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Circular Dichroism of *trans*-N,N′-Ethylenediaminediacetic Acid Cobalt(III) Complexes[1]

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The circular dichroism (CD) spectra of a series of optically active cobalt(III) chelate complexes having in common the tetradentate ligand ethylenediamine-N,N′-diacetic acid (EDDA) in a *trans* (with respect to the carboxylate oxygens) configuration are reported. Two pairs of complexes were prepared and resolved: *trans*-$[Co(L)(EDDA)]^+$, L = ethylenediamine and *l*-propylenediamine; and *trans*-[Co(L)(EDDA)], L = glycine and L-alanine. The coordinated *l*-propylenediamine and L-alanine exhibit vicinal effects which were subtracted to obtain the configurational contribution to the CD. The CD curves were used to determine the absolute configurations of the complexes. These complexes are of particular interest with respect to the assignment of absolute configurations since they form a new link between the absolute configurations of $[Co(EDTA)]^-$ and $[Co(en)_3]^{3+}$.

Introduction

The assignment of absolute configuration of cobalt(III) chelate complexes by relating their circular dichroism (CD) spectra to that of optically active $[Co(en)_3]^{3+}$ has been of recent interest.[2-8] To make comparisons between the CD spectra of various complexes it is desirable to separate the vicinal contribution of optically active ligands from the configurational contribution.[3-5]

This paper investigates the CD spectra of a series of optically active cobalt(III) chelate complexes having in common the tetradentate ligand ethylenediamine-N,N′-diacetic acid (EDDA) with the coordinated oxygens in a *trans* configuration.[9] Two pairs of complexes were studied: *trans*-$[Co(L)(EDDA)]^+$, L = ethylenediamine (en) and *l*-propylenediamine (*l*-pn), and *trans*-[Co(L)(EDDA)], L = glycine (gly) and L-alanine (L-ala). The *l*-pn and L-ala exhibit vicinal effects. Cobalt(III) complexes with EDDA and related tetradentate ligands including $[Co(en)(EDDA)]^+$ have been prepared and their geometric isomers identified.[10] The synthesis and resolution of *trans*-[Co(L)(EDDA)], L = gly and L-ala, and *trans*-$[Co(l\text{-pn})(EDDA)]^+$ and the resolution of *trans*-$[Co(en)(EDDA)]^+$ are now reported.

Experimental Section

The optically active isomers are characterized by (+) and (−), the sign of the lowest energy CD maximum, $\Delta\epsilon$, Table I, and by the molar rotation, $[M]_{589}$.

Resolution of *trans*-Ethylenediamine-N,N′-diacetato(ethylenediamine)cobalt(III) Ion.—The complex was resolved using silver tartrate which was prepared in the following manner. (During the synthesis the reaction mixture was kept shielded from light.) A solution of 3.8 g (0.025 mole) of *d*-tartaric acid in 15 ml of water, to which had been added 2 g (0.050 mole) of 98% sodium hydroxide in 10 ml of water, was added dropwise to a stirred solution of 8.5 g (0.050 mole) of silver nitrate in 25 ml of water. After stirring about 30 min the precipitate was allowed to settle, filtered, and washed with five 30-ml portions of water and acetone. The air-dried silver tartrate (7.6 g) was stored in a brown bottle.

This silver tartrate was used to resolve the complex as follows. A solution of 7.464 g (0.02 mole) of *trans*-$[Co(en)(EDDA)]NO_3 \cdot H_2O$[10] in 160 ml of water was passed through a column (diameter 2.8 cm), which contained 200 ml (wet volume) of Dowex 1-X8 strong-base anion-exchange resin (50–100 mesh) in the chloride form at a rate between 1 and 2 ml/min. The eluted complex was quantitatively collected in a stirred suspension of 3.638 g (0.01 mole) of silver tartrate and 1.501 g (0.01 mole) of tartaric acid in 100 ml of water which was kept shielded from light. The coagulated silver chloride was then filtered, but not washed, and the filtrate was evaporated to about 50 ml on a steam bath in a stream of air and then to about 15 ml with air alone. To the stirred solution at 40° was then added 15 ml of ethanol. Within a few minutes crystallization took place. After stirring 15 min, 10 ml of water was added and the mixture stirred an additional 15 min. The solid (−)-*trans*-$[Co(en)(EDDA)]Htart \cdot H_2O$ ($\Delta\epsilon_1 = -4.45$; $\Delta\epsilon_2 = +1.60$) was then filtered at 40° and washed with two 5-ml portions of 60% ethanol (these were added to the filtrate), ethanol, and ether. The air-dried yield was 1.6 g. A portion of this was recrystallized from 50% ethanol. *Anal.* Calcd for $[CoC_8H_{18}O_4N_4][(C_4H_5O_6) \cdot 0.5H_2O$: C, 31.94; H, 5.36; N, 12.42. Found: 31.78; H, 5.45; N, 12.54.

After the addition of 5 ml of water, the filtrate from the isolation of the (−)-diastereoisomer was cooled in an ice bath, and the almost pure diastereoisomer was filtered and washed as described for the (−)-isomer; yield, 3.2 g. This was then dissolved in 35 ml of water at 40°, and 30 ml of ethanol was added. The solution was cooled in an ice bath, and the product which formed was filtered and washed as before; yield of (+)-*trans*-$[Co(en)(EDDA)]Htart \cdot 0.5H_2O$, 1.7 g ($\Delta\epsilon_1 = +4.46$; $\Delta\epsilon_2 = 1.72$).

The (+)-diastereoisomer (1.7 g) was dissolved in 6 ml of water and 1 ml of concentrated HNO_3 was added. The nitrate salt was precipitated by the slow addition of 15 ml of ethanol. The

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[1] This work was supported by a research grant (GM10829-08) from the Division of General Medical Studies, Public Health Service.

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

[3] B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).

[4] B. E. Douglas, *ibid.*, **4**, 1813 (1965).

[5] C. T. Liu and B. E. Douglas, *ibid.*, **3**, 1356 (1964).

[6] R. A. Haines and B. E. Douglas, *ibid.*, **4**, 452 (1965), and other papers in this series.

[7] A. M. Sargeson and G. H. Searle, *ibid.*, **4**, 45 (1965).

[8] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

[9] The nomenclature of the isomers of metal complexes containing tetradentate ligands is now in a state of flux. Rather than introduce any new system which is likely to be dropped or altered later, we retain the usage of *cis* and *trans* to designate the positions of the oxygens of the tetradentate as in a previous paper. In complexes in which glycine or alanine is coordinated in the fifth and sixth positions, the supplemental notation α or β is used following the method of Lifschitz (*Z. Physik. Chem.*, **114**, 493 (1925)) to designate three oxygens on an edge or face, respectively.

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

TABLE I

ABSORPTION AND CIRCULAR DICHROISM IN $^1A_{1g} \longrightarrow {}^1T_{1g}$ REGION

	Absorption max, $\bar{\nu}$ in cm^{-1} × 10^{-4}		Circular dichroism max, $\bar{\nu}$ in cm^{-1} × 10^{-4}	
	I_a (ϵ)	I_b	I_a ($\Delta\epsilon$)	I_b ($\Delta\epsilon$)
(+)-*trans*-[Co(en)(EDDA)]$^+$	1.89 (87.3)	2.23 sh	1.88 (+4.46)	2.24 (−1.75)
(−)-Isomer	*b*		*b* (−4.49)	*b* (+1.72)
(+)-*trans*-[Co(*l*-pn)(EDDA)]$^+$	1.89 (94.5)	2.22 sh	1.88 (+4.63)	2.25 (−1.71)
(−)-Isomer	*b* (95.2)	*b*	1.88 (−4.53)	2.24 (+1.74)
$(+)_{589}$-[Co(en)$_3$]$^{3+}$	2.14		2.03 (+1.89)	2.34 (−0.17)
trans-[Co(gly)(EDDA)]^a	1.84 (90.0)	2.13 sh	1.85	2.17
(+)-*trans*-[Co(L-ala)(EDDA)]	1.84 (95.0)	2.15 sh	1.84 (+4.00)	2.16 (−1.92)
(−)-Isomer	*b*		1.84 (−4.27)	2.15 (+1.44)

^{a} Partially resolved, see Experimental Section. ^{b} Same as for (+)-isomer.

product was filtered, washed with 70% ethanol, ethanol, and ether, and air dried; yield of (+)-*trans*-[Co(en)(EDDA)]-$NO_3 \cdot H_2O$, 1 g ($[M]_{589}$ +5770°). *Anal.* Calcd for $[CoC_8H_{18}N_4O_4]NO_3.H_2O$: C, 25.74; H, 5.40; N, 18.77. Found: C, 25.70; H, 5.50; N, 18.72.

The (−)-diastereoisomer (1.6 g) was similarly converted to the nitrate using 8 ml of water and 15 ml of ethanol; yield of (−)-*trans*-[Co(en)(EDDA)]$NO_3 \cdot H_2O$, 0.6 g.

Preparation of (+)- and (−)-*trans*-Ethylenediamine-N,N′-diacetato(*l*-propylenediamine)cobalt(III) Perchlorate.—To a 150-ml solution of 0.050 mole of Co^{II}EDDA[10] was added a solution of 7.35 g (0.050 mole) of *l*-propylenediamine dihydrochloride ($[\alpha]_{589}$ +4.2°; lit.[11] 4.04 ± 0.06°) in 110 ml of water containing 2.1 g (0.010 mole) of $LiOH \cdot H_2O$. After addition of 5 g of activated charcoal, the resulting solution was aerated for 20 hr. After removal of the carbon, the volume was brought to 300 ml and 3.5 g of $NaClO_4 \cdot H_2O$ was added. The almost pure (−)-isomer which formed was stirred 5 min, filtered, and washed with water, ethanol, and acetone. The air-dried yield was 3.5 g. The product was recrystallized from 280 ml of water at 75°. After cooling, the red-violet crystals were filtered and washed as before. Further recrystallization did not change the CD curves. The yield of pure (−)-[Co(*l*-pn)(EDDA)]ClO_4 was 2.2 g ($[M]_{589}$ −5620°). *Anal.* Calcd for $[CoC_9H_{20}N_4O_4]ClO_4$: C, 26.58; H, 4.96; N, 13.78. Found: C, 26.67; H, 5.03; N, 13.94.

The filtrate from which the (−)-isomer had been obtained was evaporated to 230 ml, and 1.3 g of impure racemate was removed and discarded. An additional 1.8 g of $NaClO_4 \cdot H_2O$ was added and crystallization was induced by scratching. After stirring 15 min, 1.7 g of almost pure (+)-isomer was removed, washed, and dried as before. This was recrystallized from 50 ml of water at 75° to give 0.5 g of pure (+)-[Co(*l*-pn)(EDDA)]ClO_4. ($[M]_{589}$ +6190°). *Anal.* Calcd for $[CoC_9H_{20}N_4O_4]ClO_4$: C, 26.58; H, 4.96; N, 13.78. Found: C, 26.89; H, 4.94; N, 13.83.

Since these isomers exhibited a very small vicinal effect, their purity was checked by preparing them from *l*-propylenediamine resolved in a different laboratory. The CD curves for the two isomers were reproducible within experimental error. [(−): $\Delta\epsilon_1 = -4.53$, $\Delta\epsilon_2 = +1.74$; (+): $\Delta\epsilon_1 = +4.63$, $\Delta\epsilon_2 = 1.71$; compare with data in Table I.]

Preparation of (+)- and (−)-*trans*-Ethylenediamine-N,N′-diacetato(L-alaninato)cobalt(III) Dihydrate.—(The following preparation is identical if D-alanine is used.) A solution of 0.0200 mole of Co^{II}EDDA[10] was diluted to 500 ml, 2 g of activated charcoal and 1.78 g of L-alanine were added, and a stream of air was passed through the suspension for at least 8 hr. The volume was brought back to 500 ml, and the suspension was heated (50–60°) with stirring for 30 min. The charcoal was removed by filtration and washed with hot water until the washings were colorless. The combined filtrate and washings were evaporated in a stream of air on a steam bath to 400 ml, and the solution was cooled in an ice bath for several hours. The resulting violet-purple precipitate was filtered and washed with ethanol and ether and air-dried; yield of 96% pure (−)-*trans*, 0.3 g. After standing in a cold room 24 hr an additional 0.8 g of 84% pure (−)-*trans* was obtained.

The solution was then evaporated to 100 ml and allowed to cool to room temperature. The precipitate which formed was filtered and washed as before; yield of 71% pure (+)-*trans*, 0.9 g.

The first crop of (−)-isomer was purified by dissolving 0.3 g in 35 ml of water at 50–60° and adding 15 ml of ethanol. The solution was rapidly filtered and cooled in an ice bath for about 1 hr. About 0.15 g of pure ($[M]_{589}$ −5280°) (−)-*trans*-[Co(L-ala)(EDDA)]$\cdot 2H_2O$ was obtained after washing and drying as before. Solubility: 0.18 g/100 ml at 10°. *Anal.* Calcd for $[CoC_9H_{16}N_3O_6] \cdot 2H_2O$: C, 30.26; H, 5.64; N, 11.76. Found: C, 30.05; H, 5.94; N, 11.91. The second crop of (−)-isomer was purified by using two recrystallizations as described for the first crop.

The (+)-isomer was purified by dissolving 0.9 g in 45 ml of water at 50–60° and adding 15 ml of ethanol. After filtering and cooling for 1 hr, 0.5 g of product was obtained. The salt was recrystallized again to give about 0.2 g of pure ($[M]_{589}$ +4960°) (+)-*trans*-[Co(L-ala)(EDDA)]$\cdot 2H_2O$. Solubility: 0.53 g/100 ml at 10°. *Anal.* Calcd for $[CoC_9H_{16}N_3O_6] \cdot 2H_2O$: C, 30.26; H, 5.64. Found: C, 30.56; H, 5.50. When D-alanine was used, the isomers obtained exhibited mirror image CD curves to those obtained from L-alanine as expected. *Anal.* Found for (−)-*trans*-[Co(D-ala)(EDDA)]$\cdot 2H_2O$: C, 30.41; H, 5.46; N, 12.03. ($\Delta\epsilon_1 = -3.96$, $\Delta\epsilon_2 = +1.93$; for (+)-*trans*-[Co(D-ala)(EDDA)]$\cdot 2H_2O$: $\Delta\epsilon_1 = +4.32$, $\Delta\epsilon_2 = -1.44$.)

Preparation of *trans*-Ethylenediamine-N,N′-diacetato(glycinato)cobalt(III) Dihydrate.—The synthesis was identical with that of the L-alanine analog except that it was carried out using 0.01-mole quantities of reagents, 0.751 g of glycine being used. The oxidation was carried out in 200 ml of solution. After removal of the charcoal, the solution was evaporated to about 10 ml and cooled in an ice bath, and the violet-purple crystals which had formed were filtered and washed with 50% ethanol, ethanol, and ether. The air-dried yield was 1.3 g. One gram was dissolved in 20 ml of water at 65°, and after filtration the solution was cooled in an ice bath; yield of *trans*-[Co(gly)(EDDA)]$\cdot 2H_2O$ after washing and drying as before, 0.7 g. *Anal.* Calcd for $[CoC_8H_{14}N_3O_6] \cdot 2H_2O$: C, 28.00; H, 5.29; N, 12.25. Found: C, 28.43; H, 5.25; N, 12.20.

Partial Resolution of *trans*-Ethylenediamine-N,N′-diacetato(glycinato)cobalt(III) Dihydrate.—The *trans* isomer (0.50 g) was dissolved in 20 ml of water and eluted on a starch column (diameter 2.5 cm) containing 350 g of potato starch as previously described for the isomers of [Co(gly)$_3$].[3] Twenty fractions were removed for which the CD and absorption spectra were recorded. Changes in $\Delta\epsilon$ were observed between successive fractions collected, indicating that only partial resolution had been attained. The fractions were too dilute to permit an effective rerun through the column. Fraction 1 had $\Delta\epsilon_1 = +2.63$ and $\Delta\epsilon_2 = -1.22$ and fraction 20 had $\Delta\epsilon_1 = -2.01$ and $\Delta\epsilon_2 = +0.74$. Fraction 2 ($\Delta\epsilon_1 = +2.56$ and $\Delta\epsilon_2 = -1.03$) was used for the reported CD spectrum (Figure 3).

Spectra.—The absorption spectra were measured on a Cary Model 14 recording spectrophotometer and the CD curves were recorded with a Roussel-Jouan Dichrograph using a Sylvania

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[11] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

ASA DXL tungsten–iodine light source. The nmr spectra were obtained as previously described.[10]

Discussion of Results

The CD spectra of (+)- and (−)-[Co(*l*-pn)(EDDA)]$^+$, (+)- and (−)-*α*-(*trans*)-[Co(L-ala)(EDDA)], partially resolved (+)-(*trans*)-[Co(gly)(EDDA)], and (+)-*trans*-[Co(en)(EDDA)]$^+$ are shown in Figures 1 through 4, respectively. The absorption spectra are given in Figures 4 and 5.

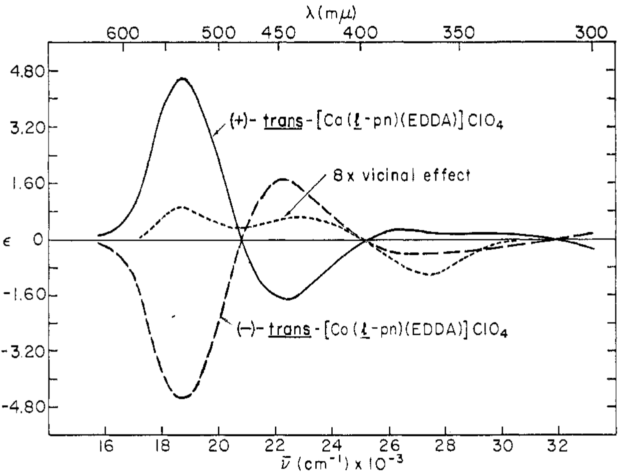


Figure 1.—Circular dichroism for (+)- and (−)-*trans*-[Co(*l*-pn)(EDDA)]$^+$.

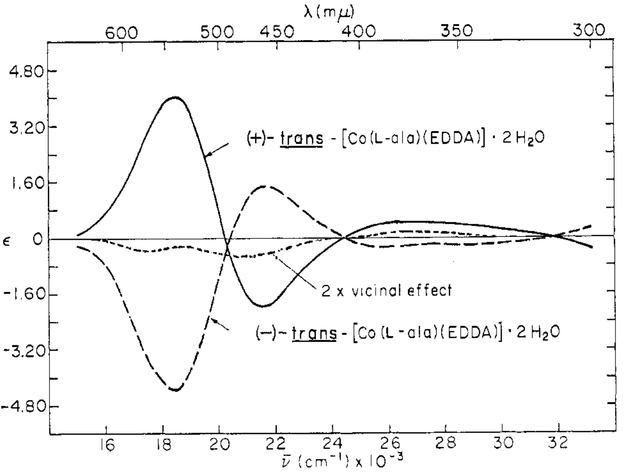


Figure 2.—Circular dichroism for (+)- and (−)-*trans*-[Co(L-ala)-EDDA)].

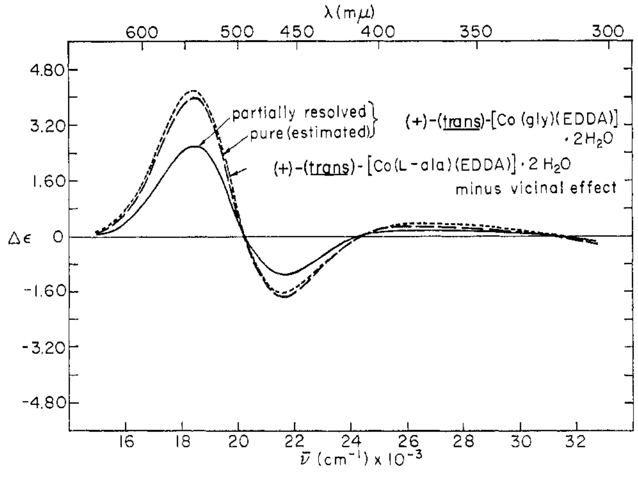


Figure 3.—Comparison of circular dichroism of (+)-*trans*-[Co(L)(EDDA)], L = gly and L-ala.

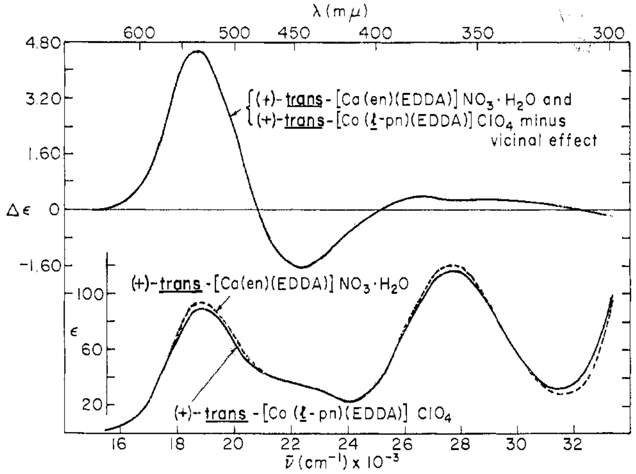


Figure 4.—Absorptivity and comparison of circular dichroism of (+)-*trans*-[Co(L)(EDDA)]$^+$, L = en and *l*-pn.

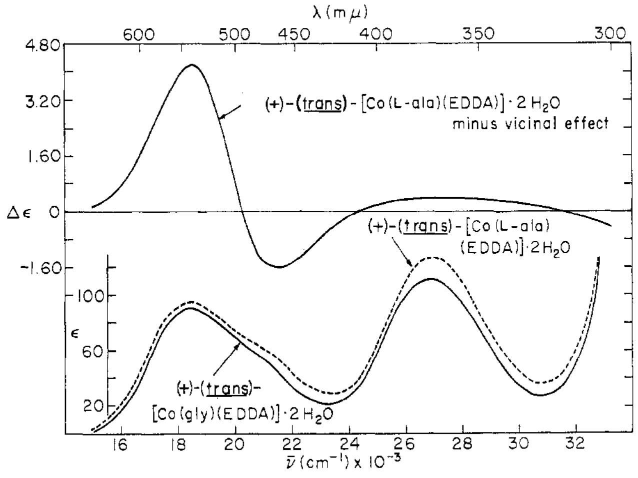
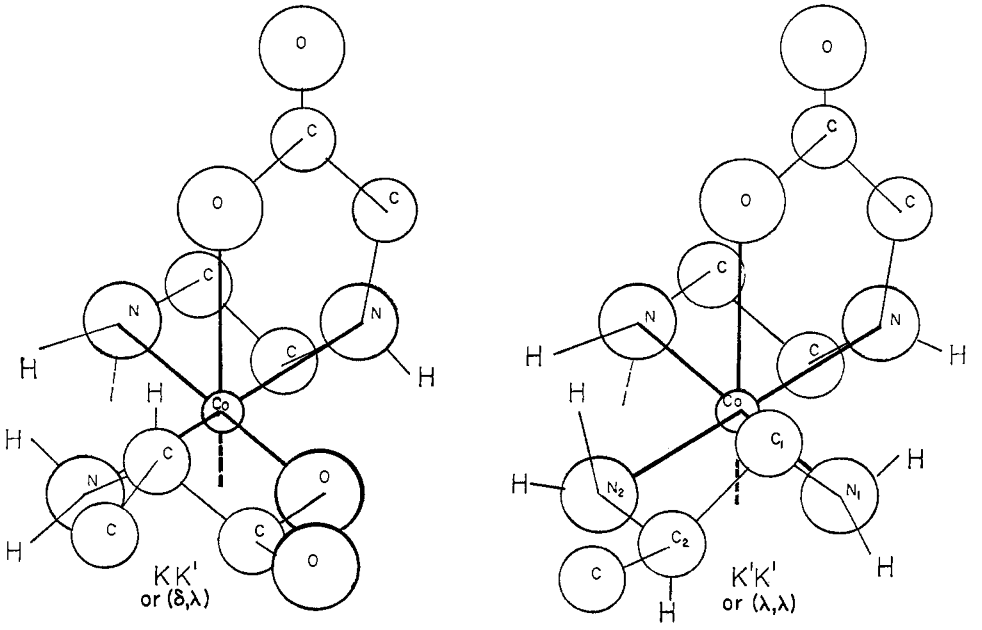


Figure 5.—Absorptivity of (+)-*trans*-[Co(L)(EDDA)], L = gly and L-ala.

Configuration of EDDA.—It has been shown that EDDA favors almost exclusively a *trans* configuration.[10] This configuration has been established for *trans*-[Co(en)(EDDA)]$^+$ and related compounds by absorption and proton nmr spectroscopy.[10] The similar *trans*-[Co(L)(EDDA)], L = *l*-pn, gly, and L-ala, were prepared under analogous conditions and were also obtained in high yields. The absorption spectrum of *trans*-[Co(*l*-pn)(EDDA)]$^+$, Figure 4, is very similar to that of the ethylenediamine analog, and the nmr spectrum exhibits acetate ring AB spectra characteristic of EDDA in a *trans* configuration.[10] The CD spectra of the amino acid isomers are strikingly similar to those of the amine isomers (Figures 1–3) so that the *trans* configuration of EDDA can be assumed. When EDDA is in a *trans* configuration in the amino acid complexes, only one isomer is possible, an *α* isomer (oxygens spanning an edge), and, as expected, the ab-



Δ,(+)-trans-[Co(L-ala)(EDDA)] Δ,(+)-trans-[Co(*l*-pn)(EDDA)]$^+$

Figure 6.—Perspective of Δ-(+)-*trans*-[Co(L-ala)(EDDA)] and Δ-(+)-*trans*-[Co(*l*-pn)(EDDA)]$^+$.

sorption spectra of the amino acid isomers, Figure 5, are characteristic of those observed for α-[CoN_3O_3] complexes.[5a] In addition chromatography revealed the presence of small amounts of the *cis* isomers, and their CD spectra are considerably different from the spectra of the *trans* isomers.

Configurational and Vicinal Effects.—The additivity of the vicinal and configurational effects, when an isomer containing an optically active ligand is compared to an isomer in which the asymmetric ligand has been replaced by an analogous optically inactive ligand, has been previously demonstrated.[3–5] Such a relationship is expected to exist between the two amino acid (L-ala and gly)–EDDA–Co(III) complexes and between the two amine (*l*-pn and en)–EDDA–Co(III) complexes, each pair having an optically active ligand and the inactive analog.

The vicinal effect curve obtained by adding together the curves of (+)- and (−)-*trans*-[Co(L-ala)(EDDA)] is shown in Figure 2. When half (two times the vicinal effect is obtained by the addition) of this curve is subtracted from either curve, a curve for the configurational effect should be obtained as illustrated for the (+)-isomer in Figure 3. Substitution for glycine in [$Co(en)_2$(gly)]$^{2+}$ by L-alanine and other similarly active amino acids did not appreciably change the magnitude of the first CD band.[5] Assuming a similar relationship to hold between the CD curves of *trans*-[Co(gly)(EDDA)] and its L-alanine analog, comparison of the $\Delta\epsilon$ values obtained for the first CD band of these complexes suggests that about 65% resolution of [Co(gly)(EDDA)] was obtained. The experimental curve of this complex has been increased by this factor so that its shape may be compared to that obtained for [Co(L-ala)(EDDA)] minus the vicinal effect.

The vicinal curve for (+)- and (−)-*trans*-[Co(*l*-pn)(EDDA)]$^+$ was similarly obtained and is shown in Figure 1. The effect is so small that subtracting it from the experimental curve makes little difference. However, comparison of the vicinal effect curve with that for the L-alanine complex as discussed below and the fact that the curve was reproducible for independent preparations (see Experimental Section) gives confidence in the reality of the effect.

The two vicinal curves which were obtained have the same general shape, two components of the same sign in the low-energy absorption band region and a broad band of opposite sign in the high-energy region, but are qualitatively mirror images of each other. The absolute configuration and consequently conformation of L-alanine is opposite to that of *l*-propylenediamine as illustrated in Figure 6. The conformation of chelate rings has been associated with positive and negative effects of the CD spectra of chelate complexes by others.[12–14]

Vicinal effects have already been determined for L-alanine[3] and *l*-propylenediamine[4] in complexes with different symmetries. The L-alanine molecule in [Co(L-ala)(EDDA)] is in an environment similar to that of an L-alanine in α-[$Co(ala)_3$], and the vicinal effects observed are of the same order of magnitude, whereas the *l*-propylenediamine in [Co(*l*-pn)(EDDA)]$^+$ is not constrained by two highly puckered *l*-propylenediamine rings as in [$Co(l\text{-pn})_3$]$^{3+}$ where a very large vicinal effect was found. From these observations it would be expected that *l*-pn in [Co(*l*-pn)(trien)]$^{3+}$

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[12] E. Larsen and S. F. Mason, *J. Chem. Soc., Sect. A*, 313 (1966).

[13] C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

[14] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, **49**, 1965.

would exhibit a vicinal effect comparable to that observed for an *l*-pn in $[Co(l\text{-}pn)_3]^{3+}$. Such was the case for the *l*-pn in $[Co(en)_2(l\text{-}pn)]^{3+}$.[4] The vicinal effect includes any contributions from the asymmetric centers, the relative ring conformations, and differences in interligand interactions. The relative importance of these contributions is expected to vary, although the chelate ring conformation is expected to be of greatest importance in most instances.[15,16]

Circular Dichroism Spectra and Absolute Configurations.—The CD spectra of *trans*-[Co(L)(EDDA)], L = gly and L-ala, Figure 3, are very similar to those obtained for the diamine analogs, Figure 4, except that the CD components of the former have been shifted to lower energy, Table I. This shift is anticipated since an amine has been exchanged for a carboxylate, a group lower in the spectrochemical series. The vicinal curves also show the same general shape as previously discussed. It would appear, then, that Co(III) maintains effective C_2 symmetry. Thus, the arguments used to assign the absolute configurations to the *trans*-$[Co(L)(EDDA)]^+$, L = en and *l*-pn, isomers should also be applicable to the amino acid analogs.

The use of the correct C_2 symmetry of $[Co(en)(EDDA)]^+$ allows one to trace the parentage and signs of the components from D_3. The ordering of the states in the $T_{1g}(O_h)$ region of $[Co(en)_3]^{3+}$ has been established from the polarized CD spectrum of the crystal[17] and is shown in Figure 7. In lowering the symmetry from D_3 to C_2 three components are expected in the T_{1g} region as shown in Figure 7. The CD spectra reveal only two components. The dominant, lowest energy band should contain the A and B components arising from $E_a(D_3)$. The A component maintains the same orbital identity as its E_a parent and therefore no mixing with $B(A_2)$ is expected).[8] On this basis the $(+)_{589}$-isomers of *trans*-$[Co(L)(EDDA)]^+$, L = en and *l*-pn, and *trans*-[Co(L)(EDDA)], L = gly and L-ala, all of which have a dominant positive low-energy component at 1.89 and 1.84 $\times 10^{-4}$ cm^{-1}, respectively, should have the same absolute configuration as $\Delta(C_2)$-$(+)_{598}$-$[Co(en)_3]^{3+}$ (reference axis is C_2, Figure 8)[18] for which the dominant positive low-energy band has been assigned to the $A_1 \rightarrow E_a$ transition. The configurational relationship between the isomers is shown in Figure 8 and the absolute configurations are illustrated explicitly in Figures 6 and 9.

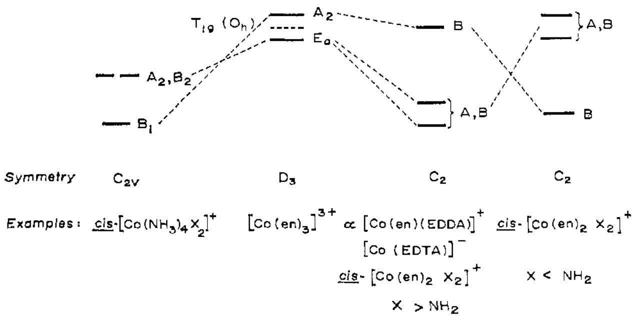

Figure 7.—Energy levels in the $T_{1g}(O_h)$ region for cobalt(III) in various crystal fields. (Separations are qualitative.)

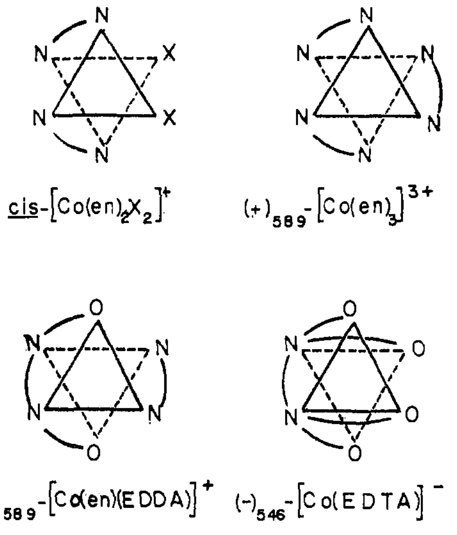

Figure 8.—Absolute configurations of some cobalt(III) complexes related to $\Delta(C_2)$-$(+)_{589}$-$[Co(en)_3]^{3+}$.

A similar line of reasoning has been used to assign absolute configurations to *cis*-$[Co(en)_2(acido)_2]^+$ [8] and α- and β-$[Co(trien)(acido)_2]^+$ [7] complexes (C_2 or approximate C_2 symmetry). The position of the dominant A_2, $B_2(E_a)$ component is dependent on the relative position of the acido to the amine group in the spectrochemical series (Figure 7). An example of a *cis*-$[CoA_4B_2]$ complex where B > A in the spectrochemical series is $[Co(EDTA)]^-$ for which the dominant CD band related to E_a in $[Co(en)_3]^{3+}$ should lie at lower energy (Figure 7), as observed.[19] The CD spectrum of $(-)_{546}$-$[Co(EDTA)]^-$ is quite similar to that of $(+)_{589}$-$[Co(en)(EDDA)]^+$ except that the bands of the former are at lower energies as expected, and both of these isomers should have the $\Delta(C_2)$ absolute configuration as previously argued, Figure 8.

There has been some question as to how to define the chirality (net helical distribution of chelate rings) of $[Co(EDTA)]^-$. A ring-pairing method has been presented[2] to help relate absolute configurations of octahedral chelate complexes whose optical activity appears to arise from the helicity of the chelate rings. The assignment of $\Delta(C_2)$ to the $(+)_{589}$-isomers of the *trans*-EDDA complexes and their apparent configurational relationship to $(-)_{546}$-$[Co(EDTA)]^-$, Figure 8, are consistent with the chiralities defined by this ring-pairing method. The absolute configuration of *trans*-$[Co(en)(EDDA)]^+$ has been established independently by the preparation and nmr study of the complex where EDDA has been replaced by the analogous ligand

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[15] S. F. Mason, A. M. Sargeson, R. Larsson, B. J. Norman, A. J. McCaffery, and G. H. Searle, Proceedings of the Ninth International Conference on Coordination Chemistry, St. Moritz, 1966, p 509.

[16] F. Woldbye, *Proc. Roy. Soc.* (London), in press.

[17] R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 331 (1962).

[18] Since the complexes discussed here have C_2 or pseudo C_2 symmetry as do many cobalt(III) complexes, the absolute configurations are related to the configuration of $[Co(en)_3]^{3+}$ as viewed down a C_2 axis. The chirality defined by a C_2 axis is the reverse of the chirality defined by the C_3 axis.[2,8] That is, $\Delta(C_2)$ refers to the same absolute configuration as $\Lambda(C_3)$.

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

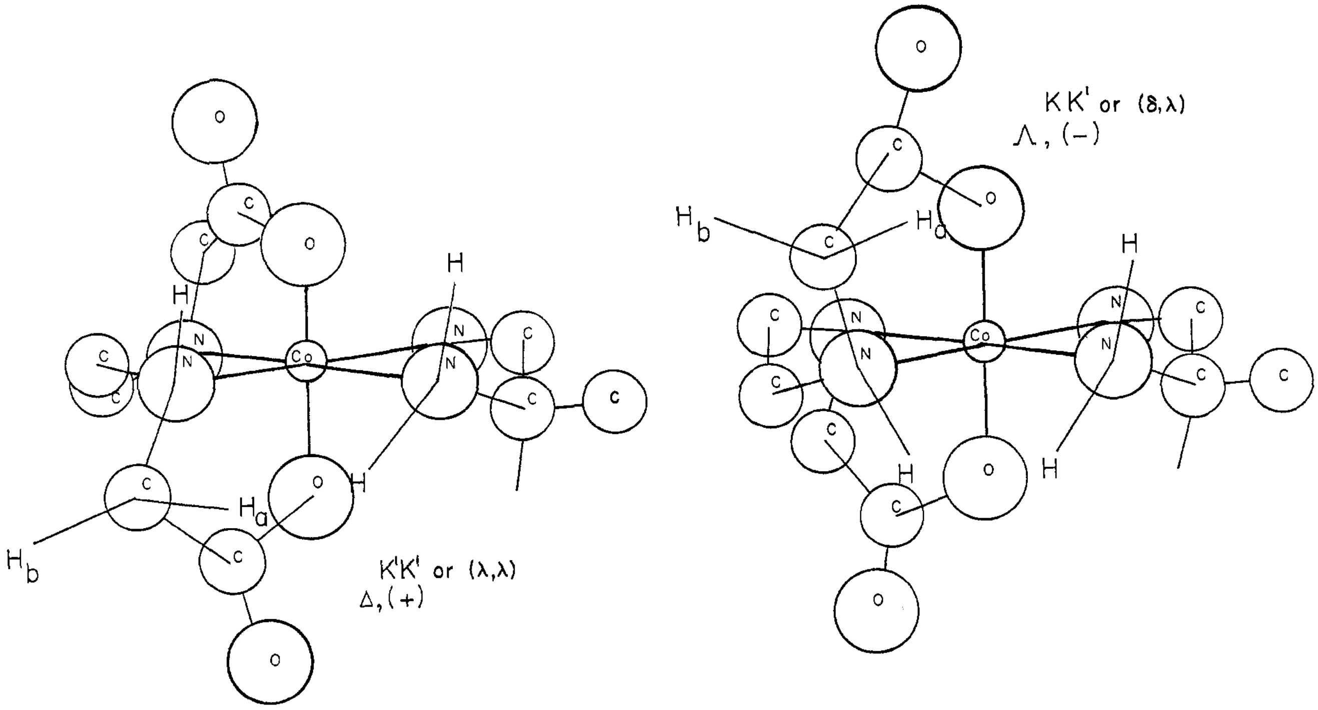

Figure 9.—Perspective of Δ- and Λ-(+)-*trans*-[Co(*l*-pn)(EDDA)]$^+$.

ethylenediamine-N,N′-di-L-α-propionate which is of known absolute configuration.[20] A more detailed discussion of the interrelationship of the absolute configurations of these and other cobalt(III) complexes can be found elsewhere.[2]

If the perturbation caused by the chelate rings is neglected, the symmetry of *trans*-[Co(en)(EDDA)]$^+$ is close to D_{4h}. The absorption spectrum of *trans*-[Co(en)(EDDA)]$^+$ has been interpreted in terms of such a tetragonal perturbation.[10] In such an approximation the $B(C_2)$ and A, $B(C_2)$ components become the $A_{2g}(D_{4h})$ and the degenerate $E_g(D_{4h})$ excited states, respectively. The two components found by analysis of the absorption spectrum of *trans*-[Co(en)(EDDA)]$^+$ [10] are easily located (Figure 4) and coincide within 1% with the CD components, Table I.

Proton Nmr Spectra and Absolute Configuration.—The spectra of the two isomers of *trans*-[Co(*l*-pn)(EDDA)]$^+$ were very similar to that obtained previously for *trans*-[Co(en)(EDDA)]$^+$ [10] except for details in the ethylene ring region for the *l*-propylenediamine complex where coupling with the methyl group complicates the spectrum.

The acetate ring proton resonances have already been assigned on the basis of bond anisotropies,[10] and their positions are shown in Figure 9. Since H_b is on the inside of the acetate ring, it should be the least influenced by changes in the bidentate ligand, *i.e.*, ethylenediamine to *l*-propylenediamine. The chemical shifts of the acetate ring protons were calculated from the AB spectra exhibited by these protons and are very close to the shifts obtained for *trans*-[Co(en)(EDDA)]$^+$ particularly in the H_b region as expected, Table II.

TABLE II
ACETATE RING PROTON CHEMICAL SHIFTS[a]

	H_a	H_b
trans-[Co(en)(EDDA)]$^+$	4.19	3.37
Λ-(−)-[Co(*l*-pn)(EDDA)]$^+$	4.16	3.34
Δ-(+)-[Co(*l*-pn)(EDDA)]$^+$	4.26 4.23	3.36

[a] Ppm from NaTMS.

Figure 6 shows Δ-*trans*-[Co(*l*-pn)(EDDA)]$^+$. The two N–C–C–N backbones are in a k′k′ conformation (identical with the stable conformation for a square-planar arrangement of two ethylenediamine chelate rings as discussed by Corey and Bailar[21]) and the N–H protons are staggered. Figure 9 shows the $\Delta(C_2)$ isomer rotated 90° about the O–N–O axis as well as the $\Lambda(C_2)$ isomer which is in the kk′ (δ, λ) conformation. Although the $\Delta(C_2)$ isomer has the N–H protons staggered, an N–H from *l*-propylenediamine is directly opposed to H_a as compared to the $\Lambda(C_2)$ isomer where the N–H protons are eclipsed and N–H_a is staggered with respect to the N–H protons of *l*-propylenediamine.

Saito and Iwasaki have determined the atomic parameters of a coordinated *l*-propylenediamine ring in their determination of the structure of *trans*-[Co(*l*-pn)$_2$Cl$_2$]Cl.[22] They found that the amines were in a k′k′ (λ, λ) conformation as in the Δ isomer, Figure 6, and that the N_2–Co bond length (Figure 6) was shorter than the N_1–Co bond length and the Co–N_2–C_2 bond angle was smaller than the Co–N_1–C_1 bond angle.

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[20] L. Schoenberg, D. W. Cooke, and C. F. Liu, paper presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[21] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959). According to an IUPAC recommendation pending, the k′ conformation will be designated λ since the C–C bond is a segment of a left helix about a line joining the coordinated N atoms and, correspondingly, the k conformation will be designated δ (right helix).

[22] Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

This dissymmetry would be expected for the *l*-propylenediamine in the *trans*-[Co(*l*-pn)(EDDA)]$^+$ isomers.

The N_1–H and N_2–H protons directly opposed to the H_a's in the $\Delta(C_2)$ isomer have a different relative orientation as a consequence of the dissymmetry, placing the H_a's in slightly different chemical environments. A doublet is observed for each component of the low-field portion of the AB spectrum (H_a region) reflecting this. The calculated chemical shifts in Table II show a difference of 0.03 ppm between the two protons. The spectrum of the Δ isomer was obtained at 100 Mc, and the separation between the doublets widened indicating a change in the chemical shifts of the protons ruling out H–N–C–H coupling previously observed in the H_a region of similar complexes.[23] The amine proton chemical shifts (for EDDA and en prior to N H–D exchange) are also slightly different in the two isomers, as would be expected. These observations are consistent with the assignment of absolute configuration made on the basis of CD spectra.

[23] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

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Substitution Reactions of Oxalato Complex Ions. VI. The Kinetics of the Anation Reaction of *cis*-Bis(oxalato)diaquochromium(III) Ion with Oxalate Ion in Aqueous Solution[1]

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The complex ion *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ undergoes reaction in aqueous solution with either $HC_2O_4^-$ or $C_2O_4^{2-}$ ion to give the tris(oxalato)chromium(III) complex ion. The rate-determining step appears to be ligand water dissociation from the diaquo complex ion, following an outer-sphere associative equilibration of the latter with bioxalate or oxalate ion. The observed pseudo-first-order rate constant is described by

$$k = k_w\{K_1(HC_2O_4^-)/[1 + K_1(HC_2O_4^-)] + K_2(C_2O_4^{2-})/[1 + K_2(C_2O_4^{2-})]\}$$

where K_1 and K_2 are the association constants for bioxalate and oxalate, respectively, and k_w is the rate constant of the water replacement. K_1 and K_2 have values of 0.85 and 1.9, respectively, at 50° and are independent of the ionic strength, I. At 50°, k_w varies between about 10^{-3} sec^{-1} at $I = 0$ and about 7×10^{-3} sec^{-1} at $I = 2.7$ M. The ionic strength effects are not altered by changes in the nature of the "inert" 1-1 electrolyte used. Temperature dependence studies indicate that the enthalpy of activation of the rate-determining process is close to 22 kcal/mole.

The only previous data on the rate of the addition of oxalate ion to the complex ion $Cr(C_2O_4)_2(H_2O)_2^-$ are those reported by Hamm and Davis[2a] as part of their study of the successive substitutions (n = 0, 1, or 2)

$$Cr(C_2O_4)_n(H_2O)_{6-2n}^{3-2n} + C_2O_4^{2-} \longrightarrow Cr(C_2O_4)_{n+1}(H_2O)_{4-2n} + 2H_2O \quad (1)$$

They proposed rate-determining chelate ring closure following rapid monodentate equilibration with the entering oxalate group. This conclusion was based on an apparent lack of dependence of the rate of reaction on oxalate concentration.[2b] In a succeeding study of reactions of several organic acid anions, including acetate and citrate, with $Cr(H_2O)_6^{3+}$ cation, Hamm and co-workers[3] adduced strong evidence for an alternative mechanism for this kind of process. This proposal involves outer-sphere ion-pair equilibration, followed by rate-determining ligand–water dissociation, very similar to the mechanism now widely accepted for many aquo cation–ligand anion substitution reactions.[4] There still remains at issue the question as to whether reaction 1, with n = 2, conforms to this latter pattern, since in this case, both reactants are anions. In fact, recent studies of chloride-for-water replacement in the hexaaquorhodium(III) cation[5] and the pentachloroaquorhodium(III) anion[6] suggest contrasting mechanisms in the two types of reaction. Furthermore, the usual inverse acidity dependence of these anation processes, often readily explainable in terms of the acid–base properties of the aquo ion,[5] is more complicated in systems involving basic ligand anions such as oxalate. In these cases, the acid–base equilibria of the entering anion itself are of significance to the acidity dependence characteristics.

An earlier investigation in our laboratory[7] clarified several aspects of the mechanism of acid-catalyzed aquation of the tris(oxalato)chromium(III) ion, *viz.*

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[1] Part V in this series: K. V. Krishnamurty, *Inorg. Chem.*, **1**, 422 (1962).

[2] (a) R. E. Hamm and R. E. Davis, *J. Am. Chem. Soc.*, **75**, 3085 (1953); (b) Hamm has since reported (private communication, 1963) that the extent of oxalate concentration variation was in fact not large enough to make the nondependence conclusion unequivocal.

[3] R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 4469 (1958).

[4] M. Eigen and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

[5] K. Swaminathan and G. M. Harris, *J. Am. Chem. Soc.*, **88**, 4411 (1966).

[6] W. Robb and G. M. Harris, *ibid.*, **87**, 4472 (1965).

[7] K. V. Krishnamurty, and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960) (part II of present series).