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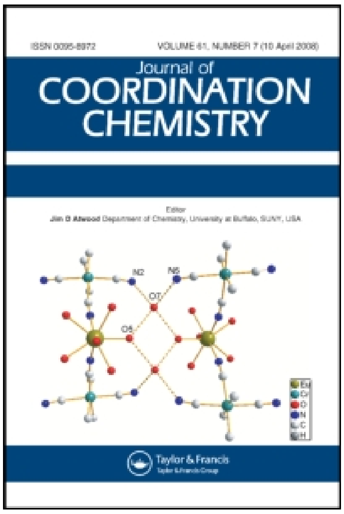

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CARBON-13 AND PROTON MAGNETIC RESONANCE AND CIRCULAR DICHROISM STUDIES OF VARIOUS COMPLEXES OF COBALT(III) WITH ETHYLENEDIAMINE-N, N'-DIACETATE-N, N'-DI-3-PROPIONATE

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CARBON-13 AND PROTON MAGNETIC RESONANCE AND CIRCULAR DICHROISM STUDIES OF VARIOUS COMPLEXES OF COBALT(III) WITH ETHYLENEDIAMINE-N, N'-DIACETATE-N, N'-DI-3-PROPIONATE

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Two nitro, two aqua and a dinitro complex of ethylenediamine-N-N'-diacetato-N,N'-di-3-propionatocobaltate have been isolated. The four quinquedentate complexes have been resolved optically and their electronic absorption and CD spectra measured. Pmr spectra at 250 MHz have also been measured for the quinquedentate complexes as well as for the dinitro complex. Those of the quinquedentate complexes are quite complicated and difficult to interpret. ^{13}C magnetic resonance spectra have been measured for all of these complexes and also for the sexidentate, *trans*(O_5) and *trans*(O_5O_6) isomers of [Co(EDDDA)]$^-$. The ^{13}C spectra are much less complex and indicate that this technique can be useful as a tool for the study of stereochemistry of metal complexes with ligands containing several carbon atoms.

INTRODUCTION

In the past ten years there have been several investigations of the chemistry and structural characteristics of cobalt(III) complexes of the potentially sexidentate ligand, ethylenediaminetetraacetate (EDTA), and related complexes. One objective has been to determine what factors influence the optical activity of such systems, and the relative importance of these factors.

Upon complete coordination to a metal ion, EDTA forms five five-membered chelate rings: the ethylenediamine backbone, and the two in-plane and two out-of plane glycinate rings. Recently, there have appeared in the literature papers dealing with studies of related complexes in which the ligand contains arms of varying size, *to wit*, ethylenediamine-N,N'-di-2-propionate (EDPA),[1] (S,S)-ethylenediamine, N,N'-dissucinate (EDDS),[2,3] (S)-ethylenediamine-N,N-diacetate-N'-monosuccinate (EDDAMS),[4] 1,3-propylenediaminetetraacetate (1,3-PDTA),[3] ethylenediaminetetrapropionate (EDTP),[5] and ethylenediamine-N,N'-diacetate-N,N'-di-3-propionate (EDDDA).[6,7] In connection with the optical activity work, there has been considerable interest in establishing the most thermodynamically favorable, strain-free complexes involving ligands of these types. Similar studies have been directed toward complexes of quinquedentate ligands containing only three glycinate chelate rings.[8-20] These include attempts at isolating and establishing the structure, by various methods, of the less favorable isomers of such complexes.

The X ray crystal structure[21] of Co(EDTA)$^-$ indicates that the in-plane glycinate rings are under more strain than the out-of-plane rings and, indeed, determination of the crystal structure of K_2[Co(ED3A)(NO_2)] · 1.5 H_2O[9] shows that the nitro substituent lies in the equatorial plane, thus relieving the greatest strain. Although there are two isomers theoretically possible for the corresponding EDTA complex, the one in which the substituent is in an axial position has not been verified. However, prior to determination of crystal structure, there were conflicting reports as to the geometry of the complex isolated.[10,12-14] It is thought that most of the quinquedentate complexes of EDTA,[9,16,17,22] ED3A (ethylenediaminetriacetate),[17,18] and (R)-(–)-PD3A[20] (PD3A = 1,2-propanediaminetriacetate) have equatorial substituents. Only the bromo substituted complex of Co(EDTA)$^-$ has been shown to exist as two isomers,[12,13] although there has been confusion as to which has an axial and which an equatorial bromo group.[23-26]

There has, as yet, been no report of investigations aimed at determining which quinquedentate structures are favored when one or more of the glycinate arms are replaced with larger alaninate arms. This paper reports the results of a study with a two-fold purpose: (1) to establish which quinquedentate geometries are favored for Co(III) complexes with EDDDA and (2) to establish the relationship between the sexidentate, quinquedentate, and quadridentate structures and their carbon-13 magnetic resonance spectra. The unambiguous assignment of the geometric isomers of EDDDA complexes is a very difficult problem without attempting crystal structure determinations. Complexes of EDDDA, in which EDDDA is a sexidentate ligand, can exist as three isomers, in theory, due to the fact that attached to each of the nitrogens of the backbone are both a glycinate arm and a β-alaninate arm. Two of the isomers, the *trans*(O_5)-[Co(EDDDA)]$^-$ (two six-membered rings in-plane and two five-membered rings out-of-plane) and the *trans*(O_5O_6)-[Co(EDDDA)]$^-$ (both in-plane and out-of-plane five- and six-membered rings) have been isolated.[6,7] The unisolated complex is designated *trans*(O_6) (two five-membered rings in-plane and two six-membered rings out-of-plane).

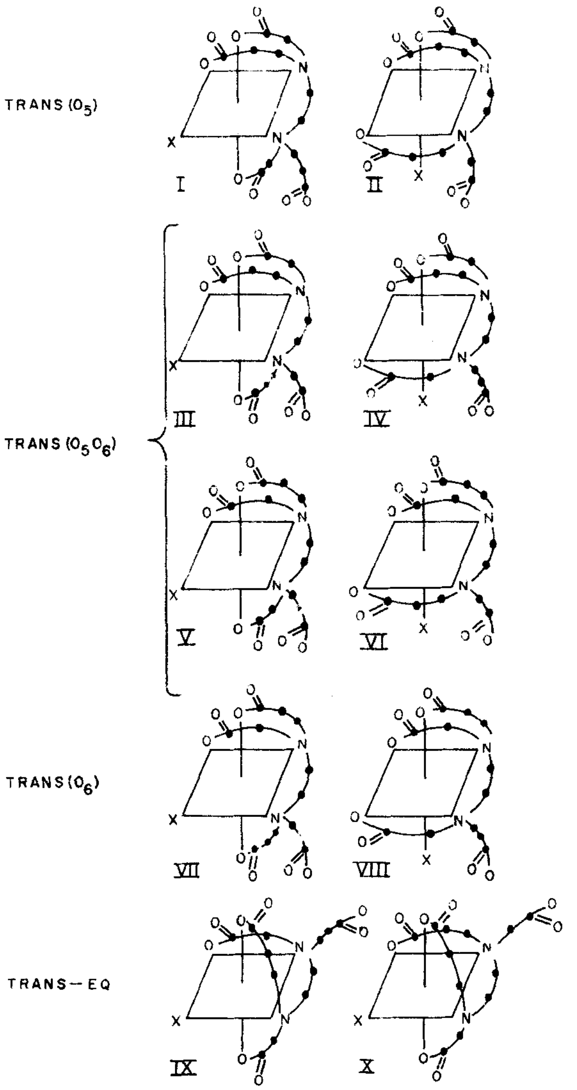

FIGURE 1 Possible geometrical isomers of quinquedentate complexes of Co(EDDDA)$^-$.

The situation becomes much more complicated when quinquedentate complexes of Co(EDDDA)$^-$ are considered. While only two isomers are possible for corresponding complexes involving EDTA, there are ten structures possible with EDDDA. These are shown in Figure 1. Thirteen structures are possible for quadridentate complexes of EDDDA. Only the six most "symmetrical" geometries are depicted in Figure 2. Four more quadridentate structures can be generated by having one of the amino acid arms (attached to N^1) coordinated in-plane and one (attached to N^2) coordinated out-of-plane. Two can be generated by having both coordinated arms attached to the same nitrogen, one in-plane and one out-of-plane. The last one results from out-of-plane coordination of both arms attached to the same nitrogen.

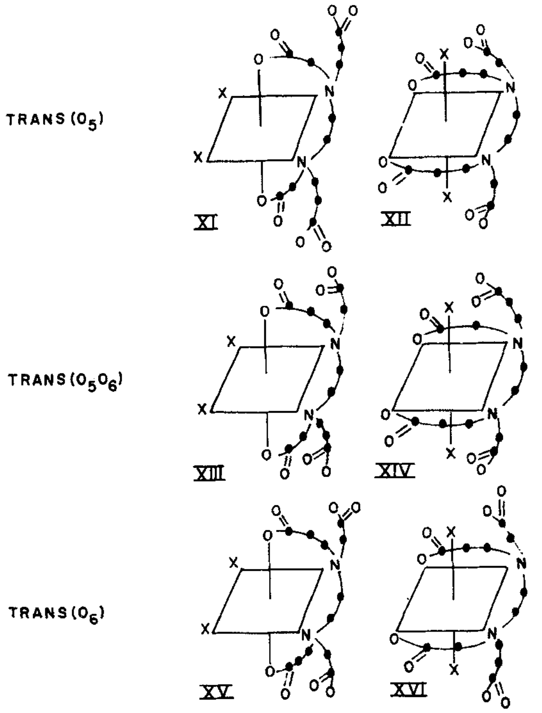

FIGURE 2 The most "symmetrical" possible geometrical isomers of quadridentate complexes of Co(EDDDA)$^-$.

Although it has not been possible to make unequivocal assignments of geometry for each of the complexes investigated here, it has been possible, at least, to restrict severely the geometrical possibilities for each complex. It is also possible to suggest, based on spectral evidence, a pathway of reactions involved in ring closures in going from quadridentate to sexidentate complexes.

With regard to the second purpose of this investigation, there have been very few reports of the application of ^{13}C nmr to transition metal complexes (with the exception of metal carbonyl compounds). However, there have been reports by two research groups on the use of this technique in studying $Co(EDTA)X^{n-}$ type complexes[12,13] and kinetics of deuterium exchange of glycinate rings for three $Co(EDTA)^-$ type systems.[22] The indications are that ^{13}C nmr can be used fruitfully as an instumenental method of investigation of inorganic stereochemistry, particularly in cases where corresponding proton spectra are so complicated as to be of only dubious use in elucidating structure.

EXPERIMENTAL SECTION

Reagents All reagents and solvents were obtained commercially and used without further purification. Ethylenediamine-N,N'-diacetic acid (La Mont Laboratories) was used for the preparation of H_4EDDDA, as previously described.[6,7]

Preparation of Sexidentate, Quinquedentate and Quadridentate Complexes of Co(III) with Ethylenediamine-N,N'-di-3-propionate H_4EDDDA (6.41 g, 0.02 mole) was partially dissolved and suspended in 350 ml of H_2O at 55°. $Na_3[Co(NO_2)_6]$, (8.08 g, 0.02 mol) dissolved in 20 ml of H_2O was added to the previous solution. The suspended H_4EDDDA dissolved within 5 min of mixing. Heating at 55°, with stirring, was continued for 3 hrs. Then the volume of the bluish-violet solution was reduced to 150 ml by rotary evaporation at 34°. This solution was then introduced onto a 40 cm x 5 cm anion exchange column made up of Dowex 1-X4 (200–400 mesh) resin in the NO_3^- form. Elution with 0.2 M KNO_3 developed two purple bands found to be uninegative aqua complexes. The first eluted purple component (referred to below as the first aqua complex) was reduced in volume from 700 to 40 ml on a rotary evaporator to remove KNO_3. The evaporation and filtration procedure was repeated four more times until a volume of about 6 ml remained. The solution was then evaporated to dryness under vacuum over conc. H_2SO_4. The resulting solid (containing 10–20% KNO_3) was ground and extracted at room temperature with 10 ml of absolute methanol. The methanol solution was then refrigerated at 4° overnight, yielding finely divided purple crystals which were filtered. The volume of the filtrate was reduced to 5 ml by a stream of air and then cooled at 4° overnight to yield a second fraction. The combined weight of the fractions after drying at 60° for 12 hrs was 4.08 g.

The second eluted purple component (the second aqua complex) was treated similarly. Despite the fact that there appeared to be a 1:1 ratio of the two aqua components on the column, only 0.92 g of the second aqua complex was isolated.[27]

The next fractions to be eluted were the blue–violet *trans*(O_5O_6) and violet *trans*(O_5) sexidentate complexes, respectively, whose isolations have been described previously.[6,7]

Following elution of the sexidentate complexes, two brown–violet fractions, both nitro complexes, were eluted in a 3:1 ratio (first:second nitro). The first nitro complex was collected by successive rotary evaporation and removal of KNO_3 to a volume of 5 ml. Then 5 ml of absolute ethanol was added and the sample was refrigerated to remove more solid KNO_3. The solution was then evaporated to dryness; yield, 5.31 g. The resulting brown–violet solid was ground and recrystallized by dissolving in a minimum amount of 80% methanol-H_2O at 45° and cooling overnight at 4°. Only one fraction was collected as all following fractions yielded crystals which immediately formed tars during filtration and drying. The crystals were washed with chilled absolute ethanol. Yield 2.82 g. *Anal.* Calcd for $K_2[Co(EDDDA)(NO_2)] \cdot 2H_2O$: C, 26.92; H 3.76; N, 7.85. Found: C, 26.91; H, 3.49; N, 7.94.

The second nitro complex was collected by successive evaporation (to a final vol of 7 ml) and removal of KNO_3. More KNO_3 was removed after addition of 3 ml of absolute ethanol. Addition of 3 ml more and refrigeration for 4 hrs produced the first fraction of brown–violet crystals. Two more additions of 5 ml quantities followed by refrigeration produced two more crops of crystals. Total yield, 1.95 g. This solid was recrystallized by dissolving in 3 ml of H_2O at room temperature, addition of 1 ml of absolute ethanol and cooling at 4° for 12 hrs. The brown–violet crystals thus produced were the double salt of the complex with KNO_3, yield 1.40 g. *Anal.* Calcd for $K_2[Co(EDDDA)(NO_2)] \cdot 0.5KNO_3 \cdot 2H_2O$:

C, 24.58; H, 3.62; N, 7.99. Found: C, 24.60; H, 3.44; N, 8.37.

A small orange band, apparently a -3 complex ion, was the last one to be eluted. Several of the orange fractions from repetitions of this procedure were combined and concentrated with removal of most of the KNO_3. Elemental analysis was not performed, however, the electronic absorption spectrum of the complex is similar to that of a dinitro EDTA type complex.

Resolution of the First Eluted Nitro Complex, $K_2[Co(EDDDA)(NO_2)] \cdot 2H_2O$ $(+)_D$-$[Co(en)_2ox] \cdot H_2O$, (1.31 g, 0.0032 mol) was dissolved in 10 ml of hot water along with silver acetate (0.53 g, 0.0032 mol). The solution was stirred for 15 min and then filtered to remove silver iodide. The filtrate and washings were then added to an aqueous solution containing the first nitro complex, $K_2[Co(EDDDA)(NO_2^-)]^- \cdot 2H_2O$ (1.71 g, 0.0032 mol) and glacial acetic acid (0.19 g, 0.0032 mol) which had been added in order to convert the carboxyl group of the free arm of the ligand from the K^+ to the H^+ form. Addition of 5 ml of ethanol and cooling at 4° for 3 hrs produced some reddish-brown crystals which were removed by filtration and washed with 1 ml of ethanol. The combined filtrate and washings yielded eight fractions during the refrigeration. Crystals of similar $\Delta\epsilon$ values were combined and recrystallized to give several fractions. Again crystals with like $\Delta\epsilon$ values were combined and the process was repeated until two fractions corresponding to the more soluble and less soluble diastereomers, giving constant $\Delta\epsilon$ values upon recrystallization, were isolated. Yield of the less soluble $(+)_D$-diastereomer was 0.80 g; $\Delta\epsilon_{520} = +4.23$. For the more soluble diastereomer, yield, 0.46 g; $\Delta\epsilon_{525} = +3.04$; $\Delta\epsilon_{600} = -0.40$. Both sets of crystals were then dissolved in 10 ml of H_2O and passed through a Rexyn 101 cation exchange column in the Li^+ form.[28] The solutions were evaporated to dryness. For the resulting Li^+ salts $\Delta\epsilon_{508} = +1.61$; $\Delta\epsilon_{595} = -0.46$ for the enantiomer derived from the less soluble $(+)_D$-diastereomer. The mirror image spectrum was also observed for the enantiomer derived from the more soluble diastereomer. *Anal.* Calcd for $Li_2[Co(EDDDA)(NO_2)] \cdot 2.5H_2O$: C, 30.02; H, 4.41; N, 8.75. Found: C, 30.32; H, 4.23; N, 8.64.

Resolution of the Second Eluted Nitro Complex, $K_2[Co(EDDDA)(NO_2)] \cdot 0.5KNO_3 \cdot 2H_2O$ $(-)_D$-$[Co(en)_2ox]Br \cdot H_2O$, 2.41 g (0.0066 mol) was converted to the acetate salt using silver acetate (1.11 g, 0.0066 mol), as above. $K_2[Co(EDDDA)(NO_2)] \cdot 0.5KNO_3 \cdot 2H_2O$, (2.58 g, 0.0044 mol) was dissolved in 5 ml of H_2O with glacial acetic acid (0.26 g, 0.0044 mol). This solution was added to that of the resolving agent. A red solid, the nitrate salt of the resolving agent, precipitated immediately and was filtrated off and rinsed with a few drops of chilled H_2O. The filtrate was placed in a refrigerator at 4° for 2 hrs to yield a few more red crystals. The less soluble and more soluble $(-)_D$-diastereomers were then isolated by the same method as used for resolution of the first nitro complex. Yield for the less soluble $(-)_D$-diastereomer, 0.74 g, $\Delta\epsilon_{522} = -3.52$, $\Delta\epsilon_{598} = +1.17$; for the more soluble diastereomer, yield 0.52 g, $\Delta\epsilon_{526} = -3.06$, $\Delta\epsilon_{585} = -1.71$. Each diastereomer was dissolved in 5.0 ml of H_2O and passed through a Rexyn 101 cation exchange column in the K^+ form, and the eluates were evaporated to dryness. For the resulting crystals derived from the less soluble $(-)_D$-diastereomer, $\Delta\epsilon_{500} = -0.44$, $\Delta\epsilon_{592} = +1.99$. A mirror image CD spectrum was obtained for the enantiomer derived from the more soluble $(-)_D$-diastereomer. *Anal.* Calcd for $K_2[Co(EDDDA)(NO_2)] \cdot 2H_2O$ from the less soluble $(-)_D$-diastereomer C, 26.92; H, 3.76; N, 7.85. Found: C, 26.95; H, 3.88; N, 7.01.

Conversions of Nitro Complexes to Aqua Complexes and to Sexidentate Complexes The first eluted nitro complex, $K_2[Co(EDDDA)(NO_2)] \cdot 2H_2O$, 0.13 g, was dissolved in 15 ml of H_2O and passed through a 1 cm x 10 cm Rexyn 101 analytical grade cation exchange column in the H^+ form. The resulting solution was heated at 40° for 2½ hrs and then reconverted to the K^+ form by passing through the same column in the K^+ form. Following this, half of the solution was used to charge a 2 cm x 25 cm Dowex 1-X4 (200–400 mesh) anion exchange column in the NO_3^- form. Elution with 0.2 M KNO_3 resulted in the appearance of only two bands. The first was a purple component giving the absorption spectrum of the second aqua complex and the second was a small brown–violet component corresponding to unreacted first nitro complex. Then the other half of the solution was heated for an additional 2 hrs at 60°. When eluted with 0.2 M KNO_3 through a Dowex 1-X4 anion exchange column two bands appeared. A small purple band corresponding to the second aqua complex was eluted first, followed by a larger, blue–violet component whose absorption spectrum was that of the *trans*(O_5) sexidentate complex.

A similar treatment of the second nitro complex, $K_2[Co(EDDDA)(NO_2)] \cdot 0.5KNO_3 \cdot 2H_2O$, revealed that it could be converted to only the first aqua complex and, predominantly, the *trans*(O_5O_6) sexidentate complex[7] with a small amount of *trans*(O_5) complex being formed also. [Recall that in the initial preparation of the complexes from $Na_3[Co(NO_2)_6]$ much more *trans*(O_5) complex is formed than *trans* (O_5O_6)].

Isolation and Resolution of the Two Aqua Complexes It proved difficult to obtain either of the two aqua complexes in a form free of KNO_3 and also to effect resolutions with $(-)$-$[Co(en)_2ox]^+$ as a resolving agent when using the complexes crystallized from solutions obtained directly from the column used initially for separation of complexes. Therefore, an alternative method for these purposes was devised.

A pure sample of the resolved first complex, $Li_2[Co(EDDDA)(NO_2)] \cdot 2.5H_2O$, was dissolved and passed through a Rexyn 101 cation exchange column in the H^+ form. The eluate was allowed to sit in a crystallizing dish for 4 hrs and then heated in a water bath at 40° for one hr more. The solution had changed in color from brown–violet to a more bluish–violet color. The shape of the CD spectrum was different from that of the first nitro complex, however, it still retained weak peaks in the same vicinity as those of the first nitro complex. Heating at the same temperature for a total of *ca.* 2 hrs was required for complete disappearance of the CD shoulders of the unreacted nitro complex. The solution was then rotary evaporated nearly to dryness at room temperature and then placed overnight in a vacuum desiccator over conc. H_2SO_4. Magnitudes of $\Delta\epsilon$ values of the resulting crystals (assuming anhydrous) were obtained and found to increase only *ca.* 3% upon redissolution and heating at 40° for one hr more. The purple crystals were then redissolved, converted back to the K^+ form and again evaporated to dryness. For the complex obtained from the first nitro enantiomer derived from the less soluble $(+)_D$-$[Co(en)_2ox]^+$ diastereomer, $\Delta\epsilon_{542} = +1.92$, $\Delta\epsilon_{618} = -0.24$. *Anal.* Calcd for $K[Co(EDDDA)(H_2O)] \cdot 2H_2O$: C, 30.78; H, 4.73; N, 5.98. Found: C, 30.69; H, 4.49; N, 6.28.

The resolved first aqua complex was obtained from the resolved second nitro complex in the same way as described above for the second aqua complex. However, after the initial 40 min heating period, no CD peaks corresponding to the second nitro complex remained. After isolating the purple crystals by evaporation, $\Delta\epsilon$ values were measured. Redissolution and heating for another hr at 40° produced no further changes in the CD spectra. For the aqua isomer obtained from the less soluble $(-)_D$-$[Co(en)_2ox]^+$ diastereomer of the second nitro complex, $\Delta\epsilon_{547} = -2.66$, $\Delta\epsilon_{610} = +1.48$. *Anal.* Calcd for $K[Co(EDDDA)(H_2O)] \cdot 2H_2O$: C, 30.78, H, 4.73; N, 5.98. Found: C, 30.72; H, 4.61; N, 6.18. Justification for the fact that no significant racemization occurs during conversion processes for both isomers lies in the fact that both aqua complexes reach constant $\Delta\epsilon$ values, comparable to those of the nitro and sexidentate complexes, and do not decrease in $\Delta\epsilon$ with further heating as would be expected if racemization occurred.

Physical Measurements Electronic absorption spectra were recorded for *ca.* 2×10^{-3} M solutions on a Cary Model 14 recording spectrophotometer with a tungsten lamp. The circular dichroism spectra were recorded at room temperature on a Cary Model 61 recording spectropolarimeter with a xenon arc lamp.

Proton magnetic resonance spectra were obtained with a Varian T-60 nmr spectrometer and the 250 MHz nmr spectrometer at Carnegie–Mellon University using 0.2 to 1.0 M solutions. The field frequency ratio was stabilized by locking to D_2O. Deuterium oxide was used as a solvent with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an interval reference.

Carbon-13 magnetic resonance spectra were recorded on a Jeol, Inc. JNM FX-60 Fourier Transform ^{13}C-^1H high performance nmr spectrometer, operating at *ca.* 15.0–15.1 MHz in the ^{13}C mode. The instrument was used in either a broad band random noise ^1H decoupling mode or a selective ^1H resonance decoupling mode. Most spectra were obtained using spectal windows of 5000 Hz, covered by 4096 addresses in the Fourier Transform spectrum. Scan times of 0.5 sec were generally used and each spectrum required 500–50,000 scans depending upon the concentration of the sample. Concentrations of samples dissolved in D_2O ranged between 0.2 and 1.0 M and spectra were obtained from samples contained within 10 mm diameter tubes or 8 mm–10 mm coaxial tubes manufactured by Wilmad Spectroscopic Supplies, Inc. TMS dissolved in benzene was used as an external standard in an outer coaxial tube arrangement.

RESULTS

Proton Magnetic Resonance The 60 MHz pmr spectra of the two nitro and two aqua complexes are very complicated. The identification of AB patterns,

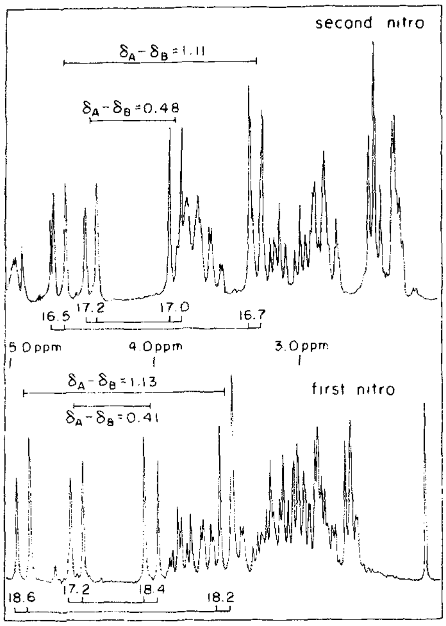

FIGURE 3 250 MHz pmr spectra of first and second nitro complexes of Co(EDDDA)$^-$.

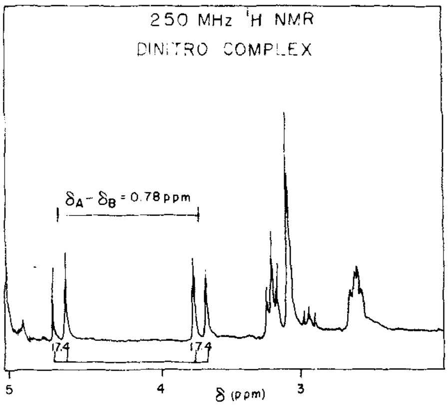

FIGURE 4 250 MHz pmr spectra of dinitro complex of Co(EDDDA)$^-$.

corresponding to glycinate chelate rings, is difficult due to the presence of overlapping peaks. For this reason 250 MHz pmr spectra of these four complexes and of the dinitro complex have been obtained. Table I summarizes the results and Figures 3 and 4 show the spectra of the two nitro complexes and the dinitro complex. In these spectra, the peaks are better separated and AB patterns are quite readily identifiable. The two nitro complexes each exhibit two distinct AB patterns in the 3–5 ppm region, while the two aqua complexes each exhibit one AB pattern, and the simpler dinitro spectrum clearly shows only one AB pattern. Peaks at higher field all correspond to ethylenediamine backbone and alaninate resonances.

The 60 MHz spectra of the *trans*(O_5) and *trans* (O_5O_6) sexidentate complexes show less overlap than those of the nitro and aqua complexes and have already been reported.[6,7] The *trans*(O_5) complex shows one AB pattern with $J_{AB} = 18.4$ Hz, corresponding to two equivalent out-of-plane (R) glycinate rings,[29] while the *trans*(O_5O_6) complex shows two AB patterns having $J_{AB} = 16.4$ Hz and 18.4 Hz, corresponding to in-plane (G) and out-of-plane (R) glycinate rings,[29] respectively.

Carbon-13 Magnetic Resonance Table II and Figure 5 summarize the results of the broad band random noise decoupled ^{13}C nmr spectra of all the EDDDA complexes. Typical spectra are shown in

TABLE I
AB patterns in pmr spectra of Co(EDDDA)$^-$ type complexes

Complex	δ_A(ppm)	δ_B(ppm)	$\delta_A - \delta_B$(ppm)	J_{AB}(Hz)	MHz	R or G
trans(O_5)[a]	4.25	3.52	0.73	18.4	60	R
trans(O_5O_6)[a]	4.15	3.40	0.75	18.4	60	R
	4.03	3.43	0.61	16.4		G
first aqua	4.29	3.62	0.67	18.4	250	R
second aqua	4.29	3.60	0.69	18.4	250	R
first nitro	4.44	3.31	1.13	18.6 and 18.2	250	R?
	4.14	3.73	0.41	17.2 and 18.4		R?
second nitro	4.35	3.24	1.11	17.2 and 17.0	250	R?
	4.17	3.69	0.48	16.5 and 16.7		G?
dinitro	4.34	3.56	0.78	17.4	250	R?

[a] from references 6 and 7

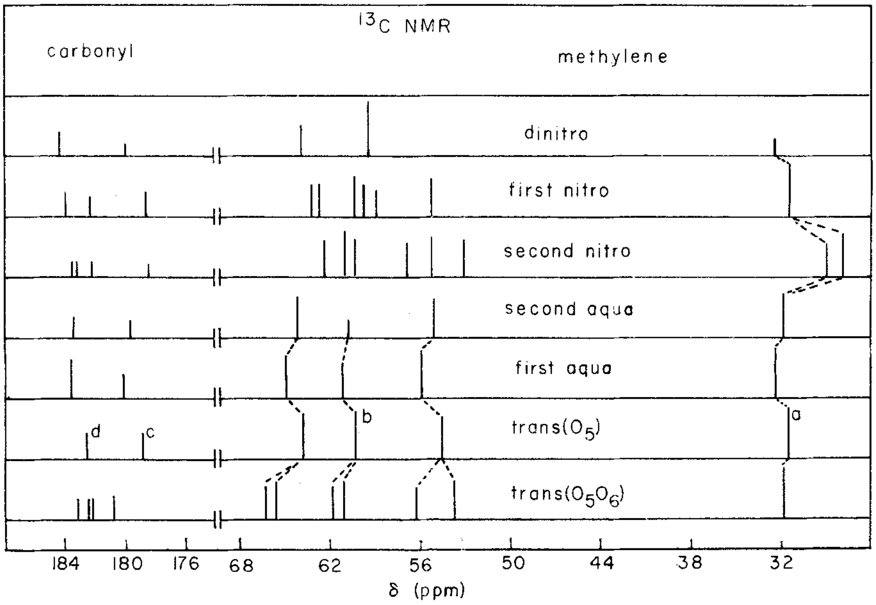

FIGURE 5 ^{13}C nmr spectra of complexes of Co(EDDDA)$^-$.

Figure 6 which depicts both the methylene and carbonyl regions of the two nitro isomers. It is evident from cursory examination of Figure 5 that the ^{13}C technique provides an excellent means of determining which isomers have the highest symmetry and which have the lowest.

Of the two sexidentate complexes, as expected, the spectrum of the *trans*(O$_5$O$_6$) isomer reflects lower symmetry. There are two peaks in this spectrum for every one in the *trans*(O$_5$) spectrum except for one peak (at highest field, *a* in Figure 5) which remains unsplit. This is due to the fact that the former isomer has in-plane and out-of-plane glycinate (5-membered) rings and in-plane and out-of-plane alaninate (6-membered) rings, while the latter has only in-plane alaninate and out-of-plane glycinate rings. The identity of each of the methylene resonances of the *trans*(O$_5$O$_6$) complex relative to those of the *trans*(O$_5$) isomer is also obvious. Therefore, it can be concluded that each "doublet" in the methylene region for the *trans*(O$_5$O$_6$) complex corresponds to in-plane and out-of-plane pairs of carbons which occupy equivalent positions in the uncomplexed EDDDA ligand. However, the correlation of the four carbonyl resonances of the *trans* (O$_5$O$_6$) complex with the two *trans*(O$_5$) carbonyl resonances is not as obvious.

Selective decoupling can be used in gaining structural information from ^{13}Cmr, just as it can for pmr.[30,31] If assignments of some or all of the resonances in the pmr spectrum of a sample have been accomplished, this technique can be used in

TABLE II
^{13}C resonance positions[a]

Complex	Carbonyl Region	Methylene region
Dinitro	184.32, 179.94	62.90, 59.41, 32.47
first nitro	184.60, 182.38, 178.64	64.04[b], 63.15, 62.66, 60.39, 59.74, 58.92, 55.27, 54.79[b], 31.65
second nitro	183.51, 183.19, 182.23, 178.48	62.33, 60.95, 60.30, 56.90, 55.27, 53.08, 28.98, 27.92
second aqua	183.41, 179.84	64.12, 60.71, 55.03, 31.82
first aqua	183.59, 180.10	64.44, 61.03, 55.89, 32.30
trans(O$_5$)	182.54, 178.88	63.80, 60.31, 54.54, 31.49
trans(O$_5$O$_6$)	183.11, 182.46, 182.13, 180.75	66.15, 65.50, 61.85, 61.12, 56.25, 53.73, 31.82

[a] δ (ppm) relative to TMS dissolved in benzene as coaxial external standard.
[b] resonance due to formation in solution of the second aqua complex.

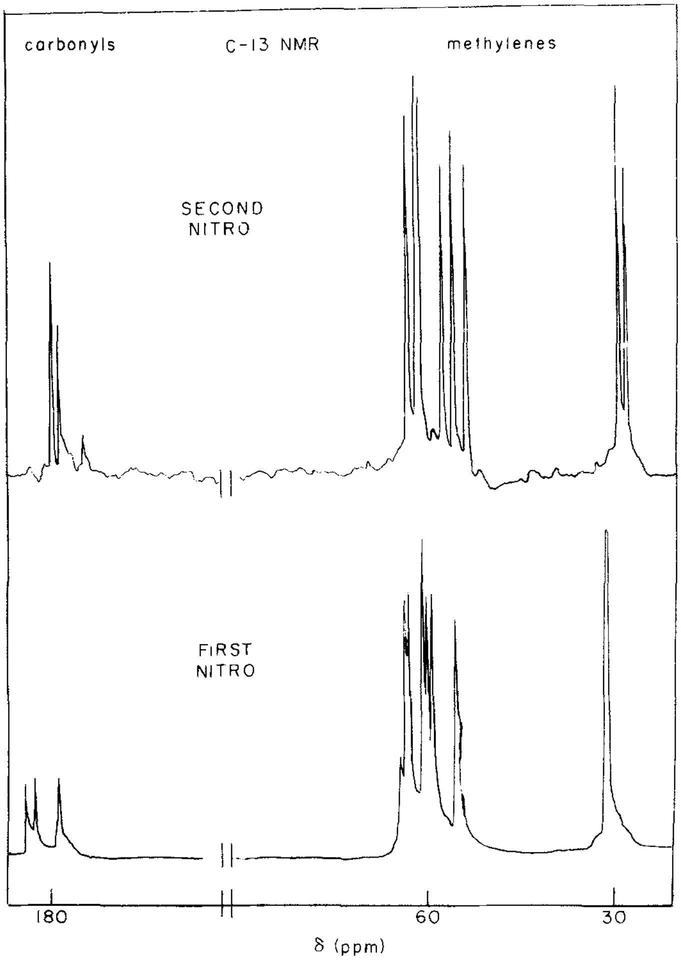

FIGURE 6 ^{13}C nmr spectra of first and second nitro complexes of Co(EDDDA)$^-$.

correlating carbon resonances with the individual carbons to which the protons considered are bound. This is particularly true when the resonances of the protons in question are, in the ideal case, isolated from the rest of the proton spectrum. In the case of the *trans*(O_5) complex, its 60 MHz proton spectrum shows a well-resolved and isolated AB pattern centered at about 232 Hz (3.88 ppm relative to internal DSS).[6] When, in the ^{13}C experiment, the broad band noise decoupler is turned off and, instead, the *trans*(O_5) sample is irradiated constantly at this particular frequency, all protons except those of the methylene carbons of the out-of-plane glycinate rings can interact with the carbons to which they are attached. This results in two effects: (1) the carbons to which the AB protons are bound show resonances which are relatively intense and unsplit since they are effectively decoupled and (2) all other carbon resonances tend to lose intensity, due to a loss in Nuclear Overhauser enhancement, and become split due to interaction with the non-resonating protons. Figure 7 shows the result of this experiment. It is evident that the methylene peak at 60.30 ppm (*b* in Figure 5) in the *trans*(O_5) spectrum corresponds to the glycinate methylene carbon.

This type of procedure was also attempted for the *trans*(O_5O_6) complex. Unfortunately, the two AB patterns in the 60 MHz proton spectrum of this complex[7] overlap to the extent that when the frequencies of individual AB resonances or the mean frequencies of each AB pattern are used for selective decoupling, both R and G rings are affected. As a consequence, it is not possible to determine by this method which resonance represents in-plane methylenes and which represents the out-of-plane carbons.

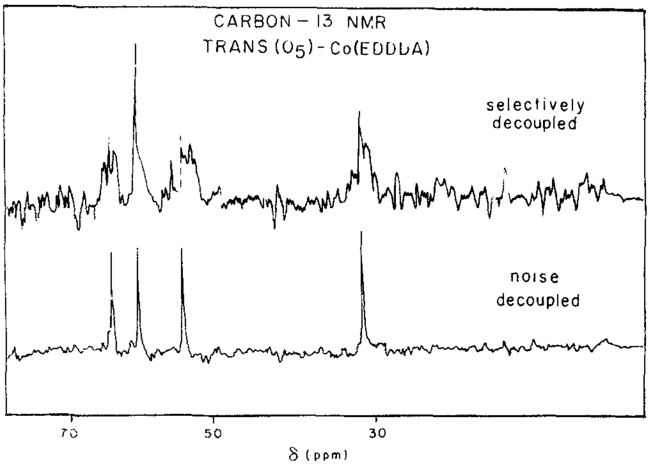

FIGURE 7 Selective decoupling of ^{13}C spectra of *trans*(O$_5$)-[Co(EDDDA)]$^-$.

Terrill and Reilley have shown from pmr studies that acid catalyzed deuterium exchange of the methylenes of Co(EDTA)$^-$ at 85°–103° and in the acidity range 0.05–0.5 M acid, occurs most rapidly at the out-of-plane glycinate methylenes, with the in-plane glycinate carbons exchanging very slowly.[32] They found that the ethylenediamine methylenes do not undergo any observable exchange under these conditions. Similar trends were observed for Co(III)-(CyDTA)$^-$ and Co(III)(PDTA)$^-$. It is known from determination of the crystal structure of Co(EDTA)$^-$ that there is more bending and strain in the in-plane glycinate rings than in the out-of-plane rings.[8]. Terrill and Reilley, therefore, postulated (1) that the acid catalyzed deuteration passes through an enol intermediate, requiring that the methylene groups α to the carboxyl groups are slightly acidic and (2) that the difference in ability of the in-plane and out-of-plane glycinate protons to undergo isotopic exchanges is a function of ring strain, the least strained rings exchanging more easily.

Blackmer and Vickrey[22] have made use of these observations in their kinetic studies of deuterium exchange for three sexidentate cobalt(III) aminocarboxylates: Co(EDTA)$^-$, Co(CyDTA)$^-$, and Co(PDTA)$^-$. Howarth, Moore, and Winterton[12,13] have also used the conclusions of Terrill and Reilley in interpreting the ^{13}C spectra of sexidentate and quinquidentate complexes of EDTA^{4-} and CDTA^{4-} with several different metal ions, particularly Co(III). Presumably there are significant differences in ring strain of the out-of-plane glycinate rings for the quinquidentate complexes since they differ in their ability to undergo isotopic exchange with one of them resisting deuterium exchange almost completely.[22]

Figure 8 shows the ^{13}C spectrum of the *trans*(O$_5$)-[Co(EDDDA)]$^-$ complex after heating for twelve hours at pD ~ 0.5. The peak positions are shifted very slightly relative to the unacidified complex. Additional weak peaks have also appeared in the 20–60 ppm region indicating some decomposition into at least one other compound. However, more importantly, the peak at 31.49 ppm (*a* in Figure 5) has dropped out of the spectrum as a result of deuteration, indicating that it must correspond to a methylene carbon in the least strained ring. In the case of the *trans*(O$_5$) complex it is likely that the two in-plane alaninate rings are under less strain than the two out-of-plane glycinate rings. Of course, the protons attached to an α carbon would be expected to be more acidic, and therefore more susceptible to exchange than those attached to β-carbons. For these reasons, the resonance at 31.49 ppm is assigned to the α carbons (to the carboxyl group) of the (in-plane) alaninate rings. Not surprisingly, the glycinate

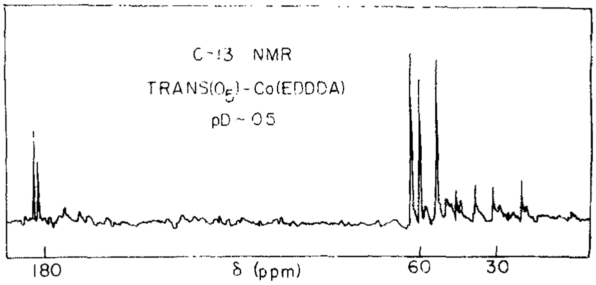

FIGURE 8 ^{13}C spectrum of deuterated *trans*(O$_5$)-[Co(EDDDA)]$^-$ at pD = 0.5.

methylene resonance at 60.30 ppm has also decreased in intensity slightly relative to the two other remaining peaks. As far as the carbonyl region is concerned, the peak at higher field in the spectrum of the unacidified complex (178.88 ppm, *c* in Figure 5) has shifted downfield by about 3 ppm, much more than any other resonance (*d* in Figure 5), and has lost considerable intensity. This is attributed to the second order Nuclear Overhauser Effect resulting from deuteration of the methylene groups adjacent to the resonating carbonyl groups. On this basis, the higher field carbonyl resonance is assigned to the two equivalent in-plane alaninate carboxylate carbons, and the lower field carbonyl resonance to the out-of-plane glycinate carbonyl groups. This ordering is consistent with the ordering of in-plane and out-of-plane carboxyl group resonances of the other sexidentate complexes, containing only glycinate arms.[12,13,22]

It is interesting to note that both aqua complexes have ^{13}C spectra which are very similar to that of the *trans*(O_5) complex. They do, however, differ in chemical shift relative to the sexidentate complexes. The shifts of the resonances of the second aqua complex more closely parallel those of the *trans*(O_5) complex, while those of the first aqua complex are close to the positions of the *trans*(O_5O_6) resonances. Also interesting, is the fact that the methylene resonance of the second aqua complex corresponding with the *trans*(O_5) glycinate methylene peak is relatively less intense than the other methylene peaks in the spectrum. The same effect is also observed, though to a much smaller degree, in the first aqua complex. This suggests the presence of a mechanism for both aqua complexes which effectively inhibits the relaxation of the carbons associated with these resonances.

It is also obvious from Figure 5 that the dinitro complex contains the smallest number of non-equivalent carbons, and the second nitro complex the greatest number. In the case of the second nitro complex, we find the only example where the resonance appearing in the 32 ppm region in other spectra becomes split into two peaks, and also is shifted to higher field. This is the only complex which shows one resonance for each carbon in both methylene and carbonyl regions. It should be noted in this regard that the lowest field carbonyl resonance of this complex, as depicted in Figure 6, is actually made up of two non-degenerate resonances (183.51 and 183.19 ppm) as is found when this region of the spectrum is expanded.

The weak peak at 64 ppm and the shoulder at about 55 ppm, at the outer extremities of the cluster of methylene resonances of the first nitro complex are though to be due to the formation in solution of the second aqua species, as the shifts correspond to the intense second aqua peaks in that region. It is also observed that these two resonances increase in intensity with time when the complex is left in solution.

Circular Dichroism and Electronic Absorption
Figures 9 and 10 show the visible absorption and CD curves for the nitro and aqua complexes related to the less soluble $(-)_D$-$[Co(en)_2(ox)]^+$ diastereomers. By correlation of these spectra with the CD spectra of the sexidentate species,[6,7] all complexes giving rise to spectra shown are assigned the Λ absolute configuration, with the single exception of the second nitro complex. For reasons which will be discussed later in this paper, this isomer is assigned a geometry which would not give rise to Λ or Δ configuration according to IUPAC rules, if the rings are considered equivalent.

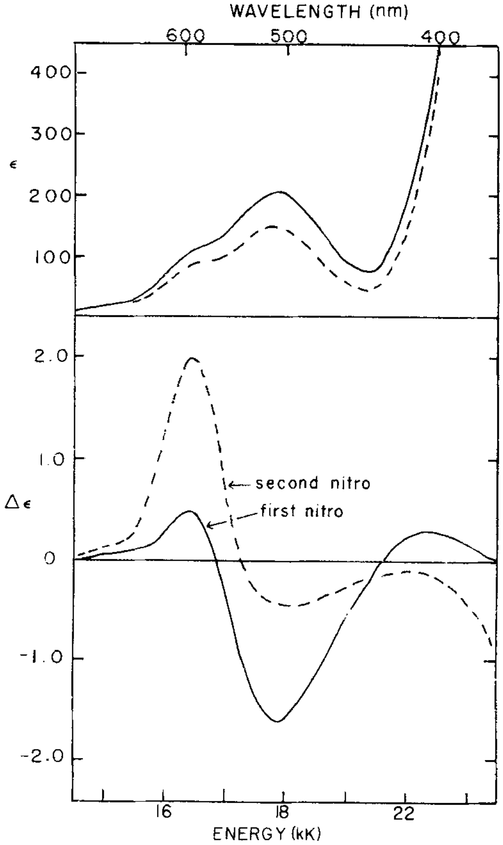

FIGURE 9 Electronic absorption and CD spectra of first and second nitro complexes of $Co(EDDDA)^-$.

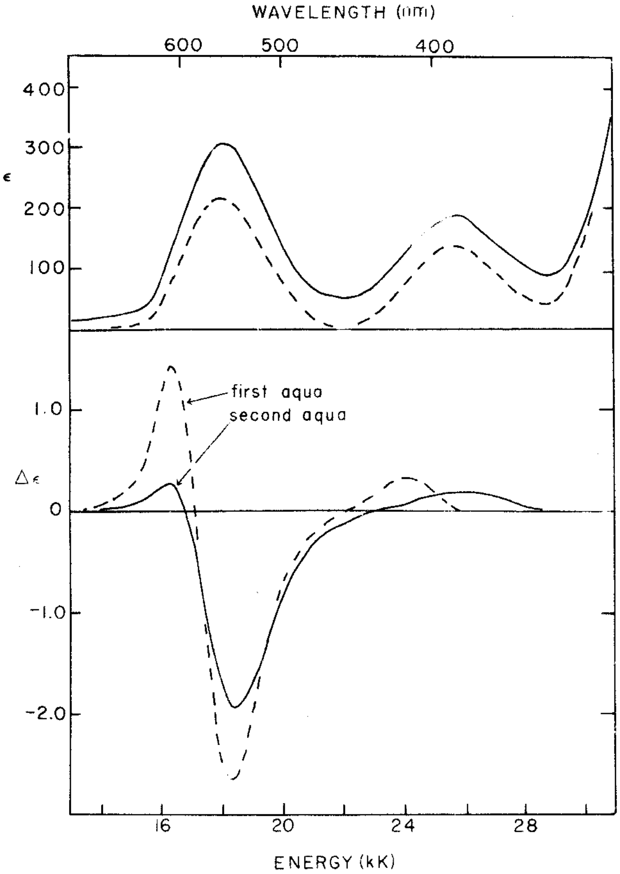

FIGURE 10 Electronic absorption and CD spectra of first and second aqua complexes of Co(EDDDA)$^-$.

Most striking are the similarities between the spectra of the second aqua complex and the *trans*-(O_5) complex, previously reported,[6] and between the first aqua complex and the *trans* (O_5O_6) complex.[7] The lower and higher energy absorption bands correspond to the T_{1g} and $T_{2g}(O_h)$ excited states, respectively. The positions of the band maxima of the T_{1g} maxima of both aqua complexes are shifted to lower energy than the corresponding bands of the sexidentate complexes, while the T_{2g} bands are shifted to higher energy. The peaks of the second aqua complex are at slightly higher energy than those of the first aqua complex.

The major differences in the shape of the CD spectra of the aqua complexes relative to those of the sexidentate species occur in the T_{2g} region. Both of the sexidentates show a "double-humped" character in this region, with the higher energy portion being somewhat more prominent in both cases. The higher energy portion of the T_{2g} region of the second aqua CD spectrum is much more prominent than the lower energy portion, while for the first aqua complex the lower energy peak is dominant and the higher energy portion has disappeared.

Since the nitro group is a stronger field ligand than is the water molecule, the absorption and CD bands peak at higher energy for the nitro complexes (Figure 10) than for the aqua complexes (and the sexidentate complexes). Low energy charge transfer tails also mask the T_{2g} region of the spectrum. Therefore, both of the peaks appearing in the visible absorption and CD spectra are associated with the T_{1g} manifold. Band maxima of the first nitro complex are at slightly higher energy than those of the second nitro complex.

The orange dinitro complex shows a major absorption peak at 19.94 kK and a shoulder at about 22 kK on the low energy tail of a nearby charge transfer band.

Two observations regarding the CD spectra of the quinquedentate and sexidentate EDDDA complexes derived from less soluble $(-)_D$-$[Co(en)_2(ox)]^+$ diastereoisomers are noteworthy: (1) the signs and relative magnitudes of all the ligand field components of the first nitro, second aqua, and *trans*(O_5) complexes are quite similar, as are those of the first aqua and *trans*(O_5O_6) complexes, and (2) only the second nitro complex has overall positive rotatory strength and fits into neither of the categories of (1).

DISCUSSION

The spectral results obtained allow us to propose geometries for each of the complexes isolated, or at least to exclude most of the structures theoretically possible for the quinquedentate (Fig. 1) and quadridentate (Fig. 2) structures.

Nitro Complexes Sudmeier, Senzel, and Blackmer[29] reported the complete assignment of the 100 MHz pmr resonances corresponding to the glycinate protons of $[Co(PDTA)]^-$ and $[Co(EDTA)]^-$. They concluded that the presence of AB patterns with $J_{AB} = 18 \pm 0.5$ Hz and 16 ± 0.5 Hz indicate the presence of metal coordinated out-of-plane (R) and in-plane (G) glycinate rings, respectively. These values have been observed for a number of other related complexes. However, there are reports in which these criteria are not strictly met. A case in point is a recent paper by Maricondi and Maricondi[20] in which they report the isolation of two isomers of $K_2[Co((R)\text{-}(-)\text{-}PD3A)NO_2]$ (PD3A = 1,2-propanediaminetriacetate). One isomer is assigned to the *cis-equatorial* geometry, analogous to structures I, III, V, and VII. The other isomer is assigned the *trans-equatorial* geometry, analogous to structures IX and X. They reported the presence of an R ring with J_{AB} = 16 Hz and also another with J_{AB} = 17 Hz. Day and Reilley have also reported that one of the four AB patterns of Co(III)-*meso*-BDTA (BDTA = (2,3-butylenediaminetetraacetate)) has J_{AB} = 11.0 Hz, presumably low for steric reasons.[33] It should be noted that no glycinate AB patterns having $J_{AB} \geqslant 18.0$ Hz have been found to correspond to anything other than out-of-plane glycinate rings. One uncoordinated glycinate arm has also been reported[17] to give rise to an AB pattern having J_{AB} = 17 Hz for $[Co(EDTA)(NO_2)]^{2-}$ but the average chemical shift is at very high field, 3.24 ppm, compared to the patterns of closed glycinate rings in the same spectrum, 3.97, 3.98, and 4.11 ppm. The AB patterns observed for both of the nitro complexes reported here, as well as for the aqua, dinitro, and sexidentate complexes of EDDDA,[6,7] all have average chemical shifts falling within the expected region for closed rings. Therefore, the only assumptions made in interpreting the proton spectra here are that AB patterns falling within this chemical shift range represent closed glycinate rings, and that those having $J_{AB} > 18.0$ Hz correspond to out-of-plane (R) rings.

Each of the nitro complexes shows a pair of AB patterns. J_{AB} values for the second nitro complex are about 16.6 Hz (the average of 16.5 and 16.7 Hz) and 17.1 Hz, centered at 3.93 and 3.80 ppm, respectively. For the first nitro complex the patterns are centered at 3.88 and 3.94 ppm but the true coupling constants are difficult to evaluate. One set has separations between the individual peaks associated with the lower field, A, protons of 18.6 Hz and separations between the B peaks of 18.2 Hz. The other set has separations of 17.2 and 18.4 Hz. Despite this apparent discrepancy there is little doubt that these resonances actually correspond to glycinate protons and AB patterns in view of the fact that their relative intensities, shapes, and positions are so similar to those of the more well behaved second nitro complex (Figure 3). The only conclusions to be drawn from these data are that both nitro complexes contain two closed glycinate rings and the first nitro complex contains at least one R ring. Structures conforming to these restrictions for the first nitro complex are structures I, IV, V, and IX. Those satisfying the conditions for the second nitro complex are I, IV, V, VIII, and IX.

Comparison of the absorption spectra of the nitro complexes reveals that they are very similar in band shape and position. The relative intensities of the two peaks associated with the $T_{1g}(O_h)$ region of each isomer are nearly identical. Therefore, the holohedrized ligand field polarizations along the *x*, *y* and *z* axes must be similar for both isomers. This requires that complexes either be both equatorially substituted, structures I, V, or IX, or else both axially substituted IV or VIII. The pronounced splitting of the $T_{1g}(O_h)$ band for both nitro complexes suggests strong tetragonal splitting. An equatorially substituted isomer would show such splitting because of the strong in-plane field and weak out-of-plane field. An axially substituted isomer would have one strong and one weak field ligand along each of the coordinate axes and would be expected to have nearly "cubic" effective symmetry.

Reference to the ^{13}C spectra (Figure 5) shows that the chemical environments of the methylene and carbonyl carbons of the second nitro complex are much different than those of the other six complexes reported. This fact, coupled with the observation that its CD spectrum is significantly different from those of the other quinquedentate and sexidentate complexes, strongly suggest that its geometry differs from that usually encountered for related complexes. The obvious conclusion is that the second nitro complex must then possess the *trans-equatorial* structure, IX. This structure would not give rise to Λ or Δ configuration if the rings were considered equivalent. It derives its optical activity from the nonequivalent chiral pairs of rings and the presence of asymmetric nitrogens. As a result, the structure of the first nitro complex must be either I or V. Structure I is favored over V because it is more closely related to the *trans*(O_5) complex, to which it can be directly converted through an aqua intermediate. Also supporting this choice is the fact that the geometry assigned to the dinitro complex, to be discussed later in this section, is also more closely related to the quinquedentate structure, I than V.

Aqua Complexes Since both aqua complexes have ^{13}C magnetic resonance, pmr, and absorption spectra, but not CD spectra, which are very much alike, they probably have similar structures. Also, the second aqua complex can be converted to the *trans*(O_5) complex and their CD spectra are very similar. The same relationships hold for the first aqua and *trans*(O_5O_6) complexes. Thus, this pair must have very similar structures also.

Each aqua complex exhibits only one AB pattern with J_{AB} = 18.4 Hz and centered at about 3.95 ppm, suggesting that each has one or two identical glycinate R rings and no G rings. Structures fitting this requirement are I, II, III, and X.

The absorption spectra of these two complexes are very similar with respect to band shapes and positions. However, this information is of little use in eliminating possibilities because we are now considering water as a substituent rather than the strong field nitrite ligand. The holoherized ligand fields for both axial and equatorial substituents, unfortunately, are the same.

The ^{13}C spectra of the aqua complexes are quite similar, differing mainly in (1) the relative intensities of the methylene resonances which, by analogy with those of the *trans*(O_5) complex discussed in the Results section, ought to correspond with glycinate methylenes, and (2) chemical shift. The glycinate methylene resonance of the first aqua complex relative to other peaks in the same spectrum is slightly less intense than that of the *trans*(O_5) complex. The same resonance of the second aqua complex shows a pronounced deintensification relative to the corresponding *trans*(O_5) resonance. It is thought that this might be caused by hydrogen bonding between the coordinated water molecule and an adjacent free glycinate arm of the ligand. This could result in an effective increase in the relaxation time of the methylene carbon adjacent to the hydrogen bonded carboxylate group, and therefore, a concurrent decrease in ^{13}C intensity. This could also account for the marked similarity between the CD spectra of the second aqua-*trans*(O_5) and first aqua-*trans*(O_5O_6) pairs, since such bonding could make the aqua complexes "pseudo-sexidentates". Also lending credence to this idea is that, although the ^{13}C resonances of the first aqua complex are not split to the extent that the *trans*(O_5O_6) resonances are, their shifts more closely parallel the average shifts of the *trans*(O_5O_6) complex than those of the *trans*(O_5) complex. The reverse is true for the second aqua complex. The fact that hydrogen bonding is suggested would lead to the conclusion that structure X no longer needs to be considered as a possibility for the aqua complexes, and only structures I, II and III remain. Structure III is the most closely related to the *trans*(O_5O_6) complex and II is related to the *trans*(O_5) structure. Thus, the second aqua complex is likely to have structure II and the first aqua complex, structure III.

Sexidentate Complexes The ^{13}C spectra support earlier assignments regarding the structures of the *trans*(O_5) and *trans*(O_5O_6) complexes.[6,7]

Dinitro Complex In view of the extreme simplicity of the ^{13}C and proton magnetic resonance spectra of the dinitro complex, only the more "symmetrical" quadridentate structures, shown in Figure 2, need be considered as possibilities. Any structures other than those pictured would greatly increase the complexity of the pmr spectrum and probably also the ^{13}C spectrum.

No examples of metal complexes of the quadridentates, ethylenediamine-N,N'-diacetate (EDDA) or trimethylenediamine-N,N'-diacetate (TMDDA) have ever been reported to have the planar geometries of structures XII, XIV, or XVI.[34] These structures are therefore considered unlikely as possibilities.

It is found that the shapes, relative intensities, and positions of the electronic absorption bands of the dinitro complex and *symmetrical-cis* [Co(EDDA)(NO_2)$_2$]$^-$ (analogous to structure XI) are nearly identical.[35] This also argues in favor of structures XI, XIII, or XV. The ligand field axial polarizations would be changed for other geometries.

Since an AB pattern (Figure 4) with J_{AB} = 17.4 Hz is found centered at 3.95 ppm in the pmr spectrum of the dinitro complex, there must be at least one closed glycinate ring. This would eliminate structure XV. The rest of the pmr spectrum cannot be accounted for completely by either of the remaining two structures – nor certainly as well accounted for by any of the other structures theoretically possible as by structure XI. For structure XI, the two equivalent R rings would account for the single AB pattern. Each equivalent methylene group of the ethylenediamine backbone should contain two nonequivalent protons giving rise to either a doublet of triplets or a triplet of doublets. The latter is observed, centered at about 2.6 ppm. The two equivalent uncoordinated alaninates could give rise to either two triplets, two singlets, or one of each, depending upon the degree of freedom of rotation about N–C or C–C bonds and the rigidity of the alaninate arm. A strong triplet and a strong singlet are observed in the alaninate region of the spectrum 3.0–3.2 ppm, however, a weak triplet between 2.9 and 3.0 ppm cannot be explained.

Proposed Pathway of Conversion of Quadridentate Complex to Sexidentate Complexes Figure 11 shows the pathway scheme suggested as most likely for ring closure based on the observations reported

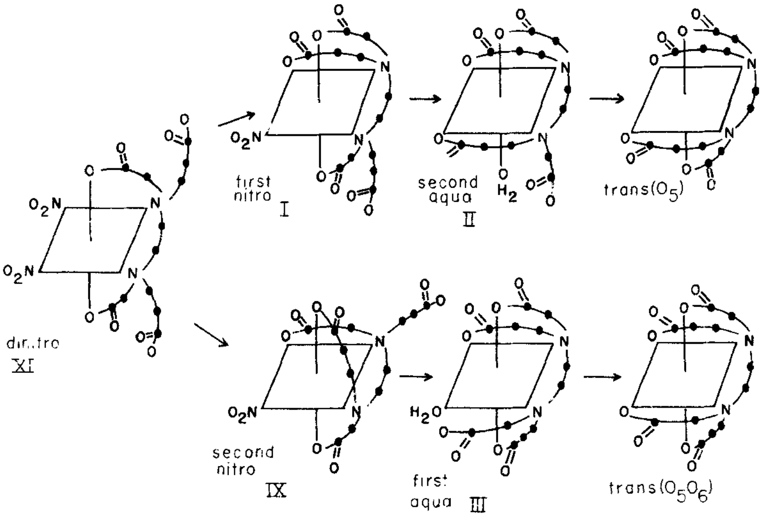

FIGURE 11 Suggested pathway of reactions of quadridentate to sexidentate Co(EDDDA)$^-$ species.

here. It should be emphasized that these are the best *tentative* assignments possible with the data at hand. Only the determination of crystal structures could give totally unambiguous results leading to definite conclusions as to geometry of chelation of these complexes.

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27. Owing to similarity in solubilities of these aqua complexes and of KNO_3, it was not possible to obtain the complexes free of contamination by KNO_3. Elemental analyses of both complexes yielded results which were high in nitrogen and low in carbon and hydrogen.

However, analyses of aqua complexes produced directly from resolved nitro complexes were much better, and will be discussed later in this section.

28. K^+ salts of the enantiomers tended to form tars upon sitting in air, although they would remain dry in a vacuum desiccator over conc. H_2SO_4.
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