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Proton and Carbon-13 NMR Studies of *cis-eq-* and *trans-eq-*Ethylenediamine-*N,N,N'*-triacetatocobalt(III) and *cis-eq-N-*Methylethylenediamine-*N,N',N'*-triacetatocobaltate(III). Crystal Structure of NH_4*cis-eq-*[Co(ed3a)CN]

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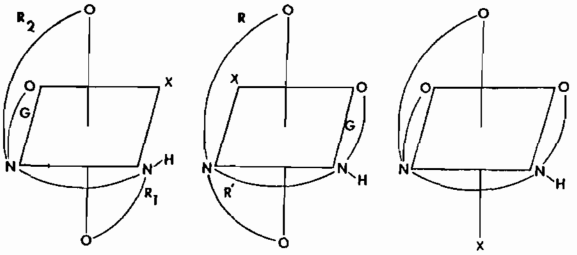
Abstract

The complexes K*cis-eq-*[Co(ed3a)CN], K*cis-eq-*[Co(med3a)CN)], and K*trans-eq-*[Co(ed3a)CN] were synthesized and characterized. The ^1H and ^{13}C NMR spectra obtained with a 300 MHz spectrometer are reported and compared to corresponding aqua and nitro complexes. The PMR spectra show good resolution for all protons, including those of the ethylenediamine backbone. The NMR spectra of the cyano complexes are most similar to those of the corresponding nitro complexes. The major changes in the ^{13}C NMR spectra can be explained based on β-substituent effects involving the N-methyl group or conversion from the *cis-eq* to the *trans-eq* isomers. Racemic $NH_4[Co(ed3a)CN]\cdot 2H_2O\cdot 0.5CH_3OH$ was found to be triclinic, *P*-1 with the cell dimensions: $a = 6.597(2)$, $b = 7.783(4)$, $c = 15.72(1)$ Å, $\alpha = 88.63(5)$, $\beta = 85.55(5)$, and $\gamma = 69.89(4)°$. There are two molecules in the unit cell.

Introduction

Ethylenediamine-*N,N,N',N'*-tetraacetate ion (edta) has been studied widely as an analytical reagent, as a sequestering agent for many metal ions, and because of the interesting stereochemistry of its metal complexes. The metal complexes are usually six-coordinate, but complexes with H_2O in a seventh coordination site are encountered for iron(III) [1] and manganese(II) [2]. The edta ligand can also be pentadentate with one acetate arm uncoordinated in complexes such as those of Co(III) and Cr(III) with the sixth coordination site occupied by a ligand such as Cl^-, Br^-, NO_2^-, or H_2O. The stereochemistry of pentadentate complexes of edta-type ligands have been studied by varying the substituent R on the N with only one coordinated acetate arm. The possible isomers of the six-coordinate complexes of ethylenediamine-*N,N,N'*-triacetate ion (ed3a), or N-substituted ed3a are shown in Fig. 1. When X is NO_2^- and R is alkyl, only the *cis-eq*-isomer [3] forms in isolable abundance. When X is NO_2^- and R = H, both *cis-eq* and *trans-eq* isomers [4, 5] can be isolated. The only *cis-polar* isomer [6] isolated and characterized so far has been the one with $R = -CH_2CO_2H$ and $X = Br^-$, $[Co(Hedta)Br]^-$.

Complexes of edta-type ligands have been investigated extensively with emphasis on the relief of strain, by removal of one or more acetate arms, and the effects on circular dichroism (CD) spectra. It has



cis–equatorial trans–equatorial cis–polar

Fig. 1. The three geometrical isomers of [Co(ed3a)X].

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been particularly intriguing that the substituent R of substituted-ed3a complexes of the type [Co(Red3a)X] has a great effect on the CD spectra [7, 8] only if X is NO_2^-. Since NO_2^- is a much stronger field ligand than others studied, CD studies of complexes of an even stronger field ligand, CN^-, have been investigated and will be reported separately [9]. Here we report the results of a study of the stereochemistry of both the *cis-eq* and *trans-eq* isomers of $[Co(ed3a)CN]^-$ and the *cis-eq* isomer of $[Co(med3a)CN]^-$ (med3a = *N*-methylethylenediamine-*N*,*N*′,*N*′-triacetate ion). The results presented, based upon ^1H and ^{13}C NMR spectroscopy and X-ray crystallography are compared with earlier results for the corresponding complexes with NO_2^- or H_2O in the sixth coordination site. An adaptation of the method of Fujita *et al.* [10] for the preparation of the cyano complexes in DMSO proved more effective than earlier syntheses in water [11].

Experimental

Preparation of Ethylenediamine-N,N,N′-triacetic Acid and the Corresponding Aqua and Cyano Complexes with Co(III)

The ligand and its aqua complex with cobalt(III) were prepared by literature methods [5, 8, 12, 13]. The cyano complex was prepared by adaptation of the preparation of various Co(III) complexes made with *N*-methyltrimethylenediamine-*N*,*N*′,*N*′-triacetic acid by Fujita *et al.* [10]. A 0.49 g (7.5 mmol) quantity of potassium cyanide was added to 150 ml of a dimethylsulfoxide (DMSO) solution of $[Co(ed3a)H_2O]\cdot H_2O$ (1.63 g, 5.0 mmol). The mixture was warmed at 70 °C for about an hour, and the resulting solution was then chromatographed on a 5 × 40 cm column of Dowex 1-x8 (200–400 mesh) anion exchange resin in the Cl^- form. The column was first washed with water and then with 0.1 M KCl solution to develop a dark red band. The solution from this band was rotavaped to about 5 ml and desalted by gel filtration using a column (2.5 × 40 cm) of G-10 Sephadex. This solution was then rotavaped to a volume of about 3 ml, which was then allowed to stand overnight. Brick-red crystals (0.4 g) of K*cis-eq*-$[Co(ed3a)CN]\cdot 2H_2O$ were separated by filtration and washed with ethanol and then ether. The filtrate was rotavaped to a volume of about 2 ml and placed in a refrigerator to stand overnight. Purple crystals (0.3 g) of K*trans-eq*-$[Co(ed3a)CN]\cdot H_2O$ were collected, washed with ethanol and then ether, and air dried. Both isomers were recrystallized from a small amount of water. *Anal.* Calc. for K*cis-eq*-$[Co(ed3a)CN]\cdot 2H_2O$: C, 27.62; H, 3.86; N, 10.74. Found: C, 26.83; H, 4.06; N, 11.30%. Calc. for K*trans-eq*-$[Co(ed3a)CN]\cdot H_2O$: C, 28.96; H, 3.51; N, 11.26. Found: C, 28.45; H, 3.63; N, 11.45%.

Preparation of Potassium cis-eq-Cyano (N-methylethylenediamine-N,N′,N′-triacetato)-cobaltate(III) Semihydrate, Kcis-eq-[Co(med3a)CN]·0.5H₂O

This complex was prepared from the corresponding aqua complex [14] using the method of Fujita *et al.* [10]. A 1.65 g quantity (5.00 mmol) of the aqua complex and 0.49 g (7.5 mmol) of KCN, yielded 0.85 g (45% of theoretical) of K*cis-eq*-$[Co(med3a)CN]\cdot 0.5H_2O$. *Anal.* Calc. for K*cis-eq*-$[Co(med3a)CN]\cdot 0.5H_2O$: C, 31.75; H, 3.73; N, 11.11. Found: C, 31.07; H, 3.74; N, 11.47.

Physical Measurements

Electronic absorption spectra were obtained using a Varian Superscan 3 recording spectrophotometer, using aqueous solutions of about 3×10^{-3} M. A Perkin-Elmer 197 Infrared Spectrophotometer was used to record infrared spectra of the compounds in KBr discs. ^1H and ^{13}C magnetic resonance spectra were measured using a Bruker WH 300 Fourier-transform nuclear magnetic resonance (NMR) spectrometer. The field frequency ratio was stabilized by locking on the deuterium signal from the D_2O solvent. The internal standard for the ^1H spectra was sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). Acidic solutions were 0.05 M DCl in D_2O. Spin-tickling AB patterns caused by glycinate protons required about 2 mW of power and decoupling ethylenediamine backbone protons required about 5 cW of power. The ^{13}C NMR spectra were recorded for samples that contained 1,4-dioxane as the internal standard. The spectrometer operated at 75.43 MHz in the ^{13}C mode. The solvent in all cases was D_2O, and, as for the ^1H spectra, the field frequency ratio was stabilized by locking to the deuterium signal of D_2O. Broad band decoupling employed about 1 W of power and selective decoupling required about 0.3 W of power.

Deeply colored red plate-like crystals of the racemic $NH_4[Co(ed3a)CN]\cdot 2H_2O\cdot 0.5CH_3OH$ were obtained by exchanging the K^+ ion using Dowex 50W cation exchange resin, evaporating the solution in a stream of air, and finally recrystallizing the solid from aqueous methanol solution. A single crystal, suitable for X-ray crystallography, was chosen that measured 0.63 × 0.75 × 0.38 mm; density 1.47 g/cm³. The crystal system and the unit cell parameters were obtained using rotation and oscillation photographs taken on the goniometer using the system's automatic centering and indexing routines. The lattice parameters were refined by least-squares procedures using 21 reflections selected from a rapid preliminary scan for the data taken between 3° and 20° in θ. The crystal was triclinic *P*-1 with cell dimensions; $a = 6.597(2)$, $b = 7.783(4)$, $c = 15.72(1)$ Å, $\alpha = 88.63(5)$, $\beta = 85.55(5)$, $\gamma = 69.89(4)°$. There are two molecules per unit cell. X-ray diffraction data were collected at

12°/min on a Nicolet P3 diffractometer using Mo Kα ($\lambda = 0.7107$ Å) radiation in the $\theta-2\theta$ mode with a graphite monochromator. Absorption corrections were made on the basis of a set of azimuthal transmission curves collected for twenty selected reflections with χ from 240° to 300°. These data were fitted to a pseudo-ellipsoidal function using a least-squares procedure. The absorption corrections applied range from 0.40 to 0.47. Radiation damage was approximated by interpolations on a curve based on the average variation of three standard reflections, (0, 0, 2; 2, –2, 0; 3, 4, 1) measured periodically during data collection. The decay corrections applied ranged from 0.99 to 1.05. A total of 3106 reflections were collected including the standards; of these, 108 reflections were rejected because of bad background measurements or unusual peak profiles. There were 2605 independent reflections from this set, of which 102 were found to be less than $2.5\sigma(F)$ above their background and were considered unobserved.

The structure was determined using Patterson methods and was refined by a least-squares procedure using a 'blocked cascade' algorithm (SHELX Version 4). All non-hydrogen atoms were refined using anisotropic temperature factors. Hydrogen atoms which were determined from difference Fourier maps were refined isotropically. The ammonium ion was refined as a rigid body by idealizing the tetrahedral ion. This was carried out because the hydrogen atoms of the ammonium ion tended to diverge during refinement which may be due to some disordering in the ion's position. Solvent molecules of crystallization were determined from difference Fourier maps. There is one water molecule with full occupancy. The rest of the solvent molecules were disordered. This included two water molecules and a molecule of methanol in the unit cell. The disorder appears to involve the substitution of one of the water molecules by a water–methanol complex. This water–methanol substitution causes a breakdown of the center of inversion, and the disordered molecules were refined assuming half occupancy for each atom. No attempts were made to refine their relative occupancies. Furthermore, these molecules were refined using isotropic temperature factors. The least-squares procedure gave final R and weighted R values of 0.033 and 0.041, respectively. The weights used were based on the counting statistics with instrumental instabilities accounted for by a factor equal to 0.002. Refinement was carried out to convergence with a maximum shift/error ratio of 0.031. The most significant peak in the final difference Fourier map had a value of 0.42 e/Å.

The data collection and analysis routines used were part of the Nicolet's R3m computerized X-ray diffraction system. All calculations were carried out on a Data General Eclipse S/140 computer. SHELX is the primary system for structure determination on the Nicolet crystallographic system.

Results

The Ortep drawing of NH_4*cis-eq*-[Co(ed3a)CN] is shown in Fig. 2. The PMR spectral parameters of the *cis-eq* complexes, K[Co(ed3a)CN], K[Co(med3a)-CN], Na(Co(ed3a)NO_2], Na(Co(med3a)NO_2], [Co-(ed3a)H_2O], and [Co(med3a)H_2O] are listed in Table I along with those of K*trans-eq*-[Co(ed3a)CN] and K[Co(edta)] [15]. The edta complex is included since the others are structural modifications of $[Co(edta)]^-$. The cyano complexes are newly prepared and constitute the main objective of this report. The nitro and aqua complexes have been prepared and characterized by others [5, 14, 16] using similar methods. We have remeasured the PMR spectra of these complexes using the same 300 MHz NMR spectrometer so that valid comparisons can be made.

For octahedral polyacetate complexes, the in-plane equatorial glycinate ring is labeled G, the out-of-plane ring R, and the ethylenediamine ring E (see insert Fig. 3). The protons on the E_1 carbon, C(3), are labeled $H_{e'}$ and $H_{a'}$, using 'e' for equatorial and 'a' for axial. The protons on the E_2 carbon, C(4), are labeled similarly. Note also that the R_1 ring emanates from N(1) and the R_2 ring from N(2). For the *trans-eq* isomer there are two R rings emanating from N(2) and a G ring emanating from N(1). The less substituted donor nitrogen atom is N(1). The E_1 and E_2 carbons are labeled as for the *cis-eq* isomers.

The PMR spectrum of K[Co(edta)] was remeasured at 300 MHz (Fig. 4) for comparison and to resolve the AB pattern for the E ring. Representative PMR spectra are shown in Figs. 3–8. The R_1 and G protons have always been found to produce AB quartet patterns with good resolution, and we have observed similar results here. Our measured J values for the *cis-eq* complexes are typically about 16 Hz

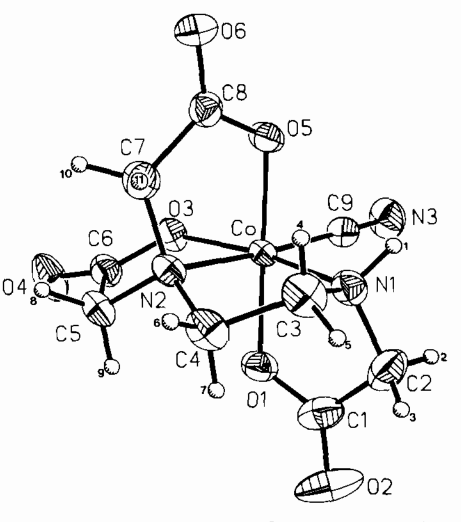

Fig. 2. An Ortep diagram of NH_4*cis-eq*-[Co(ed3a)CN]·H_2O·$0.5CH_3OH$.

TABLE I. PMR Parameters for the Complexes Studied

Complex	Protons	Pattern	δ (ppm)	Δ (ppm)	J (Hz)	
K[Co(edta)]	R	AB	3.91	0.12	18.4	
	G	AB	3.74	0.34	15.8	
	E	AB	3.60	0.36	9.8	
cis-eq-[Co(ed3a)H_2O]	R_2	AB	3.85	0.09	18.5	$J_{e'a'} = J_{ea} = 10, J_{a'a} = 14, J_{e'a} = J_{a'e} = 2$
	R_1	AB	3.67	0.81	17.7	
	G	AB	3.74	0.41	16.0	
cis-eq-[Co(med3a)H_2O]	R_2	singlet	3.98	0		$J_{e'a'} = J_{ea} = 9, J_{a'a} = 14, J_{e'a} = J_{a'e} = 4$
	R_1	AB	3.75	0.50	17.7	
	G	AB	3.74	0.40	15.9	
	CH_3	singlet	2.41			
K*cis-eq*-[Co(ed3a)CN]	R_2	AB	4.12	0.14	18.6	$J_{e'a'} = J_{ea} = J_{a'a} = 14, J_{e'a} = J_{a'e} = 4$
	R_1	AB	3.52	0.81	17.8	
	G	AB	4.07	0.09	16.0	
K*cis-eq*-[Co(med3a)CN]	R_2	AB	4.19	0.17	18.7	$J_{e'a'} = 15, J_{e'a} = J_{a'e} = 4, J_{a'a} = J_{ea} = 14,$ $J_{CH_3-H_{a'}} = 1$
	R_1	AB	3.64	0.55	17.5	
	G	AB	4.03	0.13	16.0	
	CH_3	singlet	2.41			
Na*cis-eq*-[Co(ed3a)NO_2]	R_2	singlet	4.07	0		$J_{e'a'} = 15, J_{a'a} = J_{ea} = 14, J_{e'a} = J_{a'e} = 4$
	R_1	AB	3.66	1.07	17.8	
	G	AB	3.99	0.20	16.0	
K*cis-eq*-[Co(med3a)NO_2]	R_2	singlet	4.23	0		$J_{e'a} = J_{a'a} = J_{ea} = 14, J_{e'a} = J_{a'e} = 3$
	R_1	AB	3.81	0.85	17.8	
	G	AB	3.94	0.21	15.8	
	CH_3	singlet	2.24			
K*trans-eq*-[Co(ed3a)CN]	R_2	AB	4.03	0.60	17.2	$J_{e'a'} = J_{ea} = J_{a'a} = 11, J_{e'a} = J_{a'e} = 3$
	R′	AB	3.94	0.52	16.2	
	G	AB	3.77	0.26	16.2	
	H_a	overlapping multiplet	3.29–3.14			
	$H_{a'}$	overlapping multiplet	3.29–3.14			
	H_e	coarse doublet	3.29			
	$H_{e'}$	coarse doublet	3.48			

for the G rings, a little less than 18 Hz for the R_1 rings, and a little more than 18 Hz for the R_2 rings. Sometimes, as in the case of the *cis-eq* nitro complexes, the R_2 protons appear as singlets. We found that, at 300 MHz, the R_2 protons for both of the cyano complexes and the [Co(ed3a)H_2O] complex showed a well-resolved quartet pattern. For the *cis-eq* complexes, the substitution of cyanide ion for water causes the PMR spectrum to change substantially, e.g., compare the results for the ed3a complexes of CN^- and H_2O. The center of the pattern for the R_2 protons, when cyanide replaces H_2O, is shifted to lower field by 0.27 ppm (deshielded) and the spread is increased by 0.05 ppm; the G protons are also shifted to lower field by 0.33 ppm and the spread is decreased by 0.31 ppm; the R_1 protons are shifted upfield by 0.15 ppm and the spread is essentially unchanged. It should be noted also that there is essentially no difference in the glycinate coupling constants J_{R2}, J_{R1}, and J_G between the cyano and the aqua complexes.

Probably the most dramatic feature of the PMR spectra of the *cis-eq* cyano complexes is the nearly complete resolution of the lines for the ethylenic hydrogens (E ring). This allows for the unambiguous assignment of lines for each of the protons (Fig. 3, the PMR spectrum of K[Co(ed3a)CN]). The doublet of doublets located at 2.80 ppm is attributed to the equatorial proton ($H_{e'}$) on E_1, C(3). The triplet of doublets at 3.37 ppm is assigned to the axial proton

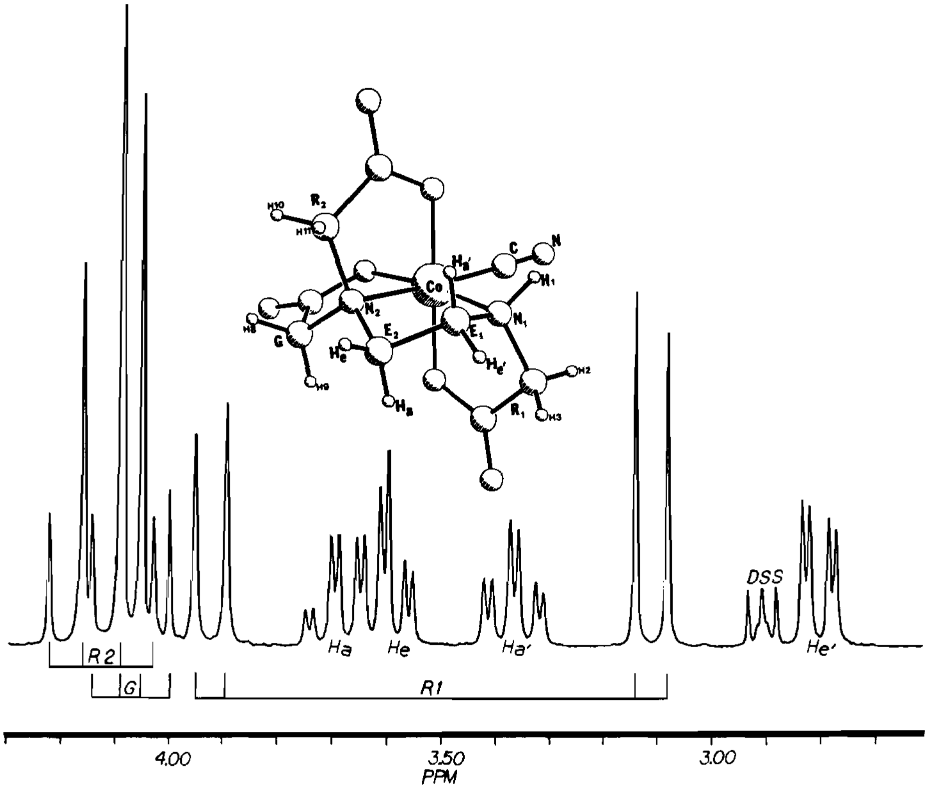

Fig. 3. The 300 MHz PMR spectrum of K*cis-eq*-[Co(ed3a)CN].

($H_{a'}$) on the same carbon atom. The doublet of doublets at 3.58 ppm is due to the equatorial proton on E_2, C(4), and the triplet of doublets at 3.69 is assigned to the axial proton on this carbon. When the same spectrum is measured in acidic solution (Fig. 5), the triplet of doublets located at 3.37 ppm is changed to a triplet of triplets further upfield. This extra splitting is caused by the N(1) hydrogen whose replacement by deuterium is slowed by the addition of DCl to the D_2O solution. In addition, the left arm of the R_1 quartet at 3.92 ppm is also further split in acidic solution. Parallel results are obtained when similar experiments are performed on the ed3a aqua complex (see Fig. 6). The two coarse doublets located at about 2.95 ppm are throught to be due to the two ethylenic equatorial protons and the multiplet with a 'spike' at about 3.46 ppm is thought to be due to the two axial protons of the ethylenic carbons. The two other peaks centered at about 3.55 ppm are part of the AB quartet for the R_1 glycinate protons. The other two of the set are located downfield at about 4.07 ppm. When considering these ethylenic protons and making comparisons between cyano and aqua complexes, similar protons (e.g., equatorial protons) absorb at similar frequencies whereas in the cyano complexes protons on the same carbon absorb at comparable frequencies.

To summarize: when H_2O replaces CN^- in the *cis-eq* complexes the biggest change in chemical shift is observed for the R_2, G, and E_2 protons. The R_1 protons are affected very little as are the protons of a methyl substituent replacing the N(1) hydrogen. Notice from Table I that the methyl peak resonates at 2.41 ppm for the corresponding aqua and cyano complexes. The greatest effect on the R_1 protons is realized when the methyl group replaces the H atom on N(1). In the corresponding cyano complexes, the center of the R_1 quartet is shifted to lower field by 0.12 ppm and the spread is changed by 0.26 ppm. Also, the methyl group, in producing the change, affects the upfield doublet to a greater extent than it affects the low-field doublet of the AB pattern. Of the ethylenic protons the largest effect is felt by $H_{e'}$, *i.e.* the equatorial proton on the E_1 carbon, the one closest to N(1) with the methyl substituent. The placement of the methyl group appears to shift this proton downfield to a greater extent than the others.

The PMR spectrum of K*trans-eq*-[Co(ed3a)CN] is shown in Fig. 8. There is no R_1 ring for this compound and the G in-plane ring is the one that now emanates from N(1). The E protons give results similar to those of the *cis-eq* aqua complex in that the resonance frequencies are differentiated according

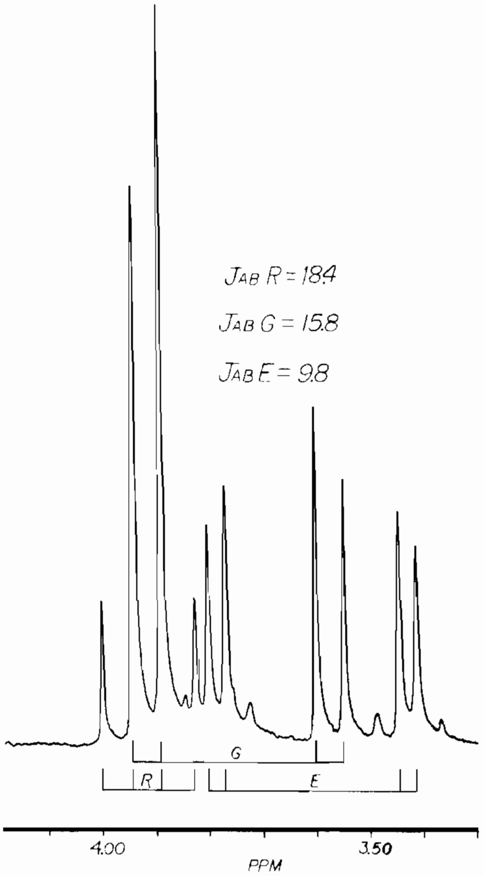

Fig. 4. The 300 MHz PMR spectrum of K[Co(edta)].

to kinds rather than positions of the protons. But here the equatorial protons both appear further downfield than the axial protons. The G ring protons are shifted upfield relative to the *cis-eq* isomer and the R_2 protons of the *trans-eq* isomer are shifted downfield when the glycinate ring to which they belong is broken at N(2) and reattached at N(1). This breaking and reattaching effectively converts the *trans-eq* isomer into a *cis-eq* isomer and is the simplest one step transformation (on paper) between the isomers.

The ^{13}C NMR spectral results are given in Table II. Typically, the G, R_2, and E_2 carbons resonate at lower fields than the E_1 and R_1 carbons. This is generally true for the *cis-eq* complexes regardless of which ligand occupies the sixth position. When CN^- replaces water for the *cis-eq* isomers, then the G, R_1, and E_2 carbons resonate at lower frequencies, and the R_1 and E_1 carbons resonate at slightly higher frequencies. When a methyl group replaces the hydrogen on N(1) the resonance of the G and E_1 carbons are most affected – typically shifted downfield by about 10 ppm. (This is fairly typical behavior of a wide range of organic compounds when a carbon replaces H in the β position.) This β-methyl downfield shift, in effect, changes the absorption sequence (low-field to high-field) from $G < R_2 < E_2 < R_1 < E_1$ for the *cis-eq* complexes to $E_1 < R_1 < G < R_2 < E_2$. The *trans-eq* complex, as expected because of severe structural differences, has the ordering somewhat reversed. Now the G and E_1 carbons are found farthest upfield.

Discussion

Crystal Structure

The X-ray crystallographic results for $NH_4[Co(ed3a)CN]$ are summarized in Tables III, IV, and V. An Ortep drawing is shown in Fig. 2. Previous studies related to this work include structural characterizations of $[Co(edta)]^-$ [17, 18] and [Co(ed3a)X] where X = H_2O, NCS^-, or NO_2^- [19–21]. The latter also includes complex ions made with the substituted ligand where the N(1) hydrogen is replaced by methyl or hydroxyethyl groups. The overall results listed here for primary bond lengths and angles for the ed3a cyano complex agree well with those for the related complexes. For $[Co(edta)]^-$ the reported [17] cobalt in-plane and out-of-plane oxygen distances of 1.945 and 1.887 Å, respectively, compared to our 1.921 for the in-plane and 1.900 and 1.884 for the two out-of-plane Co–O distances. Table VI compares related bond lengths for $[Co(edta)]^-$, $[Co(ed3a)H_2O]$, and $[Co(ed3a)CN]^-$. A further indication of gross structural similarity is the ring angle sums for the E, R_1, R_2, and G rings included in the Table. As with other studies, each of the rings was defined by a least-squares plane and the root mean square deviations were used to determine their relative planarity. The results agree with part work, namely the R_2 ring is most planar and the G ring is least planar of the glycinate rings. Summing ring angles and comparing deviations from least squares planes give consistent results. The major structural difference between $[Co(ed3a)H_2O]$ and $[Co(ed3a)CN]^-$ shows up along the N(2)–Co–L bond axis. In the cyano complex the Co–N(2) distance is longer and the Co–L (L = CN^- or H_2O) is shorter than for the aqua complex.

Proton NMR Spectra

Geminal hydrogen atoms on glycinate carbons in ethylenediaminepolycarboxylate complexes usually give rise to easily characterized AB quartets in PMR spectra, especially when high resolution computer-controlled spectrometers are used*. Complications caused by overlapping bands are easily resolved by 'spin-tickling', spectral remeasurement in acidic solution, and selective deuteration. Higher resolution

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*For a general discussion of how PMR can be applied to ethylenediaminepolycarboxylate complexes see ref. 22.

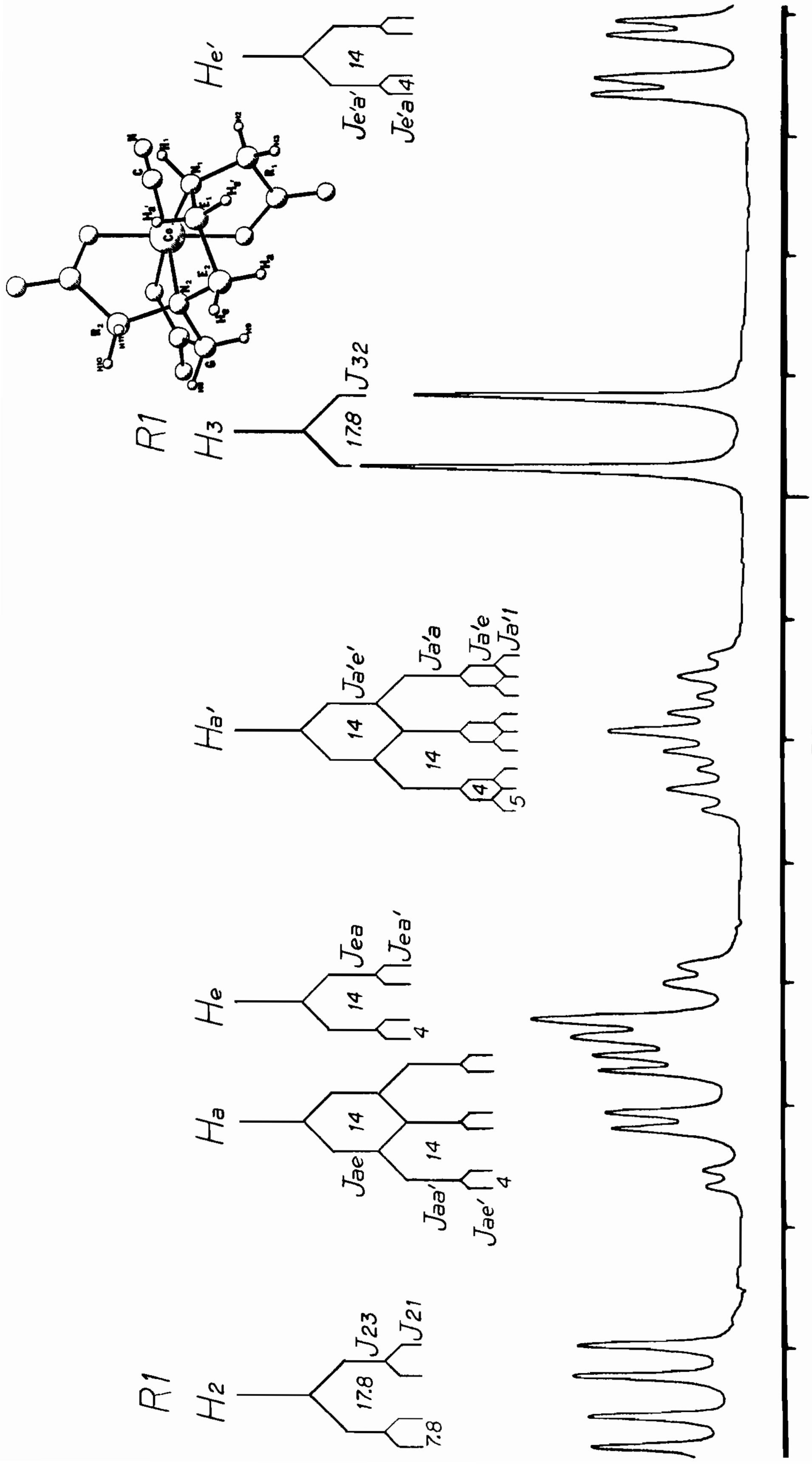

Fig. 5. The 300 MHz PMR spectrum of K*cis-eq*-[Co(ed3a)CN] in 0.05 M DCl.

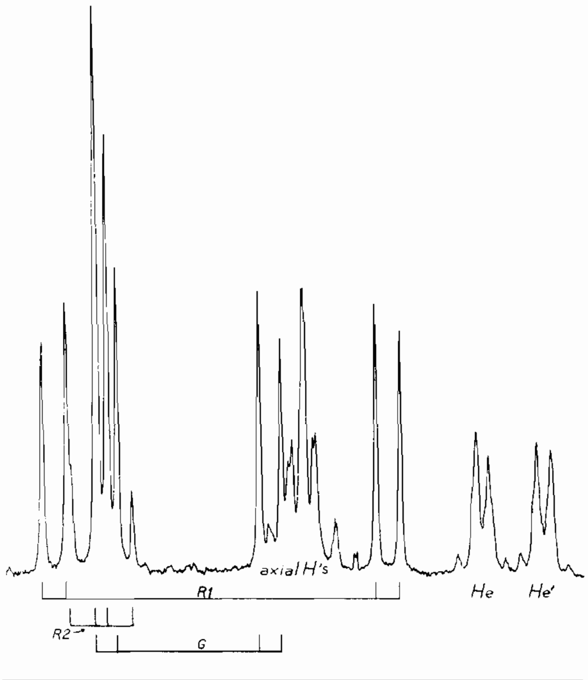

Fig. 6. The 300 MHz PMR spectrum of *cis-eq*-[Co(ed3a)-H_2O].

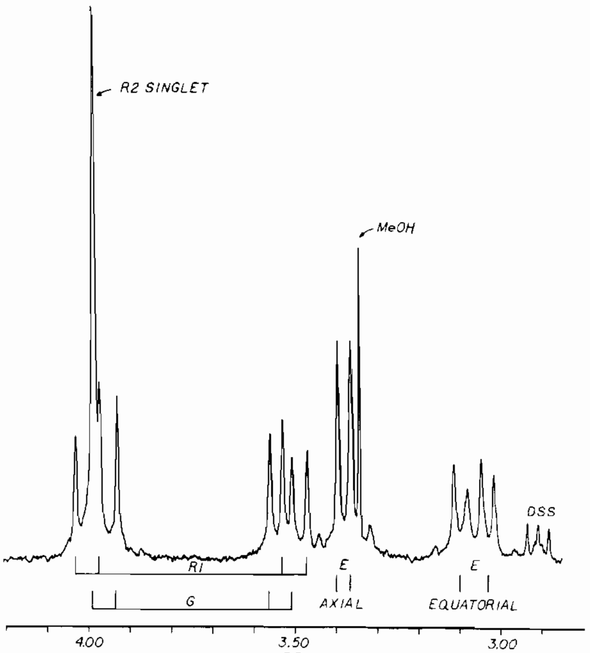

Fig. 7. The 300 MHz PMR spectrum of *cis-eq*-[Co(med3a)-H_2O].

spectrometers allow for greater precision in the measurement of spectral parameters such as coupling constants. Spectral peak positions (computer-fitted) are recorded to the ten-thousandth of a ppm so that a coupling constant reported to the nearest tenth of a Hz is reasonable.

For the ed3a complexes, which have no symmetry element higher than C_1, the R_2 ring protons always show the highest J values, then R_1, and finally the G ring protons. Geminal proton coupling constants depend upon the ring size and the electronegativities of atoms bound to the methylene carbon. Proximity to π functions (as carboxylate groups) also affects J_{AB}. Five- and six-membered cycloalkane rings show similar values (~12.6 Hz for cyclohexane) [23]. An electronegative α-substituent increases J as does a nearby carbonyl group. Measured J values of 16–18.5 Hz are reasonable, then, for chelated glycinate rings. Pople and Bothner-By [24] suggested that J_{AB} should be maximized when the line bisecting the dihedral angle made by the geminal hydrogens is coplanar with the π function of the carbonyl group. The R_1, R_2, and G rings are all similar except for the geometrical relationship in each ring between the geminal hydrogen dihedral angle and the proximal π function. A Dreiding model of a *cis-eq* complex indicates that the planarity of the three rings increases as $G < R_1 < R_2$ and is supported by the crystallographic least-squares planes for NH_4*cis-eq*-[Co(ed3a)CN]. No deviation from this sequence has been observed for several similar *cis-eq* complexes for which X-ray structural data are now available in this laboratory. A Dreiding model also indicates that the carbonyl function of each ring is not held rigidly in place and is relatively free to wiggle in and out of the least-squares plane defined by the other atoms (Co, N, C, O). This freedom of motion of the carbonyl group increases in the order $G < R_1 < R_2$. The model shows that the average position of the carbonyl bond vector of the R_2 ring is coincident with a line that bisects the H–C–H bond angle. This situation is similar for the R_1 and G rings, but to lesser degrees, as indicated by all of the PMR data to date. Accordingly, the R_2 glycinate hydrogens always have the highest coupling constant of the three rings. Sometimes the signal from the R_2 proton appears as a single line in the PMR spectrum rather than as the usual AB quartet. This is not because $J = 0$, but rather that the δ values for the two hydrogens are so similar, probably because of the high degree of planarity of the R_2 ring.

The X-ray crystallographic data for a series of *cis-eq* complexes [19, 20] give inconclusive support to inferences obtained from the molecular models regarding the coplanarity of the bisector of the angle formed by the geminal hydrogens and the π function of the glycinate rings. For example, the angular differences measured in this study for NH_4[Co(ed3a)-CN] are $R_2(\Delta) = 2°$, $R_1(\Delta) = 16°$, and $G(\Delta) = 16°$. For the corresponding aqua complex [19], $R_2(\Delta) = 5.9°$, $R_1(\Delta) = 19°$, and $G(\Delta) = 20°$. But results for the corresponding nitro complex [21] show $R_2(\Delta) = 10°$,

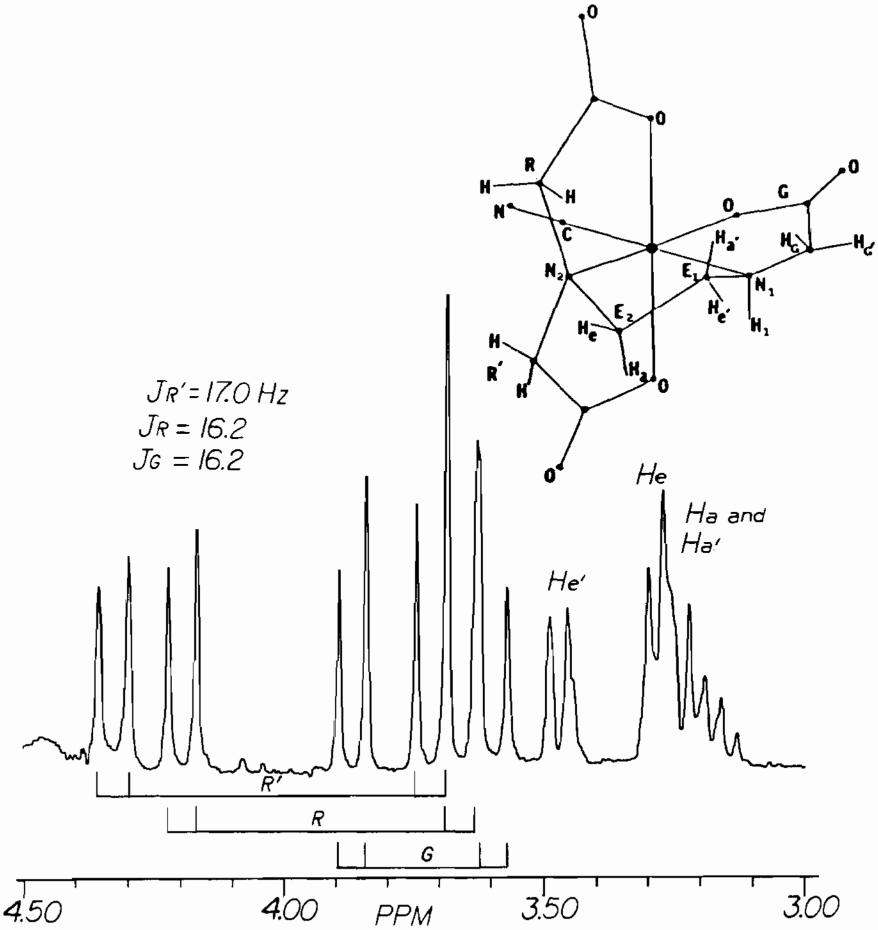

Fig. 8. The 300 MHz PMR spectrum of K*trans-eq*-[Co(ed3a)CN].

TABLE II. Carbon-13 Chemical Shifts from TMS for Cobalt(III) ed3a Complexes

Complex	Methylene carbons					Carbonyl	Methyl
	G	E_2	E_1	R_2	R_1		
cis-eq-[Co(ed3a)CN]$^-$	64.5	59.1	56.4	62.6	57.3	183.0, 183.4, 184.2	
cis-eq-[Co(ed3a)NO$_2$]$^-$ [a]	66.5	61.1	56.1	65.2	57.2	182.6, 184.1, 186.1	
cis-eq-[Co(ed3a)H$_2$O] [a]	67.3	62.7	55.6	66.5	57.1	182.9, 184.4, 185.7	
cis-eq-[Co(med3a)CN]$^-$	64.7	59.8	66.8[b]	62.6	67.3[b]	181.4, 182.7, 183.7	50.8
cis-eq-[Co(med3a)NO$_2$]$^-$ [a]	67.0	60.9	67.5	65.3	67.3	182.7, 183.4, 184.7	49.7
cis-eq-[Co(med3a)H$_2$O] [a]	67.6	62.0	66.2	67.1	66.2	182.7, 183.8, 183.9	49.4
				R_2'	R_2		
trans-eq-[Co(ed3a)CN]$^-$	52.1	66.6	49.1	67.1[d]	68.8	180.7, 181.7, 184.6	
trans-eq-[Co(ed3a)NO$_2$]$^-$ [c]	(50.6)	(66.4)	(55.0)	(69.1)[d]	(68.5)	182.6, 184.7, 184.7	

[a] From ref. 5. [b] Ref. 30 cited these values, from a preliminary report of the present work, in reverse order. [c] These values from ref. 5 were reported as uncertain. [d] R_2'.

$R_1(\Delta) = 3.0°$, and $G(\Delta) = 24°$. Deviations are caused undoubtedly by the proximity of the carbonyl oxygens in the lattice to water molecules, counter ions, and hydrogen atoms on N(1) of a neighboring complex ion. For example, in NH_4[Co(ed3a)CN] the hydrogen atom of an NH_4^+ ion is located 2.0 Å

TABLE III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $NH_4[Co(ed3a)CN] \cdot 2H_2O \cdot 0.5CH_3OH$

	x	y	z	U^a
Co	4545(1)	4208(1)	2696(1)	21(1)
C(9)	1868(4)	6003(3)	3115(1)	29(1)
N(3)	285(3)	7058(3)	3377(1)	43(1)
N(1)	5485(3)	5962(3)	2042(1)	32(1)
C(3)	7844(4)	5047(4)	1760(2)	39(1)
C(4)	8229(4)	3070(4)	1576(2)	36(1)
N(2)	7333(3)	2314(3)	2339(1)	27(1)
C(7)	8742(4)	2001(3)	3063(2)	35(1)
C(8)	7743(4)	3406(3)	3773(2)	29(1)
O(6)	8760(3)	3403(2)	4392(1)	40(1)
O(5)	5844(3)	4556(2)	3673(1)	30(1)
O(3)	3876(3)	2177(2)	3202(1)	30(1)
C(6)	4920(4)	662(3)	2818(2)	30(1)
O(4)	4480(3)	−744(2)	2942(2)	50(1)
C(5)	6782(4)	661(3)	2179(2)	32(1)
O(1)	3318(3)	3860(2)	1688(1)	34(1)
C(1)	3168(4)	5096(4)	1110(2)	42(1)
O(2)	2372(4)	5102(4)	435(1)	73(1)
C(2)	4058(5)	6578(4)	1333(2)	45(1)
W(1)[b]	2717(4)	9204(3)	4630(2)	51(1)
Hw(1)[b]	2535(59)	8452(53)	4720(25)	87(12)
Hw(2)[b]	2717(50)	9267(45)	4169(21)	43(9)
Nh[c]	2860(3)	2863(3)	5070(1)	37(1)
Hnha[c]	2639(45)	4029(14)	5098(18)	76(6)
Hnhb[c]	2016(37)	2599(39)	5465(13)	76(6)
Hnhc[c]	4209(19)	2258(34)	5164(18)	76(6)
Hnhd[c]	2611(44)	2581(38)	4571(9)	76(6)
W(2a)[d]	2786(13)	1207(11)	−40(5)	130(3)
W(2b)[d]	−143(11)	9242(9)	313(4)	93(2)
Ome[e]	3738(12)	869(11)	405(5)	115(2)
Cme[e]	1721(24)	1435(22)	−166(10)	147(5)
H(1)	5337(41)	6944(36)	2386(17)	33(6)
H(4)	8634(37)	5097(33)	2192(15)	29(6)
H(5)	8399(48)	5587(43)	1248(20)	55(8)
H(7)	7260(38)	3081(33)	1105(16)	28(6)
H(6)	9608(43)	2450(37)	1549(17)	38(7)
H(10)	9037(38)	744(34)	3316(16)	33(6)
H(11)	10108(42)	2092(37)	2833(17)	40(7)
H(8)	8069(37)	−378(34)	2312(16)	28(6)
H(9)	6356(40)	812(36)	1631(16)	35(7)
H(2)	2794(50)	7550(44)	1514(21)	58(9)
H(3)	4955(47)	6738(40)	844(18)	45(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Oxygen and hydrogens 1 and 2 of water 1. [c] N of NH_4^+ and hydrogens a, b, c, and d of NH_4^+. [d] Water 2 in disordered positions a and b. [e] O and C of methanol.

TABLE IV. Bond Lengths (Å) for $NH_4[Co(ed3a)CN] \cdot 2H_2O \cdot CH_3OH$[a]

Co–C(9)	1.916(2)	Co–N(1)	1.929(2)
Co–N(2)	1.972(2)	Co–O(5)	1.884(2)
Co–O(3)	1.921(2)	Co–O(1)	1.900(2)
C(9)–N(3)	1.138(3)	N(1)–H(1)	0.920(28)
N(1)–C(3)	1.507(3)	N(1)–C(2)	1.479(4)
C(3)–H(4)	0.896(26)	C(3)–H(5)	1.002(33)
C(3)–C(4)	1.503(4)	C(4)–H(7)	1.013(27)
C(4)–H(6)	0.869(25)	C(4)–N(2)	1.493(3)
N(2)–C(7)	1.489(3)	N(2)–C(5)	1.484(4)
C(7)–H(10)	1.008(26)	C(7)–H(11)	0.970(29)
C(7)–C(8)	1.524(3)	C(8)–O(6)	1.224(3)
C(8)–O(5)	1.284(3)	O(3)–C(6)	1.281(3)
C(6)–O(4)	1.232(3)	C(6)–C(5)	1.525(3)
C(5)–H(8)	0.983(21)	C(5)–H(9)	0.919(26)
O(1)–C(1)	1.291(3)	C(1)–O(2)	1.218(4)
C(1)–C(2)	1.522(5)	C(2)–H(2)	0.942(27)
C(2)–H(3)	0.966(30)		
Ome-Cme	1.592(18)		
Nh–Hnha	0.869(12)	Nh–Hnhb	0.869(25)
Nh–Hnhc	0.874(13)	Nh–Hnhd	0.863(20)

[a] Same atom designations as in Table III.

away from O(6); an N(1) hydrogen atom from a neighboring complex is located 1.9 Å away from O(4) and a water of crystallization is hydrogen bonded to both O(4) and an NH_4^+ ion. The O(2) atom is found tilted toward a disordered CH_3OH molecule about 3 Å away. Similar interactions are found for all of the ed3a complexes studied to date, reinforcing the caution that parameters measured for solids should be used carefully and critically when interpreting results obtained in solution by other techniques. The crystallographic averages for seven related *cis-eq* ed3a complexes show that coplanarity of the π function and the bisector of the angle formed by the geminal hydrogens increases from G to R_1 to R_2, a finding consistent with the PMR results.

When a cyanide ion replaces a water molecule the δ values of methylene hydrogens on carbons bound to N(2) (a ligating atom *trans* to L) are shifted downfield. The effect can be electronic, magnetic, or both. For example, the cylindrical π-cloud around the cyanide ion can interact with the applied field to create an induced field which can reinforce the applied field at these positions. It is also interesting to note that the Co–N(2) bond is significantly longer than the Co–N(1) bond in $NH_4[Co(ed3a)CN]$ (1.972 *versus* 1.929 Å). The opposite is to be expected from comparisons of Co–N bond lengths for polyamide and aminopolyacid complexes. The bond lengths are slightly shorter for nitrogens constrained (pulled in) by more than one chelate ring and the effect is slightly greater for the more strained glycinate ring than for diamine rings. The Co–N distances are 1.98 Å for $[Co(en)_3]^{3+}$ [25], 1.96(NH_2) and 1.95(NH) for β-[Co(trien)(S-proline)]$^{2+}$ (trien = triethylenetetraamine) [26], 1.99(NH_2) and 1.96(N) for $[Co(penten)]^{3+}$ (penten = *N,N,N′,N′*-tetrakis(2′-aminoethyl)-1,2-diaminoethane) [27], 1.94(NH) for *uns-cis*-[Co(edda)pn]$^+$ (edda = ethylenediaminediacetate ion) [28], and 1.92 for $[Co(edta)]^-$. The corresponding bond lengths for the $[Co(ed3a)H_2O]$ complex are 1.924 Å for Co–N(2) and 1.935 Å for

TABLE V. Bond Angles (°) for $NH_4[Co(ed3a)CN]\cdot 2H_2O\cdot 0.5CH_3OH$ [a]

C(9)–Co–N(1)	93.7(1)	C(9)–Co–N(2)	176.5(1)
N(1)–Co–N(2)	88.5(1)	C(9)–Co–O(5)	89.8(1)
N(1)–Co–O(5)	92.7(1)	N(2)–Co–O(5)	87.3(1)
C(9)–Co–O(3)	94.5(1)	N(1)–Co–O(3)	170.5(1)
N(2)–Co–O(3)	83.6(1)	O(5)–Co–O(3)	92.3(1)
C(9)–Co–O(1)	91.5(1)	N(1)–Co–O(1)	85.9(1)
N(2)–Co–O(1)	91.4(1)	O(5)–Co–O(1)	178.1(1)
O(3)–Co–O(1)	89.0(1)	Co–C(9)–N(3)	178.8(2)
Co–N(1)–H(1)	109.0(18)	Co–N(1)–C(3)	107.7(2)
H(1)–N(1)–C(3)	109.0(17)	Co–N(1)–C(2)	107.4(2)
H(1)–N(1)–C(2)	109.5(16)	C(3)–N(1)–C(2)	114.2(2)
N(1)–C(3)–H(4)	108.5(14)	N(1)–C(3)–H(5)	116.0(16)
H(4)–C(3)–H(5)	107.3(27)	N(1)–C(3)–C(4)	108.3(2)
H(4)–C(3)–C(4)	108.1(15)	H(5)–C(3)–C(4)	108.3(19)
C(3)–C(4)–H(7)	105.5(14)	C(3)–C(4)–H(6)	110.0(21)
H(7)–C(4)–H(6)	123.7(22)	C(3)–C(4)–N(2)	107.2(2)
H(7)–C(4)–N(2)	105.4(15)	H(6)–C(4)–N(2)	104.1(19)
Co–N(2)–C(4)	105.9(1)	Co–N(2)–C(7)	107.6(1)
C(4)–N(2)–C(7)	112.0(2)	Co–N(2)–C(5)	104.8(1)
C(4)–N(2)–C(5)	115.4(2)	C(7)–N(2)–C(5)	110.5(2)
N(2)–C(7)–H(10)	111.9(16)	N(2)–C(7)–H(11)	106.6(16)
H(10)–C(7)–H(11)	108.2(21)	N(2)–C(7)–C(8)	111.8(2)
H(10)–C(7)–C(8)	108.2(14)	H(11)–C(7)–C(8)	110.2(17)
C(7)–C(8)–O(6)	119.8(2)	C(7)–C(8)–O(5)	116.5(2)
O(6)–C(8)–O(5)	123.7(2)	Co–O(5)–C(8)	115.8(1)
Co–O(3)–C(6)	112.7(2)	O(3)–C(6)–O(4)	123.2(2)
O(3)–C(6)–C(5)	116.5(2)	O(4)–C(6)–C(5)	120.3(2)
N(2)–C(5)–C(6)	108.1(2)	N(2)–C(5)–H(8)	105.1(17)
C(6)–C(5)–H(8)	108.1(15)	N(2)–C(5)–H(9)	104.1(19)
C(6)–C(5)–H(9)	111.1(17)	H(8)–C(5)–H(9)	119.5(20)
Co–O(1)–C(1)	115.1(2)	O(1)–C(1)–O(2)	123.5(3)
O(1)–C(1)–C(2)	114.9(2)	O(2)–C(1)–C(2)	121.7(3)
N(1)–C(2)–C(1)	110.0(2)	N(1)–C(2)–H(2)	110.3(20)
C(1)–C(2)–H(2)	102.5(24)	N(1)–C(2)–H(3)	106.7(18)
C(1)–C(2)–H(3)	107.5(20)	H(2)–C(2)–H(3)	119.6(26)
Hw(1)–W(1)–Hw(2)	104.4(47)		
Hnha–Nh–Hnhc	108.9(27)	Hnha–Nh–Hnhb	108.4(26)
Hnha–Nh–Hnhd	110.1(26)	Hnhb–Nh–Hnhc	109.3(22)
Hnhc–Nh–Hnhd	109.1(24)	Hnhb–Nh–Hnhd	111.0(27)

[a]Same atom designations as in Table III.

TABLE VI. Comparison of Bond Lengths (Å) and Ring Angle Sums (°)

	$[Co(edta)]^-$ [a]	$[Co(ed3a)H_2O]$	$[Co(ed3a)CN]^-$
Co–O(1) (out-of-plane, R_1)	1.887	1.895	1.900
Co–O(5) (out-of-plane, R_2)	1.887	1.876	1.884
Co–O(3) (in-plane, G)	1.945	1.917	1.921
Co–N(1)	1.921	1.935	1.929
Co–N(2)	1.929	1.924	1.972
Co–L		1.932	1.916
Ring angle sums			
E	520.9	519.0	517.6
R_1	537.8	532.6	533.3
R_2	537.8	539.3	539.0
G	523.5	526.0	525.7

[a]Ref. 17.

Co–N(1), as expected [19]. This amount of lengthening in the cyano complex could mean that the cyanide ligand is exerting a '*trans* influence' weakening the bond *trans* to it. The cyanide ion is a π-acceptor, but also a strong σ-donor ligand. The two effects tend to cancel the net electron transfer to or from cobalt. Both effects make CN^- a very strong field ligand with a strong, highly covalent Co–C bond. The lengthening of the Co–N(2) bond *trans* to Co–CN suggests a strong *trans* influence. The *trans* influence has not been as well documented for octahedral complexes as for square-planar complexes.

Because the ed3a complexes can be considered to be structural modifications of $[Co(edta)]^-$, the PMR spectrum of the latter was remeasured at 300 MHz and the results are shown in Fig. 4. This spectrum consists of three easily distinguished AB patterns, one for the R rings, one for the G rings, and one for the E ring. The earlier low-field spectrum [15] did not reveal the E ring AB pattern. The $[Co(edta)]^-$ has a C_2 axis bisecting the N–Co–N angle of the E ring. The R (our-of-plane) glycinate hydrogens resonate relatively far downfield (3.91 ppm), probably because of the eclipsed configuration that these methylene H–C–H bonds make with the C–N–C bonds. When one of the in-plane glycinate rings is removed from the edta complex to make a *cis-eq* ed3a complex, the configuration of the H–C–H of the R ring (H(3)–C(2)–H(2), Fig. 2) is no longer required to eclipse the C–N–C bonds. The H(2) atom, which is closer to the electronegative monodentate ligand, now resonates significantly farther downfield than the other, H(3). This assignment is unambiguous if the validity of the Karplus equation [29] is assumed.

The downfield R_1 arm of the AB pattern, H(2), always shows further splitting in acidic solution while the upfield arm is unaffected. This splitting is caused by the H(1) hydrogen whose replacement by deuterium is retarded in DCl solution. The measured coupling constants for the N-unsubstituted ed3a aqua and cyano complexes are, respectively, 7.2 and 7.6 Hz. Values of 7–8 Hz have been reported for various similar nitro complexes [4, 14, 16]. The X-ray crystallographic data for $[Co(ed3a)CN]^-$ shows that the H(1)–C(2)–H(2) torsion angle is 33° and the H(1)–N(1)–C(2)–H(3) torsion angle is 99°. The Karplus equation suggests that the coupling constant should be a minimum when the torsion angle is close to 90°. Thus, assigning H(2) as the atom corresponding to the downfield R_1 arm is justified.

Removal of a glycinate arm from $[Co(edta)]^-$ to form an ed3a complex eliminates the C_2 axis and all ten methylene hydrogens become nonequivalent. Of the complexes studied here, the PMR results suggest that $[Co(med3a)H_2O]$ is most similar to $[Co(edta)]^-$, while $[Co(ed3a)CN]^-$ is least similar. Figure 3 shows that the PMR spectrum of $[Co(ed3a)CN]^-$ is completely resolved, *i.e.* it has spectral lines that can be assigned to these ten different protons. All of the glycinate protons absorb downfield of 3.8 ppm except H(3) which absorbs at 3.1 ppm. The four protons on the E ring give a well-defined ABCD pattern because of the conformational purity of the ring. The splitting pattern can be considered to be first order even though $\Delta\nu \sim J$ in most cases for these E protons.

For $[Co(ed3a)CN]^-$ the multiplet centered at 3.37 showed increased splitting when the spectrum was remeasured in acidic solution (Fig. 5), suggesting that this multiplet should be ascribed to the axial hydrogen atom, H(4), next to N(1). None of the other multiplets due to the E protons was affected. The torsion angle H(1)–N(1)–C(3)–H(4) from the X-ray results is 37°. The torsion angle measured for the equatorial proton, H(5), on C(3) with N(1) and H(1) is 85° so it's reasonable to assume that the multiplet due to this proton is the one whose spectral line is not split further when measured for an acidic solution. When the sample was doubly irradiated using the frequency of the multiplet occurring farthest upfield, the multiplet at 3.37 ppm collapsed to a pattern than can be called a doublet of doublets; at the same time, the multiplet at 3.69 ppm (triplet of doublets) collapsed to a simpler triplet while the other multiplet at 3.58 ppm remained unaffected. Thus, the resonance lines at 2.80 and 3.37 ppm are assumed to be caused by the protons on the same carbon, C(3), next to N(1).

Assignments for the N-methyl derivatives of the cyano and nitro complexes were made similarly. Remeasuring the spectra in acidic solution would yield no useful results because there is no hydrogen on N(1). Instead, spectra of very dilute solutions were measured to show long range coupling ($J \sim$ 1Hz) between the methyl hydrogens and the axial hydrogen on C(3). Decoupling experiments, similar to those for the ed3a complexes, permitted assignments to be made unambiguously. The nitro complexes yielded spectra whose E protons were similarly well resolved and could be assigned using the same decoupling experiments.

The aqua complexes show the most poorly resolved PMR spectra for the E protons (Figs. 6 and 7). These spectra of the ed3a and med3a complexes resemble the PMR spectrum of the edta complex in that protons on the same carbons resonate at about the same δ values. The equatorial E protons are upfield of the axial protons in all cases. Rohly *et al.* [30] reported similar results for the PMR spectra of $[Co(ed3a)NCS]^-$ and the N-substituted complexes. The thiocyanate ion and water molecule exert ligand fields of about the same strength in cobalt(III) complexes, so similar effects might be expected.

It is imporant to emphasize that the assignments made for the E protons of the aqua complexes are speculative and cannot be made with the same certainty as for the other complexes. The same techniques used for the cyano and nitro complexes failed on the aqua complexes because the chemical shift values are nearly the same for protons on the same E carbon. When the spectrum of [Co(ed3a)H_2O] was measured in acidic solution, no further splitting of the multiplet at 3.47 ppm occurred although further splitting of the downfield AB R_1 arm at 4.08 ppm was observed (two peaks become four). Part of the multiplet at 3.47 ppm ascribed to the downfield axial proton is obliterated by the upfield arm of the AB pattern of the G protons. This part of the multiplet could show more splitting, but it was not resolved because of this overlap. Hence we conclude, with caution, that the downfield side of the multiplet at 3.47 ppm is due to the axial proton on the E carbon bonded to the tertiary nitrogen. Furthermore, we assume that the equatorial proton close to the tertiary nitrogen resonates farthest upfield as it does for the corresponding protons of the ed3a nitro and cyano complexes. A methyl substituent on N(1) should exert a greater influence on the nearer equatorial proton, so it is reasonable to assume that resonance lines centered at 3.09 ppm are due to this proton. Note that this assignment is opposite to the one for the equatorial protons of the unsubstituted [Co(ed3a)H_2O].

The coupling constant for the vicinal axial E protons is about the same ($J_{aa'} \sim 13–14$ Hz) for all of the *cis-eq* complexes studied in this report. Changing the monodentate ligand seems to have little effect. The coupling constant between the geminal mates (J_{ae} or $J_{a'e'}$) is affected, however, when the ligand in the sixth position is changed. The coupling constant between the gem mates in a cyclic five- or six-membered ring is thought to be negative [23]. Furthermore, the magnitude of these coupling constants can be affected by electronegative substituents α or β to the methylene carbon. An electronegative α substituent has the effect of algebraically increasing J_{gem} and an electronegative β substituent should decrease J_{gem}. The measured coupling constants, J_{gem}, are about -14 Hz, for the nitro and cyano *cis-eq* complexes and about -9 to -10 Hz for the corresponding aqua and parent $[Co(edta)]^-$ complexes. These values are also comparable to coupling constants of E protons obtained for K*cis-eq*-[Co(pd3a)NO_2] [4] [pd3a = 1,3-propanediaminetriacetate ion) and $[Ru(en)_3]^{2+}$ [31, 32]. This algebraic decrease in J_{gem} (-10 to -14) for the cyano and nitro complexes compared to the aqua complexes is reasonable if it is assumed that the π-acceptor role of CN^- or NO_2^- effectively increases the positive charge on the cobalt(III). This should have the same effect as placing a more electronegative substituent in the β position.

The PMR spectrum of *trans-eq*-$[Co(ed3a)CN]^-$ is shown in Fig. 8. The PMR results obtained here are similar to those obtained by Maricondi and Maricondi [4] for the *trans-eq* isomer of K[Co(R-pd3a)NO_2]; and similar methods were used to make the assignments. The AB pattern due to the G glycinate protons was determined by measuring the spectrum in acidic solution. The downfield arm centered at 3.88 ppm was split further by the hydrogen on the tertiary nitrogen with $J = 6$ Hz. The resonance peaks of the upfield arm centered at 3.60 ppm were also split further with a coupling constant of 10 Hz. Originally, in neutral solution, J_{AB} for the G glycinate protons was measured to be 16.2 Hz, fairly typical for an in-plane glycinate arm. A Dreiding model reveals that H_G should make a torsion angle with H(1) of nearly 180°, hence its assignment as the one with the larger J. Also, $H_{G'}$ is more nearly in the same plane as the cobalt and cyanide ligand whose magnetic anisotropy should deshield $H_{G'}$ to a greater extent than H_G. The J values measured for the G protons of the pd3a nitro complex [5] in acidic solution were also 6 and 10 Hz.

The R′ glycinate AB pattern was more difficult to assign because the out-of-plane glycinate rings are very similar. There is only 0.1 ppm difference in chemical shift and spread. A Dreiding model reveals, however, that H_a is slightly closer to $H_{R'}$ than H_e is to H_R, and a van der Waals interaction of this type is expected to cause deshielding. Therefore, we assign the R′ glycinate protons as resonating downfield of the other AB quartet due to the out-of-plane glycinate ring. The protons of the R rings closest to the electronegative cyanide ion are expected to resonate farthest downfield. The coarse doublets at 3.48 and 3.28 ppm are assigned to the equatorial protons of the E ring. The geminal proton coupling constant was measured to be about 11 Hz. The $H_{e'}$ proton was assigned to the doublet at 3.48 ppm because this proton shows further splitting in acidic solution. This equatorial proton should suffer the deshielding effect of the cyano ligand to a greater extent than its vicinal counterpart because its methylene carbon is bonded to a donor nitrogen *trans* to the cyanide ion, and this proton is more nearly in plane with the E ring. Both axial protons are assigned to the broad multiplet that occurs between 3.29 and 3.14 ppm. Remeasuring the spectrum in acidic solution did not help much to decide which part of the multiplet should be assigned to H_a or $H_{a'}$.

Carbon-13 NMR Spectra

The CMR results for the cyano ed3a complexes are shown along with results for the nitro and aqua complexes in Table II. The CMR line positions for $[Co(edta)]^-$ are: 66 for R, 65.8 for G and 64.0 for en [33]. Assignments specific to the various carbonyl carbons could not be made and the line positions of the cyano carbons were not located.

The edta complex, with its C_2 symmetry, has only three ^{13}C methylene resonance lines, as expected for the R, G, and E carbons in the broad-band decoupled spectrum. The ed3a complexes, with no symmetry, show five distinct ^{13}C lines. The assignments were made by selective deuteration and decoupling. Peak assignments were aided by the knowledge that a carbon atom without another carbon atom in the β position will resonate at about 9–10 ppm farther upfield. The cause of this β-substituent shift is little understood, but it has been well characterized and seems to be steric rather than electronic. It is possible that some sort of orbital contraction caused by a small steric crowding of β-carbons may cause a sufficient increase in the paramagnetic terms to explain this so-called β-effect [34]. The magnitude of this shift (9–10 ppm) is fairly constant for cyclic and acyclic systems*. Furthermore, it does not matter if the ring system is a chelate ring with a highly charged metal ion participating, the shift is still ~9–10 ppm downfield when a carbon is added to the β position [35]. Therefore, the resonance lines for [Co(ed3a)H_2O] located at 56.6 ppm and 57.1 ppm are almost certainly due to the E_1 and R_1 carbons (both bonded to N(1)) because a β-carbon has been removed from the [Co(edta)]$^-$ to form [Co(ed3a)H_2O]. It was also determined that these E_1 and R_1 lines for the ed3a complexes appeared as 'doublets', *i.e.* two lines appear for each instead of the expected one. The partially deuterated N(1) atom gives rise to a measurable chemical shift difference at high resolution for the carbons bonded directly to this N(1) atom. Differentiating between the E_1 and R_1 carbons is done by selectively decoupling the spins of the protons bonded to these carbons.

The same E_1 and R_1 carbons for [Co(med3a)H_2O] resonate at 66.2 ppm back downfield, at about the same place as for [Co(edta)]$^-$, because a β-carbon, the methyl group, has been added. This same technique, using the β-substituent effect can be used to verify the assignments made by selective decoupling and deuteration. Consider, for example, the *trans-eq* cyano complex. Removing an R_2 glycinate arm and reattaching it to the N(1) atom of the *cis-eq*-[Co(ed3a)CN]$^-$ complex effectively transforms it into a *trans-eq* isomer (see sketches in Figs. 3 and 8). What was the *cis-eq* E_2 carbon becomes a *trans-eq* E_1 carbon that should then resonate upfield by 9–10 ppm. In a similar fashion it can be deduced that the *cis-eq* R_2 carbon stays at about the same position and the others move downfield by 9–10 ppm.

We must conclude that for the ed3a and med3a complexes there are no substantial spectral differences among the ^{13}C NMR spectra. Even for the different isomers, *cis-eq* and *trans-eq*, the spectral differences can be explained comfortably in terms of the β-substituent effect. The small upfield shifts for the G, R_2, and E_2 carbons of the *cis-eq* complexes in going from the aqua to the cyano complexes can be explained in terms of the acetylenic nature of the cyanide ligand *trans* to the nitrogen atom, N(2), that binds all of these carbons.

Supplementary Material

The following supplementary tables are available from the author on request: Table I, Least Squares Planes; Table II, Anisotropic Thermal Parameters; and Table III, Observed and Calculated Structure Factors for $NH_4[Co(ed3a)CN]\cdot 2H_2O\cdot 0.5CH_3OH$.

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References

1 M. D. Lind and J. L. Hoard, *Inorg. Chem., 3,* 34 (1964).
2 S. Richards, B. Pedersen, J. V. Silverton and J. L. Hoard, *Inorg. Chem., 3,* 27, (1964).
3 G. L. Blackmer and J. L. Sudmeier, *Inorg. Chem., 10,* 2019 (1971).
4 C. W. Maricondi and C. Maricondi, *Inorg. Chem., 13,* 1110 (1974).
5 D. E. Bause, C. A. Chang and B. E. Douglas, *J. Coord. Chem., 6,* 211 (1979).
6 O. W. Howarth, P. Moore and N. Winterton, *Inorg. Nucl. Chem. Lett., 10,* 553 (1974).
7 C. W. Van Saun and B. E. Douglas, *Inorg. Chem., 7,* 1393 (1968).
8 C. W. Maricondi and C. Maricondi, *Inorg. Chem., 12,* 1524 (1973).
9 D. J. Radanović, S. R. Trifunović, D. E. Bause, C. Maricondi, J. E. Abola and B. Douglas, *Inorg. Chem.,* in press.
10 M.-K. Doh, J. Fujita, H. Ogino and K. Saito, *Bull. Chem. Soc., Jpn., 48,* 874 (1975).
11 R. L. Russell, *Ph.D. Dissertation,* University of Pittsburgh, Pittsburgh, Pa., 1970.
12 C. Bernhard, *Ph.D. Dissertation,* University of Neuchatel, Neuchatel, Switzerland, 1975.
13 G. L. Blackmer, R. E. Hamm and J. I. Legg, *J. Am. Chem. Soc., 91,* 6632 (1969).
14 J. L. Sudmeier, A. J. Senzel and G. L. Blackmer, *Inorg. Chem., 10,* 90 (1971).

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*For a general discussion of factors affecting chemical shifts in ^{13}C spectroscopy see ref. 34.

15 D. E. Bause, *Ph.D. Dissertation*, University of Pittsburgh, Pittsburgh, Pa., 1977.

16 G. L. Blackmer and J. L. Sudmeier, *Inorg. Chem., 10*, 2019 (1971).

17 K. Okamoto, T. Tsukihara, J. Hidaka and Y. Shimura, *Chem. Lett.*, 145 (1973).

18 H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc., 81*, 549 (1959).

19 K. E. Rohly, *Ph.D. Dissertation*, University of Pittsburgh, Pittsburgh, Pa., 1985.

20 J. D. Bell and G. L. Blackmer, *Inorg. Chem., 12*, 836 (1973).

21 C. Maricondi, B. Douglas, R. Whittle and J. Abola, manuscript in preparation.

22 C. J. Hawkins, 'Absolute Configuration of Metal Complexes', Wiley-Interscience, New York, 1971, p. 257, 270.

23 L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', Pergamon, Oxford, 1978, p. 275.

24 J. A. Pople and A. A. Bothner-By, *J. Chem. Phys., 42*, 1339 (1964).

25 F. Marumo, Y. Utsumi and Y. Saito, *Acta Crystallogr., Sect. B, 26*, 1492 (1970).

26 H. C. Freeman and I. E. Maxwell, *Inorg. Chem., 9*, 649 (1970); H. C. Freeman, L. G. Marzilli and I. E. Maxwell, *Inorg. Chem., 9*, 2408 (1970).

27 A. Muto, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B, 26*, 226 (1970).

28 L. J. Halloran, R. E. Caputo, R. D. Willett and J. I. Legg, *Inorg. Chem., 14*, 1762 (1975).

29 M. Karplus, *J. Chem. Phys., 30*, 11 (1959).

30 K. E. Rohly, B. E. Douglas and C. Maricondi, *Inorg. Chem., 25*, 4119 (1986).

31 H. Elsbernd and J. K. Beattie, *J. Am. Chem. Soc., 91*, 4573 (1969).

32 J. K. Beattie and H. Elsbernd, *J. Am. Chem. Soc., 92*, 1946 (1970).

33 O. W. Howarth, P. Moore and N. Winterton, *J. Chem. Soc., Dalton Trans.*, 2271 (1974).

34 J. B. Stothers, 'Carbon-13 NMR Spectroscopy', Academic Press, New York, 1972, p. 124.

35 L. E. Erickson, J. E. Sarneski and C. N. Reilley, *Inorg. Chem., 14*, 3007 (1975).