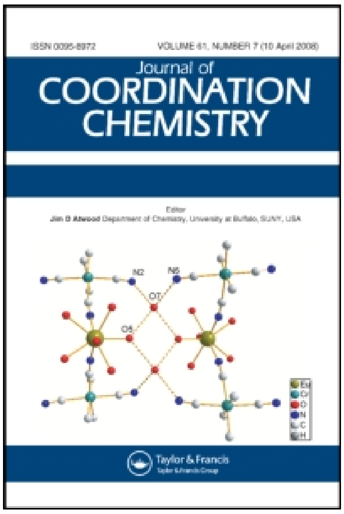

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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Daniel E. Bause[a]; Cheng A. Chang[a]; Bodie E. Douglas[a]
[a] Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania

To cite this Article Bause, Daniel E. , Chang, Cheng A. and Douglas, Bodie E.(1979) 'CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDIES OF COBALT(III) COMPLEXES OF ETHYLENEDIAMINE-*N,N',N'*-TRIACETATE TYPE LIGANDS', Journal of Coordination Chemistry, 9: 4, 211 — 219

To link to this Article: DOI: 10.1080/00958977908073826

URL: http://dx.doi.org/10.1080/00958977908073826

J. Coord. Chem. 1979, Vol. 6, pp. 211–219
0095–8972/79/0904–0211$04.50/0

CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDIES OF COBALT(III) COMPLEXES OF ETHYLENEDIAMINE-*N*, *N'*, *N'*-TRIACETATE TYPE LIGANDS

DANIEL E. BAUSE, CHENG A. CHANG, and BODIE E. DOUGLAS*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(*Received January 10, 1979*)

Carbon-13 nuclear magnetic spectroscopy has been used to study a series of octahedral cobalt(III) complexes with various quinquedentate ligands and either NO_2^- or H_2O coordinated in the sixth position. Measurements were made on eight nitro complexes and six aqua complexes. The quinquedentate ligands studied were ethylenediamine-*N*,*N'*,*N'*-triacetate (ed3a), *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetate (med3a), *N*-hydroxyethylethylenediamine-*N*,*N'*,*N'*-triacetate (hed3a), *N*-benzylethylenediamine-*N*,*N'*,*N'*-triacetate (bed3a), 1,2-diamino-2-methylpropanetriacetate (dmp3a), and (*R*)-(-)-1,2-propanediaminetriacetate ((*R*)-pd3a). The identification of the *trans-equatorial*-isomer of $[Co(ed3a)NO_2]^-$ has been confirmed using ^{13}C and proton magnetic resonance. Selective decoupling, off-resonance decoupling, and acid-catalyzed deuteration have been used to identify the resonances of specific carbons. Information about the stereochemistry of the complexes can be derived by comparing the chemical shifts in the ^{13}C spectra.

INTRODUCTION

The cobalt(III) complexes discussed in this paper contain quinquedentate ethylenediamine-*N*,*N'*,*N'*-triacetate (ed3a) type ligands with either water or a nitro group coordinated in the sixth position. The complexes of (ed3a), *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetate (med3a), *N*-hydroxyethylethylenediamine-*N*,*N'N'*-triacetate (hed3a), *N*-benzylethylenediamine-*N*,*N'*,*N'*-triacetate (bed3a), 1,2-diamino-2-methylpropanetriacetate (dmp3a), and (*R*)-(-)-1,2-propanediaminetriacetate ((*R*)-pd3a) have been studied previously by circular dichroism (CD) and proton magnetic resonance (PMR).[1–5,7,8]

Three geometrical isomers are possible for the cobalt(III) complexes of these ed3a type quinquedentate ligands, and these have been designated[5] cis-equatorial, trans-equatorial and cis-polar (Figure 1). Since "in-plane" (G) glycinate rings of $[Co(edta)]^-$ are more strained than the "out-of-plane" (R) rings,[6] the most favored isomer has been assumed to be cis-equatorial with the two glycinate rings, which have a common N atom, coordinated on a face of the octahedron.

Blackmer, Hamm, and Legg[7] obtained two isomers

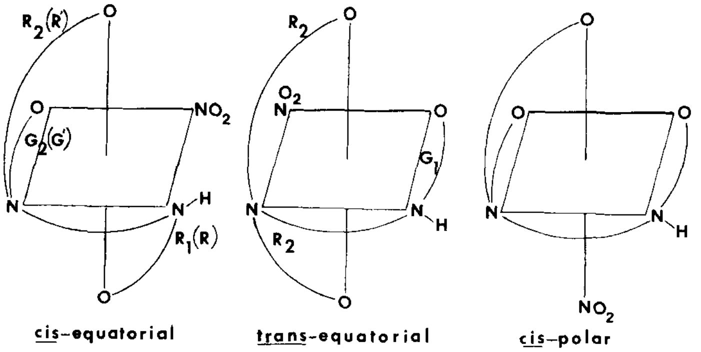


FIGURE 1. Geometrical isomers of $[Co(ed3a)NO_2]^-$.

of $[Co(ed3a)NO_2]^-$ which they assigned as nitro and nitrito linkage isomers with the cis-equatorial geometry. Blackmer and Sudmeier[8] found only one isomer (cis-equatorial) for a series of nitro and aqua complexes of quinquedentate ligands related to ed3a.

An x-ray structure determination of $[Co(ed3a)NO_2]^-$ has shown the stable isomer to be a nitro complex with cis-equatorial geometry.[9] Maricondi and Maricondi[5] obtained two stable isomers of $[Co((R)\text{-pd3a})NO_2]^-$ corresponding to the two isomers reported[7] for $[Co(ed3a)NO_2]^-$. They showed them to be *cis-eq-* and *trans-eq*-isomers rather than linkage isomers.

The series of aqua and nitro cobalt(III) complexes of ethylenediaminetriacetate ligands reported here has been studied using ^{13}C magnetic resonance. The peak assignments were made using noise-decoupling, off-resonance decoupling, acid catalyzed deuteration, methyl substitution on the backbone ring, and structural comparison. The stereochemical studies of these complexes using ^{13}C chemical shift provide a means to detect the change of structural parameters in solution.

EXPERIMENTAL SECTION

Preparation of Ethylenediamine-N,N′,N′-triacetic Acid and its Cobalt(III) Aqua and Nitro Complexes.

The preparation of the ligand and the complexes used the methods of Maricondi and Maricondi,[1] Bernhard,[2] and Blackmer, *et al.*[7] A solution of 65 mmole (11.4 g) of *N,N′*-ethylenediaminediacetic acid, 195 mmole (7.80 g) NaOH and 70 mmole (8.2 g) sodium chloroacetate in 180 mL water was stirred at 40–45° for 45 min. The solution was acidified to pH 6 and 65 mmole (18.9 g) $Co(NO_3)_2 \cdot 6H_2O$, 5 ml 30% H_2O_2 and 3 g activated charcoal were added. Air was bubbled through the mixture for two days. The charcoal was removed and the deep purple-red filtrate diluted to 1 L. This solution was passed through a column containing 700 mL of Dowex 1-X8 anion-exchange resin (100–200 mesh, acetate form) to remove the negatively charged species. The ramaining solution was allowed to pass through a column containing 700 mL of Dowex 50W-X8 cation-exchange resin (100–200 mesh, H^+ form). Slow evaporation of the solution at room temperature yielded large purple crystals of $[Co(ed3a)H_2O]$.

The nitro complex was prepared directly from the concentrated solution of the aqua complex. The solution was cooled in ice and a solution of 70 mmole (5 g) of $NaNO_2$ in 125 mL of water was added. Ten mL of glacial acetic acid was also added and the solution was left in ice overnight. The nitro complex was isolated by passing the red solution through a Dowex 1-X8 anion-exchange column (700 mL resin, 100–200 mesh, Cl^- form). The red band that adhered to the resin was eluted with 0.025 M KCl. The eluent was concentrated to a small volume, absolute methanol was added, and the solution was refrigerated overnight. Red crystals of the potassium salt was filtered and washed with methanol and acetone. The silver salt of the complex was prepared by mixing equimolar proportions of the potassium salt and of $AgNO_3$.

Preparation of ligands and complexes. The ligands med3a,[3] hed3a,[4] bed3a,[1] dmp3a,[8] and (*R*)-pd3a,[5] and their respective cobalt(III) nitro complexes were prepared by the literature methods. The identities of the complexes were verified by electronic absorption spectra.

Conversion of the ed3a-type nitro complexes to the aqua species. The general procedure used 0.2 g of the nitro complex dissolved in 10–15 ml water. Concentrated hydrochloric acid (1–4 drops) was added, and the solution was heated for 8 min at 85°. The color of the solution changed from red to purple. After heating, the solution was stirred with separate portions of Dowex 1-X8 (200–400 mesh, Cl^- form), and then with Dowex 50W-X8 (200–400 mesh, H^+ of form) to remove any charged species that may have formed. The final filtrate was concentrated to a viscous solution under an air stream and was redissolved in D_2O to run the ^{13}C spectrum.

Acid catalyzed deuteration experiment. For complexes containing exchangeable protons, acid catalyzed deuteration experiments were carried out to aid the ^{13}C NMR spectral assignments. The general procedure for deuteration experiments used 0.1 to 0.2 g of the aqua complex dissolved in 3 mL D_2O. To the solution was added 3 to 5 drops of 98% D_2SO_4 and the mixture was refluxed at *ca.* 80° for 1 hr using a microcondenser. The resulting solution was cooled and its ^{13}C NMR spectrum measured. In several cases, heating at 95° for a longer time (4 to 12 hr) was required.

Physical measurements. The visible absorption spectra were recorded on a Cary 14 spectrophotometer at room temperature using a tungsten source.

PMR spectra were obtained using a 60 MHz Varian

Associates A-60-D NMR spectrometer and the 250 MHz instrument at Carnegie-Mellon University. Deuterium oxide was used as the solvent. The field frequency ratio was stabilized by locking to internal, residual H_2O with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal reference.

Carbon-13 nuclear magnetic resonance spectra were recorded on a Jeol JNM FX-60 ^{13}C-^{1}H high performance NMR spectrometer, operating at 15.0 MHz in the ^{13}C mode. The instrument was used in a broad-band randomnoise ^{1}H decoupling mode, an off-resonance ^{1}H decoupling mode, or a selective ^{1}H resonance decoupling mode. The field frequency ratio was stabilized by locking to internal D_2O. The spectra were recorded using spectral widths of 4, 3, or 1 kHz covered by 4096 addresses in the Fourier transform spectrum. Pulse repetition times ranged from 1.0–3.0 seconds with delay times of 166–400 μsec. A crystal filter increased the signal-to-noise ratio significantly and to avoid phasing problems the upper range of delay times was used. The number of scans ranged from 100 scans (for the organic ligands) to 100,000 scans (for the slightly soluble $Na[Co(bed3a)NO_2]\cdot 2H_2O$. The samples dissolved in D_2O were place in either 10-mm diameter tubes or 8–10 mm coaxial tubes manufactured by Wilmad Spectroscopic Supplies Inc. Benzene (δ = 128.7 ppm downfield from TMS) was used as an external reference in an outer coaxial tube arrangement, except for the spectra of the complexes of bed3a which used chloroform (δ = 77.2 ppm downfield from TMS) as the external reference.

The Jeol JNM FX-60 was also used in the proton mode to facilitate using the correct proton fequencies for selective decoupling. In the proton mode the instrument operates at 59.75 MHz.

RESULTS AND DISCUSSION

Proton magnetic resonance. The PMR spectra of all the complexes except $[Co(bed3a)NO_2]^-$ and *trans-eq*-$[Co(ed3a)NO_2]^-$ were studied previously at 60 MHz.[8] The 250 MHz PMR spectra of these 2 complexes and of $[Co\text{-}(hed3a)NO_2]^-$ and $[Co(ed3a)H_2O]$ were obtained in this study. As in related complexes, the AB pattern of the R′ glycinate ring is shown as a singlet at 4.09 ppm. The in-plane ring has the expected geminal coupling constant of 16 Hz with the AB pattern centered at 3.89 ppm. However, the other AB pattern in this region has a coupling constant of only 14 Hz. The center of the chemical shifts for these glycinate protons is 3.68 ppm, occurring in the region expected for the protons of the R ring. Some support for the assignments of these AB patterns, is given in a study by Legg, *et al.*[10] There is a characteristic chemical shift difference for the glycinate protons of the various types of G and R rings. For the R rings attached to a tertiary nitrogen atom (labelled R_2) the difference is 0–0.2 ppm. Both of the out-of-plane rings in the *N*-benzyl complex are attached to tertiary nitrogens, and the chemical shift differences were found to be 0 ppm and 0.26 ppm for the R rings. The G ring bonded to a tertiary nitrogen (G_2) has a characteristic value of 0.2–0.3 ppm for the difference in chemical shifts. In the present study this difference was found to be 0.2 ppm.

The PMR data also support the assumption that $[Co(bed3a)NO_2]^-$ exists as the *cis-eq*-isomer. It was shown that the average chemical shift of the glycinate protons and the resonance frequency are characteristic of G and R rings in these Co(III) complexes of quinquedentate ligands.[8] For the nitro complexes studied previously[8] the average chemical shift for the G ring was between 3.94–4.01 ppm, compared to an average of 3.89 ppm for the *N*-benzyl derivative. Similarly the previously reported[8] resonances of the R′ ring were found at 4.05–4.16 ppm, with $[Co(bed3a)NO_2]^-$ giving a value of 4.09 ppm.

The absorption spectrum of the less stable "nitrito" isomer of $[Co(ed3a)NO_2]^-$ reported by Blackmer *et al.*[7] shows a splitting of the $^1T_{1g}$band, which is expected if the nitro group is in an equatorial position. Its PMR spectrum shows three AB patterns (centered at 3.85, 3.71, and 3.53 ppm) with a complex multiplet in the upfield portion of the spectrum. Two of the AB patterns have coupling constants of 16 Hz while the other one has J_{AB} = 18 Hz. A coupling constant of 16 Hz is expected for G rings, but Maricondi and Maricondi[5] found J_{AB} = 16 Hz for both G and R rings in *trans-eq*-$[Co((R)\text{-}pd3a)NO_2]^-$. Thus the less stable isomer originally reported as the "nitrito" complex of $[Co(ed3a)NO_2]^-$ can be assigned reasonably as the *trans-eq* nitroisomer.

Further support for this assignment is provided by the similarities of the visible absorption spectra of the (*R*)-pd3a and ed3a complexes. The *cis-eq*-$[Co((R)\text{-}pd3a)NO_2]^-$ has a shoulder at 17,200 cm^{-1} (ϵ 93) and a maximum at 20,300 cm^{-1} (ϵ 191),[5] while the *cis-eq*-$[Co(ed3a)NO_2]^-$ has a shoulder at 17,100 cm^{-1} (ϵ 88) and a maximum at 20,300 cm^{-1} (ϵ 192).[7] Similarly, the *trans-eq* complexes have two low-energy maxima occurring at 17,800 cm^{-1} (ϵ 181) and 20,900 cm^{-1} (ϵ 174) for (*R*)-pd3a,[5] and 17,800 cm^{-1} (ϵ 186) and 21,000 cm^{-1} (ϵ 180) for the ed3a complex.[7]

Carbon-13 magnetic resonance spectra. The chemical shifts for the carbon resonances of the nitro and aqua complexes are summarized in Table I and in Figures 2 and 3. The chemical shift assignments, based on methods discussed below, refer to the carbon atoms as labelled in Figure 4. The methylene carbons resonate at 47–74 ppm downfield from TMS, while the carbonyl carbon resonances are found 181–188 ppm downfield. The unambiguous assignments of the individual carbonyl carbons is difficult and little structural information is gleaned from these assignments.

Some of the peak assignments for these complexes were made by selective decoupling. The complexity of the PMR spectra for these ed3a type complexes limits the usefulness of selective decoupling and the only isolated proton resonances were those of the methyl groups. Other resonances could be assigned using off-resonance decoupled spectra. In these spectra methylene, methine, and quaternary carbons appear as quartets, triplets, doublets, and singlets, respectively.

If the AB patterns of the glycinate protons have been assigned in the PMR spectrum, then selective

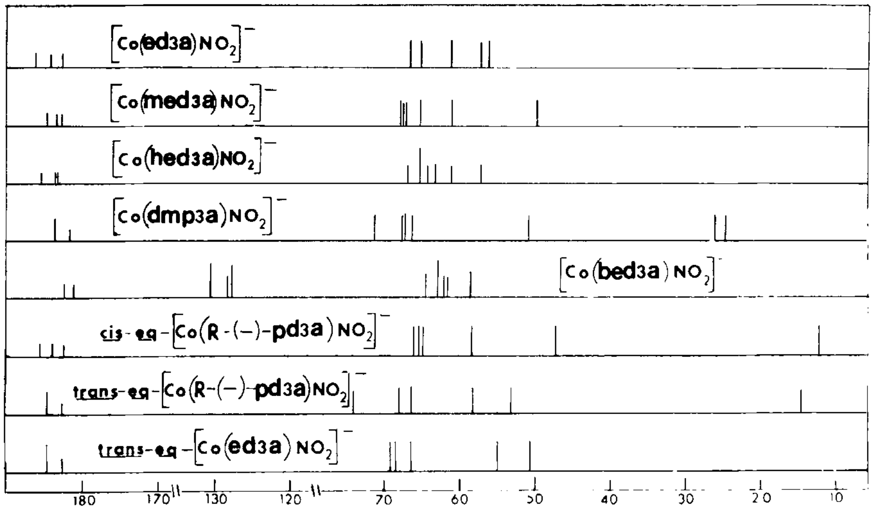


FIGURE 2. Carbon-13 chemical shifts for nitro complexes of quinquedentate ligands.

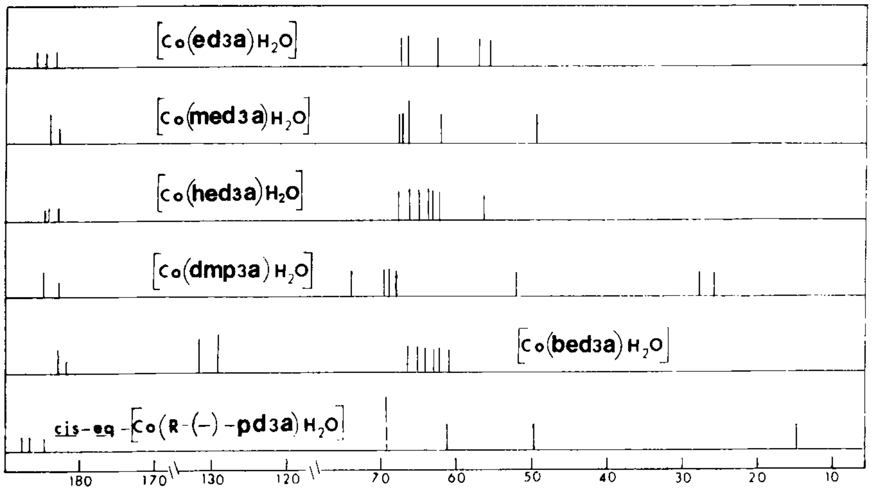


FIGURE 3. Carbon-13 chemical shifts for aqua complexes of quinquedentate ligands.

TABLE I
^{13}C Chemical Shift Data (ppm)[a]

	Designation		methylene				carbonyls	
Complex	*b*	*b'*	*c*	*c'*	*e*	*e'*		Other
cis-eq-$[Co(ed3a)NO_2]^-$	66.48		61.12	56.09	65.18	57.22	182.62, 184.09, 186.09	
cis-eq-$[Co(ed3a)H_2O]$	67.32		62.71	55.55	66.53	57.12	182.92, 184.38, 185.66	
cis-eq-$[Co(R\text{-}pd3a)NO_2]^-$	66.24		64.87	58.30	65.36	47.22	182.34, 183.90, 185.67	12.32(g)
cis-eq-$[Co(R\text{-}pd3a)H_2O]$	68.97		68.97	60.93	68.97	49.73	184.69, 186.41, 187.56	14.41(g)
cis-eq-$[Co(dmp3a)NO_2]^-$	67.52		71.34	67.03	66.34	50.88	181.44, 183.60, 183.86	24.77, 26.24(g,g')
cis-eq-$[Co(dmp3a)H_2O]$	69.59		73.80	67.83	68.81	51.98	182.51, 184.76, 184.76	25.76, 27.71(g,g')
cis-eq-$[Co(med3a)NO_2]^-$	66.96		60.89	67.45	65.29	67.25	182.71, 183.40, 184.67	49.73(h)
cis-eq-$[Co(med3a)H_2O]$	67.61		62.02	66.24	67.12	66.24	182.72, 183.80, 183.90	49.38(h)
cis-eq-$[Co(hed3a)NO_2]^-$	66.83	64.38	63.30	61.24	65.26	65.26	183.01, 183.51, 185.47	57.03(i)
cis-eq-$[Co(hed3a)H_2O]$	67.61	63.00	63.59	62.22	66.24	64.87	182.72, 183.90, 184.29	56.43(i)
cis-eq-$[Co(bed3a)NO_2]^-$	(64.33)[b]	(62.86)	(61.58)	(58.44)	(62.86)	(61.88)	180.41, 181.10, 182.47	127.57, 128.25, 130.41 (benzene)
cis-eq-$[Co(bed3a)H_2O]$	66.33	(64.28)	(62.32)	(60.95)	65.26	62.91	181.40, 183.68, 183.68	128.36, 131.60(benzene)
trans-eq-$[Co(ed3a)NO_2]^-$	(50.62)		(66.37)	(55.00)	(69.13)	(68.48)	182.59, 184.70, 184.70	
trans-eq-$[Co(R\text{-}pd3a)NO_2]^-$	52.86		74.00	58.24	67.93	66.36	182.61, 184.67, 184.67	14.60(g)

[a] Positive sign indicates a downfield shift from TMS.

[b] Data in parenthesis indicate uncertainty of the assignment.

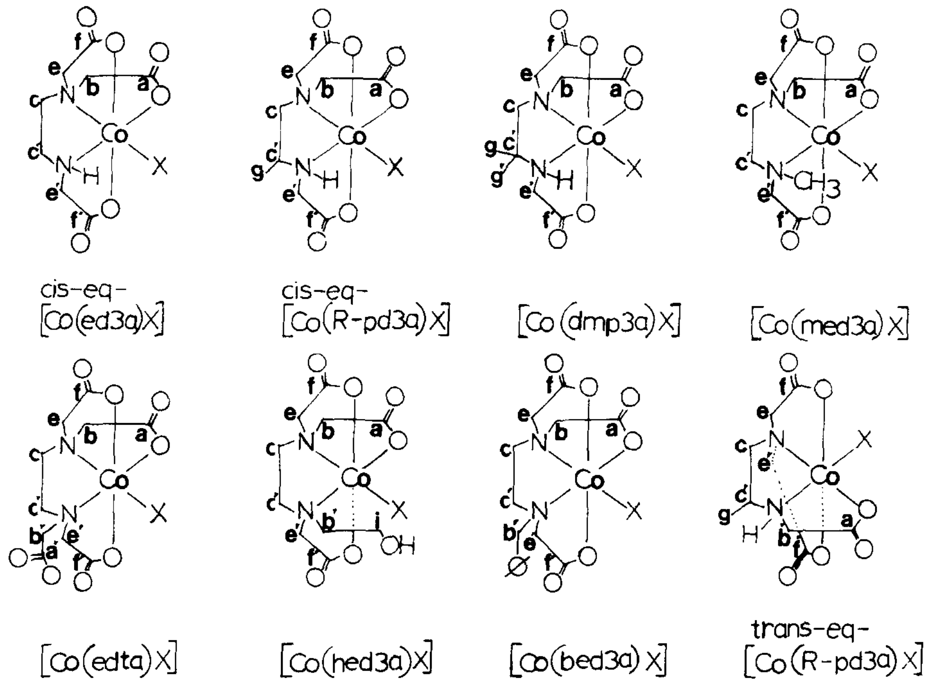


FIGURE 4. Abbreviated structures of complexes studied.

irradiation at the "average" chemical shift for these protons will cause other carbon peaks to lose intensity and become split. These relative assignments can be verified during acid-catalyzed deuteration by observing which two peaks (the E ring carbons) retain their intensity after complete deuteration.

Specific assignments of the glycinate protons could be made using acid-catalyzed deuteration, based upon the work of Terrill and Reilley.[11] Data are available for only the aqua complexes since the nitro complexes undergo aquation in acidic solution. Deuteration of the nitro complexes was attempted using alkaline conditions, but no ^{13}C peaks were observed. Presumably decomposition occurs with some cobalt(III) reduced to paramagnetic cobalt(II) causing the resonances to broaden and shift position.

Some typical assignments and comments on shift patterns are given:

Cis-eq-[CO(ed3a)X] (X = NO_2^- *or* H_2O). The complex *cis-eq-*[Co(ed3a)X] is structurally similar to [Co(edta)]$^-$ except one of the strained, equatorial rings is replaced by a hydrogen atom. For the half of the complex retaining two glycinate rings, the only important change is the strain relief, so this will be referred to as the strain-relieved half of the complex. Strain is certainly relieved in the half of the complex containing a single glycinate ring, but the major change is the through bond perturbation caused by the hydrogen substitutent which replaces an acetate group. The order of chemical shifts of the three methylene carbons (G′, R′ and E ring carbons) of the portion of the complex released from ring strain is predicted and found to be the same as that of [Co(1,3-pdta)]$^-$, for which the ring strain is relieved by the six-membered diamine backbone.[12,13] The through-bond pertrubed half of [Co(ed3a)X] should have methylene carbon resonances (R and E ring carbons) which are shifted upfield by the through-bond effect of the hydrogen relative to the displaced acetate group.

The five methylene peaks for [Co(ed3a)H_2O] and *cis-eq-*[Co(ed3a)NO_2]$^-$ are assigned using selective decoupling and acid-catalyzed deuteration. If the aqua complex is heated at 95° for two days, all three glycinate methylene carbon peaks disappear, leaving two ethylenic backbone carbon peaks with the one near the secondary amine being upfield because of the hydrogen through-bond effect. Thus the glycinate ring carbons are found to occur in the order G′, R′, and R as the magnetic field increases.

A comparison of the chemical shifts for

[Co(ed3a)X] and [Co(med3a)X] also confirms this hydrogen through-bond effect. These complexes differ only in the substituent bonded to the secondary nitrogen atom. The two upfield resonances of carbons *c′* and *e′* of [Co(ed3a)X] are not found in that spectral region for the *N*-methyl complex (Figures 2 and 3).

Cis-eq- [Co((*R*)-pd3a)X] (X = NO_2^- *or* H_2O). The complex *cis-eq-* [Co((*R*)-pd3a)X] has an equatorial methyl group attached to the ethylenic backbone *c′* carbon. Besides the substitution effect on the backbone ring methylene carbons,[13,14] the R ring *e′* carbon which is found under steric perturbation of the methyl group from molecular model studies is shifted farther upfield compared to the corresponding one of *cis-eq-* [Co(ed3a)X], as predicted.[13,14]

Cis-eq- [Co(dmp3a)X] (X = NO_2^- *or* H_2O). These complexes are unique in the series studied because of the presence of a quaternary carbon. Selective irradiation at various proton frequencies did not seem to affect the peaks at 67.03 and 67.83 ppm for the respective complexes, as expected for a quartenary carbon. The high intensity is probably due to effective spin-rotation relaxation of the methyl groups.

Cis-eq- [Co(hed3a)X] (X = NO_2^- *or* H_2O). The spectrum of the nitro complex shows six peaks in the methylene region with one peak twice as intense as others. The assignment of the terminal carbon peak of the hydroxyethyl group (-CH_2CH_2OH) is based on the assumption that the chemical shift would be similar for the free ligand and in the complex. It was found that upon complexation of the ligand to cobalt(III) ion, all the α carbon resonances shift to lower field and those for the β carbons shift upfield if the carbons are in a fixed chelate ring.[15,16] For the carbons in an uncoordinated pendent arm, the shifts in either direction should be less and the shift value would be closer to those obtained for free ligands.[13] The complexes [Co(edta)X] (X = NO_2^-,Cl^-) with edta acting as a quinquedentate ligand have an uncoordinated acetate arm. In their ^{13}C NMR spectra, pairs of similar carbon resonances are split and the carbon resonance closer to the pendent arm is found to be shifted upfield.[15] The [Co(hed3a)NO_2]$^-$ complex is a structural analog of [Co(edta)NO_2]$^-$ and its ^{13}C NMR spectral assignment is made by analogy.

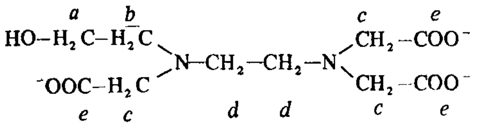
The PMR and ^{13}C NMR spectra of the free hed3a ligand were measured at pD ~ 11. The assignments of both spectra are shown in Table II together with the structure of the ligand. The free ligand peak at 58.91 ppm is the terminal hydroxyethyl carbon peak. In the ^{13}C NMR spectrum of the nitrocomplex, the peak at 57.03 ppm is assigned to this terminal hydroxyethyl carbon. The upfield shift of this peak is consistent with the result found for most carbons β to the coordinated atoms. The rest of the peaks are assigned as described before.

Stereochemical Studies Using ^{13}C Chemical Shifts

The complexes studied are all somewhat less strained than [Co(edta)]$^-$. A detailed analysis of the ring strain of [Co(edta)]$^-$ type complexes has been reviewed.[17] The strain in these complexes is revealed mainly by the C-N-C bond angles at the coordinated nitrogen. Although the ^{13}C chemical shift should be dependent on structural parameters such as bond angles, only qualitative empirical comparisons can be made at this time. In the series of [Co(ed3a)X] complexes, the bond angles are expected to reflect the effects of the

TABLE II

Assignments of PMR and ^{13}C NMR Spectra of hed3a^{3-}



pD ∿ 11

	a	*b*	*c*	*d,d′*	*e*
PMR^a	3.63(t)^b	2.60(t)	3.09(s)	2.54(s)	–
^{13}C NMR^a	58.91	56.70	59.56	52.41, 52.02	179.89

^{a}Positive sign indicates a downfield shift from TMS (TMS = 0 ppm).
^{b}t = triplet, s = singlet.

pendent equatorial groups. As described above, for *cis-eq*-[Co(ed3a)X] the half of the complex containing two glycinate rings is described as strain-relieved because this is the only major change. The major effect for the other half of the complex is the through-bond perturbation caused by substitution of H (or R) on N for an acetate group or the steric (through space) effect of a large substituent. The magnitude of the chemical shift separation of the G′ and R′ ring methylene carbon resonances of the ring strain-releived half seems to be an indication of the degree of the overall strain in the cobalt(III) complex. A more strained environment makes the R′ ring *e* carbon less distinguishable from the G′ ring *b* carbon. A comparison of the strained [Co(edta)]$^-$ and the less strained [Co(1,3-pdta)]$^-$ (in which the accumulated strain of the sexidentate ligand is relieved by the six-membered diamine ring) supports the previous statement.[13] This is also demonstrated with [Co(ed3a)X], although the chemical shift span (1.30 ppm) is much less than that of [Co(1,3-pdta)]$^-$ (7.14 ppm). Similar results are obtained for other complexes with quinquedentate ligands. The separations are within the 0.5–1.7 ppm range with the *b* carbon peaks being always more deshielded than the *e* carbon peaks (except *cis-eq*-[Co((*R*)-pd3a)H_2O] for which *b* and *e* carbon peaks overlap). The smaller chemical shift span would indicate that the strain is relieved to a greater extent when the diamine backbone is enlarged in contrast to removing one of the acetate arms.

If the N-H hydrogen of [Co(ed3a)H_2O] is replaced by a methyl group, the complex [Co(med3a)H_2O] results. Neglecting the methylene carbons under the methyl inductive through-bond effect,[13,14] the overall structure changes only slightly as evidenced by very small changes of the chemical shifts of the *b, c*, and *e* carbon resonances of [Co(med3a)H_2O] relative to those of [Co(ed3a)H_2O]. In both complexes, no steric interactions seem to be observed between the N-H or N-CH_3 group and the nearby out-of-plane glycinate ring prontons. (Usually the carbons experiencing steric interactions should shift upfield.[14]) If the N-H hydrogen of [Co(ed3a)H_2O] is replaced by a hydroxyethyl or a benzyl group, the complex [Co(hed3a)H_2O] or [Co(bed3a)H_2O] results. Since in both [Co(hed3a)H_2O] and [Co(bed3a)H_2O], the pendent groups are large enough, some steric interactions of the groups with the nearby out-of-plane glycinate protons must occur, as observed in molecular models. However, the observed chemical shift for the out-of-plane glycinate methylene, *e′* carbon near the hydroxyethyl group of [Co(hed3a)H_2O] does not change very much. It seems that this steric interaction is not as severe as that between the backbone ring methyl group and the nearby R ring methylene protons.[18] As one considers the size of the hydroxyethyl group and the benzyl group, one would expect a stronger steric interaction between the larger benzyl group and the R ring proton of [Co(bed3a)H_2O]. If the through-bond effect on the *e′* carbon resonance is assumed to be similar for both the hydroxyethyl and benzyl groups, the R ring *e′* carbon resonance of [Co(bed3a)H_2O] is expected to be shifted upfield more than the corresponding one of [Co(hed3a)H_2O], as observed. The R ring *e′* carbon resonance of [Co(bed3a)H_2O] at 62.91 ppm under steric perturbation is shifted upfield by 2.35 ppm more than the one of the R′ ring without the interaction where the corresponding chemical shift difference of [Co(hed3a)H_2O] is only 1.37 ppm.

The out-of-plane *e* carbon and the in-plane *b* carbon of the strain-relieved half of *cis-eq*-[Co((*R*)-pd3a)NO_2]$^-$ resonate at fields within 0.2 ppm of those of the corresponding ones of *cis-eq*-[Co(ed3a)NO_2]$^-$, which indicates the structural similarity of the two strain-relieved halves. The other out-of-plane *e′* carbon of *cis-eq*-[Co((*R*)-pd3a)NO_2]$^-$ is found to be the one farthest upfield as expected to be the result of both the steric interaction and the hydrogen through-bond effect. The steric interaction with methyl group would cause the *e′* carbon resonance to be shifted farther upfield in addition to the upfield shift due to the hydrogen through-bond effect. However, the chemical shift difference between the *e′* carbon of *cis-eq*-[Co((*R*)-pd3a)NO_2]$^-$ and the *e′* carbon of [Co(ed3a)NO_2]$^-$ is 10 ppm, which is higher than any other observed value for similar cases. Since it seems unlikely that the steric effect of a methyl group could cause such a large shift, there must be other factors which contribute to the effect. One of these factors could be conformational changes of the R ring and the backbone E ring. The methine and the methylene carbons of the backbone E ring resonate at lower field than the two corresponding backbone carbons of [Co(ed3a)NO_2]$^-$ due to the equatorial methyl substituent effects.[13,14] However, the downfield shift values of 3.75 ppm and 2.21 ppm for the two corresponding carbons (*c* and *c′*) of *cis-eq*-[Co((*R*)-pd3a)NO_2]$^-$ relative to *cis-eq*-[Co(ed3a)NO_2]$^-$ are less than those observed for other complex pairs (e.g. 5.6 ppm for [Co(1,3-pdta)]$^-$ and [Co(1,3-mpdta)]$^-$).[13]

The PMR spectrum of *cis-eq*-[Co(dmp3a)NO_2]$^-$

has been studied by Blackmer and Sudmeier.[8] Additional strain in the dmp3a complex and subsequent distortions in the complex may arise from the inability of either of the backbone methyl groups to acquire completely the energetically preferred equatorial position. In the ^{13}C NMR spectrum, the in-plane *b* and out-of-plane *e* glycinate methylene carbon resonances are shifted slightly downfield by about 1 ppm relative to the corresponding ones of the strain-relieved half of $[Co(ed3a)NO_2]^-$. The other out-of-plane *e*′ glycinate methylene carbon resonance is shifted downfield by 3.66 ppm relative to that of $[Co((R)\text{-}pd3a)NO_2]^-$. The quaternary carbon and the methylene carbon of the backbone ring resonate at 67.03 ppm and 71.34 ppm, respectively, which are very different from the values obtained for other complexes. For *cis-eq*-$[Co(dmp3a)NO_2]^-$ the chemical shifts indicate that the strain-relieved half retains structural parameters similar to those of *cis-eq*-$[Co(ed3a)NO_2]^-$ and $[Co((R)\text{-}pd3a)NO_2]^-$, but the backbone ring and the R ring must have a significant conformational change as compared to those of $[Co(ed3a)NO_2]^-$ and $[Co(R)\text{-}pd3a)NO_2]^-$.

The absorption and PMR data indicate that the "nitrito" isomer of $[Co(ed3a)NO_2]^-$ is actually the nitro complex with the trans-equatorial geometry. The ^{13}C spectrum of the complex seems to confirm this. If the complex were the *cis-eq*- "nitrito" isomer, the spectral pattern should have been similar to those of the *cis-eq*-nitro and aqua complexes. Further support comes from the similarity of the carbonyl resonance region of the *trans-eq*-isomer of $[Co(ed3a)NO_2]^-$ and $[Co((R)\text{-}pd3a)NO_2]^-$. They have nearly identical carbonyl chemicals shifts. Both complexes also show only two carbonyl resonances with the one at lower field being twice as intense, indicating the similar environment of the two out-of-plane carbonyl carbons. All of the other nitro compounds studied have three downfield carbonyl peaks (except for the dmp3a complex).

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