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Circular Dichroism of a Second Geometrical Isomer of Ethylenediamine-*N*,*N'*-diacetato-*N*,*N'*-di-3-propionatocobaltate(III) Ion

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A second geometrical isomer, *trans*(O_5O_6)-Co(EDDDA)$^-$, of the Co(III) complex of ethylenediamine-*N*,*N'*-diacetic-*N*,*N'*-di-3-propionic acid has been prepared and resolved. More complete resolution of the previously reported trans(O_5) isomer has been achieved. Electronic absorption, circular dichroism (CD), and nmr spectra were used to characterize the new isomer and confirm the identity of the one previously reported. Both isomers with lowest energy (+) CD peaks are tentatively assigned the Λ configuration.

Introduction

Complexes structurally related to Co(EDTA)$^-$ (EDTA = ethylenediaminetetraacetate) are of interest in the study of factors contributing to their optical activity. X-Ray studies[2] of the Co(EDTA)$^-$ complex have shown that the two glycinate rings which lie in the plane of the two coordinated nitrogens (the so-called G rings) are more strained than the two glycinate rings lying outside this plane (R rings). The CD spectra[3] differ for Co(EDTA)$^-$, Co(1,3-PDTA)$^-$ (1,3-PDTA = 1,3-propanediaminetetraacetate), and Co(EDTP)$^-$ (EDTP = ethylenediaminetetrapropionate) because of changes in the size and arrangements of the chelate rings. Because of the interest in the optical activity of the Co(EDTA)$^-$ type complexes, three structurally similar ligands, EDDDA[4] (EDDDA = ethylenediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate), EDDS[5] (EDDS = (*S*,*S*)-ethylenediamine-*N*,*N'*-disuccinate), and EDDAMS[6] (EDDAMS = (*S*)-ethylenediamine-*N*,*N*-diacetate-*N'*-monosuccinate), have been prepared and the CD spectra of the corresponding cobalt(III) complexes have been reported. It was found that, assuming there is more strain in the G plane for five-membered rings than for six-membered rings, the EDDDA and EDDS ligands preferentially form isomers having two six-membered rings in the G plane. Their circular dichroism curves are very similar in shape. On the basis of this similarity and by means of correlation with the spectrum of the Co(EDTA)$^-$, which is of known absolute configuration,[7-9] the configuration of the trans(O_5) geometrical isomer of Co(EDDDA)$^-$ was assigned.[4]

In the case of the EDDDA,[4] EDDS,[5] and EDDAMS[6] complexes, besides the contribution to optical activity due to the relative size and distribution of the chelate rings, consideration of the contributions due to the asymmetric nitrogen or carbon atoms and ring conformational effects are important in the study of the rotational strengths of the CD bands. In order to evaluate the contribution due to the asymmetric nitrogens in the Co(EDDS)$^-$ complex, Jordan and Legg[10] prepared *N*-methyl and *N*,*N'*-dimethyl derivatives of EDDS (MEDDS and DMEDDS). Because of only slight changes in the CD spectra among the Co(III) complexes, they concluded that there is only a very small contribution to rotational strength due to the asymmetric nitrogen atoms in the EDDS system. The contribution of the chelate rings to optical activity for these complexes, then, strongly depends on both their relative size, as postulated by Legg and Neal,[6] and their disposition about an octahedron. We cannot yet say just how large the relative contributions are. This question could be partially clarified if the CD spectra of the optical isomers of all three possible geometrical isomers of Co(EDDDA)$^-$ (Figure 1) could be measured. It was for this reason that we have continued the work with the EDDDA ligand, in the hope that we could prepare and resolve the trans(O_5O_6) and trans(O_6) geometrical isomers (not previously prepared), which have different dispositions of five-membered (glycinate) and six-membered (β-alaninate) rings about an octahedron. Earlier work led to the isolation of only one isomer of Co(EDDDA)$^-$.

Experimental Section

H_4EDDDA[4] and $Na_3[Co(NO_2)_6]$[11] were prepared using previously described procedures. All other reagents and solvents were obtained commercially and used without further purification.

Optical isomers are identified by (+) or (−), corresponding to the sign of the lowest energy CD band or by the sign of the optical rotation at a wavelength λ [(+)$_\lambda$ or (−)$_\lambda$]. The chirality is designated as Δ or Λ according to IUPAC rules.[12]

Preparation of the Trans(O_5) and Trans(O_5O_6) Geometrical Isomers of Potassium Ethylenediamine-*N*,*N'*-diacetato-*N*,*N'*-di-3-propionatocobaltate(III), K[Co(EDDDA)]. H_4EDDDA, 4.8 g (0.015 mol), was dissolved at 55° in 300 ml of water. To this solution, freshly prepared $Na_3[Co(NO_2)_6]$,[11] 6.06 g (0.015 mol), in 10 ml of water was then added, and heating and stirring at the same temperature were continued for 3 hr. After that, the temperature was increased to 85° for 5 hr more. The resulting blue-violet solution (*ca.* 100 ml) was then introduced into a 5 cm × 60 cm column containing Dowex 1-X4 (200–400 mesh) anion-exchange resin in the NO_3^- form. The column was then washed with H_2O and eluted with 0.1 *M* KNO_3 solution (*ca.* 0.5 ml/min). Two similarly colored bands, the first of which was blue-violet and the second violet, were obtained (*ca.* 3:1), in addition to a third, brown-violet, band which was more strongly bound to the column. After the elution of the first two bands was completed, the brown-violet band was separated into two bands[13] by elution with 0.2 *M* KNO_3.

The first eluate (blue-violet) was evaporated under vacuum at 50° to 30 ml and then cooled in a refrigerator for 2 hr. The deposited KNO_3 was removed by filtration. To the filtrate was added 30 ml of ethanol, precipitating the complex. The complex was filtered off, washed with ethanol and then acetone, and air-dried; yield 4.5 g. This complex was recrystallized from a 1:1 water–ethanol mixture and identified by means of its electronic absorption spectrum as the earlier characterized[4] trans(O_5) geometrical isomer of K[Co(EDDDA)].

The second eluate (violet) was evaporated under vacuum at 30° to a volume of 15 ml and then cooled. KNO_3 was removed and 20 ml of ethanol was added to the filtrate. A precipitate formed which was filtered off, and the solution was cooled again for 3 hr. After removing some solid KNO_3, 15 ml more of ethanol was added to the filtrate and the solution was left in the refrigerator to stand for 6 hr to crystallize the second geometrical isomer of K[Co(EDDDA)]. This complex was filtered, washed with acetone, and air-dried; yield 0.7 g. The isomer was recrystallized by dissolving it in a small amount of water at room temperature, adding ethanol, and cooling. *Anal.* Calcd for $K[Co(EDDA)]\cdot 3H_2O$: C, 30.77; H, 4.73; N, 5.98; H_2O, 11.53. Found: C, 30.99; H, 4.73; N, 6.10; H_2O, 11.30.

Resolution of the Trans(O_5O_6) Geometrical Isomer of Potassium Ethylenediamine-*N*,*N'*-diacetato-*N*,*N'*-di-3-propionatocobaltate(III) Trihydrate, $K[Co(EDDDA)]\cdot 3H_2O$. Silver acetate, 0.80 g (0.0048 mol), and (−)$_D$-$[Co(en)_2ox]Br\cdot H_2O$, 1.60 g (0.0044 mol), were stirred together at 60° for 10 min in 20 ml of water. AgBr was removed by filtration and washed with 10 ml of water. The wash was added to the filtrate, to which solid *trans*(O_5O_6)-$K[Co(EDDDA)]\cdot 3H_2O$ (1.88 g, 0.004 mol) was then added at room temperature with stirring. To the resulting solution, 50 ml of ethanol was added and the solution

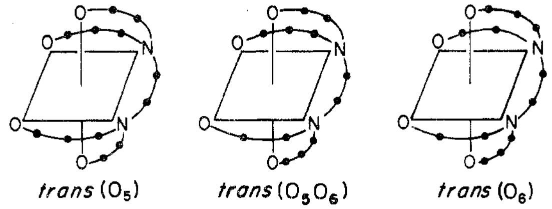

Figure 1. Three possible geometrical isomers of Λ-[Co(EDDDA)]$^-$.

was allowed to stand in the refrigerator for 6 hr. The less soluble diastereoisomer, (−)D-[Co(en)$_2$ox]-(−)D-[Co(EDDDA)]·xH$_2$O, was removed by filtration, washed with a small amount of ethanol and then acetone, and air-dried; yield 1.6 g. To the remaining filtrate about 60 ml of acetone was added slowly and the solution was left in the refrigerator overnight. The more soluble diastereoisomer, (−)D-[Co(en)$_2$ox]-(+)D-[Co(EDDDA)]·xH$_2$O, was filtered off and treated in the same way as above; yield 1.2 g. Both diastereoisomers were fractionally recrystallized to constant Δε values (assuming anhydrous 1:1 diastereoisomers, FW 642) by dissolving each in 15 ml of water at room temperature and by adding 20 ml of ethanol to each solution followed by cooling (however, in the case of the more soluble diastereoisomer, both ethanol and acetone were required for crystallization). $\Delta\epsilon_{532}$ −5.10 and $\Delta\epsilon_{604}$ −2.15 values were obtained for the less soluble and more soluble diastereoisomers, respectively.

The corresponding enantiomers in the form of silver salts were obtained by passing aqueous solutions of the diastereoisomers through a column in the Ag$^+$ form. The eluates were evaporated over sulfuric acid in a light-shielded vacuum desiccator to a volume of 3 ml. About 4 volumes of absolute ethanol was added to each solution, and the solutions were left in the refrigerator for the enantiomers to crystallize as the silver salts. The enantiomers were removed from the solutions by filtration, washed with absolute ethanol and then acetone, and air-dried. The pure enantiomers were also obtained in other experiments by evaporating the eluates to dryness: $\Delta\epsilon_{606}$ ±2.25, $\Delta\epsilon_{543}$ ∓3.12; $[\alpha]_D$ ∓1940° in 0.02% aqueous solution. *Anal.* Calcd for *trans*(O_5O_6)-(−)D-Ag[Co(EDDA)]·H$_2$O: C, 28.76; H, 3.62; N, 5.59; H$_2$O, 3.59. Found: C, 28.81; H, 3.65; N, 5.63; H$_2$O, 3.80.

Resolution of the Trans(O$_5$) Geometrical Isomer of Potassium Ethylenediamine-*N*,*N*'-diacetato-*N*,*N*'-di-3-propionatocobalt(III) Dibydrate, K[Co(EDDDA)]·2H$_2$O. The resolved trans(O$_5$O$_6$) isomer was isolated as the silver salt because the potassium salt is difficult to purify. It is more soluble than K[*trans*(O_5)-Co(EDDDA)]. The resolution of the trans(O$_5$) isomer was repeated using the procedure given above and more complete resolution was achieved than previously reported.[4] Both diastereoisomers were fractionally recrystallized from a mixture of water and ethanol (1:1) to constant values of Δε (for FW 642). Values of Δε of −4.66 (at 536 nm) and +1.10 (at 563 nm) were obtained for the less soluble and more soluble diastereoisomers, respectively. Optical purity of the enantiomers was achieved more easily as the silver salt: $\Delta\epsilon_{618}$ ±0.40, $\Delta\epsilon_{547}$ ∓2.78; $[\alpha]_D$ ∓1200° in 0.02% aqueous solution. *Anal.* Calcd for *trans*(O_5)-(−)D-Ag[Co(EDDDA)]·2H$_2$O: C, 27.76; H, 3.88; N, 5.39; H$_2$O, 6.94. Found: C, 27.65; H, 3.66; N, 5.39; H$_2$O, 7.20.

Physical Measurements. $[\alpha]_D$ values were measured in a 1-dm tube at 20° on an O. C. Rudolph and Sons polarimeter.

Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer (60 MHz). D$_2$O containing 1% of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (internal standard) was used as a solvent, and 10% D$_2$O solutions of the substances were used.

Electronic absorption spectra were recorded on a Cary Model 14 recording spectrophotometer using a tungsten lamp. For these measurements, 2.00 × 10^{-3} M aqueous solutions of the substances were used.

The circular dichroism curves were recorded at room temperature with a Roussel-Jouan Dichrograph using a Sylvania Sun Gun light source.

Analyses. Analyses were performed by Chemalytics Inc., Tempe, Ariz. The number of waters of crystallization was determined both from elemental analyses and by weight loss on drying at 80° under vacuum.

Results and Discussion

EDDDA, as an EDTA type sexadentate diaminepolycarboxylic ligand, forms by coordination to a metal three five-membered and two six-membered chelate rings. Considering the different orientations of the two glycinate and two β-alaninate rings about an octahedron, three cis(N) geometrical isomers are possible: trans(O$_5$), trans(O$_5$O$_6$), and trans(O$_6$) (Figure 1). The trans(O$_5$) and trans(O$_6$) isomers have a tetragonal ligand field and C_2 molecular symmetry (neglecting any conformational differences) while the trans(O$_5$O$_6$) isomer possesses a rhombic field and has C_1 molecular symmetry. All isomers have pseudo-D_{4h} (holohedrized) symmetry with the quasi-C_4 axes being perpendicular to the planes containing the diamine. Because of the strain of the glycinate rings lying in the same octahedral plane,[2] it is reasonable to expect that the trans(O$_5$) geometrical isomer of Co(EDDDA)$^-$ should form preferentially relative to the other two isomers, as has been found.[4] Similar conclusions were reported for EDDS[5] and EDDAMS[6] Co(III) complexes.

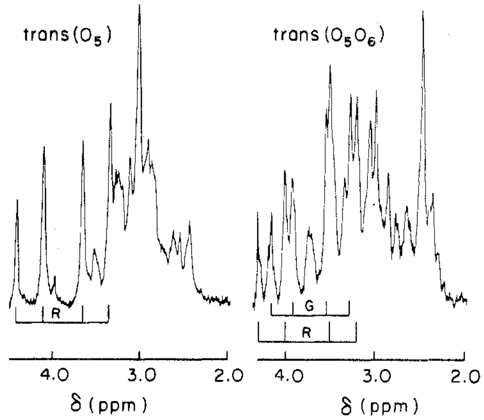

Figure 2. Nmr spectra of the trans(O$_5$) and trans(O$_5$O$_6$) geometrical isomers of K[Co(EDDDA)] in D$_2$O at 60 MHz *vs.* DSS as internal standard.

In an effort to isolate the remaining, trans(O$_5$O$_6$) and trans(O$_6$), geometrical isomers, many different reactions were carried out. In reactions occurring between freshly prepared Co(OH)$_3$ and H$_4$EDDDA or during oxidation of Co(II) to Co(III) in the presence of partially neutralized ligand (pH ~9), the trans(O$_5$) isomer is formed preferentially, along with a very small amount of the trans(O$_5$O$_6$) isomer. The best ratio (about 3:1) of these two geometrical isomers is obtained in the reaction between freshly prepared Na$_3$[Co(NO$_2$)$_6$][11] and H$_4$EDDDA. Once formed the trans(O$_5$O$_6$) isomer of the Co(EDDDA)$^-$ complex is quite stable. No isomerization occurs after 3 hr at 80° in aqueous solution.

Nmr Spectra. Distinguishing between the Two Geometrical Isomers of K[Co(EDDDA)]. Nmr results were used in the identification of the *trans*(O_5)-Co(EDDDA)$^-$ isomer reported earlier.[4] Nmr spectra were obtained for both isomers isolated here for direct comparison. The spectra were interpreted in light of the report[14] that the magnitudes of geminal proton coupling constants (J) for aminocarboxylate–cobalt(III) complexes fall into two categories, those in the vicinity of 16 Hz for in-plane (G) glycinate rings and those in the vicinity of 18 Hz for out-of-plane (R) glycinate rings. A relationship between the chemical shift difference for A and B protons and the orientation of coordinated glycinate groups for aminocarboxylatocobalt(III) complexes was first indicated by Legg and coworkers.[15] Similar arguments were applied recently by Koine, *et al.*,[16] for distinguishing between geometrical isomers of a series of (N,N-β-alaninatodiacetato)(α-aminocarboxylato)cobaltate(III) complexes.

The trans(O$_5$) isomer shows a well-resolved AB pattern centered at 3.88 ppm with δ_A 4.25 ppm, δ_B 3.52 ppm, and J_{AB} = 18.4 Hz (Table I, Figure 2). These results are in good agreement with the C_2 symmetry of the trans(O$_5$) isomer which has two equivalent glycinate R rings. In the same region, the

Table I. Coupling Constants and Chemical Shifts[a] for Methylene Protons of R and G Glycinate Rings of Co(EDDDA)$^-$

	Geometrical isomers		
	Trans(O_5)	Trans(O_5O_6)	
	R rings	R rings	G rings
δ_A, ppm	4.25	4.15	4.03
δ_B, ppm	3.52	3.40	3.43
J_{AB}, Hz	18.4	18.4	16.4
$\delta_A - \delta_B$, ppm	0.73	0.75	0.61

[a] Values are in ppm downfield from DSS as internal standard.

Table II. Absorption and CD Data for Cobalt(III) Sexadentate EDTA Type of Complexes

	Absorption		Circular dichroism	
Complex ion[a]	Peak position, kK	ϵ	Peak position, kK	$\Delta\epsilon$
Co(EDTA)$^-$	18.60	347	17.10	+1.50
			19.80	−0.69
	26.65	246	23.80	+0.28
			25.60	−0.09
			27.60	+0.29
trans(O_5O_6)-Co(EDDDA)$^-$	18.60	253	16.50	+2.25
			18.40	−3.12
	25.80	142	24.40	+0.31
			26.60	+0.56
trans(O_5)-Co(EDDDA)$^-$	18.50	342	16.20	+0.40
			18.30	−2.78
	25.70	186	24.20	+0.29
			26.30	+0.36
Co(1,3-PDTA)$^-$	18.20	131	17.00	+1.91
			19.00	−2.41
	26.40	115	24.60	+0.69
Co(EDTP)$^-$	18.00	253	15.80	+0.88
			17.60	−3.28
	24.80	110	23.30	+0.09
			26.30	+0.18

[a] Data for all complexes except Co(EDDDA)$^-$ are taken from ref 3. All data are given for isomers having a positive rotatory strength associated with the lowest energy CD bands.

trans(O_5O_6) isomer, with lower (C_1) molecular symmetry, as expected, shows signals of two well-resolved AB patterns belonging to two nonequivalent (R and G) glycinate rings. The AB pattern of the R ring (centered at 3.77 ppm) has δ_A 4.15 ppm, δ_B 3.40 ppm, and J_{AB} = 18.4 Hz. The other AB pattern, belonging to the G ring (centered at 3.73 ppm) has δ_A 4.03 ppm, δ_B 3.43 ppm, and J_{AB} = 16.4 Hz (Table I, Figure 2). The $\delta_A - \delta_B$ values obtained for the R rings [0.73 ppm for the trans(O_5) and 0.75 ppm for the trans(O_5O_6) isomer] are larger than for the G ring (0.61 ppm) of the trans(O_5O_6) isomer. These values are consistent with the smaller $\delta_A - \delta_B$ values obtained for the R and G rings of EDTA[15] and 1,3-PDTA[17] complexes of Co(III) which have more strain in plane and probably out of plane. The trans(O_6) isomer, which has not been isolated, has C_2 symmetry and highly strained G rings.

Electronic Absorption and Circular Dichroism. Electronic absorption and CD spectra of the trans(O_5) and the trans(O_5O_6) geometrical isomers of Co(EDDDA)$^-$ are shown in Figure 3 and Table II. The absorption spectra of these isomers are very similar in shape, with two bands corresponding to transitions to the T_{1g} and $T_{2g}(O_h)$ states. The bands show no obvious splitting, as would be expected for *cis*-[CoN_2O_4] type complexes. The absorption energies, in general, lie between those of Co(EDTA)$^-$ and Co(EDTP)$^-$ complexes (see Table II). The lowest energy, $T_{1g}(O_h)$, maxima (18.60 kK for the trans(O_5O_6) isomer and 18.50 kK for the trans(O_5) isomer) have approximately the same position as that of the Co(EDTA)$^-$ complex (18.60 kK), which indicates that the Dq values of these complexes are nearly identical. However, their second absorption bands (25.80 kK for the trans(O_5O_6) and

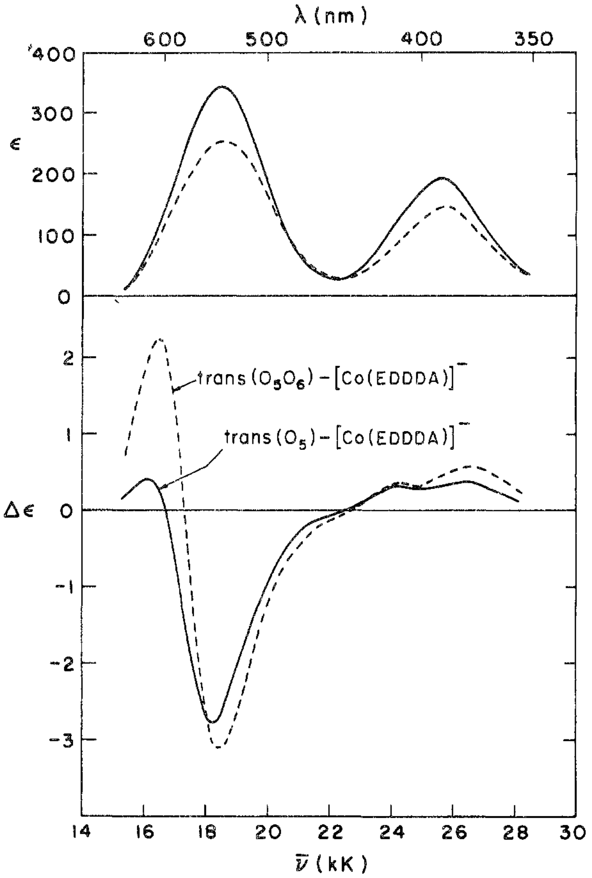

Figure 3. Electronic absorption and CD spectra of the trans(O_5) and trans(O_5O_6) geometrical isomers of Co(EDDDA)$^-$.

25.70 kK for the trans(O_5) isomer) are slightly shifted to lower energy with respect to the corresponding band of the Co(EDTA)$^-$ complex. The values for ϵ of the trans(O_5O_6) isomer are significantly lower than those of the trans(O_5) isomer.

The absence of apparent splitting of the T_{1g} and T_{2g} absorption bands suggests pseudooctahedral symmetry. But according to the results of Neal and Rose[5] for the Co(EDDS)$^-$ complex, the interpretation of the electronic absorption spectra of these isomers based on a tetragonal field probably would be better. Using pseudo-D_{4h} symmetry and Wentworth and Piper's[18] treatment, they concluded that the EDDS ligand, which contains two in-plane six-membered carboxylate rings and secondary nitrogen atoms, is a stronger donor toward Co(III) than is EDTA. They also analyzed the Co(EDTA)$^-$ absorption spectrum assuming D_{4h} symmetry. The actual symmetry of Co(EDTA)$^-$ is C_2. Its CD spectrum has been treated using C_2 symmetry[3,7,9] in relating it to model complexes, such as Co(en)(mal)$_2^-$, which share this symmetry. The lowest energy (positive) CD band for $(-)_{546}$-Co(EDTA)$^-$ has been assigned as the A(C_2) component. This enantiomer has the Λ absolute configuration,[7-9,12] corresponding to the chirality of the isomers shown in Figure 1. This assignment is consistent with the empirical observation[19] that the sign of the A → A(C_2) component can be correlated with the absolute configuration.

The same absolute configuration (Λ) was assigned to the enantiomers with similar CD spectra for several model complexes[3] related to Co(EDTA)$^-$. This assignment has been confirmed crystallographically for K[$(-)_{546}$-Co(1,3-PDTA)]·$2H_2O$.[20]

The CD spectra[3] of Co(EDTA)$^-$, Co(1,3-PDTA)$^-$ (Table II), and Co(IDA)$_2^-$ (IDA = iminodiacetate) show two low-energy peaks of opposite sign, one on either side of the first absorption band. The D_{4h} model is consistent with this

CD pattern, the lower energy peak being $E_g(D_{4h})$ and the higher energy peak being $A_{2g}(D_{4h})$. The sign of the $E_g(D_{4h})$ CD peak correlates with the absolute configuration. This sign is retained by the $A(C_2)$ component of E_g parentage. The spectra for Co(EDTP)$^-$ (Table II) and the two isomers of Co(EDDDA)$^-$ (Figure 3 and Table II) differ in that both CD peaks in the low-energy region occur at *lower* energy than the absorption maximum, strongly suggesting that they are components split from the $E_g(D_{4h})$ state because of the lower symmetry. On this basis, a third transition is expected on the higher energy side of the absorption maximum, but presumably it is obscured by the dominant neighboring peak. In the case of Co(en)(mal)$_2^-$ [7] and Co(EDDS)$^-$ [5] three peaks of alternating sign appear, corresponding to the number of transitions expected for C_2 symmetry. The appearance of these spectra and the sharpness of the peaks argue strongly against this pattern resulting from the overlap of two peaks of opposite sign, one very broad (giving the flanking peaks of the same sign) and one very narrow (giving the center peak). The absolute configurations of Co(en)(mal)$_2^-$ [21] and Co(EDDS)$^-$ [22] are known. The Co(EDTA)$^-$ type complexes with C_2 symmetry can be related to Co(en)(mal)$_2^-$, which can be correlated with the *cis*-[Co(en)$_2$X$_2$]$^{n+}$ complexes (C_2 symmetry).[19] The $A(C_2)$ component for the *cis*-[Co(en)$_2$X$_2$]$^{n+}$ complexes was considered[19] to retain the sign of the $E_a(D_3)$ component for Co(en)$_3^{3+}$. This empirical correlation has weaknesses in that Co(en)(mal)$_2^-$ is of the *cis*-[CoN$_2$O$_4$] type rather than *cis*-[CoN$_4$X$_2$], but Mason, *et al.*,[19] considered cases where the field strength of X is greater than that of N, as well as the converse. Also the effects of six-membered chelate rings on the order of splitting of the transitions and their signs is inconclusive.[23] The correct absolute configuration was predicted, however, from CD spectra[7] for Co(en)(mal)$_2^-$.

The Co(EDDS)$^-$ complex (known absolute configuration) and Co(EDDDA)$^-$ complexes contain two six-membered chelate rings. Their CD spectra are very similar and correlate well with the spectrum for Co(en)(mal)$_2^-$. It could be fortuitous, but the empirical correlations are consistent with the results using D_{4h} symmetry when there are two CD peaks, one on each side of the absorption maximum, or using C_2 symmetry when there are three peaks or only two peaks, both on the low-energy side of the absorption maximum. Intensity criteria are not applicable. The absolute configuration of Co(EDDAMS)$^-$ (EDDAMS is a sexadentate ligand derived from iminodiacetic and (S)-aspartic acids joined by an ethylene linkage) has been assigned with a high degree of confidence[6] from the overall similarity of the CD spectrum to that of Co(EDDS)$^-$. The empirical rules do not apply here unless one assumes that the single CD peak which appears in the first absorption band region for Co(EDDAMS)$^-$ completely cancels a lower energy peak of opposite sign [and presumably a higher energy peak of opposite sign which appears for Co(EDDS)$^-$]. This assumption is implied in the comparison of the overall curves.[6]

The structure and absolute configuration of *trans*(O_5)-Co(EDDDA)$^-$ were assigned[4] based on the nmr spectrum which indicated two equivalent out-of-plane glycinate rings and the close similarity of the CD spectrum to that of Co(EDDS)$^-$. The later work[6] on Co(EDDAMS)$^-$ adds support to these assignments. The second isomer reported here, *trans*(O_5O_6)-Co(EDDDA)$^-$, has nonequivalent glycinate rings (nmr), one in plane and one out of plane. The CD spectrum (Figure 3, Table II) differs from that of the trans(O$_5$) isomer primarily in peak intensities. On the basis of overall comparisons with Co(EDDS)$^-$ and Co(EDDAMS)$^-$, these $(-)_{589}$ isomers of Co(EDDDA)$^-$ also have the Λ configuration and they have positive lowest energy CD peaks, $A(C_2)$. Both of these isomers give the less soluble diastereoisomer with (−)D-[Co(en)$_2$ox]$^+$ which, using Werner's rule,[24] would indicate the same absolute configuration. However, it should be noted that (+) isomers of Co(EDTA)$^-$ and other model complexes listed in Table II were obtained from the less soluble diastereoisomers with (+)D-[Co(en)$_2$ox]$^+$. Werner's rule is not expected to apply except to an isomorphous series.

In the case of the Co(EDDDA)$^-$ complexes there are possible contributions to the CD intensities from the two coordinated asymmetric nitrogen atoms, as well as from the configurational effect about the metal ion. However, as previously mentioned, the latter effect is thought to dominate. The configurations of the two asymmetric nitrogens of the Λ isomers of the Co(EDDDA)$^-$ complex (Figure 1) are *RR* for the trans(O$_5$) and *SR* for the trans(O$_5$O$_6$) isomers. In the latter case, the contributions of the *SR* nitrogens should practically cancel. The similarity in shapes of CD curves of the Co(EDTP)$^-$ complex[3] (in which case there is no contribution due to asymmetric nitrogens) and those of the trans(O$_5$) isomer of the Co(EDDDA)$^-$ complex and the relative intensities of their lowest energy CD components (see Table II) support the idea that the contribution due to the asymmetric nitrogens is not very great in this system. Recent studies of the contribution of asymmetric nitrogens in the very similar EDDS[10] system suggest that this effect is not very large. In view of these facts, it seems that the difference in CD spectra of the trans(O$_5$) and trans(O$_5$O$_6$) isomers is mostly due to different configurational effects associated with the distribution of five- and six-membered chelate rings.

In appears that there are some trends in intensities associated with particular transitions which are beginning to become apparent for Co(EDTA)$^-$ type compounds differing in the number and arrangement of five- and six-membered chelate rings (Table II). More examples and more structures established by X-ray methods are needed.

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Registry No. *trans*-(O_5O_6)-K[Co(EDDDA)], 52810-57-8; *trans*-(O_5)-K[Co(EDDDA)], 52881-93-3; *trans*-(O_5O_6)-(−)D-Ag-[Co(EDDDA)], 52949-30-1; *trans*-(O_5)-(−)D-Ag[Co(EDDDA)], 52881-94-4.

References and Notes

(1) Research Associate, 1973–1974.
(2) H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).
(3) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 1145 (1969).
(4) W. Byers and B. E. Douglas, *Inorg. Chem.*, **11**, 1470 (1972).
(5) J. A. Neal and N. J. Rose, *Inorg. Chem.*, **7**, 2405 (1968); J. A. Neal and N. J. Rose, *ibid.*, **12**, 1226 (1973).
(6) J. I. Legg and J. A. Neal, *Inorg. Chem.*, **12**, 1805 (1973).
(7) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).
(8) T. E. MacDermott and A. M. Sargeson, *Aust. J. Chem.*, **16**, 334 (1963).
(9) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185, 1969 (1965).
(10) W. T. Jordan and J. I. Legg, *Inorg. Chem.*, **13**, 2271 (1974).
(11) E. Billmann, *Z. Anal. Chem.*, **39**, 284 (1900).
(12) 1970 IUPAC rules, *Pure Appl. Chem.*, **28**, 1 (1971); *Inorg. Chem.*, **9**, 1 (1970).
(13) Comparison of the electronic spectra of these brown-violet eluates with the spectrum of the mononitro-substituted EDTA comples of Co(III) [C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **7**, 1393 (1968)] suggests that these components are mononitro-substituted EDDDA–Co(III) complexes. Presently, efforts are being directed toward characterizing these nitro-substituted complexes and also toward preparing the remaining, trans(O$_6$), geometrical isomer of the Co(EDDDA)$^-$ complex.
(14) J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *Inorg. Chem.*, **10**, 90 (1971).
(15) P. F. Coleman, J. I. Legg, and J. Steele, *Inorg. Chem.*, **9**, 937 (1970).
(16) N. Koine, N. Sakota, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **12**, 859 (1973).
(17) H. Ogino, M. Takahasi, and N. Tanaka, *Bull Chem. Soc. Jap.*, **43**, 424 (1970).

(18) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).
(19) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).
(20) R. Nago, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 1852 (1972).
(21) K. R. Butler and M. R. Snow, *Chem. Commun.*, 550 (1971).
(22) L. M. Woodward, Thesis, University of Washington, 1970.
(23) R. R. Judkins and D. J. Royer, *Inorg. Chem.*, **13**, 945 (1974), and references therein.
(24) A. Werner, *Ber. Deut. Chem. Ges.*, **45**, 1229 (1912).

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Substitution Reactions of Oxalato Complex Ions. XI. Kinetics of the Anation of Aquopentaamminecobalt(III) Ion by Oxalate in Aqueous Acidic Solution[1,2]

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The title reaction has been studied in the temperature range 50–80°, with the acidity range from pH 7.5 up to 1.0 *M*, and with oxalate concentrations between 0.04 and 0.45 *M*. It goes essentially to completion even at the highest acidities in the presence of excess oxalate. Ion pairing is not significant between the complex ion and $H_2C_2O_4$ but is kinetically identifiable with $HC_2O_4^-$ and $C_2O_4^{2-}$, such that the rate expression becomes as shown in eq 4. The essentially temperature-independent ion-pair formation constants for bioxalate and oxalate ions are $Q_1 = 1.8\ M^{-1}$ and $Q_2 = 9.2\ M^{-1}$, respectively. The rate constants at 70° for anation by $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$ are $k_0 = 1.5 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$, $k_1 = 4.9 \times 10^{-4}\ \text{sec}^{-1}$, and $k_2 = 4.0 \times 10^{-4}\ \text{sec}^{-1}$. The corresponding temperature parameters are $\Delta H^{\ddagger} = 14.3 \pm 1.7$, 22.4 ± 2.1, and 24.8 ± 1.8 kcal/mol, respectively, and $\Delta S^{\ddagger} = -35.0 \pm 4.8$, -8.6 ± 6.3, and -2.1 ± 5.4 cal/(deg mol), respectively. On the basis of the contrast in temperature parameters and a study of the solvent D_2O effect, it is concluded that the mechanism for $H_2C_2O_4$ addition may not be of the conventional water–ligand dissociative type which appears to be the mechanism for the two ionic oxalate species.

Introduction

Previous papers in this series have reported studies of the anation by oxalate of the diaquobis(ethylenediamine)cobalt(III) ion in acidic[3] and neutral or basic[4] solution. These reactions take place by means of a two-step mechanism in which there is first replacement of one aquo ligand by oxalate, followed by release of the second aquo ligand as chelation of the metal ion by oxalate occurs. Similar results have recently been reported for oxalate anation of the diaquoethylenediaminediacetatocobalt(III) analog.[5] In order to throw more light on the nature of the intimate mechanism of the first water-replacement step, we have in the present study examined the kinetics of the reaction with oxalate of aquopentaamminecobalt(III) ion, in which system chelation of the metal ion by the entering ligand does not occur. This contrasts with the behavior of the aquopentaamminechromium(III) analog, where the final product is the tetraammineoxalato species, made possible by the elimination of an ammonia ligand in the ring-closure step.[6] A further significant feature of our work is that it adds a new dimension to the study of $Co(NH_3)_5H_2O^{3+}$ anation in that the reaction has been studied over a wide enough pH range to encompass all possible acidic and basic forms of each reactant species and involves a bifunctional anion. While there has been a long-standing interest in the mechanism of $Co(NH_3)_5H_2O^{3+}$ anation,[7,8] nearly all previous studies have involved monodentate entering ligands over a limited range of acidity. Another interest we have in this study is to determine whether conditions exist such that anation of aquopentaamminecobalt(III) by oxalate can proceed by direct addition of the entering ligand to the oxygen atom of the aquo ligand such as is now known to occur in the formation reaction of carbonatopentaamminecobalt(III) complex.[9] Finally, it has proved to be instructive to relate our findings to earlier studies[10,11] of the aquation equilibration in acidic aqueous solutions of the species $Co(NH_3)_5C_2O_4H^{2+}$.

Table I. Spectral Data for Aquopentaammine- and Oxalatopentaamminecobalt(III) Complexes

Complex ion	λ_{max}, nm	ϵ_{max}	Ref
$Co(NH_3)_5H_2O^{3+}$	487	41.7	*a*
	491	48.6	*b*
	491	49.0	*c*
	491	49.0	This work[d]
$Co(NH_3)_5C_2O_4H^{2+}$	507	74.0	*e*
	507	74.1	*a*
	505	73.0 (pH <2.5)	This work[f]
	505	74.5 (pH 5.0)	This work[f]
	505	76.0 (pH 7.5)	This work[f]

[a] R. Tsuchiya, *Bull. Chem. Soc. Jap.*, **35**, 666 (1962). [b] Reference 7. [c] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968). [d] The figure quoted is for the aquo ion, the p*K* of which is 6.6 at 25°.[9] At higher pH's a shift in the peak and an increase in absorbance take place as deprotonation to form the $Co(NH_3)_5OH^{2+}$ ion occurs, such that λ_{max} and ϵ_{max} have the values 497 and 57.6 at pH 7.7: S. Ficner, unpublished work in the laboratory. [e] Reference 10. [f] The variation of ϵ_{max} between 73.0 and 76.0 presumably results from the deprotonation of $Co(NH_3)_5C_2O_4H^{2+}$. The p*K* of this cation at 25° is close to 2.[10,13]

Experimental Section

The complexes $[Co(NH_3)_5H_2O](ClO_4)_3$ and $[Co(NH_3)_5(HC_2O_4)](ClO_4)_2$ were prepared by standard procedures,[12,13] and purified by recrystallization. Chemical analysis[14] confirmed the purity, as did a comparison with published visible absorption spectral data, as shown in Table I. The anation reaction was followed at 497 nm where the decrease in absorbance on aquation of the oxalato complex is nearly 35% up to pH 4.5, though reduced to about 25% at pH 7.5. (see footnote *d* to Table I). The ionic strength was maintained at 1.0 *M* with KNO_3, since a perchlorate medium limits the solubility of oxalate salt. Blank experiments indicated that nitrate ion did not in any identifiable way compete with oxalate anation.[15] The rate studies were made by batch-sampling techniques in a thermostat controlled to ±0.1°. The aquo complex ion concentration was 0.010