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Carbon-13 Nuclear Magnetic Resonance as a Means of Investigation of Inorganic Stereochemistry. Studies of Cobalt(III) Complexes of Trimethylenediamine-*N*,*N*'-diacetate and Ethylenediamine-*N*,*N*'-diacetate Ions

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Carbon-13 NMR measurements have been performed on nine uns-cis complexes, one, newly prepared, s-cis complex of Co(III) with the quadridentate ligand, trimethylenediamine-*N*,*N*'-diacetate ion (TMDDA), and sixteen complexes of Co(III) with the quadridentate ligand ethylenediamine-*N*,*N*'-diacetate ion (EDDA) with various unidentate (ammonia, water, pyridine, or nitrite ion) or bidentate ligands (ethylenediamine, trimethylenediamine, 2,2'-bipyridyl, 1,10-phenanthroline, ethanolamine, carbonate, oxalate, or malonate) occupying the remaining two octahedral coordination sites. Comparison of the spectra of s-cis and uns-cis complexes, along with application of selective decoupling and deuteration techniques, allows assignments of most resonances to individual carbons. It is found that ^{13}C NMR can be useful in its application to the investigation of inorganic stereochemistry insofar as it allows determination of which particular parts of ligands in uns-cis complexes sense the greatest differences in environment, relative to the same ligand in s-cis complexes or pure ligand.

Introduction

Cobalt(III) complexes containing ethylenediamine-*N*,*N*'-diacetate ion (EDDA) have been studied extensively by electronic absorption, circular dichroism (CD), and proton magnetic resonance (^1H NMR) spectra in the last decade.[1-14] Complexes of the related trimethylenediamine-*N*,*N*'-diacetate ion (TMDDA) have been investigated in previous papers dealing with electronic absorption and CD spectra.[10,15] An "octahedral" complex containing an EDDA type ligand has three possible structures, s-cis, uns-cis, and trans. In the case of Co^{III}–EDDA complexes, only s-cis (α) and uns-cis (β) structures, which are shown in Figure 1, actually have been obtained.[16] The s-cis EDDA complexes have been prepared most easily, but good preparative methods for uns-cis EDDA complexes have been developed in recent years.[6-8,10-14] The TMDDA complexes reported[10,15] were all uns-cis isomers. The structures of the isomers of $[Co(TMDDA)X_2]$ are the same as those of the EDDA complexes (Figure 1) except that the ethylenediamine backbone is replaced with a trimethylenediamine backbone.

In the case of both EDDA and TMDDA s-cis complexes, the absolute configurations of both N atoms must be the same. The unresolved s-cis complexes reported here would be mixtures of Λ-*SS* and Δ-*RR*.[9] In the case of uns-cis isomers the absolute configurations of the two N atoms can be the same or different.[15] These configurations are not known for the uns-cis complexes reported here. Perhaps the barrier to inversion for the N atom at the apex of two edges spanned in the same plane (the N which is part of a G ring) would be smaller for TMDDA complexes because of the more flexible diamine ring.

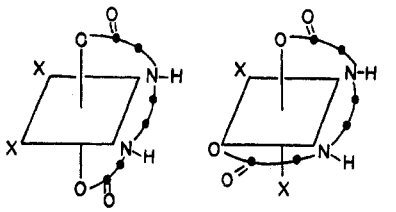
Numerous reports concerning the application of ^{13}C NMR to organic compounds[17] have shown the technique to be a very powerful tool for organic structural investigation. However, there have been very few reports of the application of the technique to transition metal complexes, with the main exceptions being organometallic compounds. Howarth et al.[18-20] used this technique in studying sexidentate and quinquedentate complexes of $EDTA^{4-}$, $HEDTA^{3-}$, and $CyDTA^{4-}$ (the anion of cyclohexanediaminetetraacetic acid) with several different metal ions, especially Co(III), and Blackmer and Vickrey[21] applied the technique to the study of deuterium-exchange kinetics in cobalt(III) aminopolycarboxylates. As another example, there is a report of ^{13}C NMR of cobalt(III) complexes containing amino acids.[22-24]

In order to investigate the utility of the technique for the study of transition metal stereochemistry, we sought to study two series of structurally related complexes. As suitable series of known stereochemistry, the above mentioned TMDDA– and EDDA–Co^{III} complexes have been investigated. One series consists of cobalt(III) complexes containing trimethylenediamine-*N*,*N*'-diacetate anion (TMDDA) and ammonia, ethylenediamine (en), trimethylenediamine (tn), 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen), carbonate ion, oxalate ion (ox), malonate ion (mal), water, or nitrite ions in the remaining two coordination positions. Unfortunately, the preparations of the s-cis isomers of TMDDA–Co^{III} complexes are very difficult and only the preparation of the s-cis isomer of the ethylenediamine complex has, thus far, been successful. Therefore, in the present study, nine uns-cis complexes and one s-cis complex are used for the application of the ^{13}C NMR experiments to the TMDDA series. Eleven s-cis and five uns-cis Co(III) complexes of EDDA with some of the ligands listed plus pyridine, py, and ethanolamine, elam, are reported also.

The ^{13}C spectra of EDDA itself and its symmetrically substituted s-cis complexes should show two resonances in the methylene region: one corresponding to the two equivalent carbons of the ethylenediamine backbone and another corresponding to the two equivalent glycinate methylene carbons. There should appear only one resonance in the carbonyl region. However, the uns-cis complexes have no equivalent carbons and should give four methylene resonances and two carbonyl resonances. Since there can be no significant ^1H–^{13}C or ^{13}C–^{13}C coupling for proton-decoupled (noise-modulated) spectra obtained from complexes synthesized from ligands containing only the naturally occurring proportion of ^{13}C, no splittings of resonances associated with single carbon atoms are observed.

The ^{13}C spectra of TMDDA itself and in s-cis complexes should show three resonances in the methylene region provided there are no significant distortions from the expected geometry: one corresponding to the two equivalent terminal carbons of the trimethylenediamine backbone, one corresponding to the two equivalent glycinate methylene carbons, and one of approximately half the intensity of the previous two, due to the middle carbon of the backbone. In addition, there should appear only one resonance in the carbonyl region. However, the uns-cis isomer has no equivalent carbons and should give rise to five methylene and two carbonyl resonances.

Since pairs of equivalent carbons in an s-cis complex (or the pure ligand) give two resonances in uns-cis complexes due to unsymmetrical coordination of the ligand, the separation between these resonances (hereafter referred to as shift



s-cis-[Co(EDDA)X_2] uns-cis-[Co(EDDA)X_2]

(α) (β)

Figure 1. Structures of s-cis and uns-cis isomers of [Co(EDDA)X_2].

nonequivalences) gives an indication of the extent of distortion or symmetry-imposed nonequivalence for those particular carbon atoms. Here, two series of complexes with systematic structural variations are investigated regarding the correlations with chemical shifts and the shift nonequivalences of carbon resonances.

Experimental Section

Preparation of Materials. All of the uns-cis isomers of TMDDA complexes, except the dinitro complex newly reported here, were prepared according to the methods reported in previous papers.[10,15] The 1,10-phenanthroline complex, however, was prepared with a minor modification. Although TMDDA–Co^{III} complexes seem to prefer the uns-cis configuration, the s-cis isomer of the ethylenediamine complex could be obtained by an ion-exchange column separation from its reaction solution and also is reported here. The EDDA complexes were prepared as previously described[7-11] and verified by electronic absorption spectra.

Preparation of *s-cis*-Trimethylenediamine-*N,N'*-diacetato(ethylenediamine)cobalt(III) Perchlorate, *s-cis*-[Co(TMDDA)(en)]ClO_4. Ten grams of H[Co(TMDDA)Cl_2]·0.5H_2O[10] was dissolved in 500 ml of water. Ethylenediamine (3.6 g) in 20 ml of water and activated charcoal (2 g) were added to the above solution. The mixture was refluxed for 5 hr. After the activated charcoal was filtered, the filtrate was poured into a cation-exchange column (Dowex 50W-X8, Na^+ form, 200–400 mesh). At first, a brown impurity was flushed away with water. By elution with aqueous $NaClO_4$ (0.1 *M*), the adsorbed components were gradually separated into three bands. The first band was purple-red, the second was red, and the last, which adhered to the top of the column, was yellow. The first band eluted was concentrated to 70 ml using a rotary evaporator, and 55 ml of ethanol and 75 ml of ether were added to it. The solution was cooled in a refrigerator. Soft, purple-red crystals were separated by filtration and washed with ethanol and then ether; yield 0.44 g. Anal. Calcd for [Co(TMMDA)(en)]ClO_4·H_2O: C, 25.45; H, 5.22; N, 13.20. Found: C, 25.64; H, 4.78; N, 12.98. The second band turned out to be the uns-cis isomer, previously reported,[10] as shown by its absorption spectrum. The third band was $Co(en)_3^{3+}$. For the measurement of its ^{13}C NMR spectrum, the perchlorate was changed into the more soluble chloride complex by treating with an anion-exchange resin (Cl^- form).

Preparation of Sodium *uns-cis*-Trimethylenediamine-*N,N'*-diacetato(dinitro)cobaltate(III), *uns-cis*-Na[Co(TMDDA)$(NO_2)_2$]. Five grams of H[Co(TMDDA)Cl_2]·0.5H_2O[10] in 50 ml of water was warmed at ca. 56° for 15 min. The color changed from green to blue and finally to violet. To the solution was added 4.3 g of $NaNO_2$, little by little. Accompanying the resulting reaction was the evolution of a gas (presumably NO_2) and the color changed to brown. The solution was warmed in a water bath for 20 min more. After the solution was cooled in a refrigerator, 3.7 g of brown crystals was separated by filtration. This product was dissolved in 100 ml of water, to this was added 3.1 g of $NaNO_2$ in 10 ml of water, and the solution was cooled in a refrigerator. Brown needle crystals were separated by filtration and washed, successively, with a small amount of water, water–ethanol (1:1) mixture, ethanol, and then ether; yield 2.1 g. Anal. Calcd for Na[Co(TMDDA)$(NO_2)_2$]·H_2O: C, 22.12; H, 3.71; N, 14.74. Found: C, 22.28; H, 3.69; N, 14.04.

Preparation of *uns-cis*-Trimethylenediamine-*N,N'*-diacetato(1,10-phenanthroline)cobalt(III) Chloride, *uns-cis*-[Co(TMDDA)(phen)]Cl. Seven and five-tenths grams of H[Co(TMDDA)Cl_2]·0.5H_2O[10] in 250 ml of water was warmed (60–65°) for 20 min. To it was added 9.3 g of 1,10-phenanthroline in 150 ml of an ethanol–water (1:1) mixture. The color turned from violet to light red. A small amount of insoluble purple complex was filtered. The filtrate was shaken well with 150 ml of ether in a separatory funnel in order to extract excess 1,10-phenanthroline. This procedure was repeated once more. The solution containing the product was evaporated to dryness with a rotary evaporator. The product was recrystallized from hot ethanol–water (1:1) mixture twice. Fine needle, purple-red crystals were separated and washed with an ethanol–water (2:1) mixture, ethanol, and then ether; yield 4.7 g. Anal. Calcd for [Co(TMDDA)(phen)]Cl·3H_2O: C, 44.15; H, 5.07; N, 10.84. Found: C, 44.38; H, 4.53; N, 10.99.

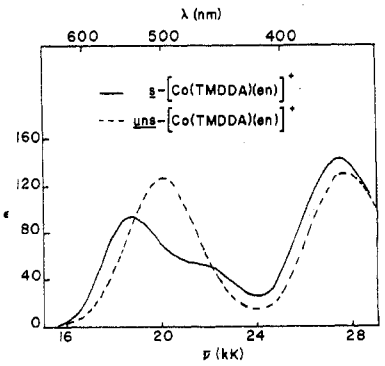


Figure 2. Electronic absorption spectra of *s-cis* and *uns-cis*-[Co(TMDDA)(en)]$^+$.

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

Proton magnetic resonance spectra were obtained with a Varian T-60 NMR spectrometer using ca. 0.5 *M* solutions. Deuterium oxide was used as a solvent with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal 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. The field frequency ratio was stabilized by locking to D_2O. Most spectra were obtained using spectral 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 5000–100000 scans depending upon the concentration of the sample. Concentrations of samples dissolved in D_2O ranged between 0.1 and 0.8 *M* and spectra were obtained from samples contained within 10-mm diameter tubes or 8–10 mm coaxial tubes manufactured by Wilmad Spectroscopic Supplies, Inc. TMS dissolved in benzene was used as external standard in an outer coaxial tube arrangement.

Analyses. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz.

Results and Discussion

TMDDA Complexes. Electronic Absorption Spectra. The absorption spectra of most of the TMDDA–Co^{III} complexes have been reported.[10,15] Those of *s-cis*-[Co(TMDDA)(en)]$^+$ and the previously reported[10] *uns-cis*-[Co(TMDDA)(en)]$^+$ are shown in Figure 2. As expected, the s-cis isomer of the complex has a clear shoulder on the higher energy side of the first absorption band, while the uns-cis isomer has not. It is well-known experimentally[25,26] and theoretically[27,28] that the *trans*(*O*)-[Co(N_4O_2)] type complexes exhibit a large splitting of the first absorption band, while for the *cis*(*O*)-[Co(N_4O_2)] type complexes this band is nearly symmetrical because of the smaller splitting.

The electronic absorption spectrum of *uns-cis*-[Co(TMDDA)$(NO_2)_2$]$^-$ shows a symmetrical first absorption maximum at 21.05 kK (ε 200). The second ligand field absorption band is overlapped by an intense charge-transfer or intraligand absorption band and is not recognizable. The s-cis isomers of dinitro complexes containing EDDA, or di-

Table I. Median Chemical Shifts for TMDDA in $Co(TMDDA)X_2$ (ppm)[a]

$-CH_2COO-$		$-HNCH_2COO$		$-HNCH_2CH_2CH_2NH-$		$-HNCH_2CH_2CH_2NH-$	
β-tn	182.50	α-en	53.73	α-en	46.59	α-en	18.02
β-phen	182.62	β-tn	54.99	β-mal	46.83	β-tn	22.00
β-bpy	182.66	β-mal	55.03	β-bpy	46.87	β-bpy	22.40
β-CO_3	183.35	β-bpy	55.11	β-phen	47.08	β-phen	22.40
β-mal	183.43	β-phen	55.27	β-tn	47.32	β-ox	22.40
β-ox	183.51	β-ox	55.45	β-ox	47.81	β-mal	22.56
β-$(NH_3)_2$	184.71	β-$(NO_2)_2$	55.94	β-$(NO_2)_2$	49.02	β-$(NO_2)_2$	22.56
β-$(NO_2)_2$	184.83	β-$(NH_3)_2$	57.22	β-$(NH_3)_2$	49.43	β-$(NH_3)_2$	24.02
β-en	186.14	β-en	58.27	β-en	51.09	β-en	25.08
α-en	186.68	β-CO_3	60.22	β-CO_3	53.32	β-CO_3	27.43

[a] The s-cis isomers are designated by α and the uns-cis by β for brevity.

Table II. Shift Nonequivalences of Similar Carbons (ppm) for TMDDA in *uns-cis*-$[Co(TMDDA)X_2]$ (β) Complexes Relative to the Corresponding s-cis (α) Complex

$-CH_2COO^-$		$-HNCH_2COO^-$		$-HNCH_2CH_2CH_2NH-$		Total splitting of TMDDA		Ring size
α-en	0.00	α-en	0.00	α-en	0.00	α-en	0.00	
β-en	0.89	β-bpy	0.81	β-$(NO_2)_2$	0.00	β-$(NO_2)_2$	3.90	∞
β-(NO_2)	1.14	β-phen	1.46	β-ox	0.49	β-$(NH_3)_2$	4.06	∞
β-$(NH_3)_2$	1.30	β-tn	1.54	β-mal	0.49	β-tn	5.03	6
β-tn	1.38	β-$(NH_3)_2$	1.79	β-$(NH_3)_2$	0.97	β-mal	5.03	6
β-CO_3	1.46	β-mal	2.60	β-en	1.38	β-en	5.03	5
β-mal	1.94	β-en	2.76	β-CO_3	1.46	β-bpy	5.69	5
β-ox	2.11	β-$(NO_2)_2$	2.76	β-tn	2.11	β-phen	6.00	5
β-bpy	2.20	β-ox	3.90	β-phen	2.27	β-ox	6.50	5
β-phen	2.27	β-CO_3	4.22	β-bpy	2.68	β-CO_3	7.14	4

alkyl–EDDA ligands have two bands assigned to the two D_{4h} components of the lowest energy (T_{1g}) O_h absorption transition.[9] The higher energy band is a fairly well-defined shoulder on the intense charge-transfer or intraligand absorption band. The absorption spectrum of $[Co(TMDDA)(NO_2)_2]^-$ reported here does not show a shoulder on the intense charge-transfer or intraligand band. This fact strongly suggests that the complex is the uns-cis isomer. This assignment is also confirmed by the ^{13}C NMR spectrum, as will be discussed later.

Proton Magnetic Resonance. Figure 3 shows the 60-MHz ^1H NMR spectrum of *uns*-$[Co(TMDDA)(NH_3)_2]^+$ vs. DSS, which is one of the more clearly defined examples of ^1H NMR spectra of the uns TMDDA complexes. Usually observed in the 3–4-ppm range for these complexes are a four-line AB pattern, corresponding to an out-of-plane (R) glycinate ring, and a singlet due to an in-plane (G) glycinate ring in the vicinity of the middle of the AB pattern of the R ring. The rest of a typical spectrum, which corresponds to resonances of the trimethylenediamine backbone and, where appropriate, bidentate ligands is ill defined and individual resonances are not readily assigned. The ^1H NMR spectrum of *s*-$[Co(TMDDA)(en)]^+$ is not easily interpretable, but it does differ from the spectrum of *uns*-$[Co(TMDDA)(en)]^+$, and the complex can be assigned definitely the s geometry on the basis of elemental analyses and electronic absorption and ^{13}C spectra.

Similar ^1H NMR spectra involving broadened and overlapping peaks, particularly in the nonglycinate regions, are found for other cobalt(III) aminopolycarboxylates, for example, complexes of (*R*)-(−)-1,2-propylenediaminetriacetate [*R*-(−)-1,2-PD3A],[29] ethylenediamine-*N*,*N*'-diacetate-*N*,*N*'-di-3-propionate (EDDDA),[30-32] *dl*-1,2-propylenediaminetetraacetate (1,2-PDTA),[33] ethylenediaminetetraacetate (EDTA),[33-34] trimethylenediaminetetraacetate (TRDTA or 1,3-PDTA),[35] ethylenediaminetriacetate (ED3A),[36] ethylenediamine-*N*,*N*'-di-L-α-propionate (LL-EDDP) and -D-α-propionate (DD-EDDP),[37] and ethylenediamine-*N*,*N*'-diacetate (EDDA)[2,6,7,8] ions. While the proton spectra of these complexes have had definite usefulness in the study of molecular geometry of these complexes, broadening and overlapping of peaks have placed limits upon their utility. This situation accentuates the value of ^{13}C NMR spectroscopy in such studies in that ^{13}C spectra possess inherently sharp and usually well-resolved peaks associated with individual carbon atoms.

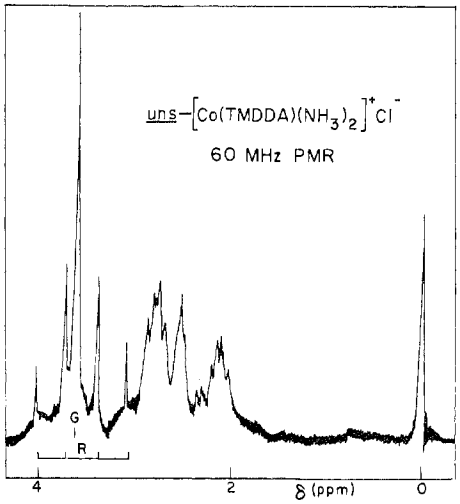


Figure 3. The 60-MHz ^1H NMR spectrum of *uns-cis*-$[Co(TMDDA)(NH_3)_2]Cl$.

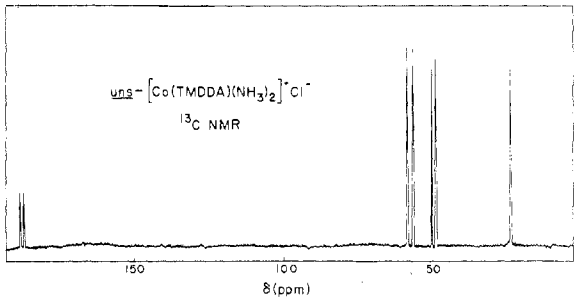


Figure 4. Noise-modulated ^{13}C NMR spectrum of *uns-cis*-$[Co(TMDDA)(NH_3)_2]Cl$.

^{13}C Magnetic Resonance. Figure 4 shows a typical example

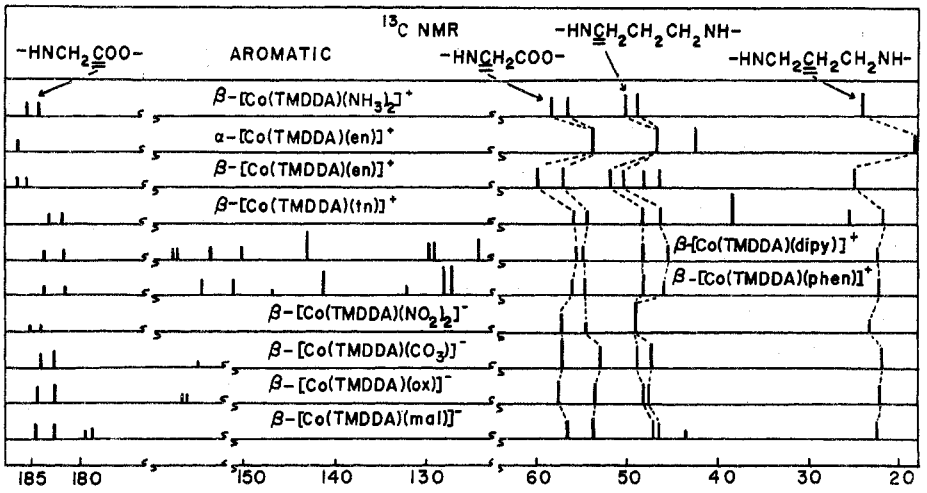


Figure 5. ^{13}C NMR of [Co(TMDDA)X$_2$] complexes (α and β are used for the s-cis and uns-cis isomers, respectively, for brevity).

of a ^{13}C spectrum of a TMDDA complex, *uns*-[Co(TMDDA)(NH$_3$)$_2$]$^+$. The spectra are characterized by clearly defined peaks and excellent signal-to-noise ratios. Figure 5 and Tables I and II summarize the results. All methylene resonances occur within the 18–60-ppm region, the resonances of the aromatic carbons range from 125 to 158 ppm, and the carboxyl carbons resonate from 167 to 187 ppm, relative to external TMS in benzene. In Figure 5, those methylene resonances associated with the TMDDA ligand are connected by dashed lines. All others in this region are due to carbon atoms of bidentate ligands. These are the following: the two equivalent carbons of the ethylenediamine bidentate ligand of *s*-[Co(TMDDA)(en)]$^+$ at 42.37 ppm; the same two carbons, now nonequivalent, for *uns*-[Co(TMDDA)(en)]$^+$ at 48.21 and 46.34 ppm; the two apparently accidentally degenerate resonances of the terminal carbon atoms of the trimethylenediamine bidentate ligand at 38.31 ppm and the middle carbon of the same ligand at 25.57 ppm for *uns*-[Co(TMDDA)(tn)]$^+$; and finally the very weak resonance of the methylene carbon of the malonate ligand at 43.52 ppm for *uns*-[Co(TMDDA)(mal)]$^-$.

In the carbonyl region all resonances are associated with the TMDDA ligand except the following: those at 179.31 and 178.66 ppm for *uns*-[Co(TMDDA)(mal)]$^-$, 169.31 and 168.82 ppm for *uns*-[Co(TMDDA)(ox)]$^-$, and 167.20 ppm for *uns*-[Co(TMDDA)(CO$_3$)]$^-$, all of which are toward greater shielding than the TMDDA carbonyls.

The relative intensities of the peaks in each spectrum are shown in Figure 5. Since the resonances in the carbonyl region are all quite weak (the bidentate carbonyls weakest), their intensities as depicted are increased by a factor of 3.

The main factors responsible for intensity of peaks in noise-modulated ^{13}C spectra are the number of equivalent carbons giving rise to a resonance and the nuclear Overhauser effect, which is related to the ease of relaxation of ^{13}C atoms from excited states back to the ground state.[17] The most effective means of relaxation of excited ^{13}C nuclei involves interaction of resonating protons with the carbon nuclei and resulting energy exchange. Therefore, its effectiveness is dependent upon the number of protons which are attached to or are in close proximity to the resonating carbon nuclei and whether or not the protons are also in resonance. This accounts for the fact that the carbonyl resonances, especially those of carbonate and oxalate, are much weaker than the methylene resonance peaks. The low intensity of the malonate methylene resonance also may be explained by the fact that the methylene group itself is bonded to two carbonyls.

For *uns*-[Co(TMDDA)(phen)]$^+$ the two weakest peaks in the aromatic region at 146.80 and 131.97 ppm are thought to represent the four carbons of phenanthroline to which no protons are attached. This low-intensity effect is more pronounced in the spectrum of the metal complex than in that of the pure ligand.[38] It is also noteworthy that these two nonequivalent pairs of carbons, which are equivalent in the pure ligand, still give rise to only two resonances rather than four in the uns complex, as is the case for most other pairs of phenanthroline carbons in the same complex. Only slightly low relative intensity is observed for the resonances thought to be associated with the two nonprotonated carbon atoms of bipyridyl,[39] which do give rise to separate resonances in the spectrum of *uns*-[Co(TMDDA)(bpy)]$^+$, at 157.62 and 157.21 ppm. The region associated with phenanthroline and dipyridyl resonances will be discussed in greater detail later in this paper.

The assignments of resonances in the methylene region have been accomplished by means of selective decoupling and deuteration. Selective decoupling of proton resonances from carbon resonances can be used in gaining structural information from ^{13}C NMR, just as for ^{1}H NMR.[17] If assignments of some or all of the resonances in the ^{1}H NMR spectrum of a sample have been made, this technique can be used in correlating carbon resonances with the individual carbon atoms to which the protons considered are bound. This is particularly true when the resonances in question are, in the ideal case, isolated from the rest of the proton spectrum. In the case of the TMDDA complexes, the glycinate proton resonances are all localized in the 3–4-ppm range and other ligand resonances are toward greater shielding (Figure 3). In the ^{13}C experiment, when the broad-band noise modulation is discontinued and, instead, the complex of interest is irradiated constantly at the particular frequency of the G ring proton resonance, for example (while simultaneously sweeping the field of ^{13}C resonances), all protons except those of the methylene carbons of the G ring can interact with the carbons to which they are attached. This results in two effects: (1) the carbons to which the glycinate 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 and become split as a result of coupling with the nonresonating protons.

Figure 6 shows the result of this experiment on *uns*-[Co(TMDDA)(en)]$^+$. It is evident that the two lowest field methylene resonances, at 59.65 and 56.89 ppm, tend to retain much of their sharp singlet character while the other methylene resonances broaden and virtually disappear. This indicates that the sharp resonances are associated with the methylene carbons of the glycinate rings. It is not possible to determine unambiguously which of the two sharp carbon resonances corresponds to a G ring methylene and which corresponds to

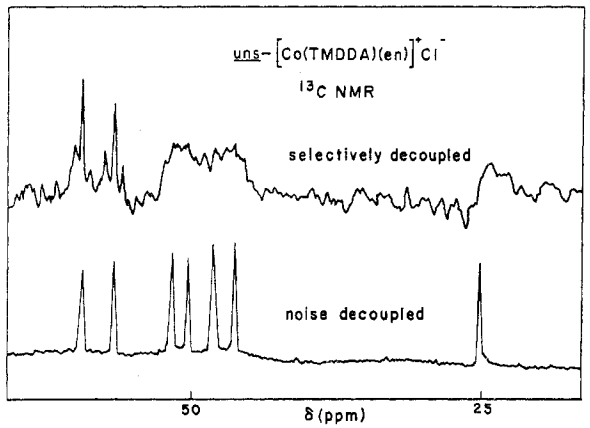


Figure 6. Noise-modulated and selectively decoupled (at G ring proton frequency) ^{13}C NMR spectra of *uns-cis*-[Co(TMDDA)(en)]Cl.

an R ring methylene. This is due to the fact that decoupling at the frequency of the G protons also has a large effect on the R protons, since the G ring proton singlet is near the center of the R ring AB pattern. The decoupling data are inconclusive on this question for the *uns*-[Co(TMDDA)(en)]$^+$ complex but suggest that the lower field methylene peak remains the more intense of the two and, therefore, that it is more likely to be associated with a G ring methylene and the other with the R ring.

Terrill and Reilley[34] have shown from ^{1}H NMR 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* occurs most rapidly at the out-of-plane glycinate methylenes with the in-plane glycinate rings exchanging very slowly. They found that the ethylenediamine methylenes do not undergo any observable exchange under these conditions. Similar trends were also observed for Co(CyDTA)$^-$ and Co(PDTA)$^-$. These observations have been utilized by Blackmer and Vickrey[21] in their ^{13}C NMR studies of the kinetics of deuterium exchange for three sexidentate cobalt(III) aminopolycarboxylates: Co(EDTA)$^-$, Co(CyDTA)$^-$, Co(PDTA)$^-$. Howarth, Moore, and Winterton[18-20] have also used the conclusions of Terrill and Reilley in interpreting the ^{13}C spectra of complexes of EDTA^{4-}, HEDTA^{3-}, and CyDTA^{4-}, as have Gailey and Douglas[32] for Co(III) complexes of EDDDA.

Comparison of ^{13}C NMR spectra of deuterated and undeuterated complexes of *uns*-[Co(TMDDA)(tn)]Cl aided the identification of methylene resonances. The deuteration was accomplished by acidifying a D_2O solution of the complex to a pD of ca. 0.5 and heating at ca. 85° for 24 hr. The two lowest field (less shielded) methylene peaks, at 55.76 and 54.22 ppm, lost intensity relative to the other methylene peaks. Similar results were obtained for several other uns TMDDA complexes, thus verifying the results obtained from selective decoupling that the two least shielded methylene resonances of these complexes are glycinate methylene resonances.

In terms of chemical shift, the resonances of the *s*-[Co(TMDDA)(en)]$^+$ complex in the methylene region are about 5–7 ppm toward greater shielding than those of *uns*-[Co(TMDDA)(en)]$^+$, while the carbonyl resonance of the s complex is about 0.5 ppm toward less shielding than the average position of carbonyl resonances of the uns complex. It is difficult to explain in terms of molecular models why so much shift is observed in the methylene region. ^{13}C studies of organic compounds have shown that shifts to greater shielding can be associated with carbons which are sterically perturbed relative to similar carbons which are unperturbed.[17] This is called a steric compression shift. The s complex would not be expected to be more strained than the uns complex, yet *all* methylene resonances of the s isomer are shifted to greater shielding than those of the uns isomer.

Table I shows the medium values of chemical shift for each of the pairs of resonances (and the single resonance of the middle carbon of the trimethylenediamine backbone) associated with the TMDDA ligand. The TMDDA carboxyl carbons have median shifts ranging between 182.50 and 186.68 ppm, a range of only about 4 ppm, somewhat less than the range of comparable methylene shifts. The glycinate methylene resonances range between 53.73 and 60.22 ppm, the terminal carbons of the backbone appear between 46.59 and 53.32 ppm, and the middle carbons of the backbone are between 18.02 and 27.43 ppm. The appearance of these resonances within these particular regions is governed mainly by the shielding or deshielding characteristics of the nearest-neighbor groups of the resonating carbons. The small differences in shifts caused by changing the bidentate or unidentate ligands result from combinations of more subtle influences, such as long-range steric and inductive effects. While it is difficult to evaluate the relative contributions of these factors to the total shifts, it can be seen that the orderings within the various groupings of methylene resonances are quite similar, though not identical. However, it is interesting that the ordering within the series of TMDDA carboxyl resonances is significantly different from those of the methylenes. The chemical shifts of these complexes compared to those of complexes of the ethylenediamine-*N*,*N*'-diacetate ion (EDDA) will be discussed below.

A listing of shift nonequivalences for the uns complexes is found in Table II for similar carbon atoms of the TMDDA ligand in each of the complexes. The total shift nonequivalences (sum of the carbonyl, glycinate methylene, and backbone shift nonequivalences) associated with TMDDA are found to vary quite regularly with chelate ring size of the other ligand(s). The sum of shift nonequivalences of similar carbons of the quadridentate ligand for *s*-[Co(TMDDA)(en)]$^+$ is, of course, zero. For the uns complexes, the monodentate dinitro and diammonia complexes (∞ ring size) show total shift nonequivalences of only 3.90 and 4.06 ppm. Total separations increase from 5.03 to 7.14 ppm as the size of the chelate rings of bidentate ligands decreases from six to five to four members. This is a predictable order since it might be expected that more overall strain would occur in the complex and manifest itself in total separations, as the size of the bidentate ligand decreases.

However, the ordering of the shift nonequivalences varies for each of the three different groups of corresponding pairs of carbons of TMDDA. In uns complexes, for the glycinate methylene carbons, for example, coordination of bipyridyl results in a separation of only 0.81 ppm while coordination of carbonate (as a bidentate ligand) causes a shift nonequivalence of 4.22 ppm. However, for the methylene carbons of the trimethylenediamine backbone, bipyridyl causes a *larger* shift nonequivalence than does carbonate, 2.68 ppm as compared with only 1.46 ppm.

Finally, it is worth mentioning that, for the TMDDA complexes, a compensation effect of sorts seems to be operational. For example, the general trend observed (Figure 5) for shift nonequivalences in the regions of the methylenes of the glycinates and terminal methylenes of the backbone are as follows: (1) complexes containing the aromatic bidentates phenanthroline and bipyridyl tend to give rise to rather small separations in the former region and large separations in the latter; (2) complexes with oxygen donor ligands carbonate, oxalate, and malonate tend to give large glycinate methylene separations and small backbone separations; and (3) complexes with the diamine ligands ethylenediamine, trimethylenedi-

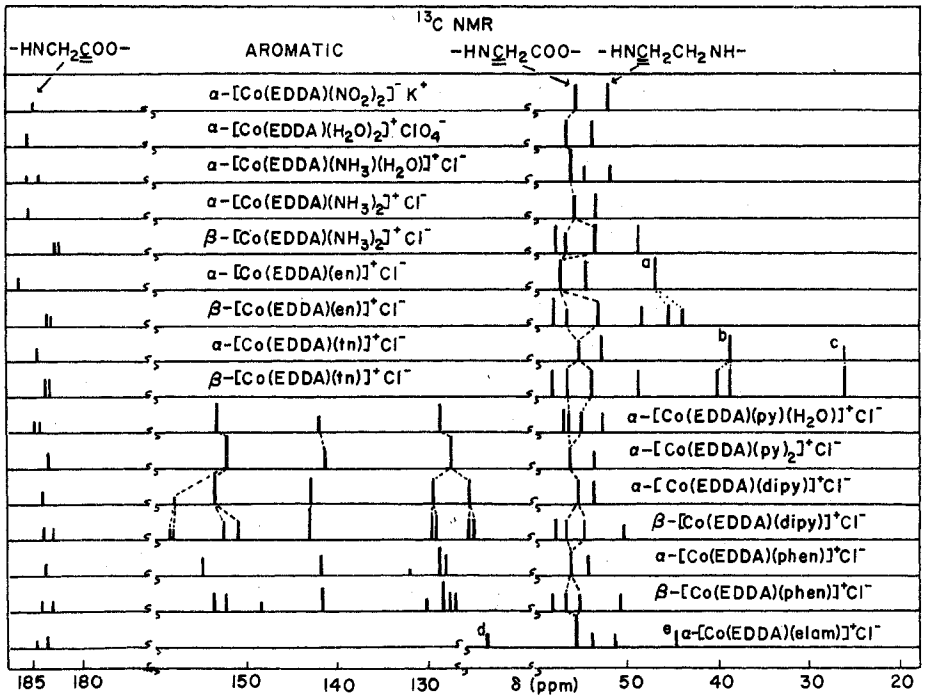


Figure 7. Noise-modulated ^{13}C NMR spectra of [Co(EDDA)X$_2$] complexes.

Table III. Median Chemicals Shifts of EDDA in Co(EDDA)X$_2$ (ppm)

-CH$_2$*C*OO-		-HN*C*H$_2$COO-		-HN*C*H$_2$CH$_2$NH-	
α-phen	182.90	*β-en*	54.71	α-(NO$_2$)$_2$	51.78
β-en	183.35	*β-(NH$_3$)$_2$*	54.83	α-elam	52.54
β-(NH$_3$)$_2$	183.43	α-tn	55.03	α-tn	52.59
α-(py)$_2$	183.59	*β-tn*	55.19	*β-en*	53.00
β-tn	183.59	α-bpy	55.35	α-(NH$_3$)(H$_2$O)	53.01
β-bpy	183.59	α-(NO$_2$)$_2$	55.35	α-(NH$_3$)$_2$	53.08
β-phen	183.75	α-elam	55.47	*β-(NH$_3$)$_2$*	53.24
α-bpy	184.24	α-(NH$_3$)$_2$	55.52	*β-tn*	53.32
α-elam	184.36	*β-bpy*	55.68	α-en	53.38
α-tn	184.73	α-(NH$_3$)(H$_2$O)	55.85	α-bpy	53.57
α-(py)(H$_2$O)	184.81	*β-phen*	55.92	α-(py)$_2$	53.57
α-(NO$_2$)$_2$	184.89	α-phen	56.17	α-(H$_2$O)$_2$	53.57
α-(NH$_3$)(H$_2$O)	185.06	α-(py)$_2$	56.32	α-(py)(H$_2$O)	53.73
α-(NH$_3$)$_2$	185.54	α-(H$_2$O)$_2$	56.49	*β-bpy*	54.05
α-(H$_2$O)$_2$	185.54	α-(py)(H$_2$O)	56.57	α-phen	54.22
α-en	186.68	α-en	57.14	*β-phen*	54.38

Table IV. Shift Nonequivalences of Similar Carbons of EDDA in Co(EDDA)X$_2$ (ppm)

-HN*C*H$_2$COO-		-HN*C*H$_2$CH$_2$NH-		-CH$_2$*C*OO-		Total	
8 α-symmetrically disubstituted	0.00	8 α-symmetrically disubstituted	0.00	8 α-symmetrically disubstituted	0.00	8 α-symmetrically disubstituted	0.00
α-(NH$_3$)(H$_2$O)	0.00	α-elam	2.27	β-(NH$_3$)$_2$	0.32	α-(py)(H$_2$O)	3.25
α-elam	0.00	α-(py)(H$_2$O)	2.27	β-tn	0.32	α-elam	3.41
α-(py)(H$_2$O)	0.49	α-(NH$_3$)(H$_2$O)	2.76	α-(py)(H$_2$O)	0.49	α-(NH$_3$)(H$_2$O)	4.06
β-phen	1.46	β-phen	7.47	β-en	0.49	β-phen	9.90
β-bpy	1.95	β-bpy	7.47	β-phen	0.97	β-bpy	10.39
β-tn	2.60	β-(NH$_3$)$_2$	9.09	β-bpy	0.97	β-tn	12.17
β-(NH$_3$)$_2$	3.18	β-tn	9.25	α-elam	1.14	β-(NH$_3$)$_2$	12.59
β-en	3.25	β-en	9.58	α-(NH$_3$)(H$_2$)	1.30	β-en	13.32

amine, and diammonia yield separations of comparable magnitudes in both regions. Although this ordering is not perfect, it appears that, to the extent allowed by the length of the bidentate ligands, and distortions of complexes resulting therefrom, a large separation associated with a particular pair of carbons is at least partially compensated for by a relatively small separation of resonances associated with another pair of carbons.

EDDA Complexes. Proton Magnetic Resonance. The ^{1}H NMR spectra of most of the Co(III) complexes of EDDA investigated here already have been reported[2,5-8,13,14] and closely resemble those of the TMDDA complexes.

Carbon-13 Magnetic Resonance. Figure 7 and Tables III and IV summarize the results of noise-modulated ^{13}C NMR measurements of all 16 EDDA complexes. The methylene resonances of the EDDA ligand itself all occur within the 47–60-ppm (relative to external TMS in benzene) region. Those resonances assigned to glycinate methylene carbons are connected by broken lines in Figure 7, while those of the ethylenediamine backbone are not connected. Those methylene peaks labeled a–e, or connected to peaks with such labels, are assigned to the following bidentate resonances: a,

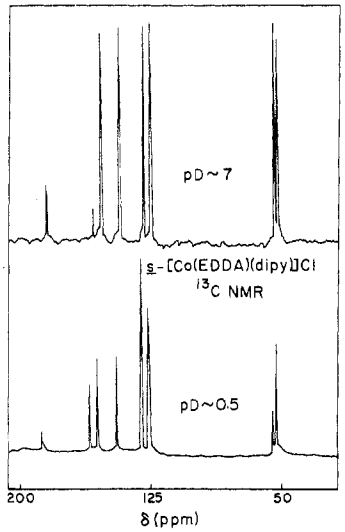


Figure 8. ^{13}C NMR spectra of undeuterated and deuterated *s-cis*-[Co(EDDA)(bpy)]Cl.

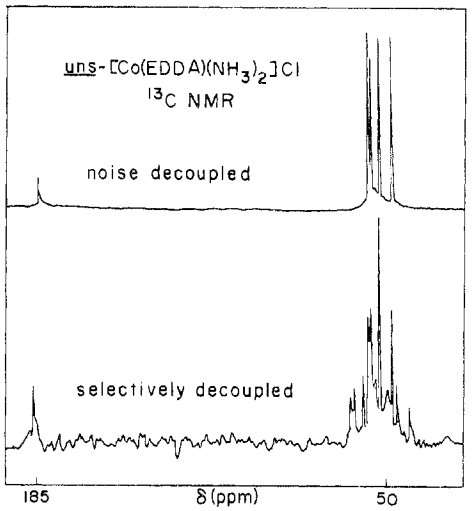


Figure 9. Selective decoupling of ^{13}C NMR spectrum of *uns-cis*-[Co(EDDA)(NH$_3$)$_2$]Cl.

ethylenediamine carbons; b, terminal carbons of trimethylenediamine; c, middle carbon of trimethylenediamine; d and e, resonances of the two carbons of ethanolamine, adjacent to the hydroxyl and amino groups, respectively. The resonances of the aromatic carbons of complexes containing pyridine, bipyridyl, and phenanthroline are found in the 120–160-ppm region. The carboxylate carbon resonances occur between 182 and 187 ppm and also are depicted as being enhanced in intensity by a factor of about 3 relative to methylene and aromatic carbon resonances in the same spectra, because of their low intensity in the original spectra.

Figure 8 shows noise-modulated ^{13}C spectra of *s*-[Co(EDDA)(bpy)]Cl in D_2O and the same complex after acidification to pD ca. 0.5 and heating for 14 hr at ca. 85°. It is evident that the lower field methylene resonance at 55.68 ppm has lost considerable intensity relative to the other methylene resonance and, therefore, corresponds to the two equivalent (out-of-plane) glycinate ring methylenes while the higher field peak, at 54.05 ppm, is due to the two equivalent carbons of the ethylenediamine backbone. A similar situation is observed upon deuteration of other s complexes.

Noise-modulated spectra of deuterated and undeuterated *uns*-[Co(EDDA)(bpy)]Cl were also obtained. As expected these spectra exhibit twice as many peaks in the methylene and carboxyl regions of the spectrum as does the corresponding s complex. However, not all of the five bipyridyl resonances of the s complex separate into two resonances in the uns complex. The results of the deuteration experiment suggest that the two inner methylene peaks, at 56.65 and 54.70 ppm, are due to the two nonequivalent glycinate methylene carbons. Therefore, the two outer methylene peaks at 57.79 and 50.32 ppm must correspond to the two ethylenediamine backbone carbon resonances.

These assignments are verified by the results of selective decoupling. When *s*-[Co(EDDA)(H_2O)$_2$]Cl, for example, is irradiated constantly at the median frequency of the R ring proton AB pattern rather than at all proton frequencies as the ^{13}C frequency range is swept, the resonance of the less shielded of the two methylene peaks at 56.49 and 53.57 ppm is the one which remains more intense. This leads to the same conclusion, that the resonance corresponding to less shielding is due to the glycinate methylenes and the other to the backbone methylene carbons. Selective decoupling of the uns complexes, *uns*-[Co(EDDA)(NH_3)$_2$]Cl for example (Figure 9), at the proton frequency of the G ring results in the peak at 53.24 ppm retaining more intensity and singlet character than any

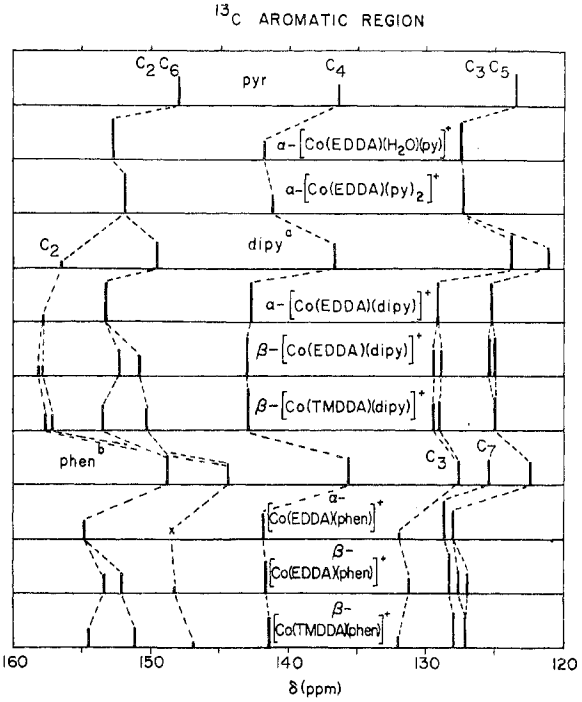
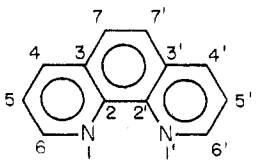


Figure 10. ^{13}C NMR spectra of pyridine, bipyridyl, phenanthroline, and their EDDA- and TMDDA-Co^{III} complexes in the aromatic region.

of the other methylene resonances, thus substantiating its assignment as a glycinate methylene resonance. Since the G ring proton resonance is near the center of the R ring AB pattern for the *uns*-[Co(EDDA)X_2] complexes, selective irradiation at the median frequency of the AB pattern produces a very similar ^{13}C spectrum, thus making it impossible to distinguish, on this basis, between G ring and R ring methylene carbons.

Figure 10 shows the chemical shifts and relative intensities of pyridine, bipyridyl, and phenanthroline resonances for the uncomplexed ligands and for their EDDA and TMDDA complexes. The chemical shifts of the free ligands already have been reported,[38-41] and for bipyridyl and phenanthroline these values are used. Relative intensity measurements of the free ligands were performed by the present authors. The numbering system used for these ligands is shown for phenanthroline, I.



I

The C_4 resonance of pyridine (136.36 ppm) is of about half the intensity of the resonances of the two equivalent pairs of carbons, C_2 and C_6 (148.04 ppm) and C_3 and C_5 (123.53 ppm). This is, of course, expected assuming that the relaxation times of all the carbons are nearly the same. Complexation of any of the free ligands results in shifts toward less shielding of 1.2 to 6.1 ppm for these resonances due to the increased deshielding of the ligands as they donate electron density toward the metal. C_2 and C_6 are not equivalent for bipyridyl and show separate resonances, as is the case for C_3 and C_5. The intensity of the C_2 peak is much lower than the intensities of the other peaks since C_2 is a nonprotonated carbon and, therefore, is not easily relaxed.[17] While the peaks do not split further upon complexation of bipyridyl in *s*-[Co(EDDA)(bpy)]$^+$, they do for the corresponding uns complex. For the uns complex only C_4 and $C_{4'}$, which are the most remote carbon atoms from the donor atoms, remain equivalent with respect to the ^{13}C spectrum, while each of the other pairs of corresponding carbons, C_2 and $C_{2'}$, C_3 and $C_{3'}$, etc., are nonequivalent and show separate resonances. The largest shift nonequivalence of corresponding pairs of aromatic carbon atoms for this complex, as well as for other uns complexes containing bipyridyl and phenanthroline, clearly occurs for C_6 and $C_{6'}$ and is probably due to the fact that these atoms are closest to the in-plane and out-of-plane glycinate carboxyl groups, respectively. It is interesting to note that *uns*-[Co(TMDDA)(bpy)]$^+$ shows that C_5 and $C_{5'}$ are magnetically equivalent while in the corresponding EDDA complex they are not, yet the TMDDA complex shows slightly larger nonequivalence associated with C_2 and $C_{2'}$, the atoms bridging the rings, and significantly larger separation of C_6 and $C_{6'}$ resonances. A similar situation is found for the analogous carbon resonances of the corresponding phenanthroline complexes, except that no distinction is observed at all for C_2 and $C_{2'}$ for any of the phenanthroline complexes. The fact that the C_6 and $C_{6'}$ resonances have greater separations in TMDDA complexes than in EDDA complexes suggests a situation—to be substantiated below—in which the carbonyl carbons of the uns TMDDA complexes are in more widely differing chemical environments than those of uns EDDA complexes. Generally less shift nonequivalence is observed for phenanthroline resonances than for bipyridyl resonances, probably because of the greater restraints against distortion imposed upon the former as a result of the fused rings. In contrast to the situation for uncomplexed bipyridyl, the nonprotonated carbons of uncomplexed phenanthroline (C_2, $C_{2'}$ and C_3, $C_{3'}$) have resonances of nearly the same intensity as other resonances in its spectrum, but when the ligand is complexed, each of the resonances in question loses significant relative intensity. It should also be noted that the weak resonance, due to C_2 and $C_{2'}$ of *s*-[Co(EDDA)(phen)]$^+$, was not clearly located and its estimated position is marked by × (Figure 10). The difficulty in the location of the peak after 100000 fast scans is a result of two factors, the inherently low intensity expected for resonances of C_2 and $C_{2'}$ and the relatively low solubility of the complex.

The fact that subtle changes arising from increasing or decreasing the size of the backbone of the quadridentate ligand by one methylene group can be accompanied by such clear ^{13}C spectral changes associated with carbon atoms of the ligands attached on the opposite side of the ion points out the potential of this technique in structural characterization of inorganic complexes.

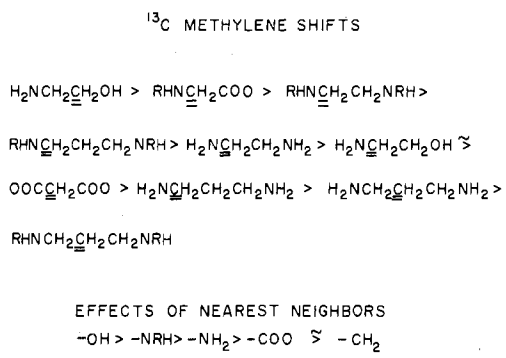


Figure 11. Order of ^{13}C chemical shifts of methylene groups in ten different chemical environments and deshielding effects of nearest neighbors.

As can be seen from Table IV the resonance separations of similar carbons obtained for the [Co(EDDA)X_2] series follow a somewhat different order from that for corresponding [Co(TMDDA)X_2] ions (Table II): s symmetrically disubstituted complexes (0-ppm total shift nonequivalence of EDDA resonances) < s unsymmetrically disubstituted complexes < uns complexes of phenanthroline and bipyridyl < uns complexes of diamine ligands. For the EDDA series no particular trend is observed with respect to the ring size of X_2. This suggests that factors resulting in distortion of the EDDA complexes involve more than just strain due to the X_2 chelate ring size, while this factor seems to be dominant for complexes of the more flexible TMDDA ligand.

The ordering of magnitudes of shift nonequivalences of individual types of carbon atoms, for glycinate methylene carbons and ethylenediamine backbone carbons of EDDA complexes (Table IV), varies similarly to but not identically with the ordering of the sums of the shift nonequivalences. The separations of the glycinate methylene carbon resonances of uns complexes of EDDA are all greater than those of corresponding TMDDA complexes. The same effect is much more pronounced for the ethylenediamine carbons of the EDDA backbone as compared with the terminal carbons of the TMDDA backbone. This could be due to greater overall strain and resulting distortion from uns coordination of the ligand with an ethylenediamine backbone relative to one with a larger trimethylenediamine backbone. It is also found that the ordering of separations of carboxyl carbon resonances of EDDA complexes (Table IV) is much different from the orderings of either the sums of all the EDDA separations or individual glycinate or backbone methylene shift nonequivalences and shows no easily explainable trend. It is interesting to note that for complexes in which carbonyl separations occur, these separations for EDDA complexes range from only 0.32 to 1.30 ppm while they range from 0.89 to 2.27 ppm for TMDDA complexes. The fact that EDDA carbonyl resonances all separate less than the TMDDA carbonyl resonances is in direct contrast to the separations of the methylene resonances just discussed. However, this is consistent with the observation that C_6 and $C_{6'}$ resonances of both phenanthroline and bipyridyl in *uns*-[Co(TMDDA)(phen)]$^+$ and *uns*-[Co(TMDDA)(bpy)]$^+$ both show larger separations in the ^{13}C spectra than they do in the corresponding EDDA complexes. This tendency is very resonable since C_6 and $C_{6'}$ are the carbon atoms which are nearest to the in-plane and out-of-plane coordinated glycinate carboxylate groups.

It is likely that the magnitudes of shift nonequivalences or differences in chemical environments as sensed by particular carbon atoms should be dependent upon factors such as degree of distortion and lowering of symmetry in uns complexes

relative to corresponding s complexes. Therefore, resonance separations should give indications as to which specific carbon atoms experience the greatest changes in environment in going from the pure ligand or s complexes to uns complexes. This, of course, has important implications with regard to the use of ^{13}C NMR in investigations of inorganic stereochemistry in that it allows determination of what regions of molecules suffer the most (and least) effects from distortion due to unsymmetrical coordination of carbon-containing ligands to metal ions. This is more information than can be obtained easily from ^{1}H NMR spectra in view of (1) the fact that ^{1}H NMR spectra are often quite complex and difficult to interpret completely and (2) the fact that the carbon atoms form the basic framework of the structures of the complexes and the protons do not.

The ordering of chemical shifts (or median chemical shifts for complexes in which shift nonequivalences of similar carbons occur) of different pairs of EDDA carbons as the X_2 species are varied appears to be almost random for s complexes of EDDA, as seen in Table III. The uns complexes, though, follow a regular order for each series of carbonyl, glycinate methylene, and backbone resonances: X_2 = ethylenediamine < diammonia < trimethylenediamine < bipyridyl < phenanthroline.

Figure 11 shows the ordering of ^{13}C shifts of methylene groups in ten different chemical environments for both quadridentate and bidentate ligands of EDDA and TMDDA complexes. This ordering is quite consistent with the results of investigations of organic compounds, containing similar moieties,[17] as expected, and adds support to the assignments made by deuteration and selective decoupling. It is observed that the general positions of the methylene resonances are influenced mainly by the deshielding or shielding characteristics of nearest neighbor groups. The hydroxyl group is the most deshielding of the groups considered and tends to produce low-field resonances for adjacent methylene groups, whereas methylene groups adjacent to other (shielding) methylene groups resonate at relatively high field.

In summary, it is clear that while the ^{13}C NMR technique has received little attention in its application to the structure elucidation of transition metal complexes, it has a great deal of potential in this area. Of course, it will be necessary to carry out more such investigations of related series of complexes in order to establish valid general trends and to evaluate realistically the limits of its applicability to the study of inorganic stereochemistry.

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Registry No. β-[Co(TMDDA)$(NH_3)_2$]$^+$Cl$^-$, 56845-89-7; α-[Co(TMDDA)(en)]$^+$Cl$^-$, 56845-90-0; β-[Co(TMDDA)(en)]$^+$, 56845-91-1; β-[Co(TMDDA)(tn)]$^+$, 56845-92-2; β-[Co(TMDDA)(bpy)]$^+$, 56845-93-3; β-[Co(TMDDA)(phen)]$^+$Cl$^-$, 56792-84-8; β-[Co(TMDDA)$(NO_2)_2$]$^-$Na$^+$, 56792-85-9; β-[Co(TMDDA)(CO_3)]$^-$, 53533-55-4; β-[Co(TMDDA)(ox)]$^-$, 56792-86-0; β-[Co(TMDDA)(mal)]$^-$, 56792-87-1; α-[Co(EDDA)$(NO_2)_2$]$^-$K$^+$, 37480-85-6; α-[Co(EDDA)$(H_2O)_2$]$^+$$ClO_4^-$, 37715-40-5; α-[Co(EDDA)$(NH_3)(H_2O)$]$^+$Cl$^-$, 56792-88-2; α-[Co(EDDA)$(NH_3)_2$]$^+$Cl$^-$, 56792-89-3; β-[Co(EDDA)$(NH_3)_2$]$^+$Cl$^-$, 56792-90-6; α-[Co(EDDA)(en)]$^+$Cl$^-$, 56792-91-7; β-[Co(EDDA)(en)]$^+$Cl$^-$, 56792-92-8; α-[Co(EDDA)(tn)]$^+$Cl$^-$, 56845-94-4; β-[Co(EDDA)(tn)]$^+$Cl$^-$, 56845-95-5; α-[Co(EDDA)(py)(H_2O)]$^+$Cl$^-$, 56792-93-9; α-[Co(EDDA)$(py)_2$]$^+$Cl$^-$, 56792-94-0; α-[Co(EDDA)(bpy)]$^+$Cl$^-$, 56792-95-1; β-[Co(EDDA)(bpy)]$^+$Cl$^-$, 56792-96-2; α-[Co(EDDA)(phen)]$^+$Cl$^-$, 56792-97-3; β-[Co(EDDA)(phen)]$^+$Cl$^-$, 56792-98-4; α-[Co(EDDA)(elam)]$^+$Cl$^-$, 56792-99-5; α-[Co(TMDDA)(en)$^+$$ClO_4^-$, 56845-97-7; H[Co(TMDDA)Cl_2], 43200-14-2; ethylenediamine, 107-15-3; ^{13}C, 14762-74-4.

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