$$E(^3E(^3T_2)) = -14Dq + Ds + {}^{13}/_2Dt + 9B + 5C + R_1$$

where

$$R_1 = {}^1/_2[(2Ds + {}^{10}/_4Dt + 8B)^2 + {}^3/_4(4Ds + 5Dt)^2]^{1/2}$$

we find that there is a triplet state $^3E(^3T_1)$ *ca.* 400 cm^{-1} above the $^1A_1$ ground state. Clearly the triplet state is thermally accessible from the ground state and this is sufficient to account for the magnetic behavior of the $[Fe(P_4)X]BPh_4$ complexes, even though a more accurate treatment must await the data made available by the structure determination which is in progress in these laboratories.

Registry No. $[Fe(P_4)Cl]BPh_4$, 39831-90-8; $[Fe(P_4)Br]BPh_4$, 39708-45-7; $[Fe(P_4)I]BPh_4$, 39708-46-8; $[Fe(P_4)(NCS)_2]$, 39836-70-9; $[Co(P_4)Cl]BPh_4$, 39971-67-0; $[Co(P_4)Br]BPh_4$, 39708-47-9; $[Co(P_4)I]BPh_4$, 39708-48-0; $[Co(P_4)(NCS)]BPh_4$, 39708-49-1; $[Ni(P_4)Cl]BPh_4$, 39708-50-4; $[Ni(P_4)Br]BPh_4$, 39831-91-9; $[Ni(P_4)I]BPh_4$, 39708-51-5; $[Ni(P_4)(NCS)]BPh_4$, 39708-52-6; $[Fe(PP_3)Br]BPh_4$, 39708-53-7; $[Fe(PP_3)(NCS)_2]$, 39836-71-0.

Acknowledgments. Thanks are expressed to Dr. J. Gelsomini and Mr. F. Nuzzi for microanalyses and to Mr. F. Zanobini, Mr. F. Cecconi, and Mr. G. Scapacci for technical assistance.

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Absolute Configuration of Aspartic Acid Complexes. The Cobalt(III) Complex of a New Stereospecific Hexadentate Ligand Containing the Aspartic Acid Unit

J. IVAN LEGG*[1] and JOHN A. NEAL

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A series of aspartic acid complexes and related chelates have been reported in the literature, and their absolute configurations have been assigned on the basis of circular dichroism and proton magnetic resonance. From correlations of spectral data and comparison with complexes of known absolute configuration, we believe that some of the assignments are incorrect. In support of this argument we have synthesized the aspartic acid containing ligand (*S*)-ethylenediamine-*N*,*N*-diacetic-*N*′-monosuccinic acid (EDDAMS) which is of known absolute configuration. EDDAMS exhibits stereospecificity on coordination to cobalt(III) to give a complex of known absolute configuration which has been characterized by visible, ir, pmr, and CD spectroscopy. The spectral behavior of this complex supports our predictions of absolute configurations. The unusual geometry associated with the tridentate aspartic acid chelate (*e.g.*, the presence of greater-than-five-membered rings) may account for the difficulties which have arisen in assigning absolute configurations to its complexes.

Introduction

The stereochemistry of trifunctional amino acids[2] is distinct from bifunctional amino acid chelates as illustrated in Figure 1 for chelated aspartic acid. The three rings join on a face of the octahedron at the asymmetric carbon in such a manner that the rings do not clearly define edges of an octahedron as they do for other commonly encountered tridentate chelates (*e.g.*, diethylenetriamine and iminodiacetic acid chelates), and in some of the chelates the R side chain forms part of a six- or greater-than-six-membered ring. The formation of greater-than-five-membered rings may result in ligand–metal bond angles which are greater than 90°. The presence of such chelate rings may lead to complexities in the circular dichroism spectra which would make it difficult to correlate absolute configurations on the basis of optical activity alone. It has been recently shown that changing from metal–ligand bond angles of less than 90° to angles greater than 90° profoundly affects the energies and signs of electronic states.[3] These observations are consistent with a model for optical activity suggested by Piper and Karipides.[4]

A number of reports have appeared where trifunctional amino acids may function or definitely function as tridentate ligands.[5-8] Among the most thoroughly studied of the tridentate amino acid chelates are the Co(III) complexes of aspartic acid[6-8] and a closely related hexadentate ligand con-

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[1] National Institutes of Health Special Research Fellow, Biophysics Research Laboratory, Harvard Medical School, Boston, Mass., 1972–1973. (This is Dr. Legg's address until Sept 1, 1973.)

[2] Trifunctional amino acids are defined as those which have three potential coordinating groups (*e.g.*, aspartic acid and cysteine) as compared to bifunctional amino acids with two potential coordinating groups (the α-amine and carboxylate, *e.g.*, glycine and alanine). When not explicitly stated the *S* configuration of aspartic acid is implied.

[3] T. M. Wing and R. Eiss, *J. Amer. Chem. Soc.*, **92**, 1929 (1970).

[4] T. S. Piper and A. G. Karipides, *Inorg. Chem.*, **4**, 923 (1965); A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964); T. S. Piper and A. Karipides, *Mol. Phys.*, **5**, 475 (1962); T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961). For a recent discussion of this model see K. R. Butler and M. R. Snow, *Inorg. Chem.*, **10**, 1838 (1971); *Chem. Commun.*, 550 (1971).

[5] J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1857 (1969); G. N. Schrauzer and P. A. Doemeny, *J. Amer. Chem. Soc.*, **93**, 1608 (1971); A. Kay and P. C. H. Mitchell, *J. Chem. Soc. A*, 2421 (1970); R. Candlin and M. M. Harding, *J. Chem. Soc. A*, 384 (1970); L. T. J. Delbaere and C. K. Prout, *Chem. Commun.*, 162 (1971); J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 6092 (1967); C. C. McDonald and W. D. Phillips, *ibid.*, **85**, 3736 (1963); E. W. Wilson, Jr., M. H. Kasperian, and R. B. Marting, *ibid.*, **92**, 5365 (1970); D. S. Barnes and L. D. Pettit, *Chem. Commun.*, 1000 (1970); E. R. Clarke and A. E. Martell, *J. Inorg. Nucl. Chem.*, **32**, 911 (1970).

[6] A. Y. Girgis and J. I. Legg, *J. Amer. Chem. Soc.*, **94**, 8420 (1972); J. I. Legg and J. Steele, *Inorg. Chem.*, **10**, 2177 (1971); M. S. Schneller, Thesis, Washington State University, 1971; J. I. Legg, A. L. Kilbert, Jr., and W. F. Siems III, "Progress in Coordination Chemistry," Michael Cais, Ed., Elsevier, Amsterdam, 1968, p 331; J. I. Legg and D. W. Cooke, *J. Amer. Chem. Soc.*, **89**, 6854 (1967).

[7] S. Yamada, J. Hidaka, and B. E. Douglas, *Inorg. Chem.*, **10**, 2187 (1971); L. R. Froebe, S. Yamada, J. Hidaka, and B. E. Douglas, *J. Coord. Chem.*, **1**, 183 (1971).

[8] J. Hidaka, S. Yamada, and B. E. Douglas, *J. Coord. Chem.*, in press.

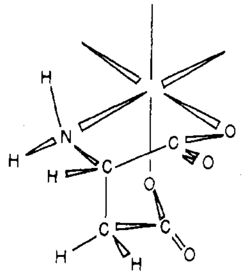


Figure 1. (*S*)-Aspartic acid chelated as a tridentate.

sisting of two aspartic acids joined at the nitrogens by an ethylene bridge, (*S,S*)-*N,N'*-ethylenediaminedisuccinic acid (EDDS).[9,10] Complexes pertinent to this paper are summarized in Figure 2. The absolute configurations of the diastereoisomers shown in Figure 2 have been tentatively assigned on the basis of circular dichroism and proton magnetic resonance studies; and in the case of Co(EDDS)$^-$, the absolute configuration has been confirmed by an X-ray crystallographic study.[10] This latter study revealed, as expected, that greater than 90° ligand–metal–ligand angles were defined by both six-membered rings.

The circular dichroic spectra which have been obtained for the complexes of the type Co(N_2O_4)$^-$ are summarized in Figure 3. Scheme I outlines some of the correlations which

Scheme I

$$\begin{tikzcd}
\mathrm{Co(EDTA)}^- \arrow[r, leftrightarrow] \arrow[dd, leftrightarrow] & \mathrm{Co(IDA)}_2^- \arrow[d, leftrightarrow] \\
 & \mathrm{Co(IDA)(ASP)}^- \arrow[d, leftrightarrow] \\
\mathrm{Co(EDDS)}^- \arrow[r, leftrightarrow] & \mathrm{Co(ASP)}_2^-
\end{tikzcd}$$

can be made. The $(IDA)_2$, (IDA)(ASP), and $(ASP)_2$ complexes offer a means of studying the progressive effect on the circular dichroic spectra of substituting ASP for IDA, Figure 3. On substitution the low-energy band shifts to lower energy and becomes weaker, disappearing for $(ASP)_2$ (noted by the straight line). There is a corresponding shift for the higher energy component (noted by checks). In keeping with this observation is an analogous change in going from EDTA to EDDS, Figure 3, both of which are of known absolute configuration.

These rather dramatic changes in the CD spectra suggest that if comparisons are to be made between hexadentates and bis(tridendates), related chelates should be compared, that is, EDDS and $(ASP)_2$, not EDTA and $(ASP)_2$. On this basis, referring to Figure 4, there appears to be a better correlation between CD spectra A and B than between A and C. Note also that there is a better correlation between the absorption spectra. This leads to an *opposite* assignment for the cis isomers of Co(ASP)$_2^-$ and Co(ASP)(IDA)$^-$ than was made by Douglas and coworkers.[7,8] The absolute configuration assignments in Figure 3 are based on this opposite assignment.

These conclusions are in keeping with the observation that relative state positions and signs may invert in going from chelate rings of less than 90° to greater than 90°[3,4] as is suggested by the spectra obtained for these complexes. That is, complexes which we have tentatively assigned the same absolute configuration have approximately mirror image CD spectra, Figure 3.

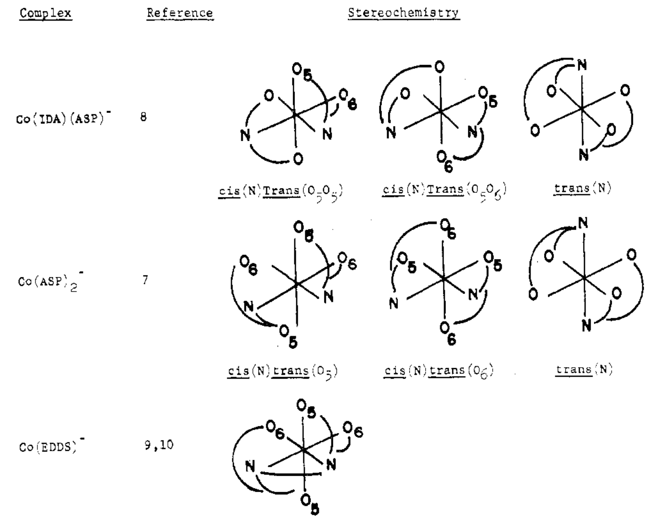


Figure 2. Complexes of (*S*)-aspartic acid and (*S,S*)-*N,N'*-ethylenediaminedisuccinic acid.

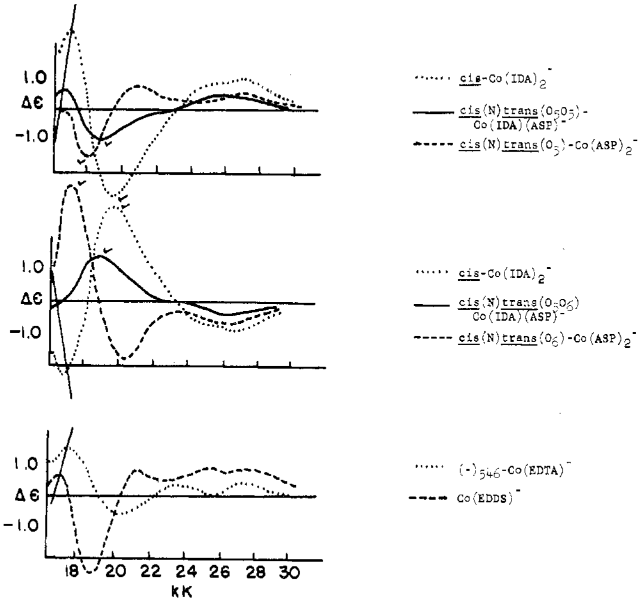
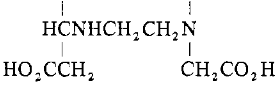


Figure 3. Circular dichroic spectra for complexes of the type Co(N_2O_4)$^-$.

An examination of the spectroscopic data and corresponding complexes summarized in Figure 3 and the scheme shown previously suggests that the cobalt(III) complex of (*S*)-ethylenediamine-*N,N*-diacetic-*N'*-monosuccinic acid (EDDAMS)



$$\begin{array}{ccc} \mathrm{HO_2C} & & \mathrm{CH_2CO_2H} \\ | & & | \\ \mathrm{HCNHCH_2CH_2N} & & \\ | & & | \\ \mathrm{HO_2CCH_2} & & \mathrm{CH_2CO_2H} \end{array}$$

would form an important link between Co(EDTA)$^-$ and Co(EDDS)$^-$ and consequently aid in understanding the changes in CD spectra just discussed. It would be the analog of Co(IDA)(ASP)$^-$ and might be expected to exhibit corresponding band position changes in the circular dichroism spectrum.

It is possible, in principle, for EDDAMS to form two geometric isomers with Co(III), each of which represents hexadentate coordination. The principal difference between these two geometric isomers is the position of the unique

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[9] J. A. Neal and N. J. Rose, *Inorg. Chem.*, 7, 2405 (1968).

[10] L. M. Woodward, Thesis, University of Washington, 1970.

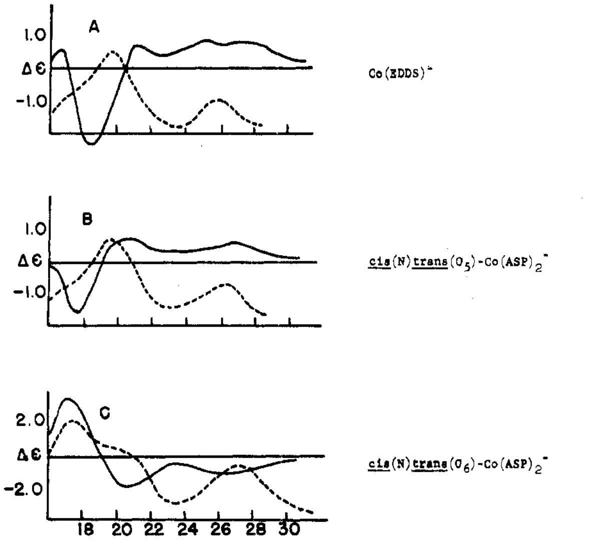

Figure 4. Comparison of circular dichroic (——) and visible absorption spectra (– – –) between Co(EDDS)$^-$ and the two isomers of Co(S-ASP)$_2$$^-$.

oxygen donor atom in the aspartic acid portion which forms a six-membered chelate ring as illustrated in Figure 5. The O_6-eq isomer is the isomer which is related to Co(EDDS)$^-$ and (–)$_{546}$-Co(EDTA)$^-$ as shown in Figure 5. EDDS has been shown to coordinate stereospecifically to Co(III) such that both six-membered chelate rings provide oxygen donor atoms to equatorial coordination sites.[9,10] This suggests that the O_6-eq isomer would be the favored isomer. That EDDAMS and EDDS are predicted to have the six-membered ring in the plane of the amine nitrogens, is based on the expected ring strain when the five-membered rings are in the plane.[9] In this paper the synthesis of Co(EDDAMS)$^-$ is described, and its relationship to the absolute configurations of the homologous hexadentate and aspartic acid complexes previously reported is discussed.

Experimental Section

Preparation of (*S*)-Ethylenediamine-*N*,*N*-diacetic-*N*′-monosuccinic Acid. A solution was prepared by dissolving NaOH (16.0 g, 0.4 mol), (*S*)-aspartic acid (13.3 g, 0.1 mol), and iminodiacetic acid dihydrate (16.9 g, 0.1 mol) in 125 ml of water at ice-bath temperature. Sodium carbonate (10.6 g, 0.1 mol), 150 ml of 95% ethanol, and 125 ml of water were added to the solution contained in a 1-l. three-necked flask fitted with a water condenser and a thermometer. Eleven milliliters of 1,2-dibromoethane (29% excess) was added according to the procedure reported for the preparation of EDDS.[9] Crystallization by acidification with concentrated hydrochloric acid produced substantial amounts of unreacted aspartic acid. By careful fractional crystallization a portion was separated (4.0 g) which consisted almost entirely of the hexadentate ligands (EDTA, EDDA, and EDDAMS) in the amounts of approximately 2, 1, and 1 g, respectively. This mixture was successfully allowed to react to yield the three corresponding Co(III) complexes. However, it was more straightforward to precipitate the entire mixture in fractions (by acidification and evaporation) and combine all fractions which were not determined to be (*S*)-aspartic acid by infrared analysis. By this procedure a solid mixture was obtained which contained EDDAMS along with EDTA, EDDS, and unreacted materials. The yield of EDDAMS was *ca.* 6%. This mixture was used without further purification for the synthesis of the desired complex.

Preparation of Sodium (*S*)-Ethylenediamine-*N*,*N*-diacetato-*N*′-monosuccinatocobaltate(III) Hydrate. The ligand mixture containing EDDAMS (1.86 g) was added with stirring to a cold slurry of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (2.18 g, 4 mmol) and activated charcoal (2 g) in 50 ml of water. The reaction mixture was allowed to warm to room temperature, and after evolution of CO_2 ceased, the mixture was heated to 75°, and 5% acetic acid was added dropwise to maintain CO_2 evolution. After CO_2 evolution had ceased, heating was continued for 20 min (pH ∿4.5). The solution was filtered to remove charcoal, diluted to 400 ml with water, and added to a column of Dowex 1-X8 anion-exchange resin in the chloride form (diameter 4.5 cm, height of resin 50 cm). Elution with water removed two small bands which were discarded. Upon elution with 0.1 *M* NaCl (*ca.* 2 ml/min) the sample separated into nine distinct bands. Three major bands, representing approximately 70% of the products (by band volume), eluted first in the order Co(EDDS)$^-$, Co(EDDAMS)$^-$, and Co(EDTA)$^-$. The identity of the first and third bands was established by comparison of visible, CD, and ir spectra with those reported for the corresponding complexes.[9]

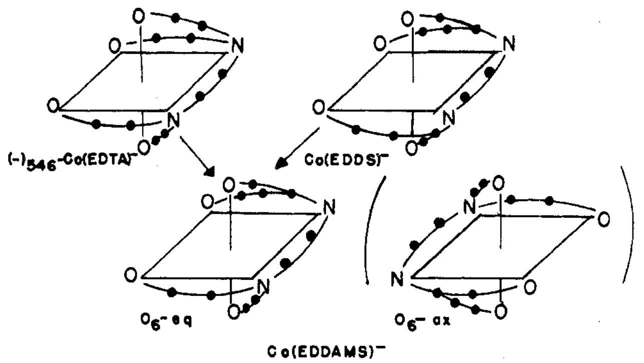

Figure 5. Possible isomers for Co(EDDAMS)$^-$ and their relationship to Co(EDTA)$^-$ and Co(EDDS)$^-$.

The second band containing Co(EDDAMS)$^-$ was evaporated to dryness in an air stream. The solid was dissolved in a minimum amount of water and desalted by passage through a G-25 Sephadex column (diameter 2.5 cm, height 30 cm). The product was collected, concentrated, and passed down a G-25 Sephadex column a second time, eluting with distilled water. Evaporation to dryness in an airstream and drying at 80° for 5 hr under vacuum (1 mm) yielded 0.23 g of pure Na[Co(EDDAMS)]$\cdot H_2O$. *Anal.* Calcd for $Na[CoC_{10}H_{12}N_2O_8]\cdot H_2O$: C, 30.93; H, 3.63; N, 7.22. Found: C, 30.81; H, 3.89; N, 7.21.

Physical Measurements. Visible absorption and circular dichroism spectra were recorded for aqueous solutions (*ca.* 10^{-3} *M*) on a Cary Model 14 spectrophotometer and a JASCO Model ORD/UV-5 with CD attachment, respectively. Infrared solution spectra in D_2O were obtained on a Beckman 18A infrared spectrophotometer. The solution pD was varied by the addition of DCl or NaOD. Solid spectra were obtained as Nujol mulls. Proton magnetic resonance spectra were recorded on a Varian A-60 and a T-60 spectrometer. The samples were dissolved in deuterium oxide, and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (NaTMS) was used as an internal reference.

Results and Discussion

Synthesis and Characterization of (*S*)-Ethylenediamine-*N*,*N*-diacetato-*N*′-monosuccinatocobaltate(III). Since no convenient method could be found for isolation of the desired ligand from the closely related hexadentates and starting amino acids, an *in situ* synthesis of Co(EDDAMS)$^-$ was employed. The desired complex was then chromatographically isolated from the other closely related complexes. It is important to note that fractionation of the band containing Co(EDDAMS)$^-$ and examination of each fraction by CD showed only one isomer to be present. This suggests a steric preference for coordination of the ligand.

The electronic absorption spectrum of Co(EDDAMS)$^-$ consists of two bands at 19.36 kK (ε 260) and 26.35 kK (ε 150). The band at lower energy is slightly dissymetric but no shoulder is observed. This spectrum is quite similar both in band position and in relative intensity to those observed for Co(EDTA)$^-$ and Co(EDDS)$^-$ [9] except that the low-energy band of the last two exhibits a slight broadening toward longer wavelengths.

The ir spectrum of solid Na[Co(EDDAMS)]$\cdot H_2O$ exhibits a maximum at 1640 cm^{-1} typical of compounds containing coordinated carboxylates.[11] The ir spectrum of a solution

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[11] M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.*, **78**, 5178 (1956); R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, **1**, 174 (1962).

of the complex in D_2O is independent of pD in the range pD 2-8 and exhibits a strong absorption at 1640 cm^{-1} with a definite shoulder at approximately 1600 cm^{-1}. The absorption at 1640 cm^{-1} is assigned to the asymmetric stretching frequency of carboxylate groups contained in the three five-membered chelate rings, Figure 5. The shoulder at 1600 cm^{-1} is assigned to the single carboxylate group contained in the six-membered chelate ring. These observations are consistent with those made for Co(EDDS)$^-$ [9] and support coordination of all the acetates.

It was expected, as discussed in the Introduction, that EDDAMS would show stereospecificity on coordination, favoring the O_6-eq isomer, Figure 5. That only one isomer was found suggests that the ligand exhibits absolute stereospecificity like EDDS. If the O_6-eq isomer was obtained, then its pmr spectrum should closely resemble the combined spectra of Co(EDTA)$^-$ [12] and Co(EDDS)$^-$ [9] since this isomer is essentially a combination of half of each of these complexes, Figure 5. Indeed, if the pmr spectra of these complexes were overlapped, a spectrum would be obtained which would bear a close similarity to the spectrum obtained for Co(EDDAMS)$^-$, Figure 6. The downfield portion of the spectrum (3.5-4.2 ppm) contains the glycinate ring proton spectrum corresponding to the EDTA portion, and the upfield portion (2.5-3.5 ppm) contains the aspartate proton spectrum corresponding to the EDDS portion. Superimposed on this is the ABCD spectrum of the ethylene backbone. This differs from the symmetric AA′BB′ spectra found for the corresponding EDTA and EDDS complexes.[9,12] The AB pattern for the in-plane glycinate ring (G ring, Figure 6) exhibits a coupling constant J_{AB} = 16.1 Hz. This si typical of in-plane ring coupling constants for Co(EDTA)$^-$ and similar chelates.[13] The center of the AB pattern at 3.81 ppm is 0.06 ppm downfield relative to the G-ring protons in Co(EDTA)$^-$.[12] The out-of-plane ring (R ring in Figure 6) exhibits a single broad resonance at 4.04 ppm which is 0.12 ppm downfield from the corresponding resonance in Co(EDTA)$^-$.[12]

The ABX pattern of the aspartate protons has been obtained from the spectrum, and the assignment tested by computer matching.[14] The results of the computer analysis are shown in the line spectra in Figure 6 and are summarized in Table I. Good agreement between the observed and calculated spectrum was obtained. The general appearance of the ABX pattern is very similar to that of the ABX pattern of Co(EDDS)$^-$.[9] The entire spectrum is shifted slightly upfield relative to that of Co(EDDS)$^-$ but no line is shifted by more than 0.12 ppm and the average shift is 0.10 ppm. The actual chemical shifts (τ_A 2.90 ppm, τ_B 3.17 ppm, τ_X 3.49 ppm) indicate that the protons are shifted upfield relative to those of Co(EDDS)$^-$ by 0.11, 0.07, and 0.11 ppm, respectively.[15] The values of the coupling constants J_{AX} = 2.19 Hz and J_{BX} = 4.58 Hz indicate that the dihedral angles between the protons are not greatly different from those of Co(EDDS)$^-$ (J_{AX} = 2.40 Hz and J_{BX} = 4.60 Hz).

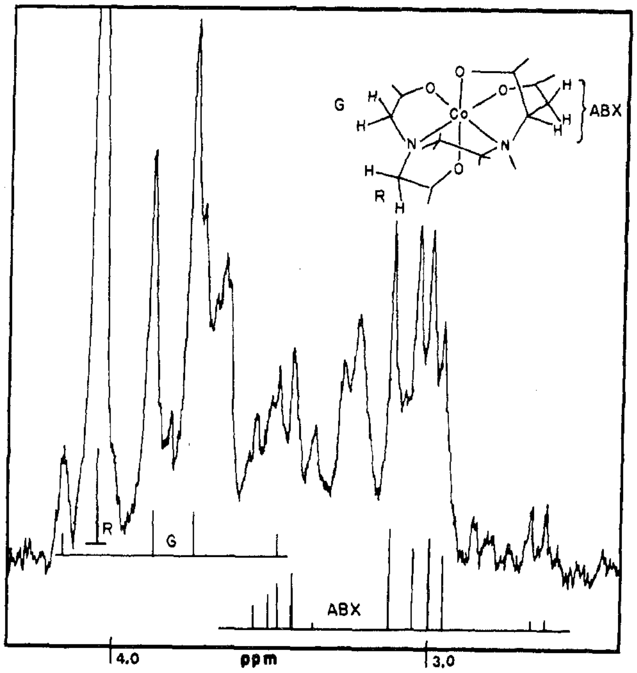

Figure 6. Proton magnetic resonance spectrum of Co(EDDAMS)$^-$ (NaTMS internal reference).

Table I. Comparison of Experimental and Calculated Pmr Spectra for Co(EDDAMS)$^-$

Line	Theoret intens	Theoret position[a, b]	Obsd position
1	0.231	2.668	2.672
2	0.279	2.712	2.708
3	1.555	2.959	2.963
4	1.877	3.004	3.000
5	1.467	3.048	3.043
6	2.021	3.118	3.122
7	0.071	3.338	3.335
8	0.495	3.410	3.413
9	1.301	3.433	3.433
10	1.160	3.478	3.480
11	0.856	3.504	3.500
12	0.628	3.549	3.550

[a] The eight most intense spectral lines were matched preferentially in the final calculation to obtain best value parameters. [b] Line positions tabulated in ppm downfield from NaTMS.

The close similarity between the Co(EDDAMS)$^-$ spectrum and those of Co(EDTA)$^-$ and Co(EDDS)$^-$ and the occurrence of only one isomer is good evidence that the O_6-eq isomer was obtained. Examination of molecular models shows that in the O_6-ax isomer the protons are in considerably different environments. For example, one of the protons of the aspartic acid portion of EDDAMS is in very close proximity to a proton from the ethylenic backbone of the ligand. This proton would be expected to exhibit a pmr chemical shift substantially downfield from the corresponding proton of Co(EDDS)$^-$, as has been observed in other instances where steric compression is a factor.[16]

Relationship of the Absolute Configuration of (*S*)-Ethylenediamine-*N*,*N*-diacetato-*N*′-monosuccinatocobaltate(III) to Absolute Configuration of Complexes of Aspartic Acid. The absolute configurations of optically active Co(EDTA)$^-$ [17] and Co(EDDS)$^-$ [10] are known, and based on the studies reported here, the absolute configuration of Co(EDDAMS)$^-$ is known with a high degree of certainty. The correlation scheme discussed in the Introduction can now be completed to give Scheme II, where the complexes in the

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

(13) J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *Inorg. Chem.*, **10**, 90 (1971).

(14) The program LAOCN 3 by A. A. Bothner-by and S. M. Castellano was used.

(15) It should be noted that the chemical shifts for Co(EDDS)$^-$ given in ref 9 are referred to *external TMS*. In order to make a direct comparison between Co(EDDS)$^-$ and Co(EDDAMS)$^-$, the spectrum of Co(EDDS)$^-$ was also obtained using internal NaTMS.

(16) J. C. Dabrowiak and D. W. Cooke, *J. Amer. Chem. Soc.*, **92**, 1097 (1970).

(17) T. E. MacDermott and A. M. Sargeson, *Aust. J. Chem.*, **16**, 334 (1963).

Scheme II

$$\begin{tikzcd}
\mathrm{Co(EDTA)^-} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & \mathrm{Co(IDA)_2^-} \arrow[d, leftrightarrow] \\
\mathrm{Co(EDDAMS)^-} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & \mathrm{Co(IDA)(ASP)_2^-} \arrow[d, leftrightarrow] \\
\mathrm{Co(EDDS)^-} \arrow[r, leftrightarrow] & \mathrm{Co(ASP)_2^-}
\end{tikzcd}$$

left column are of known absolute configuration and afford closely related references for the assignment of absolute configurations to the corresponding bis-tridentate amino acid complexes.

The circular dichroic spectra of Co(EDDAMS)$^-$ and related complexes are shown in Figure 7. The spectrum exhibits two maxima at 18.4 kK ($\Delta\epsilon$ -1.98) and 26.3 kK ($\Delta\epsilon$ $+0.58$). The spectrum is quite close to what would have been predicted from the comparisons made in Figure 3 (see discussion in the Introduction) except for the lack of a positive band at approximately 600 nm. A distinct change in the position and sign of the bands is noted on progressive substitution of an ASP for an IDA unit in the hexadentate ligand which may be a reflection of the increasing number of ligand-metal-ligand bond angles greater than 90°.[4] There does not appear to be any correlation between the low-energy absorption maxima of the complexes (EDTA, 18.6 kK; EDDAMS, 19.4 kK; EDDS, 19.4 kK) and the CD maxima.

From a comparison of the CD spectrum of Co(EDDAMS)$^-$ to the CD spectra obtained for the two isomers of Co(IDA)(ASP)$^-$,[8] the absolute configurations of these isomers are tentatively assigned as shown in Figure 7. (For isomer nomenclature see Figure 2.) An analogous comparison between Co(EDDS)$^-$ and the two isomers of Co(ASP)$_2^-$, Figure 4, was used to assign their absolute configurations. It should be noted that these are *empirical* comparisons. No assumption concerning sign patterns or relative state positions has been made. We feel that comparing complexes with the same number of aspartic acid and iminodiacetic acid units permits a reasonably safe correlation of absolute configurations on the basis of CD. The tentative assignments of absolute configuration that have been made here are opposite to those made by Douglas and coworkers.[7,8]

Registry No. Sodium (*S*)-ethylenediamine-*N*,*N*-diacetato-*N*′-monosuccinatocobaltate(III) hydrate, 40299-74-9; (*S*)-ethylenediamine-*N*,*N*-diacetic-*N*′-monosuccinic acid, 40354-50-5; (*S*)-aspartic acid, 6899-03-2; iminodiacetic acid, 142-73-4; 1,2-dibromoethane, 106-93-4.

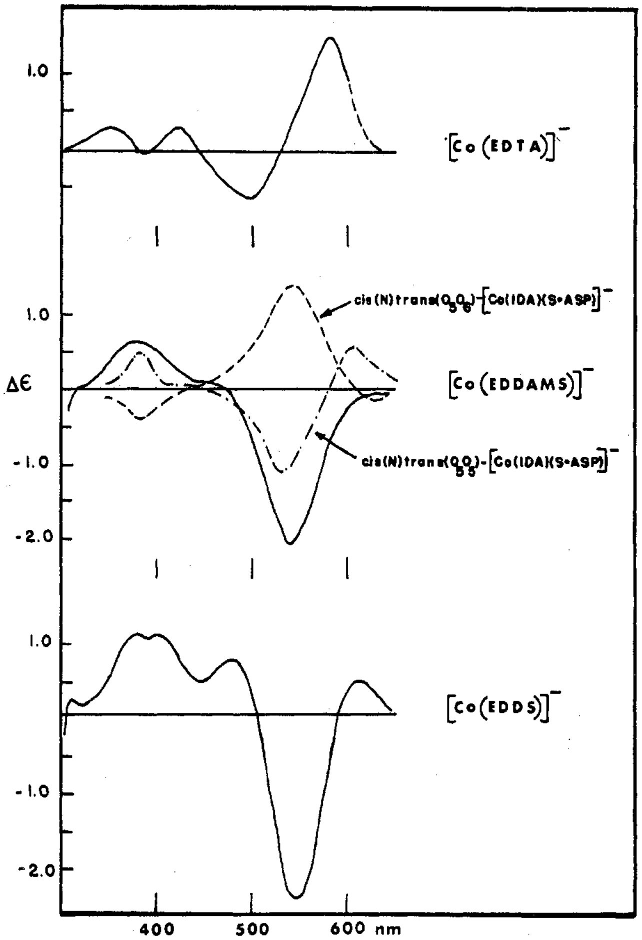

Figure 7. Circular dichroic spectra of Co(EDDAMS)$^-$ and related complexes.

Acknowledgments. We wish to thank Professor B. E. Douglas for providing information on the bis-tridentate complexes prior to publication.[7,8] Acknowledgment is made to the donors of the Petroleum Research Fund (Grant No. 3153-A3), administered by the American Chemical Society, the National Science Foundation (Grant GP-34490X), and the National Institutes of Health (GM 18983-01) for partial support of this research. A grant provided for biological and medical research by State of Washington Initiative Measure No. 171 is also gratefully acknowledged.