

Specific Cation Catalysis in the Thiocyanate Photoanation of Acidopentacyanocobaltate(III) Complexes

A. D. Kirk*

Department of Chemistry, University of Victoria, P. O. Box 3055, Victoria, BC, Canada V8W 3P6

Diane M. Kneeland

Department of Chemistry, University of Texas, Austin, Texas 78712

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The thermal anation of $\text{Co}(\text{CN})_5\text{Br}^{3-}$ by 2 M thiocyanate ion at 22 °C in 0.1 M NaOH proceeds by two pathways. Direct anation occurs with a pseudo-first-order rate constant of about $8 \times 10^{-6} \text{ s}^{-1}$, while anation of $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ in equilibrium with $\text{Co}(\text{CN})_5(\text{OH})^{3-}$ formed by the concurrent base hydrolysis of $\text{Co}(\text{CN})_5\text{Br}^{3-}$ occurs with a pseudo-first-order rate constant of $2.15 \times 10^{-6} \text{ s}^{-1}$. The thiocyanate anation product obtained shows an overall S:N-bonded linkage isomer ratio of 4.5 ± 0.2 . Measurements of the product S:N linkage isomer ratio and of the ratio of aquation to anation were obtained for photosubstitution of $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ at 5 °C and pH 13 in 2 M aqueous thiocyanate with various counterions. For the group of singly charged ions Li^+ , Na^+ , K^+ , and NH_4^+ , the aquation:anation ratio ranged from 9.9 ± 1.4 for Li^+ to 2.5 ± 0.5 for NH_4^+ while the range of S:N product ratios was 12.7 ± 1.1 to 10.6 ± 2.6 over the same group. These results reveal a linear relationship between $\ln(\text{aquation/anation})$ and $1/\text{hydrated radius}$, while the S:N ratio is essentially constant. Compared with Li^+ , Ca^{2+} showed the increase in anation efficiency expected on the basis of its higher charge. A constant total quantum yield of 0.073 ± 0.005 was found for photosubstitution of $\text{Co}(\text{CN})_5\text{I}^{3-}$ in $\text{NaClO}_4/\text{NaSCN}$ mixtures of total concentration 4 M, showing that the anation and aquation are competitive processes. The cation apparently assists anation by helping overcome the Coulomb repulsion between the entering thiocyanate and a coordinatively unsaturated intermediate of like charge. The higher S:N ratio for the photoprocess is not a result of the cation assistance but is an intrinsic property of the intermediate, consistent with involvement of the triplet state five-coordinate species theoretically predicted.

Introduction

The influence of ion pairing and other intermolecular interactions on properties of charged species is a subject that has attracted long-standing interest.^{1–3} The effects can be marked and can include the appearance of new spectral bands owing to charge transfer between paired ions^{4,5} which can, in turn, lead to new photochemistry and photophysics of the species of interest. Such interactions are most recently of interest with respect to their involvement in certain kinds of supramolecular assemblies.⁶ In addition, the general effects of ionic strength on reactions and specific catalysis by ions have a long history of use as means to study mechanisms. It is this aspect that is of importance in the present paper which describes some further investigations of photosubstitution in acidopentacyanocobaltate(III) complexes.

It was reported earlier⁷ that the thiocyanate photoanation of some $\text{Co}(\text{CN})_5\text{X}^{3-}$ complexes, X = CN, OH, Cl, Br, I, and N_3 , show a ratio of S- to N-bonded linkage isomer anation product of 9.0 ± 1.5 , independent of the leaving group X and twice the value of 4.5 ± 0.2 found for the thermal reactions. In addition, for a given thiocyanate concentration, there is a leaving group

independent aquation to anation product ratio. These results were attributed to the participation in the photoreaction of a coordinatively unsaturated intermediate that is different from that for the ground state reaction; this was proposed to be the five-coordinate triplet state species predicted⁸ theoretically.

It was recognized, however, that this interpretation might be invalid if cations catalyze and therefore serve to direct this photosubstitution process. The possibility of such effects is suggested by an early study⁹ of photoaquation of $\text{Co}(\text{CN})_5\text{I}^{3-}$. There, addition of sodium ion to the solution reduced the quantum yield by promoting recombination of the solvent-caged primary fragments $\{\text{Co}(\text{CN})_5^{2-\cdots}\cdot\text{I}^-\}$. Counterion-influenced rates are also well-established for electron transfer reactions between like-charged ions. Thus, as one example, sodium and potassium cations have an accelerating influence on electron transfer in the manganate/permanganate reaction,¹⁰ faster rates being observed in the presence of potassium than with sodium ions. Apparently the determining parameter in this specific ion catalysis is the hydrated cation radius.

The present paper describes work undertaken to test for the possibility of such cation assistance in the photosubstitution reactions of $\text{Co}(\text{CN})_5\text{X}^{3-}$ and to explore its possible influence on both the anation:aquation product ratio and the S:N linkage isomer ratio for the anation product formed in the presence of added thiocyanate.

* Author to whom correspondence should be addressed.

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- (1) Davies, C. W. *Ion Association*; Butterworths: London, 1962.
- (2) Beck, M. T. *Coord. Chem. Rev.* **1968**, *3*, 91–115.
- (3) Perlmutter-Hayman, B. *Prog. React. Kinet.* **1971**, *6*, 240–267.
- (4) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1562–1571.
- (5) Balzani, V.; Sabbatini, N.; Scandola, F. *Chem. Rev.* **1986**, *86*, 319.
- (6) Balzani, V.; Scandola, F. *Supramolecular photochemistry*; Ellis Horwood, Chichester, England, 1991.
- (7) Kirk, A. D.; Kneeland, D. M. *Inorg. Chem.* **1989**, *28*, 4274–4278.

- (8) Vanquickenbourne, L. G.; Ceulemans, A. *Inorg. Chem.* **1978**, *17*, 2730–2736.
- (9) Adamson, A. W.; Chiang, A.; Zinato, E. *J. Am. Chem. Soc.* **1969**, *91*, 5467–5475.
- (10) Spiccia, L.; Swaddle, T. W. *Inorg. Chem.* **1987**, *26*, 2265–2271.

Experimental Section

Materials. The following thiocyanate salts were used without further purification: sodium (Aldrich), lithium (Aldrich), potassium (BDH), ammonium (Aldrich), and calcium (GFS, reagent grade). HPLC eluents were prepared as described⁷ using HPLC grade methanol (Fisher), organopure water (Barnsted/Sybron system), hexylamine (Aldrich, 99%), and citric acid monohydrate (Sigma).

Preparation of Complexes. The compounds $K_3[Co(CN)_5X]$, $X = N_3, Cl, Br, I,$ and SCN , were prepared by literature methods and characterized by their UV-vis and IR spectra as reported earlier.^{7,11} The purity of the compounds was established both by chromatography and by their UV-vis molar absorptivities. The N-bonded thiocyanate isomer was obtained by methylene chloride extraction of the product obtained from the Burmeister reaction¹² (this gave about 95% S-, 5% N-bonded product by chromatography) or by thermal thiocyanate anation¹³ of aquopentacyanoocobaltate (80% S-, 20% N-bonded product).

The complex $[Co(CN)_5(H_2O)]^{2-}$ was synthesized by complete photolysis of $[Co(CN)_6]^{3-}$ at 313 nm. A solution of 150 mg of $K_3[Co(CN)_6]$ in 50 mL of distilled water was irradiated at 313 nm (Hanovia 100W high-pressure mercury lamp/Bausch Lomb high-intensity monochromator/15 cm water filter) with magnetic stirring. The photoaquation was followed by the decrease in the absorption of $Co(CN)_6^{3-}$ at 313 nm and the growth at 380 nm due to $Co(CN)_5(H_2O)^{2-}$. After 24 h, the reaction was complete. The HCN was then CAUTIOUSLY removed from the solution by acidifying to pH 2 with $HClO_4$ in a flask with a nitrogen stream leading to a bubbler filled with 10 M NaOH to safely absorb the toxic gas. The aqua pentacyano complex could not be isolated as a solid except as a silver salt, which is quite unstable. It was therefore prepared in solution and HPLC used to assess its purity. A small, strongly retained peak which had a UV-vis absorption maximum at 380 nm was present in the chromatogram of these solutions. This peak disappeared when the mixture was photolyzed further, irradiating at 360 nm. The long retention time of the peak suggests that it has a high charge; it is likely to be the polymeric or dimeric species reported¹³ in the preparation of the aqua pentacyano complex and observed chromatographically.¹⁴

Chromatographic Analysis. The chromatographic analysis was carried out using a C_{18} reversed-phase column with methanol and water eluents modified with ion interaction reagents as described earlier.⁷ The starting materials and all products gave baseline resolved peaks, identified by the elution times of authentic samples. The complex, $Co(CN)_5(H_2O)^{2-}$, which eluted first, was detected by its UV-vis absorption at 380 nm. The large interval between this peak and the next to be eluted allowed time to change the detector wavelength to 265 nm and rezero the baseline to detect all other species with greater sensitivity. The limiting factor for the measured S/N ratios was the measurement of $Co(CN)_5(SCN)^{3-}$ which eluted last and also had the lower 265 nm molar absorptivity, $2.34 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ versus $1.71 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ for the S-bonded isomer.¹⁵ A typical chromatogram has been published.⁷

Thermal Kinetics. The thermal reactions of the acidopentacyanoocobaltates were studied in 2 M sodium thiocyanate and 0.1 M sodium hydroxide at $22 \pm 0.1 \text{ }^\circ\text{C}$. For example, 10.6 mg of the iodo pentacyano complex was dissolved in 2 mL of the above medium to give a concentration of $1.2 \times 10^{-2} \text{ M}$ and thermostated in the dark. Aliquots of the sample were removed every 20 h or so for a total of about 8 and analyzed by HPLC.

The thermal reaction of the hydroxo complex was carried out as follows. The concentration of the solution of aqua pentacyano complex prepared as above was determined from its UV-vis absorbance at 380 nm and the known⁹ molar absorptivity ($280 \text{ L mol}^{-1} \text{ cm}^{-1}$). Then 500 μL of this solution was mixed with 500 μL of a solution 4 M in sodium thiocyanate and 0.2 M in sodium hydroxide, both solutions having been

brought to $22 \text{ }^\circ\text{C}$ before mixing. Aliquots, 100 μL , were removed at 20 min intervals for 2 h and analyzed by chromatography.

Photochemical Experiments. Except as noted below, photolyses were carried out in 0.1 M NaOH and at 5 or $10 \text{ }^\circ\text{C}$. Under these conditions, the major photoproduct is $Co(CN)_5(OH)^{2-}$, since $pK_a - (Co(CN)_5(H_2O)^{2-}) = 10.5$. This conjugate base form anates at a negligible rate, so this minimizes the problems which would arise otherwise because of rapid thermal anation of the major photoproduct. The unavoidable exception to this procedure was the measurement for calcium thiocyanate, mentioned in the earlier paper, which had to be carried out at neutral pH, to avoid precipitation of calcium hydroxide. The experiment was therefore done at $-4 \text{ }^\circ\text{C}$, just above the solution freezing point, to minimize the thermal anation of the $Co(CN)_5(H_2O)^{2-}$ photoproduct.

The total quantum yield for each of the complexes was calculated from the rate of conversion of the starting material, measured chromatographically, and the rate of photon absorption, measured using ferrioxalate actinometry.^{16,17} Because photoaquation dominates in these experiments, it was necessary to work at high conversions in order to produce sufficient minor N-bonded anation product to permit determination of the S/N ratio. For the bromo and chloro pentacyano complexes, with approximate molar absorptivities at 313 nm of 500 and $100 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively, this was difficult, but it was successful for the more strongly absorbing azido and iodo pentacyano systems, 2.0×10^3 and $1.5 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. Thus for the iodo pentacyano complex, a graph of product formation versus time was linear up to 80% conversion. This can be attributed to the low light absorption by the major products $Co(CN)_5(OH)^{2-}$, with irradiation wavelength molar absorptivity of about $200 \text{ L mol}^{-1} \text{ cm}^{-1}$, and $Co(CN)_5(SCN)^{3-}$, which represents only 10% of the total product and has a molar absorptivity at 313 nm of about $460 \text{ L mol}^{-1} \text{ cm}^{-1}$. $Co(CN)_5(OH)^{2-}$ has been reported¹⁸ to aquate cyanide with a quantum yield of 0.06 at 313 nm, but calculation¹¹ shows that any losses by secondary photolysis would be a maximum of 4% even at the highest conversions (50%) employed here. Because of this, the photochemical studies were carried out using the iodo and azido pentacyano compounds.

The influence of the counterion on the thiocyanate/water competition ratio for the photosubstitution reaction of 0.004 M $Co(CN)_5I^{3-}$ was explored using 2 M sodium, lithium, potassium, and ammonium and 1 M calcium thiocyanates, the latter at $-4 \text{ }^\circ\text{C}$ in neutral solutions. Aliquots were removed at various irradiation times corresponding to 10–50% conversion, and the products were analyzed by HPLC. Attempts were made to include tetrabutylammonium thiocyanate, but this reagent generated large, broad impurity peaks in the chromatograms which completely obscured the product peaks. Our attempts to purify this very hygroscopic compound by recrystallization merely aggravated this problem.

To determine the effect of concentration of thiocyanate on the total quantum yield and on the aquation to anation ratio, similar experiments were carried out using 0.01 M $Co(CN)_5N_3^{3-}$ (the most strongly absorbing complex at 313 nm). The concentration of sodium thiocyanate was varied from 0 to 4 M, while the ionic strength was held constant at 4 M by the addition of sodium perchlorate.

Results

Thermal Anation Reactions. The original purpose of these experiments was to establish that the formation of thermal products is negligible on the time scale of the photochemical reaction. It was also of interest, however, and pertinent to the reported constancy of the thermal S:N ratios,^{7,19} to determine the extent to which the acido pentacyano compounds thermally anate by direct reaction with thiocyanate as opposed to the route via consecutive anation of $Co(CN)_5(H_2O)^{2-}$ in equilibrium with

(11) Kneeland, D. M. Doctoral Dissertation Thesis, Victoria, 1991.

(12) Burmeister, J. *Inorg. Chem.* **1964**, *3*, 919–920.

(13) Haim, A.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1961**, *83*, 509–516.

(14) Burnett, M. G.; McCullagh, J. F. *Inorg. Chim. Acta* **1990**, *169*, 31–37.

(15) Gutterman, D. F.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3364–3371.

(16) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. (London) A* **1956**, *235*, 518.

(17) Kirk, A. D.; Namasivayam, C. *Anal. Chem.* **1983**, *55*, 2428–2429.

(18) Wrighton, M.; Bresenden, D. *Inorg. Chem.* **1973**, *12*, 1707–1709.

(19) Abou-El-Wafa, M. H. M.; Burnett, M. G.; McCullagh, J. F. *J. Chem. Soc., Dalton Trans.* **1986**, 2083–2089.

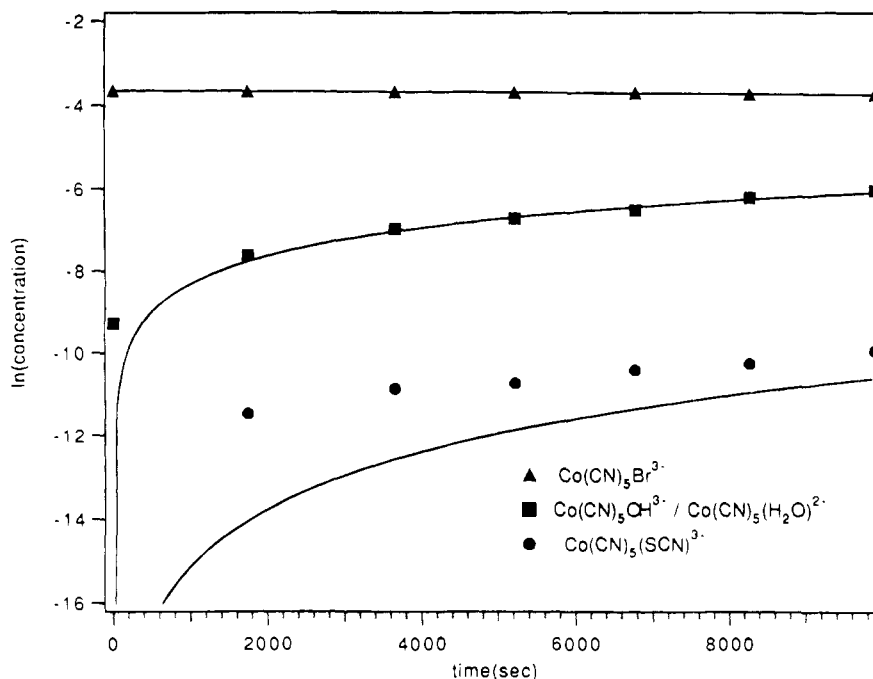
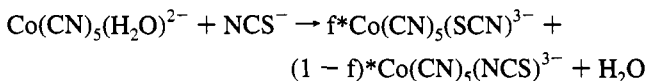
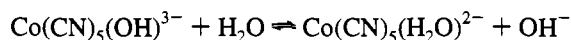
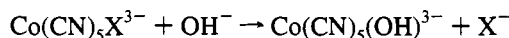


Figure 1. Model curves and experimental points for the anation of 0.0262 M $\text{Co}(\text{CN})_5\text{Br}^{3-}$ in 2 M NaSCN and 0.1 M NaOH at 22 °C. Points are experimental and solid lines are calculated for two consecutive pseudo-first-order processes with $k_1 = 9.4 \times 10^{-6}$ and $k_2 = 2.15 \times 10^{-6} \text{ s}^{-1}$.

$\text{Co}(\text{CN})_5(\text{OH})^{3-}$ product; that is,



The same question arises in connection with the thermo- and photoanation of $\text{Co}(\text{CN})_5(\text{OH})^{3-}$ itself. In an experiment reported in the previous paper,⁷ an overall rate for the thermal anation of $\text{Co}(\text{CN})_5(\text{OH})^{3-}$ was measured at 23 °C in 2 M sodium thiocyanate, and by comparison to published results for the corresponding anation of $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ at 40 °C, it was concluded that direct anation of $\text{Co}(\text{CN})_5(\text{OH})^{3-}$ occurs. However, the 23 °C rate constant on which that conclusion was based, $2 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$, was wrong because of an error in calculation. In the present work, the experiment was therefore repeated, and additional measurements were made for those $\text{Co}(\text{CN})_5\text{X}^{3-}$ that show measurable thermal reactions at room temperature, namely for $\text{X} = \text{Cl}, \text{Br},$ and I .

The pseudo-first-order rate constant for thiocyanate anation of $\text{Co}(\text{CN})_5(\text{OH})^{3-}$ in 2 M thiocyanate and 0.1 M NaOH was first measured at 40 °C and was $2.4 \times 10^{-6} \text{ s}^{-1}$. This is within 10% of the value we calculate⁷ using literature rate constants for the thiocyanate substitution of the aqua pentacyano complex ($\text{p}K_a = 10.5$) in equilibrium with hydroxopentacyanocobaltate. This shows that direct anation of the hydroxo pentacyano complex does not compete with the route via the aqua pentacyano complex, even at pH near 13.

The complexes $\text{Co}(\text{CN})_5\text{X}^{3-}$, $\text{X} = \text{OH}, \text{Cl}, \text{Br},$ and I , were allowed to base hydrolyze (for simplicity referred to as aquation) and anate in the dark at 22 °C in the presence of 2 M NaSCN and 0.1 M NaOH for up to 10^5 s with chromatographic analysis of six or seven aliquots taken at regular intervals. For the three acido pentacyano complexes studied, loss of the starting material was first order and yielded rate constants for their disappearance

of 2.0×10^{-5} , 9.4×10^{-6} , and $3.0 \times 10^{-7} \text{ s}^{-1}$ for chloro, bromo, and iodo pentacyano, respectively. For the hydroxo pentacyano complex, a rate constant for thiocyanate anation of $1.1 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$ was obtained, a factor of 20 lower than reported earlier.⁷

Given these measured rate constants, the product versus time curves for the three acido complexes calculated using the integrated equations for two consecutive pseudo-first-order reactions, above mechanism, can be compared to the measured product concentration/time behavior. The results are shown for $\text{Co}(\text{CN})_5\text{Br}^{3-}$ in Figure 1, where the solid lines are the calculated concentrations. This comparison shows that there is significantly more thiocyanate product than would be expected by the above secondary anation route and indicates a role for direct anation of $\text{Co}(\text{CN})_5\text{Br}^{3-}$. Taking the thiocyanate product concentration difference between calculated and experiment leads to an initially linear growth with first order rate constant $8 \times 10^{-6} \text{ s}^{-1}$, corresponding to a second order rate constant for direct thiocyanate anation of $4 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$. Figure 1 shows that this direct process remains dominant up to at least 10% conversion. A similar result was found¹¹ for the chloro pentacyano complex, but the iodo pentacyano data were more involved, showing more hydroxo and less thiocyanate product than expected by this mechanism. This can result from the low rate constant for aquation of the iodo pentacyano complex, which permits equilibration of the hydroxo and thiocyanate pentacyano products. The latter product has a rate constant for aquation of the same order as the starting complex. The azido pentacyano complex is too stable to measure thermal anation at this temperature. In summary, the present results indicate that, for these complexes, the thermal generation of anation products is complicated by thermal reaction of $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ in equilibrium with $\text{Co}(\text{CN})_5(\text{OH})^{3-}$ as suggested by Burnett.^{20,21} For the chloro and bromo pentacyano compounds, however, there remains good evidence for an important contribution from direct anation. Figure 1 shows also that, over this time domain,

(20) Burnett, M. G.; Gilfillan, W. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1578–1582.

(21) Burnett, M. G. Personal communication.

Table 1. Aquation:Anation and Sulfur-Nitrogen-Bonded Product Ratios for Different Cations in $\text{Co}(\text{CN})_5\text{I}^{3-}$ Photoanation by Thiocyanate^a

cation	hydrated radius (nm)	aq/an ratio (no. measd)	S/N ratio
Li^+	0.6	9.9 ± 1.4 (6)	12.0 ± 1.6
Na^+	0.4	6.4 ± 0.6 (6)	12.7 ± 1.1
K^+	0.3	4.1 ± 0.6 (5)	11.3 ± 1.1
NH_4^+	0.25	2.5 ± 0.5 (3)	10.6 ± 2.5
Ca^{2+}	0.6	5.4 ± 0.4 (4)	9.5 ± 1.2

^a Conditions: Irradiation wavelength 313 nm, temperature 5 °C, complex concentration 0.004 M, 0.1 M NaOH, 2 M thiocyanate. Except Ca^{2+} , see text.

Table 2. Total Photosubstitution Quantum Yield for $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ ^a

[NaSCN] (M)	[NaClO ₄] (M)	tot. quantum yield (no. measd)	aq/an
0	4	0.070 ± 0.03 (5)	
1	3	0.072 ± 0.01 (6)	11.3 ± 1.3
2	2	0.072 ± 0.006 (5)	8.8 ± 1.6
3	1	0.081 ± 0.01 (5)	6.0 ± 1.8
4	0	0.069 ± 0.005 (5)	4.4 ± 0.7

^a Conditions: Irradiation wavelength 313 nm, temperature 10 °C, complex concentration 0.01 M, 0.1 M NaOH.

there is a fairly constant $\text{Co}(\text{CN})_5(\text{OH})^{3-}$ to $\text{Co}(\text{CN})_5(\text{SCN})^{3-}$ ratio again showing that these products are produced in parallel and not consecutively.

Product Distribution in the Photoanation Reactions. The complexes $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ and $\text{Co}(\text{CN})_5\text{I}^{3-}$ were chosen as optimal for the study of the effects of cation nature and concentration on the photoaquation:anation and S:N linkage isomer ratios. This reflects their thermal stability and strong absorption at 313 nm which minimizes secondary photolysis problems even at the high conversions (up to 50%) needed in some of these experiments.

Table 1 presents the measured aquation:anation and product S:N isomer ratios in the photosubstitution of $[\text{Co}(\text{CN})_5\text{I}]^{3-}$ with 2 M thiocyanate ion and the listed cations. The number of measurements made is given in parentheses in column 3. The aquation:anation ratio is seen to show a strong dependence on the cation present, while the S:N ratio in the product remains unchanged within the rather large uncertainties. These arise from two features; first for cations such as lithium, very little anation actually occurs and second, for all the systems, the N-bonded isomer gives only a small peak in the chromatogram, which is therefore hard to quantify reliably. The slightly larger S:N ratios found here than earlier are probably due to the same cause. No trends in aquation:anation or S:N ratios were seen with percent conversion over the range 10–50%.

Table 2 shows the effect on photosubstitution of $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ of changing the concentration of sodium thiocyanate while keeping the total ionic strength constant with sodium perchlorate. The quantum yield for the disappearance of $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ remains constant as the ratio of anation to aquation product increases with increasing thiocyanate concentration. A few experiments with $\text{Co}(\text{CN})_5\text{I}^{3-}$ showed parallel behavior; the total quantum yield of anation plus aquation was 0.080 ± 0.008 in 2 M NaClO₄ and 0.088 ± 0.009 in 2 M NaNCS.

Discussion

The present work was undertaken to explore the role of the cation in these photoanation processes, but it is also necessary to clarify some other specific issues relating to the thermo- and photoaquation and thermo- and photoanation of the $\text{Co}(\text{CN})_5\text{X}^{3-}$ species. Earlier we reported⁷ that photoanation led to a constant

ratio, 9.0 ± 1.5 , of S- to N-bonded thiocyanate-substituted product, independent of the identity of the X ligand in $\text{Co}(\text{CN})_5\text{X}^{3-}$ complexes. A product S/N linkage isomer ratio of 4.5 ± 0.2 for the thermal thiocyanate anation in the same complexes was also reported and was offered as proof that a common intermediate such as $\text{Co}(\text{CN})_5^{2-}$ was participating in all these thermal reactions. The results of the present study caused us concern, as they show that thermal anation via $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ in equilibrium with $\text{Co}(\text{CN})_5(\text{OH})^{3-}$ can make a contribution to the measured S/N ratios even in 0.1 M NaOH. Since conversions of 10–50% were needed to measure the S:N ratios, these could be influenced by anation of $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ as well as by some linkage isomerization. However the data show no trend in thermal S:N ratios with conversion. Together with our modeling of the thermal processes, Figure 1, this suggests that the 4.5 S:N value truly characterizes a common intermediate for the ground state process in the acido pentacyano complexes. The significantly higher S/N product ratios and lower aquation/anation ratio found for the photoreactions are confirmed by the present work.

This photobehavior is consistent with a dissociative pathway for photoreaction via a coordinatively unsaturated intermediate common to all starting complexes used but one that behaves differently from that produced thermally from $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$. We recognized, however, that cation assistance might explain the higher photochemical S/N ratio. It was reported⁹ that, in the photochemistry of $\text{Co}(\text{CN})_5\text{I}^{3-}$, cations reduced the photoaquation yield by promoting back-recombination of the negatively charged photofragments. If cations present in the solution assist photoanation in a parallel way, they could also serve to orient the thiocyanate ion, accounting for the higher and constant S/N ratio observed for the photoprocess. Thus, for example, the cation could prefer to associate with the nitrogen end of the thiocyanate ion, leaving the sulfur end free for binding to a five-coordinate cobalt(III) fragment.

This paper was aimed primarily at exploring this possibility. Photoreaction of $\text{Co}(\text{CN})_5\text{I}^{3-}$ in the presence of 2 M MNCS, for M = Li^+ , Na^+ , and K^+ , and 1 M $\text{Ca}(\text{NCS})_2$ led to the aquation:anation and S:N product isomer ratios shown in Table 1; the ratio of aquation to anation changes from 10 to 4 with decreasing hydrated radius for the three alkali metal ions. The smallest ion studied, NH_4^+ , gives a ratio of only 2.5. The data show that the cation helps thiocyanate ion compete with water as an entering nucleophile and that its effectiveness improves as the hydrated cation radius decreases.

The process almost certainly involves a pre-association prior to the absorption of a photon; all our attempts to measure transient absorption changes for these processes on the picosecond time scale have been unsuccessful, implying very rapid reactions of the intermediates involved and therefore no time for adjustment of the counterion sphere. For the iodide recombination process mentioned earlier, Adamson et al.⁹ have proposed a triple ion is preformed containing the cation, the cobalt(III) complex, and the iodide ion, thus preorganizing the system for reaction the moment the ligand is lost. It is unlikely that the rate of attack of the neutral ligand, H₂O, on the five-coordinate intermediate is influenced by the cations present. More reasonable is that thiocyanate attack is facilitated by the cation. The aquation reaction can then be associated mainly with the free complex, and the anation reaction with those complexes that are ion-paired with cation and form the population base for triplets. There is a continuum of models based on this concept, depending on the reaction mode ratios of the derived putative intermediates. Assume the simple, perhaps

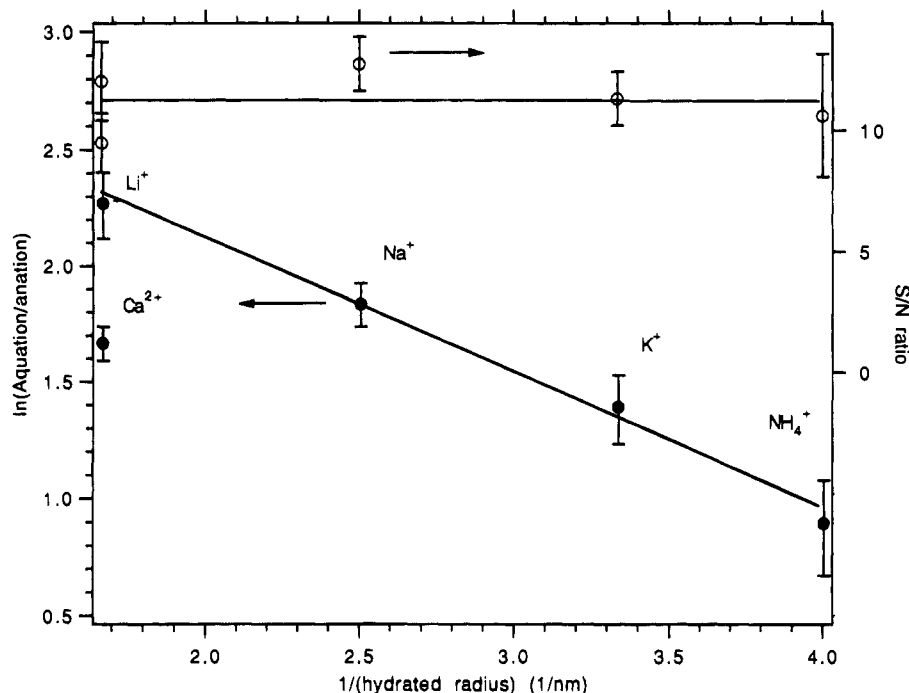


Figure 2. Cation effect on aquation:anation and S:N linkage isomer ratios in photoaquation and -anation of $\text{Co}(\text{CN})_5\text{I}^{3-}$ by 2 M thiocyanate at 5 °C and in 0.1 M NaOH (except Ca^{2+} ; see text).

unlikely, case where the modes are exclusive; only the free complex aquates and the ion-paired complex anates.

This leads directly to an expectation of a logarithmic relationship between the aquation:anation ratio and the reciprocal of the distance between centers in the ion pair formed from the cation, a , and the complex, b . Thus, considering only the electrostatic interaction part, and based on a double sphere model, the free energy change for ion pair formation should show the proportionalities

$$\Delta G \propto z_a z_b / (r_a + r_b) \propto -\ln K_{ip}$$

where $K_{ip} = [\text{Co}(\text{CN})_5^{2-}, \text{M}^+] / [\text{Co}(\text{CN})_5^{2-}][\text{M}^+]$

If the anation/aquation ratio is proportional to the ratio $[\text{Co}(\text{CN})_5^{2-}, \text{M}^+] / [\text{Co}(\text{CN})_5^{2-}]$, it follows that for constant $[\text{M}^+]$, $\ln(\text{aquation}/\text{anation}) \propto z_a z_b / (r_a + r_b)$. Figure 2 shows a plot of $\ln(\text{aquation}/\text{anation})$ against the reciprocal hydrated radius of the cation. For the three alkali metal ions and the ammonium ion, a very good straight line results. Furthermore, the Ca^{2+} point lies below the line as expected for a doubly charged ion which should associate more strongly and enhance anation.

The good linearity of Figure 2 for singly charged ions using cation radius alone implies too small a radius, essentially zero, for the complex ion. The complex anion could contribute less than expected for two reasons. Counterions can occupy pockets²² between the ligands in metal complexes. Also, the hydrated radius of the cations was used as seems appropriate for ion association in aqueous solutions. However, it is possible that, in the photoactive species, the cation desolvates to some extent at the periphery associated with the anion, giving a smaller effective internuclear separation in the ion pair. Figure 2 clearly establishes that the cation does enhance anation and that the trend in efficiency is in reasonable agreement with expectations based on an electrostatic ion-pair model. Pre-association of the cation with the cobalt complex can also account for the increased photochemical capture of thiocyanate relative

to water, because of the partial neutralization of the dinegatively charged intermediate formed upon photoexcitation.

As shown also in Figure 2, the S:N capture ratio for the thiocyanate ligand varies very little over the range of cation radius studied. Although the cation clearly assists the photoanation process, it does so without exerting a significant directing effect on the entering thiocyanate ion. The high S:N photoanation ratio observed is therefore a property of the reaction originating in the photoexcited state.

To further explore this process, experiments were carried out with $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ at constant sodium ion concentration to explore the dependence of the ratio of aquation:anation on thiocyanate concentration. The third ion was perchlorate. The resulting data, Table 2, show the expected increase in anation and decrease in aquation as thiocyanate concentration increases. While this occurs, the total quantum yield of photosubstitution remains constant. Had anation been an additional process, it would have led to a 16% increase in total quantum yield at 2 M thiocyanate, well outside the $\pm 10\%$ uncertainties. Thus the anation and aquation processes are in competition.

The cumulative results reveal the contrast between the thermal and photochemical reactions. The main thermal process is aquation, and direct anation is minor. The question of cation assistance of thermal anation has not been explored. Though it may play a role, the reactivity of the aqua pentacyano product precludes its study. Photochemically 15% of the product is formed by direct anation in 2 M sodium thiocyanate. Thus anation competes more effectively with aquation in the photochemical process which invites explanation. It could reflect the properties of the photochemical intermediate. Theory,²³ and results²⁴ for strong field d^6 complexes, support photoreaction via excited triplet state five coordinate species. These may prefer softer ligands because of greater polarizability, explaining both the preference for anation and for sulfur over nitrogen

(22) Wickramasinghe, W. A.; Bird, P. H.; Serpone, N. *Inorg. Chem.* **1982**, *21*, 2694–8.

(23) Vanquickenborne, L. G.; Ceulemans, A. *Coord. Chem. Rev.* **1983**, *48*, 157–202.

(24) Skibsted, L. H. *Coord. Chem. Rev.* **1989**, *94*, 151–179.

bonding relative to the ground state reaction. If alternatively the same ground state intermediate is involved in both thermal reactions and photoreactions, then the favoring of anation photochemically could arise because the negatively charged leaving ligand is ejected with excess kinetic energy to a position far from the cobalt intermediate. The opportunity for the thiocyanate ion to approach would then be greater, because of reduced electrostatic repulsion.

The first explanation seems to be favored by the cation assistance phenomenon. The formation of ion pairs or triple ion species occurs in the ground state, and therefore, there seems to be no reason why this should favor anation over aquation or S- over N-bonding to markedly different extents between the thermal and photochemical reactions. We conclude, therefore, that the preferential anation and the higher S/N product isomer ratio are both genuine properties of an intermediate produced photochemically in an excited state.

Conclusions. Direct anation occurs in the photosubstitution reactions of $\text{Co}(\text{CN})_5\text{X}^{3-}$ complexes in the presence of thiocyanate ion. Further, the reaction occurs via an intermediate which is competitively scavenged by water and thiocyanate. The thiocyanate approach is assisted by ion pairing of the $\text{Co}(\text{CN})_5\text{X}^{3-}$ with the counterion of thiocyanate leading to formation of an ion triplet between the cobalt complex, the counterion, and thiocyanate. The photochemical pathway shows a higher anation efficiency and a favoring of thiocyanate S-bonding which both likely arise because of reaction via a five-coordinate intermediate in its excited triplet state.

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