

An Interpretation of the Absorption and Circular Dichroism Spectra and the Determination of the Absolute Configurations of a Series of Linear Sexadentate Chelate Compounds of Cobalt(III)

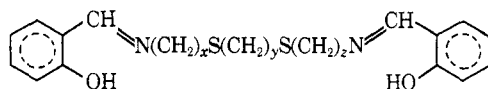
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Abstract: The absorption and circular dichroism spectra of a series of cobalt(III) complexes containing the linear sexadentate ligands 1,8-bis(salicylideneamino)-3,6-dithiaoctane ($\text{EEE}(\text{salH})_2$), 1,10-bis(salicylideneamino)-4,7-dithiadecane ($\text{TET}(\text{salH})_2$), 4-methyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane ($\text{EPE}(\text{salH})_2$), 1,8-dimethyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane ($\text{PEP}(\text{salH})_2$), and 1,8-dimethyl-1,8-bis(2-hydroxy-1-naphthylideneamino)-3,6-dithiaoctane ($\text{PEP}(\text{napH})_2$) (the last two derived from L-alanine) have been recorded and analyzed. A consideration of the conformational demands of the complexed ligands derived from L-alanine, their proton magnetic resonance spectra, and the exciton circular dichroism exhibited by the first (complexed) ligand transition leads to the mutually consistent conclusion that the complexes formed by the ligands derived from L-alanine exist mainly in the $\text{P}(\text{C}_2)$ absolute configuration. These complexes have provided an absolute reference from which the absolute configurations of all the green isomer complexes have been inferred and also that of the ligand derived from propane-1,2-dithiol. In addition, the geometric and absolute configurations of the brown $[\text{Co}(\text{TET}(\text{sal})_2)]$ complex derived from the optically active green $[\text{CoTET}(\text{sal})_2]\text{I}$ have been deduced by means of proton magnetic resonance, absorption, and circular dichroism spectra.

In their studies of complexes containing sexadentate ligands, Dwyer and Lions prepared a variety of linear sexadentate chelates having the general formula¹



They were able to prepare and resolve many of the cobalt(III) complexes and found that, although in most cases green colored complexes were formed, when $x = z = 3$ and $y = 2$ the green isomer could be converted into a brown isomer exhibiting optical activity.² More recently it was shown that the ligand, having $x = z = 2$ and with y as the optically active 1,2-disubstituted propane linkage ($\text{EPE}(\text{salH})_2$), was strongly stereospecific when complexed to cobalt(III).³ Our concern with these complexes stems from an interest in the relationship between the absolute configurations of transition metal complexes and the signs and intensities of the circular dichroism exhibited by their d-d electronic transitions. Of particular interest is the apparent discrepancy, which is observed in multidentate chelates, between the chirality of the complex and the sign of the "major" circular dichroism band under the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition of cobalt(III) complexes.⁴ It is the purpose of this note to suggest the absolute configura-

tions of these complexes, to record and analyze their absorption and circular dichroism spectra, to determine the absolute configuration of the ligand 4-methyl-1,8-(diamino)-3,6-dithiaoctane,³ and to propose the geometric and absolute configuration of the optically active brown $[\text{CoTET}(\text{sal})_2]\text{I}$ complex.

1. The Chemistry and Stereochemistry

The linear sexadentate chelate compounds discussed here can be written in four isomeric structures. These stereochemistries, each of which is devoid of an improper symmetry operation, are designated α , α' , β , and γ and are represented in Figure 1. Scale (Dreiding) molecular models show that only the α isomer of the complex cations $[\text{CoEEE}(\text{sal})_2]^+$, $[\text{CoPEP}(\text{sal})_2]^+$, and $[\text{CoEPE}(\text{sal})_2]^+$ can be constructed without engendering severe strain in the molecular framework. The $[\text{CoTET}(\text{sal})_2]^+$ cation, because of the greater flexibility of the trimethylene links, can be constructed in all four isomeric forms without any serious deformations of either the normal bond angles or normal bond distances. Thus we conclude, in conformity with earlier experimental observations,² that the complexes $[\text{CoEEE}(\text{sal})_2]^+$, $[\text{CoPEP}(\text{sal})_2]^+$, and $[\text{CoEPE}(\text{sal})_2]^+$ will exist only in the α forms.

For a given absolute configuration of the 1,2-disubstituted propane linkages of the complex ion $[\text{CoPEP}(\text{sal})_2]^+$ in the α form, a consideration of the conformations⁵ of the chelate rings leads to the conclusion that in one absolute configuration of the complex ion the methyl groups point away (*exo*) from the 1,2-dithiaethanecobalt ring, and in the enantiomeric configuration of the complex ion the methyl groups point toward (*endo*) the 1,2-dithiaethanecobalt ring. Two of these isomers are shown in Figure 2. Since, when the methyl groups are *endo*, the nonbonding interactions will be greater (because the methyl groups are in close proxim-

(1) A 1,2-disubstituted ethane linkage is represented by E, a 1,2-disubstituted propane linkage is P, a 1,3-disubstituted propane linkage is T, and the salicylideneamino and 2-hydroxy-1-naphthylideneamino groups are represented as sal and nap, respectively. Thus, for example, the complex, $(-)-1,8\text{-dimethyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane-}(\text{OC}_6\text{H}_7=\text{NCH}(\text{CH}_3)\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}(\text{CH}_3)\text{N}=\text{C}_6\text{H}_7\text{O})$ cobalt(III) iodide will be abbreviated to $(-)-[\text{CoPEP}(\text{sal})_2]\text{I}$ (see ref 2).

(2) (a) F. P. J. Dwyer and F. Lions, *J. Am. Chem. Soc.*, **72**, 1545, (1950); (b) F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *ibid.*, **74**, 4178 (1952); (c) *ibid.*, **74**, 3134 (1952); (d) *ibid.*, **75**, 1526, (1953); (e) *ibid.*, **75**, 2443 (1953); (f) *ibid.*, **76**, 383 (1954).

(3) F. P. Dwyer and T. E. MacDermott, *ibid.*, **85**, 2916 (1963).

(4) (a) J. R. Gollagly and C. J. Hawkins, *Chem. Commun.*, 873 (1966); (b) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

(5) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

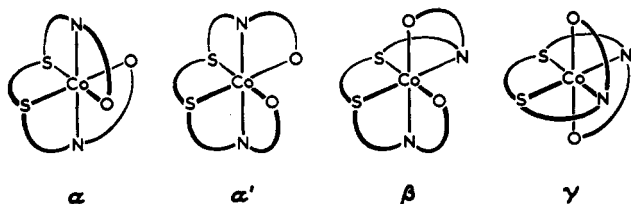


Figure 1. A schematic representation of the four possible isomers that might be formed by the sexadentate ligands.

ity to the dithia chelate ring) than when they are *exo*, an equilibrated solution of the $[\text{CoPEP}(\text{sal})_2]^+$ ion will contain a higher proportion of the *exo-α*- $[\text{CoPEP}(\text{sal})_2]^+$ ion than the *endo-α*- $[\text{CoPEP}(\text{sal})_2]^+$ ion. Furthermore, it follows that, if the absolute configuration of the 1,2-disubstituted propane linkage is known, the absolute configurations of both the *exo-α*- and the *endo-α*- $[\text{CoPEP}(\text{sal})_2]^+$ cations are also known. Similar arguments have been used successfully for the determination of the absolute configurations of other multidentate chelates,⁶⁻⁸ and we use them here for the determination of the absolute configuration of the complex $(-)\text{-}\alpha\text{-}[\text{CoPEP}(\text{sal})_2]\text{I}$. This complex was prepared from L-alanine by reactions which do not involve the optically active center. It follows, therefore, that the *exo-α*- $[\text{CoPEP}(\text{sal})_2]\text{I}$ complex has the $P(C_2)$ absolute configuration and that the less stable *endo-α*- $[\text{CoPEP}(\text{sal})_2]\text{I}$ complex has the $M(C_2)$ absolute configuration. These are the two isomers depicted in Figure 2.

The solubility characteristics of the cobalt complexes were such that we have had to employ solvents which obscure large portions of their proton magnetic spectra, and we shall only discuss the signals given by the azomethine protons and those given by the methyl groups.⁸ In nitromethane solution, $[\text{CoPEP}(\text{sal})_2]\text{I}$ shows two sharp signals due to the azomethine protons at τ 2.0 and 2.1 whose ratios are 5:2, respectively. These absorptions occur somewhat below the aromatic protons, and their integrated area with respect to the aromatic protons is in the correct ratio of 1:4. The methyl protons show doublets at around τ 8.1 and 8.3, and both are split by 6.5 cps. The respective areas of the sets of peaks are in the ratio of 2:5, and their total integrated area with respect to the aromatic protons is in the correct ratio of 3:4. The stereospecificity arguments outlined above therefore lead us to conclude that the sample of the $\alpha\text{-}[\text{CoPEP}(\text{sal})_2]\text{I}$ complex contained 72% *exo-α*- $[\text{CoPEP}(\text{sal})_2]\text{I}$ and 28% *endo-α*- $[\text{CoPEP}(\text{sal})_2]\text{I}$. However, because we were unable to precipitate all the complex in a pure form from a (charcoal) equilibrated aqueous solution, this value may not represent the precise extent of stereospecificity although the true value is unlikely to be greatly different from this. The circular dichroism spectra of the $\alpha\text{-}[\text{CoPEP}(\text{sal})_2]\text{I}$ complex which are recorded here have this ratio of isomers. The $[\text{CoEEE}(\text{sal})_2]\text{Cl}$ in D_2O , the green $[\text{CoTET}(\text{sal})_2]\text{I}$ in D_2O , and the brown $[\text{CoTET}(\text{sal})_2]\text{Cl}$ complex in dimethyl sulfoxide all show a single sharp azomethine signal at τ 2.0, 2.5, and 1.9, respectively, indicating that all three molecules have a twofold rotation axis of symmetry. In deuterated chloroform solution the complex $[\text{ZnPEP}(\text{sal})_2]$ shows a rather broad nmr spec-

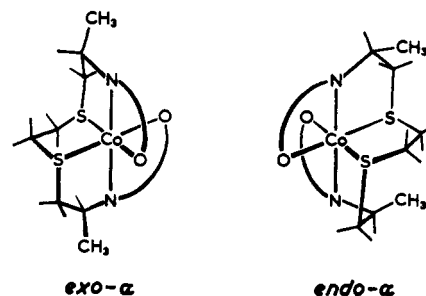


Figure 2. The *exo* and *endo* isomers of the $\alpha\text{-}[\text{CoPEP}(\text{sal})_2]^+$ ion derived from L-alanine. In each case only one of the possible conformational isomers is shown.

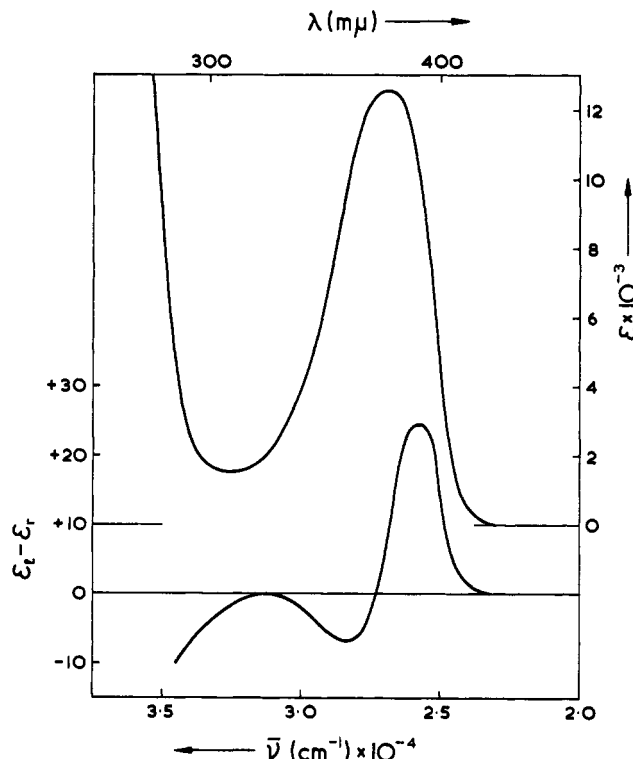


Figure 3. The absorption and circular dichroism spectra of the $[\text{ZnPEP}(\text{sal})_2]$ complex in chloroform solution.

trum, suggesting that the ligand is loosely bound to the zinc atom. Three methyl group doublets are observed at around τ 8.6, 8.7, and 8.8, split by 6.0, 6.0, and 5.6 cps, respectively, whose respective area ratios are 1:2:8. Since the free ligand also shows a methyl doublet at τ 8.6, split by 6.0 cps, it is probable that the $[\text{ZnPEP}(\text{sal})_2]$ complex is to some extent dissociated in chloroform solution.

2. The Absorption and Circular Dichroism Spectra of the $[\text{ZnPEP}(\text{sal})_2]$ Complex

In order to establish the contribution of the complexed ligand to the spectra of the cobalt complexes, the near-ultraviolet absorption and circular dichroism spectrum of the $(+)\text{-}[\text{ZnPEP}(\text{sal})_2]$ complex have been measured. These are shown in Figure 3. The moderately strong absorption at $27,000\text{ cm}^{-1}$ is a $\pi \rightarrow \pi^*$ transition⁹ which involves orbitals which are connected with both the azomethine and phenolic

(6) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).

(7) B. Bosnich, *Proc. Roy. Soc. (London)*, **A297**, 88 (1967).

(8) R. G. Asperger and C. F. Liu, *J. Am. Chem. Soc.*, **89**, 708 (1967).

(9) B. Bosnich, *ibid.*, **90**, 627 (1968).

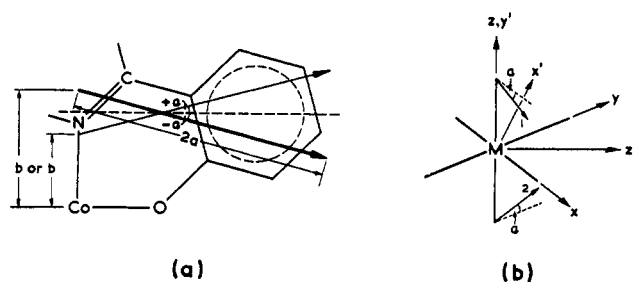


Figure 4. (a) The salicylaldimino group coordinated to the cobalt atom and the two possible inclinations of the transition dipole vector ($+\alpha$ or $-\alpha$) which were considered. The transition dipole length is $2a$, and b is the distance from the "end" of vector to the center of the cobalt atom. (b) The z' -polarized symmetric coupling mode. The other combination may be pictorially represented by reversing the direction of one of the arrows.

moieties¹⁰ of the salicylaldimino groups of the ligand. The two (positive and negative) circular dichroism bands associated with this absorption band show that two transitions are involved and indicate that the two transition dipole moments of the $\pi \rightarrow \pi^*$ transitions of the two salicylaldimino groups are coupled^{9,11-13} and give rise to exciton circular dichroism and to exciton splittings. We now investigate the consequences of this assumption.

For the particular absolute configuration ($P(C_2)$) of the *exo-α*-[ZnPEP(sal)] shown in Figure 2, the zero-order dipole strength, D_z , and the zero-order rotational strength, R_z , of the z' -polarized symmetric coupling mode are given by

$$D_z = p^2 \cos^2 \alpha$$

$$R_z = +\bar{\nu} \pi p^2 b \cos^2 \alpha$$

where p is the transition dipole moment of the isolated chromophore and $\bar{\nu}$ is the frequency (in cm^{-1}) at which the individual isolated chromophore absorbs. The angle α defines the inclination of the transition dipole vector (Figure 4) and b is the half-distance, defined in Figure 4, between the "ends" of the two transition dipole vectors. Similarly the dipole strength, $D_{x'y'}$, and the rotational strength, $R_{x'y'}$ (in the x', y' directions), of the antisymmetric coupling mode are given by

$$D_{x'y'} = p^2(1 + \sin^2 \alpha)$$

$$R_{x'y'} = -\bar{\nu} \pi p^2 b \cos^2 \alpha$$

Thus, provided the dipole-dipole interaction energies of the two coupling modes are sufficiently different, the exciton theory predicts that the first $\pi \rightarrow \pi^*$ transition of the salicylaldimino groups in the α configuration will consist of two components each carrying equal but opposite circular dichroism. This is in approximate conformity with observation, and the inequality of the two rotational strengths is probably due to the fact that the present simplified theory does not take into account the possibility of mixing between these and other transitions of the system.

Given that the α -[ZnPEP(sal)] complex exists mainly in the $P(C_2)$ absolute configuration and assuming the

(10) H. H. Jaffe, S. J. Yeh, and R. W. Gardner, *J. Mol. Spectry.*, **2**, 120 (1958).

(11) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).

(12) E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

(13) B. Bosnich, *Inorg. Chem.*, **7**, 178 (1968).

applicability of the exciton model, experiment shows that the symmetric coupling mode appears at lower energies than the antisymmetric mode. The circumstances under which this situation can arise depend critically upon the value of the angle α , and we shall couch the solution in general terms since we shall require this information later and because the solution has a general relevance to octahedral geometries.

In Figure 4a we define two angles α with respect to a line which intersects the transition dipole vector and which is parallel to the cobalt-oxygen bond. If α is either positive or negative (Figure 4a), the relationships between the dipole and rotational strengths are the same, namely, those given above, but the point-dipole-point-dipole interactions¹⁴ are different. When the angle α is taken as positive, it can be shown that for any value of b and the transition dipole length and for any angle α between 0 and 90° the symmetric coupling mode will appear at higher energies than the antisymmetric coupling mode. This is contrary to observation and establishes that the transition dipole vector does not lie with a positive value of α .

If, however, the angle α is taken as negative, the energy, E , of the point-dipole-point-dipole interaction for the z' -polarized symmetric coupling mode is given by

$$E = \frac{p^2}{r^3} \left\{ -\sin^2 \alpha + \frac{3}{r^2} (a + a \sin^2 \alpha - 2b \sin \alpha)^2 \right\}$$

where $r = (2a^2 + 2a^2 \sin^2 \alpha + 4b^2 - 8ab \sin \alpha)^{1/2}$ and a is half the transition dipole length. The position of the other coupling mode is given simply by the negative of this expression. Under these conditions, provided a is approximately equal to b and the angle α lies between 0 and 60° , the symmetric coupling mode will appear at lower energies as is required by experiment. The actual value of the angle is likely⁹ to be closer to 0 than to 60° . Provided, as is probable, the values of these three parameters do not vary greatly in going from the divalent zinc to the trivalent cobalt complexes, all the sexadentate cobalt complexes having the α - $P(C_2)$ absolute configuration should show essentially the same circular dichroism as that exhibited by the zinc complex (Figure 3) in the region of the first (complexed) ligand $\pi \rightarrow \pi^*$ transition. Furthermore, a knowledge of the approximate values of these three parameters allows for the nonempirical determination of the absolute configurations of any of the four α , α' , β , γ isomeric forms.

3. The Absorption and Circular Dichroism Spectra of the Green Cobalt(III) Complexes

In Figure 5 we show the absorption and circular dichroism spectra in various solvents of the $(-)$ -[CoPEP(sal)] complex which, from the nmr spectrum, contains 72% *exo-α*-[CoPEP(sal)] and 28% of *endo-α*-[CoPEP(sal)]. Only the absorption region between 10,000 and about 32,000 cm^{-1} is shown since at higher energies our instrument was not sufficiently sensitive to give circular dichroism spectra of sufficient accuracy. It will be seen that in this part of the spectrum there are three main regions of absorption—a relatively weak band at ca. 15,000 cm^{-1} , a broad band of moderate

(14) E. G. McRae and M. Kasha, "Physical Processes in Radiation Biology," Academic Press, New York, N. Y., 1964, p 23.

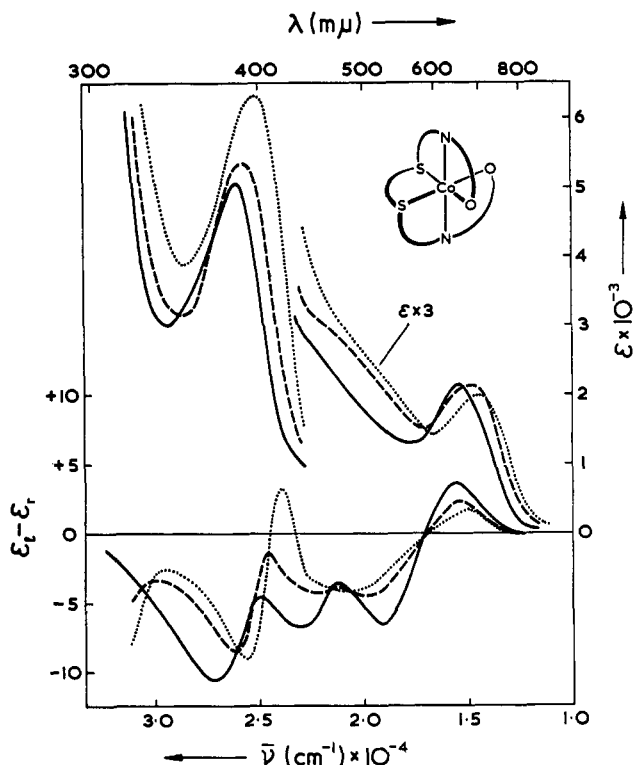


Figure 5. The absorption and circular dichroism spectra of the (—)[CoPEP(sal)₂]I complex in water (—), in methanol (---), and in chloroform (— · —). In the inset is shown the absolute configuration which corresponds to the circular dichroism.

intensity whose center is at *ca.* 21,000 cm⁻¹, and a strong band at *ca.* 25,000 cm⁻¹. This last band has a similar intensity and energy position to the first $\pi \rightarrow \pi^*$ transition of the zinc complex and indicates that this excitation remains largely unmodified by the presence of the tervalent cobalt atom. We thus expect that this band will carry positive circular dichroism at lower energies (the z' -polarized symmetric coupling exciton mode) and negative circular dichroism at higher energies (the x' , y' antisymmetric coupling mode) for the α -P(C₂) absolute configuration. This expectation is confirmed by an examination of the effect of solvent on the circular dichroism and absorption spectra. Because of the extensive overlap which occurs, the low-energy positive peak is not clearly defined in water solution but is clearly resolved in chloroform (at 24,000 cm⁻¹). The corresponding negative circular dichroism is seen in all solvents and occurs at around 26,000 cm⁻¹ in chloroform solution.

The poorly resolved absorption band of moderate intensity between 17,000 and 25,000 cm⁻¹ is assigned⁹ to charge-transfer transitions involving the filled d_e orbitals of the central cobalt atom and the antibonding π^* orbitals of the azomethine chromophores. An inspection of the associated circular dichroism shows two resolved negative absorptions which occur in water at around 19,000 and 23,000 cm⁻¹. The peak at 21,000 cm⁻¹ does not vary in intensity with change of solvent and thus most probably represents the "trough" of the two overlapping negative components and not the resultant of a positive band which is submerged by overlap.

Following methods which have been described elsewhere,⁹ it can be shown that the result of interaction

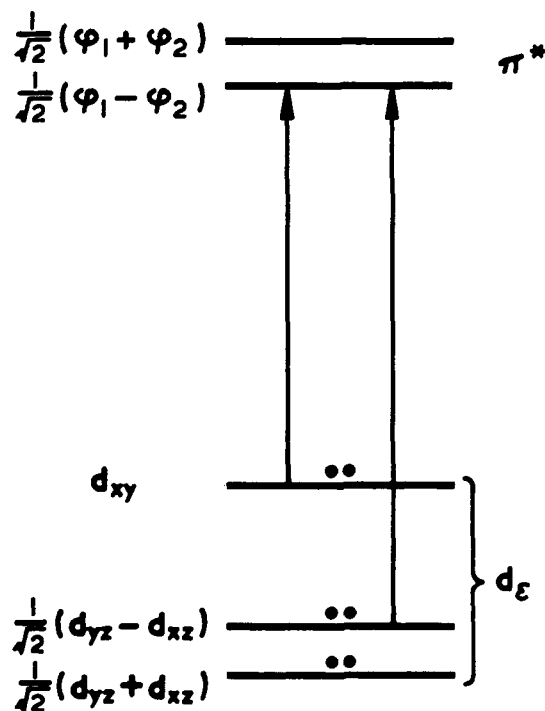


Figure 6. The essentially degenerate empty upper states derived from the π bonds of the azomethine groups and the splitting of the filled d_e subset. The molecular states are labeled by the ligand or metal orbitals from which they are derived.

of the π -electron orbitals associated with the azomethine groups (labeled φ_1 and φ_2) and the d_e orbitals of the cobalt atom (d_{xy} , $(1/\sqrt{2})(d_{yz} - d_{xz})$, and $(1/\sqrt{2})(d_{yz} + d_{xz})$) leads to two essentially degenerate empty upper levels and to the d_e subset being split into a single upper level and two essentially degenerate lower levels. This result is depicted in Figure 6 and we assign the band at around 19,000 cm⁻¹ to the transition $d_{xy} \rightarrow (1/\sqrt{2}) \cdot (\varphi_1 + \varphi_2)$, $(1/\sqrt{2})(\varphi_1 - \varphi_2)$ ($^1A \rightarrow ^1A$, 1B), and the band at around 23,000 cm⁻¹ is assigned to the transitions $(1/\sqrt{2})(d_{yz} - d_{xz})$, $(1/\sqrt{2})(d_{yz} + d_{xz}) \rightarrow (1/\sqrt{2})(\varphi_1 + \varphi_2)$, $(1/\sqrt{2})(\varphi_1 - \varphi_2)$ ($^1A \rightarrow ^1A$, 1B , 1A , 1B), where it is understood that the transitions occur between molecular rather than atomic states.

The absorption band at around 15,000 cm⁻¹ is assigned to the magnetic dipole allowed "d-d band" $^1A_{1g} \rightarrow ^1T_{1g}$. In the presence of the C_2 field, Yamatera's¹⁵ approximation predicts that this band will be split into two components.

An examination of the circular dichroism associated with the $^1A_{1g} \rightarrow ^1T_{1g}$ transition reveals only one component which, however, has a maximum at higher energies than the ordinary absorption, and this circular dichroism maximum would probably appear to have an even greater displacement were it not for the intrusion of the negative charge-transfer circular dichroism. In addition, the lower energy side of the circular dichroism absorption diminishes more rapidly than the corresponding ordinary absorption. We therefore propose that the positive circular dichroism appearing at around 15,500 cm⁻¹ is associated with the two-component transition, $(1/\sqrt{2})(d_{zz} - d_{yz}) \rightarrow (1/\sqrt{2})(d_{x^2-y^2} - d_{y^2-z^2})$, $(1/\sqrt{2})(d_{zz} + d_{yz}) \rightarrow (1/\sqrt{2})(d_{x^2-z^2} + d_{y^2-z^2})$ ($^1A \rightarrow ^1B$, $^1A \rightarrow ^1A$),

(15) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

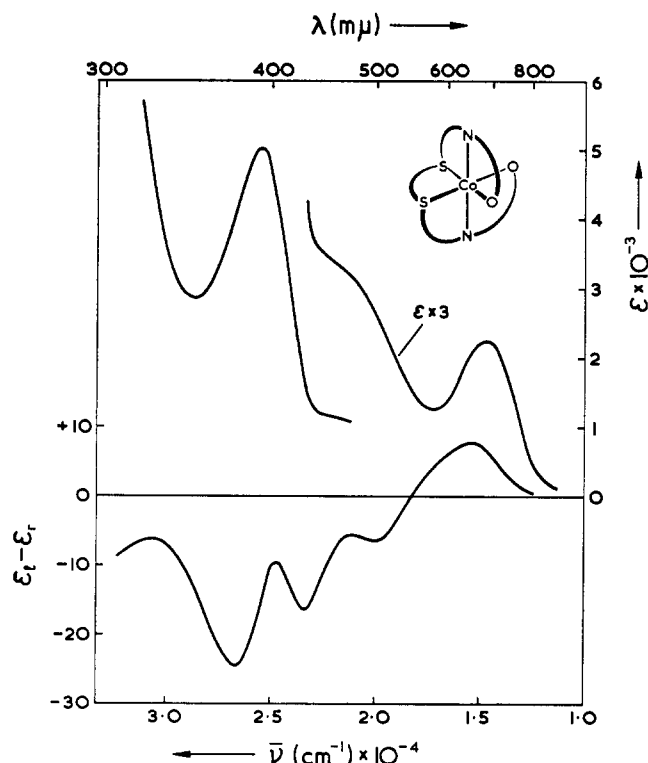


Figure 7. The absorption and circular dichroism spectra of the $(-)$ -[CoEEE(sal)₂]I complex in water solution with the absolute configuration shown in the inset.

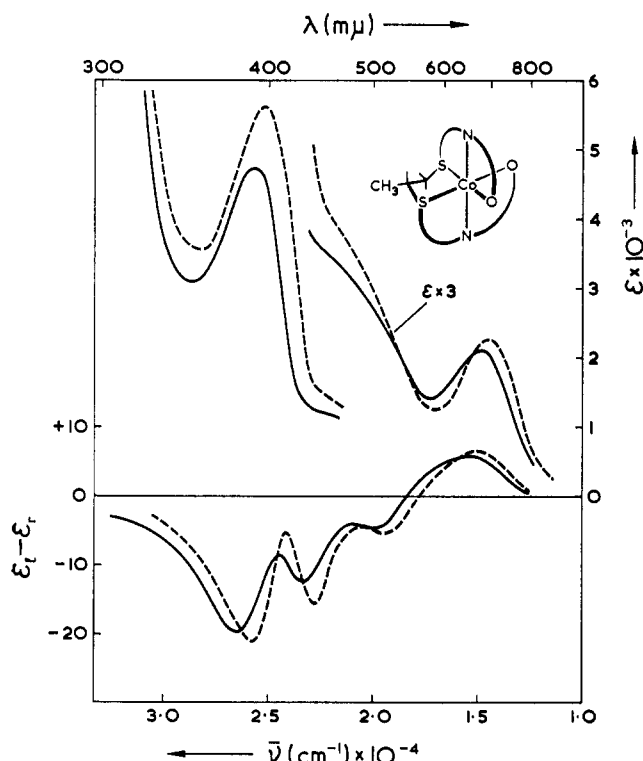


Figure 8. The absorption and circular dichroism spectra of the $(-)$ -[CoEPE(sal)₂]I complex in methanol (—) and in chloroform (---). This complex is the conformationally more stable species derived from $(+)$ -EPE and the absolute configurations of both the ligand and the complex are shown in the inset.

and that the other transition, $d_{xy} \rightarrow d_{x^2-y^2}$ ($^1A \rightarrow ^1B$), which probably carries a smaller negative rotational

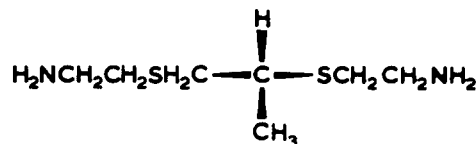


Figure 9. The absolute configuration of the $(+)$ -EPE ligand.

strength, occurs at lower energies and is not seen because of overlap. The other spin-allowed octahedral transition, $^1A_{1g} \rightarrow ^1T_{2g}$, is expected to occur under the charge-transfer bands, and, because it is neither electric nor magnetic dipole allowed in the first order, the circular dichroism that it carries will be small^{16,17} compared with the relatively strong circular dichroism exhibited by the charge-transfer bands.

The absorption and circular dichroism spectra of the green *exo-α*-[CoPEP(nap)₂]I in the region between 10,000 and 30,000 cm^{-1} is almost identical with the two spectra of the *exo-α*-[CoPEP(sal)₂]I complex. In Figures 7 and 8 we show the spectra of the $(-)$ -[CoEEE(sal)₂]I and the $(-)$ -[CoEPE(sal)₂]I complexes. Because of their solubility characteristics, we were able only to measure $(-)$ -[CoEEE(sal)₂]I in water solution and $(-)$ -[CoEPE(sal)₂]I in water and chloroform. It will be noted that these two sets of spectra are almost identical with those of the *exo-α*-[CoPEP(sal)₂]⁺ ion, and we assign the spectral transitions in a similar way and conclude that both $(-)$ -[CoEEE(sal)₂]⁺ and $(-)$ -[CoEPE(sal)₂]⁺ have the $P(C_2)$ absolute configuration. Given the $P(C_2)$ absolute configuration for the $(-)$ -[CoEPE(sal)₂]⁺ ion and given that the methyl group is equatorial,⁵ then it follows that the ligand $(+)$ -EPE resolved by Dwyer and MacDermott³ has the absolute configuration depicted in Figure 9.

4. The Absorption and Circular Dichroism Spectra of the Green and Brown [CoTET(sal)₂]I Complexes

Figure 10 shows the absorption and associated circular dichroism spectra of the green $(-)$ -[CoTET(sal)₂]I complex in methanol and chloroform solutions. It will be noted that the absorption spectrum is almost identical with that shown by the other green complexes with less flexible ligands and suggests that the donor atom microsymmetry around the cobalt atom is the same in all cases. Thus the geometry is either α or α' , a conclusion which is in conformity with the nmr results. However, the circular dichroism spectrum is also almost the same as that shown by the other green complexes with the α geometry. We therefore propose that the green $(-)$ -[CoTET(sal)₂]⁺ ion has the α geometry and the $P(C_2)$ absolute configuration and that the absorption and circular dichroism bands have the same electronic provenance as in the other green complexes.

The green $(-)$ -[CoTET(sal)₂]⁺ can be converted² to the brown $(+)$ -[CoTET(sal)₂]⁺ complex by heating the former in methanol solution, and the resultant absorption and circular dichroism spectra of the brown $(+)$ -[CoTET(sal)₂]I complex are shown in Figure 11. It will be seen that the two spectra are somewhat different from those previously discussed. We have arrived

(16) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

(17) J. P. Mathieu, *Bull. Soc. Chim. France*, **3**, 464, 476 (1936).

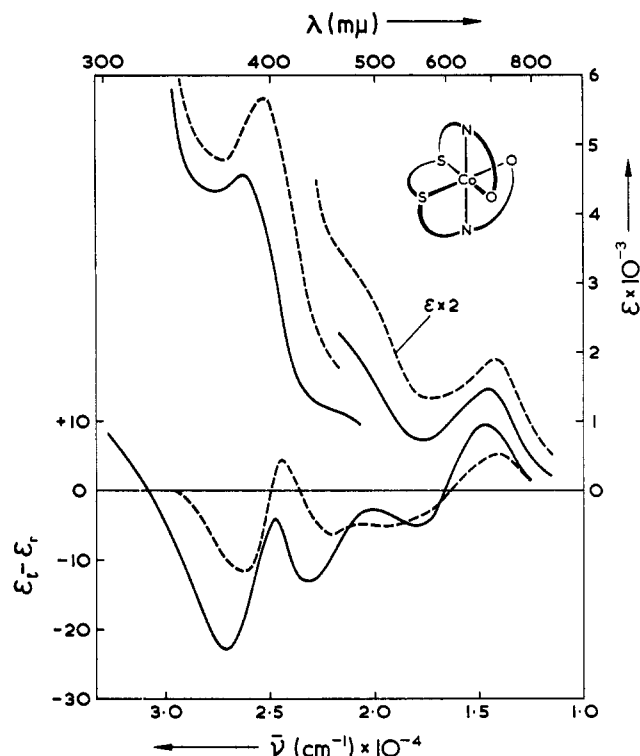


Figure 10. The absorption and circular dichroism spectra of the (—) $[-\text{CoTET}(\text{sal})_2]\text{I}$ complex in methanol (—) and chloroform (---) with the geometric and absolute configuration shown in the inset.

at a conclusion about the geometric and absolute configuration of this complex in the following way.

The nmr spectrum shows only one azomethine proton signal and thus, if the green (—) $[-\text{CoTET}(\text{sal})_2]^+$ ion has the α geometry, the brown (+) $[-\text{CoTET}(\text{sal})_2]^+$ can either have the α' or γ geometry but not β because the azomethine protons in this system are environmentally different. (The possibility of accidental degeneracy seems unlikely since the *exo*- and *endo*- α - $[\text{CoPEP}(\text{sal})_2]^+$ ions have their azomethine protons at different chemical shift values. The environmental difference between the azomethine protons of the *endo* and *exo* forms would appear to be less than that of the same protons in the β isomer.) If the brown (+) $[-\text{CoTET}(\text{sal})_2]^+$ ion were the α' isomer, we would expect to find that the first d-d band would occur in the same position as for the α isomer because the donor group microsymmetry is the same, and, in fact, calculation shows that the spectral shifts would be exactly the same as those of the green isomers. Figure 11 shows that the first d-d band is shifted to higher energies compared with the equivalent band of the green $[\text{CoTET}(\text{sal})_2]^+$ ion (Figure 10). This suggests, contrary to the earlier postulate,² that the brown form of the ion $[\text{CoTET}(\text{sal})_2]^+$ exists as the γ isomer (Figure 1). That the brown form cannot be the (previously proposed) α' isomer is confirmed by a consideration of the exciton circular dichroism shown by the first (complexed) ligand transition which occurs at around $25,000\text{ cm}^{-1}$. Under this band the circular dichroism is positive at lower energies and negative at higher energies, the same pattern as is observed for the α $\text{P}(\text{C}_2)$ isomers. However, as can be seen in Figure 1, a simple edge displacement of the

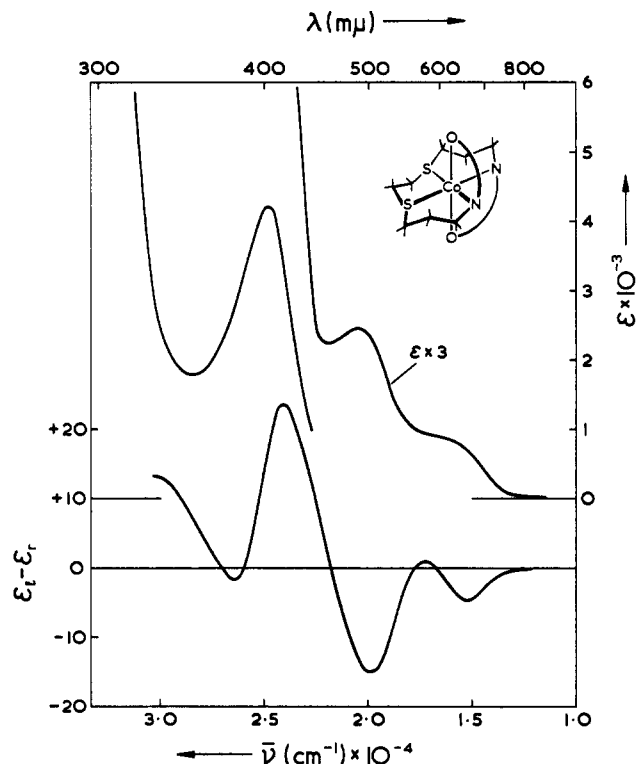


Figure 11. The absorption and circular dichroism spectra of the brown (+) $[-\text{CoTET}(\text{sal})_2]\text{I}$ derived from the green (—) $[-\text{CoTET}(\text{sal})_2]\text{I}$ complex in methanol solution. The inset shows the suggested conformational, geometric, and absolute configuration of the complex.

salicylaldimino groups of the α isomer leads to the formation of the α' isomer, but the absolute relationship of the salicylaldimino groups in the two cases is enantiomeric. Thus the exciton circular dichroism in the two cases should also be enantiomeric. This is contrary to what is observed.

Using the limits (section 2) placed upon the transition dipole length and the inclination of the transition dipole vector of the first $\pi \rightarrow \pi^*$ transition of the salicylaldimino chromophore, the absolute configuration of the brown (+) $[-\gamma\text{-CoTET}(\text{sal})_2]^+$ ion can be determined from the exciton circular dichroism associated with this band. Calculation shows that, for the absolute configuration shown in Figure 11, the circular dichroism should appear positive at lower energies and negative at higher energies under the first $\pi \rightarrow \pi^*$ transition of the salicylaldimino groups. Figure 11 shows a strong positive circular dichroism band at around $14,000\text{ cm}^{-1}$ and a negative band (which is heavily overlapped) at around $16,500\text{ cm}^{-1}$. These energy positions are very similar to those of the green complexes, and we assign their electronic provenance in a similar way and conclude that the brown (+) $[-\text{CoTET}(\text{sal})_2]^+$ ion has the absolute configuration depicted in the inset of Figure 11.

The magnetic dipole allowed d-d transition $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ appears as a shoulder (at around $16,500\text{ cm}^{-1}$) at somewhat higher energies compared with the same band of the green complex, but the first (negative) circular dichroism band appears at much the same energy (at around $15,000\text{ cm}^{-1}$) as the first positive band of the green complex. Following the procedure of Yamatera, it can be shown that the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition of the γ isomer will be displaced to higher energies

compared with the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the α isomer. This is in conformity with observation.

In addition, the energy positions of the two transitions (two components being essentially degenerate) will be reversed in going from the α to the γ isomer. We therefore assign the negative circular dichroism band at around $15,000\text{ cm}^{-1}$ to the two-component transition, $(1/\sqrt{2})(d_{zz} - d_{yy}) \rightarrow (1/\sqrt{2})(d_{x^2-z^2} - d_{y^2-z^2})$, $(1/\sqrt{2})(d_{zz} + d_{yy}) \rightarrow (1/\sqrt{2})(d_{x^2-z^2} + d_{y^2-z^2})$ (${}^1A \rightarrow {}^1B$, ${}^1A \rightarrow {}^1A$) and the positive circular dichroism band at around $17,500\text{ cm}^{-1}$ to the transition $d_{xy} \rightarrow d_{x^2-y^2}$ (${}^1A \rightarrow {}^1B$) which is diminished in intensity because of overlap. Our preference for the d-d assignment of this latter band, rather than for a charge-transfer band, is based on the fact that a consideration of the spectrochemical effects¹⁸ of the donor atoms leads to an energy position which is consistent with that observed.

Scale molecular models of the γ -[CoTET(sal)₂]⁺ ion show that the salicylaldimino groups are not in the same plane as the oxygen, cobalt, and nitrogen atoms; in fact, both the benzene rings are splayed inward and "cover" adjacent faces of the octahedron. This does not pose any difficulties in the exciton interpretation of the circular dichroism, but the π orbitals of the sulfur, oxygen, and nitrogen atoms can interact appreciably with all the d_e subset of cobalt orbitals. Under these circumstances we would not expect any significant splitting of the resultant energies of the d_e orbitals as is expected and observed in the green α complexes. If this assumption is correct, we expect, as is observed, that the charge-transfer absorption and circular dichroism spectra to be less broad than in the case of the green complexes. The absorption band at around $20,500\text{ cm}^{-1}$ and the corresponding negative circular dichroism band at around $20,000\text{ cm}^{-1}$ are thus assigned to the multicomponent transition from the filled d_e subset to the antibonding π^* orbitals of the azomethine groups.

Discussion

The earlier suggestion² that the green to brown interconversion involved only the geometric α to α' isomeric change provided a simple and obvious rearrangement in which optical activity could be retained. The present work strongly suggests that there is a much more drastic molecular rearrangement involved, namely a α to γ change, and poses the problem of how this can lead apparently to almost complete retention of asymmetry. In order to attempt to answer this problem, it must be remembered that the α -[CoTET(sal)₂]⁺ has two centers of asymmetry which arise because the general chelate structure is dissymmetric and because the chelated sulfur atoms are asymmetric. These two aspects of asymmetry must be mutually compatible in the sense that the asymmetric sulfur atoms "direct" the chelate rings more favorably into one absolute configuration than to the other. It is obvious that in a α to α' transformation the final absolute configuration of the α' isomer is determined by the absolute configuration of the chelate rings of the α isomer. This cannot be so for the α to γ transformation since the chelate rings which determine the outcome in the case of the α to α' change are themselves involved in taking

up new positions. However, provided we assume, as was observed in another case,¹⁹ that the complexed sulfur atoms are optically stable and that they are not dissociated during the transformation, the sulfur atoms can provide a source of asymmetric "memory" for the resultant γ isomer. Scale molecular models show that if the sulfur atoms are chelated into an absolute configuration appropriate for the $P(C_2)$ α -[CoTET(sal)₂]⁺ ion, the chelate rings containing the sulfur-trimethylene-nitrogen sequence will probably have the chair conformation which, by reason of the sulfur atoms' asymmetry, will "direct" the salicylaldimino groups into the absolute configuration predicted from the spectra of the brown form (Figure 11). (The β isomer probably requires a *meso* configuration of the sulfur atoms for stability.)

The other aspect of this work which warrants some comment is the relationship between the absolute configuration of the complex and the signs of equivalent d-d transitions derived from the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ excitation. It will be noted that the $P(C_2)$ α isomers when viewed down their twofold axes have a molecular arrangement which presents itself as essentially a dextral chirole and that the transition ${}^1A \rightarrow {}^1A$, where the magnetic transition dipole moment is polarized down the twofold axis, carries positive circular dichroism. This is in agreement with most observations that have been made on the circular dichroism of cobalt complexes.^{7,20} However, the molecular chirality of the brown (+)- γ -[CoTET(sal)₂]⁺ ion is also right-handed when viewed down the twofold axis, but the ${}^1A \rightarrow {}^1A$ transition carries negative circular dichroism. This indicates, if the conclusions given above are correct, that any future rule which attempts to correlate the relationship between the absolute configurations of complexes and the signs of the circular dichroism of the d-d bands will probably involve a recognition of all or most of the chelate rings of the complex. Certain tentative rules^{21,22} which have been proposed are therefore of limited applicability.

Experimental Section

All rotations refer to the sodium D-line.

L-(+)-Alaninol. L-(+)-Alaninol (bp $68-71^\circ$ (20 mm), $[\alpha] +18.9^\circ$ in ethanol) was prepared by lithium aluminum hydride reduction of L-(+)-alanine.²³

L-(+)-N-(2-Bromo-1-methyl)ethylphthalimide. L-(+)-Alaninol (40 g) and purified phthalic anhydride (78 g) were heated together at 140° . After 2 hr the resulting oily product was allowed to cool and solidify. Phosphorus tribromide (100 ml) was then cautiously added at room temperature while the flask was occasionally agitated. When the addition was complete (0.5 hr), the resultant syrup was slowly heated on an oil bath to 140° and allowed to stand at this temperature for 3 hr. The resultant hot reaction mixture was poured into crushed ice (1000 g) with vigorous stirring. The orange solid was collected, washed many times with water, and dried over phosphorus pentoxide. The dried product recrystallized from petroleum ether (bp $40-60^\circ$) as colorless needles: yield 105 g (73%), mp $68-69^\circ$, $[\alpha] +19.5^\circ$ in ethanol.

Anal. Calcd for $C_{11}H_{10}BrNO_2$: C, 49.2; H, 3.7; N, 5.2; Br, 29.8. Found: C, 49.3; H, 3.9; N, 5.0; Br, 30.5.

L-(+)-1,8-Dimethyl-1,8-bis(phthalimido)-3,6-dithiaoctane. To a solution of sodium (8.6 g) in absolute ethanol (150 ml) was added

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1,2-ethanedithiol (17.6 g) followed at once by a hot solution of L-(+)-N-[(2-bromo-1-methyl)ethyl]phthalimide (100 g) in absolute ethanol (150 ml). The resultant pale yellow mixture was heated under reflux for 3 hr, during which time an increasingly greater precipitate of sodium bromide was formed. Most of the ethanol (250 ml) was distilled from the suspension and water (500 ml) was added to the residue. The oil which separated was extracted with ether (three 250-ml portions) and the combined extracts were washed with dilute sodium hydroxide (300 ml, 2 N) and then dried over sodium sulfate. The oil (51 g) obtained after removal of the ether contained a mixture of compounds which were separated on alumina (Brockman Activity 1) using benzene-chloroform (1:1) as eluent. The required compound was obtained in the early fractions and after one recrystallization from ethanol it was obtained as colorless needles: yield 33 g (38%), mp 125°, $[\alpha] +134^\circ$ in chloroform.

Anal. Calcd for $C_{24}H_{24}N_2O_4S_2$: C, 61.8; H, 5.1; S, 13.7. Found: C, 62.0; H, 4.8; S, 14.2.

L-(+)-1,8-Dimethyl-1,8-diamino-3,6-dithiaoctane Dihydrochloride. L-(+)-1,8-Dimethyl-1,8-bis(phthalimido)-3,6-dithiaoctane (28 g) in ethanol (150 ml) was heated under reflux with hydrazine hydrate (13 g) for 2 hr after which time the resulting white suspension was cautiously acidified with hydrochloric acid (35 ml, 10 N). After heating the suspension for a further 0.5 hr, most of the ethanol was distilled off and water (30 ml) was added. The white precipitate was filtered and washed twice with water (two 10-ml portions), and the last traces of ethanol in the filtrate were removed by distillation. Solid sodium hydroxide (50 g) was cautiously added to the cooled aqueous filtrate, whereupon the amine separated as an oil which was continuously extracted for 6 hr with ether. The ether extract was dried over sodium hydroxide pellets, and after removal of the solvent the residual oil (7.8 g) was not purified further but was used directly for the preparation of the bisalicylalimine derivative. The bishydrochloride salt of the amine was obtained as a white powder after crystallization from ethanol-ether: mp 185–190°, $[\alpha] +60.0^\circ$ in water.

Anal. Calcd for $C_8H_{22}Cl_2N_2S_2$: C, 34.2; H, 7.9; Cl, 25.3; S, 22.8. Found: C, 33.8; H, 7.6; Cl, 25.3; S, 22.8.

(-)-1,8-Dimethyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane-cobalt(III) Iodide Dihydrate, (-)-[CoPEP(sal)₂]₂I·2H₂O. A solution of 1,8-dimethyl-1,8-diamino-3,6-dithiaoctane (2.08 g) in ethanol (10 ml) was warmed for 0.25 hr with salicylaldehyde (2.44 g). On cooling the resulting yellow solution deposited an oil, which could not be induced to crystallize from a variety of solvents even after chromatography on silica gel. It was therefore used without isolation in the preparation of the complexes.

The ligand (2 g calculated from the starting materials) in hot ethanol (20 ml) was added to a solution of cobalt acetate tetrahydrate (1.2 g) in methanol (20 ml). After drawing air through the

solution for 4 hr, during which time the color changed from deep brown to deep green-brown, the solution was filtered and a concentrated aqueous solution of potassium iodide (20 ml) was added to the filtrate. The olive green crystals were collected, washed with a 1:1 solution of methanol-ether, dried, and recrystallized three times from chloroform-ether: yield 1.8 g (60%), mp 195–200°, $[\alpha] -2850^\circ$ in methanol. The molar conductance of a 10^{-3} M water solution was 97 mhos cm^2 (1:1 electrolyte).

Anal. Calcd for $CoC_{22}H_{30}N_2O_4S_2I$: C, 41.6; H, 4.7; N, 4.4; S, 10.1; Co, 9.3. Found: C, 41.8; H, 4.6; N, 4.9; S, 10.0; Co, 9.1.

(-)-1,8-Dimethyl-1,8-bis(2-hydroxy-1-naphthylideneamino)-3,6-dithiaoctanecobalt(III) Iodide, (-)-[CoPEP(nap)₂]₂I. This complex was prepared in a manner identical with that given above for the (-)-[CoPEP(sal)₂]₂I·2H₂O complex. After two recrystallizations from chloroform-ether, deep green crystals were obtained: yield 60%, mp 215°, $[\alpha] -2900^\circ$ in methanol.

Anal. Calcd for $CoC_{30}H_{30}N_2S_2O_2I$: C, 51.5; H, 4.3; S, 9.2; N, 4.0; Co, 8.4. Found: C, 51.9; H, 4.5; S, 9.0; N, 3.8; Co, 8.4.

(+)-1,8-Dimethyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane-zinc(II) Monohydrate, (+)-[ZnPEP(sal)₂]₂·H₂O. A solution of the ligand (1 g) in ethanol (10 ml) was added to zinc acetate dihydrate (0.5 g), and the resultant mixture was heated under reflux for 0.25 hr during which time a pale yellow oil separated. Addition of water to the cooled reaction mixture resulted in the deposition of more oil which, after the supernatant solution was decanted, was recrystallized three times from chloroform-petroleum ether to give a faintly yellow powder: yield 20%, mp 135–140°, $[\alpha] +3250$ in chloroform.

Anal. Calcd for $ZnC_{22}H_{28}N_2O_3S_2$: C, 53.3; H, 5.7; N, 5.7; S, 12.9. Found: C, 53.2; H, 5.4; N, 5.8; S, 12.8.

The green [CoEEE(sal)₂]₂I ($[\alpha] -7600$), [CoEPE(sal)₂]₂I ($[\alpha] -5100^\circ$), [CoTET(sal)₂]₂I ($[\alpha] -7100^\circ$), and the brown [CoTET(sal)₂]₂I ($[\alpha] +900^\circ$) were prepared, purified, and resolved by methods described elsewhere.^{2,3} The [CoEEE(sal)₂]₂⁺ is more conveniently resolved by using sodium antimonyl tartrate rather than by the earlier procedure.

The nmr spectra were recorded using a Varian HA 100 spectrometer. Tetramethylsilane was used as an internal reference. Electronic absorption spectra were measured with a Unicam SP 800 (recording) spectrophotometer, and the circular dichroism spectra were obtained using a Roussel-Jouan dichrograph having a sensitivity of 1.5×10^{-4} .

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