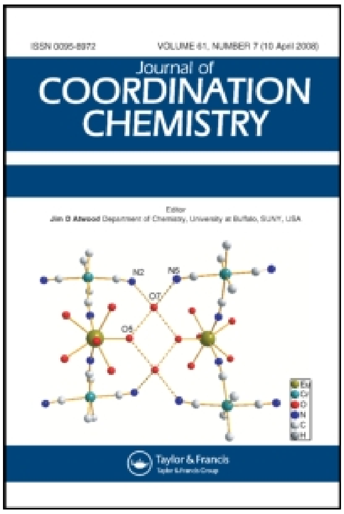

Journal of Coordination Chemistry

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

STEREOCHEMICAL STUDIES OF COBALT(III) COMPLEXES OF SEXIDENTATE AMINOPOLYACIDS USING CARBON-13 CHEMICAL SHIFTS

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To cite this Article Chang, C. A. and Douglas, B. E.(1979) 'STEREOCHEMICAL STUDIES OF COBALT(III) COMPLEXES OF SEXIDENTATE AMINOPOLYACIDS USING CARBON-13 CHEMICAL SHIFTS', Journal of Coordination Chemistry, 9: 2, 93 — 106

To link to this Article: DOI: 10.1080/00958977908076512

URL: http://dx.doi.org/10.1080/00958977908076512

J. Coord. Chem.
1979, Vol. 9, pp. 93–106

STEREOCHEMICAL STUDIES OF COBALT(III) COMPLEXES OF SEXIDENTATE AMINOPOLYACIDS USING CARBON-13 CHEMICAL SHIFTS

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(Received August 29, 1978)

Detailed assignments of the ^{13}C NMR spectra of two series of cobalt(III) complexes have been made with the aid of methyl substitution at the terminal carbon of the diamine backbone ring and other standard techniques. One series of complexes includes ligands ethylenediaminetetraacetate ion (edta), trimethylenediaminetetraacetate ion (1,3-pdta), and 1,3-butanediaminetetraacetate ion (1,3-mpdta). The other series of complexes includes the ligands triethylenetetraaminediacetate ion (ttda), 1,9-diamino-3,7-diazanonane-3,7-diacetate ion (ddda), and 1,9-diamino-4-methyl-3,7-diazanonane-3,7-diacetate ion (mddda). Spectral similarities reveal that these two types of complexes have similar bonding characteristics. Methyl substitution on the 6-membered backbone ring affects the overall complex structural parameters only slightly but the effects for a complex with a 5-membered backbone ring are obvious. The induced chemical shift changes for inductive (through-bond) and steric (through-space) perturbation of carbons caused by methyl substitution are consistent with those obtained for simple organic molecules. Comparison of carbon chemical shifts of complexes of 5-membered and 6-membered backbone ring reveals the strain effects and the results are explained partially in relation to those obtained by other spectroscopic methods. The strain effects are considered in reference to the chemical shift ranges of similar carbons in related complexes. A more strained environment makes the out-of-plane ring methylene carbon resonance more similar to that of the in-plane ring. The chemical shifts, in this case, seem to correlate with the C–N–C bond angles made between the methylene carbons of the side ring and of the backbone ring at the coordinated nitrogen.

KEY WORDS: Carbon-13 NMR spectra, sexidentate aminopoly acid complexes, cobalt(III) complexes, ethylenediaminetetraacetate ion, trimethylenediaminetetraacetate ion, 1,3-butanediaminetetraacetate ion, triethylenetetraaminediacetate ion, 1,9-diamino-3,7-diazanonane-3,7-diacetate ion, 1,9-diamino-4-methyl-3,7-diazanonane-3,7-diacetate ion.

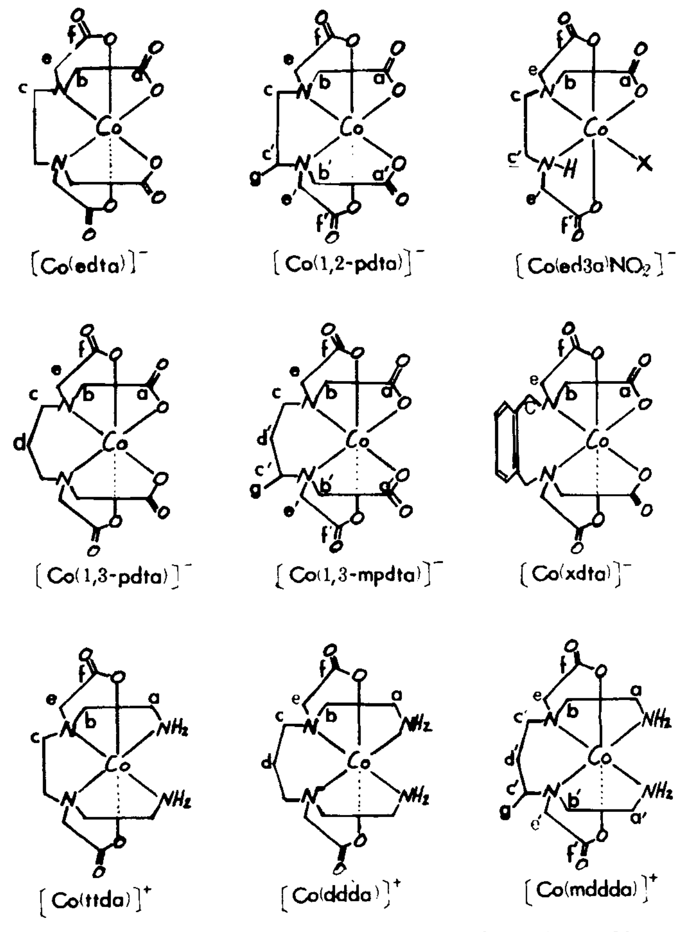
INTRODUCTION

The applications of ^{13}C nuclear magnetic resonance (NMR) to the study of inorganic stereochemistry have been exploited only recently.[1] The elucidation of structural parameters comes from spin-spin coupling constants, chemical shifts, as well as relaxation time measurements. For coordination compounds with organic ligands, the studies have been concentrated on diamagnetic complexes, particularly those of cobalt(III)[2-10] and platinum(II).[11,12] The most direct application of ^{13}C NMR to the study of cobalt(III) complexes is to distinguish one isomer from others.[2]

Blackmer and Vickery studied the kinetics of acid catalyzed deuteration reactions on [Co(edta)]$^-$, [Co(cydta)]$^-$, and [Co(1,2-pdta)]$^-$ using the ^{13}C NMR technique.[3] (edta = ethylenediaminetetraacetate ion, cydta = *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetate ion, 1,2-pdta = *d*,*l*-1,2-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetate ion.) The ^{13}C NMR spectra from these experiments show lower intensity peaks for deuterated carbons due to the loss of nuclear Overhauser effect (NOE), the increased relaxation time, and the lack of spin equilibrium prior to each new pulse. Deuteration was found to occur first for the less strained out-of-plane glycinate methylene protons, as verified also from proton magnetic resonance (PMR) data.[4] Using this technique together with standard ^{13}C NMR methods, Howarth,[5,6] *et al.* assigned most of the carbon peaks for $[M(edta)]^{n-}$ and $[M(cydta)]^{n-}$ where M = Co(III), Al(III), Pb(II), Zn(II), Hg(II), etc. Douglas, *et al.* also studied the stereochemistry of cobalt(III) complexes of trimethylenediamine-*N*,*N*′-diacetate ion (tmdda) and ethylenediamine-*N*,*N*′-diacetate ion (edda);[7] ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-dipropionate ion (eddda);[8] diethylenetriamine (dien) and iminodiacetate ion (ida);[9] ethylenediamine-*N*,*N*,*N*′-triacetate ion (ed3a) and related ligands.[10] However, there have been no detailed explanations of the chemical shifts of methylene carbons in different chemical environments.

Erickson, Sarneski, and Reilley[11] have obtained ^{13}C NMR spectra for a series of square-plane plantinum(II) chelates, Pt(bpy)(substituted 1,2-diaminoethane)$^{2+}$ where bpy = bipyridyl. The analysis of $^{195}Pt-^{13}C$ coupling constants, J_{Pt-C}, together with complementary J_{H-H} and J_{Pt-H} data offers information about the conformational properties of the gauche 1,2-diamine rings. The chemical shifts of the free amine ligands were reported to shift downfield upon platinum binding but no detailed analysis of the chemical shifts was given.

In order to obtain stereochemical information using ^{13}C chemical shifts, two series of cobalt(III) complexes of sexidentate aminopolyacetates have been synthesized and their ^{13}C NMR spectra measured and compared. These multidentate ligands are all of the ethylenediaminepolyacetate type with ligand donating atoms varying from N_2O_4 for edta to N_4O_2 for ttda (ttda = triethylenetetraamine-N^2, N^3-diacetate ion). In each series, the backbone diamine ring was varied from five to six members and additional complexes with a methyl group attached to a terminal backbone carbon were prepared to aid the spectral assignments and to be used as a source of detailed stereochemical information. Figure 1 shows the structures of the two series of cobalt(III) complexes of interest.

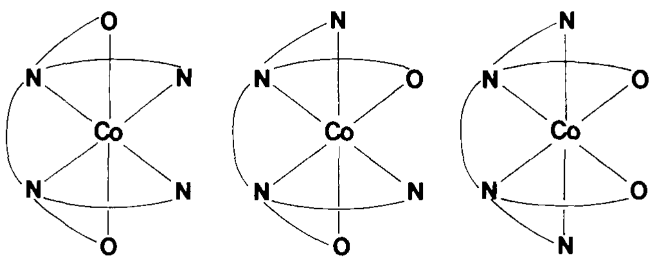


$[Co(edta)]^-$ $[Co(1,2\text{-}pdta)]^-$ $[Co(ed3a)NO_2]^-$

$[Co(1,3\text{-}pdta)]^-$ $[Co(1,3\text{-}mpdta)]^-$ $[Co(xdta)]^-$

$[Co(ttda)]^+$ $[Co(eddda)]^+$ $[Co(mddda)]^+$

FIGURE 1 Abbreviated structures and labels of complexes of interest.



trans(O) cis(O)cis(N) cis(O)trans(N)

FIGURE 2 Possible isomers of [Co(ttda)]$^+$.

The edta series includes edta, 1,2-pdta, 1,3-pdta (1,3-diaminopropane-*N,N,N′,N′*-tetraacetate ion), and 1,3-mpdta (*d,l*-1,3-diaminobutane-*N,N,N′,N′*-tetraacetate ion). The ttda series includes ttda, ddda (1,9-diamino-3,7-diazanonane-3,7-diacetate ion) and mddda (1,9-diamino-4-methyl-3,7-diazanonane-3,7-diacetate ion). Only one isomer is possible for each of the cobalt(III) complexes of ligands in the edta series. The cobalt(III) complexes of ligands in the ttda series can have three isomers: *trans(O)*, C_1-*cis(O)cis(N)*, and C_2-*cis(O)trans(N)* (Figure 2), but only the *trans(O)*-isomers were isolated. The *trans(O)*-[Co(ttda)]$^+$ is a structural analogue of [Co(edta)]$^-$ in that both complexes have five five-membered chelate rings and only a C_2 axis of symmetry. Among the five rings, three are the same, i.e., the backbone ethylenediamine E ring and the two out-of-plane glycinate R rings, but the two in-plane side rings are different. For [Co(edta)]$^-$ there are two strained in-plane glycinate G rings as reported by an x-ray structural analysis[13] while *trans(O)*-[Co(ttda)]$^+$ has two in-plane ethylenediamine side rings. Similarly, *trans(O)*-[Co(ddda)]$^+$ is related to [Co(1,3-pdta)]$^+$ in having one six-membered backbone T ring and four five-membered rings; *trans(O)*-[Co(mddda)]$^+$ is related to [Co(1,3-mpdta)]$^-$ in having a methyl group attached to a terminal carbon of the six-membered backbone ring. No complex in the ttda series related to [Co(1,2-pdta)]$^-$ has been isolated since the attempted preparation of 1,8-diamino-4-methyl-3,6-diazaoctane-3,6-diacetic acid (H_2mttda) was unsuccessful.[14]

These compelxes are chosen for study not only for the understanding of basic inorganic stereochemistry but also for the applications in the rapidly developing bioinorganic field because they serve as possible simple structural models of the active sites of metalloproteins.[15]

These complexes offer the advantage of being characterized by absorption spectra, circular dichroism (CD) spectra, proton magnetic resonance (PMR) spectra, and x-ray diffraction studies.[4,13,16–21] In this paper we report the detailed assignments of the ^{13}C NMR spectra of these cobalt(III) complexes and stereochemical studies using ^{13}C chemical shifts.

EXPERIMENTAL PROCEDURE

Preparation of Materials

Metal salts were purchased from the J. T. Baker Chemical Co. The starting materials for the synthesis of the ligands were obtained from Aldrich Chemical Co. Elemental analyses were performed by Integral Microanalytical Laboratories Inc., Raleigh, NC and Calgon Analytical Laboratories, Pittsburgh, PA. The complexes K[Co(edta)] · H_2O,[20] K[Co(1,2-pdta)] · H_2O,[20] Na[Co(1,3-pdta)] ·$3H_2O$,[16] [Co(ttda)] I,[18] and [Co(ddda)] I[19] were prepared according to published methods.

Preparation of 1,3-butanediaminetetraacetic acid, H_4(1,3-mpdta), and silver (1,3-butanediaminetetracetato)cobaltate(III), Ag[Co(1,3-mpdta)] The ligand 1,3-butanediaminetetraacetic acid was prepared according to the method similar to that for H_4xdta.[22] (H_4xdta = α,α'-diamino-*o*-xylene-*N,N,N′,N′*-tetracetic acid). Racemic 1,3-dibromobutane was treated with double the amount of dimethyliminodiacetate ion followed by hydrolysis of the ester to yield the free acid solution. The dimethyliminodiacetate was prepared using a modification of a process outlined in a U.S. Patent[23] or by reacting thionyl chloride with iminodiacetic acid suspended in absolute methanol. The free ligand was used directly in the solution. To the free ligand acid was added an equimolar amount of $CoCl_2 \cdot 6H_2O$ and the pH was adjusted to eight by adding 4 M NaOH solution. The resulting solution was heated to boiling for 30 min, 0.5 g of activated charcoal was added and the mixture was air oxidized for 24 hr. After filtering the charcoal, the solution was rotary evaporated to remove inorganic salts. The final product was recrystallized from hot ethanol-water (1:1) solution to obtain the complex as the sodium salt. The Na[Co(1,3-mpdta)] was dissolved in a minimum amount of hot water and excess $AgNO_3$ was added slowly with stirring. On cooling, the crude complex as the silver salt was precipitated. The precipitate was recrystallized twice from ethanol-water and heated in boiling absolute ethanol to remove the last traces of $AgNO_3$. The purple product was collected by filtration and dried in a vacuum desiccator over anhydrous $CaCl_2$.

Preparation of 1,9-diamino-4-methyl-3,7-diazanonane-3,7-diacetic acid, H_2mddda, and its trans*(O)-cobalt-(III) complex, [Co(mddda)]I* The ligand H_2mddda, was prepared in aqueous solution without isolating the solid product. Racemic 1,3-dibromobutane was used to bind two molecules of piperazinone.[14] Ten grams (4.16×10^{-2} mole) of the condensation product was refluxed in 80 mL of 6 M HCl for 5 hr. The solution was rotary evaporated to dryness and then dissolved in deionized water to give a volume of about 200 mL. To this solution was added a solution of 12 g (5.04×10^{-2} mole) $CoCl_2 \cdot 6H_2O$ in 50 mL of deionized water and the pH of the mixture was adjusted with 4 M NaOH solution to about eight. Activated charcoal (0.5 g) was added and the mixture was air oxidized for 12 hr. The solution was filtered to remove the charcoal and the filtrate was rotary evaporated to about 30 mL and cooled. The inorganic salt was then filtered and the filtrate was pipeted into a column with Dowex 50W-1X cation exchange resin in the Na^+ form (100–200 mesh). The complex was eluted with 0.1 M NaCl solution and the eluent was concentrated and filtered to remove excess NaCl. The product, [Co(mddda)]Cl, was isolated by several recrystallizations from hot methanol-water (1:1) mixture. The chloride salt was dissolved in a minimum amount of hot water and a saturated solution of NaI was added dropwise with stirring. On cooling, the iodide salt crystallized and it was recrystallized twice from water at 70°. The total yield was about 5 g. *Anal.* Calcd. for $[Co(C_{12}H_{24}N_4O_4)]I$: C, 30.40; H, 5.10; N, 11.81. Found: C, 30.37; H, 5.28; N, 11.75.

Acid Catalyzed Deuterium Exchange Experiments of Cobalt(III) Aminopolyacetates Complexes

The procedure for the deuterium exchange experiments was as follows: to a 3 mL D_2O solution containing 0.2–0.5 g of complex was added 5 drops of 98% D_2SO_4 solution. The mixture was refluxed in an oil bath at *ca.* 80° for 30 min or longer. The refluxing apparatus was equipped with a 10 mL flask fitted with a microcondenser to prevent the loss of D_2O.

Physical Measurements

The visible absorption spectra were recorded using either a Cary Model 118 C or Cary 14 spectrophotometer at room temperature.

The PMR spectra were obtained with a Varian HA-100 NMR spectrometer and the 250 MHz NMR spectrometer at Carnegie-Mellon University. Deuterium oxide was used as a solvent with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (NaDSS) as an internal reference.

The ^{13}C NMR spectra were recorded on a Jeol, Inc., JNM FX-60 Fourier transform ^{13}C-^{1}H high performance NMR spectrometer, operating at 15.0 MHz in the ^{13}C mode. The field frequency ratio was stabilized by locking to D_2O. Spectra were obtained from samples contained in 8–10 mm coaxial tubes manufactured by Wilmad Spectroscopic Supplies, Inc. Benzene (δ = 128.70 ppm downfield from TMS) was used as external standard in an outer coaxial tube arrangement. The instrument was used in all four modes: broad-band random-noise ^{1}H decoupling mode, ^{1}H off-resonance decoupling mode, ^{1}H selective decoupling mode, and ^{1}H coupled mode. The spectra were recorded using spectral widths of 1, 2.5, or 4 KHz, covered by 4096 addresses in the Fourier transform spectra. The pulse repetition times range from 0.8–3.0 seconds with delay times of 166–400 μ-seconds.

The same Jeol JNM FX-60 spectrometer was also used in the ^{1}H mode at 59.75 MHz to facilitate using the correct proton frequencies for ^{1}H selective decoupling experiments.

RESULTS AND DISCUSSION

^{13}C NMR Spectral Assignments

In all of these cobalt(III) complexes, no ^{59}Co-^{13}C couplings are observed and the spectra are much simpler than those with couplings. Thus the loss of metal ion-carbon coupling information could be an advantage for chemical shift studies of more complicated systems. The approach of the present study is an empirical one which involves the comparison of ^{13}C NMR spectra of several complexes with structural similarity since at present, generalized theoretical treatments of ^{13}C chemical shifts have not been particularly successful except within restricted series of compounds.[24] Also, the trends of the chemical shifts observed in many systems are not yet understood quantitatively.

Besides methyl substitution on the backbone ring as an aid for spectral assignments, the ^{13}C–^{1}H splitting pattern is another guide for assigning methyl, methylene, methine, and quarternary carbon resonances. This splitting pattern can be obtained from ^{1}H off-resonance decoupled spectra or ^{1}H coupled spectra. No effort was made to utilize the J_{C-H} coupling constants for methylene and methine carbon assignments since the coupling constants fall into the range of 140–145 Hz and their measurements take more time and are usually complicated by secondary or other long range couplings. In some cases, the assignments can be made with the aid of the selective decoupling technique if part of the PMR spectrum can be assigned unambiguously. A particular carbon is often assigned in this manner. Acid catalyzed deuteration of out-of-plane glycinate methylene carbons was also used for spectral assignments.

For all complexes of interest, only the structures of $[Co(edta)]^-$ and $[Co(1{,}3\text{-}pdta)]^-$ have been determined by x-ray cyrstallographic methods.[13,21] The structures of the other complexes are known from studies of visible spectra, CD spectra, and PMR spectra measured in aqueous solution. For an octahedral complex of a sexidentate ligand containing only a C_2 axis, five chelate rings are formed. The in-plane and out-of-plane rings are called G and R rings, respectively. The backbone ring is an E ring if it is a 5-membered ring, and a T ring if it is a 6-membered ring. The G ring terminal carbon is designated the *a* carbon and its methylene carbon α to the coordinated nitrogen of the backbone is the *b* carbon. Each terminal carbon of the E or T ring is designated the *c* carbon and the central methylene carbon of a T ring is the *d* carbon. The R ring terminal carbon is designated the *f* carbon and its methylene carbon α to the coordinated backbone nitrogen is the *e* carbon. If the C_2 axis is destroyed by adding a methyl group on a terminal backbone carbon, the labels for the carbons of the half away from the perturbation are the same as defined above but a prime is added to the

TABLE I

^{13}C Chemical shift data of complexes of interest[a]

Compound	Designation												
	a	a′	b	b′	c	c′	d	d′	e	e′	f	f′	g
$[Co(edta)]^-$	182.4		65.77		64.00				66.00		183.0		
$[Co(1{,}2\text{-}pdta)]^-$[b]	183.0	183.0	67.0	66.0	69.7	69.7			68.0	59.0	183.7	183.7	12.0
$[Co(ed3a)NO_2]^-$	182.62		66.48		61.12	56.09			65.18	57.22	184.09	186.09	
$[Co(1{,}3\text{-}pdta)]^-$	181.84		70.35		52.03		21.49		63.21		183.66		
$[Co(1{,}3\text{-}mpdta)]^-$	181.83	181.44	69.89	68.33	52.96	57.66		29.68	62.85	58.05	183.20	183.20	14.70
$[Co(xdta)]^-$[c]	180.32		64.58		60.20				65.39		181.62		
$[Co(ttda)]^+$	46.15		64.38		59.28				62.91		184.59		
$[Co(ddda)]^+$	41.05		65.56		53.22		23.20		58.79		184.68		
$[Co(mddda)]^+$	40.44	40.44	65.47	63.21	53.11	57.52		32.13	58.89	54.58	184.78	184.59	15.26

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

[b] Data are taken from Ref. 3.

[c] Additional peaks at 130.48, 131.78, and 133.57 ppm.

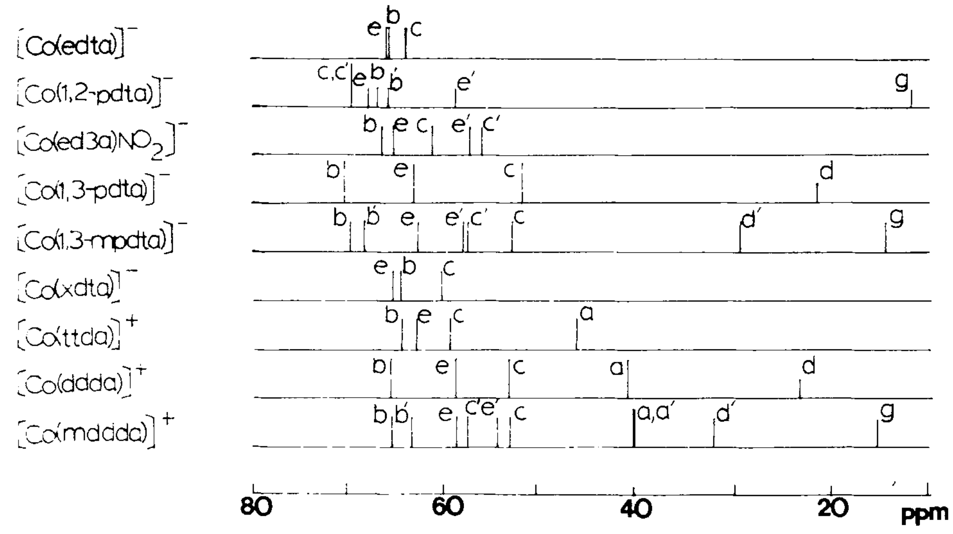


FIGURE 3 Stick diagram of ^{13}C NMR spectra in the methylene region.

labels for the carbons of the half near the pertubation (Figure 1). The ^{13}C chemical shift data and the stick diagram of ^{13}C NMR spectra in the methylene region are shown in Table I and Figure 3.

[Co(ttda)]$^+$ series The 100 MHz PMR spectrum shows an unresolvable enthylenediamine ring proton multiplet and a singlet for the out-of-plane glycinate methylene protons. The detailed assignments of the PMR sepctrum cannot be made even with the aid of a 250 MHz PMR spectrum, except for the AB quartet of the out-of-plane ring protons, with coupling constant 18.87 Hz. The noise-band decoupled ^{13}C NMR spectrum of [Co(ttda)]$^+$ simply shows four peaks in the methylene region and one peak in the carbonyl region, as expected for C_2 symmetry (Figure 4). The upfield methylene carbon peak at 46.15 ppm is assigned to the terminal carbons of the side ethylenediamine rings based on typical substitutent effects of protons on the neighboring nitrogen. Acid catalyzed deuterium exchange caused the third peak at 62.91 ppm from upfield to lose spectral intensity due to the loss of nuclear Overhouser effect. The peak is assigned to the out-of-plane glycinate methylene *e* carbon resonance. The remaining two peaks are assigned tentatively to the ethylenediamine backbone *c* carbon (59.28 ppm) and the other in-plane ring terminal *b* carbon (64.38 ppm) resonances. The downfield peak at 184.59 ppm is the out-of-plane carbonyl carbon resonance.

The ligand ddda^{2-}, has the N_4O_2 coordination chromophore but with a trimethylenediamine backbone ring. The complex [Co(ddda)]$^+$ has a *trans*(*O*)-configuration as seen from the similarity of the visible spectrum with that of [Co(ttda)]$^+$. The 100 MHz PMR spectrum shows a AB quartet corresponding to the out-of-plane R ring protons and a messy splitting in the region 2.5–3.1 ppm. The 250 MHz PMR spectrum did not improve the situation greatly except the AB quartet coupling constant was determined by computer to be 19.15 Hz.

The ^{13}C NMR spectrum of [Co(ddda)]$^+$ shows a carbonyl peak (*f* carbon) at 184.68 ppm and five peaks in the methylene region (Figure 5). The five peaks in the methylene region are easily assigned. The C_2 axis of [Co(ddda)]$^+$ requires pairs of equivalent carbons except of the central *d* methylene carbon of the backbone, so the peak of low intensity (23.20 ppm) is assigned to this carbon. The peak at 41.05 ppm is assigned to the pair of terminal *a* carbon resonances of the side ethylenediamine ring and the peak at 58.79 ppm is assigned to the glycinate methylene *e* carbon resonance since upon deuteration, this peak loses intensity. The other two peaks are assigned to the trimethylenediamine side *c* carbon (53.22 ppm) and the other ethylenediamine side *b* carbon (65.56 ppm).

The methyl group at a terminal carbon of the trimethylenediamine backbone of [Co(mddda)]$^+$ does not change the preference for a *trans*(*O*)-configuration, but it seems to lower the effective symmetry as evidenced by the higher molar absorptivities of the visible absorption peak maxima compared to those of [Co(ddda)]$^+$. The 100 MHz PMR spectrum is

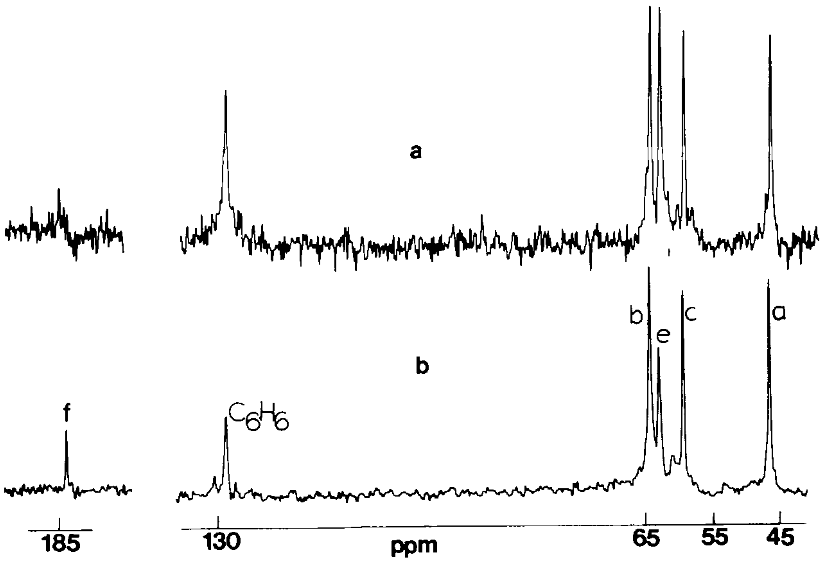


FIGURE 4 ^{13}C NMR spectra of [Co(ttda)]$^+$.

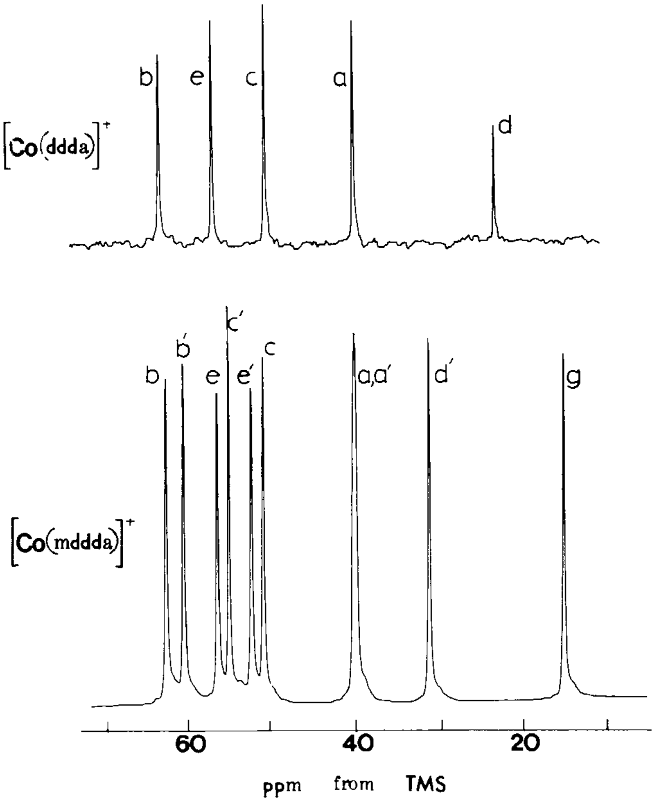


FIGURE 5 ^{13}C NMR spectra of [Co(ddda)]$^+$ and [Co(mddda)]$^+$ in the methylene region.

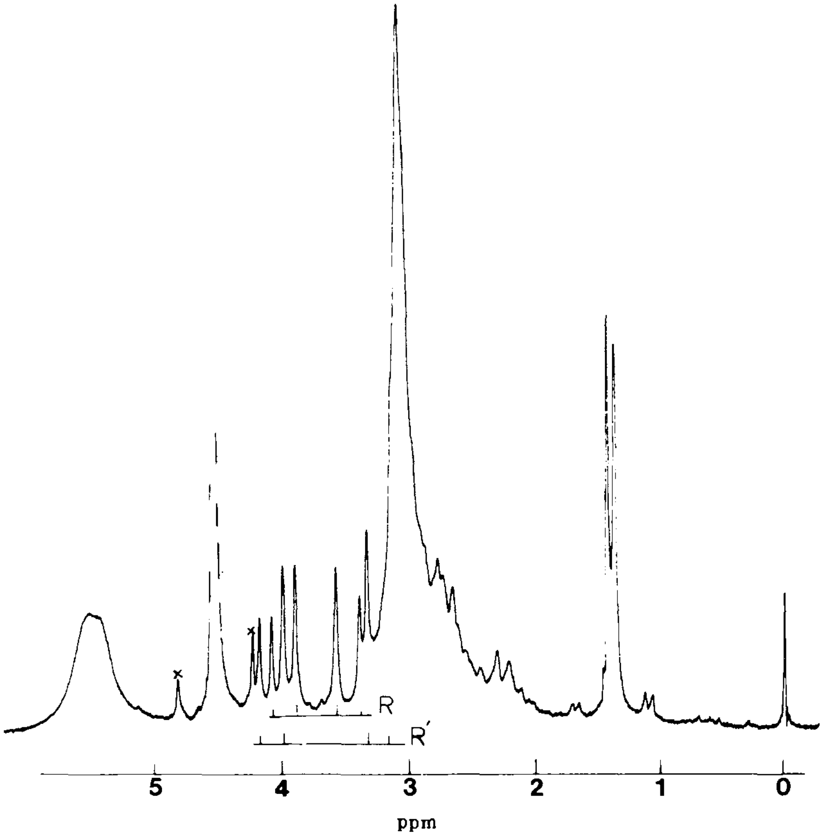


FIGURE 6 100 MHz PMR spectrum of [Co(mddda)]$^+$.

shown in Figure 6. The 250 MHz PMR spectrum shows two AB quartets with the same coupling constants (19.17 Hz) and a methyl doublet split by the methine proton (coupling constant 6.16 Hz). Table II shows the visible absorption data and the assignments of the AB quartets of the PMR spectra of [Co(ttda)]$^+$, [Co(ddda)]$^+$, and [Co(mddda)]$^+$.

In the ^{13}C NMR spectrum of [Co(mddda)]$^+$, in addition to two peaks in the carbonyl region, ten peaks in the chemical shift range 10–70 ppm are observed (Figure 5). The spectrum is as expected since upon methyl substitution at the backbone, the C_2 axis is destroyed. Among the ten peaks observed in the upfield region, two overlap forming a broad peak at 40.44 ppm. It is assigned to the two terminal ethylenic carbon resonance since these carbons are farthest from the methyl substituent. The peak at 15.26 ppm is assigned to the methyl carbon since it splits into a quartet in the off-resonance decoupled spectrum. The peak at 57.52 ppm, which becomes a doublet in the off-resonance decoupled spectrum, is assigned to the methine peak. The peak at 32.13 ppm is assigned to the central methylene carbon of the trimethylenediamine backbone ring. Of the remaining peaks, three appear at almost the same frequencies as the corresponding peaks for [Co(ddda)]$^+$, so they are assigned to carbons remote from the methyl group: The ethylenic *b* carbon (65.47 ppm), out-of-plane glycinate *e* carbon (58.89 ppm) and the trimethylenediamine ring terminal *c* carbon (53.11 ppm). The peak at 54.58 ppm is assigned to the out-of-plane glycinate *e*′ carbon near the methyl group since upon deuterium exchange, both peaks at 58.89 ppm and 54.58 ppm lose intensity. The rates of deuterium exchange for the two out-of-plane glycinate ring protons are similar. Finally the remaining peak at 63.21 ppm is assigned to the last unassigned ethylenic *b*′ carbon near the methyl group. These assignments

TABLE II
Visible absorption data and assignments of the PMR AB quartets of [Co(ttda)]$^+$, [Co(ddda)]$^+$, and [Co(mddda)]$^+$

Compound	Absorption		PMR of the AB quartet (ppm)^b	
	kK	ϵ	R	R′
[Co(ttda)]I^a	18.83 22.0 27.89	161 sh 183	3.94, 4.01, 4.05, 4.13 (average = 4.03)	
[Co(ddda)]I^a	18.66 21.88 27.62	99 sh 119	3.48, 3.56, 4.02, 4.10 (average = 3.79)	
[Co(mddda)]I	18.57 21.80 27.43	121 sh 138	3.50, 3.58, 3.99, 4.07 (average = 3.79)	3.25, 3.32, 4.09, 4.16 (average = 3.71)

^{a}Data are taken partially from Ref. 13.
^{b}Positive sign indicates a downfield shift from NaDSS.

were double checked by a series of selective decoupling experiments.

[Co(edta)]$^-$ series Different ^{13}C assignments in the methylene region of [Co(edta)]$^-$ have been made by two research groups.[3,5] Blackmer and Vickery observed two methylene carbon peaks at 62.5 and 65.5 ppm in the ^{13}C NMR spectrum of [Co(edta)]$^-$ under low resolution. The peak at 65.5 ppm was assigned to overlapping out-of-plane glycinate methylene *e* carbons and ethylenic *c* carbons of the backbone due to its higher intensity. Howarth *et al.* observed three peaks at 64, 65.8, and 66 ppm with equal intensities. In contrast to the previous assignments made by Blackmer and Vickery, Howarth *et al.* assigned the peak at 64 ppm to the backbone *c* carbons and the other two at 65.8 and 66 ppm to the in-plane (*b*) and out-of-plane (*e*) glycinate methylene carbons, respectively. Clarification of the assignments was needed for the present study, since other work is heavily dependent of the ^{13}C NMR spectral assignment of [Co(edta)]$^-$. The work was repeated. The spectrum measured at a spectral width of 4 KHz shows two peaks in the methylene region with the one at lower field being twice as intense as the other. At a spectral width of 2.5 KHz, a shoulder is observed near the more intense peak. The three peaks are well resolved in the spectrum at a spectral width of 1 KHz. Figure 7 shows the effect of the spectral width on the spectra in the methylene region of [Co(edta)]$^-$. The assignments of the spectra are based on the selective decoupling and acid catalyzed deuteration experiments. Assignments for the PMR spectrum of [Co(edta)]$^-$ are known.[4,20] The R and G ring methylene protons show two AB quartets centered at 3.90 ppm and 3.74 ppm downfield from TMS, respectively. The E ring proton pattern is centered upfield from the two quartets. The ^{13}C NMR spectrum obtained by selectively irradiating at about 3.90 ppm in the proton region shows that the lower field peak (66.00 ppm) retains its intensity in comparison to the other two. At a decoupling frequency in the range of 3.70 ppm, the peak at 65.77 ppm was singled out. The peak at 64.00 ppm was more intense at a higher decoupling frequency. Thus the peaks at 66.00 ppm, 65.77 ppm, and 64.00 ppm are assigned to the *e*, *b*, and *c* carbon resonances, respectively. The assignment of the *e* carbon is supported further by acid catalyzed deuteration. The peak at 66.00 ppm loses intensity after deuterium exchange as expected for the less strained, out-of-plane glycinate ring protons. The *a* and *f* carbon resonances are assigned to the peaks at 182.4 ppm and 183 ppm, respectively.

In the ^{13}C NMR spectrum of [Co(1,3-pdta)]$^-$, in addition to two carbonyl peaks corresponding to pairs of out-of-plane and in-plane glycinate carbonyl carbons, four methylene peaks are observed with the one at highest field being half as intense as the other three peaks. This peak at 21.49 ppm with low spectral intensity is assigned confidently to the central methylene *d* carbon of the trimethylenediamine ring. The peak at 63.21 ppm is assigned to the out-of-plane glycinate methylene *e* carbon resonance since after acid catalyzed deuterium exchange this peak loses its spectral intensity. The peaks at 70.35

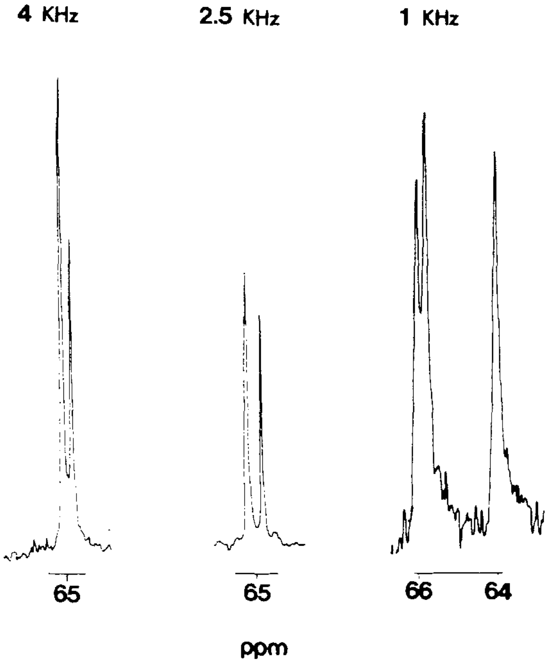


FIGURE 7 Effect of the spectral width on the ^{13}C NMR spectra in the methylene region of $[Co(edta)]^-$.

ppm and 52.03 ppm are assigned to the in-plane glycinate methylene *b* carbon and trimethylenediamine backbone terminal *c* carbon, respectively, based on selectively decoupled spectra. The 60 MHz PMR spectrum was measured and assigned previously.[17]

With the substitution of a hydrogen by a methyl group at a terminal backbone carbon, the C_2 axis of $[Co(1,3\text{-pdta})]^-$ is destroyed leaving all the carbons of $[Co(1,3\text{-mpdta})]^-$ nonequivalent. In the ^{13}C NMR spectrum of $[Co(1,3\text{-mpdta})]^-$, eight peaks are observed in the region of 10–70 ppm indicating the nonequivalence of all carbons. The peaks at 14.70 ppm and 57.66 ppm are assigned to the *C*-methyl and the methine carbon resonances, respectively, due to the corresponding quartet and doublet splittings in the off-resonance decoupled spectrum. The peak at 29.68 ppm is assigned to the central methylene *d′* carbon of the trimethylenediamine backbone ring owing to the upfield chemical shift. Three of the remaining peaks (68.89, 62.85, and 52.96 ppm) appear approximately at the same freqeuncies as for $[Co(1,3\text{-pdta})]^-$. These peaks are assigned to the in-plane glycinate methylene *b* carbon, out-of-plane glycinate methylene *c* carbon, and the backbone T ring terminal *c* carbon, respectively, all carbons in the half of the complex away from the methyl substituent. Finally, the peak at 58.05 ppm is assigned to the other out-of-plane R′ ring *e′* carbon near the methyl group since the peaks at 62.85 ppm and 58.05 ppm lose their spectral intensities after deuteration. Because of the peak at 62.85 ppm has been assigned to the *e* carbon, the peak at 58.05 ppm has to be the *e′* carbon. The remaining peak at 68.33 ppm is then assigned to the *b′* carbon, the in-plane glycinate methylene carbon near the methyl group. The assignments of the carbonyl peaks are not certain. Tentatively, by comparison with the spectrum of $[Co(1,3\text{-pdta})]^-$, the peak at 183.20 ppm with higher intensity is assigned to the two overlapping out-of-plane carbonyl carbon resonances.

The rate of deuterium exchange for both out-of-plane glycinate ring protons has been examined roughly and there is no distinct difference between the ring protons with or without methyl perturbation.

Methyl Substituent Effects

The ^{13}C NMR spectra of both $[Co(ddda)]^+$-$[Co(mddda)]^+$ and $[Co(1,3\text{-pdta})]^-$-$[Co(1,3\text{-mpdta})]^-$ pairs give information about the methyl substituent effects on complexes with 6-membered backbone rings. The fact that three of the carbon resonances (*b*, *c*, and *e*) of $[Co(mddda)]^+$ are within 0.1 ppm of the corresponding ones of $[Co(ddda)]^+$ indicates that the half of the $[Co(mddda)]^+$ complex away from the methyl group remains unperturbed. This fact would imply also that *trans*(*O*)-$[Co(ddda)]^+$ adopts a very stable configuration and its ring conformations are rather fixed since in the ^{13}C NMR spectrum of $[Co(mddda)]^+$ only the carbon resonances of the half of the complex close to the methyl group are affected. The reason for the shifts of the carbon resonances under methyl perturbation can be rationalized readily by considering the model studies of Grant and his coworkers.[25] They studied the methyl substituent effects of the carbon chemical shifts of a series of methylcyclohexanes. If the methyl substituent is in an equatorial position, the α, β, γ, and δ carbon resonances all shift downfield relative to the carbon resonance of the pure cyclohexane (Table III).

The average α and β carbon equatorial substituent shift values are about 5.6 ppm and 8.9 ppm, respectively. The γ and δ carbon equatorial substituent shift values are the same within 0.3 ppm. These shifts are mainly a result of the substituent through-bond inductive effect. The downfield shifts of 4.41 ppm of the methine carbon and the 9.93 ppm of the central trimethylenediamine carbon of $[Co(mddda)]^+$

TABLE III
Methyl substituent parameters for substituted cyclohexanes[a]

Substituent	Parameter (ppm)			
	α	β	γ	δ
Equatorial-CH_3	+5.6 ± 0.2	+8.9 ± 0.1	0.0 ± 0.6	−0.3 ± 0.3
Axial-CH_3	+1.1 ± 0.4	+5.2 ± 0.3	−5.4 ± 0.2	−0.1 ± 0.3

[a] Positive sign indicates a downfield shift. Ref. 25.

relative to those of $[Co(ddda)]^+$ are due to the equatorial α and β substituent effects, respectively, since it is reasonable to assume that the methyl group prefers to be at the equatorial position in the trimethylenediamine backbone ring based on the conformational energy argument. On the other hand, in Grant's study, if the methyl group is in an axial position, both of the through-bond α and β substituent effects become smaller and a strong γ effect is observed. This γ effect causes the carbon γ to the substituent to be shifted upfield because of a 1,4 steric, through-space interaction. In terms of this model, the upfield shifts of 2.66 ppm of the ethylenic b' carbon and of 4.30 ppm of the out-of-plane glycinate methylene e' carbon of $[Co(mddda)]^+$ relative to the corresponding carbons in the unperturbed half are understood, since both carbons of interest are γ to the methyl group. Framework Molecular Model studies confirm the presence of these steric interactions.

In order to make correlations between the complex ^{13}C chemical shifts of ligands with different donor atoms, the spectra of both $[Co(1,3\text{-pdta})]^-$ and $[Co(1,3\text{-mpdta})]^-$ were measured. $[Co(1,3\text{-pdta})]^-$ has a structure similar to that of $[Co(ddda)]^+$ but with two glycinate in-plane side rings while $[Co(1,3\text{-mptda})]^-$ differs from $[Co(1,3\text{-pdta})]^-$ only in having one methyl group at the terminal backbone carbon. The ^{13}C NMR spectra of this pair of complexes are helpful for structural comparison to the $[Co(ddda)]^+$-$[Co(mddda)]^+$ pair. One obvious change in the ^{13}C NMR spectra of the $[Co(1,3\text{-pdta})]^-$ and $[Co(1,3\text{-mpdta})]^-$ pair compared to those of $[Co(ddda)]^+$ and $[Co(mddda)]^+$ is the addition of carbonyl peaks. The methine and the central methylene carbon resonance of the T ring of $[Co(1,3\text{-mpdta})]^-$ shift downfield relative to those of $[Co(1,3\text{-pdta})]^-$ by 4.70 ppm and 8.19 ppm, respectively, as the result of the equatorial α and β substituent effects. The upfield shifts of 1.56 ppm and 4.80 ppm of G′ ring (b') and R′ ring (e') methylene carbon resonances arc the result of the axial γ substituent effects.

Among the eight carbon peaks in the high field region of the ^{13}C NMR spectrum of $[Co(1,3\text{-mpdta})]^-$, three of them (b, c, and e carbon resonances) appear at frequencies similar to the corresponding ones in the ^{13}C NMR spectrum of $[Co(1,3\text{-pdta})]^-$. However, the sum of the absolute values of chemical shift difference of these three pairs of carbon resonances is 1.75 ppm, which is comparatively larger than the sum value, 0.29 ppm, obtained for the $[Co(ddda)]^+$ and $[Co(mddda)]^+$ pair. This result probably indicates that the structural distortion introduced by substituting a methyl group at the terminal backbone carbon is relatively more severe for $[Co(1,3\text{-pdta})]^-$ than for $[Co(ddda)]^+$. The shift values of the carbon resonances caused by equatorial α and β substituent effects in $[Co(1,3\text{-mpdta})]^-$ and $[Co(mddda)]^+$ are slightly different. The reasons for the differences probably are related to the difference in the ring conformation, the variations of the Co–N bond length, and variations of some of the bond angles at the backbone amine atoms. The shift values which result from the γ effect of $[Co(1,3\text{-mpdta})]^-$ and $[Co(mddda)]^+$ are also different. The chemical shift difference 4.70 ppm for the two out-of-plane glycinate methylene carbons (e and e' carbons) of $[Co(1,3\text{-mpdta})]^-$ is larger than the (4.30 ppm) of $[Co(mddda)]^+$, indicating that the corresponding steric interaction is a little stronger for $[Co(1,3\text{-mpdta})]^-$ than for $[Co(mddda)]^+$. Similarly, the steric interaction between the backbone methyl group and the in-plane b' carbon is a little stronger for $[Co(mddda)]^+$ than for $[Co(1,3\text{-mpdta})]^-$.

Comparison of the ^{13}C NMR spectra of $[Co(edta)]^-$ and $[Co(1,2\text{-pdta})]^-$ provides an evaluation of the methyl substituent effects for complexes of sexidentate ligands with a 5-membered backbone ring. The ^{13}C NMR spectrum of $[Co(1,2\text{-pdta})]^-$ looks very different from that of $[Co(edta)]^-$. The axial γ effect causes the two in-plane b and b' carbon resonances and the two out-of-plane *e* and *e'* carbon resonances of $[Co(1,2\text{-pdta})]^-$ to be separated by 1 ppm and 9 ppm, respectively, indicating much greater steric interaction between the methyl group and the out-of-plane *e'* carbon. The equatorial α and β substituent effects make the two backbone ethylenic carbon resonances overlap with each other accidentally. All of these results indicate a great structural change for $[Co(1,2\text{-pdta})]^-$ compared to $[Co(edta)]^-$

The origin of the large structural distortion of $[Co(1,2\text{-pdta})]^-$ possibly arises from the fact that the strained $[Co(edta)]^-$ complex is sterically crowded at the "hydrophobic face". (The complex $[Co(edta)]^-$ has two faces that are hydrophobic, being mostly methylene hydrocarbons, and the opposite faces are hydrophilic because the carbonyl oxygens can be solvated easily by water.) With the addition of a methyl group in the backbone, severe steric interactions occur for $[Co(1,2\text{-pdta})]^-$, causing distortion. The situation is not seen for complexes with six-membered backbone rings since the hydrophobic faces are not sterically crowded. These comparisons are supported by rates of acid deuteration. The rate of deuterium exchange for the hydrogen of the sterically perturbed *e'* carbon is faster then for the one of the unperturbed *e* carbon for $[Co(1,2\text{-pdta})]^-$ However, the rates for deuterium exchange for the out-of-plane protons of $[Co(mddda)]^+$ and $[Co(1,3\text{-pdta})]^-$ are almost the same regardless of the presence of steric perturbation.

The Strain Effect

The term "strain effects" shall be used to describe the problem concerning the overall strain of the complex structure. The change of configurational and conformational strain of a complex by enlarging the 5-membered backbone ring with the insertion of the methylene group to result in a 6-membered backbone ring is revealed by the change of ^{13}C chemical shifts of two pairs of complexes: $[Co(edta)]^-$-$[Co(1,3\text{-pdta})]^-$ and $[Co(ttda)]^+$-$[Co(ddda)]^+$.

Van Saun and Douglas[16] studied the visible absorption spectra of both $[Co(edta)]^-$ and $[Co(1,3\text{-pdta})]^-$. The $[Co(1,3\text{-pdta})]^-$ is believed to have less overall ring strain than $[Co(edta)]^-$ due to the release of the fused ring strain by the flexible six-membered backbone ring. This is supported by the low molar absorptivities of $[Co(1,3\text{-pdta})]^-$ for both visible absorption band maxima. Similar results have been observed for $[Co(ttda)]^+$ and $[Co(ddda)]^+$ by Granchi and Douglas.[19] If one compares the ^{13}C NMR spectra of $[Co(edta)]^-$ and $[Co(1,3\text{-pdta})]^-$, one can find that the separation between the in-plane and the out-of-plane glycinate methylene carbon resonances of $[Co(edta)]^-$ (0.2 ppm) is less than that of $[Co(1,3\text{-pdta})]^-$ (7.14 ppm) which could be the direct result of the strain effects. A similar observation is seen also for $[Co(ttda)]^+$ (1.47 ppm) and $[Co(ddda)]^+$ (6.77 ppm) for the corresponding carbon resonance separations. Therefore, the strain effects can be considered in reference to the chemical shift separations of similar carbon resonances in related complexes. In the case of $[Co(edta)]^-$ and $[Co(1,3\text{-pdta})]^-$, a more strained environment makes the out-of-plane ring methylene carbon resonance more similar to that of the in-plane ring.

The reason why the backbone carbon resonances cannot be used for the present purpose is that the terminal carbon resonance of the six-membered backbone ring is strongly affected by the central methylene group through the inductive effect. Hence it is difficult to make comparisons between the five-membered E ring carbon resonance and six-membered T ring terminal carbon resonance. The conformations of the backbone rings are different, the E ring adopts a gauche conformation[13] and the T ring adopts a skew-boat conformation.[21]

In order to correlate the strain effects with the observed chemical shifts under consideration, a detailed understanding of the nature of the ring strain is necessary.[26] In their study for an estimate of the ring strain of $[Co(edta)]^-$, Weakliem and Hoard[13] suggested that the sum of the bond angles of the rings could be used. For the five-membered glycinate rings, the ideal bond angle sum is 538.4° which would allow the rings to be nearly planar.

The G ring strain as well as the relative lack of strain in the R rings in these complexes is clearly demonstrated by the bond angle sum since the R ring bond angles sums are closer to the ideal value and those of G rings are not. The primary reason for the G ring strain in $[Co(edta)]^-$ is thought to be the angular strain about the coordinated nitrogens. The $[Co(edta)]^-$ nitrogens are the intersection points of three five-membered chelate rings with two common members, cobalt and nitrogen. Each ring attempts to impose its own stereochemical requirements on the nitrogen atom which is also constrained to approximately tetrahedral geometry. The resulting compromise structure contains not only the bond angle and the bond length abnormalities in the G rings but also significant distortions of the nitrogen tetrahedra, opening the C_b–N–C_c angle to 116.1° with the C_e–N–C_c and the C_b–N–C_e angles remaining nearly tetrahedral. If the analysis is carried out for [Co(1,3-

pdta)]$^-$, the results are slightly different. [Co(1,3-pdta)]$^-$ with the less constricting six-membered T ring backbone has less strained nitrogen tetrahedral angles (C_b–N–C_c angle of 108.8°, C_b–N–C_e angle of 110.0°, and C_e–N–C_c angle of 112.9°) but still significantly strained G rings.[21]

With the understanding that the strain effects are revealed mainly by the geometry of the coordinated backbone nitrogen, a structural comparison of [Co(edta)]$^-$ and [Co(1,3-pdta)]$^-$ at the nitrogen center is made. Table IV shows some (solid state) values of bond angles and bond lengths of interest.[13,21] The values for [Co(ed3a)NO_2]$^-$ are included also for further verification.[27] Among these values, the Co–O_R and Co–O_G bond lengths seem to have little influence on the chemical shifts of R ring and G ring methylene carbons, but the Co–N bond length may play an important role in governing the chemical shift values of the two carbons in a fashion which is unknown at present. If bond angles are considered in the present case, the chemical shifts seem to correlate with the C–N–C bond angles made between the methylene carbons of the side ring and of the backbone ring at the coordinated nitrogen. The Co–N–C_b bond angles made between the side ring methylene carbon and the cobalt center at the coordinated nitrogen may also affect the relative chemical shifts but probably with a smaller degree of influence. Other bond angles are not considered mainly because they change only slightly. The ^{13}C chemical shift values of the R ring and G ring methylene carbons of all three complexes are listed also in Table IV. If other contributions are neglected, the chemical shift of the R ring methylene carbon changes from 66.0 ppm for [Co(edta)]$^-$ to 63.21 ppm for [Co(1,3-pdta)]$^-$ as the corresponding C_c–N–C_e angle changes from 108.6° to 112.9°. The chemical shift of the G ring methylene carbon changes from 65.8 ppm for [Co(edta)]$^-$ to 70.35 ppm for [Co(1,3-pdta)]$^-$ as the corresponding C_b–N–C_c angle changes from 116.1° to 108.8°.

The structural variations in going from [Co(ttda)]$^+$ with a five-membered backbone ring to [Co(ddda)]$^+$ with a six-membered backbone ring are believed to be similar to those for the [Co(edta)]$^-$ and [Co(1,3-pdta)]$^-$ pair, as it indicated by the similarities shown by their visible and ^{13}C NMR spectra. However, the different chemical shift values observed for both pairs of complexes may be caused by the different nature of the two in-plane chelate rings. The complex ions [Co(edta)]$^-$ and [Co(1,3-pdta)]$^-$, both with more strained G rings, have a small ΔC_e value 2.79 ppm, (the chemical shift difference for the *e* carbon of [Co(edta)]$^-$ and the *e* carbon of [Co(1,3-pdta)]$^-$)

TABLE IV

Selected values of bond angles, bond lengths, and ^{13}C chemical shifts of [Co(edta)]$^-$, [Co(1,3-pdta)]$^-$, and [Co(ed3a)NO_2]$^-$

Bond angles	[Co(edta)]$^-$[13]	[Co(1,3-pdta)]$^-$[20]	[Co(ed3a)NO_2]$^-$[27]
Co–N–C_c	107.5°	112.7°	107.0°
C_b–N–C_c	116.1°	108.8°	115.8°
C_e–N–C_c	108.6°	112.9°	111.9°
Co–N–C_b	103.9°	105.9°	104.4°
C_b–N–C_e	110.0°	110.4°	110.1°
Co–N–C_e	108.1°	108.1°	–
N–C_e–C_f	111.3°	111.1°	111.7°
N–C_b–C_a	107.6°	106.4°	107.0°
Bond lengths (A)			
Co–N	1.925	1.966	1.965
Co–O_G	1.915	1.904	1.919
Co–O_R	1.885	1.861	1.884
^{13}C chemical shift (ppm)			
C_b	65.8	70.35	66.48
C_e	66.0	63.21	65.18

and a larger ΔC_b value 4.55 ppm (the chemical shift difference of the *b* carbon of $[Co(edta)]^-$ and the *b* carbon of $[Co(1,3\text{-}pdta)]^-$). However, for $[Co(ttda)]^+$ and $[Co(ddda)]^+$ the two in-plane ethylenediamine side rings are a little less strained than the glycinate rings and a larger ΔC_e value (4.12 ppm) and a smaller ΔC_b value (1.18 ppm) are observed.

The complex $[Co(xdta)]^-$ has a seven-membered xylylenediamine backbone ring. The ^{13}C chemical shifts of the R ring and G ring methylene carbons have been assigned.[22] Since the crystal structure of $[Co(xdta)]^-$ is not known, no correlations can be made between the ^{13}C chemical shifts and the structural parameters. However, it is thought that the angular geometry at the coordinated nitrogens for $[Co(xdta)]^-$ is similar to that of $[Co(edta)]^-$ rather than to that of $[Co(1,3\text{-}pdta)]^-$ since the ^{13}C chemical shift values of the R ring (*e*) and G ring (*b*) methylene carbons of $[Co(xdta)]^-$ are closer to those of $[Co(edta)]^-$ (Table I).

The ^{13}C NMR spectrum[10] of $[Co(ed3a)NO_2]^-$ indicates that the major effect for half of the complex is the through-bond perturbation caused by replacing an acetate ion by a hydrogen atom. The major effect for the other half of the complex is the relief of strain resulting from the removal of one glycinate ring. The chemical shift separations between the two nonequivalent out-of-plane glycinate methylene carbon resonances and between the two nonequivalent ethylenic carbon resonances are 7.96 ppm and 5.03 ppm, respectively, with the one near the N–H bond being upfield. The three methylene carbon peaks (*b*, *c*, and *e* carbons) of the "strain-relieved half" are spread out as compared to the corresponding ones in the ^{13}C NMR spectrum of $[Co(edta)]^-$. However, the spread is not as much as for $[Co(1,3\text{-}pdta)]^-$. Thus the strain condition of $[Co(ed3a)NO_2]^-$ is predicted to be between that for $[Co(edta)]^-$ and that for $[Co(1,3\text{-}pdta)]^-$. This prediction is verified by comparing the bond angles and bond lengths at the coordinated nitrogen obtained from all three complexes in their crystalline state[27] (Table IV). For all bond angles considered, those of $[Co(ed3a)NO_2]^-$ are all within the range of those of $[Co(edta)]^-$ and $[Co(1,3\text{-}pdta)]^-$ except two which are only a little off. Although other factors also affect the chemical shifts, the angular dependence of the chemical shift is clearly demonstrated in the present study. However, owing to the high sensitivity of the ^{13}C chemical shift to other minor changes, only qualitative statements can be drawn at this time.

ACKNOWLEDGMENT

The authors thank Dr. K. D. Gailey of the University of Georgia for providing some ^{13}C NMR spectra of complexes of interest.

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