

Decompositions were initiated by activating the pH-stat which delivered 1 *N* NaOH to bring the system to the desired pH. The reaction was followed both by the additional base added continually by the pH-stat to maintain pH and by O<sub>2</sub> evolution. Representative reactions were followed iodometrically by removing aliquots and determining total H<sub>2</sub>O<sub>2</sub>. Good agreement was obtained for rates of product formation and H<sub>2</sub>O<sub>2</sub> consumption.

**Product identification** was carried out on several oxidation reactions run on a larger scale, and figures below all refer to moles of product per mole of H<sub>2</sub>O<sub>2</sub> consumed. With Fe<sup>III</sup>EDTA + excess EDTA alone at pH 9, 0.14 mol of acid was produced. Acidification of a portion and sweeping through Ascarite showed it to be essentially all CO<sub>2</sub>. A similar run at pH 7.5–8.5 in the presence of ethylene glycol gave 0.47 mol of acid but only 0.10 mol of CO<sub>2</sub>. The remaining acid products (presumably glycolic or oxalic acids) were not identified. Nessler's test for ammonia was strongly positive in the first case but only weakly so in the second.

Alcohol oxidations at pH 8–10 gave small quantities of identifiable products. Isopropyl alcohol at pH 9 yielded 0.24 mol of acetone plus 0.15 mol of unidentified acids. Lesser quantities of each were formed at pH 10. Small amounts of the corresponding aldehydes were identified (by DNP derivatives and glpc retention time) from methyl, ethyl, and *n*-propyl alcohols, and the last also gave approximately 2% propionic acid.

**Attempts to Detect Singlet Oxygen.**—Decompositions were carried out in aqueous methanol buffered with ammonia (pH 8–11) in the presence of tetramethylethylene. The purple complex forms under these conditions and there is rapid evolution of oxygen. The organic layer was separated and was shown to contain small amounts of peroxidic material. For quantitative analysis, hydroperoxides were reduced with triethyl phosphite and the resulting alcohols were separated by glpc, collected, and identified by comparison with known materials. The same procedure applied to the H<sub>2</sub>O<sub>2</sub>–NaOCl reaction gave a 60–70% yield of 3-hydroxy-2,3-dimethyl-1-butene, derived from the corresponding peroxide.

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## A Nuclear Magnetic Resonance Study of the $\beta$ -cis-Ethylenediamine-N,N'-diacetatocobalt(III) Chelate System

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The complexes Na[Co(EDDA)(L)] (EDDA = ethylenediamine-N,N'-diacetate and L = oxalate and malonate) have been synthesized, and substantial yields of both the  $\alpha$ -cis and  $\beta$ -cis (previously designated *trans* and *cis*, respectively) isomers have been isolated through a series of chromatographic steps and fractional crystallizations of the tetraphenylarsonium salts. Previously only trace quantities of isomers of similar complexes having this linear tetradentate in the  $\beta$ -cis configuration have been reported even though this configuration is often encountered for other linear tetradentates such as triethylenetetramine. A study of the pmr spectra of the  $\beta$ -cis isomers of the oxalate and malonate complexes together with a reinvestigation of the spectrum of  $\beta$ -cis-Co(EDDA)en<sup>+</sup> has shown the previously reported analysis of the pmr spectrum of the  $\beta$ -cis configuration to be incorrect. The new data obtained for this chelate system have been compared with pmr data previously reported for cobalt(III) complexes of the related ligands EDTA, ethylenediaminetriacetic acid (ED3A), and  $\beta$ -aminoethyliminodiacetic acid (AEIDA). This has permitted a systematic classification of the glycine ring methylene resonances (an AB spectrum) into four categories. This classification should prove useful in future stereochemical and kinetic studies of these and related chelates. Selective isotopic substitution of these methylene protons by deuterium proved to be invaluable in this study. The use of bond anisotropy arguments to assign stereochemistry has been reevaluated.

### Introduction

Ethylenediamine-N,N'-diacetate (EDDA) and its N-substituted analogs show a high preference for the  $\alpha$ -cis<sup>3–6</sup> configuration in complexes in which a diamine ligand is used in the remaining two positions.<sup>4,5</sup> It was postulated that the low yield of  $\beta$ -cis-Co(EDDA)en<sup>+</sup>

obtained was due to greater nonbonding interactions between the amine protons of ethylenediamine with EDDA in this isomer.<sup>4,6</sup> To test this hypothesis a series of complexes has been prepared in which these steric interactions have been eliminated, Co(EDDA)L<sup>–</sup> where L is oxalate (ox) or malonate (mal). Van Saun and Douglas<sup>7</sup> reported the isolation of the  $\alpha$ -cis isomers of these complexes as well as the carbonate analog. However, in all cases less than 30% of the total yield based on moles of cobalt used was obtained. Thus it is possible that the  $\beta$ -cis isomers still remained in solution. Recently Garnett and Watts found that good yields of the  $\beta$ -cis-EDDA isomer could be obtained if the remaining two positions of the coordination sphere were occupied by carbonate, two chlorides, or two waters,<sup>6</sup> thus supporting the steric argument.

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(3) There has been no definite decision on how the various configurations of a tetradentate chelate should be designated. However it has been recently suggested<sup>6</sup> that the nomenclature introduced by A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965), for linear tetradentate ligands has wider application. Thus the designations employed by Legg, Cooke, and Douglas,<sup>4,5</sup> *trans* and *cis*, which refer to the relative positions of the terminal ligating atoms (the oxygens in the case of EDDA), become  $\alpha$ -cis and  $\beta$ -cis, respectively. These designations are used in this report.

(4) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

(5) J. I. Legg, D. W. Cooke, and B. E. Douglas, *ibid.*, **6**, 700 (1967); J. I. Legg and B. E. Douglas, *ibid.*, **7**, 1452 (1968); J. I. Legg, *Chem. Commun.*, 675 (1967).

(6) P. J. Garnett, D. W. Watts, and J. I. Legg, *Inorg. Chem.*, **8**, 2534 (1969).

(7) C. W. Van Saun and B. E. Douglas, *ibid.*, **8**, 115 (1969).

The pmr spectrum of  $\beta$ -*cis*-Co(EDDA) $\text{en}^+$  has been reported.<sup>4</sup> The analysis of the out-of-plane acetate methylene resonances showed that the chemical shifts of  $H_A$  and  $H_B$  differed by 0.40 ppm whereas in the same ring of the  $\alpha$ -*cis* isomer the difference was 0.84 ppm. Recently the synthesis and pmr spectrum of  $\text{Co}(\text{ED-3A})(\text{NO}_2)^-$  were reported.<sup>8</sup> The out-of-plane acetate arm which is analogous to the one found in the  $\beta$ -*cis*-EDDA isomers was found to have a difference between  $H_A$  and  $H_B$  of 0.74 ppm. These observations suggested that the pmr spectrum of  $\beta$ -*cis*-Co(EDDA) $\text{en}^+$  had been incorrectly assigned. It was thought that selective deuterium substitution of these methylene protons could be used to check these assignments. Such a technique has been used previously with great success in the study of these types of chelates.<sup>9,10</sup>

The preparation and study of the isomers of  $\text{Co}(\text{ED-DA})(\text{ox or mal})^-$  was thus undertaken with the expectation that large yields of the  $\beta$ -*cis* isomers would be obtained which would permit a detailed investigation of the pmr of the  $\beta$ -*cis*-EDDA chelate system.

### Experimental Section

The  $\beta$ -*cis* isomer of  $\text{Co}(\text{EDDA})\text{en}^+$  was synthesized and isolated chromatographically as previously described.<sup>4</sup> Ethylenediamine- $N,N'$ -diacetic acid was obtained from K & K Laboratories.

**Synthesis and Separation of the Isomers of Sodium Ethylenediamine- $N,N'$ -diacetato(oxalato)cobaltate(III).**—Cobalt(II) carbonate (5.2 g, 0.04 mol) and 7.0 g (0.04 mol) of ethylenediamine- $N,N'$ -diacetic acid were added to 100 ml of water and heated on a steam bath until carbon dioxide evolution ceased (about 25 min). The solution was filtered (medium frit) to remove unreacted  $\text{CoCO}_3$ . To the solution were added 5.04 g (0.04 mol) of oxalic acid dihydrate in 50 ml of water, 0.8 g (0.02 mol) of NaOH in 25 ml of water, and 4.0 g of powdered carbon (Norit-A, alkaline). Oxidation was achieved by the dropwise addition of 9.0 ml of 30%  $\text{H}_2\text{O}_2$  to the stirred mixture. The mixture was heated on a steam bath for 10 min and stirred an additional 2 hr. The carbon was removed (medium frit), and the resulting solution was passed through a cation-exchange column (200 ml of Dowex-50W-X8 in the  $\text{Na}^+$  form at a rate of 1 ml/min) to remove cationic species which inhibited crystallization of the desired products. A red band which adsorbed at the top of the column was eluted with NaCl and tentatively identified by its absorption spectrum as  $\text{Co}(\text{EDDA})(\text{H}_2\text{O})_2^+$ .<sup>11</sup>

Separation of the isomers was accomplished in two ways. During one of the syntheses the solution obtained from the cation column was chromatographed on Dowex 1-X8 anion-exchange resin (100–200 mesh) using a previously described technique.<sup>12</sup>  $\text{NH}_4\text{Cl}$  (0.02 *M*) was used as an eluent. The complex separated cleanly into the two isomers with the purple  $\alpha$ -*cis* isomer eluting prior to the mauve  $\beta$ -*cis* isomer. The absorption spectra of these solutions were used along with the pmr spectra to establish the purity of the isomers obtained by fractional crystallization. The yields of the isomers were estimated from the chromatographic elutions.

To obtain solid samples of the isomers the solution obtained from the cationic column (225–250 ml) was stirred with 14 g (0.035 mol) of tetraphenylarsonium chloride. Almost immediately upon dissolution of the salt, the fine, purple crystals

of the  $\alpha$  isomer precipitated from the solution. After standing in a refrigerator overnight, the  $\alpha$  isomer was removed by filtration and washed with a small amount of ice-cold water and then acetone. The yield was 4.5 g after air drying. The remaining solution was evaporated in a stream of air with stirring to 100 ml whereupon the mauve  $\beta$  isomer crystallized. The crystals were filtered and washed with ethanol and acetone. The air-dried yield was 1.7 g. Further evaporation to 50 ml produced an additional 4.0 g of the  $\beta$  isomer. The remaining solution could be evaporated to near dryness and triturated with ethanol to remove excess tetraphenylarsonium chloride. This produced an additional 3.2 g of the  $\beta$  isomer.

The tetraphenylarsonium salts were converted to the more soluble sodium salts by passing them through a cation-exchange column (Dowex 50W-X8 in the  $\text{Na}^+$  form). A 20:1 ratio of exchange equivalents to equivalents of complex was maintained. Evaporation of the eluents to dryness produced purple needles of the  $\alpha$  isomer and a mauve powder of the  $\beta$  isomer. The two isomers were recrystallized by dissolving them in a minimum of water at 60–65° and cooling the resulting solution in a refrigerator overnight. The products were then filtered, washed with ethanol and acetone, and air dried. *Anal.* Calcd for  $\alpha$ - and  $\beta$ -*cis*- $\text{Na}[\text{CoC}_9\text{H}_{10}\text{N}_2\text{O}_8] \cdot 2\text{H}_2\text{O}$ : C, 25.28; H, 3.71; N, 7.26. Found for  $\alpha$ : C, 25.27; H, 4.02; N, 7.27. Found for  $\beta$ : C, 25.08; H, 4.08; N, 7.40.

**Synthesis and Separation of the Isomers of Sodium Ethylenediamine- $N,N'$ -diacetato(malonato)cobaltate(III).**—The synthesis of the solution of isomers was identical with that used for the synthesis of the corresponding oxalato complex except that 4.20 g of malonic acid was used. Chromatography of the isomers was accomplished in a similar fashion except that 0.02 *M*  $\text{CaCl}_2$  was used as the eluent. The middle fractions from each component eluted were evaporated almost to dryness and stirred with a large excess of absolute ethanol. The  $\text{CaCl}_2$  dissolved leaving behind the calcium salts of the two isomers. These were filtered and washed with ethanol. The spectral properties of the isomers obtained in this fashion were identical with those obtained for the isomers isolated by fractional crystallization.

Fractional crystallization was similar to that used to obtain the isomers of oxalato complex. However, clean separation was more difficult in this case. After removing the cationic species on an ion-exchange column as previously described, 15 g of tetraphenylarsonium chloride was dissolved in the reaction solution (about 250 ml). The continuously stirred solution was evaporated in a stream of air to 225 ml and then allowed to stand for 2 hr. The deep purple crystals which formed were filtered and washed with 70 ml of ice-cold water and then with acetone. The air-dried yield of the  $\alpha$  isomer was 10.5 g. Successive evaporations to 200, 150, and 60 ml yielded on filtration 0.15, 0.70, and 2.9 g of the  $\beta$  isomer. These were washed sparingly with absolute ethanol. Further evaporation produced only mixtures of the two isomers along with tetraphenylarsonium chloride. The isomers were purified as the tetraphenylarsonium salts. The  $\alpha$  isomer was partially dissolved with stirring in 85 ml of water at 55° for about 20 min. The mixture was then cooled in an ice bath to 0°. After filtering and washing with ice-cold water and acetone, 8.4 g of pure  $\alpha$  isomer was obtained. In a similar fashion the  $\beta$  isomer was stirred with 85 ml of water at 40°. After cooling in an ice bath the product was removed by filtration and washed with ice-cold water and acetone. A yield of 2.13 g of pure  $\beta$  isomer was obtained.

The tetraphenylarsonium salts were then converted to the sodium salts by passing them through a cation-exchange column as described for the oxalato complex isomers. The eluents were evaporated to dryness, transferred to a filter with ethanol, and further washed with acetone. *Anal.* Calcd for  $\alpha$ -*cis*- $\text{Na}[\text{CoC}_9\text{H}_{12}\text{N}_2\text{O}_8] \cdot 1.5\text{H}_2\text{O}$ : C, 28.21; H, 3.95; N, 7.31. Found: C, 28.01; H, 3.49; N, 7.01. Calcd for  $\beta$ -*cis*- $\text{Na}[\text{CoC}_9\text{H}_{12}\text{N}_2\text{O}_8] \cdot 3\text{H}_2\text{O}$ : C, 26.35; H, 4.42; N, 6.83. Found: C, 26.42; H, 4.18; N, 6.72.

**Physical Measurements.**—The visible absorption spectra were recorded on a Cary Model 14 spectrophotometer. Proton

(8) G. L. Blackmer, R. E. Hamm, and J. I. Legg, *J. Am. Chem. Soc.*, **91**, 6632 (1969).

(9) J. L. Sudmeier and G. Occupati, *Inorg. Chem.*, **7**, 2524 (1968).

(10) J. B. Terrill and C. N. Reilly, *ibid.*, **5**, 1988 (1966).

(11) M. Mori, M. Shibata, E. Kyuno, and F. Maryama, *Bull. Chem. Soc. Japan*, **35**, 75 (1962).

(12) J. I. Legg and D. W. Cooke, *J. Am. Chem. Soc.*, **89**, 6854 (1967).

nuclear magnetic resonance spectra were recorded on a Varian A-60 nmr spectrometer. Deuterium oxide was used as a solvent with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (TMS\*) as an internal reference. In the base-exchange studies a few granules of  $\text{Na}_2\text{CO}_3$  were added to the nmr tube containing the sample to be investigated and the tube was shaken. In the acid-exchange studies concentrated nitric acid was added to a calculated volume of sample to give a pD of *ca.* 0.5. Good spectra of  $\text{Na}[\text{Co}(\text{EDDA})\text{ox}]$  were somewhat more difficult to obtain than spectra of the corresponding malonate complex due to lower solubility of the former. Analyses were performed by Galbraith Laboratories, Inc.

### Results and Discussion

**Synthesis and Separation of Isomers.**—The complexes were prepared by oxidation of cobalt(II) in the presence of the desired ligands using carbon as a catalyst, a procedure similar to the one used for the preparation of the diamine analogs<sup>4,5</sup> and the  $\alpha$ -*cis* isomer of oxalate and malonate.<sup>7</sup> The isomers could be isolated either by chromatography on ion-exchange resin or by fractional crystallization of the tetraphenylarsonium salts followed by ion-exchange conversion to the sodium salts. The purity of the isomers obtained by fractional crystallization could be checked by comparison of spectral properties with isomers separated chromatographically. The violet  $\alpha$ -*cis* isomer eluted prior to the mauve  $\beta$ -*cis* isomer in both cases. The same elution pattern had been observed for the isomers of  $\text{Co}(\text{EDDA})\text{en}^+$ .<sup>4</sup> Occasionally there was some difficulty in isolating pure isomers of the malonate through fractional crystallization of the tetraphenylarsonium salts. Thus it is suggested that, if pure isomers of the malonate are desired, the longer but more definitive chromatographic separation be employed using calcium chloride as an eluent.

For both the malonate and oxalate synthesis much higher yields of the  $\beta$ -*cis* isomers (ox, 30%  $\alpha$ -*cis* and 60%  $\beta$ -*cis*; mal, 70%  $\alpha$ -*cis* and 20%  $\beta$ -*cis*) were obtained than had been obtained for  $\text{Co}(\text{EDDA})(\text{en}$  or *l*-pn)<sup>+</sup>.<sup>4,5</sup> This supported the observation from molecular models that the nonbonding interactions of the amine protons of the diamines with EDDA are significantly greater in the  $\beta$ -*cis* isomers.

TABLE I  
ELECTRONIC ABSORPTION SPECTRAL DATA OBTAINED  
FOR THE COMPLEXES INVESTIGATED

		$\text{Na}[\text{Co}(\text{EDDA})\text{ox}]$	$\text{Na}[\text{Co}(\text{EDDA})\text{mal}]$
$\alpha$ - <i>cis</i>	$\lambda_1^a$ ( $\epsilon$ ) <sup>b</sup>	558 (128)	560 (134)
	$\lambda_2$ ( $\epsilon$ )	383 (145)	386 (110)
$\beta$ - <i>cis</i>	$\lambda_1$ ( $\epsilon$ )	528 (200)	526 (202)
	$\lambda_2$ ( $\epsilon$ )	385 (193)	383 (172)

<sup>a</sup>  $\lambda$  in  $m\mu$ . <sup>b</sup> Extinction coefficient.

**Electronic Absorption Spectra.**—As expected, the electronic absorption spectra, Table I, were not particularly helpful in distinguishing the isomers since both are essentially *cis*- $\text{CoN}_4\text{O}_2$ . Two observations can be made, though. First, there is a correlation between these isomers and the corresponding isomers of  $\text{Co}(\text{EDDA})\text{en}^+$  in that  $\lambda_1$  is at lower energy for the  $\alpha$ -*cis* isomers in all cases. Second, as was the case for the isomers of  $\text{Co}(\text{EDDA})\text{en}^+$ , the absorption bands of the

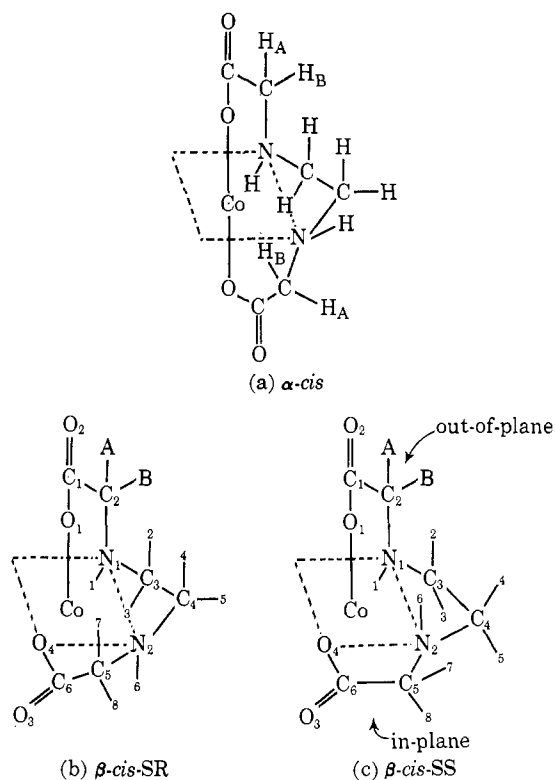


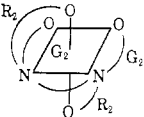
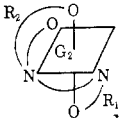
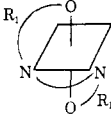
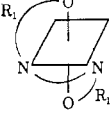
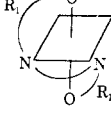
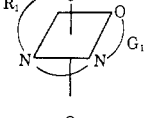
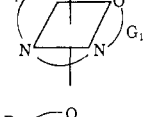
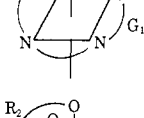
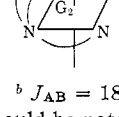
Figure 1.—Configurations of chelated ethylenediamine-*N,N'*-diacetate. (Remaining two positions occupied by a bidentate ligand.)

higher symmetry ( $C_2$ )  $\alpha$ -*cis* isomers are less intense than the corresponding bands for the  $\beta$ -*cis* isomers. Van Saun and Douglas have discussed the absorption and circular dichroism spectra of  $\alpha$ -*cis* isomers and compared them with those obtained for other  $\text{Co}(\text{III})$  complexes having EDDA in the  $\alpha$ -*cis* configuration.<sup>7</sup>

**Characterization of the Isomers by Their Proton Magnetic Resonance Spectra.**—Proton magnetic resonance offered the only certain method of distinguishing between isomer pairs. From the difference in symmetry between the isomers ( $C_2$  for the  $\alpha$ -*cis* and  $C_1$  for the  $\beta$ -*cis*) this could easily be done, Figure 1. Deuterium exchange with labilized protons on methylenes  $\alpha$  to carboxylates was used to confirm assignments.

(1) **The  $\alpha$ -*cis*-EDDA Isomers.**—The presence of a single AB pattern and a symmetrical AA'BB' pattern corresponding to the glycinate ring and ethylene backbone protons, respectively, Figures 1a and 2, confirmed the  $\alpha$ -*cis* configuration of EDDA in the purple isomers, the first to be eluted in ion-exchange chromatography. The calculated chemical shifts for the AB pattern resulting from coupling between the methylene protons of the acetate rings are given in Table II. In all cases in this study where AB patterns were found for the acetate rings, the coupling constants were 17–18 cps, consistent with what has been found previously.<sup>4,5,8–10</sup> The acetate ring data obtained for the  $\alpha$ -*cis* isomers are in agreement with those reported by Van Saun and Douglas.<sup>7</sup> The assignment of  $H_A$  and  $H_B$ , Figure 1a, to the low-field and high-field protons of the acetate ring, respectively, was previously made on the basis of

TABLE II  
GLYCINATE RING METHYLENE PROTON RESONANCE LINE ASSIGNMENTS FOR  
VARIOUS AMINECARBOXYLATE CHELATES BASED ON ETHYLENEDIAMINE<sup>a</sup>

Ligands	Stereochemistry	R-Type rings				G-Type rings	
		R <sub>1</sub> <sup>b</sup>		R <sub>2</sub> <sup>b</sup>		G <sub>1</sub>	G <sub>2</sub> <sup>b</sup>
		H <sub>A</sub>	H <sub>B</sub>	H <sub>A</sub>	H <sub>B</sub>	H <sub>A</sub>	H <sub>B</sub>
EDTA <sup>4-</sup>				3.96	3.88	3.91	3.59
				(0.08) <sup>c</sup>		(0.32)	
ED3A(NO <sub>2</sub> ) <sup>3-</sup>		4.16	3.42	4.04		4.08	3.88
		(0.74)				(0.20)	
$\alpha$ - <i>cis</i> -EDDA(en) <sup>4</sup>		4.22	3.38				
		(0.84)					
$\alpha$ - <i>cis</i> -EDDA(ox)		4.28	3.33				
		(0.95)					
$\alpha$ - <i>cis</i> -EDDA(mal)		4.20	3.25				
		(0.95)					
$\beta$ - <i>cis</i> -EDDA(en)		4.02	3.15			3.71	
		(0.87)					
$\beta$ - <i>cis</i> -EDDA(ox)		3.92	3.09			3.56	
		(0.83)					
$\beta$ - <i>cis</i> -EDDA(mal)		3.99	3.09			3.48	
		(0.90)					
<i>cis</i> -AEIDA(en) <sup>e</sup>				4.21	4.05 <sup>d</sup>	4.18	4.02 <sup>d</sup>
				(0.16)		(0.16)	

<sup>a</sup> Values in ppm from TMS\*. <sup>b</sup>  $J_{AB} = 18-19$  cps. <sup>c</sup>  $\delta_A - \delta_B$ . <sup>d</sup> The specific assignments of R<sub>2</sub> and G<sub>2</sub> are only tentative since the AB spectra are very similar. It should be noted that H<sub>A</sub> and H<sub>B</sub> have been interchanged by M. W. S. Chu, D. W. Cooke, and C. F. Liu, *Inorg. Chem.*, **7**, 2453 (1968). <sup>e</sup> See reference given in the preceding footnote.

bond anisotropy arguments<sup>4</sup> and was confirmed by deuterium exchange studies.<sup>9</sup>

It has been demonstrated that the methylene protons adjacent to a coordinated carboxylate in certain chelate systems are susceptible to deuterium substitution.<sup>9,10,13</sup> Such behavior was observed for the  $\alpha$ -*cis* isomers. Furthermore in acid solution selective deuteration of H<sub>A</sub>, the less sterically hindered proton (Figure 1a), was observed as had been noted for analogous complexes by Sudmeier and Occupati.<sup>9</sup> The resonances for this proton disappeared more rapidly than those of H<sub>B</sub> with a temporary appearance of a resonance at 3.33

(13) D. H. Williams and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 4644 (1965).

ppm corresponding to the expected position of decoupled H<sub>B</sub>. The  $\alpha$ -*cis*-Co(EDDA)mal<sup>-</sup> isomer also exhibited a sharp resonance corresponding to the malonate methylene protons at 3.43 ppm, Figure 2. In basic solution (Na<sub>2</sub>CO<sub>3</sub>) this disappeared in less than 1 min leaving a spectrum very similar to that of the  $\alpha$ -*cis* oxalate.

(2) **The  $\beta$ -*cis* Isomers.**—The analysis of the pmr spectra of the  $\beta$ -*cis* isomers was the primary goal of this project and led to the reassignment of the spectrum previously reported for  $\beta$ -*cis*-Co(EDDA)en<sup>+</sup>.<sup>4</sup> The spectra obtained for these isomers and the ethylenediamine analog are shown in Figures 3–8. The analysis of the spectra showed either that only one

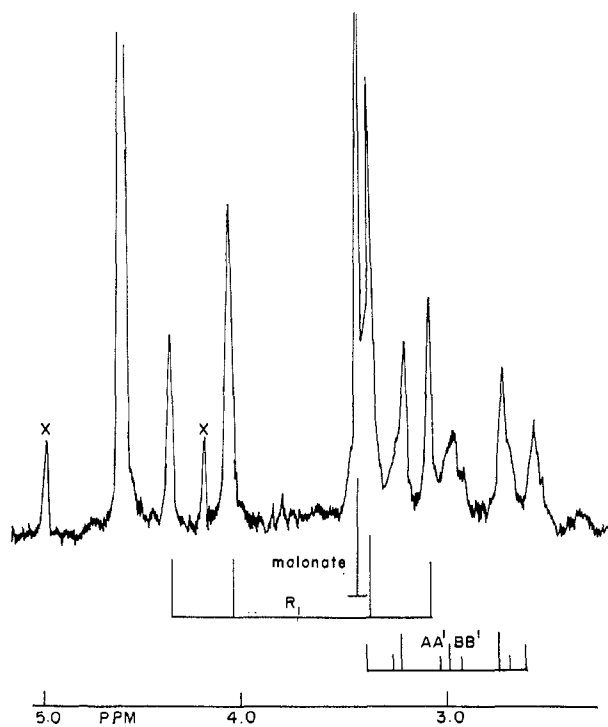


Figure 2.—Pmr spectrum of a freshly prepared  $D_2O$  solution of  $\alpha$ -cis-Co(EDDA)mal $^-$ .

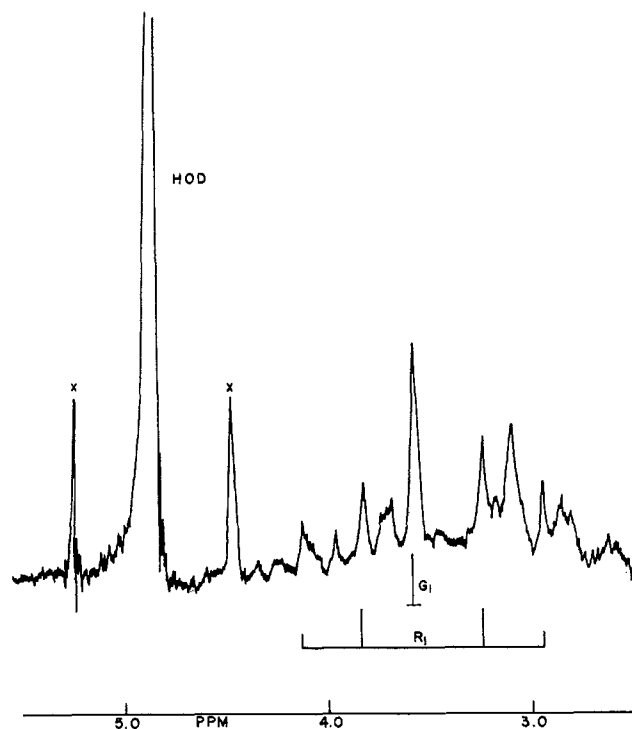


Figure 4.—Pmr spectrum of a  $D_2O$  solution of  $\beta$ -cis-Co(EDDA)-ox $^-$  after addition of  $HNO_3$  (1 hr).

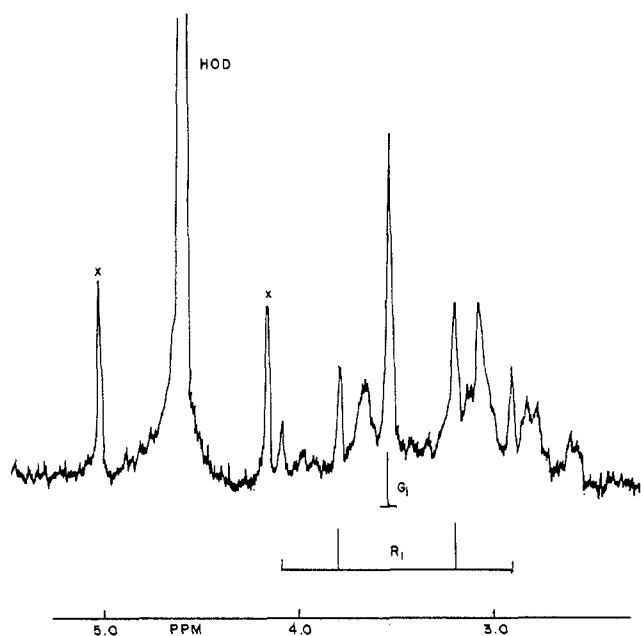


Figure 3.—Pmr spectrum of a freshly prepared  $D_2O$  solution of  $\beta$ -cis-Co(EDDA)ox $^-$ .

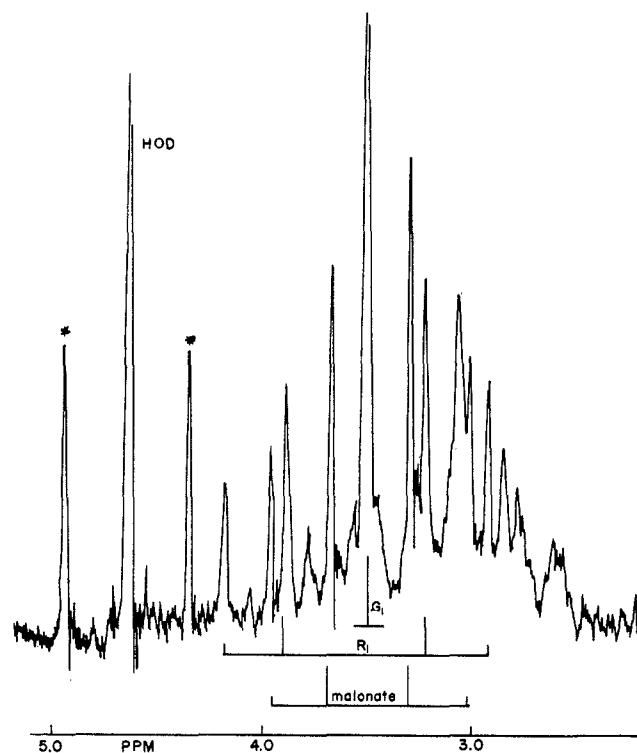


Figure 5.—Pmr spectrum of a freshly prepared  $D_2O$  solution of  $\beta$ -cis-Co(EDDA)mal $^-$ .

configuration of the in-plane glycinate (Figure 1b, c) was present or that one configuration was highly favored (*vide infra*).

(a)  $\beta$ -cis-Co(EDDA)ox $^-$ .—The spectrum of  $\beta$ -cis-Co(EDDA)ox $^-$  (henceforth  $\beta$ -cis-ox) appears similar to the spectrum of  $\beta$ -cis-Co(EDDA)en $^+$  (henceforth  $\beta$ -cis-en) except that the first three sharp low-field resonances are shifted to higher field by about 0.10 ppm in the former, Figures 3 and 8. (It should be kept in mind that the spectrum of  $\beta$ -cis-en contains the resonances associated with the ethylenediamine, an ABCD

pattern; otherwise it would be expected to be quite similar to the spectrum of  $\beta$ -cis-ox. It is this factor that made the original assignment of  $\beta$ -cis-en difficult.) The strong resonance at 3.71 ppm in  $\beta$ -cis-en has been assigned to the in-plane  $-CH_2-$  protons (Figure 1).<sup>4</sup> As pointed out these protons appear to be symmetrically disposed with respect to the carbonyl group (O(3)-

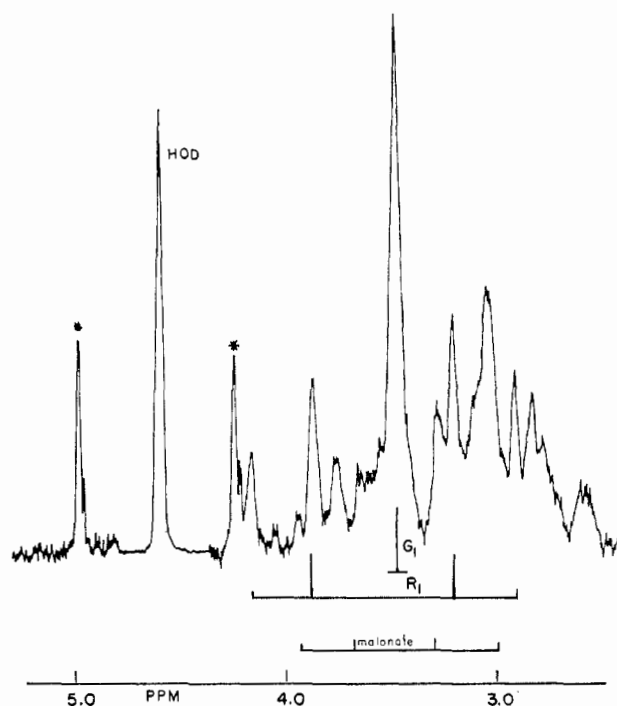


Figure 6.—Pmr spectrum of a  $D_2O$  solution of  $\beta$ -*cis*-Co(EDDA)-mal<sup>-</sup> after addition of  $Na_2CO_3$  (5 min).

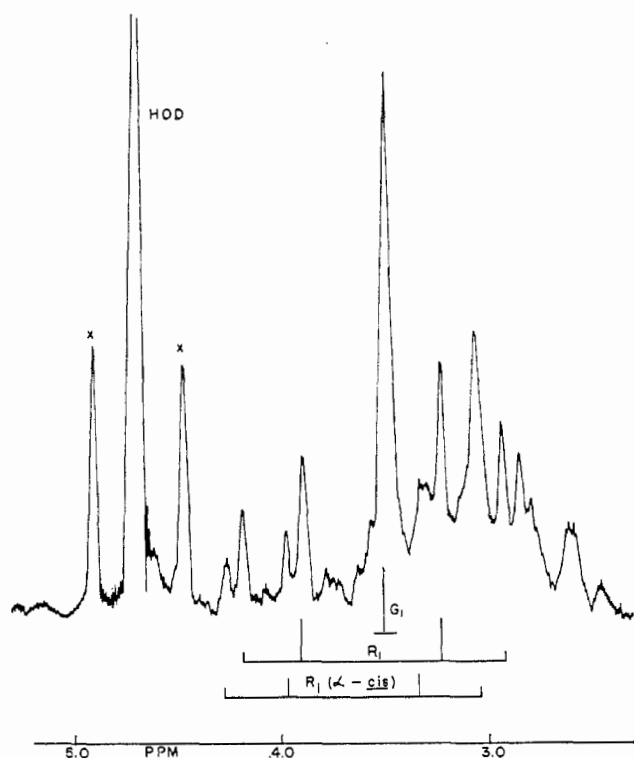


Figure 7.—Pmr spectrum of a  $D_2O$  solution of  $\beta$ -*cis*-Co(EDDA)-mal<sup>-</sup> after addition of  $HNO_3$  (ca. 1.5 days).

C(6), Figure 1) and more symmetrically disposed with respect to the bond C(4)-N(2) than is the corresponding out-of-plane  $-CH_2-$  to C(3)-N(1). Glycinate rings quite similar to this one are found in *trans*-Co(IDA)-dien<sup>+</sup>.<sup>14</sup> Both sets of acetates in the meridionally spanning iminodiacetate yield spectra which show that

(14) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

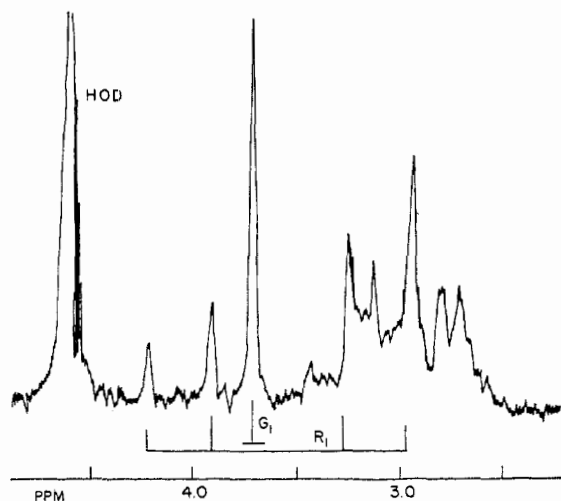


Figure 8.—Pmr spectrum of a freshly prepared  $D_2O$  solution of  $\beta$ -*cis*-Co(EDDA)en<sup>+</sup>.

$H_A$  and  $H_B$  are almost in identical environments. Thus it seems reasonable that the corresponding strong resonance occurring at 3.53 ppm in  $\beta$ -*cis*-ox belongs to the in-plane  $-CH_2-$  group in this isomer. This assignment is further substantiated by the fact that this peak was not affected by conditions which brought about deuterium exchange of the out-of-plane acetates (*vide infra*).

On the addition of  $HNO_3$  to  $\beta$ -*cis*-ox (after the amine protons had exchanged in neutral solution) the resonances at 4.09 and 3.79 ppm begin to decrease. At the same time the resonances at 3.20 and 2.91 ppm decrease and a broadening and increase in size of the resonance at 3.08 ppm take place, Figure 4. At this stage, then, partial deuteration of  $H_A$ , Figure 1b (or c), has occurred in the same manner as was observed for the  $\alpha$ -*cis*-EDDA isomers. Thus the assignment of the AB spectrum expected for the out-of-plane ring  $-CH_2-$  protons would be 4.09, 3.79, 3.20, and 2.91 ppm as shown in Figures 3 and 4. The calculated chemical shifts for  $H_A$  and  $H_B$  are shown in Table II. The calculated position of  $H_B$ , 3.09 ppm, is in agreement with the broadening of the resonance at 3.08 ppm observed during the deuterium exchange. If the acidified solution is heated at 55° for several days, these peaks decrease further and resonances belonging to  $\alpha$ -*cis* isomer begin to appear. After 3 days complete conversion to the  $\alpha$ -*cis* isomer occurs.

Terrill and Reilley have shown that the more strained in-plane glycinate ring of Co(EDTA)<sup>-</sup> does not exchange its  $-CH_2-$  protons directly with  $D_2O$ .<sup>10</sup> The in-plane glycinate ring of  $\beta$ -*cis*-ox is expected to be sterically similar and as expected the resonance at 3.53 ppm assigned to  $-CH_2-$  protons of this ring did not decrease in acid. However, in base some decrease was noted after about 4 hr.

(b)  $\beta$ -*cis*-Co(EDDA)mal<sup>-</sup>.—The spectrum of  $\beta$ -*cis*-Co(EDDA)mal<sup>-</sup> (henceforth  $\beta$ -*cis*-mal) is shown in Figure 5. The spectrum quite obviously appears to be more complex than those observed for the other  $\beta$ -*cis*-EDDA isomers. Examination of molecular models shows that the malonate can assume several conform-

mations. These have been discussed in some detail.<sup>15</sup> In one of these there is a close interaction between a malonate proton and the EDDA amine proton, H(1), Figure 1b or c. In addition even if the malonate were changing conformations rapidly, it would be doing so in an asymmetrical environment. Thus an AB pattern is expected for the methylene protons of the malonate. On the addition of base ( $\text{Na}_2\text{CO}_3$ ) the resonances at 3.96, 3.67, 3.30, and 3.00 ppm disappear rapidly (5 min), Figure 6. The methylene protons of malonate chelated to Co(III) have been found to be exceptionally labile to deuteration.<sup>16</sup> This is due apparently to the relatively high acidity expected for these protons. From these observations these four resonances can be assigned to the malonate ring. These protons almost completely exchange in neutral solution within 3 hr. The calculated chemical shifts for the two protons are 3.76 and 3.17 ppm. The center is at 3.46 ppm which is close to the resonance (3.43) observed for the malonate in the corresponding  $\alpha$ -cis isomer, Figure 2.

The malonate-exchanged spectrum of  $\beta$ -cis-mal, Figure 6, bears a close resemblance to that of  $\beta$ -cis-ox, Figure 3, as expected; and the in-plane and out-of-plane resonances can be assigned without difficulty as shown in Figures 5-7. In acid the out-of-plane resonances show selective exchange in the same fashion as was observed for  $\beta$ -cis-ox. The in-plane resonance remains as expected. On heating the acidified solution at 55° for 1 day the beginning of conversion to the  $\alpha$ -cis isomer is observed, Figure 7. Conversion is completed in 3 days.

(c) **Reassignment of  $\beta$ -cis-Co(EDDA)en**.—The previous assignment of the out-of-plane acetate in  $\beta$ -cis-en, 4.02 and 3.62 ppm,<sup>4</sup> should be reexamined since the latter resonance,  $H_B$ , differs considerably from that of  $H_B$  found for  $\beta$ -cis-ox and  $\beta$ -cis-mal (3.09 ppm). Also the integration previously reported showed that there were 3.5 protons in the region from 4.22 to 3.43 ppm whereas the assignment made with one inner resonance coincident with the resonance attributed to the in-plane acetate required four protons in this region.

On comparison of the spectrum of  $\beta$ -cis-en to the corresponding oxalate and malonate isomer spectra (Figures 3-8), it becomes evident that the high-field portion of the out-of-plane acetate AB pattern of  $\beta$ -cis-en should be found in the region of the spectrum attributed to the ethylene backbone of EDDA and ethylenediamine. In either acid or base the resonances at 4.22, 3.92, and 3.40 ppm decrease. The remaining resonance of the AB quartet would be located under the strong peak at 2.94 ppm and would not be observed in the exchange. The new assignment of the out-of-plane methylene proton resonances is then 4.22, 3.92, 3.40, and 3.10 ppm as shown in Figure 8. The calculated chemical shifts are summarized in Table II. The integration was checked by weighing the various portions of the spectra. The following results were ob-

tained: peaks at 4.22 and 3.92 ppm, 0.97 proton (required 1.00); peak at 3.71 ppm, 1.85 protons (required 2.00); peaks from 3.43 to 2.50 ppm, 9.26 protons (required 9.00). Thus the integration is in agreement with the new assignment. It is seen that this assignment is much more consistent with those made to the other  $\beta$ -cis isomers.

(d) **The Question of the Asymmetric In-Plane Nitrogen in the  $\beta$ -cis Isomers**.—Isomers resulting from the two possible placements of the planar nitrogen, N(2), Figure 1b and c, were first reported and discussed by Buckingham and coworkers<sup>17,18</sup> for complexes with a similar linear tetradentate ligand, triethylenetetramine. The pmr spectra of the  $\beta$ -cis isomers can be analyzed in terms of one isomer. It would be very unlikely that both  $\beta$ -cis-SR (or  $\beta$ -cis-RS) and  $\beta$ -cis-SS (or  $\beta$ -cis-RR) would have identical spectra. A free energy difference between the two forms of as little as 1.8 kcal mol<sup>-1</sup> would still result in a predominance of 95% of one form. It would not be possible to detect with any certainty 5% or less of the other isomer in the pmr spectrum. As previously noted  $\beta$ -cis-ox and  $\beta$ -cis-mal isomerize completely when heated in acid solution to the corresponding  $\alpha$  isomers. Assuming that the planar amine proton, H(6), remains intact in acid solution,<sup>17</sup> then it seems likely that SS and RR are the isomers present since the RS and SR isomers would require inversion at the nitrogen center, N(2).

**Correlation of the Proton Magnetic Resonance Spectra of the EDTA, ED3A, EDDA, and AEIDA Chelates**.—A complete listing of glycinate methylene resonances for the various complexes of EDTA, ED3A, EDDA, and AEIDA ( $\beta$ -aminoethyliminodiacetate)<sup>19</sup> which have been characterized are listed in Table II. The glycinate rings can be divided into four groups: two types of out-of-plane acetates, one which is attached to a secondary amine,  $R_1$ , and one which is attached to a tertiary amine having an additional chelated glycinate attached,  $R_2$ ; and two types of in-plane glycinates,  $G_1$  and  $G_2$ , classified in the same manner as the R rings. Each type of proton has a characteristic location and range, the maximum range, 0.36 ppm, being exhibited by  $H_A$  of the  $R_1$  rings. Also in the cases where an AB spectrum is observed there is a characteristic chemical shift between  $H_A$  and  $H_B$  shown in parentheses in Table II: 0.7-0.9 ppm for  $R_1$  rings, 0.2-0.3 ppm for  $G_2$  rings, and 0-0.2 ppm for  $R_2$  rings. These characteristics, particularly the latter, should be useful in the characterization of isomers of these complexes not yet found and isomers of complexes of related ligands. For example one of the other isomers of  $\text{Co}(\text{ED3A})\text{NO}_2^-$  where  $R_1$  becomes a  $G_1$  ring should show a single resonance occurring somewhere between 3.48 and 3.71 ppm.

The remaining isomer of  $\text{Co}(\text{ED3A})\text{NO}_2^-$  where the two acetates attached to the tertiary amine are *trans* (the remaining secondary amine acetate must then be a  $G_1$  ring) has two sets of methylene protons in a similar

(15) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Australian J. Chem.*, **20**, 257 (1967).

(16) H. Yoneda and Y. Morimoto, *Inorg. Chim. Acta*, **1**, 413 (1967); L. A. Dressel and J. G. Brushmiller, private communication.

(17) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

(18) L. G. Marzilli and D. A. Buckingham, *ibid.*, **6**, 1042 (1967).

(19) M. W. S. Chu, D. W. Cooke, and C. F. Liu, *ibid.*, **7**, 2453 (1968).

environment which is different from any of those just discussed. This isomer is comparable to *trans*-Co(AEIDA)en<sup>+</sup><sup>19</sup> and *trans*-Co(MIDA)dien<sup>+</sup>.<sup>14</sup> The latter two isomers have similar resonances for the methylene protons falling in the ranges 3.96–4.06 and 4.23–4.43 ppm. It would be predicted, then, that this “*trans*” isomer of Co(ED3A)NO<sub>2</sub><sup>-</sup> would have resonances at about 4.00 and 4.30 ppm for both acetates. It should be pointed out that this isomer was not discussed in the original report on the Co(ED3A)NO<sub>2</sub> system.<sup>8</sup>

Finally, it should be noted that although for a given type of complex, H<sub>A</sub> and H<sub>B</sub> have similar resonance frequencies (see, for example, the *α-cis*-EDDA isomers), there is a considerable range within the list given. Bond anisotropy arguments have been used to relate and assign spectra to these and related complexes.<sup>4,8,14</sup> However, some caution should be observed when doing this because these rings, although similar, should differ somewhat due to changes in ring strain. For example, the G<sub>2</sub> rings in Co(EDTA)<sup>-</sup> and Co(ED3A)NO<sub>2</sub><sup>-</sup> are expected to differ due to such a change as previously discussed.<sup>8</sup> Bond anisotropy arguments were used to justify the original assignment made to *β-cis*-Co(EDDA)en<sup>+</sup> by comparing its spectrum to that of Co(EDTA)<sup>-</sup><sup>4</sup> and comparing the chemical shifts to those obtained on N-alkyl substitution of EDDA in the *α-cis*

isomers. The only proton which has been shown to be significantly different in the new assignment made in this study is H<sub>B</sub> of the R<sub>1</sub> ring, but this gives a shift on “alkyl substitution” (see Table V of ref 4) of +0.73 ppm which is not in as good agreement as the previously obtained value. It should also be noted that anisotropy related to the other bonds, metal–ligand and N–H and C–H, has been assumed to be of secondary importance in these studies, and there seems to be some justification for this.<sup>10</sup> Terrill and Reilley invoked an electron orbital interaction to explain the glycinate rate chemical shifts observed for Co(CyDTA)<sup>-</sup>,<sup>10</sup> and Sudmeier and Occupati<sup>9</sup> have pointed out that steric compression should also be considered. Experimental techniques such as isotopic deuterium exchange and H–N–C–H spin–spin coupling<sup>8,9,12</sup> have been of great value in defining the extent to which bond anisotropy arguments can be used and in the study of aminocarboxylate chelates in general.

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