solution of $NaClO_4 \cdot H_2O$ (4.7 g, 33.5 mmol) in water (50 ml) was added. Upon air evaporation under a hood, the red-brown crystals formed were collected and were washed with water and ether. This crude product was dissolved in a small amount of methanol. The solution was filtered to remove some solids and an equal volume of water was added. Crystals formed on air evaporation. The product (39% yield) was washed with water and ether and dried in vacuo. Anal. Calcd for $C_{14}H_{28}CoCl_4N_4O_{12}P$: C, 24.87; H, 4.17; Co, 8.71. Found: C, 25.7; H, 3.5; Co, 8.4.

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Registry No. $P(OC_6H_5)_3Co(DH)_2Cl$, 56629-86-8; $P(O\text{-}\textit{o}\text{-}(CH_3)C_6H_4)_3Co(DH)_2Cl$, 56629-87-9; $P(O\text{-}\textit{o}\text{-}(\textit{i}\text{-}C_3H_7)C_6H_4)_3Co(DH)_2Cl$, 56629-88-0; $P(c\text{-}C_6H_{11})_3Co(DH)_2Cl$, 24489-36-9; $P(\textit{i}\text{-}C_3H_7)_3Co(DH)_2Cl$, 56629-89-1; $P(OCH_3)_3Co(DH)_2Cl$, 52654-86-1; $P(OC_2H_5)_3Co(DH)_2Cl$, 56403-89-5; $P(O\text{-}\textit{i}\text{-}C_3H_7)_3Co(DH)_2Cl$, 56403-90-8; $P(O\text{-}2\text{-}Cl\text{-}C_2H_4)_3Co(DH)_2Cl$, 56629-90-4; $P(CH_2C_6H_5)_3Co(DH)_2Cl$, 56629-91-5; $P(OCH_2)_3CC_2H_5Co(DH)_2Cl$, 56629-92-6; $P(OCH_3)_2(C_6H_5)Co(DH)_2Cl$, 56403-84-0; $P(CH_3)(C_6H_5)_2Co(DH)_2Cl$, 56629-93-7; $P(C_2H_5)(C_6H_5)_2Co(DH)_2Cl$, 24489-34-7; $P(\textit{n}\text{-}C_4H_9)(C_6H_5)_2Co(DH)_2Cl$, 56629-94-8; $P(OCH_3)(C_6H_5)_2Co(DH)_2Cl$, 56403-88-4; $P(2\text{-}(CN)\text{-}C_2H_4)_3Co(DH)_2Cl$, 56629-95-9; $P(CH_3)_3Co(DH)_2Cl$, 23648-10-4; $P(CH_3)_2(C_6H_5)Co(DH)_2Cl$, 56629-96-0; $[P(2\text{-}(CN)\text{-}C_2H_4)_3Co(DH)_2OH_2]NO_3$, 56629-98-2; $[P(CH_3)(C_6H_5)_2Co(DH)_2H_2O]NO_3$, 56630-00-3; $[P(\textit{n}\text{-}C_4H_9)(C_6H_5)_2Co(DH)_2H_2O]NO_3$, 56630-02-5; $[P(OCH_3)(C_6H_5)_2Co(DH)_2H_2O]NO_3$, 56630-04-7; $[P(C_6H_5)_3Co(DH)_2H_2O]NO_3$, 56630-05-8; $[P(\textit{n}\text{-}C_4H_9)_3Co(DH)_2NO_3]$, 51194-37-7; $[P(O\text{-}2\text{-}Cl\text{-}C_2H_4)_3Co(DH)_2H_2O]ClO_4$, 56630-13-8; $Co(DH)(DH_2)Cl_2$, 12107-63-0; $(CH_3OH)Co(DH)_2Cl$, 28872-22-2; $P(C_6H_5)_3Co(DH)_2Cl$, 23295-34-3; $P(OC_6H_5)_3$, 101-02-0; $P(OCH_3)_3$, 121-45-9; $P(OC_2H_5)_3$, 122-52-1; $P(CH_3)_3$, 594-09-2; $[(C_2H_5)(C_6H_5)_2PCo(DH)_2(CH_3OH)]^+$, 56630-06-9; $[(C_6H_5CH_2)_3PCo(DH)_2(CH_3OH)]^+$, 56630-07-0; $[(\textit{o}\text{-}\textit{i}\text{-}C_3H_7C_6H_4O)_3PCo(DH)_2(CH_3OH)]^+$, 56630-08-1; $[(CH_3O)_3PCo(DH)_2(CH_3OH)]^+$, 56630-09-2; $[(C_2H_5O)_3PCo(DH)_2(CH_3OH)]^+$, 56630-10-5; $[(ClC_2H_4O)_3PCo(DH)_2(CH_3OH)]^+$, 56630-11-6.

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Resolution of Ethylenediaminetetraacetic Acid-d_2 and Ethylenediaminediacetic-N,N'-di-α-propionic Acid via Resolution of Their Cobalt(III) Complexes

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The sexidentate ligand EDPA, ethylenediaminediacetic-N,N'-di-α-propionic acid, has been resolved via resolution of its cobalt(III) complex. Its coordination to the metal ion is approximately 92% stereospecific. Opposite optical isomers of EDTA-d_2, dideuterated EDTA, can also be generated from enantiomeric forms of $[Co(EDTA)]^-$ that have undergone either acidic or basic H–D exchange. The two most labile hydrogen atoms of EDTA and the methyl groups of EDPA seem to occupy the same position on the out-of-plane glycine-like linkages, and the configurations of the two optically active carbon atoms of each ligand are tentatively assigned as *RR* for the ligands from the $(+)_{546}$ complex with Co(III).

Introduction

Studies into the stereochemistry of cobalt(III) complexes with polyaminopolycarboxylate chelates have undergone steady growth,[1-5] culminating in detailed ^1H NMR work completely assigning the glycinate protons of EDTA and analogous ligands.[6] Carbon-13 NMR data have yielded even more information concerning the stereospecific hydrogen–deuterium exchange of such complexes,[7] an exchange that has been the subject of considerable attention.[8-14] With ligands differing from EDTA by the presence of one or more attached methyl groups, the NMR spectra that result are more complicated but yield more information.[2,3,6,7] Brubaker has summarized much information regarding the significance of such methyl groups.[15] In this paper we evoke two approaches to elucidate even further the full consequences associated with the stereochemistry of the glycine-like linkages located out of the N–Co–N plane of the $[Co(EDTA)]^-$ anion, especially when occupied by a methyl group. We utilize Dwyer's rather classical approach,[16,17] an approach used by Mizukami et al.,[18] whereby ligand stereochemistry is discerned via its influence upon the stereochemistry of the complex. We also use H–D stereospecific exchange techniques[6] to prepare the particular enantiomers of EDTA. This work involved EDTA, an analogous ligand with two methyl groups that we refer to as

EDPA, ethylenediaminediacetic-*N*,*N*'-di-α-propionate,[19] and their Co(III) complexes. Use of EDPA, with two asymmetric centers, allows us to demonstrate chemically just how stereodirective is the coordination of this ligand. Having already established that EDPA coordinates with geometric specificity[3] this work details the stereospecific coordination to Co(III) by resolving the ligand via resolution of the complex and isolation of the free ligand. The resolved ligand is then used to prepare an optically active complex.

In a similar fashion, optically active dideuterated EDTA has been made by first fostering H–D exchange of optically active $[Co(EDTA)]^-$ ions and then removing the metal ion, freeing enantiomeric forms of EDTA-d_2. In this manner, the importance of the position occupied by the hydrogen atom that Sudmeier, Senzel, and Blackmer[6] referred to as H_a (and H_a') can be assessed chemically.

Experimental Section

Materials. The purest commercially available chemicals were used without further purification.

The ^1H NMR spectra were recorded on a Varian A-60 at ambient temperatures with DSS as an internal standard in D_2O solutions. Visible spectra were measured on a Cary 14, and ORD spectra were obtained on the Cary Model 60 ORD–CD instrument at the Illinois Institute of Technology. D_2O was from Merck Sharp and Dohme of Canada Ltd. and was of 99.7 atom % D.

Preparation of the Ligand and Complexes. The ligand, EDPA, and its cobalt(III) complex were prepared as published,[3] and both were characterized via ^1H NMR analysis and optical properties. The sodium and potassium salts of the complex anion $[Co(EDTA)]^-$ were prepared according to the method of Dwyer.[17] $Na_3[Co(CO_3)_3]\cdot 3H_2O$ was made via the method of Bauer and Drinkard.[20]

Isotopic Exchange and Ligand Stripping. The following description is typical of the approach taken for deuterium exchange.[10,12] Two and one-half grams of Na[Co(EDTA)] was dissolved in 9.5 ml of D_2O to which 5 drops of concentrated HNO_3 was added. The pH was about 2. The ^1H NMR spectra of the sample after warming at 70° for 8 hr indicated that the exchange was at the desired level; that is, the A_2 type peak for the out-of-plane protons was diminished by half.[12] The ligand was freed by adding 2.5 g of NaCN and one pellet of NaOH in 10 ml of H_2O and cooling the solution. Concentrated HNO_3 was added dropwise until precipitation of the ligand appeared complete, requiring 80 drops sometimes. Solution of the isolated ligand was effected in D_2O with the addition of Na_2CO_3. The ratio of acetate H atoms to ethylene H atoms was 1.59 for EDTA-d_2^{4-}. The expected value for exactly half-exchange of the out-of-plane methylenes would be 1.50.

Complex Resolution. Both anions $[Co(EDTA)]^-$ and $[Co(EDPA)]^-$ were resolved via diastereoisomer formation with optically active *cis*-$[Co(en)_2(NO_2)_2]^+$ according to the method of Dwyer.[21] Both optical antipodes of each complex were isolated.

Results and Discussion

With an approach not unlike that of Dwyer's with PDTA,[16] propylenediaminetetraacetic acid, we have prepared and characterized complexes of Na[Co(EDPA)]. After resolution via formation of diastereoisomers with *cis*-$[Co(en)_2(NO_2)_2]^+$ the ORD spectrum of each isomer was measured and compared with those of optically active $[Co(EDTA)]^-$ and $[Co(PDTA)]^-$.[22] The maximum rotation for the EDTA complexes occurs at 545 nm. For the EDPA complex the maximum rotation occurs at a slightly shorter wavelength, 540 nm. The results of any of several resolutions yielded $[Co(EDPA)]^-$ with specific rotations at 546 nm within 10° of 1000°, either (+) or (–), following the pattern of the EDTA complexes. After the EDPA has been stripped from each separate optical isomer of the complex, isolated, redissolved, and characterized via ^1H NMR, opposite optical rotations are found. The ORD curves for free $EDPA^{4-}$ are mirror images. The $(-)_{546}$-$[Co(EDPA)]^-$ complex is the source of EDPA that rotates plane-polarized light to the left. The $(+)_{546}$-$[Co(EDPA)]^-$ complex releases dextrorotatory EDPA. At 589 nm the specific rotations observed for free $EDPA^{4-}$ are –130 and +120°. The rotations are larger at shorter wavelengths, increasing markedly at 400 nm to the end of our measurements at 300 nm (where the observed rotations are +0.010° and –0.012°). These specific rotations can be compared to those of PDTA, $[\alpha]_{589}$ ±47°.[16]

Thus, we conclude that the coordination of EDPA is highly stereospecific, yielding primarily only one isomer for each isomer of EDPA, *RR* or *SS* (we have already noted the absence of complexed *ms*-EDPA[3]). Confirmation comes from the observation that, when a solution of $EDPA^{4-}$ that is levorotatory is mixed with $Na_3[Co(CO_3)_3]\cdot 3H_2O$, an optically active complex is made. The ORD spectrum of this complex matches that of $(-)_{546}$-$[Co(EDPA)]^-$. The concentration can be estimated from its absorption spectra. (The extinction coefficients agree at maxima and minima.) The specific rotation at 546 nm is 850°. Thus, the coordination of EDPA is approximately 92% stereospecific, a specificity arising from the bulky methyl groups on the out-of-plane glycine linkages. Neutral solutions of complex made in this fashion maintain their optical activity for more than 1 year.

Information about the configuration of the carbon atom of the out-of-plane methylene linkage is available by capitalizing upon the stereospecific H–D exchange that occurs there. Using optically active $[Co(EDTA)]^-$ complexes we performed both acid- and base-catalyzed H–D exchange. The exchange was monitored via ^1H NMR spectra and quenched after obtaining the dideuterated complexes, (+)- or (–)-$[Co(EDTA\text{-}d_2)]^-$. After removing the metal, the free dideuterated ligand samples, now with two chiral centers, were found to be optically active with opposite rotatory powers, depending upon the isomer from which they had come. The ORD curves obtained are typical of colorless asymmetric molecules and, of course, have very small rotations. Specific rotations at some wavelengths for one run are as follows: for EDTA-d_2 from $(+)_{546}$-$[Co(EDTA)]^-$ (acid catalyzed), +1.20° at 300 nm, +0.64° at 365 nm, +0.34° at 430 nm, +0.33° at 500 nm, +0.30° at 589 nm; for EDTA-d_2 from $(-)_{546}$-$[Co(EDTA)]^-$ (acid catalyzed), –1.22° at 300 nm, –0.58° at 365 nm, –0.32° at 430 nm, –0.32° at 500 nm, –0.30° at 589 nm. The rotations were not as high with the EDTA-d_2 made via the more rapid base-catalyzed exchange. Not only is it harder to control, but some racemization of the complex very likely occurs. Hence, this basic medium is unsatisfactory for generating an optically active ligand of high optical purity. These rotations are reasonable for carbon atoms made asymmetric due to the presence of a hydrogen atom and a deuterium atom. Specific rotations for such asymmetric carbon atoms have been observed to range from 0.28 to 4.0° at the sodium D line, 589 nm.[23]

Examination of molecular models and previous work detailing the stereospecific exchange indicates the methyl group of coordinated EDPA[3] to be in the same position as the hydrogen atom called H_a in coordinated EDTA. This conclusion comes from the comparison to the analysis first made by Sudmeier et al. that the first hydrogen atom to undergo exchange is H_a, the proton furthest from the diamine backbone.[6] Our reasoning is based upon the observation that the appropriate $(-)_{546}$ complex generates both EDPA and EDTA-d_2 in the same form, which happens to be levorotatory. Furthermore, we can assign tentative configurations to the optically active carbon atoms. The configuration of the two chiral centers is the same since optical activity is observed. And since the absolute configuration of active $[Co(EDTA)]^-$ is known, we can deduce each ligand's configuration. For the ligand from the $(-)_{546}$ complex, whether made optically active with a methyl group or a deuterium atom, the configuration is *SS*, and for the ligand from the $(+)_{546}$ complex the configuration is *RR*. This work represents chemical evidence for the very stereospecific preference for the site furthest from the backbone in the out-of-plane linkage in exchange and upon coordination.

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Registry No. $(+)_{546}$-[Co(EDPA)]$^-$, 56816-58-1; $(-)_{546}$-[Co(EDPA)]$^-$, 56816-59-2; $(+)_{589}$-EDPA^{4-}, 56845-77-3; $(-)_{589}$-EDPA^{4-}, 56845-78-4; $(+)_{589}$-EDTA-d_2, 56783-74-5; $(-)_{589}$-EDTA-d_2, 56783-75-6.

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Isotropic Shifts in Two Low-Spin Cobalt(II) Complexes

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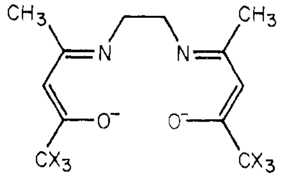
The proton magnetic resonance spectra of Co(BAE) and Co(F_3BAE) have been obtained and interpreted. These low-spin d^7 complexes show spectra strikingly different from those of the other low-spin cobalt(II) systems for which NMR spectra have been reported. In the complexes discussed here there is a substantial contact contribution to the isotropic shifts. The pattern of contact shifts was interpreted with the help of CNINDO molecular orbital calculations. It was concluded that α-spin density is delocalized into the ligand HOMO. The pattern and magnitude of the contact shifts are suprisingly insensitive to the presence or absence of axial bases. However the line widths and therefore the electron relaxation time is quite dependent on axial ligation and on the nature of the solvent. In addition the temperature dependence of the isotropic shifts is discussed. Finally, the NMR behavior of the Co(BAE) and Co(F_3BAE) systems is contrasted to that of other low-spin d^7 systems.

Introduction

The electronic properties of low-spin cobalt(II) complexes have received substantial attention in recent years.[1-11] This is due in part to the fact that many of these complexes bind oxygen reversibly. In addition certain members of this class of complexes have been suggested as model systems for vitamin B_{12r}. One group of low-spin cobalt(II) systems which have received a great deal of recent attention is the cobalt(II) porphyrins.[2,12,13] Interest in cobalt(II) porphyrins has been heightened by the discovery that cobalt-substituted hemoglobin, "coboglobin", binds oxygen in a cooperative fashion.[14,15] Thus, there are several lines of current research to which the properties of low-spin cobalt(II) complexes are relevant.

La Mar and Walker have reported the NMR spectra of several cobalt(II) porphyrins.[13] This work showed quite clearly that the observed isotropic shifts were due primarily to the dipolar or pseudocontact interaction. Besides this work on cobalt(II) porphyrins the NMR spectra of other low-spin cobalt(II) systems have revealed rather small contact contributions to the isotropic shifts.[16,17] Thus, all of the previous low spin cobalt(II) systems have qualitatively exhibited the same behavior when examined by NMR spectroscopy.

Bis(acetylacetone)ethylenediiminecobalt(II), Co(BAE), is one of the low-spin cobalt(II) complexes which has been studied in great detail. The ligand system is



where X = H for BAE and X = F for F_3BAE.

The magnetic properties and ESR spectra of the complexes are quite representative of the low-spin d^7 electronic configuration and thus are formally similar to cobalt(II) porphyrins and vitamin B_{12r}.[4] However, we have found that the NMR spectrum of this particular cobalt(II) complex is substantially different from the other low-spin cobalt(II) complexes which have been investigated.

In this system there is a substantial contact contribution to the observed isotropic shift. We report here a study of the NMR spectra of bis(acetylacetone)ethylenediiminecobalt(II) and the related bis(trifluoroacetylacetone)ethylenediiminecobalt(II). It will be shown that the isotropic shifts are largely contact in origin. In addition the reasons for the striking dissimilarity between this system and other low-spin cobalt(II) systems such as the cobalt(II) porphyrins will be discussed.

Experimental Section

Preparation of Ligands and Complexes. The ligands bis(acetylacetone)ethylenediimine (BAE) and bis(3-trifluoroacetylacetone)-