$M^{-1}\ s^{-1}$ reported for the $Co(CN)_6^{3-}$ ion.[6] Since the complex does not absorb below 2.80 μm^{-1}, an electron-transfer mechanism involving reduction of the pyrazine carboxylate ligand seems implicated.

For the $Ni(CN)_4^{2-}$, an energy-transfer mechanism has been proposed.[8] The pentacyano(nitrosyl)ferrate complex presents the same difficulties reported for the *N*-methylpyrazinium ion case; energy transfer to the triplet of the charge-transfer excited state whose singlet–singlet transition is centered at 2.0 μm^{-1} may be possible. In addition, reduction of coordinated nitrosyl is also feasible; for the $Fe(CN)_5NO^{2-/3-}$ couple $E_{1/2}$ is −0.61 V[27] so that oxidation of $^*Ru(bpy)_3^{2+}$ is energetically favorable. Furthermore, there is evidence that the reorganization barrier for the bound NO^+/NO couple is small.[28] Thus in this system, as well, quenching may occur by parallel energy-transfer and oxidative pathways involving the ligand.

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Fe(CN)_5H_2O^{2-}$, 19413-97-9; $Fe(CN)_5(imid)^{2-}$, 61332-60-3; $Fe(CN)_5(\gamma\text{-picoline})^{2-}$, 61332-61-4; $Fe(CN)_5(py)^{2-}$, 61332-63-6; $Fe(CN)_5(isonicotinamide)^{2-}$, 61332-64-7; $Fe(CN)_5(pz)^{2-}$, 61332-65-8; $Fe(CN)_5(NMPz)^{-}$, 61363-44-8; $Fe(CN)_5(Me_2SO)^{2-}$, 61348-42-3; $Fe(CN)_5CO^{2-}$, 61332-62-5; $Fe(CN)_5CO^{3-}$, 17455-62-8; $Fe(CN)_5(Me_2SO)^{3-}$, 59422-09-2; $Fe(CN)_5(pzCO_2)^{4-}$, 59422-16-1; $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_5(imid)^{3-}$, 60105-88-6; $Fe(CN)_5py^{3-}$, 37475-75-5; $Fe(CN)_5(NMPz)^{2-}$, 40299-79-4; $Fe(CN)_5NO^{2-}$, 15078-28-1; Me_2SO, 67-68-5; imid, 288-32-4; py, 110-86-1; NMPz, 17066-96-5; $pzCO_2$, 61288-78-6; $Mo(CN)_8^{4-}$, 17923-49-8.

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Charge-Transfer Photochemistry of Thiocyanatopentaamminecobalt(III)

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The continuous photolysis of $Co(NH_3)_5SCN^{2+}$ has been studied as a function of excitation wavelength, temperature, and the composition of the medium. The major photolysis products are $Co(NH_3)_5NCS^{2+}$ and Co^{2+} with $Co(NH_3)_5H_2O^{3+}$ being formed in low yield. The relative yields of the major products are constant throughout the 550–250-nm spectral region suggesting that both are derived from the thiocyanate-to-cobalt charge-transfer excited state. The results are discussed in terms of a model in which photoisomerization of the sulfur-bonded thiocyanate results from kinetic factors in the electron-transfer collapse of the $Co(NH_3)_5^{2+}$,·SCN radical pair while the retention of configuration results from the deactivation of the LMCT excited state without its net dissociation into radicals.

Introduction

Linkage isomerization of the "wrong-bonded" isomers of octahedral coordination complexes in aqueous solution generally occurs more rapidly than their aquation.[2-4] The linkage isomerization reactions are generally dissociative: during the isomerization–aquation process a metal–ligand bond is broken, an intermediate of reduced coordination number is formed, and effects associated with the solvent cage appear to be of primary importance in determining the products. In a recent study of the mercury(II)-catalyzed isomerization–aquation of the unstable sulfur-bonded isomer $Co(NH_3)_5SCN^{2+}$, the available data were surveyed and the cage effects discussed.[4]

It seemed appropriate to extend this kind of study to the excited states of $Co(NH_3)_5SCN^{2+}$. Photoexcitation of cobalt(III) ammines in the ligand-field and charge-transfer region of the absorption spectrum is known to lead to photosubstitution and photoredox decomposition, respectively.[5-8] In both kinds of processes cage effects are expected to play an important role, making linkage isomerization a likely process again. Previously, nitro-to-nitrito linkage photoisomerization of $Co(NH_3)_5NO_2^{2+}$ has been observed.[9,10]

Here we report the results of a study of the photochemistry of the $Co(NH_3)_5SCN^{2+}$ ion as a function of excitation wavelength, temperature, and the viscosity of the medium. While this work was in progress a short report of the photochemistry of the same ion appeared in the literature.[11]

Experimental Section

Materials. $[Co(NH_3)_5SCN]Cl_2\cdot{}^3/_2H_2O$ and $[Co(NH_3)_5NCS]Cl_2$ were used from a stock available from the previous study.[4] All other chemicals were reagent grade.

Photolysis Procedures. A 450-W xenon lamp powered by a Christie power supply (Model SCX 1200-RS) was used as the source of the visible and ultraviolet light. A high-intensity Bausch and Lomb grating monochromator with the appropriate slit settings was used to select a 20-nm band-pass (bandwidth at half-maximum intensity) of the desired wavelength.

The photolyses were carried out in a 10-cm cylindrical spectrophotometer cell modified to contain a stirring bar. A thermostated Cary cell holder was used to control the cell temperature to ±0.1 °C. The solution in the cell was magnetically stirred during the irradiation and condensation on the outside of the cell windows at 3.3 °C was prevented by a stream of dry N_2 gas. The solution was brought to the reaction temperature prior to the photolysis. Concentrations of the complex in the photolyzed solutions were chosen so as to have absorbances above 1.5, thus ensuring essentially complete light absorption. The photolyses were stopped at 10% destruction of the complex. Irradiation times varied between 50 and 540 min, depending on the wavelength and temperature employed. An aliquot of the starting (reference) solution was therefore kept in the dark under the same conditions to determine the amount of thermal isomerization. The reaction medium was 0.01 M perchloric acid except where otherwise noted. All the experiments were carried out in a semi-darkened room.

Intensities of the excitation light were determined by ferrioxalate actinometry[12] in the ultraviolet and by Reineckate actinometry[13a] in the visible spectral region.

Analytical Procedure. All the analyses, including the product separation on the cation-exchange column, were simultaneously performed in a darkened room for the irradiated and reference solutions.

Cobalt(II) ion was determined directly in the irradiated solution by the Kitson method[13b] calibrated for the present experimental conditions. The other photochemical products were separated on a cooled (0 °C) Sephadex C-25 cation-exchange column. Thiocyanate ion was washed off the column with 0.001 M $HClO_4$, and NH_4^+ was eluted with 0.02 M $NaClO_4$ and 0.01 M $HClO_4$ solution. Attention was paid to the search for a possible product of stoichiometric composition $Co(NH_3)_4(H_2O)(CNS)^{2+}$. Elution was tried with $[Na^+] = 0.03–0.05$ M present in turn in a borate buffer of pH ~3, an acetate buffer of pH 5, a phosphate buffer of pH 6.85, and a phosphate buffer of pH 7.6. It was expected that at least the pH 7.6 buffer would convert the aquo complex to its hydroxy form, reducing the charge of the complex to 1+ thereby permitting elution by 0.03–0.05 M sodium ion. The mixture of $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ ions was separated from the product $Co(NH_3)_5H_2O^{3+}$ ion by eluting the former complexes with 0.16 M $NaClO_4$–0.01 M $HClO_4$ solution, while the latter complex was finally eluted with 0.5 M $NaClO_4$–0.01 M $HClO_4$ solution.

Thiocyanate ion was determined in the eluate as $FeNCS^{2+}$ after the addition of excess iron(III).[2] Ammonium ion was determined spectrophotometrically at 430 nm using Nessler's reagent. The amounts of unreacted $Co(NH_3)_5SCN^{2+}$ and product $Co(NH_3)_5NCS^{2+}$ ions were determined spectrophotometrically at 288 and 512 nm using known molar absorptivities of the two at these wavelengths.[3,4] $Co(NH_3)_5H_2O^{3+}$ ion was present in too low a concentration for the absorption spectrometry and was determined by atomic absorption-flame emission photometry.

Table I. Quantum Yields for the Continuous Photolysis of $Co(NH_3)_5SCN^{2+}$ in 0.01 M $HClO_4$

			Quantum yield		
λ, nm	T, °C	Other conditions	Co^{2+}	Co-$(NH_3)_5$-NCS^{2+}	$Co(NH_3)_5$-H_2O^{3+}
550[a]	3.3		0.0031	0.0017	0.000 80
510[b]	3.3		0.0089	0.0043	0.000 80
470[c]	3.3		0.015	0.012	0.001 6
400	25		0.19	0.097	0.007 5
370	25		0.26	0.12	0.006 1
370	3.3		0.19	0.099	0.003 0
333	25		0.39	0.18	0.020
333[d]	25		0.48[e]	0.24[e]	
333	3.3		0.24	0.15	0.014
288	25		0.45	0.22	0.031
288	3.3	I_i (incident light)	0.29	0.19	0.017
288	3.3	$^1/_3I_i$	0.31	0.20	0.024
288	3.3	0.0113 M NaSCN	0.24	0.20	0.018
288	3.3	0.108 M NaSCN	0.28	0.16	0.023
288	3.3	10% vol of glycerol	0.25	0.20	0.025
288	3.3	30% vol of glycerol	0.18	0.18	0.023
288	3.3	50% vol of glycerol	0.10	0.16	0.025
288	3.3	70% vol of glycerol	0.057	0.15	0.019
250	25		0.46	0.21	0.025
250	3.3		0.35	0.17	0.027

[a] The quantum yields of SCN^- and NH_3 were 0.0032 and 0.0163, respectively. [b] The quantum yields of SCN^- and NH_3 were 0.0085 and 0.049, respectively. [c] The quantum yields of SCN^- and NH_3 were 0.0072 and 0.10, respectively. [d] The quantum yield of thiocyanate was 0.33.[11] [e] Reference 11.

Results

Preliminary photolysis experiments involved irradiation of $Co(NH_3)_5SCN^{2+}$ ion at 510 nm, the region of the first ligand-field absorption band (λ_{max} 512 nm, ϵ_{max} 74 M^{-1} cm^{-1}).[3] Though the quantum yields were low, it was immediately evident that at least three cobalt species were formed in the photolysis: Co^{2+}, accompanied by the other products of the photoredox reaction; $Co(NH_3)_5NCS^{2+}$, the product of the linkage isomerization reaction; and $Co(NH_3)_5H_2O^{3+}$, a likely product of the photosubstitution reaction. Since cobalt(III) ammines often undergo "antithermal" photobehavior involving photosubstitution of ammonia by water upon irradiation in the ligand field spectral region,[14] it was anticipated that species of the stoichiometric composition of $Co(NH_3)_4(H_2O)(CNS)^{2+}$ might also be produced. To establish their formation using criteria based on the amount of ammonia released was not considered reliable because of the relatively large amounts of ammonia produced by the photoredox reaction and the difficulties associated with its determination. Instead, the direct search for $Co(NH_3)_4(H_2O)(CNS)^{2+}$ as described above was preferred. However, no evidence was found for the presence of these species among the photolysis products and we tentatively conclude that the quantum yield for the photoaquation of ammonia is less than or equal to that for photoaquation of thiocyanate. Our failure to detect $Co(NH_3)_4(H_2O)(CNS)^{2+}$ as a photoproduct is consistent with the photochemical behavior of $Co(NH_3)_5NCS^{2+}$ since evidence for the formation of $Co(NH_3)_4(H_2O)(CNS)^{2+}$ was also not found in the photolysis of the latter complex.[8]

The quantum yields for the products of the continuous photolysis of $Co(NH_3)_5SCN^{2+}$ were determined as a function of the following parameters: wavelength and intensity of the excitation light, temperature, viscosity of the medium, and the presence of excess thiocyanate ions. The results are summarized in Table I. The quantum yields for both Co^{2+} and $Co(NH_3)_5NCS^{2+}$ production increase with increasing energy of the exciting light. The extrapolated threshold energy is

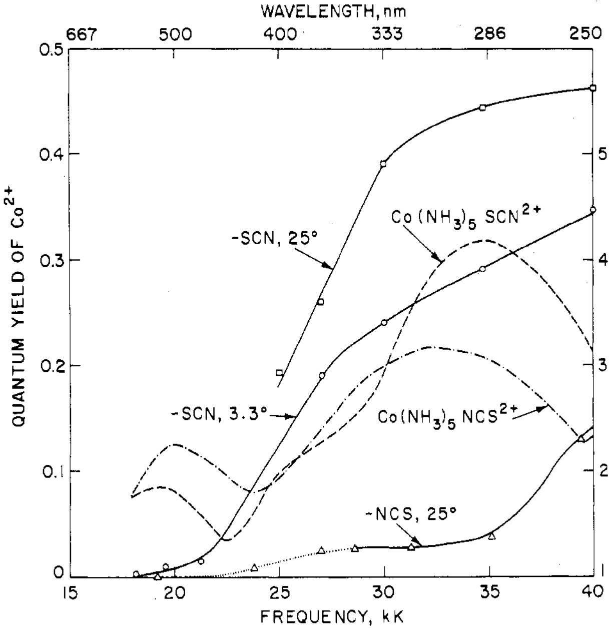

Figure 1. Absorption spectra of $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ and the quantum yields of Co^{2+} produced in the photolysis of $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ as a function of excitation energy: triangles, Co^{2+} quantum yields from $Co(NH_3)_5NCS^{2+}$ at 25 °C;[8] squares, Co^{2+} quantum yields from $Co(NH_3)_5SCN^{2+}$ at 25 °C; circles, Co^{2+} quantum yields from $Co(NH_3)_5SCN^{2+}$ at 3.3 °C.

Table II. Photolysis of $Co(NH_3)_5SCN^{2+}$ in 0.01 M $HClO_4$ at 3.3 °C: Ratios of the Quantum Yields as Functions of Excitation Wavelength

λ, nm	$\phi_{Co^{2+}}/\phi_{Co(NH_3)_5NCS^{2+}}$	$\phi_{Co^{2+}}/\phi_{Co(NH_3)_5(H_2O)^{3+}}$
550	1.8	4
510	2.1	11
470	1.3	10
400	2.0 (25 °C)	26 (25 °C)
370	1.9	63
333	1.6	17
288	1.5	17
250	2.0	13

21 000 cm^{-1} (Figure 1) and the quantum yields tend to level off in the thiocyanate-to-metal charge-transfer spectral region (λ_{max} 288 nm, ϵ_{max} 15 600 M^{-1} cm^{-1}).[3] The light intensity and the presence of excess thiocyanate ions had no significant effect on the quantum yields. The quantum yields decrease with decreasing temperature and, for Co^{2+} and $Co(NH_3)_5NCS^{2+}$ ions, with increasing concentration of glycerol in the medium.

Discussion

The ratios of the quantum yields of cobalt products formed in the continuous photolysis of $Co(NH_3)_5SCN^{2+}$ as a function of excitation wavelength are presented in Table II. Although the quantum yields for the formation of both Co^{2+} and $Co(NH_3)_5NCS^{2+}$ increase by about a factor of 100 on changing the wavelength from 550 to 250 nm (Table I), it is noteworthy that the ratio of their quantum yields remains essentially constant. This constancy suggests that, in the spectral region studied, the two products are formed either from the same precursor or from the same set of consecutive and parallel processes involving more than one precursor. Since Co^{2+}, a photoredox product, is formed through the ligand-to-metal charge-transfer (LMCT) excited state, it follows that the linkage isomerization producing $Co(NH_3)_5NCS^{2+}$ results from the same excited state.[15] A possible contribution to the linkage isomerization from the ligand-field excited state thus appears insignificant and the sharply decreasing quantum yields of Co^{2+} and $Co(NH_3)_5NCS^{2+}$ in the ligand-field spectral region reflect inefficient population of the charge-transfer excited state from the initially formed ligand-field states.

It is of interest that for $Co(NH_3)_5SCN^{2+}$ the extrapolated (threshold) energy for LMCT absorption (E_{th}') lies about 5000 cm^{-1} above the extrapolated (threshold) energy for appreciable photoredox decomposition of the complex (E_{th}) (26 000 and 21 000 cm^{-1}, respectively; Figure 1). Like $Co(NH_3)_5SCN^{2+}$, $Co(NH_3)_5NO_2^{2+}$ undergoes photoinduced linkage isomerization; upon LMCT excitation, the *unstable* nitrito isomer is produced.[9] As previously noted,[17] ($E_{th}' - E_{th}$) is ~6000 cm^{-1} for $Co(NH_3)_5NO_2^{2+}$, while E_{th}' and E_{th} are nearly equal for several other $Co(NH_3)_5X^{2+}$ complexes (X = Cl, Br, N_3, NCS). For the latter complexes E_{th}' provides a measure of the energy of the thermally equilibrated LMCT excited state;[17] the fact that $E_{th}' > E_{th}$ for $Co(NH_3)_5NO_2^{2+}$ is consistent with the interpretation that the LMCT excited state of the nitro complex is dissociative in character.[9,17] Indeed the fact that E_{th}' is also greater than E_{th} for the sulfur-bonded thiocyanato complex implies that the charge-transfer excited state of the thiocyanate complex too is dissociative. Furthermore, this model can also account for the marked differences in the Co^{2+} quantum yields for the nitrogen- and sulfur-bonded thiocyanate complexes. The nitrogen-bonded isomer, which is not expected to have a dissociative LMCT excited state since $E_{th}' \approx E_{th}$ (Figure 1), attains Co^{2+} quantum yields of only ~0.1. By contrast the sulfur-bonded complex, which is expected by this criterion to have a dissociative excited state, attains much higher Co^{2+} quantum yields (~0.5).

If it is assumed that the LMCT excited state of $Co(NH_3)_5SCN^{2+}$ dissociates to give a $Co(NH_3)_5^{2+}$,·SCN radical pair, then geminate recombination of these radicals[18,19] must compete with processes such as "outer-sphere" electron transfer, the aquation of the $Co(NH_3)_5^{2+}$ fragment, and the diffusional escape of the radicals into the bulk phase. A model of this type was proposed[9] for the photoisomerization of $Co(NH_3)_5NO_2^{2+}$ and was later supported by studies of the effect of glycerol on the relative quantum yields.[10] It was shown that increasing the viscosity of the medium (by increasing the glycerol concentration) increased the yield of isomerization and decreased that of Co^{2+}, with the sum of the isomerization and Co^{2+} yields remaining essentially constant. The detailed mechanism[20,21] for the photoisomerization of $Co(NH_3)_5NO_2^{2+}$ involves the dissociation of the LMCT excited state to form a $Co(NH_3)_5^{2+}$,·NO_2 radical pair. This pair may either undergo recombination in the primary cage to form the parent isomer exclusively or diffuse apart so as to become separated by at least one solvent molecule. The solvent-separated radicals can undergo a number of competing (secondary) reactions: these include recombination of form $Co(NH_3)_5ONO^{2+}$ (but not $Co(NH_3)_5NO_2^{2+}$) and diffusional escape of the radicals into the bulk phase. The secondary reactions are expected to be similar to ordinary chemical reactions in many respects. Thus the secondary reactions should show very little memory; that is, the reactions of a given pair of radicals should be independent of their mode of formation. The secondary reactions should also be relatively unaffected by the kinetic energy with which the radicals were originally formed; in other words, the reactions should be insensitive to the excitation wavelength. This model can account for the observed wavelength and solvent dependence of the $Co(NH_3)_5NO_2^{2+}$ photoisomerization.[20,21] An essential feature of this interpretation is that formation of ground-state $Co(NH_3)_5NO_2^{2+}$ occurs prior to the formation of the secondary radical pair.[9,17,20,21]

A similar model can account for the photoisomerization of $Co(NH_3)_5SCN^{2+}$ if it is postulated that the $Co(NH_3)_5^{2+}$,·SCN radical pair recombines to form $Co(NH_3)_5NCS^{2+}$ rather than

$\mathrm{Co(NH_3)_5SCN^{2+}}$. This is shown in eq 1–3. In this scheme

$$\mathrm{Co(NH_3)_5SCN^{2+}} + h\nu \rightarrow {}^*\mathrm{Co(NH_3)_5SCN^{2+}} \qquad (1a)$$

$${}^*\mathrm{Co(NH_3)_5SCN^{2+}} \rightarrow (\mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{SCN}) \qquad (1b)$$

$$(\mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{SCN}) \begin{array}{l} \nearrow (\mathrm{Co(NH_3)_5SCN^{2+}} \qquad (2a) \\ \searrow \mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{SCN} \qquad (2b) \end{array}$$

$$\mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{SCN} \begin{array}{l} \nearrow \mathrm{Co(NH_3)_5NCS^{2+}} \qquad (3a) \\ \rightarrow \mathrm{Co(NH_3)_5^{3+}},\ \mathrm{SCN^-} \qquad (3b) \\ \searrow \mathrm{Co^{2+}} + 5\mathrm{NH_4^+} + \mathrm{SCN^-} \qquad (3c) \end{array}$$

($\mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{SCN^-}$) denotes the caged radical pair. This pair can either undergo recombination to form $\mathrm{Co(NH_3)_5SCN^{2+}}$ (eq 2a) or separate to form the secondary pair $\mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{SCN}$ (eq 2b). The secondary pair may either recombine to form the linkage isomer $\mathrm{Co(NH_3)_5NCS^{2+}}$ (eq 3a),[22] undergo electron transfer (eq 3b), or diffuse apart into the bulk phase to ultimately form $\mathrm{Co^{2+}}$ and $\mathrm{SCN^-}$ (eq 3c).[23]

The above scheme is consistent with the failure of $\mathrm{Co(NH_3)_5NCS^{2+}}$ to undergo photoisomerization. If the $\mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{SCN}$ radical pair undergoes (secondary) recombination to form $\mathrm{Co(NH_3)_5SCN^{2+}}$, then it is necessary to postulate that the secondary reactions of the radicals formed from excited $\mathrm{Co(NH_3)_5SCN^{2+}}$ and $\mathrm{Co(NH_3)_5NCS^{2+}}$ differ in their properties; this requirement of secondary radical reactions with memories is not too attractive. On the other hand, there is precedent for primary radical pairs with memories.[25] In the present context this requires that the $\mathrm{Co(NH_3)_5^{2+}}$ and $\cdot\mathrm{SCN}$ radicals formed from $\mathrm{Co(NH_3)_5SCN^{2+}}$ and $\mathrm{Co(NH_3)_5NCS^{2+}}$ have memories in the sense that they undergo cage recombination to re-form the isomers from which they were produced.[26] Alternatively, the "formation" of ground-state $\mathrm{Co(NH_3)_5SCN^{2+}}$ from the excited state can be explained by postulating that the LMCT excited state of $\mathrm{Co(NH_3)_5SCN^{2+}}$ can undergo deactivation to the ground state without ever undergoing net dissociation into radicals. (Similarly, "formation" of ground-state $\mathrm{Co(NH_3)_5NO_2^{2+}}$ from the excited-state complex could occur prior to the formation of a radical pair.[17]) In order to account for the wavelength dependence of the photoisomerization yield in terms of this model it is necessary to postulate that the efficiency of deactivation of the excited state to the ground-state increases with decreasing excess energy of the excited state, a requirement that does not seem prohibitive.

Regardless of the detailed steps leading to retention of configuration (primary recombination with memory or deactivation of the excited state without radical formation) the data require that the secondary radicals formed from $\mathrm{Co(NH_3)_5SCN^{2+}}$ and $\mathrm{Co(NH_3)_5NCS^{2+}}$ recombine in each case to form $\mathrm{Co(NH_3)_5NCS^{2+}}$ only. This can be rationalized on the following basis. We assume that the radical recombination reaction is an "ordinary" inner-sphere electron-transfer reaction, that is, that the radical recombination reaction proceeds in two steps: the first step is the addition of the radical to the cobalt(II) center to form a precursor complex, and the second is the electron transfer within the precursor complex. In other words, we assume that radical addition to $\mathrm{Co(NH_3)_5^{2+}}$ precedes the electron transfer. The stability of the precursor complex in this inner-sphere reaction is related to the degree of bonding in the thermally equilibrated LMCT excited state of the parent complex. As discussed above, there is good evidence that the LMCT excited state formed from $\mathrm{Co(NH_3)_5NCS^{2+}}$ is more bound than the LMCT excited state formed from $\mathrm{Co(NH_3)_5SCN^{2+}}$. Assuming then that the electron-transfer precursor complexes are formed from identical (secondary) radical pairs, the sulfur-bonded precursor complex must be less stable than the nitrogen-bonded one. In addition, since the nitrogen-bonded complex is the more stable isomer, the driving force for "intramolecular" electron transfer will be larger in the nitrogen-bonded than in the sulfur-bonded precursor complex. Both factors should favor formation of $\mathrm{Co(NH_3)_5NCS^{2+}}$ in the radical recombination reaction (eq 4, 5). Similarly, in view of the evidence that the LMCT

$$\mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{SCN} \rightleftharpoons \mathrm{Co^{II}(NH_3)_5NCS^{\cdot 2+}} \qquad (4)$$

$$\mathrm{Co^{II}(NH_3)_5NCS^{\cdot 2+}} \rightarrow \mathrm{Co^{III}(NH_3)_5NCS^{2+}} \qquad (5)$$

excited state formed from $\mathrm{Co(NH_3)_5NO_2^{2+}}$ is dissociative, the formation of a nitrogen-bonded precursor complex from the $\mathrm{Co(NH_3)_5^{2+}},\cdot\mathrm{NO_2}$ radical pair will not readily take place. The relative rates of electron transfer within the nitrogen- and oxygen-bonded precursor complexes are difficult to assess.[27] In any event, in terms of this model, photoisomerization of the sulfur-bonded thiocyanate (and nitrogen-bonded nitro) complexes is a consequence of the thermodynamic and kinetic factors that govern the electron-transfer collapse of the secondary radical pairs.[29,30]

The above interpretation is inconsistent with the effect of glycerol on the product distribution from excited $\mathrm{Co(NH_3)_5SCN^{2+}}$. The data in Table I show that the yield of $\mathrm{Co^{2+}}$ decreases with increasing viscosity as expected but that the $\mathrm{Co(NH_3)_5NCS^{2+}}$ yield *decreases* too, though more gradually, while the $\mathrm{Co(NH_3)_5H_2O^{3+}}$ yield remains essentially constant and low. Evidently glycerol has different effects on the photoisomerizations of $\mathrm{Co(NH_3)_5NO_2^{2+}}$ and $\mathrm{Co(NH_3)_5SCN^{2+}}$. This objection can be met if, in addition to changing the viscosity of the medium, the added glycerol also has other consequences. These consequences include possible changes in the excited- (and ground-) state potential energy surfaces, intersystem crossing rates, preferential solvation effects, etc., all of which could have important effects on the $\mathrm{Co^{2+}}$ quantum yields.[31] Because of these complications the effect of glycerol on the quantum yields may not provide a reliable guide to the radical recombination reactions in the photolysis of the thiocyanate complexes.

Thus far the third cobalt photoproduct of the photolysis of $\mathrm{Co(NH_3)_5SCN^{2+}}$, the $\mathrm{Co(NH_3)_5H_2O^{3+}}$ ion, has been ignored in the discussion mostly because its yield is lower by an order of magnitude than those of the two other products, its pattern of yields is more complicated, and its combined separation and determination is the least accurate of the three. The third column of Table II shows that the largest ratio of the yield of $\mathrm{Co^{2+}}$ to $\mathrm{Co(NH_3)_5H_2O^{3+}}$ is for excitation at 370 nm, a fact contrasting with the observation for the photolysis of the $\mathrm{Co(NH_3)_5NCS^{2+}}$ ion.[8] The relatively higher ratios from 370 to 550 nm are probably caused by a contribution to the photosubstitution from the ligand-field excited states.

To conclude, the stereochemistry of the photolysis of the $\mathrm{Co(NH_3)_5CNS^{2+}}$ isomers can be rationalized as follows. The retention of configuration results either from memory effects in the primary radical recombination reactions or from the deactivation of the LMCT excited states of the complexes without their net dissociation into radicals. Although there is an increasing amount of evidence that the latter type of deactivation process may be important in some systems,[7] we cannot distinguish between these retention mechanisms in the thiocyanate system and in the limit they may well be indistinguishable. On the other hand, the photoisomerization of $\mathrm{Co(NH_3)_5SCN^{2+}}$ and the failure of $\mathrm{Co(NH_3)_5NCS^{2+}}$ to undergo photoisomerization can be understood if the secondary radical recombination reactions produce $\mathrm{Co(NH_3)_5NCS^{2+}}$ but not $\mathrm{Co(NH_3)_5SCN^{2+}}$. This specificity may be related to the relative stabilities of the complexes that are formed between the radicals prior to the back electron transfer.

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Registry No. $Co(NH_3)_5SCN^{2+}$, 15005-69-3; $Co(NH_3)_5NCS^{2+}$, 14970-18-4.

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(22) The fact that the ratio of the quantum yields of Co^{2+} and $Co(NH_3)_5NCS^{2+}$ is essentially independent of excitation wavelength is consistent with the interpretation that no $Co(NH_3)_5NCS^{2+}$ is formed in the primary radical recombination.
(23) The formation of thiocyanate in the photolysis of complexes of this type is not without precedent.[8,24] It has been proposed[8] that the thiocyanate arises through hydrolysis of $(NCS)_2$ or through scavenging of $\cdot NCS$ or $(NCS)_2^-$ by dissolved species.
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(27) Calculations described in ref 17 indicate that electron transfer within the $Co(NH_3)_5ONO^{2+}$ precursor complex should be more rapid than within the $Co(NH_3)_5NO_2^{2+}$ precursor complex. Despite the fact that these calculations "predict" the desired result, they are open to question on at least two grounds. The first objection concerns the assumption that the charge on NO_2^- is centered on the *nitrogen* atom. Actually, although the latter assumption is incorrect, this error is of little consequence since the important factor is not where the net charge lies in NO_2^- but where the electron is added when NO_2 radical is reduced to NO_2^-. In the case of free NO_2, the reduction process can at least formally be regarded as electron addition to the nitrogen atom (which in NO_2 carries a formal positive charge).[28] The second objection is more fundamental. In calculating the solvent reorganization terms for the $(NH_3)_5CoONO^{2+}$ and $(NH_3)_5CoNO_2^{2+}$ precursor complexes, an equation derived for spherical ions was used[17] to predict the behavior of these systems. It is thus assumed that the solvent reorganization energy varies as $(1/a_1 + 1/a_2 - 1/r)$, where a_1 and a_2 are the radii of the reactant ($Co(NH_3)_5^{2+}$, NO_2, or ONO) spheres. There is, unfortunately, no sensible way to define the radius of the reactant sphere when the reactant is V shaped and the precursor complex is of the inner-sphere variety. Although it is clear that r is greater for $(NH_3)_5CoONO^{2+}$ (thus favoring formation of this isomer), the value of the $1/a_2$ term is *not* negligible and, depending on the a_2 values used, the formation of either isomer may be predicted.
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(30) Above it was tacitly assumed that the charge-transfer *singlet* state is responsible for the observed photochemistry and that this excited state produces a geminate radical pair of net *singlet* multiplicity upon dissociation. In a more detailed treatment it would be necessary to consider the possible formation of a geminate radical pair of triplet spin multiplicity and to allow for possible changes in the spin state of the cobalt(II).[7,17]
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Reactions of Chloraminepentaammineiridium(III) Ion. Evidence for a Coordinated Nitrene Intermediate

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The kinetics of the reaction of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ with bromide ion and hydroxide ion have been investigated in acetic acid–sodium acetate buffers. The reactions are both first order in iridium complex. The reaction with hydroxide ion is first order in hydroxide ion, whereas the reaction with bromide ion is zero order in bromide ion. The hydrolysis reaction is inhibited by chloride ion. The mechanism proposed involves a coordinated nitrene intermediate. The kinetics of the reaction of iodide ion with $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ and with $[Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ were also studied. The reaction of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ is interpreted as two consecutive reactions, both first order in iodide ion. The reaction of $[Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ is first order in complex and first order in iodide ion. A coordinated iodamine intermediate is postulated.

Introduction

Nitrene intermediates are well-known in organic chemistry and are postulated for aryl azide[1] and sulfonylchloramine[2] decompositions. Coordinated nitrene intermediates have been reported for the reactions of some azido–metal complexes. Photochemical generation of nitrenes are reported for $[Rh(NH_3)_5N_3]^{2+}$ [3] and for $[Ir(NH_3)_5N_3]^{2+}$.[4] Coordinated nitrene intermediates are also postulated for some thermal reactions of azido–metal complexes of ruthenium(III)[5] and iridium(III).[6,7] These coordinated nitrenes react with various nucleophiles.[6,7] This paper reports a kinetic study of the reactions of the chloraminepentaammineiridium(III) ion with bromide ion, hydroxide ion, and iodide ion. The results obtained suggest the formation of a nitrene intermediate in the reaction with bromide ion and with hydroxide ion. The intermediate behaves similarly to the intermediate generated from $[Ir(NH_3)_5N_3]^{2+}$, which is believed to be the nitrene $[Ir(NH_3)_5NH]^{3+}$.

The reactions of iodide ion with $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ and with $Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ are first order in iodide ion, and for these reactions the intermediate is believed to be $[Ir(NH_3)_5(NH_2I)]^{3+}$.

Experimental Section

Synthesis and Reactions. The compounds $[Ir(NH_3)_5(NH_2Cl)](ClO_4)_3$, $[Ir(NH_3)_5N_3](ClO_4)_2$, and $[Ir(NH_3)_5(NH_2OH)](ClO_4)_3$