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Linkage Isomer Ratios in Thermal and Photochemical Anation of Acidopentacyanocobaltate(III) Anions

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Photolysis of $[Co(CN)_5X]^{n-}$ ions, where X = CN^-, N_3^-, Cl^-, Br^-, I^-, OH^-, and H_2O, in slightly acidic aqueous thiocyanate solution has been found to give the linkage isomers of $[Co(CN)_5(NCS)]^{3-}$, together with larger amounts of $[Co(CN)_5(H_2O)]^{2-}$. Photolyses at pH 13 and room temperature, and in acidic medium at −4 °C, demonstrate that direct photoanation occurs in competition with the more efficient aquation reaction. Photochemical anation gives the product linkage isomers in an S- to N-bonded ratio of 8.5 ± 1.4, 8.8 ± 1.5, 9.3 ± 1.3, 8.7 ± 1.5, 8.1 ± 1.7, and 8.7 for X = Cl^-, Br^-, I^-, N_3^-, CN^-, and OH^-, respectively. These values differ from those for the thermal anation, which are 4.3 ± 0.2, 4.5, 4.7, and 4 (literature) for the first four of the same sequence. In addition the ratio of aquation to anation is lower for the photochemical reaction than for the thermal. The intermediate in the photochemical reaction therefore differs from the species that has been proposed for the thermal reaction and favors S over N attack to a greater extent. This may reflect either participation of an excited-state intermediate of greater polarizability or cation interactions operating to direct ligand substitution.

Introduction

Although the thermal and photochemical aquation and anation of hexacyanocobaltate(III) and its acido- and hydroxypentacyanocobaltate(III) derivatives have been studied from a number of points of view over three decades, their behavior is not understood in all aspects.

Hexacyanocobaltate(III) is a very stable compound and thermally aquates to the aquo pentacyano compound only very slowly. Early studies[1-4] of the kinetics of the thermal aquation and anation of the pentacyano compounds suggested a D mechanism[5] involving participation of a five-coordinate intermediate, $[Co(CN)_5]^{2-}$, analogous to the $[Co(NH_3)_5]^{3+}$ intermediate proposed in the thermal chemistry of the acido pentaammine series, but the existence of which has recently been undermined.[6] The proposed pentacyano intermediate then underwent aquation and anation in the presence of an appropriate nucleophile, these two processes being in competition with one another.

Some more recent research[7,8] has revealed, however, that rate law results can be complicated by ionic strength and other medium effects. For aquopentacyanocobaltate(III) anation, for example, azide gives rate law results that are equivocal, while thiocyanate adheres to expectations for the D mechanism. The latter observation and the combined weight of evidence from competition experiments[2] and activation volumes[9] continue to support substitution reaction via a D mechanism for the pentacyano systems.

Quite a recent study[10] has examined the competition between water and thiocyanate ion for the intermediate formed in the thermal reactions of azidopentacyanocobaltate(III). An acid-catalyzed dissociative mechanism was assigned to the process, about 14% anation was found at 1 M thiocyanate, and a chromatographic determination showed that about 20% of the product thiocyanatopentacyanocobaltate(III) was N-bonded.

There have been extensive studies of the photochemistry of these species. Hexacyanocobaltate(III) has been known for a long time to photolyze with a wavelength- and temperature-independent quantum yield of 0.31[11-13] to the aquo pentacyano product in acidic or neutral aqueous solution. The photochemistry is sufficiently clean that exhaustive photolysis of hexacyanocobaltate(III) is an excellent and convenient way to prepare the aquo- and hydroxopentacyanocobaltate(III) compounds.[14] It has been reported[7] that photolysis of the aquo pentacyano product leads to some *trans*-diaquotetracyanocobaltate(III) but that, in the presence of released cyanide, this quickly reverts to the monoaquo species.

That the photoreaction occurs via the triplet state of the complex with an efficiency of 0.8 for triplet reaction has been shown[15-18] by an analysis of sensitization with biacetyl triplets. A detailed study[16] revealed important complexities in the quenching behavior. The aquopentacyanocobaltate(III) produced by sensitized photochemistry during the quenching measurements quenches biacetyl triplets with a rate constant that is 570 times larger than that for hexacyanocobaltate(III) so a major fraction of the quenching arises from the photoproduct quite early in the experiment. The quenching rate constants for some other acido pentacyano species have been found[17] to increase with decreasing energy of the first spin-allowed absorption band.

Evidence that the photoaquation of hexacyanocobaltate can be considered as a dissociative process involving a solvent-caged $Co(CN)_5^{2-}$ species and cyanide ion has been obtained from studies[20,21] of the viscosity dependence of the reaction quantum yield; this is supported by parallels with the isoelectronic carbonyl species such as $Cr(CO)_6$ and is consistent with theoretical arguments.[22,23] Also, and more directly, the photoaquation quantum yield has been found[24] to show a positive volume of activation,

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pointing to a dissociative process, despite the uncertainties associated with the effects of electrostriction. It has also been shown[25] that cage recombination is promoted by sodium ions, causing a reduced quantum yield, and if HCN is present, competition occurs between water and HCN for the intermediate in the solvent cage, which again reduces the quantum yield. Further strong evidence for the limiting dissociative process has been obtained from a recent study[26] in haloalkane solvents where, for example, the monosubstituted methylene chloride complex was produced and its decay by acetonitrile replacement was followed. This work revealed that the quantum yield for solvent substitution in methylene chloride is the same as in water.

There have been less extensive studies of the acido pentacyano species. An early paper reported[27] quantum yields for aquation of chloro, bromo, and iodo of 0.06, 0.17, and 0.24, respectively. More recent work gives values of 0.03 and 0.19 for azido[28] and isothiocyanato,[28] while a lower value of 0.17 has been reported for iodo.[13] Limiting dissociative mechanisms have been assigned[13] to the aquo and iodo compounds. Also of importance for the present study are the reported[29] quantum yields for photolytic cyanide release from aquo- and hydroxopentacyanocobaltate(III), which are 0.003 and 0.06, respectively, for irradiation at 313 nm in room-temperature aqueous solution.

Literature evidence regarding the photoanation process, which competes with aquation when high concentrations of added nucleophiles are present, is, for cyano complexes, mildly contradictory. Photoanation yields reported[13] for hexacyanocobaltate with azide were later attributed[30] to secondary photoanation of aquo pentacyano photoproduct, although for aquopentacyanocobaltate(III) the cited studies agreed that direct photoanation occurred with both iodide and azide ions. Unfortunately, none of the acido pentacyano species were included in the flash-photolysis study.[30] A comparison of the thermal and photochemical anation processes involving the aquo pentacyano complex, pursuing some of the same objectives as the present study, showed[25] that, for entry of anionic ligands, the intermediate in the photochemical and thermal reactions had the same iodide/azide competition ratio. By comparing ratios for the entry of a charged and an uncharged ligand, the authors concluded that the intermediate reacted to a greater extent within the solvent cage when produced photochemically.

Note also that any case[31] for a general photoanation of acidopentacyanocobaltates(III) via a $[Co(CN)_5]^{2-}$ intermediate rests on data for only two compounds, aquo- and iodopentacyanocobaltate(III).

The present work sought answers to several questions that spring from the survey of the literature on pentacyanocobaltates just presented. They are the following. (1) If the thermal reactions truly occur through a common five-coordinate intermediate, is this reflected in a common S/N linkage isomer ratio for the product of thermal anation by thiocyanate? (2) Does direct photoanation really occur? (3) If so, is the photochemical S/N bonded ratio independent of the source compound, indicating participation of a common photochemical intermediate? (4) Is any such photochemical intermediate the same or different in its behavior from that involved in the thermal reactions?

We have addressed these questions using two new experimental approaches. First, strongly alkaline conditions were used to establish unambiguously the extent to which direct photoanation processes occur for these compounds. Second, an ambidentate nucleophile was used. This produces linkage isomers, allowing the product isomer ratio to be a probe of the nature of the intermediate. Thiocyanate was chosen as the nucleophile because the S- to N-bonded isomer ratio for any photoanation reactions found could be easily measured.

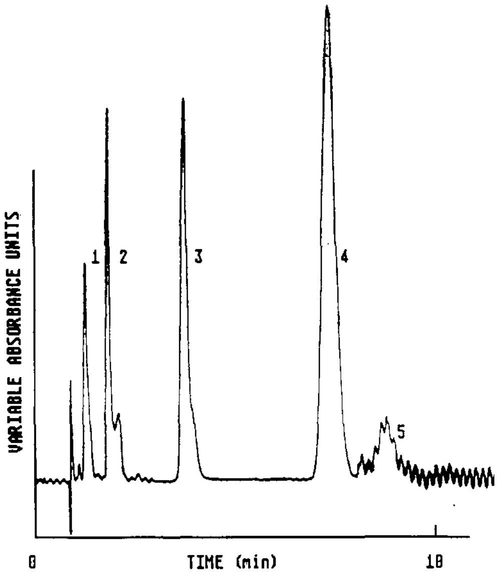

Figure 1. Photoanation products of $[Co(CN)_5N_3]^{3-}$. Conditions: 1.0×10^{-2} M complex with 2.0 M sodium thiocyanate in pH 13 aqueous solution photolyzed at 313 nm for 155 min; eluted isocratically for 20 min with 50 mM hexylammonium ion/40 mM citrate in 25% methanolic water at pH 6.5; UV detection at 265 nm. Peaks are as follows: (1) $[Co(CN)_5(H_2O)]^{2-}$ ($\epsilon = 2.73 \times 10^2$ L mol^{-1} cm^{-1}), 0–0.2 absorbance units full scale (aufs); (2) NCS^- split peak owing to high $[NCS^-]$, 0–0.2 aufs; (3) $[Co(CN)_5N_3]^{3-}$, 0–2 aufs; (4) $[Co(CN)_5SCN]^{3-}$ ($\epsilon = 1.71 \times 10^4$ L mol^{-1} cm^{-1}), 0–0.5 aufs; (5) $[Co(CN)_5NCS]^{3-}$ ($\epsilon = 2.34 \times 10^3$ L mol^{-1} cm^{-1}), 0–0.05 aufs.

In this, we were fortunate to have at our disposal a reversed-phase HPLC technique that allowed rapid separation of the S- and N-bonded isomers.[32] This method of analysis is immune to the interferences by the polymeric cyano complexes and thiocyanate species that appear to have plagued earlier workers who had only spectrophotometric analysis available.

In this paper we report results that show that thermal anation gives a product isomer ratio of about 4 for all the acido pentacyano species studied, that direct photoanation occurs for all the complexes studied, and that the photochemical process gives a significantly higher S/N-bonded product isomer ratio of about 9.

Experimental Section

Preparation of Complexes. The compounds $K_3[Co(CN)_5X]$ were prepared by the following literature methods: X = Cl, Br, I,[33] N_3,[3] CN,[2] SCN,[34] H_2O.[7] They were identified by the concordance of their UV-vis spectra with the published data, and their purity was established by chromatographic analysis. All gave a single peak. The aquo compound was obtained only in solution.

Materials. The following thiocyanate salts were used without further purification: sodium (Aldrich), calcium (GFS, reagent grade). HPLC eluents were prepared as described[32] by using HPLC grade methanol (Fischer), organopure water (Barnstead/Sybron system), hexylamine (Aldrich, 99%), and citric acid monohydrate (Sigma).

Chromatography. A Varian 5000 liquid chromatograph was used with a 30-cm Chromatography Sciences ODS2 10-μm C18 column and Varichrom variable-wavelength detector set at 265 nm. This wavelength corresponds to the maximum of the charge-transfer absorption band of the S- and N-bonded (thiocyanato)pentacyanocobaltate products.

Eluents were prepared in organopure water and a solvent mixture containing 90% v/v HPLC methanol in water, and both contained 50

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Table I. Thermal and Photoanation Ratios for $[Co(CN)_5X]^{n-}$

ligand X^a	S/N thermal	S/N photo	ag/an^b
Cl^-	4.3 ± 0.2 (3)	8.5 ± 1.4 (8)	5.4 ± 0.8 (4)
Br^-	4.5 (2)	8.8 ± 1.5 (6)	6.1 ± 2.1 (4)
I^-	4.7 (2)	9.3 ± 1.3 (5)	7.8 ± 1.5 (3)
N_3^-	4^c	8.7 ± 1.5 (9)	4.2 ± 1.1 (5)^d
OH^-		8.7 (1)	
CN^-		8.1 ± 1.7 (3)	
H_2O	4.4		

^{a}Photolysis at 313 nm of 1.0×10^{-2} M solutions of the complex in 2 M sodium thiocyanate solution for periods ranging from 15 min to 3 h. Although conversions in the data reported went as high as 60%, the S/N ratios showed no photolysis time dependence except for the chloro compound, where data influenced by this were rejected. The figures in parentheses are the number of runs in the average given. ^{b}Ratio of photoaquation to photoanation. ^{c}From ref 10. ^{d}On the substitution of 2 M sodium thiocyanate by 1.0 M $Ca(NCS)_2$, the ratios S/N photo and aq/an were 9.5 ± 1.2 (9) and 5.5 ± 0.2 (4), respectively.

mM hexylamine and 40 mM citric acid, adjusted to pH 6.5 with ammonia. Analyte ions were separated by a combination of isocratic and gradient elution using the following protocol: isocratic at 25% methanol for 20 min followed, in some runs, by a linear gradient from 25 to 40% methanol over 10 min. The latter was to elute some minor product peaks that were not identified but are likely to be hydroxo- or halo-bridged dimeric species. Samples of pH 13 were injected directly to avoid thermal reaction after neutralization; the eluent has adequate buffering capacity to allow this.

Peaks were identified by their elution times, measured by using authentic samples of the compounds. Quantitative analyses were based on peak areas determined by cutting and weighing or triangulation in combination with the molar absorptivities at 265 nm given in the caption to Figure 1; estimates of the random error in the final data are given in Table I. The uncertainty in the S/N bonding ratios was made large by the unfortunate coincidence that the minor isomer has the considerably lower molar absorptivity at all possible analysis wavelengths.

Photolysis Apparatus. Radiation from an Osram 100 W high-pressure mercury arc lamp was filtered through a Bausch and Lomb high-intensity monochromator set at 313 nm. Light intensity was measured by ferrioxalate actinometry[35,36] to be 8×10^{-8} einstein s^{-1}. Solutions were irradiated in 1-cm rectangular quartz spectrophotometer cells in a cell compartment with magnetic stirring and thermostated by a Lauda refrigerated circulating bath.

Solution Handling and Procedures. Most studies were carried out in aqueous solution at pH 13 to avoid interference by the thermal anation of photoproduced aquo complex. This was not possible where calcium thiocyanate was used so these thermal and photochemical experiments were carried out at −4 °C (the solutions froze only at about −10 °C).

In photolysis experiments, complex concentration was typically 5×10^{-3} M. The desired salt was added to give a usual thiocyanate concentration of 2 M. Higher concentrations interfered with the chromatographic analysis by causing serious peak splitting, particularly on early-eluting peaks, while much lower concentrations were insufficient to give significant photoanation yields. Solutions were photolyzed to conversions between 20 and 80%; such high figures were mandated by the inefficiency of photoanation, which occurs for only 10–20% of the molecules photolyzed. In all experiments dark blanks were analyzed along with the photolyzed solutions, and a number of experiments were carried out in which photolyzed solutions were analyzed and then allowed to react thermally for a period prior to reanalysis.

Solutions were analyzed by chromatography on 10-μL samples. Good separations and quantitative analyses were possible for all the starting materials and for the S- and N-bonded anation products; the precision of analysis for the aquo complex produced was less satisfactory as it eluted very early and was split, leading to much uncertainty in the estimation of its area and therefore in the derived ratios of aquation to anation.

Results

Photoanation has been reported[15] for irradiation of some of these complexes in acidic or neutral solutions, but under such conditions the process can be accompanied by the relatively facile production of anation products via secondary thermal reactions of the dominant photoproduct, aquopentacyanocobaltate(III). To be certain that direct photoanation does occur, and to be able to measure the S/N bonded isomer ratios for the process without the need for large thermal corrections, we decided to carry out the main experiments in strongly basic solution. This was in the expectation that thermal anation of hydroxopentacyanocobaltate(III) would be much slower than that for the aquo species.

Thermal Anation Reactions. The foregoing supposition was supported by our preliminary measurements and by published data that appeared during the course of this work. A 1.0×10^{-2} M solution of $[Co(CN)_5OH]^{3-}$ at pH 13 with 2 M sodium thiocyanate was allowed to react thermally at 23 °C for 155 min and then analyzed chromatographically. A small peak corresponding to the S-bonded thiocyanato product was observed; the other isomer was too small to be observed.

Quantitation of the product peak lead to a bimolecular rate constant for the thiocyanate anation of 2×10^{-5} M^{-1} s^{-1} under these conditions. Burnett and Gilfillan[7] report that thermal anation of the aquo species by thiocyanate at 40 °C follows the rate law $k_e = 6.33 \times 10^{-4}/(1 + 0.272[NCS^-])$, giving a value of 4×10^{-4} M^{-1} s^{-1} for 2 M thiocyanate. The pK_a for $[Co(CN)_5(H_2O)]^{2-}$ has been measured as 10.6 and 10.5 ± 0.5. Therefore, 0.3% of the hydroxo compound is in the thermally reactive aquo form at our working pH, which would correspond to an effective rate constant of 1.3×10^{-6} M^{-1} s^{-1} at 40 °C if all the reactivity were to occur via the aquo complex. Assuming that our larger experimental value for the rate constant at a lower temperature is correct, the comparison suggests that the hydroxo complex itself thermally anates, despite the uncertainties and approximations in this analysis.

For our purposes, the more important aspect of these results is that thermal anation of the hydroxo complex is very slow on the scale of our photolysis experiments. Thermal formation of anation products via photoproduced hydroxo complex must therefore be negligible during the 0.5–3-h irradiation times required for the photoanation runs.

It remains to show also that direct thermal anation of the acidopentacyanocobaltates(III) is not a serious distorting factor. Experiments with the bromo, iodo, and azido complexes showed these did not thermally anate unless left to react for long periods. The mechanisms of these slow processes were not pursued. The chloro compound was the most reactive of the series studied; it anated with an effective rate constant of 1.5×10^{-5} M^{-1} s^{-1} at 23 °C. The thermal rate of anation corresponding to this is a factor of 10 smaller than the photochemical rate of anation for our conditions, so while some thermal production of products does occur, it does not significantly influence measurements of the S/N bonding ratio for the photoproducts.

Photochemical Anation. Each of the four acidopentacyanocobaltates(III) and the hydroxo pentacyano compound were irradiated at room temperature (24–27 °C) for times sufficient to produce adequate anation product for chromatographic analysis. Aliquots were taken at intervals and analyzed chromatographically. In a number of experiments, photolyzed solutions were kept in the dark for periods up to 2 h and reanalyzed chromatographically. In all cases the results were indistinguishable from those obtained with immediate analysis, demonstrating that thermal reactions were not distorting the results during or after photolysis. The data are collected in Table I.

It was important to examine whether the observed S/N ratios might be influenced by secondary photolysis. Using the pragmatic approach to this, it was noted that, within the rather large variability of the values, the measured S/N ratios were independent of photolysis time except for extensive photolysis of the weakly absorbing chloro compound. The variability observed had its main origin in the very small size of the chromatographic peak for the N-bonded isomer, which was correspondingly difficult to quantify the precision.

For the azido and iodo complexes, the molar absorbances (all in L mol^{-1} cm^{-1}) at the irradiation wavelength of 313 nm are very much higher, at 1930 and 1570 respectively, than those for the photoproducts, which are 400 for the S- and 250 for the N-bonded thiocyanato isomers, respectively, and 183 for the hydroxo com-

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pound. Simple calculations[37],[38] show that secondary photolysis would not be a problem.

On the other hand, the bromo and chloro complexes have molar absorbances at 313 nm of 424 and 100, respectively. For the chloro compound in particular, this allows absorption by the major hydroxo and the minor thiocyanato species at relatively low conversions. A small amount of secondary photolysis of the hydroxo-compound would not distort the S/N ratio in a significant way as it gives (Table I) essentially the same S/N ratio as the other complexes. Secondary photolysis of the thiocyanate products would be more of a problem. The more strongly absorbing S-bonded isomer could be expected to photoaquate, lowering the S/N ratio. Where such a decrease at high conversion was observed, the results were rejected. At the conversions used, the bromo compound gave consistent, trend-free results.

The results in Table I show that direct photoanation occurs in pH 13 photolyses of all these compounds and that the anation products are produced in an S/N bonded ratio of 9/1 across the series. In contrast to this, the ratio that we observe for the thermal reactions in basic solution is constant at just over 4/1, consistent with the value of 20% N-bonded isomer reported[10] for azidopentacyanocobaltate(III) in acid solution.

Effect of Cation. The effect of cation on the photoanation could not be properly investigated in basic solution, since the more interesting cations of higher charge precipitate out as hydroxides or hydrous oxides. These experiments therefore required work in acid medium at lower temperatures to inhibit the interfering thermal anation. So far, only calcium has been studied.

Solutions of $[Co(CN)_5N_3]^{3-}$ were irradiated for 45, 83, 121, and 174 min at −4 °C in the presence of 1 M calcium thiocyanate at pH 7. The observed S/N ratio was 9.5 ± 1.2 (9 runs), which is the same within experimental error as the ratio observed for the data in alkaline medium with sodium ion. Experiments on solutions reacted thermally for long times, including postphotolysis thermal reactions, showed that the results were not being distorted by thermal reactions. It was observed that there was a small decrease in the relative efficiency of photoanation with calcium present. This result undoubtedly reflects the lower cation concentration present at constant thiocyanate concentration and demonstrates that the cations do play an important role in facilitating interaction of the negatively charged reactants. Future studies will explore these aspects in more detail than has been possible so far.

Flash Photolysis. In separate experiments carried out with the picosecond flash-photolysis apparatus at Concordia University (Montreal), the iodo-, azido-, and thiocyanatopentacyanocobaltate(III) compounds were excited in aqueous solution with a 2.5-mJ, 355-nm, 30-ps pulse. The resulting transient absorption was examined in the wavelength range 425–675 nm over the time range 20 ps to 5 ns.

The thiocyanato compound gave no significant transient absorption. Very weak transients (0.02–0.04 A) were seen for the other two compounds, but they were very broad, extending over the whole spectral range examined. For both compounds, the dominant absorption seen was consistent with inefficient generation of some solvated electrons. It decayed completely in less than 5 ns for the azido complex, but about one-third remained at 5 ns for the iodo compound. This could just reflect the concentrations of adventitious electron-scavenging impurities in the two solutions. For the azido compound there might have been a residual absorption at 475 nm but this was much smaller than the uncertainties in the measurements. No transients that could be assigned to photochemical intermediates or precursor electronically excited states were therefore positively identified. The significance of this is discussed later.

Discussion

Table I includes data for the S/N ratios observed for the thermal anation of iodo pentacyano, bromo pentacyano, and chloro pentacyano starting complexes; a ratio of about 4.5 is found for all three, and this value agrees with an earlier report that the azido complex anates to give about 20% N-bonded isomer.[10]

As explained earlier, since this work was carried out at pH 13, there can be no doubt that the results reflect the direct anation of the complexes in question and cannot arise by aquation followed by anation of aquo or hydroxo species.

Observation of a constant ratio of S/N bonding of 4, independent of the nature of the leaving group, adds further evidence for the importance in the thermal anation reactions of a dissociative step involving a five-coordinate intermediate common to all precursors, as has been proposed on other grounds discussed in the introduction. The geometry of this intermediate has been considered on theoretical grounds to be square pyramidal,[39],[40] as rearrangement to a trigonal-bipyramidal species would be expected to be energetically unfavorable.

Our fragmentary observations of the ratio of aquation to anation in the thermal reactions suggest that aquation is significantly more rapid than anation; ratios of about 15/1 and 70/1 were observed for the azido and chloro compounds, respectively, in 2 M sodium thiocyanate solutions. This result probably reflects both the higher molarity of the water and the unfavorable Coulombic term for the nucleophilic attack of the thiocyanato ligand. When these factors are allowed for, it can be seen that, on an equal footing, water and the thiocyanate ion are roughly equivalent as nucleophiles. However, there is an important role for the leaving ligand, and probably for the cation, phenomena that invite more detailed investigation.

The photochemical results of Table I contrast with the thermal behavior in two ways. First, the yield of aquo product is relatively smaller and shows less variation with the nature of the leaving ligand. It amounts to between 80% and 90% of the total reaction for all complexes studied. Second, the S/N ratio for the thiocyanato products of anation is constant within experimental error at a different value of 9 ± 1.5. We cannot exclude the possibility of a small variation in this ratio for different complexes because our data are unfortunately not yet sufficiently precise. Nevertheless, any variation would have to be a second-order effect. We proceed on the basis that the photochemical anation leads to a constant S/N isomer ratio which is clearly larger than that for the corresponding thermal process.

The constancy of the ratio supports the contention that the photochemical reaction also is dissociative in nature, involving a common, presumably five-coordinate, intermediate, across the series. This intermediate behaves differently from that for the thermal reaction, however, as shown by its different reactivity with the S or N atoms of the thiocyanate ligand. The question immediately arises as to whether this intermediate can be directly observed.

Low-temperature spectroscopic studies[41],[42] of hexacyanocobaltate(III) have provided transient absorption spectra and emission lifetimes for a species that has been assigned as the triplet state of the molecule. The transient absorption consists of a structured band with the main peak at 460 nm. The lifetime of the state is short, 22 μs, even at 94 K, and it decreased to less than 30 ns at about 220 K, at which temperature photosolvation was occurring. The reasonable implication is that the immediate precursor to reaction is the triplet state. In other work, recent observations using picosecond techniques have identified charge-transfer absorptions assignable to parent triplet states of cobalt ammine complexes[43],[44] that could be expected to dissociate to the kind of species envisioned here. We therefore thought it useful to search for similar transients by picosecond spectroscopy

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under photochemical conditions. Unfortunately, we were unable to observe any analogous picosecond absorptions in any of these cyano complexes or in hexacyanocobaltate(III). This could be because any transient species are too weakly absorbing, but it seems more likely that they are too short-lived to be observed. The failure to observe them is therefore disappointing but not an argument against their possible existence.

A number of previous workers have considered the question of the nature of any intermediates in the photochemical reaction. Adamson et al. found[13] that the photochemical intermediate showed competition ratios for different anions similar to those for the thermal species. In contrast to us, they found that scavenging of the intermediate by solvent water was relatively favored in the photochemical reaction compared to the thermal (of course, their temperature and pH conditions were very different from ours). They concluded that the intermediate was the same for both reactions and that the differences in behavior observed had their origin in cage recombination processes promoted by cations. They proposed that the photochemical intermediate was initially square pyramidal in nature and therefore subject to rapid cage recombination but that it could evolve to a trigonal-bipyramidal configuration of longer lifetime that could discriminate between various nucleophiles. These suggestions are consistent with theory.[39]

Viaene et al.[25] similarly concluded, from a study of the thermal and photochemical reactions of aquopentacyanocobaltate(III) with azide, iodide, and hydrazoic and hydrocyanic acids, that there was a difference in the behavior of the thermal and photochemical intermediates. Milder et al.[26] interpreted their scavenging ratios in terms of reaction of singlet $[Co(CN)_5]^{2-}$ in both cases but with the differences arising from the intermediacy in the photochemical reaction of the triplet state of the intermediate.

The behavioral difference between the intermediates in the photo and thermal processes is further demonstrated by our observation of different S/N ratios for the two pathways. The favoring of S coordination by the photochemical intermediate suggests to us, however, that a species of greater polarizability is involved in the photochemical reaction. Since ground-state five-coordinate intermediates of different geometries are not likely to differ greatly in polarizability, since the triplet excited-state intermediates are likely to be energetically accessible and to be more polarizable, and since the available picosecond evidence suggests the photochemical reaction is very rapid, we think it reasonable to conclude that the photochemical reaction occurs via a five-coordinate species in the triplet excited state. Such intermediates have been shown to be involved in the photochemistry of Rh(III) and Ir(III) systems, in which they provide a route for the stereochemical rearrangements observed in the photochemistry of these complexes.

We consider that the photochemical intermediate is reacting with thiocyanate while still in the triplet excited state, corresponding to a one-electron configuration of the $t_{2g}^5 e_g^{*1}$ type. The transition to the ground state would presumably occur during the course of such a reaction. The triplet-state intermediate could reasonably be expected to show a preference for sulfur coordination over the ground-state analogue; this can be imagined to arise in two ways. In the first place, it would be more polarizable, i.e. softer, than its ground-state analogue and therefore would prefer coordination to the soft end of the thiocyanate ligand to a greater extent. This would also be consistent with the lower proportion of aquation seen for the photochemical reaction. Also, since they should be larger, the frontier orbitals of the cobalt excited state can interact with the S lone pair at longer range than the ground state, conferring a kinetic preference for S coordination in a rapid substitution reaction.

Our data, and also that reported by Adamson et al.,[13] demonstrate a role for the cation in facilitating cage substitution of the negatively charged entering ligand. This is reminiscent of the analogous role of counterions in facilitating electron transfer between ions of like charge; we plan to explore this aspect in more detail in future studies. It also allows an alternative explanation of our findings. If the photochemical reaction occurs predominantly by a cation-assisted cage recombination, it could be that the alteration in the photochemical S/N ratio that favors S coordination arises because of orientation of the entering thiocyanate by the cation. Assuming that the nitrogen end of the ligand would preferentially orient toward the cation, this could favor coordination by the free S end of the ligand. It is not clear, however, why such a mechanism would lead to a greater anation to aquation ratio for the photochemical reaction. We plan to undertake further experiments to further explore these possibilities.

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Registry No. $K_3[Co(CN)_5Cl]$, 14705-98-7; $K_3[Co(CN)_5Br]$, 14650-10-3; $K_3[Co(CN)_5I]$, 14650-11-4; $K_3[Co(CN)_5N_3]$, 14705-99-8; $K_3[Co(CN)_6]$, 13963-58-1; $K_2[Co(CN)_5(H_2O)]$, 14709-63-8; $[Co(CN)_5(SCN)]^{3-}$, 22258-10-2; $[Co(CN)_5(NCS)]^{3-}$, 19584-48-6; $K_3[Co(CN)_5OH]$, 42126-43-2; NaSCN, 540-72-7; $Ca(SCN)_2$, 2092-16-2.