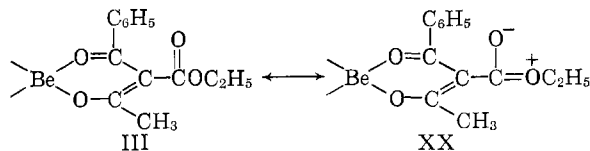


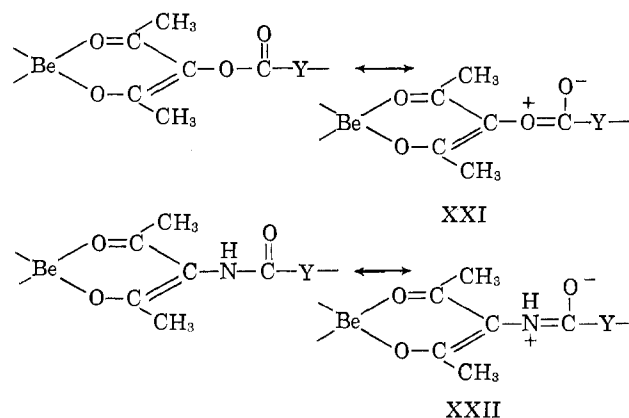
This does not affect the beryllium–oxygen bond, but it does reduce the importance of resonance form XVII to the total structure and thus stabilizes the complex.



An interesting correlation is observed between the stability of the acetylacetonate complexes and the infrared absorption frequency for the metal–oxygen bond. The peak which occurs in the stable beryllium acetylacetonate complex at 500 cm^{-1} has been assigned by Martell to a nearly pure beryllium–oxygen stretching vibration.⁷ A less stable acetylacetonate complex would be expected to show a decrease in the frequency of this absorption, due to the weakening of the beryllium–oxygen bond. Infrared spectra of the monomeric complexes prepared in this study show a definite shift toward lower frequencies for the metal–oxygen bond. Thus, the hydroxo, amino, and carboxyethyl substituted complexes have this peak occurring at 480, 477, and 473 cm^{-1} , respectively. (Beryllium acetylacetonate shows a peak at 497 cm^{-1} on the same instrument.) The data for polymers IX–XVI in Table III show that these compounds generally are more stable than the monomeric complexes from which they are formed. This is due to the existence of the new resonance structures XXI and XXII for these polymers which cannot be written for the simple complexes.

Here, as in structure XX, the resonance form does not promote the breaking of the beryllium–oxygen

(7) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).



bond, but decreases the importance of the resonance forms which do favor this dissociation. It is of interest to note that resonance forms like XXI and XXII cannot be written for the silicon-containing polymers, and these show no increased stability over the parent complex.

Polymers of type VI also offer no resonance possibilities which differ from those in the parent complex, and since these polymers now contain a linking chain, they are actually less stable than the monomeric complex itself.

The greatly increased stability which polymers of types XIV, XV, and XVI show at 200° is most likely due to the partial ionic character imparted to them by the formation of hydroxo bridges, as proposed in structure XVI.

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Circular Dichroism of Coordination Compounds. I. Splitting Patterns for Potassium Ethylenediaminetetraacetatocobaltate(III) and Model Compounds¹

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The optical absorption, optical rotatory dispersion (ORD), and circular dichroism (CD) data for the visible and near-ultraviolet regions have been compared for $\text{K}[\text{Co}(\text{EDTA})]$, $\text{Na}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]$, and $\text{K}[\text{Co}(\text{en})(\text{mal})_2]$. The two absorption bands for each compound are symmetrical, but the ORD curves reveal two components in the long wave length band and the CD curves reveal three components for each band. The signs of the CD peaks follow the same pattern for all three compounds only in the short wave length band. The $(-)_s48\text{-K}[\text{Co}(\text{en})(\text{mal})_2]$ complex is assigned the A (or D) absolute configuration based on the CD data, ORD curves, and solubility data.

The spectrum of $\text{K}[\text{Co}(\text{EDTA})]$ (EDTA = ethylenediaminetetraacetate ion) has been interpreted as in-

(1) This work was supported by a grant (AM02219-05S1) from the Division of General Medical Studies, Public Health Service. Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

dicating an essentially cubic crystal field² about $\text{Co}(\text{III})$ since the two bands in the visible region appear to be symmetrical on a wave length scale. The $[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]^-$ and $[\text{Co}(\text{en})(\text{mal})_2]^-$ (mal = malonate ion)

(2) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 643 (1956).

ions are crystal field models of $[Co(EDTA)]^-$ and each of these model compounds has two symmetrical absorption bands (wave length scale) at almost exactly the same positions as those of $[Co(EDTA)]^-$.

It has been shown^{3,4} that the crystal field about Co(III) cannot be cubic in $[Co(EDTA)]^-$ since two Cotton effects can be identified from the rotatory dispersion (ORD) curve in the long wave length band. Two components within the band suggest a tetragonal crystal field. Two components can also be identified from the ORD curves of the model compounds.⁵

It is difficult to analyze broad absorption bands and the $[Co(EDTA)]^-$ case illustrates that an apparently symmetrical band can have more than one component. The ORD curve in this case provides more detailed information, but the analysis of ORD curves can be even more complex. The contribution to the optical rotation from an optically active transition does not diminish appreciably at wave lengths rather far removed from the corresponding absorption band.⁶ Circular dichroism (CD, measured as the difference between the absorptivity for *levo* and *dextro* circularly polarized light) provides an excellent means of analyzing ORD curves⁶ and provides much more information than the ORD curves alone concerning the location of the individual components of the absorption bands.⁷ The CD bands in the visible region of complexes of the transition metals are generally much more narrow than the absorption bands. The analysis of the CD curves is aided greatly by the fact that the CD can be either positive or negative. Two overlapping CD bands of opposite sign are much more easily resolved than two similar gaussian curves of the same sign.

Experimental

Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was prepared⁸ and resolved⁹ by Dwyer's methods using $(-)$ ₅₈₉-*cis*-dinitrobis-(ethylenediamine)-cobalt(III) bromide as the resolving agent, $[\alpha]_{546} = \pm 1000^\circ$ observed and reported. Potassium bis-(malonato)-ethylenediaminecobaltate(III) monohydrate and sodium bis-(oxalato)-ethylenediaminecobaltate(III) monohydrate were prepared by Dwyer's methods.¹⁰ The resolution procedure¹⁰ for $[Co(en)(mal)_2]^-$ using $(-)$ ₅₈₉-*cis*- $[Co(en)_2(NO_2)_2]I$ was modified only by allowing the $(+)$ - or $(-)$ - $K[Co(en)(mal)_2] \cdot 2H_2O$ (the resolved complex is the dihydrate) to crystallize very slowly at 3–4° after the separation of the diaster-

(3) J. G. Brushmiller, E. L. Amma, and B. E. Douglas, paper presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962.

(4) J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 847 (1960).

(5) J. Hidaka, Y. Shimura, and R. Tsuchida, *ibid.*, **35**, 567 (1962).

(6) J. G. Brushmiller, E. L. Amma, and B. E. Douglas, *J. Am. Chem. Soc.*, **84**, 3227 (1962).

(7) B. E. Douglas, J. G. Brushmiller, and E. L. Amma, Paper presented at the 7th International Conference on Coordination Chemistry, Stockholm, June, 1962; J. P. Mathieu, *Bull. soc. chim.*, (5) **3**, 476 (1936); W. Kuhn and H. L. Lehmann, *Z. physik. Chem.*, **18**, 32 (1932).

(8) F. P. Dwyer, E. Gyrfas, and D. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

(9) F. P. Dwyer and F. L. Garvan, *Inorg. Syn.*, **6**, 192 (1960). Several workers have reproduced Dwyer's results. The higher rotations reported for the ammonium and rubidium salts by spontaneous resolution were for samples of less than 1 mg. [H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959)]. The results are being checked in our laboratory.

(10) F. P. Dwyer, I. K. Reid, and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 1285 (1961).

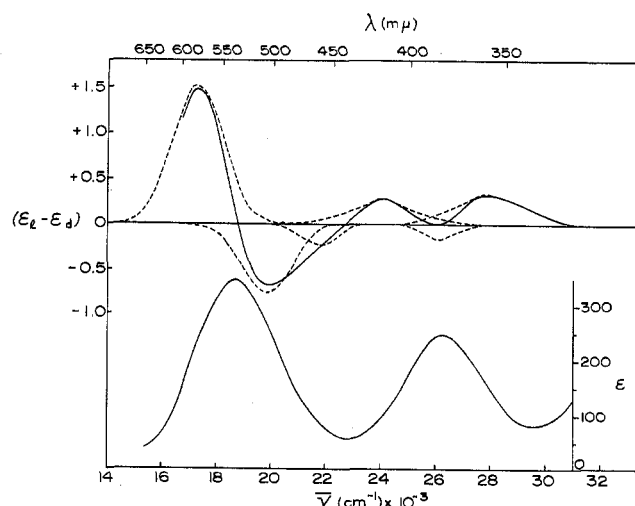


Fig. 1.—Circular dichroism and absorptivity vs. wave number for $(-)$ ₅₄₆- $K[Co(EDTA)] \cdot 2H_2O$: observed curve (—), gaussian analysis (-----).

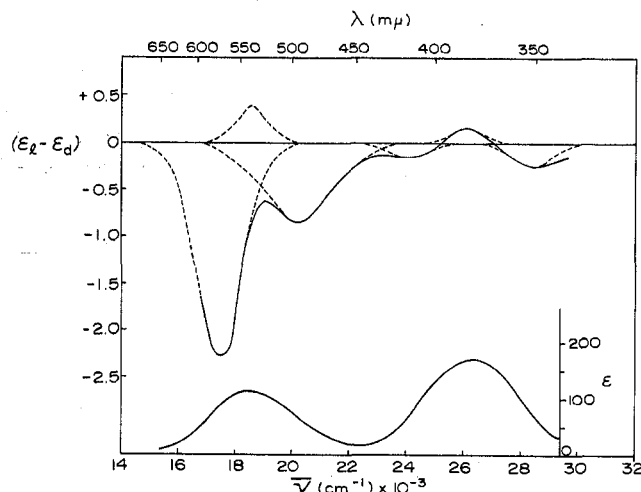


Fig. 2.—Circular dichroism and absorptivity vs. wave number for $(+)$ ₅₄₆- $Na[Co(en)(C_2O_4)_2] \cdot H_2O$: observed curve (—), gaussian analysis (-----).

eoisomers and reconversion to the potassium salt. The observed specific rotations were $[\alpha]_{589} = \pm 1800^\circ$ and $[\alpha]_{546} = \pm 1040^\circ$ compared to the reported values of $+1550$ and 1150° , respectively. The resolution procedure¹⁰ for $[Co(en)(C_2O_4)_2]^-$ using $(+)$ -*cis*- $[Co(en)_2(NO_2)_2]Br$ was modified slightly in the quantities used. Based on the 14.1 g. of $Ca[Co(en)(C_2O_4)_2] \cdot 4H_2O$ called for by Dwyer, 12.6 g. of $(+)$ ₅₈₉-*cis*- $[Co(en)_2(NO_2)_2]_2C_2O_4$ and 7.7 g. of $Na[Co(en)(C_2O_4)_2] \cdot H_2O$ were used. The observed specific rotation was $[\alpha]_{589} = -510^\circ$ compared to -500° reported.

Absorption spectra were recorded on a Cary Model 14 spectrophotometer. ORD curves were obtained with a Rudolph Model 80Q6 polarimeter with quartz optics and a photoelectric attachment using a 100-watt zirconium arc lamp in the visible region and a xenon arc lamp below 400 mμ. CD curves were recorded with a Baird-Jouan Dichrographe. All measurements were made in aqueous solution at room temperature.

Results

Although no splitting can be detected in either absorption band of $K[Co(EDTA)]$, the ORD curves clearly identify two components for the long wave length band. Casual examination of the CD curves reveals two well isolated components for each band, as

TABLE I
ABSORPTION AND CIRCULAR DICHROISM DATA

Complex	Absorption		Circular dichroism		Half-width, cm. ⁻¹ ^a
	cm. ⁻¹	ϵ	cm. ⁻¹	($\epsilon_l - \epsilon_d$)	
$(-)_546\text{-K}[\text{Co}(\text{EDTA})] \cdot 2\text{H}_2\text{O}$	18,600	347	17,300	+ 1.50	1050
			19,830	- 0.76	1100
			(21,750)	-(0.26)	750
			24,050	+ 0.29	1150
$(+)_546\text{-Na}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$	26,650	246	26,100	- 0.15	700
			27,900	+ 0.33	1500
			17,200	- 2.27 ^b	1000
			(18,600)	+(0.39)	650
$(-)_546\text{-K}[\text{Co}(\text{en})(\text{mal})_2] \cdot 2\text{H}_2\text{O}$	18,500	109	20,200	- 0.82	1500
			24,100	- 0.15	900
			26,100	+ 0.16	600
			28,400	- 0.33	950
$(-)_546\text{-K}[\text{Co}(\text{en})(\text{mal})_2] \cdot 2\text{H}_2\text{O}$	18,500	95	16,950	+ 3.09	700
			18,550	- 2.96	750
			20,550	+ 1.06	1200
			23,600	+ 0.91	850
$(-)_546\text{-K}[\text{Co}(\text{en})(\text{mal})_2] \cdot 2\text{H}_2\text{O}$	25,950	124	25,800	- 0.15	900
			27,700	+ 0.32	950

^a Half-width at half maximum. ^b The signs for the CD should be reversed for comparison of this complex with the other complexes of the same configuration, since the sample of this complex used for the CD studies was resolved using $(+)_589\text{-cis-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{Br}$ while the other two complexes were resolved using $(-)_589\text{-cis-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{Br}$. ORD data were obtained for both enantiomers of the oxalato complex; the data presented in Fig. 4 are for the $(-)_546$ enantiomer.

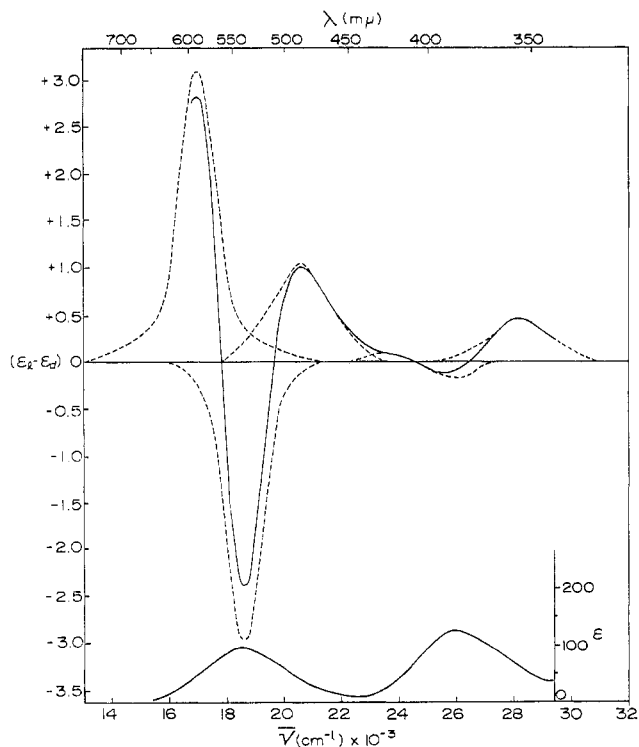


Fig. 3.—Circular dichroism and absorptivity vs. wave number for $(-)_546\text{-K}[\text{Co}(\text{en})(\text{mal})_2] \cdot 2\text{H}_2\text{O}$: observed curve (—), gaussian analysis (-----).

reported after this work was completed.¹¹ However, more careful analysis reveals three components for each band. The presence of six peaks for $\text{K}[\text{Co}(\text{en})(\text{mal})_2]$ is obvious from even casual inspection of the CD curve. In the case of $\text{Na}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]$ three

components are easily identified for the short wave length band, but the presence of a third component in the long wave length region is detected only by more careful analysis.

The data are summarized in Table I for the absorption spectra and CD peaks. The components of the CD curves were identified by gaussian analysis on a frequency scale. In only two cases the analysis was made difficult by serious overlap of the peaks. In these cases (the values are enclosed in parentheses) slightly different estimates of peak height, $\bar{\nu}_{\text{max}}$, and half-widths of the components might also result in reasonable agreement with the experimental curve. The CD curves are shown in Fig. 1–3. The ORD curves from the present work are presented in Fig. 4 for comparison. The curve for $\text{K}[\text{Co}(\text{EDTA})]$ agrees well with that of ref. 12, but with somewhat more fine structure than those reported in ref. 5 and 13. The curve for $\text{K}[\text{Co}(\text{en})(\text{mal})_2]$ is similar to that reported,⁵ but with more fine structure in the region of the short wave length absorption band and with slightly higher molecular rotations. It was this compound for which the rotation at 546 $m\mu$ was slightly lower than that reported by Dwyer, but the rotation at 589 $m\mu$ was appreciably higher than his value. The values reported here are supported by the duplication of the same specific rotations for both optical isomers (see Experimental section).

The molecular absorptivities of the EDTA and malonato complexes agree well with other values reported.⁵ The values for $\text{Na}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$, which

(12) T. Büerer, *Helv. Chim. Acta*, **46**, 242 (1963).

(13) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

(11) R. D. Gillard, *Nature*, **198**, 580 (1963).

were reproducible, are appreciably higher than those given by Hidaka, *et al.*⁵ We have noted and Dwyer reported that this compound is subject to decomposition involving reduction of Co(III) and oxidation of $C_2O_4^{2-}$. Any decomposition would lower the absorption. This complex also racemizes at an appreciable rate.

Discussion

All three complexes contain two nitrogen atoms in *cis* positions and four oxygen atoms, but only the chelate ring of the ethylenediamine is common to all three complexes. The positions of the absorption bands are remarkably constant for the three complexes. The Laporte forbidden bands are expected to derive their intensity largely from vibronic coupling. By far the greatest intensity is observed for the bands of $K[Co(EDTA)]$ where all ligand atoms are interlocked by five chelate rings. Consequently most vibrational modes of $K[Co(EDTA)]$ might distort the crystal field symmetry. The other two complexes, with three separate chelate rings each, have much lower intensity absorption bands. Of these two complexes, somewhat lower intensity is observed for $K[Co(en)(mal)_2]$ where the chelate rings involving the malonate ion have six members and are much more flexible than the five-membered chelate rings involving oxalate ion. The $[Co(en)(C_2O_4)_2]^-$ and $[Co(en)(mal)_2]^-$ ions, with similar molecular symmetry, both show stronger intensity of the short wave length band while the reverse is true for $K[Co(EDTA)]$.

It is noteworthy that the most intense CD peaks are those of the malonato complex. The two most intense CD peaks of the EDTA complex are lower than those of either of the other complexes. These observations are consistent with the expectation that vibronic coupling is more important for absorption bands than for CD peaks.¹⁴ For $[Co(EDTA)]^-$ the most intense CD peaks fall within the more intense (first) absorption band, but not for the other two complexes.

The interpretation of absorption spectra has had notable success by considering only the effective crystal field symmetry and ignoring the over-all molecular symmetry. The effective crystal field symmetry is usually determined from the three relative axial electric charges. The compounds considered here have two sets of *trans* pairs (1 O-O and 2 N-O), suggesting an effective tetragonal field for which two components of each band would be expected. The detailed information obtained from CD curves reveals the inadequacy of this approach. The presence of three components for each absorption band indicates an effective rhombic field for each of the complexes. No splitting was noted for the symmetrical absorption bands, suggesting cubic symmetry, while the ORD curves permit the identification of only two components for each band.

The positions are similar and the signs (+, -, +) are the same for peaks in the high frequency band for

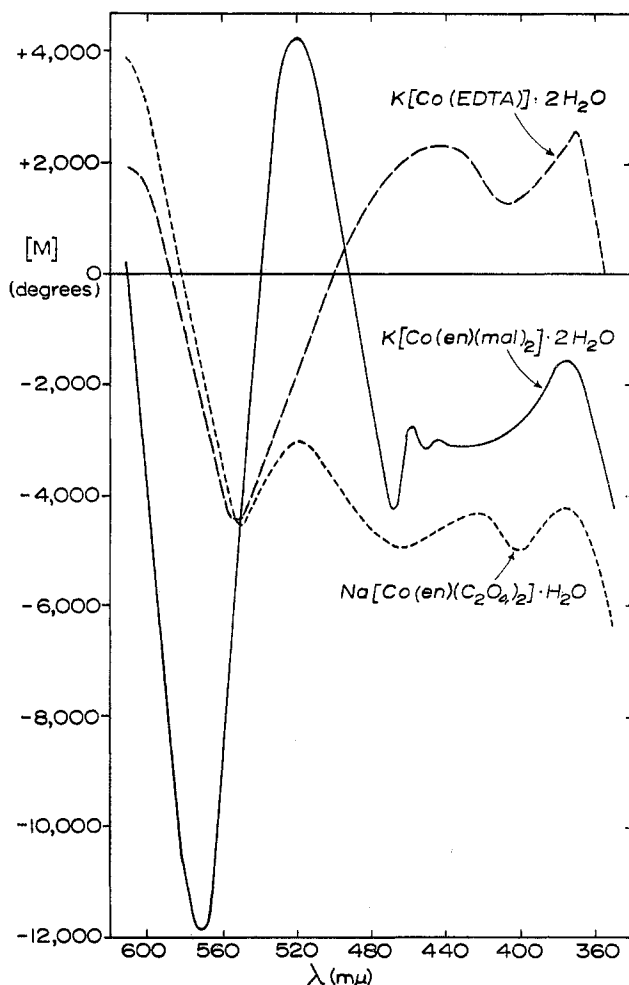


Fig. 4.—Optical rotatory dispersion curves for the $(-)$ ₆₄₆ isomers of $K[Co(EDTA)] \cdot 2H_2O$, $Na[Co(en)(C_2O_4)_2] \cdot H_2O$, and $K[Co(en)(mal)_2] \cdot 2H_2O$.

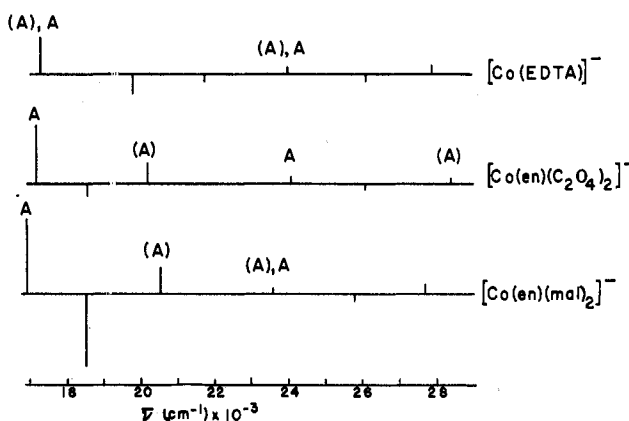


Fig. 5.—Assignments of the A_2 components: (a) on the basis of the expected splitting between the A and B components—given as (A)—and (b) as the lowest frequency components of each band—given as A. The CD peaks of $[Co(en)(C_2O_4)_2]^-$ are represented as those for the $(-)$ ₆₄₆ enantiomer based on CD measurements for the $(+)$ ₆₄₆ enantiomer and ORD data for both.

all three complexes with the same configuration (based on the solubility criterion and ORD curves). In the low frequency region the sign pattern for $K[Co(EDTA)]$ differs from that for the other two complexes. In this region the analysis of the CD curve for the oxalato

(14) J. G. Brushmiller, E. L. Amma, and B. E. Douglas, *J. Am. Chem. Soc.*, **84**, 111 (1962).

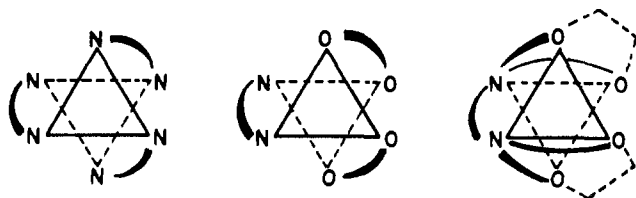


Fig. 6.—Comparison of the enantiomers assigned the Δ configuration.

complex was uncertain, particularly with regard to the parameters of the $18,600\text{ cm.}^{-1}$ peak. A good fit was also obtained using three positive peaks at $17,400$, $20,050$, and $21,950\text{ cm.}^{-1}$. This analysis gave remarkably close agreement with the positions of all six peaks of $\text{K}[\text{Co}(\text{EDTA})]$. The analysis presented gives close agreement between the positions of the CD peaks of the oxalato and malonato complexes and the same sign pattern. Great similarity is expected between these two complexes.

One might assume that the rhombic component is smaller than the tetragonal component since these complexes might have been expected to have tetragonal crystal field symmetry. If the rhombic component is not great the splitting between the B_1 and B_2 components of each band should be smaller than that between the A component and the closer one of the B components. The differences in the splittings (in cm.^{-1}) are small in some cases but on this basis the A components would be as designated by (A) in Fig. 5. Each of these peaks is positive for complexes of the same configuration. However, since the differences in the splittings are small, the lowest frequency peak (which is dominant for the first band) is assigned as A in all cases. The A_2 peaks assigned on this basis are also all positive. Further consideration of the rhombic splittings and assignments of the peaks for these and other related complexes will be treated in a later publication.

Mason¹⁵ suggested that compounds of the type *cis*- $[\text{Co}(\text{en})_2\text{AA}]$ with positive A components of the low frequency band would have the configuration corresponding to D - $[\text{Co}(\text{en})_3]^{3+}$ (a left-hand spiral about the C-3 axis designated as Δ using Piper's convention¹⁶). On the basis of the positive sign of A, the ORD curves, and solubility data (*vide infra*), the $(-)$ ₅₄₆ isomers of $\text{K}[\text{Co}(\text{EDTA})]$, $\text{Na}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]$, and $\text{K}[\text{Co}(\text{en})(\text{mal})_2]$ can now be assigned the Δ or D configuration also.

The $(+)$ ₅₄₆- $\text{K}[\text{Co}(\text{EDTA})]$ complex has been assigned the Δ or L configuration by comparison of the

ORD curve with that of L - $(+)$ ₅₄₆- $\text{K}[\text{Co}(-)\text{PDTA}]^{13}$ (PDTA = 1,2-propylenediaminetetraacetate ion). MacDermott and Sargeson¹⁸ also indicated that $(+)$ ₅₄₆- $\text{K}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]$ should have the same configuration because of the great similarities among the ORD curves of these three complexes. They point out that their assignment is not inconsistent with that made by Busch and Cook¹⁷ based on kinetic studies even though these authors designated the absolute configuration of $(+)$ ₅₄₆- $\text{K}[\text{Co}(\text{EDTA})]$ as D . The difference arises because of the arbitrary choice to be made in relating the $[\text{Co}(\text{EDTA})]^-$ complex to one of the isomers of $[\text{Co}(\text{en})_3]^{3+}$, since they differ in the number and arrangement of chelate rings. The $[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]^-$ complex ion provides the common basis of comparison since its $(+)$ ₅₄₆ isomer can be related to the $(+)$ ₅₄₆- $\text{K}[\text{Co}(\text{EDTA})]$ by the ORD curves and it can be related to Δ - $[\text{Co}(\text{en})_3]\text{Cl}_3$ because the latter two have the same spiral pattern for the three chelate rings (see Fig. 6). The choice of the enantiomer of $[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]^-$ to be related to Δ - $[\text{Co}(\text{EDTA})]^-$ is also somewhat arbitrary since one must choose between the two ways of connecting the pairs of oxygen atoms in $[\text{Co}(\text{EDTA})]^-$. The choice made seems reasonable since the oxygens joined are the ones connected by O-N-O bridges. MacDermott and Sargeson also applied the criterion of relative solubilities of diastereoisomers. They compared the diastereoisomers of $[\text{Co}(\text{EDTA})]^-$ and $[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]^-$ formed with $(-)$ ₅₈₉- $[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)]^+$ and $(-)$ ₅₈₉- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ and found the results consistent with the assignment based on ORD curves.

Comparisons of the ORD curves of the $(-)$ ₅₄₆ isomers and the fact that the less soluble diastereoisomers are those of $(+)$ ₅₄₆- $[\text{Co}(\text{EDTA})]^-$, $(+)$ ₅₄₆- $[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]^-$, and $(+)$ ₅₄₆- $[\text{Co}(\text{en})(\text{mal})_2]^-$ with $(-)$ ₅₈₉- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ support the assignment based on CD data and the assignments made by Sargeson for $[\text{Co}(\text{EDTA})]^-$ and $[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]^-$.

The similarities in the spectra for these three compounds suggest that they are good crystal field models for the general type *cis*- $[\text{Co}(\text{N})_2(\text{O})_4]$. Nevertheless, the rather great variation in the intensities and even the signs of the CD peaks makes it necessary to exercise caution in using ORD curves alone as the basis for assigning absolute configurations. In this case the comparison is reasonable because the A (lowest frequency) component of the long wave length band is dominant and has the same sign for all three complexes. The most intense CD component must also dominate in the ORD curves.⁶

(15) S. F. Mason, *Quart. Rev. (London)*, **17**, 20 (1963).

(16) T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

(17) D. H. Busch and D. W. Cook, *J. Inorg. Nucl. Chem.*, **23**, 145 (1961).