 × 10^3 M^{-1} cm^{-1}) and λ_{max} 532 nm (230 M^{-1} cm^{-1}). This complex was readily reduced to Co^{2+} by Fe^{2+}, and the extinction coefficient cited is based on analyses of cobalt(II) resulting from the Fe^{2+} reductions.

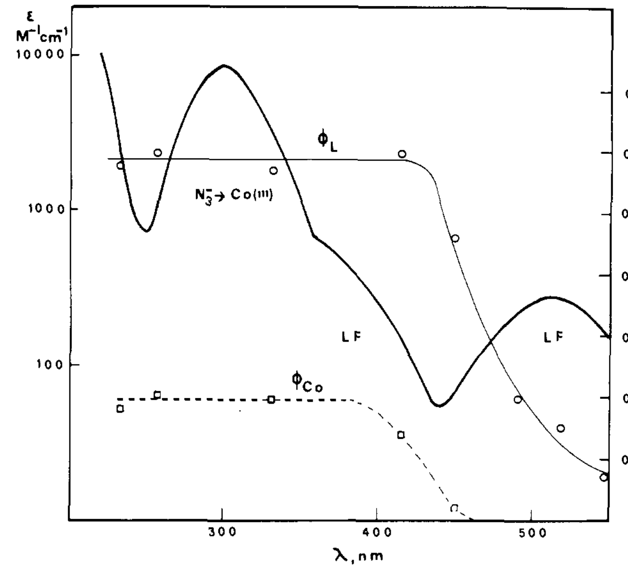


Figure 2. Absorption spectrum of $Co(NH_3)_5N_3^{2+}$ and quantum yield profiles: ○, quantum yield of $Co(NH_3)_4OH_2N_3^{2+}$; □, quantum yield of Co^{2+}. Cobalt(III) products were separated chromatographically and identified as described in the text. Each "point" represents two–five determinations.

3. Region II: Charge Transfer Irradiations (254 < λ < 450 nm). Irradiations in this region produced both Co^{2+} and $Co(NH_3)_4OH_2N_3^{2+}$ as primary photoproducts; both yields reached limiting values for excitations between 425 and 330 nm (Figure 2). For 254-nm excitations we found a decrease in the yield of Co^{2+} and a parallel increase in the yield of $Co(NH_3)_4OH_2N_3^{2+}$ with increases in [glycerol] (Table I). Furthermore we found the yield of Co^{2+} to increase and the yield of $Co(NH_3)_4OH_2N_3^{2+}$ to decrease with increasing temperature (Table I).

4. Region III: Deep Ultraviolet Charge Transfer Irradiations (λ <254 nm). In contrast to the limiting yields of Co^{2+} and $Co(NH_3)_4OH_2N_3^{2+}$ found for 400 > λ ≥ 214 nm irradiations in aqueous solutions, 229 and 214 nm irradiations of $Co(NH_3)_5N_3^{2+}$ in glycerol media have resulted in enhanced yields of Co^{2+} (Figure 3 and Table I).

B. $Co(NH_3)_5NCS^{2+}$. 1. Photochemical Behavior and Photoredox Stoichiometry in Aqueous Solutions. (a) Photoproducts and Quantum Yields. In aqueous solutions the photoreaction stoichiometry can be summarized for all irradiations by: $\phi_{Co^{2+}} = (2.1 \pm 0.5)(\phi_{NCS^-} - \phi_{Co(NH_3)_5OH_2^{3+}})$ and $\phi_{NH_3} = (5.4 \pm 0.5)\ \phi_{Co^{2+}}$. We have been unable to find evidence for $Co(NH_3)_4OH_2NCS^{2+}$ as a photoproduct and would set $\phi_{Co(NH_3)_4OH_2NCS^{2+}} \leqslant \phi_{Co^{2+}}$ as an upper limit on the quantum yield for photoaquation of ammonia. A problem encountered in the experimental determinations was that the net photoredox yield was found slightly dependent on the concentration of free thiocyanate in solution (Figure 7).[31] To avoid complications due to this effect, data in Table I and elsewhere in this report represent only a small percentage conversion of substrate to photoproducts.

Attempts were made to intercept free radical species with chemical scavengers. Attempts with alcohols (e.g., allyl alcohol and 2-propanol) seem less related to the scavenging of radical species than to the medium effects mentioned in section 2 below. Photolyses in the presence of small concentrations of I^- did result in increased yields of NCS^-, with stoichiometric results adequately represented by $\phi_{Co^{2+}} = (\phi_{NCS^-} - \phi_{Co(NH_3)_5OH_2^{3+}}) = \phi_{I_2}/2$ (see Table I). This is as expected for $\cdot NCS$ and/or $(NCS)_2^-$ oxidation of I^-.

Additional significant features to be noted for the data obtained from irradiations of $Co(NH_3)_5NCS^{2+}$ in acidic aqueous solutions are: (i) the exceptionally complex dependence of quantum yields on excitation energy which defines clearly three distinct photolysis regions (see also ref 19a); (ii) the significant but simple dependence of $\phi_{Co^{2+}}$ on medium temperature (Figure 8;[31] see also Figure 1 of ref 19a); and (iii) the yield of $Co(NH_3)_5OH_2^{3+}$ appears to reach a maximum value for excitations in the region of overlap of ligand field and charge transfer absorption bands. This last feature (iii) has also been found for $Co(NH_3)_5Br^{2+}$.[3,7]

(b) Identification and Stoichiometry of Transient Species. Flash photolyses ($\lambda \geqslant 300$ nm) of fresh solutions 10^{-4} *M* in $Co(NH_3)_5NCS^{2+}$, 10^{-3} *M* in $HClO_4$, and 0.1 *M* in $NaClO_4$ (solutions were used within 15 min of preparation and handled in dimmed light) were performed, and our observations may be summarized as follows. (i) When free NCS^- was carefully excluded from the sample solution we were unable to detect any transient absorbance changes. Net absorbance bleaching was observed between 369 and 500 nm. (ii) A transient with absorption maximum at 485 nm developed in the presence of free NCS^-. The absorbance at 485 nm was found to increase in intensity with $[NCS^-]$ in the range $1 \times 10^{-4} \geqslant [NCS^-] \geqslant 5 \times 10^{-6}$ *M*. This behavior is as expected[2,7,34] for reactions 2–4

$$Co(NH_3)_5NCS^{2+} + h\nu \xrightarrow{H^+} Co^{2+} + 5NH_4^+ + \cdot NCS \quad (2)$$

$$\cdot NCS + NCS^- \overset{K_3}{\rightleftharpoons} (NCS)_2^- \quad (3)$$

$$2(NCS)_2^- \xrightarrow{k_4} (NCS)_2 + 2NCS^- \quad (4)$$

$$(NCS)_2 \longrightarrow \text{hydrolysis products}$$

with $(NCS)_2^-$ *as the absorbing species at 485 nm.* In order to further establish the identity of the transient species, we may use eq 2 and 3 to obtain *initial* (after the flash pulse) stoichiometric relationships between photolysis products: $[Co^{2+}]_{t=0} = [\cdot NCS]_{t=0} + [(NCS)_2^-]_{t=0}$ and $K_3 = [(NCS_2^-]/[\cdot NCS][NCS^-]$. Then with $(NCS)_2^-$ the only absorbing species, and setting $A_s = \{\epsilon_{(NCS)_2^-}\}l[Co^{2+}]$ = the absorbance of $(NCS)_2^-$ under conditions that the equilibrium 3 is saturated and $A_{t=0}$ = initial absorbance of $(NCS)_2^-$ under prevailing photolysis conditions, $A_{t=0}^{-1} = A_s^{-1}(1 + [NCS^-]K_3^{-1})$. From a plot of $A_{t=0}^{-1}$ vs. $[NCS^-]$ (Figure 9),[31] we find a value of 7.5×10^{-6} for K_3^{-1} which compares well with the literature value[34] of 5.0×10^{-6}. (iii) A plot of $A_{t=0}$ vs. the flash intensity was linear (Figure 10).[31] However, initial rate of absorbance decay in solutions 10^{-4} *M* in $Co(NH_3)_5NCS^{2+}$, 10^{-4} *M* in $HClO_4$, 0.1 *M* in $NaClO_4$, and 10^{-4} *M* in NCS^- was found to be a complex function of flash intensity. Our observations of such initial rate data were fitted by eq 5.

$$d[(NCS)_2^-]/dt = ((2.3 \pm 0.4) \times 10^3)[(NCS)_2^-] + ((0.7 \pm 0.2) \times 10^9)[(NCS)_2^-]^2 \quad (5)$$

The second-order rate constant is in good agreement with that reported[34,35] for eq 4, while the first-order process is about the magnitude expected for the reverse of eq 3.[34,35] (iv) The initial $[(NCS)_2^-]$ was compared to the amount of $Co(NH_3)_5NCS^{2+}$ decomposed in a single flash as determined from changes in substrate absorbance (before and after flashing). For a solution initially 1.0×10^{-4} *M* in $Co(NH_3)_5NCS^{2+}$, $[(NCS)_2^-]_{t=0} = 1.0 \times 10^{-6}$ *M* and $\Delta[Co(NH_3)_5NCS^{2+}] = 1.3 \times 10^{-6}$ *M*; for a solution initially 4.0×10^{-4} *M* in $Co(NH_3)_5NCS^{2+}$, $[(NCS)_2^-]_{t=0} = 1.4 \times 10^{-6}$ *M* and $\Delta[Co(NH_3)_5NCS^{2+}] = 1.9 \times 10^{-6}$ *M*. In both cases the ratio of products is the same; i.e., $\Delta[Co(NH_3)_5NCS^{2+}]/[(NCS)_2^-]_{t=0} \simeq 1.3$. The larger change in substrate concentration than in $(NCS)_2^-$ production is undoubtedly a result of photoaquation to form $Co(NH_3)_5OH_2^{3+}$. For the region of flash excitation and absorbance by the substrate (26–31 kK), data in Table I indicate that the average quantum yields are $\phi_{Co^{2+}} \simeq 0.021$ and $\phi_{Co(NH_3)_5OH_2^{3+}} \simeq 0.005$. Thus

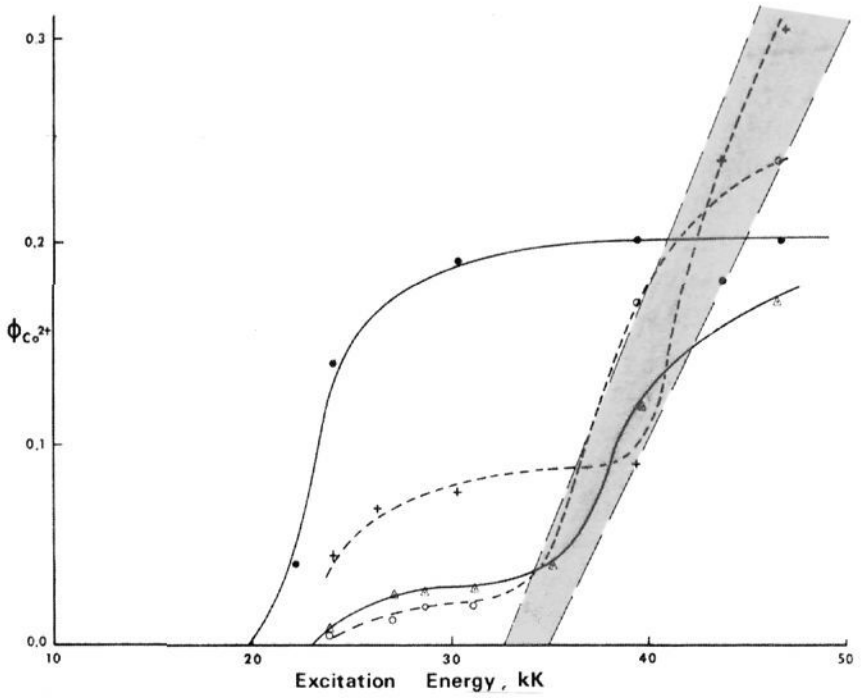


Figure 3. Variations in the quantum yield of Co^{2+} with excitation energy for $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$ irradiated in water (● and Δ, respectively) and 50% water–glycerol (+ and ○, respectively) solutions. All solutions were acidic (10^{-3} to 10^{-2} *M* $HClO_4$) and at 25°. Each point represents two–five determinations.

$$\frac{\Delta[Co(NH_3)_5NCS^{2+}]}{[(NCS)_2^-]_{t=0}} \simeq \frac{\Phi_{Co^{2+}} + \Phi_{Co(NH_3)_5OH_2^{3+}}}{\Phi_{Co^{2+}}} \simeq 1.2$$

2. Photochemical Behavior in Mixed Solvent Media. Variations of the photolysis products with composition of the solvent medium are summarized in Table I and have been mentioned briefly elsewhere.[19a] A few points regarding the photoreaction stoichiometry will be noted here.

We found that the yields of $Co(NH_3)_5OH_2^{3+}$ were significantly diminished in media containing glycerol. Whether the redox yields increased or decreased with [glycerol] depended in a complex manner on excitation energy as noted previously;[19a] however, we have also found that the photoredox stoichiometry is a function of excitation energy in glycerol solutions. For excitation at 350 nm we found $\phi_{Co^{2+}} \simeq 2\phi_{NCS^-}$ in 50% glycerol and in acidic aqueous solutions; while for excitations at 254 nm we found $\phi_{Co^{2+}} \simeq \phi_{NCS^-}$ in 50% glycerol and $\phi_{Co^{2+}} \simeq 2\phi_{NCS^-}$ in acidic aqueous solutions.

Also included in Table I are quantum yield data for region II and region III irradiations of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ in aqueous and mixed solvent media. We did not find that perdeuteration significantly altered product yields for region II irradiations.

Discussion

I. Individual Substrates. A. $Co(NH_3)_5N_3^{2+}$. The present work establishes unequivocally the ammonia aquation process inferred for 254-nm irradiations of this complex in ref 8. This reaction mode turns out to be the predominant photoprocess for all irradiations in the range $580 \geqslant \lambda \geqslant 214$ nm. Although the excitation energy dependences of the quantum yields of $Co(NH_3)_4OH_2N_3^{2+}$ and of cobalt(II) exhibit somewhat parallel trends (Figure 2), consideration of the actual yields shows that the ratio of quantum yields for the aquation to the redox process varies from >150 at 520 nm to 3 for $\lambda \leqslant 330$ nm; this indicates that some of the ammonia aquation occurs from a state not implicated in the production of cobalt(II). We presume this to be a ligand field excited state; however, the strong wavelength dependence of this redox-independent process is not very readily explained. For example, if one assumes a constant ratio of ϕ_{NH_3} to $\phi_{Co^{2+}}$ for the photoactive CTTM state, then the redox independent ammonia aquation process goes through a maximum ($\phi_{aq}^{max} \simeq 0.3$) for irradiations at about 450 nm (note that $\phi_{NH_3} = 5\phi_{Co^{2+}} + \phi_{aq}$). We know of no cobalt(III)-ammine complexes with comparably large aquation yields; aquation yields of several complexes do reach a maximum value in the region of overlap of charge transfer and ligand field absorption bands (this work and ref 2, 3, and 7).

The argument in the preceding paragraph assumes poor communication between CTTM and ligand field excited states. An alternative would be to assume that electronic relaxation of the photoactive CTTM excited state populates a photoactive ligand field excited state, thus accounting for that fraction of the ammonia aquation process, ϕ_b, which does not appear to be coupled to the formation of Co^{2+}. This alternative would require that the photoactive ligand field excited state has an intrinsic yield of $\sim$0.6 for ammonia aquation.

The variation of $\phi_{Co^{2+}}$ with [glycerol] has some similarities to the glycerol dependence of the photoredox yield for $Co(NH_3)_5Br^{2+}$[19b] and for $Co(NH_3)_5NO_2^{2+}$;[36] however, the percentage variations observed in ϕ_{aq} are much smaller than the percentage variations with [glycerol] of the yield of linkage isomerization for $Co(NH_3)_5NO_2^{2+}$.[36] Thus the variations in yields with [glycerol] complement the excitation energy dependencies discussed above and suggest that there may be two mechanisms for ammonia aquation, one process competitive with the formation of redox products and another process not involved in such a competition; e.g., $\phi_{aq} = \phi_{aq} = \phi_a + \phi_b$, where $\{\phi_a + \phi_{Co^{2+}}\}$ is the primary yield of radical pairs. This is analogous to the situation obtaining for the redox and linkage isomerization yields of $Co(NH_3)_5NO_2^{2+}$.[36] For this interpretation of the observations we obtain $\{\phi_a + \phi_{Co^{2+}}\} \simeq 0.5$ and $\phi_b \simeq 0.3$ in the excitation range $254 \leqslant \lambda <$ nm.

Such a redox "independent" ammonia aquation process (ϕ_b) could arise from several mechanisms, but two seem the most plausible: (1) the thermally equilibrated photoactive CTTM excited state may have some Co-NH_3 bond considerably lengthened and that electronic relaxation of this excited state is coupled with aquation, or (2) the CTTM excited states can relax to populate a photoactive ligand field state.

B. $Co(NH_3)_5NCS^{2+}$. 1. Stoichiometry of the Photoredox Reaction. Since the quantum yields of Co^{2+} and $Co(NH_3)_5OH_2^{3+}$ were found to depend differently on the excitation wavelength, we infer that these products generally derive from different precursors. The most notable difference in behavior is that the photoaquation process goes through a maximum value ($\phi = 0.01$ for λ 370 nm) as the photoredox process approaches a plateau ($\phi = 0.026$ for $370 \geqslant \lambda \geqslant 320$ nm). Such behavior may derive either from a competitive formation of these products (or their precursors) along the photoreaction coordinate following near-ultraviolet excitation or from competitive population of ligand field and charge transfer excited states by direct excitation in this region of appreciable spectral overlap. For either alternative, these observations imply a very inefficient population of low energy ligand field excited states by relaxation of charge transfer excited states.

2. Dependence of Quantum Yields on Excitation Wavelength. As we have noted above, and as is evident from examination of Figure 1 of our preliminary report,[19a] photoredox products result from all excitations, but one may distinguish three qualitatively different excitation regions. The different stoichiometric relations found for region II and region III excitations require that different radical intermediates be formed in these regions. Thus it appears that the operative photoredox mechanism varies with variations in excitation energy. The three excitation regions, which are well delineated for $Co(NH_3)_5NCS^{2+}$, are also evident in the photochemical behavior of $Co(NH_3)_5N_3^{2+}$ and appear to be somewhat manifested in several other cobalt(III) complexes. The similarities in behavior are great, and a combined discussion is warranted.

II. General Discussion. In this section we will first develop the mechanistic comparison of the two substrates in each of the photochemical regions noted above. We will then develop some overall comparisons of these two systems and other complexes.

A. Region I. In this region $Co(NH_3)_5NCS^{2+}$ exhibits behavior "typical" of cobalt(III)-ammine complexes: very small, wavelength-dependent product yields while the yields of $Co(NH_3)_4OH_2N_3^{2+}$ from irradiation of $Co(NH_3)_5N_3^{2+}$ are anomalously large.[2,11] In fact we would not have been able to detect very small ($\phi < 10^{-3}$) yields of Co^{2+} and $Co(NH_3)_5OH_2^{3+}$ in the presence of the $Co(NH_3)_4OH_2N_3^{2+}$ generated from irradiations of $Co(NH_3)_5N_3^{2+}$. In contrast, it is clear that no high yield ammonia aquation process occurs for $Co(NH_3)_5NCS^{2+}$. Although there may be some not yet clear connection of these large differences in product yields to very small apparent electronic distributions in Franck-Condon excited states,[37] the simplest explanation of the much smaller yield of $Co(NH_3)_4OH_2NCS^{2+}$ than of $Co(NH_3)_4OH_2N_3^{2+}$ is that the presence of the sulfur atom results in larger rate constants for internal conversion and intersystem processes in the excited $Co(NH_3)_5NCS^{2+}$ system, thus facilitating a deactivating cascade through the low energy ligand field excited states.[39] This situation is represented schematically in Figure 4.[39-44] It is to be observed that several thermally equilibrated ligand field excited states of this complex appear to have energies well below the correlated enthalpy required for dissociation of NCS^- ($\Delta H_1^\ddagger$ in Figure 4)[41] or of NH_3 ($\Delta H_2^\ddagger$ in Figure 4; this value is based on the behavior of $Co(NH_3)_6^{3+}$).[42,43]

In contrast the observation of high yields of the relatively high energy ammonia aquation process (L_2 in Figure 5) following region I excitation of $Co(NH_3)_5N_3^{2+}$ suggests that the ligand field excited states of this complex do not relax as efficiently. In fact a comparison of estimated excited state energies (Figure 5) with correlated thermal activation energy required to labilize the Co^{III}-NH_3 bond ($\Delta H_2^\ddagger$ in Figure 5)[9,41,42] suggests that the photoactive state may be any or all of $^1E^b$, $^1B_2$, $^1A_2$, or $^3E^b$. That most the implicated states would contain more electron density in a "$d_{x^2-y^2}$" orbital than in a "d_{z^2}" orbital, suggests that the ammine aquated should be cis to N_3^-; unfortunately, we were unable to determine the initial product stereochemistry. Since most of the thermally equilibrated excited states containing significant electron density in a "d_{z^2}" orbital are lower in energy than the minimum energy required for NH_3 aquation, it seems unlikely that the relative electronic populations of these states[37] have any relevance to the observed product distributions. In fact it seems surprising that the proposed photochemical models[37] have been so indifferent to the energy requirements of the various photochemical products.

The lowest energy quintet states are predicted[44,45] to be below $^3E^a$ and are therefore not likely to be a factor in observed photoreactivity patterns (see ref 46 for a differing viewpoint).

The small wavelength dependent photoredox yields produced on excitation of ligand field absorbances of many cobalt(III) complexes[2,7,22,47] remain puzzling. It is possible to estimate the enthalpy changes in the reaction sequence (6);

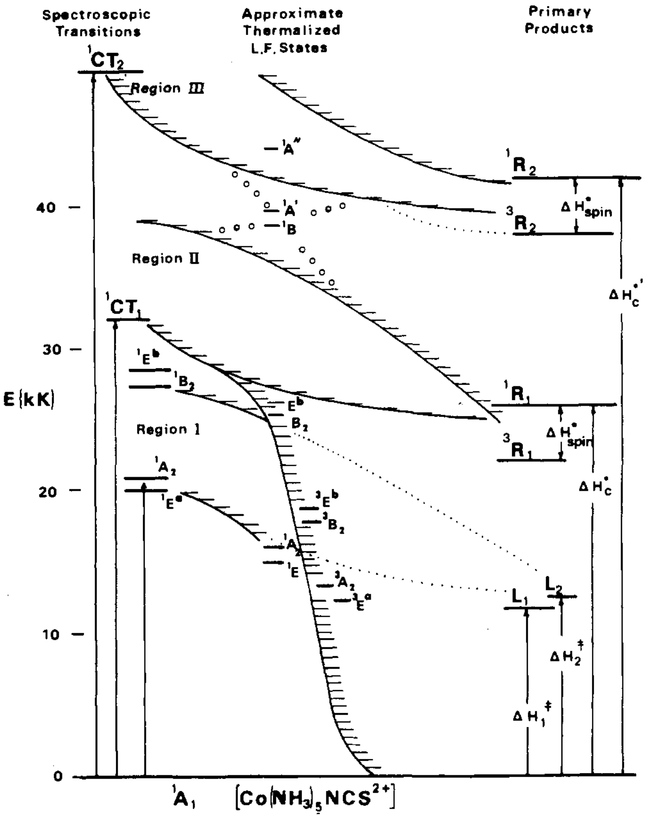


Figure 4. Photochemical correlation diagram for $Co(NH_3)_5NCS^{2+}$. Spectroscopic absorption maxima indicated by vertical arrows. Ligand field excited state energies and primary product energies estimated as described in footnote 39. Product species are $\{Co(NH_3)_5{}^{3+}, NCS^-\} = L_1$, $\{Co(NH_3)_4NCS^{2+}, NH_3\} = L_2$, $^n\{Co(NH_3)_5{}^{2+}, \cdot NCS\} = {}^nR_1$ and $^n\{Co(NH_3)_5NCS^+, H_2O^+\} = {}^nR_2$. Solid curves are drawn from left to right indicating the predominant sequence of events following electronic excitation; dotted curves indicate minor processes ($\phi < 10^{-2}$; possible or observed). Circles indicate the high energy region where electronic interactions may result in noncrossing of potential energy manifolds or other mixings of states.

$$Co(NH_3)_5NCS^{2+} \xrightarrow{\Delta H^\ddagger} \{Co(NH_3)_5{}^{3+}, NCS^-\} \xrightarrow{\Delta H^\circ_{IP}} \{Co(NH_3)_5{}^{2+}, \cdot NCS\} \quad (6)$$

from parameters in the literature,[2d,3,16,48,49] we estimate that $\Delta H^\circ_c = \Delta H^\ddagger + \Delta H^\circ_{IP} \simeq 25$ kK/mol. This should correspond to the threshold energy for formation of a $\{Co(NH_3)_5{}^{2+}, \cdot NCS\}$ radical pair containing low spin cobalt(II). That some yield of cobalt(II) is still obtained for irradiations as low in energy as 18 kK is surprising, and could be a consequence of any of the following: (a) the intermediacy of a radical pair with the cobalt(II) fragment in the high spin (ground state) electronic configuration; (b) a biphotonic process (i.e., initial population of a ligand field excited state, followed by further excitation of this state to form a charge transfer excited state); or (c) some small ultraviolet component resulting from second-order scattering from the grating in our photolysis system (in this system the nominal output at 285 nm was determined to be about 10% of the output at 500 nm in first-order dispersion from the grating; we were unable to detect any radiation with λ <285 nm).

Mechanism b could relate the temperature independent-wavelength dependent yields of $Co(NH_3)_5NCS^{2+}$ in region I to those in region III. However, the biphotonic photoredox processes found for laser irradiations of ligand field absorbances of $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ have only been detected at very high photon densities and would not be significant with the light levels used in the present study.[50]

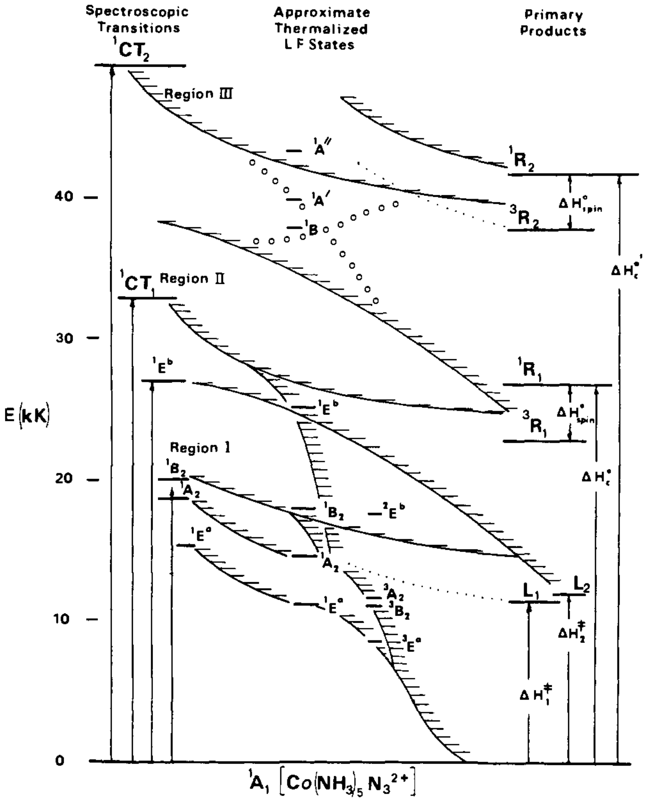


Figure 5. Photochemical correlation diagram for $Co(NH_3)_5N_3{}^{2+}$. Spectroscopic absorption maxima indicated by vertical arrows. Ligand field excited state energies and primary product energies estimated as described in footnote 39. Product species are $\{Co(NH_3)_5{}^{3+}, N_3{}^-\} = L_1$, $\{Co(NH_3)_4N_3{}^{2+}, NH_3\} = L_2$, $^n\{Co(NH_3)_5{}^{2+}, \cdot NCS\} = {}^nR_1$ and $^n\{Co(NH_3)_5NCS^+, H_2O^+\} = {}^nR_2$. Solid curves are drawn from left to right indicating the predominant sequence of events following electronic excitation; dotted curves indicate minor processes ($\phi < 10^{-2}$; possible or observed). Circles indicate the high energy region where electronic interactions may result in noncrossing of potential energy manifolds or other mixings of states.

B. Region II. The photoredox behavior of $Co(NH_3)_5N_3{}^{2+}$ is qualitatively similar to that of $Co(NH_3)_5NCS^{2+}$ over the 25-35 kK excitation range. The major difference is that $Co(NH_3)_5N_3{}^{2+}$ is about seven times as photoreactive as $Co(NH_3)_5NCS^{2+}$. Once again it seems most natural to attribute the reduced photoreactivity to a heavy atom effect in the isothiocyanato complex; i.e., to an enhancement of electronic relaxation (in a cascade process as in Figure 4) compared to homolytic dissociation of the photoactive charge transfer excited state.

Many features of the photoredox chemistry stimulated by excitation of $Co(NH_3)_5NCS^{2+}$ in this spectral region seem typical of acidopentaamminecobalt(III) complexes. The extrapolated threshold energies for absorption in the 33-kK band ($E_{th}' \sim 22$ kK) and for the photoredox process ($E_{th} \sim 24$ kK) are in good agreement with the values of $\Delta H^\circ_c \simeq 26$ kK estimated above for eq 6; very similar values, $E_{th}' \simeq 23$ kK, $E_{th} \simeq 22$ kK, and $\Delta H^\circ_c \simeq 27$ kK are found for $Co(NH_3)_5N_3{}^{2+}$. Even the deviations of observed threshold energies from the estimate of the minimum energy required for formation of a "singlet" radical pair are only slightly larger than typical for cobalt complexes.[3] For both complexes the decreases in $\phi_{Co^{2+}}$ with increases in [glycerol] are suggestive of a viscosity effect analogous to that observed for $Co(NH_3)_5NO_2{}^{2+}$ [36b] and implicate competitive recombination (k_r; to form $Co(NH_3)_5NCS^{2+}$, $Co(NH_3)_5N_3{}^{2+}$, or $Co(NH_4)_4OH_2N_3{}^{2+}$) and decomposition (k_d; to form Co^{2+} and $\cdot NCS$ or $\cdot N_3$) reactions of the primary radical pair products. In the simplest analysis,[51]

$$\phi_{\mathrm{Co}^{2+}} = (k_d/(k_r + k_d))\Phi_{\mathrm{RP}}$$

where Φ_{RP} is the intrinsic quantum yield for radical pair formation. Since $\phi_{\mathrm{Co}^{2+}}$ is independent of excitation energy in this region, there is either a fortuitous cancellation of the excitation energy dependencies of Φ_{RP} and $(k_d/[k_d + k_r])$ or both of these quantities are independent of excitation energy. A fortuitous cancellation of excitation energy dependencies would be rather difficult to explain, while excitation energy independence would be consistent with thermal relaxation within the photoactive excited state; i.e., that Φ_{RP} is a constant less than unity reflecting the reactivity of the thermalized excited state, and that in this excitation range all radical pair products are formed from such a thermalized excited state. The temperature dependence of $\phi_{\mathrm{Co}^{2+}}$ observed for both complexes could arise from either (or both) Φ_{RP} or $k_d/[k_d + k_r]$.

Finally it should be noted in this section that assignment of the 33-kK band of $Co(NH_3)_5NCS^{2+}$ has been regarded as ambiguous since all isothiocyanato complexes exhibit transitions near this energy.[14] Since the oxidation–reduction thermodynamics of halogen and pseudo-halogen radicals are now relatively unambiguous,[2c,16,49,52-54] and since the estimate of $\Delta H_c \simeq 26$ kK/mol is based on parameters which give consistently reasonable estimates of $\Delta H°_c$ for $Co(NH_3)_5X^{2+}$ (X = N_3, Cl, Br, I) complexes,[2c,3] we believe the 33-kK transition in $Co(NH_3)_5NCS^{2+}$ must contain significant CTTM character. Obviously an inner ligand transition could also contribute to this relatively broad absorption band.

C. Region III. For deep ultraviolet excitations both complexes exhibit enhanced redox yields in glycerol, compared to aqueous solutions (Figure 3). The photochemical behavior of $Co(NH_3)_5NCS^{2+}$ has a number of unique features which provide definite mechanistic insights.

The difference in stoichiometric ratios of Co^{2+} and NCS^- in regions II and III, the implied solvent oxidation in region III, the differences in the temperature dependence of $\phi_{\mathrm{Co}^{2+}}$ for irradiations in regions II and III, and the increases in $\phi_{\mathrm{Co}^{2+}}$ with excitation energy and [glycerol] in region III suggest a profound difference between the photoredox reactions induced by irradiations in different ultraviolet spectral ranges.

In all spectral regions irradiated, photoreduction of $Co(NH_3)_5NCS^{2+}$ results in formation of NCS^- either through hydrolysis of $(NCS)_2$ or possibly some sort of scavenging of $\cdot NCS$ (or $(NCS)_2^-$) by dissolved species. In continuous photolyses, the buildup of $[NCS^-]$ would be significant enough to maintain $[\cdot NCS] \ll [(NCS)_2^-]$ after a few per cent decomposition of substrate. It is not likely that $(NCS)_2^-$ can react rapidly enough with alcohols ($\cdot NCS$[16] and $(NCS)_2^-$ [55] are expected to be appreciably poorer oxidants than $\cdot Br$ and Br_2^-, respectively[16,52-54]) for such scavenging reactions to be significant compared to eq 4. Furthermore it is not likely that the efficiency of such scavenging reactions could increase with the energy of excitation of the original substrate. For these reasons we do not believe it plausible to attribute the enhanced redox yields in glycerol for region III excitations to scavenging reactions which form NCS^- and strongly reducing alcohol radicals.

The balance of available evidence dictates different primary photoredox processes in regions II and III, and we would suggest that the new process in region III involves formation of solvent radicals in the primary photoredox step and further that this process is reasonably general for deep ultraviolet excitations of coordination complexes. At first glance such direct involvement of solvent species in the charge transfer photochemistry of coordination complexes might seem unlikely; certainly there seem to be few precedents.[2,56] However, the considerations below indicate that this possibility must be given serious consideration.

1. Energetics. If we take the O-H bond energy in H_3O^+ to be 38.6 kK/mol then the enthalpy of formation of H_2O^+ is about 20 kK/mol.[57] Thus the standard reduction potential of the H_2O^+/H_2O couple should be about 5.2 V; the enthalpy change associated with this couple would be about 44 kK/mol. This is only about 27 kK/mol greater than the energy of the $\cdot NCS/NCS^-$ couple. More specifically one should consider the energetics of eq 7

$$\{Co(NH_3)_5NCS^{2+}, H_2O\} \xrightarrow{\Delta H^\circ_s,\ \phi'_{\mathrm{RP}}} {}^1\{Co(NH_3)_5NCS^+, H_2O^+\} \tag{7}$$

in which a solvating water molecule is oxidized by $Co(NH_3)_5NCS^{2+}$. For this process we estimate that $\Delta H°_s \sim 43$ kK/mol.[58] By analogy with the absorption spectrum of the $\{Co(NH_3)_6^{3+}, I^-\}$ ion pair[59] and a very similar discussion of the energetics of the corresponding optical transition,[3,60] we would expect the onset for the corresponding $H_2O \rightarrow Co^{III}$ charge transfer absorption to occur at about 48 kK (the ion pair spectra are blue shifted, in part due to Franck–Condon effects associated with population of an antibonding orbital);[3,60] the absorbance maximum for such a transition should occur in the vacuum ultraviolet. Thus direct generation of ${}^1\{Co(NH_3)_5NCS^+, H_2O^+\}$ by population of the corresponding charge transfer state is very unlikely and the dominant absorbance in region III cannot arise from such a transition. However, the CTTM transitions involving first coordination sphere ligands may produce weakly bound excited states while CTTM excited states involving second coordination sphere species are not likely to be significantly bound.[3] Thus the ${}^1CT_2$ excited state populated by absorption of radiation in region III could interact with a dissociative $H_2O \rightarrow Co^{III}$ state to produce $\{Co(NH_3)_5NCS^+, H_2O^+\}$ species as primary products; such interactions may be mediated by proximate high energy ligand field states (Figures 4 and 5).

An alternative photoredox mechanism for $Co(NH_3)_5X^{2+}$ complexes in the deep ultraviolet might be proposed to involve the primary photooxidation of an ammine ligand. We may analyze this in terms of the reaction cycle (eq 8).[3,61]

$$\begin{tikzcd}
{*(\mathrm{CT})} \arrow[r, squiggly, "\Delta H_B + \Delta H_0 + \Delta H_i"] & \{Co(NH_3)_4X^+, NH_3^+\} \\
Co(NH_3)_5X^{2+} \arrow[u, "h\nu"'] \arrow[r, "\Delta H^\ddagger"] & \{Co(NH_3)_4X^{2+}, NH_3\} \arrow[u, "\Delta H^\circ_{IP}"']
\end{tikzcd} \tag{8}$$

For a $NH_3^+|NH_3$SRP of ~2.7 V,[2c] $\Delta H^\ddagger > 15$ kK/mol,[39e] and from values of other parameters used above,[48] we estimate $\Delta H°_c = \Delta H^\ddagger + \Delta H°_{IP} > 38$ kK/mol for the minimum excitation energy required to produce a radical pair with low spin cobalt(II) and an oxidized ammine ligand. Thus this process would have energy requirements comparable to eq 7 and such a reaction mode could be stimulated by direct excitation.[3] We cannot rule out such a reaction sequence on the basis of evidence now available; however, the observed photoreaction stoichiometries and the insensitivity of region III behavior to changes in first coordination sphere ligation make eq 7 seem more plausible than eq 8. More specifically we have noted that $Co(NH_3)_5NCS^{2+}$ appears to exhibit many features of a photodissociative system for λ <254 nm, while excitations at λ ⩾254 nm have features characteristic of the generation of bound electronic excited states in which electronic and vibrational relaxation processes can occur and in which the rates of these processes are affected by the identity of coordinated ligands.

The onset of photochemical behavior characteristic of region III is actually found to occur between 32 and 35 kK for

$Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5N_3^{2+}$, rather than the estimated threshold of ~43 kK required to form $^1\{Co(NH_3)_5X^+,H_2O^+\}$. However, the energy estimate is for formation of a low spin cobalt(II) fragment, so about half[3,49] of this difference could be attributed to formation of the cobalt(II) fragment in the high spin ground state; much of the remaining difference in energy (~5 kK) could easily arise from uncertainties in our estimates of the energy required to generate H_2O^+ from water solvating the cationic complex.

D. Extension to Other Systems. If the photochemical behavior observed for λ <254 nm irradiations of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$ contains significant contributions due to primary photoxidation either of coordinated ammonia or of solvating water, then a similar effect should be observed in the photochemistry of other acidopenataamminecobalt(III) complexes. We have found similar behavior for $Co(NH_3)_5Br^{2+}$ and probably also for $Co(NH_3)_5Cl^{2+}$.

In acidic aqueous solutions the photoredox yields from ultraviolet excitations of $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5Cl^{2+}$ reach limiting values of 0.33 and 0.22, respectively[2c,3] (for $\lambda \leqslant 350$ nm), while in glycerol-water mixtures the photoredox behavior is more complex (ref 19b and Table I). We have found that the quantum yields of Co^{2+} from irradiations of $Co(NH_3)_5Br^{2+}$ at a frequency $\tilde{\nu}$ (kK) in 50% glycerol is approximately equal to the Co^{2+} yield from irradiations of $Co(NH_3)_5Cl^{2+}$ at a frequency of $(\tilde{\nu} - 4)$ kK. Empirical correlations of varying quality may also be found between the redox yields of these complexes and $Co(NH_3)_5N_3^{2+}$ or $Co(NH_3)_5NCS^{2+}$. While the energy shifts (i.e., values of $(\tilde{\nu} - \Delta)$ for which similar quantum yields are observed) seem arbitrary and not related to energy quantities appropriate to the various mechanisms discussed above, these correlations do suggest the existence of common mechanistic features in these systems.

An approach which we find more useful is to compare the ratios of quantum yields obtained for similar excitations of these substrates in glycerol and aqueous media. In Figure 6 we have compared the ratio of redox yields of several complexes in 50% glycerol and in water as a function of relative excitation energy. In computing the relative excitation energy we have made a small correction to the excitation energy which allows for the differences in SRP of the cobalt substrates (δ = 1.5 kK for $Co(NH_3)_5Cl^{2+}$, 2.4 kK for $Co(NH_3)_5N_3^{2+}$, and 2.5 kK for $Co(NH_3)NCS^{2+}$; see ref 59); thus, this comparison is made in the context of photooxidation of solvent analogous to eq 7, but it is not entirely inconsistent with eq 8. This comparison demonstrates very similar photochemical behavior of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5Br^{2+}$, with a clear discrimination of photoredox regions II and III, and with a threshold for region III behavior of about 34 kK, in very good agreement with inferences from Figure 3. For irradiations of $Co(NH_3)_5Cl^{2+}$ in region II, the redox yield ratio, $\phi_g/\phi_w \simeq 1.06$, is about twice the value obtained for excitations of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5Br^{2+}$ in this excitation energy range. We believe this anomaly arises from reaction of the primary ·Cl (or NH_3^+)[27] radicals with glycerol and subsequent reduction of the cobalt substrate by glycerol-radicals; thus we have used $\phi_g/2\phi_w$ in Figure 6 for excitations of $Co(NH_3)_5Cl^{2+}$. With this correction our observations for excitations of $Co(NH_3)_5Cl^{2+}$ in region II fall into the range of observations on $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5Br^{2+}$. Figure 6 demonstrates a qualitative distinction between region II and region III excitations of $Co(NH_3)_5Cl^{2+}$, very similar to the behavior of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5Br^{2+}$. For region III excitations of $Co(NH_3)_5Cl^{2+}$ either the value of ϕ_g/ϕ_w or values of $\phi_g/2\phi_w$ probably agree with observations on the other two complexes, within the range of observed scatter in replicate determinations.

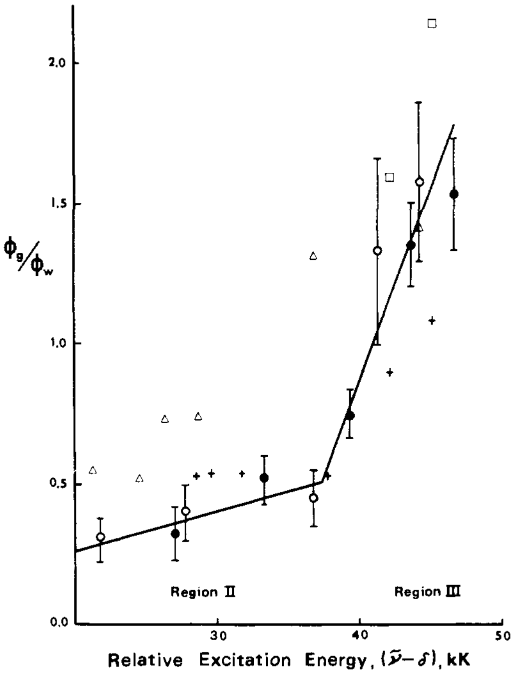


Figure 6. Ratios of redox yields in 50% glycerol (ϕ_g) and water (ϕ_w) as a function of excitation energy. Mean values of two–five determinations are shown; error flags represent average deviations: $Co(NH_3)_5N_3^{2+}$, ○; $Co(NH_3)_5Br^{2+}$, ●; $Co(NH_3)_5NCS^{2+}$, △. For $Co(NH_3)_5Cl^{2+}$ values of $\phi_g/2\phi_w$ are represented, +; and in region III a few entries of ϕ_g/ϕ_w, □, are made for comparison.

The deviations between ϕ_g/ϕ_w values for $Co(NH_3)_5NCS^{2+}$ and for the other three complexes following region II excitations, as shown in Figure 8, are slightly outside the range of reasonable error limits and indicate that the photoredox chemistry of the isothiocyanato complex is relatively less sensitive to changes in medium composition than are the bromo- and azidopentaammine complexes. Ligation effects are probably relatively independent of the medium and so should cancel in the quantum yield ratio. Furthermore there is no clear separation in Figure 6 of region II and region III behavior for $Co(NH_5)_5NCS^{2+}$, no doubt because region III behavior is already evidenced in the aqueous solution photochemistry of this complex. Thus, while Figures 3 and 6 demonstrate qualitative similarities in the photoredox chemistry of acidopentaamminecobalt(III) complexes, there are many detailed differences in behavior which must arise from the differences in photophysical processes in these systems.

Summary and Conclusions

A. Photoredox Mechanisms. Equations 2-4 and 9-15 are proposed to describe processes induced by irradiations of $Co(NH_3)_5NCS^{2+}$ at $\lambda \leqslant 285$ nm. The generation of photoproducts characteristic of a largely dissociative excited state from a lower energy bound excited state has parallels in the photochemistry of $Co(NH_3)_5NO_2^{2+}$ (lower energy ligand field state, probably dissociative CTTM state)[62] and of (EDTA)cobalt(III) complexes (lower energy $X^- \rightarrow Co^{III}$CTTM states, possibly dissociative $RCO_2^- \rightarrow Co^{III}$CTTM states).[22,63] Within the context of the model proposed here, the increase of yields with [glycerol] would be related to the efficiencies of scavenging reactions for oxidized solvent species, reactions such as eq 14 in concentrated alcohol solutions, and the subsequent alcohol-radical reduction of substrate 15. The temperature and apparent viscosity independence of $\phi_{Co^{2+}}$ in region III suggests a lack of

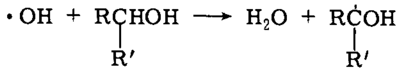
$$\mathrm{Co(NH_3)_5NCS^{2+}} + h\nu \longrightarrow \{\mathrm{Co(NH_3)_5NCS^+, H_2O^+}\} \quad (9)$$

$$\{\mathrm{Co(NH_3)_5NCS^+, H_2O}\} \xrightarrow{k'_r} \mathrm{Co(NH_3)_5NCS^{2+}} \quad (10)$$

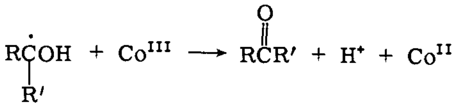
$$\{\mathrm{Co(NH_3)_5NCS^+, H_2O}\} \xrightarrow[\mathrm{H^+}]{k'_d} \mathrm{Co^{2+}} + 5\mathrm{NH_4^+} + \mathrm{NCS^-} + \mathrm{H_2O^+} \quad (11)$$

$$\mathrm{H_2O^+} \rightleftharpoons \cdot\mathrm{OH} + \mathrm{H^+} \quad (12)$$

$$\cdot\mathrm{OH} + \mathrm{NCS^-} \xrightarrow[\mathrm{H^+}]{} \mathrm{H_2O} + \cdot\mathrm{NCS} \quad (13)$$



$$\cdot\mathrm{OH} + \mathrm{R\underset{|}{\underset{R'}{C}}HOH} \longrightarrow \mathrm{H_2O} + \mathrm{R\underset{R'}{\dot{C}}OH} \quad (14)$$



$$\mathrm{R\underset{R'}{\dot{C}}OH} + \mathrm{Co^{III}} \longrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}R'} + \mathrm{H^+} + \mathrm{Co^{II}} \quad (15)$$

kinetic competition between dissociative (eq 11) and recombination (eq 10) modes of the primary $\{\mathrm{Co(NH_3)_5NCS^+,H_2O^+}\}$ radical pair products; i.e., eq 10 might not be kinetically significant.

Clearly there is evidence for similar photoprocesses for region III irradiations of $\mathrm{Co(NH_3)_5X^{2+}}$ (X = NCS, $\mathrm{N_3}$, Cl, Br) complexes in glycerol solutions. The unique feature of $\mathrm{Co(NH_3)_5NCS^{2+}}$ appears to be the development of the characteristic photodissociative reaction mode even in aqueous solutions. In one reasonable limit we can associate an intrinsic redox quantum yield, Φ_{RP}', with eq 7, and consider eq 10 and 11 to be in an excitation energy dependent competition,[3,51,64] so that the contribution of this pathway to the overall redox yield will be $\Phi_{\mathrm{RP}}'(k_d'/(k_d' + k_r'))$ and the total redox yield is $\phi_r = \Phi_{\mathrm{RP}}(k_d/(k_d + k_r)) + \Phi_{\mathrm{RP}}' \cdot (k_d'/(k_d' + k_r'))$. The observation of a quantum yield plateau in region II for $\mathrm{Co(NH_3)_5NCS^{2+}}$ may imply $(k_d/(k_d + k_r)) \sim 1$ and $\Phi_{\mathrm{RP}} \sim 0.027$. Similarly, that a different quantum yield plateau is achieved in 50% glycerol may imply that $\Phi_{\mathrm{RP}} \sim 0.02$ with again a negligible contribution from the competition between eq 10 and 11. Thus we might ascribe the differences in yield on the high energy plateau of Figure 3 to differences in the intrinsic quantum yields for primary product formation in water and glycerol-water solutions; that the intrinsic redox yield should be dependent on the medium is both plausible[3] and precedented.[19c] This approach would ascribe the curvature in the approach of ϕ_r to a plateau value to the energy dependence of $(k_d/(k_r + k_d))$,[2,3,51] possibly consistent with observation.

Alternatively one might consider the limit in which excited state equilibration results in the primary radical pair products being formed with similar energies, regardless of the actual excitation energy. For this limiting case, the ratio $(k_d/(k_r + k_d))$ will be medium, but not energy, dependent, and a less than unitary value of this ratio would contribute to the plateau in redox quantum yield. This alternative seems particularly attractive for $\mathrm{Co(NH_3)_5NCS^{2+}}$ since relatively efficient relaxation seems a characteristic feature of this system. The total product yields from region II irradiations of these complexes are 0.04 and 0.8, respectively.

For either alternative the observed redox yield in water could be formulated as in eq 16 for $\mathrm{Co(NH_3)_5NCS^{2+}}$ and

$$\phi_w = \Phi_w\left(\frac{k_d}{k_d + k_r}\right) + \Phi_w'\left(\frac{k_d'}{k_d' + k_r'}\right) \quad (16)$$

as $\phi_w = \Phi_w(k_d/(k_d + k_r))$ for the other pentaammine complexes. That the Φ_w' term is observed for $\mathrm{Co(NH_3)_5NCS^{2+}}$ is to be regarded as a consequence of the very small value of Φ_w for this complex.

For all these complexes in glycerol media the observed redox quantum yield may be expressed as in eq 17, by analogy to eq 16.

$$\phi_g = \Phi_g\left(\frac{k_d^*}{k_d^* + k_r^*}\right) + \Phi_g'\left(\frac{k_d^{**}}{k_d^{**} + k_r^{**}}\right) \quad (17)$$

The ratio ϕ_g/ϕ_w is readily decomposed into region II and region III contributions for the chloro, bromo, and azido complexes but is more complicated for the isothiocyanato complex.

B. Implications for Other Systems. The relationships between the energetics of excitation and product formation which have been explored in the correlation diagrams in Figures 4 and 5 point to a major contributory factor in the contrasting photoreactivities of ligand field excited states of acidopentaamminecobalt(III) complexes on the one hand and the acidopentacyanocobaltates and acidopentaamminechromium(III) and -rhodium(III) complexes on the other. Namely for nearly all complexes of the latter families the lowest energy, thermally equilibrated excited states have energy greater than or equal to the correlated energy required for replacement of a single ligand, while the cobalt-ammines have a large number of very low energy ligand field excited states. Thus photoreactivity in $\mathrm{Co^{III}(NH_3)_5X}$ complexes must depend on more rapid excited state decomposition than photophysical relaxation (internal conversion, intersystem crossing, and possibly vibrational), a very stringent requirement which is not present in most other families of complexes. Nevertheless, it seems evident that critical insights will be gained by careful correlations of excited state and product energetics in all these systems.

The possible implications of a photoprocess involving primary oxidation of the solvent has added significance in view of current interest in the photochemical decomposition of water mediated by transition metal complexes.[65] The one electron photooxidations which we have explored can be regarded as defining a limiting high energy process. In order for this component of solvent decomposition to be important at lower energies would require a more oxidizing acceptor, and very likely, intimate association of solvating water with a polyvalent cation.

Supplementary Material Available. Tabulated quantum yield data and Figures 7–10 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for pages in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St. N.W. Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6406.

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