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Preparation, Resolution, and Reactions of the *cis*-Dicyanobis(ethylenediamine)chromium(III) Ion[1]

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The title complex has been prepared from the reaction of chromium(III) chloride hexahydrate, hydrogen cyanide, and ethylenediamine in aqueous solution. A similar combination of reactants, albeit one involving hydrogen fluoride as an anionic ligand source, yields the *trans*-difluorobis(ethylenediamine)chromium(III) ion. This result is discussed in terms of the bonding in the cyanide complex. The stereochemistry of $Cr(en)_2(CN)_2^+$ has been confirmed by its visible and infrared spectra, ion-exchange behavior, and resolution. Ligand field calculations based on a pseudotetragonal model are presented and discussed. The complex cation reacts in dilute perchloric acid to yield the *cis*-cyanoaquo- and *cis*-diaquobis(ethylenediamine)chromium(III) ions and in the concentrated hydrohalic acids HCl and HBr to yield the *cis*-dichloro- and *cis*-dibromobis(ethylenediamine)chromium(III) ions. The dicyano- and cyanoaquobis(ethylenediamine)chromium(III) cations represent the only known cyano–amine complexes of chromium(III).

Introduction

Octahedral bis(ethylenediamine)chromium(III) complexes have been the subject of numerous kinetic and photochemical investigations[2] and Perumareddi[3] has recently given a quantitative account of their ligand field spectra. Cis and trans isomers of $[Cr(en)_2X_2]^{n+}$ have been prepared with X = OH_2, OH^-, F^-, Cl^-, Br^-, *N*CS^-, N_3^-, and *O*NO^-.[2] One notable absentee from this list of monodentate ligands is the cyanide ion. Although the syntheses of *cis*- and *trans*-dicyanobis(ethylenediamine)cobalt(III) salts have appeared in the literature,[4] there has been no mention of their chromium(III) analogues. This is somewhat surprising because cyanide forms a significant number of stable complexes with tervalent chromium.[5] Garner and House have pointed out, however, that synthetic methods applicable to the preparation of cobalt(III)–amine complexes are quite often inapplicable in chromium(III) chemistry.[2]

As an extension of our studies of chromium(III) cyanide complexes,[6] we sought preparative schemes to the *cis*- and *trans*-dicyanobis(ethylenediamine)chromium(III) complexes. To date, our efforts to prepare the trans isomer have been unsuccessful (see Discussion), but we wish to report the synthesis of the cis isomer and its acid-catalyzed decomposition product, the *cis*-cyanoaquobis(ethylenediamine)chromium(III) ion. The cis arrangement of cyanide ligands in $Cr(en)_2(CN)_2^+$ has been assigned on the basis of its visible and infrared spectra and because of the unequivocal evidence offered by the resolution of this cation into its optical enantiomorphs. Absolute proof for the stereochemistry of $Cr(en)_2(OH_2)(CN)^{2+}$ is lacking as we have not been able to isolate this complex as a solid salt. However its visible absorption spectrum is consistent with the cis configuration and we have identified its aquation product as the *cis*-diaquobis(ethylenediamine)chromium(III) ion.

The *cis*-dicyanobis(ethylenediamine)chromium(III) complex was isolated as the chloride salt from the reaction of chromium(III) chloride hexahydrate, hydrogen cyanide, and ethylenediamine in aqueous medium. It is interesting to note that a similar combination of reactants, albeit one involving hydrofluoric acid as an anionic ligand source, yields *trans*-difluorobis(ethylenediamine)chromium(III) chloride.[8]

Experimental Section

Materials. Matheson 98% ethylenediamine was refluxed over and distilled from calcium hydride. Ammonium $(+)_D$-α-bromocamphor-π-sulfonate was obtained from Aldrich and used as received; its specific rotation at the sodium D line (589 nm) was +84.0° dm^{-1} g^{-1} ml.[9] Hydrogen cyanide (*caution!*[10]) was prepared by the method described by Brauer,[11] stabilized with several drops of concentrated hydrochloric acid, and stored at −78 °C. Before use it was warmed to 0 °C and pipetted into the reaction vessel with a cold pipet. Deionized water was used in all preparations. Analytical grade Dowex 50W-X4 H^+ resin, 200–400 mesh, was purchased from Bio-Rad, converted to the sodium cycle with sodium hydroxide, and washed with mildly acidic water until the desired pH was attained. All common laboratory chemicals were reagent grade except the dimethylformamide, which was Fisher "Spectroanalyzed" grade.

Synthesis of *cis*-Dicyanobis(ethylenediamine)chromium(III) Perchlorate. Approximately 25 ml (~0.65 mol) of ice-cold hydrogen cyanide (*caution!*[10]) was pipetted into a 500-ml round-bottom flask equipped with an addition funnel, gas inlet, and magnetic stirring bar. The hydrogen cyanide was frozen at −196 °C and 140 ml of an aqueous solution containing 30 g (0.11 mol) of green chromium(III) chloride hexahydrate was slowly added and likewise frozen. The flask was evacuated and then allowed to warm in an ice bath. When the magnetic stir bar was free to rotate, the dropwise addition of 100 ml (1.50 mol) of ethylenediamine commenced and was complete in about 1 h. Atmospheric pressure was then readmitted to the flask and its contents were transferred to a large beaker or crystallizing dish. The solution, which may be inhomogeneous at this point, was heated at 90–95 °C to remove excess water. During the initial heating the solution became reddish brown and homogeneous. After the volume had been reduced to ~100 ml, a yellow crystalline solid precipitated. This precipitate was recovered from the *hot* solution by filtration. The product was washed with two 50-ml portions of ice-cold methanol and once with ether and was air-dried. The yield of *cis*-$[Cr(en)_2(CN)_2]Cl$ at this point is nearly 50% of the theoretical. Further evaporation of the filtrate beyond this point is discouraged because large amounts of tris(ethylenediamine)chromium(III) chloride coprecipitate. We have also found that recrystallization of the crude chloride from aqueous solution results in appreciable solubility losses. This complex was therefore recrystallized as the perchlorate salt.

The entire yield of crude $[Cr(en)_2(CN)_2]Cl$ was dissolved in a minimum amount of water at 70 °C and immediately filtered into an equal volume of saturated aqueous sodium perchlorate. Crystallization began almost immediately and, after cooling of the filtrate to 0 °C, the lemon yellow product was collected by filtration, washed with methanol and ether, and air-dried. The yield of the perchlorate salt is typically 40–45% of the theoretical (based on chromium(III) chloride hexahydrate).

Anal. Calcd for $[Cr(en)_2(CN)_2]ClO_4$: Cr, 16.1; Cl, 10.95; C, 22.26; N, 25.96; H, 4.98. Found: Cr, 16.0; Cl, 11.21; C, 22.56; N, 25.91; H. 4.97.

Conductance measurements of a 10^{-3} M aqueous solution of the perchlorate salt at 25 °C gave a molar conductance of 103 Ω^{-1} cm^{-1}, which is within the range expected for a univalent electrolyte.[12]

The final product was shown by ion-exchange chromatography to be the only chromium species present. A 100-mg sample of the perchlorate salt was dissolved in a minimum amount of water and charged onto a sodium cycle cation-exchange column (ca. 10 cm × 1.5 cm). The column was washed with one-column volume of water and eluted with ca. 100 ml of 0.6 M sodium perchlorate solution. The complex cation was quickly eluted from the column at a flow rate of 2 ml/min and collected in 15-ml fractions. The visible absorption spectra of all fractions were identical and were the same as the spectrum of the bulk perchlorate salt. Analysis of the eluted material accounted for 99% (two determinations) of the chromium placed on the column.

The corresponding iodide salt of $Cr(en)_2(CN)_2^+$ can be prepared in a similar fashion. Saturated aqueous sodium iodide was used to precipitate the complex iodide whose visible absorption spectrum was identical with that of the perchlorate.

Anal. Calcd for $[Cr(en)_2(CN)_2]I$: Cr, 14.8; I, 36.14; C, 20.52; N, 23.93; H, 4.59. Found: Cr, 14.6; I, 36.53; C, 20.60; N, 23.58; H, 4.60.

A 10^{-3} M solution of the iodide salt had a molar conductance of 114 Ω^{-1} cm^{-1} at 25 °C which is consistent with values expected for 1:1 electrolytes.[12]

If the chloride salt is desired, it can be prepared in nearly quantitative yield by metathesis of the perchlorate salt in dimethylformamide. A desired quantity of the perchlorate salt is dissolved in the minimum amount of spectral grade dimethylformamide. To this solution is added a dimethylformamide solution containing a slight excess over the stoichiometric amount of lithium chloride. The complex chloride precipitates immediately from solution. This product is collected by filtration, washed successively with dimethylformamide, ice-cold methanol, and ether, and then thoroughly dried in air. The complex chloride gave a visible absorption spectrum identical with those of the perchlorate and iodide salts. Analysis indicated the presence of occluded solvent which is difficult to remove by heating.

Anal. Calcd for $[Cr(en)_2(CN)_2]Cl{\cdot}0.25C_3H_7NO$: Cr, 18.7. Found: Cr, 18.7.

Preparation of the *cis*-Cyanoaquobis(ethylenediamine)chromium(III) Ion. This complex has not been synthesized as a solid but was isolated in solution by conventional ion-exchange techniques. One gram (3.1 mmol) of $[Cr(en)_2(CN)_2]ClO_4$ was dissolved in 150 ml of water at 0 °C and the pH of the solution was adjusted to 1.0 with 4.0 M perchloric acid to promote aquation. Nitrogen gas was bubbled through the ice-cold solution for 1 h to remove the released hydrogen cyanide. The reaction was quenched by raising the pH to 4.0 with 4.0 M sodium hydroxide and the solution was charged onto a sodium cycle cation-exchange column (15 cm × 1.5 cm). The column was washed once with water (pH 4.0) and then with 0.6 M sodium perchlorate (pH 4.0) to elute the starting material. During this initial elution the orange band at the top of the column separates into two distinct bands. The desired complex (the lower of the bands) was slowly eluted with 2.0 M sodium perchlorate (also at pH 4.0) and stored in ice until its spectrum could be measured. The complex cation was characterized by its visible absorption spectrum and its CN^-:Cr ratio of 1.01 (three determinations).

Resolution of the *cis*-Dicyanobis(ethylenediamine)chromium(III) Ion. A 5.2-g (18.7-mmol) sample of $[Cr(en)_2(CN)_2]Cl{\cdot}0.25$ DMF was dissolved in 50 ml of water. To this solution, a cold saturated aqueous solution of ammonium $(+)_D$-α-bromocamphor-π-sulfonate (3.3 g, 10 mmol) was added very slowly. Large yellow crystals began to appear near the end of the addition. The solution was cooled in ice for 20 min to complete the precipitation. The yellow crystals were collected by filtration, and the filtrate was set aside for recovery of the remaining optical antipode. The solid diastereomer was washed with methanol and ether and air-dried. The yield was 3.55 g (71% based on a racemic mixture).

Anal. Calcd for $[Cr(en)_2(CN)_2]C_{10}H_{14}SO_4Br$: C, 35.96; N, 15.73; H, 5.66; S, 6.00. Found: C, 36.29; N, 15.93; H, 5.70; S, 6.04.

The specific rotation of a 0.5% aqueous solution measured at the sodium D line was +71.5° dm^{-1} g^{-1} ml. Grinding the diastereomer with water did not appreciably change the specific rotation and it was considered optically pure.

The optical form of the dicyanobis(ethylenediamine)chromium(III) cation was freed of its optically active anion by triturating the diastereomer with a mixture of concentrated hydriodic acid and 95% ethanol (1:10 v/v). The solid product was washed with 95% ethanol, absolute ethanol, and ether and air-dried. A 0.5% aqueous solution of the complex had a specific rotation of 27.6° dm^{-1} g^{-1} ml at 589 nm. Grinding the solid with small quantities of water raised this value to +28.8° dm^{-1} g^{-1} ml but further grinding did not alter the rotation. There was no loss of optical activity on heating the sample for 4 h at 110 °C.

Anal. Calcd for $(+)_{589}$-$[Cr(en)_2(CN)_2]I$: Cr, 14.8; I, 36.14; C, 20.52; N, 23.93; H, 4.59. Found: Cr, 14.6; I, 36.58; C, 20.35; N, 23.68; H, 4.61.

The filtrate containing the other optical antipode was treated with saturated aqueous sodium iodide to the point of incipient precipitation and then was cooled to 0 °C. A 1.7-g amount of $[Cr(en)_2(CN)_2]I$ was recovered by filtration. A 0.5% aqueous solution of this complex had a specific rotation of −24.7° dm^{-1} g^{-1} ml at the sodium D line. This product was ground with small quantities of water until successive grinding did not alter the observed rotation. The final value of the specific rotation was −28.1° dm^{-1} g^{-1} ml.

Anal. Calcd for $(-)_{589}$-$[Cr(en)_2(CN)_2]I$: Cr, 14.8. Found: Cr, 14.6.

Reactions of *cis*-Dicyanobis(ethylenediamine)chromium(III) Perchlorate with Hydrochloric and Hydrobromic Acid. A 1.0-g sample of *cis*-$[Cr(en)_2(CN)_2]ClO_4$ was dissolved in 10 ml of 12 M hydrochloric acid and allowed to react under a gentle stream of air for 24 h. The red-purple material (0.55 g) which had precipitated was collected by filtration, washed with methanol and ether, and air-dried. The visible absorption spectrum and reflectance spectrum were consistent with the published spectra[13,14] for the *cis*-dichlorobis(ethylenediamine)chromium(III) ion. Elemental analysis indicated the presence of both perchlorate and chloride counterions.

Anal. Calcd for $[Cr(en)_2Cl_2](ClO_4)_{0.6}Cl_{0.4}$: Cr, 16.4; Cl, 33.6; C, 15.2; N, 17.7; H, 5.1. Found: Cr, 15.9; Cl, 34.1; C, 14.9; N, 18.0; H, 5.1.

An alternate preparation starting with $[Cr(en)_2(CN)_2]Cl{\cdot}0.25DMF$ gave *cis*-$[Cr(en)_2Cl_2]Cl{\cdot}H_2O$ as the solid product.

Anal. Calcd for $[Cr(en)_2Cl_2]Cl{\cdot}H_2O$: Cr, 17.5. Found: Cr, 17.2.

A 1.0-g sample of *cis*-$[Cr(en)_2(CN)_2]ClO_4$ was dissolved in 10 ml of 9.0 M hydrobromic acid and allowed to react under a stream of air for 24 h. At the end of this period, 0.71 g of a red-purple solid was collected by filtration, washed with methanol and ether, and air-dried. Elemental analysis was consistent with the formulation $[Cr(en)_2Br_2]Br{\cdot}H_2O$.

Anal. Calcd for $[Cr(en)_2Br_2]Br{\cdot}H_2O$: Cr, 11.9; Br, 55.0; C, 11.0; N, 12.9; H, 4.6. Found: Cr, 11.8; Br, 54.8; C, 11.5; N, 13.4; H, 4.2.

The reflectance spectrum of this complex agrees with the solution spectrum (extrapolated to the time of mixing) obtained by McLean et al.[15] for *cis*-$[Cr(en)_2Br_2]Br{\cdot}H_2O$ (reflectance: λ_{max} 537 nm, λ_{min} 463 nm, λ_{max} 409 nm). The reflectance spectrum reported by Wendlandt and Stembridge[14] for *cis*-$[Cr(en)_2Br_2]Br$ (λ_{max} 510 nm, λ_{max} 380 nm) cannot be correct. According to their findings replacement of Cl^- by Br^- in *cis*-$[Cr(en)_2X_2]^+$ resulted in spectral shifts to higher energy. In view of the lower value of *Dq* for bromide ion,[3] the expected spectral shift in going from the dichloro complex to the dibromo complex should be toward lower energy, which is consistent with our observations for the two complexes.

Analytical Methods and Instrumentation. Chromium analyses were performed by oxidizing the complexes to chromate with alkaline hydrogen peroxide and measuring the absorption of CrO_4^{2-} at 372 nm ($a_m = 4.83 \times 10^3$ M^{-1} cm^{-1}).[16] The amount of bound cyanide in the *cis*-cyanoaquobis(ethylenediamine)chromium(III) ion was determined by potentiometric titration with silver nitrate following acid-catalyzed decomposition of the complex in sealed glass ampoules, as described elsewhere.[17] All other microanalyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Optical rotations were obtained on an O. C. Rudolph and Sons manual polarimeter. Samples were run in 2-dm cells at ambient temperature. Reported values of specific rotations are the average of at least 10 readings. Circular dichroism spectra were run in 1-cm silica cells on a JASCO Model ORD/UV-5 overhauled with a Sproul Scientific SS-10 CD modification.

Ultraviolet and visible spectra were obtained in matched silica cells on a Cary Model 14 (or 14R) recording spectrophotometer, which was periodically wavelength calibrated using a holmium oxide glass filter (Corning No. 3130). Reflectance spectra were recorded with a Cary Model 1411 diffuse reflectance accessory. Blocks of magnesium carbonate were used as a reference.

Infrared spectra were obtained using KBr pellet techniques and a Perkin-Elmer Model 621 spectrophotometer calibrated with polystyrene film.

Conductance measurements were recorded on a Barnstead Corp. conductivity bridge, Model PM-70CB, coupled with a Sargent conductivity cell whose cell constant was 0.6059 cm^{-1}. All measurements were performed at 25.0 ± 0.1 °C.

Discussion

We have utilized the reaction of chromium(III) chloride hexahydrate, hydrogen cyanide, and ethylenediamine in aqueous solution to prepare *cis*-dicyanobis(ethylenediamine)chromium(III) chloride as the major product. Previous studies in this laboratory[18] had shown that this complex could also be obtained from the reaction of *cis*-dichlorobis(ethylenediamine)chromium(III) chloride and the stoichiometric amount of sodium cyanide in anhydrous methanol. The yields from this latter synthesis were low, and the reaction time was on the order of days.

The original intent of the present study was to prepare the unknown *trans*-dicyano isomer, by a method analogous to that yielding *trans*-difluorobis(ethylenediamine)chromium(III) chloride, which is known to form from the reaction of chromium(III) chloride hexahydrate, hydrofluoric acid, and ethylenediamine under essentially identical reaction conditions.[8] At the present time we are looking more closely at these two systems to elucidate which step in the reaction sequence determines the stereochemistry of the final product. In particular it will be necessary to see what role, if any, is played by green chromium(III) chloride hexahydrate, which is actually *trans*-$[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$. However, the absence of any *trans*-dicyanobis(ethylenediamine)chromium(III) ion as a product from our reaction is not surprising in light of recent studies in this laboratory. Jimerson[19] has tentatively characterized the three *trans*-cyanoaquo isomers, *trans*-$[Cr(CN)_2(H_2O)_4]^+$, *trans*-$[Cr(CN)_3(H_2O)_3]$, and *trans*-$[Cr(CN)_4(H_2O)_2]^-$, all of which were formed by low temperature (0 °C) anations involving the appropriate lower cyanoaquo complexes in aqueous solution. All three trans isomers were observed to be extremely labile in aqueous solution and much less stable than the corresponding cis isomers. The lability of the trans complexes presumably arises from the incompatability of cyanide trans to cyanide. Substitution of ethylenediamine for water in such a complex should have little effect in enhancing stability and at present we doubt that this complex can exist for any reasonable length of time in the reaction sequence which ultimately yields only *cis*-dicyanobis(ethylenediamine)chromium(III) chloride.

The assignment of the cis configuration to this new cyanoaminechromium(III) complex is supported by its visible absorption spectrum. The salts of $Cr(en)_2(CN)_2^+$ all exhibit two narrow, well-defined ligand field absorption bands in solution (see Figure 1) which exhibit no observable splitting. The ground state of octahedral chromium(III) is $^4A_{2g}$ and the first two excited states are $^4T_{2g}$ and $^4T_{1g}(F)$. When the symmetry of the complex is lowered to D_{4h}, the cubic states decompose into their quadrate representations, i.e., $^4A_{2g} \rightarrow {}^4B_{1g}$, $^4T_{2g} \rightarrow {}^4B_{2g} + {}^4E_g{}^a$, and $^4T_{1g} \rightarrow {}^4A_{2g} + {}^4E_g{}^b$. In the limit of zero configuration interaction, it can be shown that the splitting of the first two excited quartet levels is given by $+{}^{35}/_4Dt({}^4E_g{}^a - {}^4B_{2g})$ and $6Ds - {}^5/_4Dt({}^4A_{2g} - {}^4E_g{}^b)$. Although cis-disubstituted octahedral complexes actually possess C_{2v} or C_2 symmetry, they have been treated in the literature[3,20] as pseudo-D_{4h} symmetry complexes by averaging the field strengths of the trans ligand pairs. Following the arguments of Krishnamurthy et al.,[20] the cis complexes MX_4Y_2 become pseudo-*trans*-MZ_4X_2, where Z represents a ligand whose ligand field strength is the average of those of X and Y. It can also be shown through crystal field formalism that the tetragonal Dt parameter for *cis*-MX_4Y_2 is $^2/_7(D_{q_x} - D_{q_y})$ and for *trans*-MX_4Y_2 it is $-^4/_7(D_{q_x} - D_{q_y})$. This is the well-known prediction of ligand field theory that the tetragonal splitting of trans isomers is twice the splitting of their cis analogues.[21] With this information at hand we can predict the splitting of the first excited state to be +2325 cm^{-1} for the *trans*-dicyanobis(ethylenediamine)chromium(III) complex and −1163 cm^{-1} for the cis isomer.[22] If we take ~2000 cm^{-1} as a limit for observable splitting, then the observed two-band spectrum of $Cr(en)_2(CN)_2^+$ would imply a cis configuration. Baker and Phillips[23] have carefully studied the spectra of *cis*- and *trans*-$[Cr(en)_2X_2]^{n+}$ complexes where X = OH_2, OH^-, Cl^-, Br^-, *N*CS^-, and N_3^- and found no observable splitting in any of the cis isomers. Although the absence of splitting implies a cis configuration, the use of such a criterion requires other confirmatory evidence, especially because the *trans*-diisothiocyanatobis(ethylenediamine)chromium(III) complex, which has a predicted splitting of ~2100 cm^{-1}, does not exhibit any spectral splitting in solution.[23]

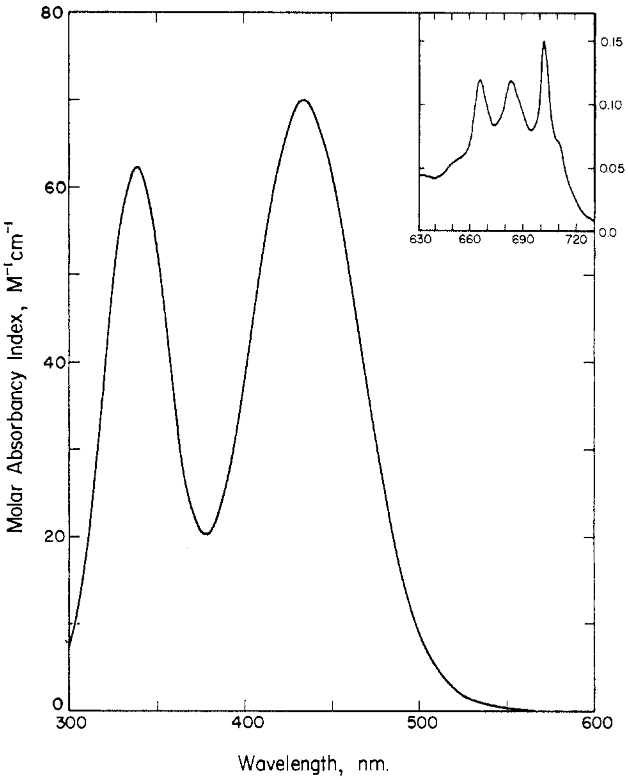

Figure 1. Visible and near-ultraviolet spectrum of the *cis*-dicyanobis(ethylenediamine)chromium(III) ion in aqueous solution. The insert displays the spin-forbidden bands associated with the complex.

In addition to the two spin-allowed bands for this complex, we have also observed four spin-forbidden bands in concentrated aqueous solutions of the chloride salt. These intercombination bands are well removed from the first spin-allowed band and show excellent resolution (Figure 1). The observed and calculated positions of all bands are included in Table I. Calculated band positions were obtained by solving the strong-field energy matrices (including configuration interaction) for the d^3 ion in a quadrate field. The fitting procedure was analogous to that described by Lowry and Perumareddi.[24] The fit for all bands is surprisingly good considering the inherent assumptions of pseudo-D_{4h} symmetry.

The infrared spectrum of $[Cr(en)_2(CN)_2]I$ is also consistent with our assignment of cis stereochemistry. The presence of four bands, ν(M–N), in the 550–395-cm^{-1} region has been proposed as a criterion for a cis configuration for disubstituted bis(ethylenediamine) complexes of chromium(III).[25] The corresponding trans isomers invariably show only three bands in this region. The infrared spectrum of our product, dicyanobis(ethylenediamine)chromium(III) iodide, reveals four well-defined bands at 550, 536, 491, and 425 cm^{-1}. The C≡N stretching frequency appears at 2139 cm^{-1}. Although we expect this band to be split, there is no evidence of any splitting

Table I. Solution Spectra of Some *Cis*-Disubstituted Bis(ethylenediamine)chromium(III) Complexes

Complex	Obsd bands[a]	Calcd band positions[b]	Assignment[c]
cis-$[Cr(en)_2(CN)_2]^+$	14 049 (0.068)	14 069	$^4B_{1g} \rightarrow {}^2A_{1g}(^2E_g)$
	14 245 (0.148)	14 078	$^2B_{1g}(^2E_g)$
	14 641 (0.118)	14 480	$^2E_g(^2T_{1g})$
	15 037 (0.116)	14 492	$^2A_{2g}(^2T_{1g})$
	23 041 (70.0)	23 001	$^4E_g{}^a(^4T_{2g})$
		24 175	$^4B_{2g}(^4T_{2g})$
	29 500 (62.3)	29 282	$^4A_{2g}(^4T_{1g})$
		29 924	$^4E_g{}^b(^4T_{1g})$
cis-$[Cr(en)_2(CN)H_2O]^{2+}$ [e]	21 413 (53.4)		
	28 129 (49.1)		
cis-$[Cr(en)_2(CN)OH^+$ [f]	20 513 (59.4)		
	25 907 (54.5)		
	28 986 (35.9)[d]		
cis-$[Cr(en)_2(H_2O)_2]^{3+}$ [g]	20 618 (41.7)		
	27 250 (65.3)		

[a] The observed band positions are given in cm^{-1} followed by extinction coefficients (M^{-1} cm^{-1}). [b] Calculated band positions were obtained by solving the strong-field quadrate d^3 energy matrices[3] with $Dq = 2417.5$ cm^{-1}, $B = 575$ cm^{-1}, $C = 3200$ cm^{-1}, $Dt = -130$ cm^{-1}, and $Ds = -130$ cm^{-1}. [c] Octahedral parent in parentheses. [d] Shoulder. [e] pH 2.9, $\mu = 2.0$. [f] pH 10.4, $\mu = 2.0$. [g] pH 1.5, $\mu = 2.0$.

in this salt or in any of the others, including the optically active iodide.

Ion-exchange chromatography has frequently been used in distinguishing between *cis*- and *trans*-diacidobis(ethylenediamine)chromium(III) complexes. For example, the *trans*-difluorobis(ethylenediamine)chromium(III) ion can be eluted from Dowex 50W-X4 (100–200 mesh, H^+ form) with 0.3 N perchloric acid.[8] The corresponding cis isomer is known to require the use of 0.6 N acid[26] for elution. In our exchange experiments we were forced to use sodium cycle resin and sodium perchlorate solutions to prevent acid-catalyzed decomposition on the column. In order to make sure that these ionic changes were insignificant as far as the exchange experiments were concerned, we loaded the *cis*- and *trans*-difluorobis(ethylenediamine)chromium(III) complexes onto the sodium cycle resin and eluted with sodium perchlorate. The results were as expected; i.e., 0.3 N sodium perchlorate eluted the trans isomer, but 0.6 N salt solution was required to remove the cis isomer. In similar experiments the $Cr(en)_2(CN)_2^+$ ion could be removed from the resin only with 0.6 N sodium perchlorate, thus adding credibility to our assignment of the cis configuration.

At this point the stereochemistry of the dicyano complex was fairly well established, but absolute proof was still lacking. In the absence of crystallographic data we decided to attempt a resolution of the complex cation using ammonium (+)D-α-bromocamphor-π-sulfonate as the resolving agent. Mixing aqueous solutions of $[Cr(en)_2(CN)_2]Cl\cdot 0.25DMF$ and the resolving agent resulted in precipitation of the diastereomer containing (+)D-$Cr(en)_2(CN)_2^+$ in high yield. This optically active cation was recovered as the iodide salt by trituration with ethanolic solutions of HI. The (−)D isomer was recovered by treating the diastereomer filtrate with saturated aqueous sodium iodide. The specific rotation of (+)D-$[Cr(en)_2(CN)_2]I$ was +28.8° dm^{-1} g^{-1} ml and for (−)D-$[Cr(en)_2(CN)_2]I$ it was −28.1° dm^{-1} g^{-1} ml. The equal though opposite values for the specific rotations suggest that resolution is complete, although we cannot rule out fortuitous agreement.

The specific rotation of $(+)_{589}$-$[Co(en)_2(CN)_2]Cl$ is +24.7° dm^{-1} g^{-1} ml.[4a] In order to make a direct comparison of the cobalt complex with its chromium analogue we must convert to molecular rotations.[27] On this basis, $[M]^{25}$D is 66° dm^{-1} mol^{-1} ml for the cobalt complex and 101° dm^{-1} mol^{-1} ml for the chromium complex. Vaughn and Krainc[28] have stated that specific rotations (and therefore molar rotations) of chromium complexes are usually one-third to one-fourth as large as those of their cobalt analogues. In the present example, however, this is not the case and House[29] has recently shown that the molar rotation of $(+)_{589}$-$Cr(en)_2(NCS)_2^+$ is greater than that of $(+)_{589}$-$Co(en)_2(NCS)_2^+$. We would therefore caution against the use of such a generalization.

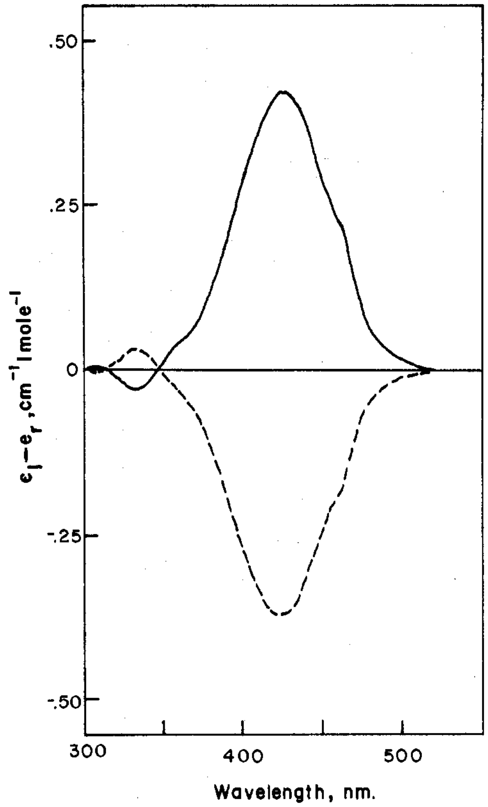

Figure 2. Circular dichroism spectra of $(+)_{589}$-$Cr(en)_2(CN)_2^+$ (solid line) and $(-)_{589}$-$Cr(en)_2(CN)_2^+$ (dotted line) in aqueous solution.

Circular dichroism spectra of the enantiomeric $(+)_{589}$- and $(-)_{589}$-*cis*-$Cr(en)_2(CN)_2^+$ cations are presented in Figure 2. Some resolution of band structure is apparent in these spectra but definitive assignments based upon C_2 symmetry do not appear fruitful. We believe, however, that the general features of the CD spectra are useful in assigning stereochemistry to the two optical isomers. The absolute configuration of $(+)_{589}$-$Cr(en)_3^{3+}$ has been inferred[30] as D by comparison of its CD spectrum with that of $(+)_{589}$-$Cr((-)pn)_3^{3+}$ ((−)pn ≡ $(-)_{589}$-propylenediamine), whose absolute configuration is dictated as L by the steric requirements of the (−)-diamine. The two spectra are enantiomorphous in the region of the low-energy spin-allowed transitions, $^4A_2 \rightarrow {}^4A_1$, $^4E^a$. Recent SCC-type molecular orbital calculations by Schreiner et al.[31] lend some theoretical support to this experimental conclusion, but no x-ray structural data are available. Inasmuch as the CD spectra of $(+)_{589}$-$Cr(en)_3^{3+}$ and $(+)_{589}$-*cis*-$Cr(en)_2(CN)_2^+$ exhibit positive Cotton effects in that region of the spectra descendent from the octahedral $^4A_{2g} \rightarrow {}^4T_{2g}$ transition we *tentatively* assign the absolute configuration of $(+)_{589}$-*cis*-$Cr(en)_2(CN)_2^+$ as D and that of its enantiomer $(-)_{589}$-*cis*-$Cr(en)_2(CN)_2^+$ as L (Figure 3). These predictions must await structural proof but we note that similar arguments[32] relating the structures of $(+)_{589}$-$Co(en)_3^{3+}$ and $(+)_{589}$-*cis*-$Co(en)_2(CN)_2^+$ have been confirmed by crystal structure analyses.[33,34]

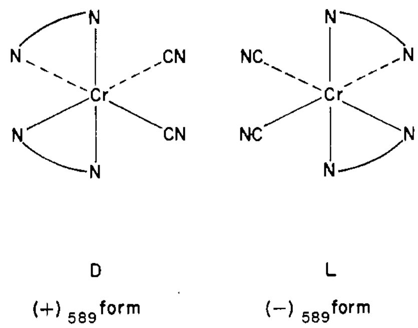

Figure 3. Proposed configurations for the $(+)_{589}$- and $(-)_{589}$-$Cr(en)_2(CN)_2^+$ cations.

When aqueous solutions of *cis*-$Cr(en)_2(CN)_2^+$ are decomposed in acidic solutions, two products can be isolated by ion-exchange techniques. The first, which was eluted from sodium cyanide resin with 2.0 M sodium perchlorate (pH 4.0), gave a cyanide ion to chromium ratio of 1.01. The second product was held strongly by the cation-exchange resin but could be slowly eluted with the same concentration of sodium perchlorate (pH 1.5). The spectrum of this complex is identical with the reported spectrum of the *cis*-diaquobis(ethylenediamine)chromium(III) ion and is reproduced in Figure 4. Other than the starting material, no other species was observed on the resin. Because of the cis configuration of the starting material and terminal product of the aquation, we have assigned a cis geometry to the intermediate. Analysis is consistent with the formulation of *cis*-$Cr(en)_2(CN)(H_2O)^{2+}$. We have not been able to isolate this material as a solid salt for resolution studies and absolute confirmation of stereochemistry, but we wish to point out that the spectra in Figure 4 are consistent with a stepwise replacement of cyanide ligands by water molecules, according to reactions 1 and 2. Because cyanide lies above water in the spectrochemical series, we observe a shift toward the red as cyanide is replaced by water. The spectrum of *cis*-$Cr(en)_2(CN)(H_2O)^{2+}$, although broad, appears uniformly gaussian in shape with no observable splitting. Pertinent band maxima and molar absorption indices for *cis*-$Cr(en)_2(CN)(H_2O)^{2+}$ and *cis*-$Cr(en)_2(H_2O)_2^{3+}$ are collected in Table I. We have also included the data for *cis*-$Cr(en)_2(CN)(OH)^+$ recorded at pH 10.5.

$$Cr(en)_2(CN)_2^+ + H^+ \xrightarrow{H_2O} Cr(en)_2(CN)(H_2O)^{2+} + HCN \qquad (1)$$

$$Cr(en)_2(CN)(H_2O)^{2+} + H^+ \xrightarrow{H_2O} Cr(en)_2(H_2O)_2^{3+} + HCN \qquad (2)$$

Chan and Tobe[4a] have reported that 0.1 N acid solutions of *cis*-$Co(en)_2(CN)_2^+$ at 80 °C exhibit no decomposition in 5 days. In contrast to this the *cis*-$Cr(en)_2(CN)_2^+$ ion decomposes very rapidly under identical conditions. The remarkable inertness of the *cis*-dicyanobis(ethylenediamine)cobalt(III) ion when compared to its chromium(III) analogue must reflect substantial differences in the metal–carbon bond strength. However, we do expect metal to cyanide π bonding via the cyanide antibonding orbitals to increase in strength on going from chromium(III) to cobalt(III) because the number of d electrons available for π bonding increases and we also expect the metal–carbon bond strength to increase in the same order because of an increase in the effective nuclear charge.

The reaction of *cis*-dicyanobis(ethylenediamine)chromium(III) salts with the hydrohalic acids HCl and HBr has been utilized to prepare *cis*-dichlorobis(ethylenediamine)chromium(III) salts and *cis*-dibromobis(ethylenediamine)chromium(III) bromide.

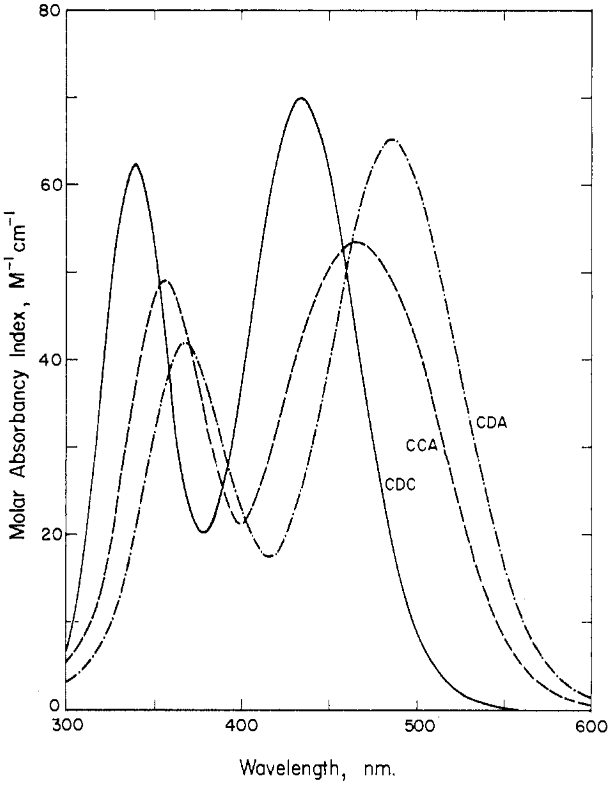

Figure 4. Visible and near-ultraviolet spectra of *cis*-$Cr(en)_2(CN)_2^+$ (CDC), *cis*-$Cr(en)_2(CN)(H_2O)^{2+}$ (CCA), and *cis*-$Cr(en)_2(H_2O)_2^{3+}$ (CDA) in aqueous solution. The spectra of *cis*-$Cr(en)_2(CN)(H_2O)^{2+}$ and *cis*-$Cr(en)_2(H_2O)_2^{3+}$ were recorded at pH 3 and pH 1.5, respectively.

A kinetic study of the acid hydrolysis of the *cis*-$Cr(en)_2(CN)_2^+$ and *cis*-$Cr(en)_2(CN)(H_2O)^{2+}$ is now under way in this laboratory.

Acknowledgment. It is a pleasure to acknowledge Dr. J. R. Perumareddi for his helpful discussions on quadrate chromium(III) complexes and for supplying us with a copy of his diagonalization program which we have adapted for use on the CDC 6600 computer. A.P.S. wishes to acknowledge the financial assistance of the Indiana University Chemistry Department throughout the course of this work.

Registry No. *cis*-$[Cr(en)_2(CN)_2]ClO_4$, 56848-41-0; *cis*-$[Cr(en)_2(CN)_2]I$, 58602-37-2; *cis*-$[Cr(en)_2(CN)_2]Cl$, 58602-38-3; *cis*-$[Cr(en)_2(CN)H_2O]^{2+}$, 58602-39-4; $(+)_{589}$-*cis*-$[Cr(en)_2(CN)_2]C_{10}H_{14}SO_4Br$, 55955-14-1; $(+)_{589}$-*cis*-$[Cr(en)_2(CN)_2]I$, 58602-40-7; $(-)_{589}$-*cis*-$[Cr(en)_2(CN)_2]I$, 58641-32-0; *cis*-$[Cr(en)_2(CN)OH]^+$, 58602-41-8; *cis*-$[Cr(en)_2(H_2O)_2]^{3+}$, 22432-36-6; *cis*-$[Cr(en)_2Cl_2]Cl$, 14240-29-0; *cis*-$[Cr(en)_2Br_2]Br$, 14263-07-1.

References and Notes

(1) Abstracted from the Ph.D. thesis of Alfred Sattelberger.
(2) C. S. Garner and D. A. House, *Transition Met. Chem.*, **6**, 59 (1970).
(3) J. R. Perumareddi, *Coord. Chem. Rev.*, **4**, 73 (1969).
(4) (a) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 966 (1963); (b) K. Ohkawa, J. Fujita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **38**, 66 (1965); (c) K. Konya, H. Nishikawa, and M. Shibata, *Inorg. Chem.*, **7**, 1164 (1968).
(5) In addition to the cyanoaquochromium(III) complexes synthesized in this laboratory,[6] Wakefield has prepared cyanofluoro-, azidocyano-, cyanoisothiocyanato-, and chlorocyanochromium(III) complexes.[7]
(6) W. B. Schaap, R. Krishnamurthy, D. K. Wakefield, and W. F. Coleman in "Coordination Chemistry", S. Kirschner, Ed., Plenum Press, New York, N.Y., 1967, p 177.
(7) D. K. Wakefield, private communication.
(8) J. W. Vaughn, O. Stvan, and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).
(9) For solutions, the specific rotation of the solute $[\alpha]^t_\lambda$ is defined as $[\alpha]^t_\lambda = \alpha^t_\lambda lc$ (deg dm^{-1} g^{-1} ml), where α^t_λ is the observed rotation at a specified

wavelength (λ) and temperature (t), l is measured in decimeters, and c is in grams per milliliter. All solutions had a concentration of 5 mg/ml and corrections were applied for the water blanks.
(10) Because of its toxicity, all manipulations involving hydrogen cyanide were performed at or near 0 °C in a well-ventilated hood.
(11) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", Vol. 1, Academic Press, New York, N.Y., 1965, p 658.
(12) R. J. Angelici, "Synthesis and Technique in Inorganic Chemistry", W. B. Saunders, Philadelphia, Pa., 1969, p 18.
(13) D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).
(14) W. W. Wendlandt and C. H. Stembridge, *J. Inorg. Nucl. Chem.*, **27**, 575 (1965).
(15) N. A. Maes, M. S. Nozari, and J. A. McLean, *Inorg. Chem.*, **12**, 750 (1973).
(16) G. W. Haupt, *J. Res. Natl. Bur. Stand.*, **48**, 414 (1952).
(17) G. D. Jimerson, Ph.D. Thesis, Indiana University, 1970.
(18) D. D. Darsow and W. B. Schaap, unpublished observations.
(19) G. D. Jimerson and W. B. Schaap, submitted for publication in *Inorg. Chem.*
(20) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).
(21) C. J. Ballhausen, "Ligand Field Theory," McGraw-Hill, New York, N.Y., 1962, p 107.
(22) $Dq_{CN^-} = 2650$ cm^{-1} and $Dq_{en} = 2185$ cm^{-1}.[3]
(23) W. A. Baker and M. G. Phillips, *Inorg. Chem.*, **5**, 1042 (1966).
(24) R. K. Lowry and J. R. Perumareddi, *J. Phys. Chem.*, **74**, 1371 (1970).
(25) M. N. Hughes and W. R. McWhinnie, *J. Chem. Soc. A*, 592 (1967).
(26) K. R. A. Fehrmann and C. S. Garner, *J. Am. Chem. Soc.*, **82**, 6294 (1960).
(27) The molecular rotation of the solute $[M]^t_\lambda$ is defined as $[M]^t_\lambda = (M/100)[\alpha]^t_\lambda$ (deg dm^{-1} mol^{-1} ml), where M is the molecular weight of the solute and $[\alpha]^t_\lambda$ is the specific rotation.[9]
(28) J. W. Vaughn and B. J. Krainc, *Inorg. Chem.*, **4**, 1077 (1965).
(29) D. A. House, *J. Inorg. Nucl. Chem.*, **35**, 3103 (1973).
(30) J. H. Dunlop and R. D. Gillard, *J. Inorg. Nucl. Chem.*, **27**, 361 (1965).
(31) R. S. Evans, A. F. Schreiner, and P. J. Hauser, *Inorg. Chem.*, **13**, 2185 (1974).
(32) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).
(33) K. Nakutsu, M. Shiro, Y. Sarto, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **30**, 158 (1957).
(34) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **44**, 2721 (1971).

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Cis Labilization of Ligand Dissociation. 4. Kinetics and Mechanism of ^{13}CO Exchange with $Cr(CO)_4$(chelate) Complexes[1]

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The kinetics and stereochemistry of ^{13}CO incorporation upon exchange with $Cr(CO)_4$phen and $Cr(CO)_4$bpy at 40 °C in 1,2-dichloroethane have been evaluated. The results are in best accord with a mechanism which involves preferential loss of CO from the cis position ($k_{cis} \geq 10k_{trans}$) and a *partially* fluxional five-coordinate intermediate, $Cr(CO)_3$(chelate). Exchange of ^{13}CO with $Cr(CO)_4$diphos at 110 °C in decalin and with $Cr(CO)_4$dpp at 90 °C in decalin proceeds preferentially at the cis positions, but it was not possible to ascertain anything of the fluxional character of the presumed five-coordinate intermediate. Reaction of ^{13}CO with $Cr(CO)_4$nbd at 40 °C in 1,2-dichloroethane yields cis and trans dilabeled $Cr(CO)_6$. The above results are consistent with the site preference model which ascribes preferential loss of ligand from the cis position to stabilization of the transition state resulting from preferential siting of ligands.

In the previous papers of this series,[2-4] it has been shown that ligands which are weaker π acceptors than CO may labilize a substituted metal carbonyl complex toward dissociative ligand loss and that when labilization occurs, the ligand is lost preferentially from a position cis to the labilizing ligand. To investigate further the phenomenon of cis labilization, we have studied ^{13}CO exchange with $Cr(CO)_4$(chelate) complexes, in which chelate = 1,10-phenanthroline (phen), 2,2'-bipyridine (bpy), 1,2-bis(diphenylphosphino)ethane (diphos), 1,3-bis(diphenylphosphino)propane (dpp), 1,2-bis(diphenylarsino)ethane (dae), or 2,5-norbornadiene (nbd).

There have been several investigations of the kinetics and mechanisms of ligand substitution by various L' into group 6 metal carbonyl chelate complexes $M(CO)_4$(chelate) (M = Cr, Mo, W).[5-24] The rate law shown in eq 1 is applicable.

$$d[M(CO)_4(\text{chelate})]/dt = \{k_1 + k_2[L]\}[M(CO)_4(\text{chelate})] \qquad (1)$$

Depending on the chelating ligand, several products have been observed; these include $M(CO)_3$(chelate)L', $M(CO)_4L'_2$, and $M(CO)_3L'_3$. Three mechanisms[24,25] have been postulated to explain the observed rate law and products: (a) an associative pathway, the application of which has been limited to Mo and W complexes, and a mechanism which is therefore not applicable to the present work; (b) CO dissociation as the rate-determining step, accounting for the k_1 term in the rate law; (c) a chelate ring opening pathway as shown in Figure 1. The rate-determining step is dissociation of one end of the chelate. Dobson[20] has shown that this mechanism can yield a rate law term which is first order in both starting complex and entering ligand.

Comparisons previously made[5,7] indicate that dissociative loss of CO is facile in $Cr(CO)_4$(chelate) complexes relative to $Cr(CO)_6$. However, the site of ligand dissociation cannot be inferred rigorously from substitution reactions; the incoming ligand, by virtue of its different steric requirements or interactions with the chelate might not enter the site of CO dissociation. This difficulty is circumvented in ^{13}CO exchange studies. However, in any attempts to make stereochemical inferences from ^{13}CO exchange studies, account must be taken of the nature of the five-coordinate intermediate generated by either CO dissociation or chelate ring opening. Is the intermediate rigid, as is sometimes implicitly assumed, or fluxional? We report here a study of the kinetics and stereochemistry of ^{13}CO exchange in several complexes of the type $Cr(CO)_4$(chelate).

Experimental Section

Preparation of Compounds. All reactions, preparations, and manipulations were performed under N_2 protection. All compounds have previously been reported; $Cr(CO)_4$phen,[26] $Cr(CO)_4$bpy,[27] $Cr(CO)_4$nbd,[28] and $Cr(CO)_4$diphos[29] were prepared as reported; $Cr(CO)_4$dpp and $Cr(CO)_4$dae were prepared using the method of Chatt.[29] Satisfactory elemental analyses and infrared spectra were obtained for the various species.

Preparation of *fac*-$Cr(CO)_3(^{13}CO)$phen. A saturated 1,2-dichloroethane solution of *fac*-$Cr(CO)_3$phenPPh_3 was placed in an exchange vessel[2] and thermostated to 40.0 °C. ^{13}CO (90% enriched) was circulated through the solution for 35 min and the reaction then quenched by immersing the vessel into liquid N_2. The solvent was