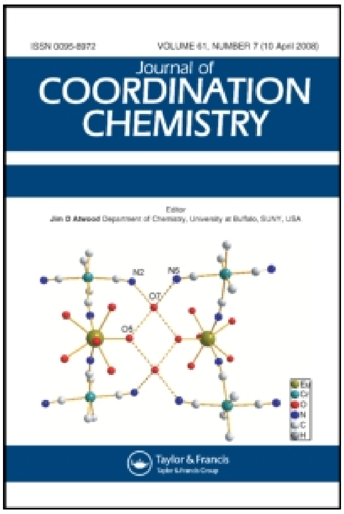

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CIRCULAR DICHROISM STUDIES OF COBALT(III) COMPLEXES OF THE TYPE CIS-$[CoN_2O_4]$[1]

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The complex ion $[Co(mal)_2(tn)]^-$ (mal = malonate ion) and the corresponding complexes of trimethylenediamine (tn) containing the bidentate O-donor ligands $C_2O_4{}^{2-}$ and acetylacetonate (acac) ions were prepared and resolved. Their circular dichroism (CD) spectra are compared with the data reported here for $[Co(C_2O_4)_2(l\text{-chxn})]^-$, $[Co(mal)_2(l\text{-chxn})]^-$, $[Co(mal)_2(l\text{-pn})]^-$, and $[Co(acac)_2(l\text{-pn})]^+$ complex ions. The malonate complexes reveal greater splitting within the first absorption band region compared to $C_2O_4{}^{2-}$ and $acac^-$, but lower net rotational strengths. The contributions to the CD spectra for the optically active ligands are comparable to those reported for other complexes. There is a much greater contribution from the optically active ligand in *trans*-cyclohexanediaminetetraacetatocobaltate ion than in the corresponding complex of 1,2-propanediaminetetracetatocobaltate ion.

INTRODUCTION

Variation in the chelate ring size for $[Co(C_2O_4)_2(en)]^-$ and $[Co(mal)_2(en)]^-$, and in the pattern of chelate rings for model compounds of $[Co(EDTA)]^-$ result in marked changes in their circular dichroism spectra.[2,3] Structural changes in complexes related to $[Co(EDTA)]^-$ also cause changes in CD spectra[4-7] which can make it difficult to assign absolute configurations. It seemed worthwhile to study a series of *cis*-$[CoN_2O_4]$ type complexes containing an aliphatic diamine (*l*-pn, *l*-chxn, and tn) and two bidentate ligands containing oxygen donor atoms ($C_2O_4^{2-}$, mal^{2-}, and $acac^-$). These ligands permit comparisons of 5- and 6-membered rings, differences in rigidity, and the effects of asymmetric centers. The complex $[Co(+)\text{–}CDTA]^-$ is included for comparison to $[Co(EDTA)]^-$ and to the model compounds reported here and in reference 2.

EXPERIMENTAL SECTION

Resolution of amines

1,2-Diaminocyclohexane, the proportions of the cis and trans isomers being unknown, was purchased from Aldrich Chemical Company. The resolution[8] of the trans isomer was accomplished by precipitation of the amine (as purchased) as the diastereomer, *l*-chxn d-tartrate, using a 1:1 mole ratio of amine to d-tartaric acid. The less soluble diastereomer was recrystallized (2 or 3 times) from hot water to a constant optical rotation $[\alpha]_{589}$ + 12.0° [lit. (+11°),[8] (+12°)[9]]. The diastereomer was treated with $Ba(OH)_2$ to precipitate barium tartrate and then with concentrated HCl to isolate the solid dihydrochloride. Racemic propylenediamine was also resolved using d-tartaric acid[10] and converted to the dihydrochloride.[11]

K[Co(mal)₂(l-pn)]·1.5H₂O. The complex was prepared using the procedure[12] for $[Co(mal)_2(en)]^-$. The work was concurrent with, but independent of, that of Stadtherr.[13] The resolution was accomplished using $(+)_{546}$ – $[Co(en)_2(C_2O_4)]$ $C_2H_3O_2$ as the resolving agent. The less soluble diastereomer, (+)-$[Co(en)_2(C_2O_4)]$ (+)-$[Co(mal)_2(l\text{-pn})]$ was recrystallized three times by dissolving in warm water, cooling in ice, and adding ethanol dropwise. The resolving agent was precipitated as the iodide salt. The very soluble enantiomers, as the potassium salts, were recrystallized from water, giving $\Delta\epsilon_{592}$ + 2.72 for one isomer and $\Delta\epsilon_{594}$ – 3.10 for the other. *Anal.* Calcd. for $K[Co(C_3H_{10}N_2)(C_3H_2O_4)_2]\cdot 1.5H_2O$: C, 26.80; H, 4.22; N, 6.95. Found: C, 26.91; H, 4.49; N, 7.11.

K[Co(C₂O₄)₂ (l-chxn)]·2H₂O. The complex was prepared by the procedure used[14] for $K[Co(C_2O_4)_2(l\text{-pn})]$. The complex was resolved using 0.5 mol of (+)-$[Co(en)_2(C_2O_4)]$ $C_2H_3O_2$, per mol of racemic complex. The active complex from the less soluble diastereomer gave $\Delta\epsilon_{576}$ – 3.04 after three recrystallizations. *Anal.* Calcd. for $K[Co(C_2O_4)_2(C_6H_{14}N_2)]\cdot 2H_2O$: C, 28.30; H, 4.29;

N, 6.60. Found: C, 27.91; H, 4.03; N, 6.39. The other enantiomer was obtained using (–)-[Co(en)$_2$(C_2O_4)] $C_2H_3O_2$ as the resolving agent.

K[Co(mal)$_2$(l-chxn)] ·3.5H_2O. The complex was prepared by a modification of the procedure[12] used for [Co(mal)$_2$(en)]$^-$. A solution of *l*-cyclohexanediamine malonate (0.04 mol, 40 ml) was added to a solution of potassium malonate (0.112 mol, 10 ml) and a solution of Co($C_2H_3O_2$)$_2$·4H_2O(0.032 mol) in 30 ml of water was added. The resulting solution was warmed to 65° and H_2O_2 (6 ml of 30% diluted to 25 ml) was added dropwise with stirring over a period of 10 min. The temp rose to 80° and was allowed to drop to 65° while stirring for another 30 min. The solution was evaporated to 70 ml under an air stream, cooled in an ice bath and the solid purple complex filtered. Yield 5.7 g. A second crop (4.5 g) was recovered from the filtrate. The combined product was recrystallized from water. The complex was resolved using (+)-[Co(en)$_2$(C_2O_4)]$C_2H_3O_2$ as the resolving agent (1:1 mole ratio). The less soluble diastereomer, (+)-[Co(en)$_2$(C_2O_4)] (-)-[Co(mal)$_2$(*l*-chxn)], was recrystallized from water by addition of ethanol to give $\Delta\epsilon_{600}$-2.7. The active complex was recovered and recrystallized as above. The much more soluble (+)-isomer was recovered similarly. *Anal.* Calcd. for K[Co($C_3H_2O_4$)$_2$($C_6H_{14}N_2$)] ·3.5H_2O: C, 30.06; H, 5.25; N, 5.85. Found: C, 29.93; H, 5.20; N, 5.83.

K[Co(C_2O_4)$_2$(tn)] ·2H_2O. The complex was prepared as described for K[Co(C_2O_4)$_2$(*l*-pn)]. The more soluble diastereomer containing the (-)-isomer was obtained using (-)-[Co(en)$_2$(C_2O_4)]$^+$, but the less soluble diastereomer was too insoluble to be used. The (+) isomer was obtained using (+)-[Co(en)$_2$(C_2O_4)]$^+$. *Anal.* Calcd. for K[Co(C_2O_4)$_2$($C_3H_{10}N_2$)] ·2H_2O: C, 21.88; H, 4.01; N, 7.29. Found: C, 21.98; H, 3.77; N, 6.99.

K[Co(mal)$_2$(tn)] ·2H_2O. The complex was prepared and resolved as described for the corresponding *l*-chxn complex. *Anal.* Calcd. for K[Co($C_3H_2O_4$)$_2$ ($C_3H_{10}N_2$)]·2H_2O: C, 26.03; H, 4.39; N, 6.79. Found: C, 25.54; H, 4.09; N, 6.78.

K-[Co(CDTA)] ·3H_2O. The complex was prepared as reported[15] using racemic cyclohexanediaminetetraacetic acid. The reported resolution using (-)-*cis*-[Co(en)$_2$(NO_2)$_2$]Br caused difficulty, so (+)-[Co(en)$_2$(C_2O_4)]$C_2H_3O_2$ was used (1:1 mole ratio). Both isomers, K(+)-[Co(-)CDTA] ·2H_2O and K(-)-[Co(+)-CDTA] ·2H_2O were obtained. *Anal.* Calcd. for K[Co($C_{14}H_{18}N_2O_8$)] ·2H_2O: C, 35.29; H, 4.71; N, 5.88. Found: C, 35.63; H, 4.75; N, 5.80.

[Co(acac)$_2$(tn)] ClO_4. This complex was prepared by a method analogous to that for [Co(acac)$_2$(en)]ClO_4[16] using 20 g of Na[Co(acac)$_2$(NO_2)$_2$], 4.2 g of trimethylenediamine and 10 g of Norit A carbon. After removal of the carbon, 150 g of $NaClO_4$·H_2O was added. Brown-violet needle crystals were separated and washed with l-propanol-ether (1:1) mixture and then ether. The product was recrystallized from warm water (55°). After the separation of the first fraction, $NaClO_4$ was added to the filtrate to recover more product. Total yield, 8.7 g.

For the resolution, [Co(acac)$_2$(tn)]ClO_4 (4.3 g) and an anion-exchange resin (Dowex 1-X8, Cl^- form) (15 g) were combined and stirred in 20 ml of water. This was repeated with a second portion (5 g) of resin. To the combined filtrate and washings were added silver d-tartrate (1.80 g) and d-tartaric acid (0.75 g) and AgCl was removed. The filtrate and washings were combined and concentrated under an air stream to give fine needle crystals which were separated by filtration and washed with ethanol-ether (1–1) mixture and then ether. One recrystallization from methanol by addition of ether was enough to reach a constant $\Delta\epsilon_{512}$ +3.68 (assuming a 1:1 diastereomer, mol wt 480.4). From the filtrate after the removal of the first fraction were obtained the second and third fractions with small $\Delta\epsilon$ value. The filtrate after the separation of the third fraction was diluted to 10 ml with water, $NaClO_4$·H_2O (0.5 g) in 5ml of water was added to it, and the solution was cooled. Brown-purple needle crystals were separated and recrystallized from hot water. Yield, 0.45 g. $\Delta\epsilon_{512}$ –3.90. The diastereomer (1.26 g) ($\Delta\epsilon_{512}$ + 3.68) was dissolved in 10 ml of water, and $NaClO_4$·H_2O (0.5 g) in 5 ml of water was added to it. The brown-purple needle crystals which appeared on cooling were separated. Recrystallization of the complex from hot water did not change $\Delta\epsilon_{512}$+3.91. Yield before recrystallization 0.94 g. *Anal.* Calcd. for [Co(acac)$_2$(tn)]ClO_4·0.5H_2O: C, 35.51; H, 5.73; N, 6.37. Found: C, 35.63; H, 5.58; N, 6.46.

[Co(acac)$_2$(l-pn)] ClO_4. Sodium dinitrobis(acetylacetonato)cobalt(III) (20 g) was dissolved in 500 ml of cold water and 100 ml of cold methanol in an ice-bath. Then Norit A carbon (10 g) and the solution containing *l*-propylenediamine dihydrochloride (8 g) and NaOH (4.4 g) in 100 ml of water were added to

the above solution. The carbon was removed and $NaClO_4 \cdot H_2O$ (150 g) was added to the combined filtrate and washings. Purple-red crystals were separated and washed with ethanol-ether (1:1) mixture and then ether. The product was recrystallized from methanol by addition of ether and subsequent cooling. Yield, 4.0 g.

For the resolution, $[Co(acac)_2(l\text{-pn})]ClO_4$ (4.07 g) was converted to the chloride salt using Dowex 1-X8 and then to the hydrogen d-tartrate salt as above. The filtrate and washings were combined and concentrated under an air stream. The crystals obtained (2.6 g) were recrystallized from methanol by addition of ether and subsequent cooling. The diastereomer with $\Delta\epsilon_{510}$ −4.27 (assuming a 1:1 diastereomer) was obtained. One more recrystallization did not increase the $\Delta\epsilon$ value. The diastereomer (0.78 g) was stirred with Dowex 1-X8 (Cl^-) in a small amount of water. After the separation of the resin, 2.5 g of $NaClO_4 \cdot H_2O$ was added. At first a gummy substance separated but scratching of the walls of the beaker induced crystallization of the product. The product was recrystallized from *ca.* 5 ml of hot water. Yield: 0.50 g. $\Delta\epsilon_{510}$ −4.58. *Anal.* Calcd. for $[Co(acac)_2(l\text{-pn})]ClO_4 \cdot 0.5H_2O$: C, 35.51; H, 5.73; N, 6.37. Found: C, 35.44; H, 5.40. N, 6.60.

The filtrate from the separation of the less soluble diastereomer, was diluted to 20 ml by the addition of water. To this solution was added 0.73 g of $NaClO_4 \cdot H_2O$ followed by cooling in an ice-bath. The perchlorate complex with low $\Delta\epsilon$ was separated by filtration (1.5 g). To the filtrate was added 5 g of $NaClO_4 \cdot H_2O$ and kept in a refrigerator. A red complex contaminated with a small amount of a white substance (presumably sodium hydrogen tartrate) was separated by filtration. This was added to 10 ml of methanol and the white. substance which remained undissolved was filtered off. Twenty milliliters of ether was added to the filtrate followed by cooling in a refrigerator. Deep red crystals (0.27 g) were separated and washed with ether. To the filtrate was added 20 ml of ether followed by cooling in a refrigerator. More deep red crystals (0.29 g) were separated. The above two fractions were combined and recrystallized from methanol by addition of ether. The complex was then recrystallized from hot water twice. These recrystallizations did not change $\Delta\epsilon_{507}$ +4.60. Yield: 0.13 g. *Anal.* Calcd. for $[Co(acac)_2(l\text{-pn})]ClO_4$: C, 36.25; H, 5.62; N, 6.51. Found: C, 36.61; H, 5.46; N, 6.66.

$[Co(acac)_2(en)]ClO_4$. This complex was prepared according to the method of Archer and Cotsoradis.[16] The optical resolution had been performed by Boucher[17] using sodium (+)-arsenyltartrate, but another method was used here. The $[Co(acac)_2(en)]ClO_4$ (6 g) was converted to the chloride salt using Dowex 1-X8 and then to the hydrogen d-tartrate salt as above. The filtrate and washings were combined and concentrated with a rotary evaporator to dryness. Red needle crystals were obtained by recrystallization from methanol by addition of ether. One recrystallization was enough to reach a constant $\Delta\epsilon_{510}$ −4.75 (assuming a 1:1 diastereomer). The purified diastereomer (1.6 g) was changed into the perchlorate by the addition of an appropriate amount of sodium perchlorate monohydrate. Recrystallization of the enantiomer from hot water was carried out twice without changing $\Delta\epsilon_{510}$ −4.85. Yield: 0.60 g. *Anal.* Calcd. for $[Co(acac)_2(en)]ClO_4$: C, 34.59; H, 5.32; N, 6.72. Found: C, 34.87; H, 5.28; N, 7.02. The opposite enantiomer could not be obtained optically pure, because of the difficulty of the purification of the diastereomer.

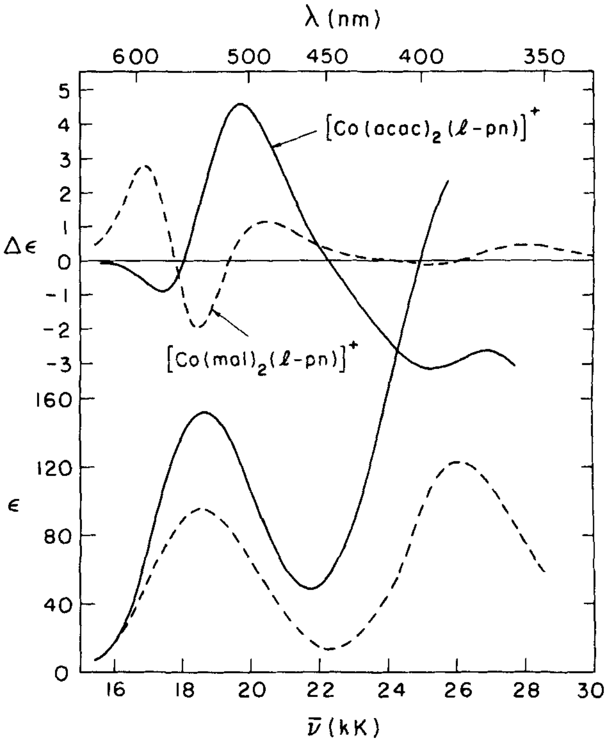

FIGURE 1 Circular dichroism and absorption spectra of $[Co(acac)_2(l\text{-pn})]ClO_4$ and $K[Co(mal)_2(l\text{-pn})] \cdot 1.5H_2O$.

RESULTS AND DISCUSSION

The CD curve for $[\mathrm{Co(mal)_2en}]^-$ shows three well-defined peaks[2] of alternating sign in the lower energy ligand field absorption band. This indicates complete removal of the degeneracy of the $T_{1g}(O_h)$ level, corresponding to the actual C_2 symmetry.† There are also three CD peaks of alternating sign in the second ligand field band region. The $[\mathrm{Co(C_2O_4)_2(en)}]^-$ complex ion shows only two CD peaks of the same sign in the first band region[2], but three peaks of alternating sign in the second band region. One of the three components in the first band region must be masked because of the small splitting. The absolute configuration assigned[2] for $\Lambda\text{-}(-)_{546}\text{-}[\mathrm{Co(mal)_2(en)}]^-$ has been confirmed by x-ray methods.[19] The $(+)_{546}\text{-}[\mathrm{Co(C_2O_4)_2(en)}]^-$ complex ion [this is $(-)_{589}$] was assigned for Δ configuration[2] in agreement with the assignment for $[\mathrm{Co(C_2O_4)_2}(l\text{-pn})]^-$ from CD spectra[20] and pmr spectra.[21]

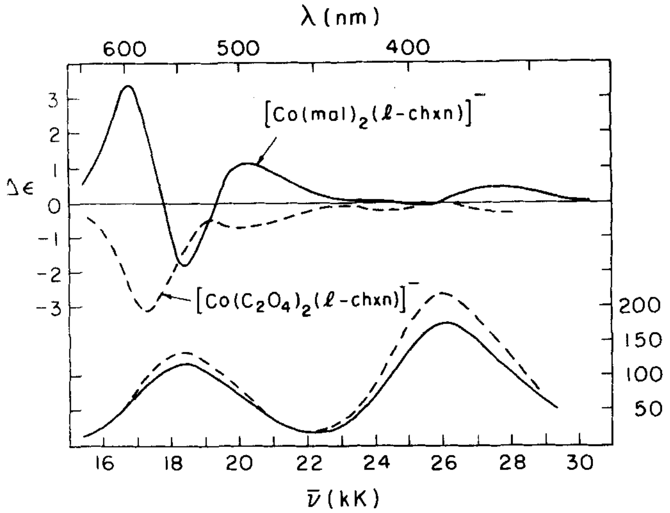

FIGURE 2 Circular dichroism and absorption spectra of $\mathrm{K[Co(mal)_2}(l\text{-chxn})]\cdot 3.5\mathrm{H_2O}$ and $\mathrm{K[Co(C_2O_4)_2}(l\text{-chxn})]\cdot 2\mathrm{H_2O}$.

The CD curves in the first band region for $[\mathrm{Co(mal)_2}(l\text{-pn})]^-$ (Figure 1), $[\mathrm{Co(mal)_2}(l\text{-chxn})]^-$ (Figure 2), and $[\mathrm{Co(mal)_2(tn)}]^-$ (Figure 3) (Tables I and II) all show the same alternating sign pattern as $[\mathrm{Co(mal)_2(en)}]^-$ and must have the same absolute configuration (Λ for the isomers shown). This assignment has been confirmed from pmr spectra[13] in the case of $[\mathrm{Co(mal)_2}(l\text{-pn})]^-$. There are differences in peak intensities through the series caused by contributions from the optically active l-chxn and l-pn and the larger chelate ring size for tn. However, mutual

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†The question is raised as to whether the three CD peaks of alternating signs indicate three transitions or two transitions with opposite signs of rotational strength. Both interpretations are possible, but not reasonable for comparison of several cases. The CD curve of $[\mathrm{Co(mal)_2en}]^-$ in the low energy region is easily resolved into 3 components of comparable half-widths.[2] These half-widths are similar (~1 kK) to those of related complexes where only two peaks appear. The separation between peaks (1.5 – 2kK) is comparable to that for the closely related $[\mathrm{Co(EDTA)}]^-$, even without an attempt to find a third peak by Gaussian analysis for $[\mathrm{Co(EDTA)}]^-$. The resolution of the CD curve of $[\mathrm{Co(mal)_2en}]^-$ into two components requires one very broad peak and one very narrow peak of opposite sign. The intensities must be greater than ordinarily encountered for solution CD spectra by almost an order of magnitude. The peaks must occur at almost the same energy (separation *ca.* 0.2 – 0.4 kK) in order to avoid complete cancellation of one of the side peaks. For a series of related compounds[2] such as $[\mathrm{Co(mal)_2en}]^-$, $[\mathrm{Co(C_2O_4)_2en}]^-$ and $[\mathrm{Co(EDTA)}]^-$ there is no indication of such wide variation in half-widths or intensities, nor are such great changes in the energy separation of the transitions expected.

In the series[18] $[\mathrm{Co(en)_2CO_3}]^+$, $[\mathrm{Co(en)_2(C_2O_4)}]^+$, and $[\mathrm{Co(en)_2mal}]^+$ only one CD peak appears in the first absorption band region, but the change in the shape of the higher energy side of the CD peak for $[\mathrm{Co(en)_2mal}]^+$ makes it obvious that there is a second component of opposite sign. The trends among the CD curves[18] are similar for the corresponding l-cyclohexanediamine complexes, but here the second peak of opposite sign does show up for $[\mathrm{Co}(l\text{-chxn})_2\mathrm{mal}]^+$.

Only one, apparently symmetrical, CD peak occurs in the first absorption band region for $[\mathrm{Co(C_2O_4)_2(gly)}]^{2-}$ [K. Yamasaki, J. Hidaka, and Y. Shimura, Bull. Chem. Soc. Japan, 42, 119 (1969)], although a second peak of opposite sign appears with the introduction of one or two 6-membered chelate rings in $[\mathrm{Co(C_2O_4)_2}(\beta\text{-ala})]^{2-}$ or $[\mathrm{Co(mal)_2(gly)}]^{2-}$. The CD curve for $[\mathrm{Co(C_2O_4)_2(L\text{-}ala)}]^{2-}$ also shows only one peak in the first absorption band region, but the presence of two components of the same sign is revealed from the CD curve for the unresolved complex or from the 'vicinal effect' curve obtained by subtracting the CD curve of $[\mathrm{Co(C_2O_4)_2gly}]^{2-}$ from that of $[\mathrm{Co(C_2O_4)_2(L\text{-}ala)}]^{2-}$. The energy positions and separations and the half-widths are consistent for two components throughout the series of complexes containing $\mathrm{C_2O_4}^{2-}$ or mal^{2-} and glycinate or L-alaninate ligands. The presence of the two components is obvious only in the case of complexes containing mal^{2-} or β-alaninate ion, ligands giving 6-membered chelate rings. It is commonly observed that complexes containing 6-membered chelate rings reveal more clearly the splitting of energy levels in a related series.[7,18] In a series of complexes related to $[\mathrm{Co(EDTA)}]^-$ two CD peaks are observed in the first absorption band region. From their positions relative to the absorption peaks it is apparent that there are three transitions, but generally either the lower energy or the higher energy peak is masked, depending on the energy separations and intensities. [J. Hidaka, S. Yamada, and B. E. Douglas, *J. Coord. Chem.*, 2, 123 (1972)].

TABLE I
Absorption and circular dichroism data

Compound[a]	Absorption		Circular Dichroism	
	kK	ε	kK	Δε
$K(+)_{546}$-$[Co(C_2O_4)_2(tn)]\cdot 2H_2O$	18.0	101	17.2	-1.61
			19.3	-0.67
	26.3	226	23.8	-0.17
			25.4	+0.17
			27.8	-0.09
$K(-)_{546}$-$[Co(mal)_2(tn)]\cdot 2H_2O$	18.1	78	16.6	+2.09
			18.2	-2.10
			20.3	+0.68
	26.2	154	24.1	+0.20
			27.2	+0.41
$(+)_{589}$-$[Co(acac)_2(en)]ClO_4$	18.7	159	17.4	+1.29
			19.6	-4.85
			25.1	+3.12
$(-)_{589}$-$[Co(acac)_2(tn)]ClO_4\cdot 0.5H_2O$	18.6	119	17.3	-2.11
			19.5	+3.91
			25.0	-2.64
$Ba(-)_{546}$-$[Co(+)PDTA]_2\cdot 8H_2O$[b]	18.6	300	17.2	+1.58
			19.7	-0.76
	26.6	204	-	-
$K(-)_{546}$-$[Co(+)$-$CDTA]\cdot 2H_2O$	18.5	316	16.8	+1.43
			18.8	-1.72
	26.2	221	-	-

[a] The isomers are designated by the sign of rotation at 546 or 589 nm.

[b] Data from reference 25. The values of ε and Δε are divided by two for comparison on a per mole of complex ion basis.

cancellation among the peaks clouds the significance of small differences (see below).

The CD curves for $[Co(C_2O_4)_2(l\text{-chxn})]^-$ (Figure 2) and for $[Co(C_2O_4)_2(tn)]^-$ (Figure 3) (Tables I and II) show two peaks of the same sign in the first band region. This is the same pattern observed for the corresponding en[2] and pn[20] complexes, so the isomers represented in the figures should also have the Δ configuration.

The complexes $[Co(acac)_2(tn)]^+$ and

TABLE II
Absorption and circular dichroism data

	Absorption		Circular Dichroism			
			(-) isomer[a]		(+) isomer[a]	
Compound	kK	ϵ	kK	$\Delta\epsilon$	kK	$\Delta\epsilon$
$K[Co(C_2O_4)_2(\ell\text{-chxn})]\cdot 2H_2O$	18.3	133	17.3	-3.04	17.4	+3.10
			20.1	-0.70	19.6	+1.19
	26.1	216	24.2	-0.18	23.8	+0.18
			27.8	-0.27	27.8	+0.26
$K[Co(mal)_2(\ell\text{-chxn})]\cdot 3.5H_2O$	18.4	114	16.8	-3.39	16.8	+3.37
			18.5	+2.09	18.4	-1.81
			20.6	-0.56	20.3	+1.13
	26.1	174	24.4	-0.16	25.4	-0.12
			27.5	-0.52	27.8	+0.46
$K[Co(mal)_2(\ell\text{-pn})]\cdot 1.5H_2O$	18.6	94.5	16.8	-3.10	16.9	+2.72
			18.5	+2.75	18.4	-1.97
			20.6	-0.78	20.4	+1.12
	26.1	124	23.8	-0.11	23.3	+0.09
			27.6	-0.56	25.4	-0.18
					27.6	+0.40
$[Co(acac)_2(\ell\text{-pn})]ClO_4$.	18.7	160	17.3	+1.07	17.4	-0.88
			19.6	-4.58	19.7	+4.60
			25.2	+3.29	25.2	-3.11

[a] The isomers are identified by the sign of the dominant CD peak.

$[Co(acac)_2(l\text{-pn})]^+$ were prepared and resolved to compare with CD data[17] for $[Co(acac)_2(en)]^+$. The intensities of the CD peaks for the newly resolved complexes (Tables I and II) indicated that $[Co(acac)_2(en)]^+$ had been incompletely resolved,[17] so this complex was resolved by another procedure ($\Delta\epsilon_{max}$3.1 reported,[17] 4.85 is the value reported here). Boucher[17] assigned $(+)_{546}$-$[Co(acac)_2(en)]^+$, with a dominant positive CD peak in the first band region, the $\Delta(C_2)$ configuration. This is equivalent to $\Lambda(C_3)$ or Λ using the IUPAC rules.[22] The CD curves are very similar for the corresponding en, tn, and l-pn complexes (Figures 1 and 4) so the isomers represented can all be assigned the Λ configuration. This is reasonable for complexes with net positive rotational strengths in the first band region.[23] Here there are two CD peaks of opposite sign in the first band region, differing from the spectra of the corresponding oxalate (Figure 3) and malonate (Figures 1, 2 and 3) complexes.

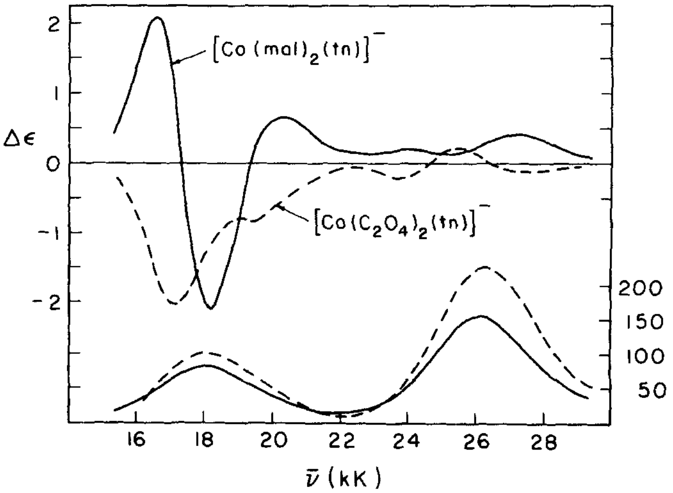

FIGURE 3 Circular dichroism and absorption spectra of $K(-)_{546}$-$[Co(mal)_2(tn)]\cdot 2H_2O$ and $K(+)_{546}$-$[Co(C_2O_4)_2(tn)]\cdot 2H_2O$.

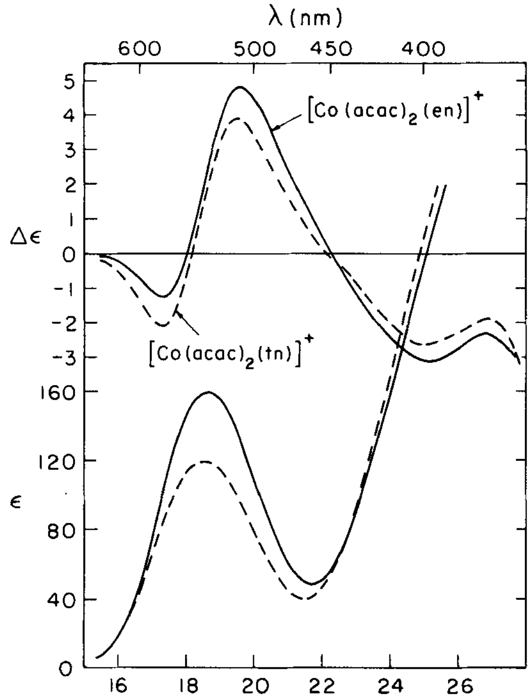

FIGURE 4 Circular dichroism and absorption spectra of $(-)_{589}$-$[Co(acac)_2(en)]ClO_4$ and $(-)_{589}$-$[Co(acac)_2(tn)]ClO_4 \cdot 0.5H_2O$.

Ring Size and Vicinal Effects

Both oxalate ion and acetylacetonate ions give essentially planar chelate rings, but differing in size. The splitting patterns are likely to change within the series of complexes of $C_2O_4{}^{2-}$, malonate, and acetylacetonate ions. The resulting differences in mutual cancellation are likely to overshadow differences in rotational strengths except for the net rotational strength within a band. If one compares the complexes of tn (Figures 3 and 4), the net rotational strengths in the $T_{1g}(O_h)$ band region are very nearly the same for the $C_2O_4{}^{2-}$ and $acac^-$ complexes. This might not be a valid comparison because of the possibility of intensity borrowing from an allowed transition in the case of acac or because of overlap with a band of opposite sign from the T_{2g} region. The net rotational strength is very low for the malonate complex, as observed for other complexes.[7,18] The ε values are considerably smaller for the oxalate and malonate complexes and this should cause some lowering of the rotational strengths.

The intensity of the lower energy CD peak for $[Co(acac)_2(tn)]^+$ is greater than that for $[Co(acac)_2(en)]^+$ (Figure 4), but the net rotational strength is significantly lower for the tn complex. Here the decrease might be attributed largely to the decrease in electric dipole strength as indicated by the lower ε value. The net rotational strengths of $[Co(mal)_2(tn)]^-$ and $[Co(C_2O_4)_2(tn)]^-$ are also somewhat lower than those of the corresponding en complexes in the first band region, but again this is accompanied by lower ε values. The tn chelate ring might lower ε, and consequently Δε, because it is less rigid.[18]

In comparing complexes of en with those of *l*-pn and *l*-chxn, there are contributions expected from the asymmetric centers and from a fixed ring conformation. The net rotational strength of $[Co(mal)_2(l\text{-pn})]^+$ is slightly higher than that of the corresponding en complex[2] primarily because of the lower intensity of the center peak which is opposite in sign to the other two peaks. The two optical isomers do not differ in CD intensities (Table II) to a great extent, indicating that the contribution from the optically active ligand is not large, but comparable to that observed in other cases.[24] The intensity comparisons for $[Co(mal)_2(l\text{-chxn})]^-$ are similar and contributions from the optically active ligand are similar to those observed elsewhere.[18]

The only unusual case is that of $[Co(acac)_2(l\text{-pn})]^+$ (Figure 1) compared to $[Co(acac)_2(en)]^+$ (Figure 4). Both CD peaks in the first band region are slightly lower for the *l*-pn complex compared to $[Co(acac)_2(en)]^+$ and this is true for both isomers of $[Co(acac)_2(l\text{-pn})]^+$ (Table I). The contribution of an optically active ligand generally decreases the intensity of a given peak for one isomer and increases it for the other. One might suspect incomplete resolution of the complex, but the resolution was carried out very carefully with many recrystallizations. The resolution is difficult because the diastereomers are very soluble and do not crystallize readily. The final Δε values did not change upon further recrystallization. Also the 'vicinal effect' curve obtained by addition of the CD curves for the two isomers agrees very well with that for the unresolved complex. This would require the same fractional resolution for both isomers. This is unlikely since the diastereomers differ significantly in solubilities.

K[Co(+)-CDTA]. The CD intensities are very nearly the same for $K(-)_{546}$-$[Co(EDTA)]$[2] and $K(-)_{546}$-$[Co(+)\text{-PDTA}]$[25] although the ε values are lower for the PDTA complex (300 compared to 347 for the first absorption band) (Table I). Thus the presence of an asymmetric center has little effect or just enough to offset the effect of the lower electric

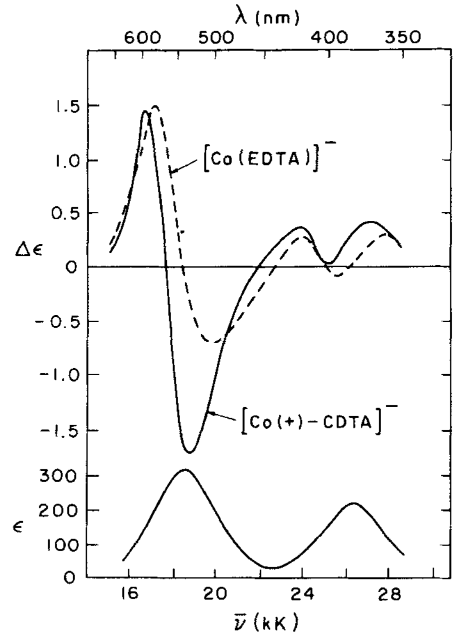

FIGURE 5 Circular dichroism and absorption spectra of K(-)$_{546}$-[Co(+)-CDTA]·$2H_2O$ and K(-)$_{546}$-[Co(EDTA)]·$2H_2O$.

dipole strength. The ε value of 316 for the first absorption band of K(-)$_{546}$-[Co(+)-CDTA] is slightly higher than that for the PDTA complex. The lowest energy CD peak has slightly lower intensity (Figure 5) than for either of the other complexes, but the second CD peak is more than twice as intense. Since CDTA coordinates stereospecifically, one obtains only the isomer represented in Figure 5 and its mirror image and it is not possible to evaluate the contribution of the optically active ligand except in comparison to [Co(EDTA)]$^-$. The overall effect on the second peak intensity is comparable to that of structural changes in the EDTA framework for less strained models[4] of [Co(EDTA)]$^-$, but the first peak is affected to a much smaller extent for the CDTA complex. The absolute configuration of the (-)$_{546}$ isomers represented in Figure 5 must be Λ, as concluded from ORD data.[26]

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