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Correlation of Circular Dichroism and Stereochemistry in Cobalt(III) Chelates with Ethylenediamine-*N,N'*-diacetate

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The complexes *uns-cis*-[Co(EDDA)L]$^-$ where EDDA is ethylenediamine-*N,N'*-diacetate and L is carbonate, oxalate, or malonate have been resolved and the circular dichroism (CD) spectra compared with the spectra of the corresponding s-cis isomers to assess the relative contributions of configurational and vicinal effects as well as chelate ring size to rotatory strengths. Changes in the chelate ring distribution (configurational effect) and the chirality of the nitrogen centers (vicinal effect) were found to have a marked and systematic effect on the CD spectra.

Introduction

While the circular dichroism (CD) spectra of Co(III) complexes with EDDA and its *N,N'*-dialkyl-substituted analogs in the s-cis geometry[1] have been studied extensively,[2-6] optically active *uns-cis*-Co(III)-EDDA complexes have not received comparable attention. This has been partly due to the fact that the uns-cis isomers are often either prepared in very poor yields or are less readily isolated from reaction mixtures than the s-cis isomers. Legg and Cooke[7] found that only small amounts of *uns-cis*-[Co(EDDA)L]$^+$ (L = en or $(NH_3)_2$) were formed from charcoal-catalyzed reactions which should favor a thermodynamic equilibrium distribution of isomers. They postulated that unfavorable nonbonding interactions involving the amine hydrogens of the uns-cis isomers were responsible for the poor yields. It was subsequently shown[8,9] that good yields of uns-cis isomers could be obtained, under the same reaction conditions, when the bidentate ligand was CO_3^{2-}, ox^{2-}, or mal^{2-}, for which the proposed steric interactions are absent. Recently, the syntheses in good yield of several other *uns-cis*-Co(III)-EDDA complexes have been reported.[10-13]

CD studies[2-4,6] of *s-cis*-Co(III)-EDDA complexes have shown that the rotatory strengths in the first (T_{1g}) absorption band region are exceptionally high for Co(III) complexes and that the CD peak intensities and frequencies are unusually insensitive to changes in field strength and size of a chelate ring at the octahedral sites not occupied by EDDA. Of particular significance it was also found[4-6] that the asymmetric nitrogens of EDDA make a contribution (vicinal effect) to the rotatory strengths comparable to the configurational effect in magnitude.

uns-cis-Co(III)-EDDA complexes possess a different configuration of chelate rings than do the s-cis isomers (Figure 1). In addition, while they have two asymmetric nitrogens, as do the s-cis isomers, the nitrogens may have either the same or opposite chiralities depending upon the mode of coordination of the in-plane nitrogen (N_1 in Figure 1).

The availability of Co(III)-EDDA complexes in the uns-cis geometry has now made possible the resolution of these isomers and an examination of the effect of change in EDDA geometry on the CD spectra. The *uns-cis*-[Co(EDDA)L]$^-$ complexes with L = CO_3^{2-}, ox^{2-}, and mal^{2-} were chosen for study since, with these ligands, the s-cis and uns-cis isomers have approximately the same crystal field (*cis*-N_2O_4). In this way, complications due to differences in the ligand field in comparing the CD spectra of s-cis and uns-cis isomers are minimized. Resolution of the CO_3^{2-}, ox^{2-}, mal^{2-} series also allows an examination of the effect of chelate ring size on the CD spectra. This is of particular interest as recent studies[14,15] have demonstrated that the rotatory strengths of tris(bidentate) complexes are very sensitive to changes in the ligand-metal-ligand bond angles which in turn are a function of chelate ring size.

Experimental Section

Resolution of Sodium *uns-cis*-Carbonato(ethylenediamine-*N,N'*-diacetato)cobaltate(III), Na-*uns-cis*-[Co(EDDA)CO_3]·1.5H_2O. The carbonato complex was prepared by the method of Halloran and Legg.[13] Resolution was achieved as follows. (−)-[Co(en)$_2$ox]I[16] (6.5 g, 0.0165 mol) and 2.75 g (0.0165 mol) of silver acetate were mixed thoroughly and 30 ml of water was added. After stirring for 15 min at 50–60°, the mixture was filtered into a beaker containing 10.42 g (0.0313 mol) of *uns-cis*-Na[Co(EDDA)CO_3]·1.5H_2O. The silver salts on the filter were washed with a few milliliters of water which were added to the filtrate. The mixture containing the filtrate was stirred at 50–60° until all solid dissolved and then was placed under a compressed air stream until crystals began to form (*ca.* 30 min). After 15–20 min, the fine purple crystals were filtered and washed with 95% ethanol and acetone and dried on a filter by suction. The product (7.5 g) was recrystallized three times from hot water by cooling in ice, filtering, and washing as before. The yield of [Co(en)$_2$ox][Co(EDDA)CO_3]·7H_2O ($\Delta\epsilon_{567}$ = +1.82) was 3.5 g. The circular dichroism was unchanged by further recrystallization. *Anal.* Calcd for [Co($C_6H_{16}N_4O_4$)][Co($C_7H_{10}N_2O_7$)]·7H_2O: C, 22.74; H, 5.87; N, 12.24. Found: C, 22.74; H, 4.88; N, 12.28.

The isomer forming the more soluble diastereomer was not isolated from the filtrate because of the tendency of the optical isomers to racemize and difficulties in crystallization. This isomer was instead obtained by repeating the above procedure, only using

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(1) s-cis is equivalent to trans(0) or α-cis while uns-cis is equivalent to c_1-cis-(0) or β-cis in the two other nomenclature systems that have been used for octahedral complexes of EDDA.

(2) J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, 6, 700 (1967); J. I. Legg and B. E. Douglas, *ibid.*, 7, 1542 (1968).

(3) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, 8, 115 (1969).

(4) C. W. Maricondi and B. E. Douglas, *Inorg. Chem.*, 11, 668 (1972).

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(6) W. T. Jordan and B. E. Douglas, *Inorg. Chem.*, 12, 403 (1973).

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

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

(9) P. F. Coleman, J. I. Legg, and J. Steele, *Inorg. Chem.*, 9, 937 (1970).

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(12) P. J. Garnett, Ph.D. Thesis, University of Western Australia, 1972; P. J. Garnett and D. W. Watts, *Inorg. Chim. Acta*, in press.

(13) L. J. Halloran and J. I. Legg, submitted for publication.

(14) K. R. Butler and M. R. Snow, *Inorg. Chem.*, 10, 1838 (1971), and references therein.

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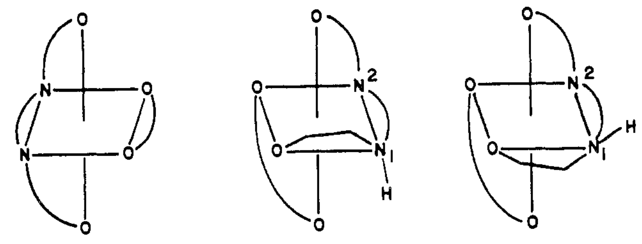

Λ-SS-s-cis Λ-RS-uns-cis Λ-RR-uns-cis

Figure 1. The cis isomers of $[Co(EDDA)(O{-}O)]^-$.

D-(+)-$[Co(en)_2ox]I$. An enantiomeric CD curve was obtained.

In spite of the use of a variety of techniques and cations, efforts to obtain a crystalline salt of either optical isomer of *uns-cis*-$[Co(EDDA)CO_3]^-$ were unsuccessful. Solutions containing either Na^+, K^+, Ca^{2+}, Ag^+, or Ph_4As^+ always dried to a glass. The CD data, therefore, were obtained in the following manner: A mixture of 0.1023 g (0.000493 mol) of either diastereomer and 2 g of Dowex 50W-X8 cation-exchange resin (100–200 mesh) in the Na^+ form was stirred with *ca.* 5–10 ml of ice-cold water until all the diastereomer had dissolved. The mixture was quickly filtered into a beaker containing 1 g of the same resin and this mixture was stirred briefly and filtered. The resin filtered from the second mixture was colorless indicating essentially complete removal of $[Co(en)_2ox]^+$ on the first contact. The resin on the filter was washed with cold water until the washings were colorless. The combined filtrate and washings were transferred quantitatively to a 25-ml volumetric flask and diluted to the mark. The above process required no longer than 5 min and racemization was insignificant. The final CD data were obtained from this solution ($\Delta\epsilon_{550} = +2.80$, $\Delta\epsilon_{383} = -0.67$). A visible absorption spectrum of the solution indicated complete absence of $[Co(en)_2ox]^+$ and confirmed the concentration of the complex ion by comparison with the molar absorptivity for racemic $Na[Co(EDDA)CO_3]\cdot 1.5H_2O$.

Preparation of (+)- and (–)-Potassium *uns-cis*-Oxalato(ethylenediamine-*N,N′*-diacetato)cobaltate(III) Monohydrate, K-*uns-cis*-[Co(EDDA)ox]·H₂O. A mixture of 0.291 g (0.00175 mol) of KI and 1.200 g (0.00175 mol) of (–)-$[Co(en)_2ox]$-(+)-$[Co(EDDA)CO_3]$ ($\Delta\epsilon_{565} = +1.82$) was stirred in 10 ml of ice-cold water for 10 min and filtered into 1 g of Dowex 50W-X8 cation-exchange resin (100–200 mesh) in the K^+ form. The (–)-$[Co(en)_2ox]I$ was washed with a few milliliters of cold water. The combined filtrate, washings, and resin were stirred for a few minutes and filtered. To the filtrate was added 0.221 g (0.00175 mol) of oxalic acid, and the solution was warmed on a steam bath until CO_2 was no longer evolved when the solution was stirred. The solution was filtered and the filtrate evaporated to a volume of 4 ml. An equal volume of 95% ethanol was stirred in, and, after the solution had stood for 1 hr, the sides of the beaker were scratched to induce crystallization. The violet crystals were filtered, washed with 95% ethanol and acetone, and dried by suction. The yield of K-*uns-cis*-$[Co(EDDA)ox]\cdot H_2O$ ($\Delta\epsilon_{544} = +2.01$) was 0.3 g. This was recrystallized once by dissolving in a little water and adding ethanol. The yield ($\Delta\epsilon_{544} = +2.05$) was 0.2 g. The circular dichroism was unchanged by further recrystallization. The (–) isomer, obtained by an identical procedure, only using the opposite diastereomer, gave an enantiomeric CD curve. *Anal.* Calcd for $K[Co(C_8H_{10}N_2O_8)]\cdot H_2O$: C, 25.41; H, 3.20; N, 7.54. Found: C, 25.33; H, 3.09; N, 7.37.

Preparation of (+)- and (–)-*uns-cis*-Malonato(ethylenediamine-*N,N′*-diacetato)cobaltate(III) Ion, *uns-cis*-[Co(EDDA)mal]⁻. An attempt to prepare the enantiomers in the same way as the oxalato analogs above was unsuccessful because of failure to obtain crystals of the optical isomers. Resolution was achieved, however, by preparing (±)-$[Co(en)_2ox]$-(∓)-$[Co(EDDA)mal]$ from the carbonato diastereomer as follows: A mixture of 1.66 g of (+)-$[Co(en)_2ox]$-(–)-$[Co(EDDA)CO_3]$ and 0.251 g (0.00242 mol) of malonic acid in 10 ml of water was heated on a steam bath until gas evolution had ceased. The solution was filtered and 95% ethanol (*ca.* 10 ml) was added. After 30–40 min, fine crystals were filtered and washed with 95% ethanol and acetone and dried by suction. The yield ($\Delta\epsilon_{602} = \pm 0.76$) was 1.1 g. After recrystallizing the diastereomer twice the CD intensities ($\Delta\epsilon_{602} = \pm 0.80$) were unchanged by further recrystallization. *Anal.* Calcd for $[Co(C_6H_{16}N_4O_4)][Co(C_9H_{12}N_2O_8)]\cdot 3H_2O$: C, 27.45; H, 5.22; N, 12.81. Found: C, 27.26; H, 4.95; N, 12.86.

The salts of (+)- or (–)-$[Co(EDDA)mal]^-$ with cations such as Na^+, K^+, and Ph_4As^+ do not crystallize readily. It was, therefore, convenient to obtain the CD data for the malonato complex in the same way as described for the carbonato complex above. Elemental analyses were obtained from the Material Sciences Department, Washington State University.

Spectra. The absorption spectra were measured on a Cary 14 spectrophotometer using a tungsten lamp. The CD spectra were recorded on a JASCO ORD-UV5 spectrophotometer equipped with a xenon source and calibrated with purified *d*-10-camphorsulfonic acid using the value $\Delta\epsilon_{290} = +2.34$.[17] The spectra were taken at room temperature at concentrations of *ca.* 10^{-3} *M.*

Results and Discussion

Visible Absorption Spectra. The visible absorption spectra of the uns-cis isomers of $[Co(EDDA)CO_3]^-$, $[Co(EDDA)ox]^-$, and $[Co(EDDA)mal]^-$ are shown in Figure 2. To facilitate comparison, the corresponding data of Van Saun and Douglas[3] for the s-cis analogs are shown in Figure 3. It has previously been noted[7,9] that the molar absorptivities are much greater for the uns-cis than for the s-cis complexes and that this is consistent with the lower symmetry in the former case. The uns-cis complexes have C_1 symmetry, and three nondegenerate transitions are expected in both first (T_{1g}) and second (T_{2g}) absorption band regions of octahedral parentage. However, a broad, nearly symmetrical band is observed in each region of the absorption spectrum for each complex. The s-cis isomers also give rise to broad absorption bands, and there is some splitting of the T_{1g} band in the spectrum of the carbonato complex. The absorption maxima in the T_{1g} region are displaced to somewhat lower energy for the s-cis isomers relative to the uns-cis isomers, and for each set of isomers the maximum of the carbonato complex in this region is lower in energy than the corresponding oxalato and malonato maxima. However, as anticipated for these *cis*-N_2O_4 isomers, the spectra are quite similar in overall appearance.

Circular Dichroism Spectra and Absolute Configurations. The CD spectra of the uns-cis isomers are shown in Figure 2. It is quite often found that CD spectra are resolved to a higher degree than are the corresponding absorption spectra. In the spectra of the *uns-cis*-carbonato and -oxalato complexes, however, there is only one CD maximum in each (T_{1g} and T_{2g}) region. In striking contrast, three extrema of T_{1g} and two of T_{2g} parentage are observed in the CD spectrum of *uns-cis*-$[Co(EDDA)mal]^-$. The greater resolution found in the CD spectrum of the malonato complex relative to its carbonato and oxalato analogs is not unique to the *uns-cis*-EDDA system. Similar results have been observed for the complexes $[CoL_3]^{3-}$,[18] $[CoL_2en]^-$,[19] $[Co(en)_2L]^+$,[16] and $[CoL_2gly]^{2-}$,[20] where L = ox^{2-} or mal^{2-}. In each case, the CD peaks of the malonato complex are narrower and the resolution is greater relative to the oxalato complex.

There is little doubt that the optical isomers of the *uns-cis*-EDDA complexes corresponding to the CD curves in Figure 2 have the same absolute configurations. Not only

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(17) W. C. Krueger and L. M. Pschigoda, *Anal. Chem.*, 43, 675 (1971). *d*-10-Camphorsulfonic acid appears to be one of the most suitable standards for CD calibration since it is readily purified and gives a sharp CD maximum in the near uv. However, there is not, at this time, agreement as to the absolute circular dichroism of this compound. Therefore, the value used to calibrate the instrument in this study is given here to facilitate accurate comparison of CD data.

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(19) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, 2, 1194 (1963).

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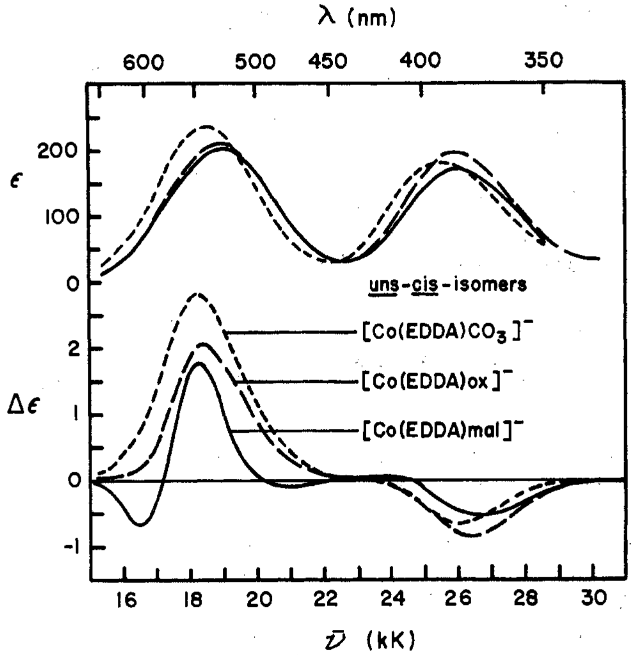

Figure 2. The CD and absorption spectra of the uns-cis isomers of Na[$Co(EDDA)CO_3$], K[Co(EDDA)ox], and Na[Co(EDDA)mal].

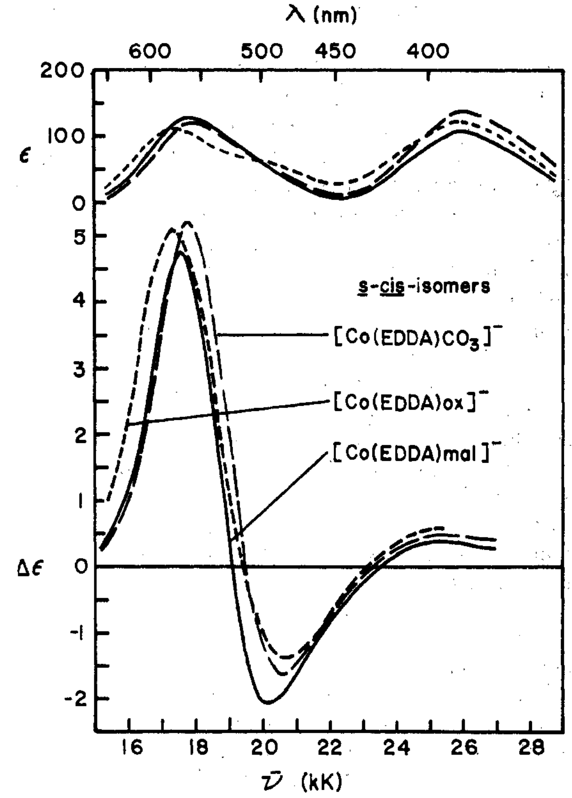

Figure 3. The CD and absorption spectra of the s-cis isomers of K[$Co(EDDA)CO_3$], K[Co(EDDA)ox], and Na[Co(EDDA)mal] (from ref 3).

is there an obvious similarity between the spectra but the oxalato and malonato complexes were prepared directly from resolved *uns-cis*-$[Co(EDDA)CO_3]^-$ by displacement of carbonate. It is reasonable to assume that the substitution reaction occurred with retention rather than inversion of configuration. Assuming the configurational effect to dominate the CD spectra, these complexes can be considered within the framework of a model developed by Mason, *et al.*,[21] to assign absolute configurations to *cis*-CoA_4B_2 chelates by relating their CD spectra to that of $[Co(en)_3]^{3+}$ for which the absolute configuration is known.[22] By this method, the complexes corresponding to the spectra in Figure 2, in each of which there is a dominant peak at *ca.* 18.2 kK, are tentatively assigned the ΛΛΛΔ,[23] or net Λ configuration[24] (Figure 1). These assignments are consistent with the conclusions reached in a pmr study[25] of *uns-cis*-[Co(LL-EDDP)(*l*-pn)]$^+$ (LL-EDDP is ethylenediamine-N,N′-di-L-α-propionate), where the optical isomers could be distinguished because of their diastereomeric relationship and the known absolute configuration of the ligands employed. The correlation of the CD spectra of *uns-cis*-EDDA–diamine and -dicarboxylato complexes is justified on the basis of the similarity of their spectra.[11,13]

Comparison of Circular Dichroism Spectra between the Uns-Cis and S-Cis Geometries. The dominant CD band intensities of the *uns-cis*-EDDA complexes, Figure 2, are all much smaller than those reported[3] for the s-cis analogs, Figure 3. The relative intensities of CD bands are expected to be dependent in part upon the relative degrees of splitting of the components of the first absorption band, and the T_{1g} visible absorption bands of the s-cis complexes are somewhat broader than those of the uns-cis complexes. Nevertheless, it is also true that the *net* T_{1g} as well as net total d–d rotatory strengths are smaller for the uns-cis relative to the s-cis complexes. The net rotatory strengths are independent of the splitting of component transitions.

There are two important structural features which are expected to have a major effect on the relative CD intensities of the *s-cis*- and *uns-cis*-EDDA complexes. These are the configurational effect due to the arrangement of chelate rings and the vicinal effect due to the asymmetric nitrogen donor atoms of EDDA. The *s-cis*-EDDA complexes with carbonate, oxalate, or malonate have three chelate ring pairs of identical chirality.[23,24] For the s-cis isomer shown in Figure 1 these ring pairs are designated ΛΛΛ (net Λ).[24] For the uns-cis complexes there are four chelate ring pairs, three of one chirality and one of opposite chirality, ΛΛΛΔ (net Λ) for the isomer shown in Figure 1. Thus, the uns-cis isomers have a *net* of two ring pairs of like chirality which might be expected to make a smaller configurational contribution to the rotatory strength than the (net) three pairs of the s-cis geometry.

It has been shown[4,5] that, for the *s-cis*-EDDA complexes, large rotatory strengths arise from the asymmetric nitrogen atom donors. Although the *net* vicinal effect from this source is quite small, the two T_{1g} components, which are of opposite sign, have very high intensity. The sign of the vicinal contribution for the low energy component is positive for the S configuration about the nitrogens and negative for the R configuration. For the low energy CD band of the oxalato[3] and diamine[4,6] complexes, the vicinal contribution has the same sign as the configurational effect so that the CD intensities from the two sources add to give an unusually high total rotatory strength (*e.g.*, $\Delta\epsilon = \pm 5.2$ for *s-cis*-[Co(EDDA)ox]$^-$).[3]

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In the *uns-cis*-EDDA complexes the asymmetric nitrogens are quite similar to those of the s-cis complexes. The "angular" nitrogen (N_2 in Figure 1) is essentially identical in stereochemical arrangement with the *s-cis*-nitrogens, and its chirality is determined by the arrangement of chelate rings.[26] The "planar" nitrogen (N_1) differs in that the acetate group is coplanar with the nitrogens. Nevertheless, it is probable that the sign of the vicinal rotatory strength is unchanged since the immediate stereochemical environment of a planar nitrogen is quite similar to that of an angular nitrogen. However, unlike an angular nitrogen, a planar nitrogen can assume either an *R* or *S* configuration. In principle, then, two geometrically different uns-cis isomers are possible. For the Λ isomer shown in Figure 1 the nitrogen configuration could be *RR* or *RS*. Assuming the vicinal effect to be similar to that found for s-cis complexes, the dominant peak should be diminished in the *RR* case (negative vicinal, positive configurational) and relatively unaffected in the *RS* case (vicinal effects approximately cancel). Thus, in either situation a less intense dominant band is expected relative to s-cis complexes. It is important to emphasize that the vicinal effect does not have a large effect on the *net* T_{1g} rotatory strength of the s-cis complexes and, likewise, is not expected to contribute appreciably to the net rotatory strength of the uns-cis complexes. Thus, changes in the vicinal effect can account for the large difference in the dominant CD peak intensities for analogous s-cis and uns-cis complexes, whereas changes in the net chelate ring configurational effect can satisfactorily account for the large differences in net d-d rotatory strength.

In light of the above arguments, it is of interest to compare the CD spectrum of *uns-cis*-[Co(EDDA)ox]⁻ with the data reported by Matsuoka, *et al.*,[27] for the structurally similar complex, c_1-*cis*-(N)-[Co(gly)$_2$ox]⁻, Figure 4. These complexes differ in that the ethylene backbone of EDDA is absent in the bis(glycinato) complex. With respect to structural sources of dissymmetry there are two important differences. The bis(glycinato) complex has no asymmetric nitrogens and has one less chiral ring pair than the *uns-cis*-EDDA analog. The absolute configuration of the complex corresponding to the CD curve in Figure 4 is $\Lambda\Lambda\Lambda$. The configuration of the analogous EDDA complex is $\Lambda\Lambda\Lambda\Delta$, and it has been argued above that the effect of the Δ ring pair should be opposite in sign to that of the three Λ pairs. The results are consistent with this argument as the bis(glycinato) complex has a greater net d-d rotatory strength than the EDDA complex. Since the bis(glycinato) complex contains no asymmetric nitrogens, the differences in the CD curves should also reflect the vicinal contribution to the circular dichroism of the EDDA complex. For the Λ isomer of *uns-cis*-[Co(EDDA)ox]⁻ shown in Figure 4, the vicinal effect is predicted to have a negative low-energy component and a positive high-energy component in the T_{1g} region and a negative band in the T_{2g} region. These predictions are consistent with the differences observed in the CD curve shapes. However, it must be pointed out that the differences in the curve shapes are not large and this suggests that the vicinal effect in *uns-cis*-[Co(EDDA)ox]⁻ is much smaller than in the case of the s-cis isomer. This would be expected if the oxalato complex had the *RS* (*SR*) configurations about the nitrogens. However, a pmr study[9] (see below) indicates the opposite (*RR*, *SS*) situation.

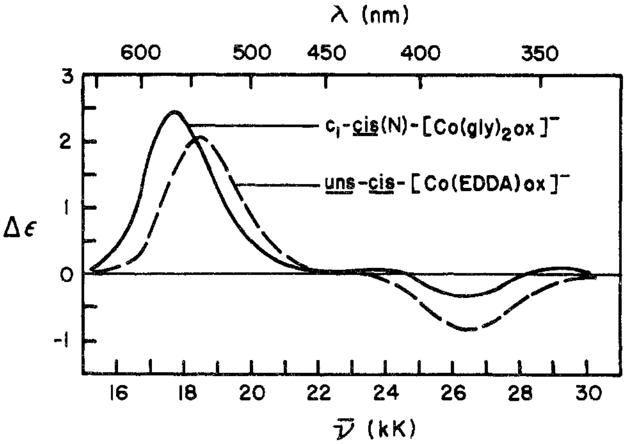

Figure 4. Comparison of the CD spectra of c_1-*cis*-(N)-[Co(gly)$_2$ox]⁻ (from ref 27) and *uns-cis*-[Co(EDDA)ox]⁻.

Effect of Chelate Ring Size. A comparison of the CD spectra of the *uns-cis*-EDDA-dicarboxylato complexes (Figure 2) reveals that the net d-d rotatory strengths, as well as the dominant peak intensities, decrease in the order $CO_3^{2-} > ox^{2-} > mal^{2-}$, with increasing chelate ring size. This is the trend (*net* rotatory strengths) commonly observed for several series of Co(III) complexes involving these dicarboxylate ligands.[16,18-20,28] Changes in electron delocalization and vibronic contributions could account for the significant changes in the CD spectra. However, large changes in these variables would be reflected in large changes in the absorption spectra as well. It is likely that the major contribution is due to changing dissymmetric distortions of the octahedron which accompany changes in the chelate ring size. As the chelate ring size increases through the series $CO_3^{2-} < ox^{2-} < mal^{2-}$, the O-M-O bond angle opens considerably.[29] Piper's model and subsequent theories[30] of optical activity in six-coordinate metal complexes predict significant rotatory strengths as a result of displacement of ligating atoms from octahedral geometry. This has been shown to be a dominant effect on the signs of the rotatory strengths of tris(diamine)[14] and tris(dicarboxylato)[15] complexes but has been studied much less extensively in complexes of lower symmetry.

An additional factor which could affect the relative rotatory strengths of the *uns-cis*-EDDA complexes with CO_3^{2-}, ox^{2-}, and mal^{2-} would be any variation in the vicinal effect. The pmr studies of Coleman, *et al.*,[9] established that, in solution, the oxalato and malonato complexes existed in only one of the two possible isomeric forms with respect to the coordination of the in-plane nitrogen, the *SS*, *RR* racemate, Figure 1. On the other hand, it has recently been shown by Garnett and Watts using pmr that the corresponding carbonato complex exists in solution as a mixture of the two isomeric forms (*SS* and *SR* or *RR* and *RS*).[12] According to the interpretation of the vicinal contribution given above, the *SR* (*RS*) isomer should give

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(26) In the s-cis isomers, the configuration of EDDA determines the configuration of the nitrogens; *e.g.*, for the Λ isomer the two nitrogens have the S configuration.

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rise to a more intense dominant CD band than the *SS* (*RR*) isomer. Thus, a mixture of the two isomers should give rise to a more intense dominant CD band than the *SS* (*RR*) isomer alone. That the carbonato complex exhibits a distinctly higher $\Delta\epsilon$ than the corresponding oxalato and malonato complexes is consistent, then, with the distribution of isomers determined by the pmr studies.

Summary. The geometrical isomerism of Co(III)-EDDA complexes permits a study of how changes in the ligand geometry affect rotatory strengths. The changes observed in the CD spectra are consistent with the changes known to occur in two important structural sources of dissymmetry in these complexes, the arrangement of chelate rings and the configurations about the asymmetric nitrogen atoms.

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Registry No. *uns-cis*-Λ-[Co(EDDA)CO_3]$^-$, 50306-65-5; *uns-cis*-Λ-[Co(EDDA)ox]$^-$, 50306-66-6; *uns-cis*-Λ-[Co(EDDA)mal]$^-$, 50306-67-7; *uns-cis*-Na[Co(EDDA)CO_3], 50306-68-8; [Co(en)$_2$ox][Co(EDDA)CO_3], 50306-69-9; *uns-cis*-[Co(EDDA)CO_3]$^-$, 26135-69-3; HO_2CCO_2H, 144-62-7; *uns-cis*-K[Co(EDDA)ox], 50306-71-3; [Co(en)$_2$ox][Co(EDDA)mal], 50306-72-4.

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Effects of Ligand Modifications on the Kinetics of Base Exchange in Methylatobis(diimine)cobalt(III) Adducts[1]

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The kinetics of base exchange in CH_3Co(chel)B complexes, where chel = bis(dimethylglyoximato) (I), diacetylmonoxime-iminodiacetylmonoximato-1,3-propane (II), or 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (III), have been observed in various organic solvents, most notably $C_6H_5NO_2$. The rates of base exchange with II are in the order $CH_3OH > NCCH_3 > N(CH_3)_3 > S(CH_3)_2 > P(OCH_3)_3 >$ 1-(2-trifluoromethylphenyl)imidazole, which parallels the order previously observed for adducts of I. Adducts with III are of generally lower thermal stability, and extensive kinetics data could not be obtained. For $P(OCH_3)_3$ as base, $\Delta G^\ddagger$ for exchanges with I, II, and III are essentially all the same. For $NCCH_3$ as base, $\Delta G^\ddagger$ varies in the order III > II > I. In all three complexes, exchange of oxygen bases from the axial position was quite rapid, although oxygen bases appear to bind relatively more stongly in the order III > II > I. These results and other base exchange data are consistent with a small variation in positive charge at the central metal in the order III > II > I. Exchange of the proton in the OHO bridge of II with free water in C_6H_5Br is considerably slower than the analogous process for the OHO protons of I. These observations are consistent with the shorter O· · ·O distance in II as compared with I.

Introduction

In previous publications we have reported the rates of base exchange for alkylatobis(dimethylglyoximato)cobalt(III) complexes, RCo(dh)$_2$B, on the basis of variable temperature nmr studies.[2,3] These results have served to establish an ordering of a wide range of bases with respect to exchange lability. In addition, variation of the group R has served to point up the existence of a substantial trans effect on base exchange.[4] More recently we have determined the comparative kinetics of exchange of bases from three methylatocobalt(III) chelate complexes, CH_3Co(chel)B, primarily on the basis of ^{19}F nmr exchange data for the base 1-(2-trifluoromethylphenyl)imidazole, $ImCF_3$.[5] The free energy of activation for exchange of $ImCF_3$ from $CH_3Co(dh)_2$, CH_3Co(bae), and methylato(cobyrinic acid heptamethyl ester) was found to be 21.2, 9.4, and 16.7 kcal/mol, respectively. This very large range of $\Delta G^\ddagger$ values demonstrates the importance of the planar ligand system in determining the lability of the cobalt center.

More subtle changes in the nature of the planar ligand system would make it possible to evaluate the effect of changing ligand donor character on the relative labilities of a series of bases. Accordingly, we have observed the nmr spectra of several adducts of the three cobalt systems $CH_3Co(dh)_2$, $CH_3Co(tmed)^+$, and $CH_3Co(tim)^{2+}$ shown as I, II, and III, respectively.

These complexes differ in the successive replacement of the $(-OHO-)^-$ groups which bind together the two diimine halves of the ligand by $-(CH_2)_3-$ groups. Since the $(-OHO-)^-$ group carries a net negative charge, it is expected to be relatively more electron releasing than $-(CH_2)_3-$. Accordingly, the effective charge on cobalt should increase in the order I < II < III. The overall charge on the cobalt complex also increases, of course, as indicated above. At the same time, the geometry about the metal center changes very little in the series. Variations in base exchange rates may thus be ascribed to predominantly electronic rather than steric effects.

Results and Discussion

In the presence of excess base, the nmr spectra of complexes I, II, and III show resonances assignable to free and coordinated base. Table I lists the chemical shifts of these resonances at a temperature in the stopped-exchange region,

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