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# Stereospecific Ligands and Their Complexes. I. A Cobalt(III) Complex of Ethylenediaminedisuccinic Acid<sup>1</sup>

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Although ethylenediaminedisuccinic acid (EDDS) is isomeric with EDTA, the former is distinctive because of its ability to form five- and six-membered chelate rings and because its two asymmetric carbon atoms impose a stereospecificity upon chelation. The reaction of L-aspartic acid with 1,2-dibromoethane affords optically active EDDS which can be used with sodium tris(carbonato)cobaltate(III) to generate the sodium salt of  $\text{Co(EDDS)}^-$  of one absolute configuration in at least 75% yield. The optical rotatory dispersion curve of the sodium salt in water exhibits its strongest rotations at  $17,360\text{ cm}^{-1}$  ( $[\text{M}] - 4300$ ) and  $19,530\text{ cm}^{-1}$  ( $[\text{M}] 8000$ ). That the EDDS is functioning as a hexadentate ligand with pairwise equivalence of the carboxylate rings is demonstrated by pH and infrared studies and by a detailed analysis of the proton magnetic resonance spectrum. The  $\text{Co(EDDS)}^-$  salt exhibits a visible spectrum similar to that of  $\text{Co(EDTA)}^-$  but EDDS imposes a stronger crystal field on the metal ion.

## Introduction

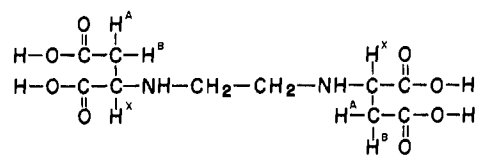
Complexes of ethylenediaminetetraacetic acid (EDTA) and of other carboxylic acids have served as vehicles for an impressive number and variety of studies<sup>3,4</sup> including those of thermochemical,<sup>5,6</sup> kinetic,<sup>7,8</sup> and stereochemical orientations.<sup>8-11</sup> Particularly fruitful information of a geometrical and stereochemical nature has resulted from the application of X-ray diffraction and proton magnetic resonance (pmr) techniques to several of these complexes.<sup>12-17</sup> The results of structure determinations performed on single crystals containing complexes of EDTA or related ligands have provided pivotal data leading to some understanding of the influence of ligand configuration on the geometry and coordination numbers of chelates. Complimentary information pertaining to the conformation and properties of five-membered chelate rings has resulted from pmr studies.

In the case of  $\text{Co(EDTA)}^-$ , a particularly detailed picture of the configuration is available because the results of an X-ray diffraction study and of pmr investigations are available.<sup>13-16</sup> Both the solid and solution data indicate that the ethylenic backbone of

$\text{Co(EDTA)}^-$  is locked in one conformation and that the four glycine rings may be classified into two groups. One group consists of two relatively strained glycine units which serve the donor positions in the plane containing the nitrogen and cobalt atoms (equatorial plane) whereas the other two glycine moieties are unstrained while providing oxygen donors for the out-of-plane positions (axial). The consequences of the conformational restrictions in the ethylenic backbone for ligands of the EDTA type have been elegantly demonstrated with optically active 1,2-propylenediaminetetraacetic acid (PDTA) and *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA) in that both of these reagents impose a stereospecificity upon chelation.<sup>8,11</sup> Both PDTA and CDTA are representative of the same general variation on the EDTA framework, namely, replacement of one or more hydrogen atoms on the ethylenic unit.

Another type of modification with stereochemical potential arises if carbon atoms are allowed to serve in more than one chelate ring. This branching at a carbon atom is characteristic of several tridentate amino acids including histidine, aspartic acid, and 2,3-diaminopropionic acid. For these acids, the carbon atoms at which the branching occurs are also asymmetric centers. Consequently, the stereochemistry and properties of complexes derived from these ligands are strongly dependent on the absolute configuration at the optically active carbon atom.<sup>17-19</sup>

It is from the class of acids to which the foregoing tridentate ligands belong that a potentially hexadentate chelating agent, ethylenediaminedisuccinic acid (I,



N,N'-ETHYLENEDIAMINEDISUCCINIC ACID (EDDS)

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EDDS), was selected for the study reported here. EDDS is closely related to aspartic acid and is isomeric with EDTA not only with respect to empirical formula but also with respect to two amine donor atoms and four carboxylate oxygen donors. It is however, distinctive in several important respects. EDDS has secondary rather than tertiary amines, its carboxylate arms may be divided into two groups, one of which forms six-membered chelate rings upon coordination and the other of which forms five-membered rings, and it possesses two optically active centers. When the two asymmetric carbon atoms have the same optical configuration, restrictions on the mode of hexadentate chelation are such that only two absolute conformations for the chelate are allowed. One has both six-membered carboxylate rings serving equatorial sites with the five-membered rings serving axial sites (case I, Figure 1) whereas the other has the five-mem-

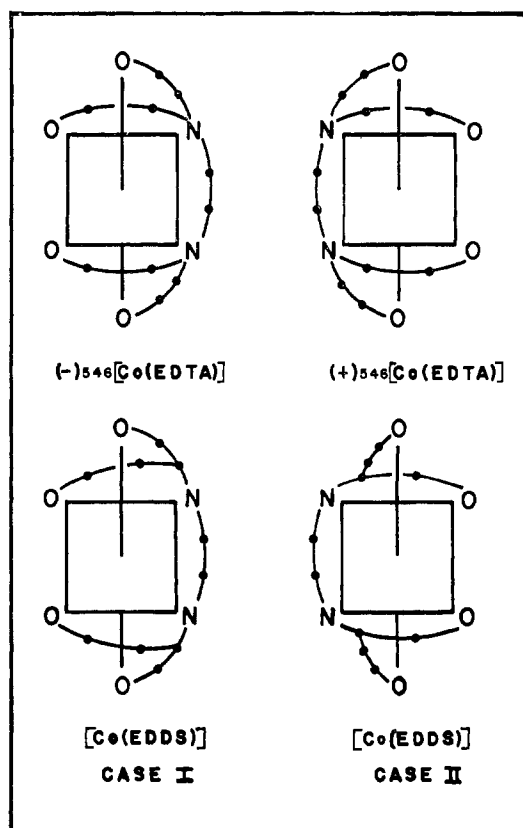


Figure 1.—Absolute configurations of the two geometrical isomers of  $\text{Co}(\text{EDDS})^-$  compared to the two optical isomers of  $\text{Co}(\text{EDTA})^-$ . See text for discussion.

bered rings in the equatorial sites with the six-membered ones in the axial (case II, Figure 1). In either of these two conformations the metal ion will be an asymmetric center and the complex or complexes formed will therefore show optical activity beyond that expected from the presence of an optically active center in a chelate ring.<sup>20</sup> Of the two possible configurations, the one with both six-membered rings in the equatorial sites might be favored because of the work on

$\text{Co}(\text{EDTA})^-$  which has shown marked strain in the equatorial five-membered rings.<sup>16</sup> We report here the nature of the hexadentate complex of EDDS with trivalent cobalt. Majer and his coworkers were the first to report EDDS as well as the stability constants and electronic spectra of several of its complexes. However, that report leaves the stereochemistry for both the ligand and its complexes essentially untouched.<sup>21</sup>

### Experimental Section

**Reagents.**—All reagents and solvents were obtained commercially and used without further purification. The  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  was prepared by the method of Bauer and Drinkard.<sup>22</sup>

**Preparation of EDDS.**—EDDS was prepared by a modification of the method of Majer, *et al.*<sup>21</sup> A solution of sodium L-aspartate was prepared by dissolving NaOH (64.0 g, 1.6 mol) and L-aspartic acid (106.4 g, 0.8 mol) in 500 ml of water at ice-bath temperature. Sodium carbonate (42.4 g, 0.4 mol), 600 ml of 95% ethanol, and 500 ml of water were added to the sodium aspartate solution contained in a 2-l. three-necked flask fitted with a water condenser and a thermometer. The reaction mixture was heated to reflux with stirring and then 11 ml of 1,2-dibromoethane was added dropwise to the clear solution. An additional 5 ml was added dropwise every 30 min to a total of 41 ml (19% excess). After the reaction mixture had refluxed for 20 hr from the time 1,2-dibromoethane was first added, enough of the liquid was allowed to distil out of the mixture so that the boiling point reached 85°. At this point the distillation was stopped and the mixture was refluxed for 30 min. Two more incremental distillations followed by 30 min of refluxing were repeated for boiling temperatures of 90 and 93°. Following the last refluxing period, enough liquid was distilled so that a boiling temperature of 100° was reached. The hot reaction mixture was filtered, cooled to 20°, vigorously stirred, and slowly acidified with concentrated hydrochloric acid to pH 3.5. Usually fine white crystals of EDDS appeared between pH 7 and 3.5. If necessary, crystallization can be induced by acidifying to pH ~2 or swirling with activated charcoal, filtering, and cooling to about 0°. The EDDS was collected on a Büchner funnel and then redissolved in NaOH solution. Precipitation was repeated by addition of acid to pH 3.5. This process was repeated twice more. The final crop of EDDS was washed at room temperature in a stirring water slurry to remove HCl and any traces of L-aspartic acid. The product was then collected and dried first in a stream of dry air and then at 65° for 5 hr at 1 mm; yield, 30 g (25%). *Anal.* Calcd for  $\text{EDDS} \cdot \text{H}_2\text{O}$ : C, 38.74; H, 5.81; N, 9.04. Found: C, 38.69, 38.86; H, 5.96, 6.03; N, 8.99, 9.23.

**Preparation of  $\text{Na}[\text{Co}(\text{EDDS})] \cdot \text{H}_2\text{O}$ .**—EDDS (3.10 g, 10 mmol) was added with stirring to a cold slurry of  $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$  (3.63 g, 10 mmol) and 3 g of activated charcoal in a minimal (~75 ml) amount of water. After the addition, the reaction mixture was allowed to warm to room temperature and was kept at that temperature until evolution of  $\text{CO}_2$  ceased. The mixture was then heated on a steam bath and acetic acid (as 5% solution) was added as necessary to maintain  $\text{CO}_2$  evolution. After  $\text{CO}_2$  evolution stopped completely, concentrated NaOH solution was added to pH ~8 and heating was continued another 5 min. Then acetic acid was added to pH ~4.5 and the solution was filtered to remove charcoal. The solution was heated to about 77° and ethanol was added until a very few small crystals were observed. At this point the solution was set aside to cool slowly. Very hygroscopic crystals were obtained. The mother liquor was partially evaporated to obtain a second crop. This was repeated for a third crop. Each crop was purified by repeated recrystallization from water-ethanol solution; yield, 2.78 g (75%). The crystals were dried in a stream of dry air and finally

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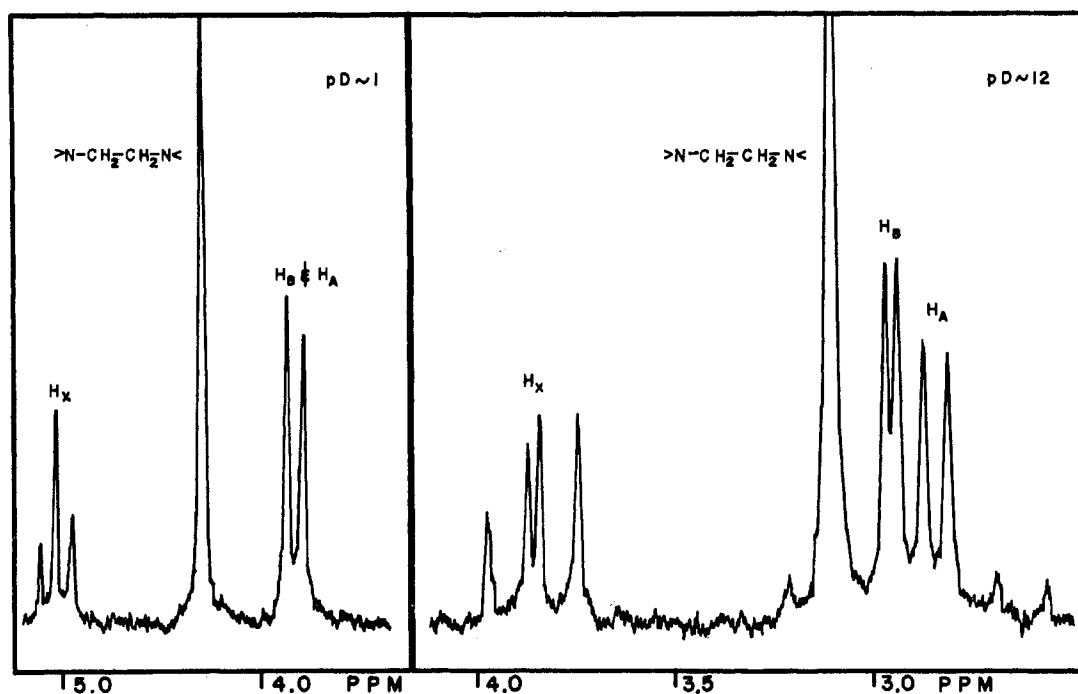


Figure 2.—The pmr spectra of EDDS in  $D_2O$  ( $pD \sim 12$  and  $\sim 1$ ). All measurements are in ppm downfield from external TMS.

at  $\sim 1$  mm over  $P_2O_5$  at  $100^\circ$  for 8 hr. This process yielded the monohydrate salt which could be converted to the anhydrous substance by drying an additional 8 hr at  $\sim 1$  mm and  $100^\circ$ . *Anal.* Calcd for  $Na[Co(EDDS)]$ : C, 32.42; H, 3.24; N, 7.57. Found: C, 32.31; H, 3.42; N, 7.74. The monohydrate and the "dry" salt proved to be chemically similar and the former was used for solution studies because it is easier to maintain with constant composition. Note: nucleation is difficult to achieve and cooling a nearly saturated solution may result in a colloidal precipitate, particularly if large amounts of ethanol are needed to compensate for an excess of  $H_2O$ . Normally, well-formed crystals will result from 60–75% ethanol and nucleation can be achieved by stirring the hot solution.

**Physical Measurements.**—Electronic spectra were recorded at room temperature in 2.5-cm cells using a Cary Model 14 spectrophotometer. A Du Pont Model 310 curve resolver was used to assist the analysis of the visible spectra. Infrared absorption spectra of Nujol or Fluorolube mulls between KBr plates were recorded on a Beckman Model 10 spectrophotometer. Proton magnetic resonance spectra of 10–15% (w/v) solutions in  $D_2O$  were analyzed using Varian Models A-60 and HA-60/DA-60 instruments. A capillary tube containing TMS was used to establish an external reference and the pD's of the solutions were estimated by adding specified amounts of NaOH and HCl to the  $D_2O$  solutions. A program provided by B. J. Nist, in conjunction with an IBM 7040/7094 computer system, was utilized for calculation of theoretical pmr spectra. Optical rotatory dispersion spectra were recorded at room temperature in 2.5-cm cells using a Cary Model 60 spectrophotometer. Circular dichroism spectra were recorded at room temperature in 1-cm cells using a Model ORD/UV-5 Japan Spectroscopic Co., Ltd., spectrophotometer. Elemental analyses were determined by Alfred Bernhardt Mikroanalytisches Laboratorium, Engelskirchen, West Germany.

### Results and Discussion

**Characterization of EDDS.**—A titration curve of an  $EDDS \cdot H_2O$  solution exhibits inflection points at pH values of 5.5 and 8.8. Formula weights of 305 and 310 (theory 310) are calculated from this data if the two inflections are presumed to reflect the removal of the

second and third protons of EDDS. Assignment of these inflections to any other combination of protons leads to calculated formula weights which are not internally consistent. The infrared spectrum of EDDS exhibits the expected similarities to that of aspartic acid. The predominant features of both spectra along with probable band assignments are summarized in Table I. Although the  $985\text{-cm}^{-1}$  absorption band of aspartic acid is unassigned in the table, it is included because its presence provides a convenient means of detecting aspartic acid as an impurity in EDDS.

TABLE I  
INFRARED SPECTRA ( $\text{cm}^{-1}$ ) OF ASPARTIC ACID, EDDS,  
AND  $Co(EDDS)^{-a,b}$

L-Aspartic acid <sup>c</sup>	EDDS	$Co(EDDS)^-$	Assignment
1684 s	1713 s		Asym C=O str of COOH
1639 s	1630 s		$-NH_2^+$ , $-NH_2^+$ def
1597 s	1560 s	1640 vs <sup>d</sup> 1560 vs	Asym C=O str of $COO^-$
1506 m			$-NH$ def <sup>e</sup>
1370 w	1340 m	1380 s 1365 s	Sym C=O str of $COO^-$
985 m		875 m 710 w	Unassigned

<sup>a</sup> Abbreviations: vs, very strong; s, strong; m, medium; w, weak. <sup>b</sup> Nujol mulls. <sup>c</sup> J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, Chapter 3. <sup>d</sup> See text for discussion of assignments.

The proton magnetic resonance spectra of EDDS in basic and acidic  $D_2O$  are shown in Figure 2. The multiplet structure in each is due to the protons of the aspartic acid moiety of EDDS (see I). Each pair of these arms bears an asymmetric carbon which causes the protons labeled A and B in I to be nonequivalent.

Coupling of these nonequivalent protons with the lone hydrogen on the asymmetric carbon leads to the expectation of an ABX pattern. Moreover the ligand is chemically symmetrical and a single ABX pattern is expected. A singlet is anticipated from the ethylenic protons of uncomplexed EDDS. In basic solution, the large singlet at 3.12 ppm is confidently assigned to the ethylenic backbone, and, as required, it has a relative area of 4, compared to that of 6 for all of the rest of the resonances observed. Furthermore its area is twice that of the downfield quartet centered at 3.87 ppm and equal to that of the two overlapping quartets upfield from it. The downfield quartet is assigned to the X proton of I and the two upfield quarters are assigned to the A and B protons with that at the uppermost field arbitrarily assigned as A. Using the methods outlined by Wiberg and Nist for determining the chemical shifts and coupling constants for an ABX pattern, the values in Table II are calculated. The values were tested by comparing the ABX pattern generated with the computer to those obtained experimentally; this comparison is shown in Table III.

TABLE II  
COUPLING CONSTANTS AND CHEMICAL SHIFTS FOR PROTONS  
OF EDDS AND Co(EDDS)<sup>-</sup>

	EDDS pD ~1	EDDS pD ~12	Co(EDDS) <sup>-</sup> pD ~7
$\delta_{N-CH_2-CH_2-N^a}$	4.29	3.12	3.41 <sup>b</sup>
$\delta_A$	3.83	2.82	3.37
$\delta_B$	3.85	2.98	3.60
$\delta_X$	5.03	3.87	3.96
$J_{AX}^c$	5.96	8.63	2.40
$J_{BX}$	3.38	4.91	4.60
$J_{AB}$	15.16	15.16	18.30

<sup>a</sup> All chemical shifts,  $\delta$ , reported in ppm downfield from external TMS. <sup>b</sup> Center of A<sub>2</sub>B<sub>2</sub> pattern; resonances at 3.036, 3.077, 3.096, 3.159, 3.241, 3.586, 3.661, 3.724, 3.744, and 3.789 ppm. <sup>c</sup> Coupling constants,  $J$ , in cps.

represent an ABX pattern in which protons A and B are in very similar chemical environments. The theoretically predicted A and B quartets are each observed as only one line because (1) the center resonances have nearly identical frequencies (see Table II) and (2) the satellites have very nearly zero intensities. The quartet for the X proton has collapsed to an apparent triplet because  $J_{AB} \gg (\nu_A - \nu_B) + [(J_{AX} - J_{BX})/2]$ .<sup>23</sup> Owing to this particular combination of chemical shifts and coupling constants, only eight of the fifteen theoretical lines have observable intensities (Table III). In addition, three pairs of those eight lines are expected at frequencies which are experimentally indistinguishable. Thus only five lines of the ABX pattern in acidic solution are observed (see Figure 2, Table II, and Table III).

The EDDS prepared as described in the Experimental Section exhibits a molecular rotation,  $[M] -680$ , in aqueous 6 *N* hydrochloric acid at 17,000 cm<sup>-1</sup>. The fact that the reaction of 1,2-dibromoethane with L-aspartic acid would not be expected to invoke attack at the asymmetric atom provides strong chemical evidence for retention of configuration at the optically active site. Thus the EDDS from L-aspartic acid is expected to have both of its optically active carbon atoms exhibit the L configuration corresponding to that of the parent acid. This assumption forms the basis for the absolute configurations of Co(EDDS)<sup>-</sup> shown in Figure 1. Any reference to EDDS in this report refers only to that product derived from L-aspartic acid.

**The Co(EDDS)<sup>-</sup> Complex.**—As is noted in the Experimental Section, the preparation of Na[Co(EDDS)]·H<sub>2</sub>O from the free acid and tris(carbonato)cobaltate(III) is straightforward. The addition of base to the reaction mixture is employed to assure complete de-

TABLE III  
COMPARISON OF EXPERIMENTAL PMR SPECTRA AND THOSE CALCULATED USING PARAMETERS OF TABLE II

Line	EDDS, pD ~1			EDDS pD ~12			Co(EDDS)		
	Theoret position	Theoret intens	Obsd position	Theoret position	Theoret intens	Obsd position	Theoret position	Theoret intens	Obsd position
1	2.643	0.000		1.907	0.002		2.986	0.001	
2	3.549	0.009		2.551	0.166	2.554	3.105	0.185	3.102
3	3.626	0.000		2.674	0.118	2.681	3.152	0.228	3.146
4	3.786	1.861	3.789	2.806	1.594	2.801	3.409	1.615	3.404
5	3.786	1.855		2.862	1.587	2.862	3.456	1.936	3.451
6	3.879	2.124	3.876	2.929	2.112	2.931	3.476	1.532	3.481
7	3.881	2.136		2.964	2.128	2.961	3.547	2.054	3.552
8	4.056	0.015		3.117	0.199		3.577	0.035	
9	4.134	0.001		3.219	0.096		3.781	0.072	3.789
10	4.784	0.011		3.572	0.017		3.851	0.376	3.856
11	4.961	1.136	4.956	3.761	1.246	3.754	3.901	1.283	3.902
12	5.038	0.989	5.036	3.862	0.977	3.857	3.947	1.112	3.949
13	5.039	0.983		3.886	0.961	3.886	3.972	0.882	3.976
14	5.116	0.876	5.116	3.986	0.792	3.987	4.019	0.688	4.019
15	5.293	0.005		4.173	0.006		4.343	0.000	

The spectrum of EDDS in an acidic medium, Figure 2, was similarly analyzed. The large singlet at 4.29 ppm is attributed to the ethylenic protons of the backbone. The three lines immediately downfield from the ethylenic singlet and the two lines upfield from it

protonation of the ligand. When syntheses of cobalt(III)-EDDS complexes were attempted excluding both this step and the addition of charcoal, the products ex-

(23) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

hibited an infrared absorption characteristic of a protonated carboxylate group ( $1710\text{--}1720\text{ cm}^{-1}$ ).<sup>24</sup> Although the hydrated  $\text{Co}(\text{EDDS})^-$  reported here does not exhibit this absorption, positive evidence of the "dentate" character of EDDS was sought. The initial evidence for hexadentate chelation is found in the fact that the hydrated crystals of the complex salt can be dried without apparent decomposition to the composition  $\text{Na}[\text{Co}(\text{EDDS})]$ . Attempted titrations of any uncoordinated carboxylate arms present in solutions made from the hydrated salt gave no evidence of either protonation or deprotonation over a range of pH from 3 to 10. Over a range of concentration from  $10^{-4}$  to  $5 \times 10^{-3} M$ , the conductance behavior of hydrated  $\text{Na}[\text{Co}(\text{EDDS})]$  in water was extremely similar to that of  $\text{Na}[\text{Co}(\text{EDTA})]$  although both deviated from the classic conductance *vs.* dilution behavior of uni-univalent electrolytes like  $\text{NaCl}$ . The hexadentate nature of the EDTA in the latter complex was established by comparing its pmr and electronic spectra with  $\text{Co}(\text{EDTA})^-$  salts of known structure. We conclude from the similarity in conductivity behavior with  $\text{Na}[\text{Co}(\text{EDTA})]$  and from the pH studies that the EDDS is hexadentate in  $\text{Na}[\text{Co}(\text{EDDS})] \cdot \text{H}_2\text{O}$ .

The infrared spectrum of the complex (Table I) is somewhat unexpected in that it exhibits two very strong bands of equal intensity at  $1640$  and  $1560\text{ cm}^{-1}$ . The absorption at  $1640\text{ cm}^{-1}$  is readily assigned to the asymmetric stretch of a coordinated carboxylate contained in a glycine residue. The band at  $1560\text{ cm}^{-1}$  occurs at quite low energy for a coordinated glycine moiety and is in the range ascribed to uncoordinated carboxylate anions of this type.<sup>24</sup> If the spectrum is taken to indicate the presence of both free and coordinated  $\text{COO}^-$  groups, then this interpretation and that derived from the aforementioned pH and conductivity data are clearly at odds. An interpretation consistent with all of the data is found if the  $1640\text{-}$  and  $1560\text{-cm}^{-1}$  bands are assigned to coordinated  $\text{COO}^-$  moieties of the five- and six-membered carboxylate arms, respectively. This view is supported by the infrared work of Célap and coworkers on *cis*- $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_3$ .<sup>25</sup> They reported the band positions of the  $\text{NH}_2$  deformation and of  $\text{COO}^-$  stretches at  $1640$ ,  $1610$ , and  $1570\text{ cm}^{-1}$ . We have repeated a portion of their work and find that the  $1570\text{-cm}^{-1}$  band does not diminish upon deuteration of the nitrogen atoms. This band is therefore confidently assigned to a carboxylate mode. Neither do the bands at  $1640$  and  $1560\text{ cm}^{-1}$  of the  $\text{Co}(\text{EDDS})^-$  salt change upon similar deuteration. More significantly, at pD values as low as  $\sim 2.5$  in  $\text{D}_2\text{O}$ , no evidence is found of a peak in the region where a  $\text{COOD}$  is expected to absorb,  $1700\text{--}1750\text{ cm}^{-1}$ .<sup>26</sup> The foregoing data provide strong support for the proposed assignments.

#### Proton Magnetic Resonance Spectrum of $\text{Na}[\text{Co}(\text{EDDS})]$

(24) M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

(25) M. B. Célap, S. R. Niketić, T. J. Janjić, and V. N. Nikolić, *Inorg. Chem.*, **6**, 2063 (1967).

(26) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

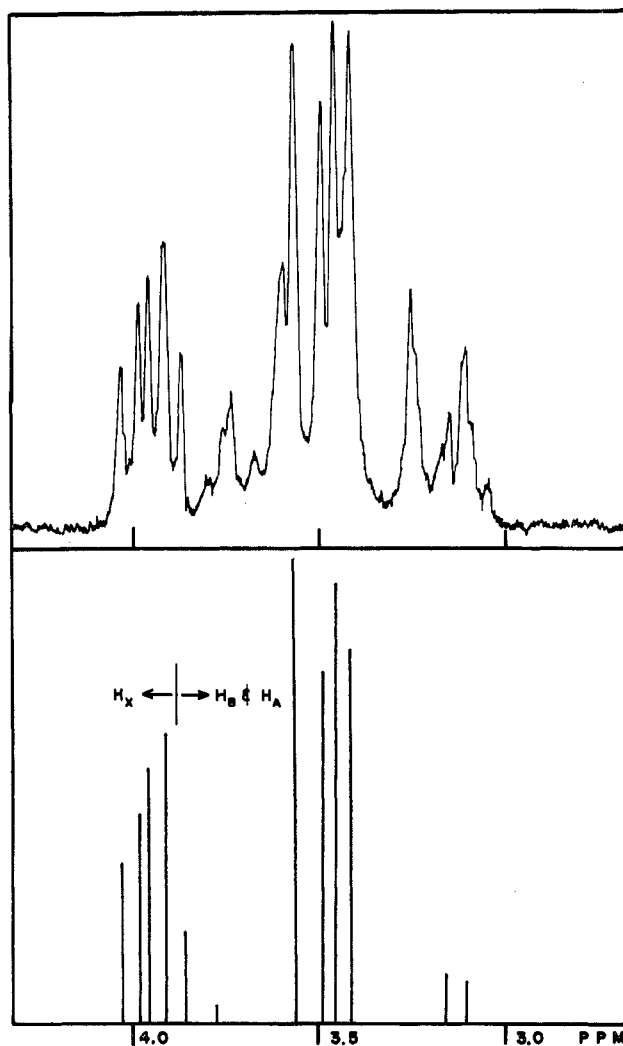


Figure 3.—The pmr spectrum of  $\text{Co}(\text{EDDS})^-$  in  $\text{D}_2\text{O}$  (pD  $\sim 7$ ). The calculated ABX pattern below the experimental spectrum was calculated from parameters noted in Table II. All measurements are in ppm downfield from external TMS.

(EDDS)].—The pmr spectrum of  $\text{Na}[\text{Co}(\text{EDDS})]$  dissolved in  $\text{D}_2\text{O}$  is reproduced in Figure 3. This spectrum is significantly more complicated than that of the free ligand and is totally contained within a range of 1.17 ppm whereas that of free EDDS in basic  $\text{D}_2\text{O}$  spans a range of 1.50 ppm. The added complexity of the former plus relative compression makes it impossible to determine the peak areas through the normal integration procedures. Therefore the analysis of the spectrum must, by necessity, be done by matching line positions, shapes, and qualitative intensities with those calculated by the techniques already described. Fortunately the program used to generate synthetic spectra provides for printing out pictures of the spectra as well as tabulations of line positions and intensities. The striking similarity in line shapes for the synthetic and experimental spectra is a most useful compliment to the match in line positions.

The analysis of the pmr spectrum of  $\text{Co}(\text{EDDS})^-$  is further aided by consideration of the expected spectral components. If, as was described earlier, both five-membered carboxylate rings serve the axial sites

while both six-membered rings serve the equatorial, then the former and latter form two equivalent groups (case I, Figure 1). The net result in terms of the pmr would be only one kind of ABX pattern. A similar conclusion is to be drawn if the roles of the six- and five-membered rings are reversed (case II, Figure 1). In either case the ethylenic backbone would have its carbon atoms locked in a single conformation, as are the backbones of similar complexes.<sup>13-15</sup> Thus an  $A_2B_2$  pattern is expected from the ethylenic protons. Therefore a pmr spectrum for the complex is anticipated which can be interpreted in terms of the structure represented by case I, by case II, or by a mixture of the two.

A single ABX spectrum calculated with the parameters shown in Table II was found to be an excellent match for many of the prominent lines in the experimental spectrum. (See the line representation of the calculated spectrum in Figure 3 and the comparison of calculated and found line positions in Table III.) The remaining lines of the experimental spectrum are found to be symmetrical about a point 3.41 ppm from external TMS (see Table II) and are therefore assigned, as an  $A_2B_2$  pattern, to the ethylenic protons of  $\text{Co}(\text{EDDS})^-$ . The unambiguous conclusion permitted by these data is that the complex has the structure represented either by case I or by case II but that the sample is not a mixture of the two. The coupling constants,  $J_{AX}$  and  $J_{BX}$  (Table II), indicate that the dihedral angles between each of the AB protons and the X protons are in the range of 35-55°. These values and an examination of molecular models of the complex do not permit a detailed conformational assignment for the rings, but the models do readily adopt angles within the specified range without any obvious strain.

**Electronic Spectra.**—The electronic spectra of the  $\text{Co}(\text{EDDS})^-$  and  $\text{Co}(\text{EDTA})^-$  complexes are grossly similar as can be seen by examination of Figure 4 and Table IV. The obvious differences in the spectra occur in band I which has a more pronounced asymmetry and has its maximum at a higher energy for the EDDS complex. These differences in band I together with the crystal field formalism permit a crude comparison of the bonding with the two ligands. One approach to a comparison follows the assumption that each ligand provides an approximately cubic field for the cobalt. A  $Dq$  representing the average environment can then be calculated in the usual fashion where the energy of band I is set equal to  $(10Dq - C)$ .<sup>28</sup> If  $C$ , one of the Racah parameters, is presumed to be the same value for both complexes, then clearly the "average"  $Dq$  for EDDS is greater than that for EDTA.

Another approach to the comparison is found by invoking an interpretation based on a tetragonal rather than a cubic field. This approach is readily implemented (1) if the EDTA and EDDS complexes are

TABLE IV  
ELECTRONIC ABSORPTION SPECTRA FOR  $\text{Co}(\text{EDTA})^-$ ,  
 $\text{Co}(\text{EDDS})^-$ , AND  $\text{Co}(\text{amino acid})_3^0$

Complex	Band I, $\text{cm}^{-1}$	Band II, $\text{cm}^{-1}$
<i>cis</i> - $\text{Co}(\text{gly})_3$	19,230	26,530
<i>cis</i> - $\text{Co}(\beta\text{-ala})_3$	19,011	27,027
$\text{Co}(\text{EDTA})^-$	18,700 band I <sup>a</sup> 17,376 band I-A <sup>b</sup> 18,904 band I-B <sup>b</sup>	26,281
$\text{Co}(\text{EDDS})^-$	19,400 band I <sup>a</sup> 17,483 band I-A <sup>b</sup> 19,520 band I-B <sup>b</sup>	26,247

<sup>a</sup> The position of the maximum in the spectrum actually observed. <sup>b</sup> These components of band I were found by looking for and finding two Gaussian curves which taken together synthesize band I.

treated as having pseudo- $D_{4h}$  symmetry with the quasi- $C_4$  axes being perpendicular to the equatorial planes and (2) if the usual assumptions regarding internuclear distances and the summations of axial charges are adopted.<sup>29,30</sup> It should be recalled that the structural work on  $\text{Co}(\text{EDTA})^-$  and the foregoing data on  $\text{Co}(\text{EDDS})^-$  clearly establish that some differences exist between the two axial oxygen donors and the two equatorial ones. Thus for each complex the equatorial field is considered to be the average of two amine and two carboxylate oxygen donors whereas the axial component of the field arises from the other two carboxylate oxygens. The balance of the analysis is found in Wentworth and Piper's treatment of the spectra for  $D_{4h}$   $\text{Co}(\text{III})$  complexes.<sup>28</sup> By this treatment band I is expected to contain two components. Furthermore the energy of the lower wavelength component (band IB) is shown to be a direct measure of the equatorial field ( $Dq_{eq}$ ), if the equatorial donor atoms are known to be higher in the spectrochemical series than are the axial. Both conditions are satisfied in the complexes considered here in that (1) band I is readily resolved into two Gaussian components and (2) the population of equatorial donors includes two amine nitrogens whereas the axial donors are both carboxylate oxygens. Hence the energy of band IB may be set equal to  $(10Dq_{eq} - C)$ . If  $3800 \text{ cm}^{-1}$ , the usual value of  $C$  for complexes of this type, is employed, then  $Dq_{eq}$  for  $\text{Co}(\text{EDDS})^-$  is  $2330 \text{ cm}^{-1}$  whereas that of  $\text{Co}(\text{EDTA})^-$  is  $2270 \text{ cm}^{-1}$ . Clearly the results of both of the foregoing approaches to the spectral interpretation suggest that EDDS, with its six-membered carboxylate rings and secondary nitrogen atoms, is a "better" ligand toward cobalt(III) than is EDTA.

**Stereochemistry of  $\text{Co}(\text{EDDS})^-$ .**—Because either of the two possible structures for  $\text{Co}(\text{EDDS})^-$ , case I or case II, represents an absolute configuration, it is not surprising that the complex, as it is obtained from the reaction mixture, exhibits a circular dichroism spectrum characteristic of a resolved complex (Figure 5). Its aqueous solution has an optical rotatory dispersion

(29) C. J. Balhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(30) For leading references to applications involving  $D_{4h}$  symmetry, see L. T. Taylor, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **7**, 785 (1968), and D. A. Rowley and R. S. Drago, *ibid.*, **7**, 795 (1968).

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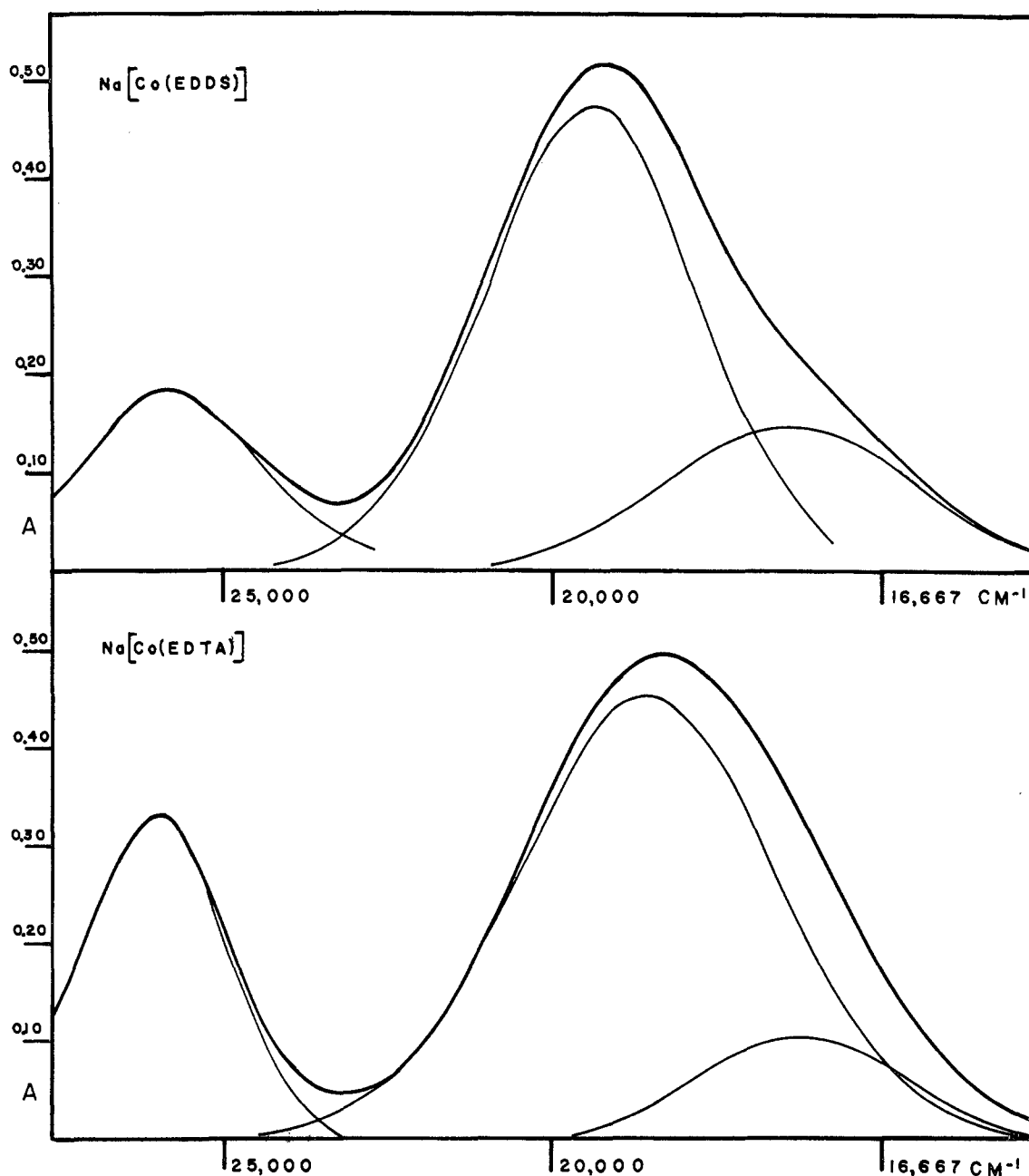


Figure 4.—Electronic spectra of  $\text{Co}(\text{EDTA})^-$  and  $\text{Co}(\text{EDDS})^-$  in water ( $7.0 \times 10^{-4}$  and  $6.9 \times 10^{-4}$  M, respectively).

curve with a maximum negative rotation at  $17,360 \text{ cm}^{-1}$  ( $[\text{M}] -4300$ ) and a maximum positive rotation at  $19,530 \text{ cm}^{-1}$  ( $[\text{M}] 8000$ ). Because the two structures of interest are geometrical isomers of different chirality, they would be expected to show grossly different optical rotatory dispersion curves<sup>31</sup> and their salts would be expected to show dissimilar solubility properties. In an attempt to gather some evidence for the presence of both structures, optical rotatory dispersion curves of solutions made from the first crystalline crop of the complex were compared with those of the third recrystallization of the third crop. Although these products span at least 75% of the theoretical yield, their curves are quantitatively identical. These data, like those derived from pmr spectra, are con-

(31) J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966).

sistent with the formation of only one of the two structures. It is concluded that ED DS derived from L-aspartic acid is a stereospecific chelating agent for cobalt(III).

Although arguments can be advanced in support of either case I or case II, no unambiguous choice is permitted by the data at hand. The synthetic work by Legg and Cooke, the structure of  $\text{Co}(\text{EDTA})^-$  by Hoard, and the information available from molecular models suggest that the five-membered carboxylate rings of ED DS will be in the axial sites whereas the six-membered ones will be in the equatorial positions (case I).<sup>14,16</sup> If this were the situation, the strain associated with the equatorial five-membered carboxylate rings of  $\text{Co}(\text{EDTA})^-$  would of course be absent in  $\text{Co}(\text{EDDS})^-$  and the equatorial oxygen atoms of the latter might

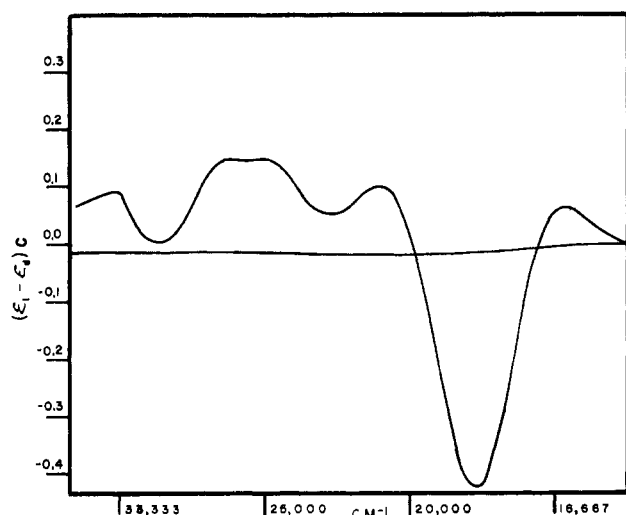


Figure 5.—Circular dichroism spectrum of  $\text{Co}(\text{EDDS})^-$  in water.

therefore make a larger contribution to the equatorial field. It is tempting to use the foregoing results from the electronic spectra to support this view but any such argument is dulled by the unknown effect of changing from tertiary to secondary nitrogen donors between EDTA and EDDS. Furthermore, data avail-

able for complexes containing isolated five- and six-membered rings, notably  $\text{cis-Co}(\text{NH}_2\text{CH}_2\text{COO})_3$ <sup>32</sup> and  $\text{cis-Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_3$ ,<sup>25</sup> would suggest that  $Dq$  values for the six-membered rings are smaller (Table IV). However a strict comparison of the effects of ring size in complexes of simple amino acids with those of EDTA and EDDS might well be inappropriate. In the latter two complexes a change in ring size has been accomplished without addition of "extra" atoms thereby minimizing any change in nonbonding interactions. It seems to these authors that case I is the most likely choice. Any argument favoring case II must be largely predicated on the chirality rules of Legg and Douglas, in that both  $(+)^{546}\text{-Co}(\text{EDTA})^-$  and  $\text{Co}(\text{EDDS})^-$  exhibit a negative rotation in the major low-energy band (see Figure 2).<sup>31</sup> Clearly an X-ray diffraction study is required to fix securely the absolute configuration of  $\text{Co}(\text{EDDS})^-$ .

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## Dibromotris(trimethylphosphine)nickel(II)

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The reaction of nickel bromide and 3 mol of trimethylphosphine yields the five-coordinate complex  $\text{Ni}(\text{P}(\text{CH}_3)_3)_3\text{Br}_2$ . The rich electronic spectrum of the complex contains both ligand field and charge-transfer absorption bands and is compatible with a trigonal-bipyramidal structure for the ground state. The presence of two moderately intense ligand field bands indicates that the molecule is distorted toward a tetragonal pyramid in the excited states derived from  $a^1E'$ . Allowed  $\text{Br} \rightarrow \text{Ni}(\text{II})$  charge-transfer bands are observed at 26,200 and 40,400  $\text{cm}^{-1}$ , whereas an allowed  $\text{P}(\text{CH}_3)_3 \rightarrow \text{Ni}(\text{II})$  band is found at 36,400  $\text{cm}^{-1}$ .

### Introduction

Numerous investigations have been carried out on the reaction of nickel(II) compounds with various trialkyl- and triarylphosphines.<sup>2-8</sup> The products in many cases have been four-coordinate complexes containing two phosphine molecules; notable examples include the square-planar  $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Br}_2$ <sup>9</sup> and the tetrahedral  $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Cl}_2$ <sup>10</sup> complexes.

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Beg and Clark have reported<sup>11</sup> that the direct reaction of trimethylphosphine with nickel(II) salts in a 2:1 mole ratio in a sealed tube yields diamagnetic  $\text{Ni}(\text{P}(\text{CH}_3)_3)_2\text{X}_2$  ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-$ ) complexes. Jensen and coworkers, however, in their investigations of nickel(II)-phosphine complexes, noted a difference in the behavior of trimethylphosphine as compared to the higher trialkylphosphines.<sup>12</sup> Using nickel chloride, only red  $\text{Ni}(\text{P}(\text{CH}_3)_3)_2\text{Cl}_2$  was isolated, but with nickel bromide an almost black compound was produced which analyzed for 3 mol of phosphine. It was tentatively suggested that the dark compound might be a mixture of the four-coordinate complex containing two phosphine molecules and a six-coordinate form containing four phosphine molecules. These investigators also re-

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