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Stereochemistry of the Thermal and Photochemical Reactions of Certain Cyanocobaltate(III) Complexes

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The thermal reaction between *trans*-$Co(CN)_4(SO_3)_2^{5-}$ and $^{13}CN^-$ leads to stereospecific incorporation of the label to form *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$ as shown by ^{13}C NMR. When the reaction is conducted photochemically, random incorporation of the label occurs. The thermal aquation of *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$ at pH 7.5 and 60 °C is very slow and the product contains a completely scrambled label. Complete aquation is not obtained after 198 h. The photochemical aquation of *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$ proceeds smoothly to the scrambled product. Possible mechanisms are discussed.

An unimpeachable diagnosis for a dissociative mechanism would rely upon the detection of an intermediate of reduced coordination. In general, however, the extremely short-lived nature of such an intermediate limits the available information to kinetic data and the stereochemical outcome of substitution reactions. As an example, there is now a great deal of kinetic evidence that the hydrolytic reactions of $Co(NH_3)_5X^{n+}$ and $Co(en)_2LX^{n+}$ involve a dissociative mechanism.[1] Buckingham and his colleagues were able to demonstrate using ^1H NMR that the hydrolyses of *trans*-$Co(ND_3)(NH_3)_4X^{n+}$, induced by NO^+ or Hg^{2+}, are accompanied with full retention of configuration.[2] These results are consistent with an intermediate whose geometry is that of a tetragonal pyramid, a structure which had been previously proposed.[1] Similarly, the partial loss of configuration[3] that occurs during the base hydrolysis of *trans*-$Co(^{15}NH_3)(NH_3)_4X^{n+}$ is consistent with a preference for a trigonal-bipyramidal intermediate which had been proposed in that reaction.[1] It is noteworthy that the introduction of $^{15}NH_3$ is possible[3,4] because of the lability of the NH_3 group trans to the S-bonded sulfite ligand in $Co(NH_3)_5SO_3^+$. The subsequent reaction of the labeled trans complex with aqueous HX led to *trans*-$Co(^{15}NH_3)(NH_3)_4X^{n+}$.

Turning attention to the cyanocobaltate(III) complexes, *trans*-$Co(CN)_4(SO_3)_2^{5-}$ and $Co(CN)_5OH_2^{2-}$, Wilmarth and his group have presented kinetic evidence that the thermal substitution reactions of these complexes proceed by a dissociative pathway.[5-9] Furthermore, the photosubstitution reactions of cyanocobaltates, with the exception of $Co(CN)_6^{3-}$,[10] have been predicted to proceed by an identical mechanism.[11-13] However, the stereochemical outcome of these reactions is unknown.

If $^{13}CN^-$ can be introduced stereospecifically into *trans*-$Co(CN)_4(SO_3)_2^{5-}$ or its aquation product, *trans*-$Co(CN)_4(SO_3)OH_2^{3-}$, then ^{13}C NMR should lead to a greater understanding of the reactions of $Co(CN)_5SO_3^{4-}$. This report focuses attention on the stereochemical results from the following reactions. Both thermal substitution and photosubstitution were studied in each case (see eq 1 and 2).

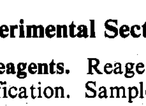
$$Co(CN)_4(SO_3)_2^{5-} + CN^- \rightarrow Co(CN)_5SO_3^{4-} + SO_3^{2-} \quad (1)$$

$$Co(CN)_5SO_3^{4-} + H_2O \rightarrow Co(CN)_5OH_2^{2-} + SO_3^{2-} \quad (2)$$

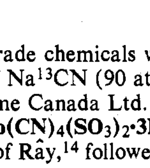
The results in each case are deduced from the ratio of the integrated intensities of the resonances due to the $^{13}CN^-$ groups which are trans and cis to a unique group, i.e., I_T/I_C. Calculations based on statistics show that $I_T/I_C = E_T/4E_C$, where E_T and E_C are the fractional abundances of $^{13}CN^-$ at the trans and cis sites, respectively. If $^{13}CN^-$ is in natural abundance at both sites, then $I_T/I_C = 0.25$. An identical value would be obtained if complete and random loss of configuration occurs during the reaction of a stereospecifically enriched complex. Stereospecific enrichment at the trans site leads to $I_T/I_C = E_T/0.044$ since the fractional natural abundance of ^{13}C available to the cis sites is 0.011. If partial, random loss of configuration occurs, the mole fraction of labeled material in which stereospecific enrichment remains is given by

$$nE_T/0.044 + (1 - n)0.25 = (I_T/I_C)_{obsd}$$

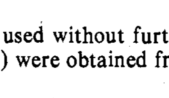
Certain notational problems also arise and deserve further comment. When substances are referred to as *trans*-$Co(^{13}CN)(CN)_4X^{z-}$, this notation will denote stereospecific enrichment at the trans site and normal isotopic abundance at the cis sites. This notation allows 12 isotopic isomers then, but only three are responsible for greater than 99% of the total population at the levels of E_T used in this research. These isomers and their fractional populations are



$0.956(1 - E_T)$



$0.956E_T$



$0.0426(1 - E_T)$

Enriched complexes with random labeling are denoted by $Co(^{13}CN)(CN)_4X^{z-}$.

Experimental Section

Reagents. Reagent grade chemicals were used without further purification. Samples of $Na^{13}CN$ (90 atm %) were obtained from Merck Sharpe and Dohme Canada Ltd.

Preparation of $Na_5Co(CN)_4(SO_3)_2\cdot 3H_2O$. This complex was prepared by the method of Râу,[14] followed by two recrystallizations

Table I. Results from the Thermal Aquation of *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$ at pH 7.5 and 60 °C

R

Time, h	I_T/I_C[a]	n[b]	P/R[c]
0	2.8	1	0
6.5	2.0	0.69	0.20
30.5	1.8	0.61	0.23
198.5	1.7	0.57	0.36

[a] The ratio of the integrated intensities of the resonances due to ^{13}CN groups which are cis and trans to a unique group. [b] The mole fraction of labeled material in which stereospecific enrichment remains. [c] The ratio of the molar quantities of product and reactant.

from a 10% solution of Na_2SO_3, which was made strongly basic by the addition of NaOH pellets. The yellow solid was successively washed with 40% ethanol, absolute ethanol, and ether and then dried under vacuum at 60–70 °C for 12 h. The synthesis was confirmed from the electronic[11] and infrared[7] spectra.

Thermal Synthesis of $Na_4[$*trans*-$Co(^{13}CN)(CN)_4SO_3]\cdot 2H_2O$. The preparation of $Na_4Co(CN)_5SO_3$ was adapted from an earlier kinetic study on the displacement of H_2O in $Co(CN)_4(SO_3)H_2O^{3-}$ by CN^-.[8] In a typical preparation 5.12×10^{-3} mol of $Na_5Co(CN)_4(SO_3)_2\cdot 3H_2O$ was dissolved in 100 ml of H_2O to form a bright yellow solution. As the pH was adjusted to 1.0 by the addition of $HClO_4$, the color of the solution turned to yellow-brown. The solution was purged with N_2 to remove completely the SO_2 which was evolved. The pH was then raised to 11.0 with NaOH, and a solution containing a fivefold excess of CN^-, which was enriched to 13.2% $Na^{13}CN$, was added. The solution immediately began to turn light yellow. The reaction, which was followed at the 263-nm band in the spectrum of $Co(CN)_5SO_3^{4-}$, was complete within 15 min. All free CN^- was removed by precipitating the complex as an oil with ethanol. This purification was repeated three times. The solid form of the compound, obtained from the evaporation of an aqueous solution, was dried under vacuum. The synthesis was confirmed from the electronic spectrum[7] and the ^{13}C NMR spectrum ($I_T/I_C = 2.9 \pm 0.1$). The infrared spectrum contains a band at 2080 cm^{-1} which is not present in an unenriched sample.

Photochemical Synthesis of $Na_4[Co(^{13}CN)(CN)_4SO_3]\cdot 2H_2O$. All solutions were made with 0.001 M NaOH to exclude any acid-induced hydrolysis of $Co(CN)_4(SO_3)_2^{5-}$ and were handled in dim light. To 100 ml of 3.3×10^{-2} M $Na_5Co(CN)_4(SO_3)_2\cdot 3H_2O$, a solution containing a fivefold excess of CN^- enriched to 4.4% $^{13}CN^-$ was added. Photolysis was conducted with a 215-W tungsten Sylvania sun lamp placed 6 in. from the surface of the solution. The light was filtered through Pyrex (1 cm) to remove ultraviolet radiation. The entire apparatus was jacketed in aluminum foil and the solution was cooled with water. The formation of $Co(CN)_5SO_3^{4-}$ was complete in less than 75 min. Tests for Co(II) were negative. The final solution was purged with O_2 for 2 h and stored at 0 °C for 24 h before being reduced in volume and precipitated with ethanol. The synthesis was confirmed from the electronic spectrum and the chemical shifts from the ^{13}C NMR spectrum. Complete scrambling was indicated by the I_T/I_C value of 0.26 ± 0.01.

Thermal Synthesis of $Co(^{13}CN)(CN)_4OH_2^{2-}$ from *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$. This preparation was adapted from an earlier kinetic study.[2] A solution of *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$ (4.2×10^{-3} M, $I_T/I_C = 2.8 \pm 0.1$) at pH 7.5 was heated for 6.5 h at 60 °C. The solution was then made strongly alkaline with NaOH. The electronic spectrum of the solution prior to reduction in volume, as well as the ^{13}C NMR spectrum after concentration, revealed the presence of a mixture of $Co(CN)_5SO_3^{4-}$ and $Co(CN)_5OH^{3-}$. The solution was then diluted, acidified to pH 7.8, and heated for an additional 24 h. The ^{13}C NMR spectrum was again obtained after the solution was made alkaline and its volume was reduced. Finally, the entire procedure was repeated with a heating time of 168 h. The results are summarized in Table I. Concentrations were not held constant during the additional heating times. The total concentrations of complexes during the second and third heating periods were 8.9×10^{-3} and 5.6×10^{-3} M, respectively.

Photolytic Synthesis of $Co(^{13}CN)(CN)_4OH_2^{2-}$ from *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$. A solution of *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$ (10^{-2} M, $I_T/I_C = 2.2 \pm 0.1$) at pH 7.5 was irradiated using the same apparatus which was described above with the exception that ice was used to cool the solution. Complete photolysis was found to take 10 h by observing the 263-nm band in the electronic spectrum of $Co(CN)_5SO_3^{4-}$. The pH was raised to 11.5 to convert the complex to the hydroxide form, and the volume was reduced for ^{13}C NMR analysis. The resulting solution was dark due to the presence of a brown decomposition product which precipitated on standing. A solution of the dark solid contained a peak at 355 nm. No evidence of this compound was observed in the ^{13}C NMR spectrum.

Attempted Catalytic Scrambling of *trans*-$Co(^{13}CN)(CN)_4SO_3^{4-}$. A solution of $Co(CN)_5^{3-}$, which had been generated from $Co(NO_3)_2\cdot 6H_2O$ and NaCN (with $^{13}CN^-$ in normal isotopic abundance) in a 1:5 ratio, was added to a solution of enriched $Co(CN)_5SO_3^{4-}$ which had been rigorously freed of O_2. The concentrations of $Co(CN)_5^{3-}$ and $Co(CN)_5SO_3^{4-}$ in the final solution were 2×10^{-3} and 10^{-1} M respectively. After the solution was allowed to sit for 48 h, O_2 was bubbled through it to remove slightly soluble $Na_6[Co(CN)_5O_2Co(CN)_5]\cdot H_2O$. The solution was filtered and reduced in volume for ^{13}C NMR analysis. The entire procedure was repeated with 2×10^{-2} M $Co(CN)_5^{3-}$ but with an elapsed time of 24 h. No scrambling was observed in either case.

Instrumental Methods. All Fourier transform ^{13}C NMR spectra of cyanocobaltate complexes were obtained with a Varian Associates XL-100-15 FT spectrometer operating at 25.196 MHZ, externally locked on a hexafluorobenzene signal. Free induction decay was obtained using a 20-μs radiofrequency pulse and a recycle time of 1.0 s. The data were accumulated as 4K data points in the time domain, transformed as 16K, and displayed as 8K in the frequency domain. The temperature, accurate to ±1 °C, was maintained with a Varian variable-temperature controller. All samples were examined in aqueous solutions (in 12-mm tubes) using dioxane as an internal reference. Chemical shifts were then adjusted to the TMS scale using the known value of the chemical shift for dioxane with respect to TMS (67.40 ppm).[15] Relative intensities and their error estimates were determined by cutting and weighing several identical spectra and through simulation by a computer. Infrared spectra were recorded using a Perkin-Elmer 621 ir spectrometer, and electronic spectra were obtained with a Cary Model 14 spectrometer. The pH of solutions were measured with a Sargeant pH meter, Model 7, equipped with a Corning 30070-1C electrode.

Discussion of Results

^{13}C NMR Spectra of Cyanocobaltates. During the course of this study two interesting aspects related to the quadrupolar coupling of the ^{59}Co ($I = {}^7/_2$) and ^{13}C nuclei were observed. The spectrum of $Co(CN)_6^{3-}$ was found to be the expected eight-line pattern with a chemical shift of 138.5 ppm and a carbon–cobalt coupling constant of 126.6 Hz. These results are in close agreement with data which were previously published.[16] The symmetric environment of this complex prevents relaxation through quadrupolar coupling and results in a long longitudinal relaxation time. Pulse intervals of 40 s were required to obtain good spectra. However, when small amounts of paramagnetic $Cr(CN)_6^{3-}$ (4 mol %) were added, a pulse interval of only 10 s was sufficient to reproduce spectra taken at much longer pulse intervals. Thus, it would appear that $Cr(CN)_6^{3-}$ might serve as an effective relaxation agent in aqueous media just as $Cr(acac)_3$ has served in nonaqueous solutions of organometallics.

Short relaxation times and significant line broadening occur with the less symmetric complexes, $Co(CN)_5SO_3^{4-}$ and $Co(CN)_5OH^{3-}$. As the effectiveness of quadrupolar coupling is decreased by decreasing the temperature of the samples to the freezing point, vast improvements in the signal-to-noise ratio and the line widths were observed as shown in Figure 1 for labeled $Co(CN)_5SO_3^{4-}$. The ^{13}C NMR spectrum of $Co(CN)_5SO_3^{4-}$ with $^{13}CN^-$ in natural abundance, given in Figure 2, demonstrates the validity of the integration of spectra taken at low temperature. The ratio of integrated intensities for the positions trans and cis (I_T/I_C) to the sulfite group is 0.26 ± 0.01, a value which agrees closely with the theoretical value of 0.25.

The chemical shifts which were observed in the ^{13}C NMR spectrum of $Co(CN)_5SO_3^{4-}$ are 140 (trans) and 144 (cis) ppm

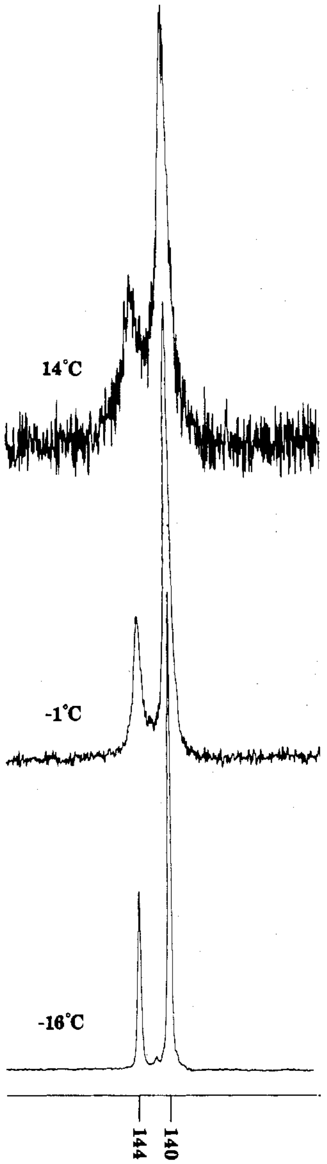


Figure 1. Temperature dependence of the ^{13}C NMR spectrum of 1.1 M *trans*-Co(^{13}CN)(CN)$_4$SO$_3^{4-}$ which was enriched to 10.6% in ^{13}CN$^-$. Each spectrum received approximately 4100 scans. Chemical shifts are in ppm downfield from TMS. At −16 °C, the sample was actually frozen.

downfield from TMS while those from Co(CN)OH^{3-} are 132 (trans) and 145 (cis) ppm downfield.

Thermal Reactions. Reaction 1 was conducted under conditions such that the formation of *trans*-Co(CN)$_4$(SO$_3$)OH$_2^{3-}$ was virtually complete before the addition of CN$^-$. Enrichment of the latter to 13.2% in ^{13}CN$^-$ leads to *trans*-Co(^{13}CN)(CN)$_4$SO$_3^{4-}$ whose ^{13}C NMR spectrum is shown in Figure 2. The value of I_T/I_C is 2.9 ± 0.1 which agrees very well with the calculated value of 3 that would occur when the incoming CN$^-$ group in reaction 1 is found exclusively in the site which is trans to the sulfite group. This result is typical of many such reactions which were conducted with varying degrees of enrichment of ^{13}CN$^-$. Partial loss of configuration was noted on two occasions even though these reactions were conducted under seemingly identical experimental conditions. However, even on these occasions rearrangement was not extensive. If a random configuration resulted from the rearrangement, then the value of n was somewhat larger than 0.7 in each case. The partial isomerization of *trans*-Co(CN)$_4$(SO$_3$)OH$_2^{3-}$, which has been reported previously,[8] may be involved, but this problem did not receive further study.

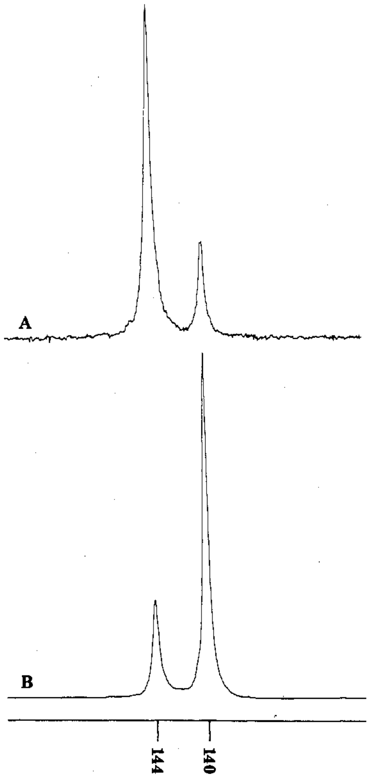


Figure 2. ^{13}C NMR spectra of (A) 1.3 M Co(CN)$_5$SO$_3^{4-}$ with ^{13}CN$^-$ in natural abundance (approximately 10 200 scans, −13 °C) and (B) 1.2 M *trans*-Co(^{13}CN)(CN)$_4$SO$_3^{4-}$ which was enriched to 13.2% in ^{13}CN$^-$ (approximately 5600 scans, −11 °C). Chemical shifts are in ppm downfield from TMS.

The stereospecific formation of *trans*-Co(^{13}CN)(CN)$_4$SO$_3^{4-}$ implies that the thermal aquation of trans-Co(CN)$_4$(SO$_3$)$_2^{5-}$ and the thermal anation of *trans*-Co(CN)$_4$(SO$_3$)OH$_2^{3-}$ proceed through a common intermediate. This intermediate is probably Co(CN)$_4$SO$_3^{3-}$ whose geometry is a tetragonal pyramid with the sulfite group in the apical position. This geometry should resist distortion when strong π-acceptor ligands, such as sulfite, are present in that position because of stabilization due to the strong interactions between the filled metal π orbitals (d_{xz} and d_{yz}) and the empty ligand π orbitals.

Thermal aquation of *trans*-Co(^{13}CN)(CN)$_4$SO$_3^{4-}$, reaction 2, does not proceed to completion even after heating for somewhat longer than 7 days at 60 °C and pH 7.5 as shown in Table I. The entries in that table require additional explanation, however. The ^{13}C NMR spectra, which were obtained after the aquo complex was converted to the hydroxo complex in order to avoid polymerization during evaporation, indicate the presence of both reactant and product. A typical spectrum is shown in Figure 3. The accidental overlap of the resonances due to the cis CN$^-$ groups of both Co(CN)$_5$SO$_3^{4-}$ and Co(CN)$_5$OH^{3-} causes an additional problem. The assignments for the latter were verified from the spectrum of a solution which contained only Co(CN)$_5$OH^{3-}. Integration of each spectrum was accomplished by computer simulation and best results were obtained when the I_T/I_C value for the hydroxo complex was taken as 0.25.

The results in Table I indicate that a major portion of the reaction occurs within the first time span (6.5 h) while very slow changes in the ratio of the product to the reactant (P/R) occur thereafter. Similarly, the largest change in the value of n occurs during the first time span but only small changes occur during an additional long span of heating (ca. 8 days).

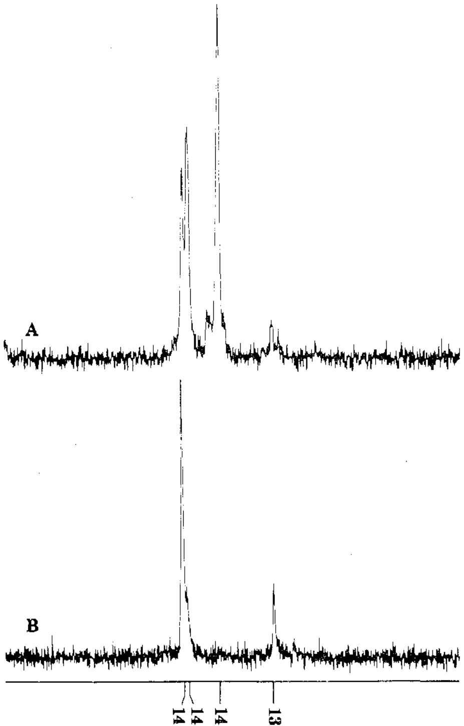


Figure 3. ^{13}C NMR spectra of (A) the solution obtained after heating *trans*-$\mathrm{Co(^{13}CN)(CN)_4SO_3^{4-}}$ for 198 h at 60 °C and pH 7.5 (0.15 M, approximately 12 300 scans, −18 °C) and (B) 0.12 M $\mathrm{Co(^{13}CN)(CN)_4OH^{3-}}$ which was obtained from the photolysis of *trans*-$\mathrm{Co(^{13}CN)(CN)_4SO_3^{4-}}$ (approximately 2050 scans, −23 °C). Chemical shifts are in ppm downfield from TMS.

At no time in the reaction has the product retained the original configuration of the reactant.

The changes in P/R may be due to an asymptotic approach to equilibrium. This process may be abetted somewhat by the slow loss of $\mathrm{SO_2}$ which must be present in small amounts above the hot, nearly neutral solution. Equilibria certainly exist in the anations of $\mathrm{Co(CN)_5OH_2^{2-}}$ with halides or pseudohalides.[5,6] The following mechanism is consistent with the kinetics of those reactions

$$\mathrm{Co(CN)_5OH_2^{2-}} \underset{k_\mathrm{w}}{\overset{k_\mathrm{e}}{\rightleftharpoons}} \mathrm{Co(CN)_5^{2-}} + \mathrm{H_2O}$$

$$\mathrm{Co(CN)_5^{2-}} + \mathrm{X^-} \underset{k_\mathrm{a}}{\overset{k_\mathrm{x}}{\rightleftharpoons}} \mathrm{Co(CN)_5X^{3-}}$$

The most stable structure for $\mathrm{Co(CN)_5^{2-}}$ would seem to be a square pyramid since the isoelectronic complex, $\mathrm{Cr(CO)_5}$, has been said[17] to possess C_{4v} symmetry in its ground state. If $\mathrm{Co(CN)_5^{2-}}$ were generated during the thermal aquation of the sulfite complex, the results require that the configurational lifetime of the square pyramid must be less than the time required for an effective molecular collision.

The disturbing feature about the data in Table I, however, is the close tie between P/R and n. Changes in n should continue to occur at a rate determined by k_a after P/R has become constant if the usual mechanism is in effect. However, it is clear that an abrupt decrease in the rate of change of n occurs when the rate of change of P/R diminishes drastically. A more complete study of this reaction is clearly required before it can be understood.

Photochemical Reactions. When solutions of *trans*-$\mathrm{Co(CN)_4(SO_3)_2^{5-}}$ and $\mathrm{CN^-}$, enriched in $\mathrm{^{13}CN^-}$ to 4.4%, at pH 10.5 where photolyzed using a thick (1 cm) Pyrex filter to absorb ultraviolet radiation, $\mathrm{Co(^{13}CN)(CN)_4SO_3^{4-}}$ was produced cleanly according to reaction 1. Photoreduction was not evident since the addition of $\mathrm{SCN^-}$ to an aliquot did not produce any measurable quantity of $\mathrm{Co(NCS)_4^{2-}}$. In addition, there was no evidence for the formation of brown, slightly soluble $\mathrm{Na_6[Co(CN)_5O_2Co(CN)_5]\cdot H_2O}$ even after the solution was purged with $\mathrm{O_2}$. However, the ^{13}C NMR spectrum of the product pointed to random incorporation of $\mathrm{^{13}CN^-}$ since the $I_\mathrm{T}/I_\mathrm{C}$ value was 0.26 ± 0.01.

Although no evidence for photoreduction was found, it is nevertheless possible that catalytic quantities of Co(II), produced in undetectable amounts from a side reaction, are responsible for the loss of configuration of the main product which is actually formed first with retention of configuration. It is known[18] that the reaction of $\mathrm{Co(CN)_5^{3-}}$ with $\mathrm{Co(CN)_5X^{n-}}$ ($\mathrm{X = H_2O, OH^-, Cl^-, Br, N_3^-}$, and $\mathrm{SCN^-}$) leads to the formation of $\mathrm{Co(CN)_6^{3-}}$. If this reaction were reversible, then catalytic quantities of $\mathrm{Co(CN)_5^{3-}}$ would be capable of scrambling a label in $\mathrm{Co(CN)_5X^{n-}}$. However, there is now evidence that rather large quantities of $\mathrm{Co(CN)_5^{3-}}$ do not cause a loss of configuration in *trans*-$\mathrm{Co(^{13}CN)(CN)_4SO_3^{4-}}$. For example, when a solution containing 10^{-1} M *trans*-$\mathrm{Co(^{13}CN)(CN)_4SO_3^{4-}}$ ($I_\mathrm{T}/I_\mathrm{C}$ = 2.5 ± 0.1) and 2×10^{-2} M $\mathrm{Co(CN)_5^{3-}}$ was allowed to stand under vacuum for 24 h, the recovered Co(III) complex was identical with the starting material with no change in $I_\mathrm{T}/I_\mathrm{C}$ value within experimental error. Thus, the random labeling in the product from the photochemical reaction is not a result of scrambling by catalytic quantities of Co(II).

The loss of configuration in the product must occur then because of the nature of the intermediate involved in the photodissociative loss of $\mathrm{SO_3^{2-}}$. Irradiation at a wavelength corresponding to the excitation, d_{xz}, $d_{yz} \rightarrow d_{z^2}$, should bring about labilization of π-acceptor ligands along the unique axis.[11] Photodissociative loss of $\mathrm{SO_3^{2-}}$ from *trans*-$\mathrm{Co(CN)_4(SO_3)_2^{5-}}$ will lead to one of three possible consequences. Loss of the ligand may induce loss of a photon and produce the intermediate in its ground state. The thermal and photochemical pathways would then be identical thereafter, as previously suggested.[11] The experimental results eliminate this possibility. Loss of the ligand may also lead to an electronically or vibrationally excited intermediate, which is quite distinct from the intermediate in the thermal reaction. Either of these could have a short configurational lifetime which would cause a random introduction of $\mathrm{^{13}CN^-}$. Although the data do not distinguish between these two alternatives, an electronically excited intermediate is particularly appealing. The photoexcited intermediate, $\mathrm{Co(CN)_4SO_3^{3-}}$, should experience greatly weakened Co–$\mathrm{SO_3}$ bonding because of the depopulation of the metal π orbitals and population of d_{z^2} (σ^*), an antibonding orbital. The consequence may be a greatly reduced stabilization of the square pyramid and a short configurational lifetime.

Irradiation of solutions of $\mathrm{Co(CN)_5SO_3^{4-}}$ ($I_\mathrm{T}/I_\mathrm{C}$ = 2.2 ± 0.1) at pH 7.5 resulted in the rapid formation of $\mathrm{Co(CN)_5OH_2^{2-}}$, a complex which is known to be stable toward further photolysis at this pH.[13] After conversion to $\mathrm{Co(CN)_5OH^{3-}}$ and evaporation, the value of $I_\mathrm{T}/I_\mathrm{C}$ was found to be 0.24 ± 0.01 due to complete scrambling of the label (Figure 3). Again, there was no direct evidence for photoreduction, but an unknown brown compound was observed. This compound was not $\mathrm{Na_6[Co(CN)_5O_2Co(CN)_5]\cdot H_2O}$. Further discussion of this reaction is deferred until a thorough study is completed.

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Registry No. *trans*-$\mathrm{Co(CN)_4(SO_3)_2^{5-}}$, 53011-07-7; $\mathrm{Co(CN)_5SO_3^{4-}}$, 53078-06-1; $\mathrm{CN^-}$, 57-12-5; $\mathrm{SO_3^{2-}}$, 14265-45-3; $\mathrm{Na_4[}$*trans*-$\mathrm{Co(^{13}CN)(CN)_4SO_3]}$, 59042-81-8; $\mathrm{Na_4[Co(^{13}CN)(CN)_4SO_3]}$, 59042-80-7; $Co(^{13}CN)(CN)_4OH_2^{2-}$, 59091-67-7; $Co(^{13}CN)(CN)_4OH^{3-}$, 59091-68-8.

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Conformational Dissymmetry. Circular Dichroism and Stereospecificity Induced by Skew Six-Membered Chelate Rings

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A series of complexes of the type $[Co(R,R\text{-dmtn})_2X_2]^{n+}$, where *R,R*-dmtn is the optically active 2,4-pentanediamine ligand, have been prepared and characterized. It is found that, unlike the five-membered chelate ring analogues, these six-membered skew rings give consistent patterns for the d–d circular dichroism of their trans complexes and, in addition, the circular dichroism is insensitive to variations in the solvent. The stereospecificity of the *cis*-$[Co(R,R\text{-dmtn})_2(NH_3)_2]^{3+}$ complexes is found to be small; the lel to ob ratio is about 4:1 in liquid ammonia. The circular dichroism of the diammine complexes show a number of unusual features, the more interesting of which are the lack of conformational additivity of the circular dichroism and the apparently large transition magnetic moments carried by the $^1A_{1g} \rightarrow {}^1T_{2g}$ manifolds. Possible reasons for these are adumbrated.

The ligand 2,4-pentanediamine (dmtn) is the six-membered chelate ring analogue of 2,4-diaminobutane (bn) which forms five-membered chelate rings, but unlike the latter, the former stabilizes two distinct chelate conformations. Conformational energy calculations[1,2] predict and experimental studies confirm[3,4] that the most stable chelate ring conformation for the meso dmtn (*R,S*-dmtn) ligand is the chair and that for the racemic ligand (*R,R:S,S*-dmtn) is the skew conformation. In both conformations the methyl groups are equatorially disposed. These essential conformations seem to persist even when there is considerable interaction between neighboring chelate rings.[3–6] This paper is concerned with the conformational isomers and the optical activity of the $[Co(R,R\text{-dmtn})_2X_2]^{n+}$ complexes; a following paper describes the isomers of the $(R,S\text{-dmtn})_2Co^{III}$ complexes.

There are two aspects of $(R,R\text{-dmtn})_2$ complexes which are of peculiar interest. The first is that the conformationally induced d–d circular dichroism in complexes containing linear quadridentate amines which incorporate the *R,R*-dmtn moiety is relatively strong and, at the same time, consistent patterns are observed for a related series of complexes.[7] This is in marked contrast with the bewildering diversity of patterns observed when only five-membered chelate rings are the major source of dissymmetry.[8] Complexes of the type *trans*-$[Co(R,R\text{-dmtn})_2X_2]^{n+}$ provide the simplest series of compounds where the d–d circular dichroism of the skew six-membered chelate ring can be investigated.

The second aspect relates to the configurational stereospecificity of octahedral complexes containing two or more *R,R*-dmtn ligands. Unlike the substituted ethylenediamine cobalt(III) complexes where diastereomeric equilibration can be achieved without appreciable decomposition,[9] the dmtn cobalt(III) complexes are decomposed by the presence of cobalt(II) catalysts. The isomers of $[Co(R,R\text{-dmtn})_2(NH_3)_2]^{3+}$, however, can be prepared under equilibrium conditions with negligible decomposition.

Figure 1 shows the two possible cis isomers of the $[Co(R,R\text{-dmtn})_2X_2]^{n+}$ system. Conformational energy calculations[1,10] predict that the lel-cis-Δ diastereomer should be more stable than the ob-cis-Λ-isomer. In all three isomers, the chelate ring is assumed to be in the basic skew[11] conformation.

1. Preparations

The original preparations[12,13] of *trans*-$[Co(R,R\text{-dmtn})_2Cl_2]^+$ give poor yields of the pure compound. Aerial oxidation of a methanolic solution of partially neutralized *R,R*-dmtn·2HCl together with cobalt chloride and sodium nitrite affords the $[Co(R,R\text{-dmtn})_2(NO_2)_2]^+$ ion in high yield, which is then converted quantitatively into the (−)-*trans*-$[Co(R,R\text{-dmtn})_2Cl_2]ClO_4$ salt. This dichloro complex is conveniently labile for preparation of other *trans*-$[Co(R,R\text{-dmtn})_2X_2]^{n+}$ species ($X = N_3^-$, NCS^-, NO_2^-, NH_3) provided the anation is carried out in methanol solutions. In other dipolar solvents, solvolysis occurs rapidly and is accompanied by the formation of *cis*-solvento species which give cis complexes upon anation. The *trans*-diazido species rapidly undergoes solvolysis and isomerization in all polar solvents, including methanol in which it is the most stable.

The reaction of *trans*-$[Co(R,R\text{-dmtn})_2Cl_2]^+$ with disodium oxalate produces the (+)-*cis*-Λ- and (−)-*cis*-Δ-$[Co(R,R\text{-dmtn})_2ox]^+$ ions in roughly equal proportions and both isomers have been obtained pure. These proportions are probably largely kinetically controlled but our attempts at equilibrating them in aqueous solutions were frustrated by their decomposition in the presence of charcoal or base. The same rapid decomposition occurs with the (three) $[Co(R,R\text{-dmtn})_2(NH_3)_2]^{3+}$ isomers in the presence of charcoal or base.