

perhaps most extreme if the  $\text{Co}(\text{TlM})(\text{NH}_3)_2^{3+}$ – $\text{Co}(\text{TlM})(\text{OH}_2)_2^{2+}$  reaction is considered.<sup>15</sup> In this case we would infer for  $\text{CoTlM}(\text{NH}_3)_2^{3+}$ , a value of  $k_0 = (6 \pm 4) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ .

We must therefore conclude that the free energy correlation (1) does not hold true for reactions of cobalt(III) even though it does nearly predict the dependence of the rate constant on the free energy of reaction.<sup>14</sup> The failure of (1) is clearly in the nature of the  $\lambda_{12}$  term.

Since (1) can be obtained from both the adiabatic and nonadiabatic theories,<sup>3,4</sup> the source of difficulty may be in some general assumption common to both approaches. For example when  $\lambda_{11}$  and  $\lambda_{22}$  are very different, the potential surfaces may not couple in such a way that  $\lambda_{12} = 1/2(\lambda_{11} + \lambda_{22})$  (see also ref 3). It is also possible that the terms represented by  $\lambda_{12}/4$  in empirical correlations do not correspond entirely to (ligand, solvent, etc.) reorganizational terms.

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## The Optical Activity of Dissymmetric Six-Coordinate Cobalt(III) Complexes<sup>1</sup>

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The optical activity associated with the d–d transitions in dissymmetric six-coordinate Co(III) complexes is examined on a model which incorporates both ligand-field theory and the one-electron, static-coupling theory of optical activity. This is a perturbation model on which the zeroth-order spectroscopic states are taken as eigenstates of an octahedral  $\text{CoL}_6$  cluster (L = ligating atoms). The dissymmetric perturbation of these states originates with ligand groups outside the  $\text{ML}_6$  cluster and with dissymmetric distortions of the  $\text{ML}_6$  cluster. The perturbation treatment is carried to second order in both the wave functions and rotatory strengths. Expressions are obtained which relate the sign of the net or total d–d rotatory strength to specific stereochemical features in the ligand environment. Sector rules based on these expressions are proposed. Applications of these sector rules to chiral Co(III) complexes of several classes are presented, and it is found that these rules are reliable in predicting the signs of the contributions made by various "kinds" of stereochemical features to the net d–d rotatory strength.

### I. Introduction

The natural optical rotatory properties of chiral transition metal compounds have played an extraordinarily important role in the development of inorganic stereochemistry. The modern structural theories of metal coordination compounds owe their final acceptance to Werner's interpretation of the optical rotatory power of the resolved optically active stereoisomers of six-coordinate metal complexes.<sup>2</sup> The investment of research effort in this field has grown enormously in the past 10 years, due in large part to the availability of improved measurement techniques (e.g., circular dichroism instrumentation) and, perhaps to a lesser extent, due to an improved theoretical understanding of the underlying spectroscopic processes. Considerable progress has been made in correlating the experimental parameters of circular dichroism (CD) and optical rotatory dispersion (ORD) spectra with specific stereochemical features of various classes of transition metal complexes. Furthermore, CD spectra have been used with some success in resolving and characterizing the spectroscopic transitions associated with metal intra-d-shell excitations and with ligand  $\leftrightarrow$  metal charge-transfer processes. Despite these successes, there remains one important objective of these studies which so far has eluded satisfactory treatment. Simply stated, this objective is to establish a quantitative relationship between the stereochemical variables of a complex (i.e., the relative positional coordinates of the atoms and groups within a coordination compound) and the

electronic variables which determine the spectroscopic observables of optical activity.

For isotropic assemblies of dissymmetric molecules, the rotatory strength as defined in eq 1 provides a direct connection between the spectroscopic moments associated with a molecular electronic transition and the contribution which this transition makes to the optical activity observables.

$$R(i \rightarrow j) = \text{Im}[\langle \psi_i | \mathbf{u} | \psi_j \rangle \langle \psi_j | \mathbf{m} | \psi_i \rangle] \quad (1)$$

where  $\mathbf{u}$  and  $\mathbf{m}$  are the electric and magnetic dipole operators, respectively, and  $\psi_i$  and  $\psi_j$  are molecular electronic state functions. If  $\psi_i$  and  $\psi_j$  are obtained as eigenfunctions of the total molecular Hamiltonian, then the stereochemical variables are implicit in the wave functions since, of course, these variables must appear explicitly in the potential energy terms of the total Hamiltonian. Of primary interest, however, is the case where  $R(i \rightarrow j)$  is determined from experiment and one then wishes to deduce the stereochemical variables. This requires a knowledge of  $\psi_i$  and  $\psi_j$  as functions of the dissymmetric parts of the total molecular Hamiltonian.

For many dissymmetric systems the electronic transitions of greatest experimental interest are localized in some subgroup of the system which is nondissymmetric. In these cases, the spectroscopic-state functions can be treated to zeroth-order as eigenfunctions of a local or group Hamiltonian which has the symmetry of the chromophoric subgroup. The influence of the dissymmetric, extrachromophoric parts of the system on the spectroscopic states is then treated by perturbation theory. It is assumed that the local zeroth-order states are well-defined and that the true spectroscopic states

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of the overall system can be accurately represented by superpositions of these localized states. It is the detailed nature of these superpositions or mixings which determine the sign and magnitude of  $R$  and, of course, the interaction potential between the optical electron and the extrachromophoric parts of the system determines the nature of the mixings. If, in a particular set of dissymmetric systems which have a common chromophoric group, all the extrachromophoric atoms or groups are similar with respect to their electrical properties and valence-electron radial distributions, then the relative signs and magnitudes of  $R$  for a specific transition in this set of systems will be directly related to the relative positions of the perturber groups with respect to the chromophoric group. Rules which express this relationship between the sign of  $R$  and the perturber positions are commonly referred to as *sector* or *regional* rules. If the perturber groups are dissimilar in their electrostatic and electrodynamic properties, then dissymmetry in the perturbation potential can arise from the relative values of these properties as well as from the spatial distribution of the perturber centers. In this case, stereochemical variables can be deduced from sector rules only after some assumptions are made about the relative electrostatic and electrodynamic properties of the perturbers.

In the present study we are interested in the CD spectra associated with the ligand-field transitions of dissymmetric six-coordinate Co(III) complexes. The chromophoric center is the Co(III) ion and, in most cases of interest, the microsymmetry of the  $ML_6$  cluster ( $M \equiv \text{Co(III)}$ ,  $L \equiv \text{ligand atom}$ ) is holohedral (*i.e.*, possesses at least one improper rotation element) or very nearly so. The dissymmetric parts of the perturber potential must, therefore, originate either with nonligating parts of the ligand environment or from small dissymmetric distortions of the  $ML_6$  cluster. To represent the spectroscopic states involved in the ligand-field transitions we choose as basis functions the 3d, 4s, 4p, and 4f orbitals centered on the Co(III) ion. These metal-centered basis functions span all the irreducible representations of the octahedral  $ML_6$  ligand symmetry orbitals except  $t_{1g}$  (*i.e.*,  $a_{1g}$ ,  $e_g$ ,  $t_{2g}$ ,  $t_{1u}$ , and  $t_{2u}$ ). The lowest order  $t_{1g}$  metal orbital is  $5g$  ( $l = 4$ ). This representation of the spectroscopic states in terms of a restricted pure metal orbital basis is not adequate for calculating state energies, absolute spectral intensities, or properties which are known to be highly dependent upon metal-ligand electron delocalization. However, it is expected that the symmetry-controlled aspects of the signs and relative magnitudes of the ligand-field CD bands will be accurately described by this representation.

## II. Previous Work

As was noted earlier, a major objective of current studies on the CD of metal complexes is to obtain a relationship between the stereochemical variables of the complex and the optical activity observables (*e.g.*, CD signs and intensities) which can be rationalized in terms of a quantum mechanical description of the electronic transitions in the complex. Due to the complexity of the systems the quantum mechanical description must by necessity be more qualitative and conceptual than quantitative and numerical, providing selection rules, signs, and relative magnitudes rather than

computed absolute values of properties. The first such description of the optical rotatory properties of a chiral transition metal complex was provided by Moffitt in 1956.<sup>3</sup> An error in sign in the d-d transition matrix of the angular momentum operator led Moffitt to incorrect conclusions, and Sugano<sup>4</sup> subsequently demonstrated that Moffitt's model could not account for the net rotatory strength observed for the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition in  $\text{Co(en)}_3^{3+}$ . However, Moffitt's work as well as the rapid increase in experimental data on the optical rotatory properties of transition metal compounds provided the stimulus for many additional theoretical treatments. Theoretical models have been proposed by Hamer,<sup>5</sup> Poulet,<sup>6</sup> Piper and Karipedes,<sup>7,8</sup> Mason and coworkers,<sup>9,10</sup> B urer,<sup>11</sup> Liehr,<sup>12,13</sup> Schaffer,<sup>14</sup> Caldwell,<sup>15</sup> Bosnich,<sup>16</sup> and Richardson<sup>17-20</sup> which vary with respect to their generality of application, their basis representation of the spectroscopic states, and their predictive relationships between stereochemical variables and optical rotatory observables. Each of these studies has enjoyed some success in extending our conceptual understanding of the phenomenon, in explaining or rationalizing the observed CD spectra of a few specific systems, or in providing a possible (if not always practical) procedure for calculating the rotatory strengths of d-d transitions. It is generally agreed, however, that these more formal theories are not sufficiently explicit or general to merit widespread use in making spectra-structure correlations except in a piecemeal, *ad hoc* fashion.

Despite the lack of a unifying theoretical model, a number of workers in the field have succeeded in developing sector rules which have, in many cases, proved to be highly useful and reliable in making spectra-structure correlations. The most prominent examples are presented in the work of Hawkins,<sup>21</sup> Martin,<sup>22-26</sup> Wellman,<sup>27-29</sup> Gillard,<sup>30</sup> Bosnich,<sup>31</sup> and Mason<sup>10,32</sup> and

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their coworkers. In most of these studies the adopted rules were selected on the basis of empirical correlations and qualitative theoretical arguments drawn from the general one-electron theory of optical activity in dissymmetrically perturbed symmetric chromophores.<sup>33,34</sup> Additionally, a great deal of effort has been expended in sorting out the individual contributions to the optical rotatory parameters attributable to different *kinds* of stereochemical features in the ligand environment. The *kinds* of stereochemical features which can contribute to the overall dissymmetry of the complex are commonly defined as follows: (1) the distribution of chelate rings about the metal ion (configurational isomerism), (2) the conformations of individual chelate rings (conformational isomerism), (3) asymmetric atoms in the nonligating parts of the ligands, (4) asymmetric ligating (donor) atoms, and (5) the distribution of unidentate ligands. It is apparent that a sector rule in which both spatial and electrostatic dissymmetries are accurately represented would simplify the partitioning of total observed rotatory strengths into contributions of various stereochemical origins. Presently, this partitioning is most reliably carried out on the basis of empirically derived relationships rather than by use of sector rules based on quantum theoretical arguments.<sup>35</sup> The most extensive studies concerned with analyzing the observed ligand-field CD spectra of Co(III) complexes in terms of configurational *vs.* conformational *vs.* vicinal effects have been conducted by Douglas,<sup>36-41</sup> Hawkins,<sup>35</sup> and Bosnich<sup>42</sup> and their collaborators. These studies indicate that ligand-field CD spectra provide a reasonable experimental basis for differentiating between the various *kinds* of stereochemical features in dissymmetric complexes, but they provide few clues as to how the spectra can be interpreted in terms of a quantum mechanical or orbital description of the molecular electronic states.

### III. Model

**A. General Comments.**—The primary objective of this study is to develop a general procedure by which the d-d CD spectra of dissymmetric six-coordinate Co(III) complexes can be systematically analyzed and interpreted in terms of specific stereochemical features of the complexes. To develop the procedure we adopt a model whose representation of the spectroscopic (electronic) states of a complex subsumes both the crystal-field theory of coordination compounds and the one-electron theory of optical activity. The limitations and deficiencies of these respective theories have received considerable attention elsewhere and need not be discussed again here. At best, they accurately and reliably display the symmetry-determined aspects of d-d absorption and CD spectra; at worst, they provide an incomplete and sometimes misleading representation of the underlying physical processes. In the present

study, we assert that the results obtained by application of the general crystal-field and one-electron theories display the essential structure-spectra relationships for the d-d CD spectra of a large number of dissymmetric six-coordinate Co(III) complexes.

The complexes are represented to zeroth-order as having regular octahedral geometry ( $O_h$  symmetry) with six identical ligating atoms situated at the vertices of a regular octahedron. Deviations from this zeroth-order representation are classified as follows: (1) distortions of the ligating atoms from their regular octahedral positions, (2) dissimilarities between the ligating atoms (*e.g.*, between the O and N atoms in the tris(glycinato)-cobalt(III) complex), and (3) the presence of chelate rings and the consequent reduction in symmetry due to both the ring bridging atoms and ring substituent groups. The influences of these deviations on the zeroth-order d-d spectroscopic states are assumed to be sufficiently small to permit their treatment by perturbation methods. Perturbation expansions of the spectroscopic-state functions and the rotatory strengths are carried to second order.

**B. Electronic States.**—Ignoring spin-orbit interactions, we partition the electronic Hamiltonian operator as

$$H = H_M + H_L + V_{ML}^0 + V'_{ML} \quad (2)$$

where  $H_M$  is the Hamiltonian for the free metal ion,  $H_L$  is the total Hamiltonian for the free ligands,  $V_{ML}^0$  is the octahedral crystal-field potential energy function, and  $V'_{ML}$  designates the noncubic parts of the crystal-field potential energy. On our model, the zeroth-order spectroscopic states are chosen as eigenstates of the operator ( $H_M + V_{ML}^0$ ), and the interaction potential  $V'_{ML}$  is treated as a perturbation.

The present study focuses primarily on the spin-allowed transitions which involve one-electron excitations within the 3d shell of low-spin Co(III). In the  $O_h$  group notation these transitions are written as  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$ . The  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition is magnetic dipole allowed in an octahedral system and occurs at a lower frequency than does the  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition which is magnetic dipole forbidden. In the absence of vibronic interactions both transitions are, of course, electric dipole forbidden by the Laporte parity rule. Vibronic perturbations on the  ${}^1A_{1g}$ ,  ${}^1T_{1g}$ , and  ${}^1T_{2g}$  electronic states can influence the spectral properties of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transitions in several ways. First, Herzberg-Teller type couplings will result in a mixing of ungerade states into the gerade optical states with a consequent induction of electric dipole allowed character in the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transitions. Second, Jahn-Teller interactions will lead to distortions within the orbitally degenerate electronic excited states which can quench certain low-symmetry (noncubic) crystal-field perturbations as well as the angular momenta of these states.<sup>43</sup> These vibronic effects cannot be neglected if quantitative, numerical calculations of the rotatory strengths are to be carried out; neither can they be neglected if distributions of intensity within CD bands are to be treated. However, if one's objective is to obtain correlations of signs and relative intensities of the observed CD spectra

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with stereochemical features, then the neglect of vibronic interactions will not lead to serious difficulties.

The noncubic perturbation potential function,  $V'_{ML}$ , is partitioned into two parts: one that transforms gerade under the inversion operation and one that transforms ungerade. These functions are written as  $V'_g$  and  $V'_u$ , respectively, for the gerade and ungerade parts, and the irreducible representations under which they transform in the  $O_h$  point group are designated by  $\Gamma_g^V(\gamma)$  and  $\Gamma_u^V(\gamma)$ , where  $\gamma$  denotes components of degenerate representations. Henceforth the zeroth-order octahedral states  ${}^1A_{1g}$ ,  ${}^1T_{1g}$ , and  ${}^1T_{2g}$  are denoted by  $|A_1\rangle^0$ ,  $|T_1(\gamma)\rangle^0$ , and  $|T_2(\gamma)\rangle^0$ , respectively, where  $\gamma$  denotes the orbital components of degenerate states and the multiplicity superscript is suppressed since we shall only be concerned with spin-singlet states. Under the influence of  $V'_u$  these three gerade states are mixed with ungerade eigenstates of the  $(H_M + V^0_{ML})$  operator. These ungerade states are denoted by  $|\Gamma_u^b(\gamma)\rangle^0$ . Since  $V'_u$  is a spin-independent, one-electron operator, the combining states must be of like multiplicity and must not have configurational representations which differ by more than one in their 3d-orbital occupation numbers. The  $V'_g$  operator will scramble the gerade eigenstates of  $(H_M + V^0_{ML})$ , denoted by  $|\Gamma_g^a(\gamma)\rangle^0$ . It is anticipated that the most important effect of  $V'_g$  on the spectral properties of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transitions will arise from  ${}^1T_{1g} + {}^1T_{2g}$  mixing, since these states are much closer in energy to one another than to any other gerade state,  $\Gamma_g^a$ , of octahedral parentage.

**C. Interaction Potential.**—In the present study, it is assumed that the spectroscopic states involved in the ligand-field transitions of Co(III) complexes can be adequately described in terms of a quasi crystal-field model. That is, it is assumed that these states can be described entirely in terms of metal atomic orbitals and that the ligand environment can be represented by an array of "static" charge distributions. Differential overlap between the metal and ligand electron orbitals is neglected and the dynamical behavior of the electronic distributions on the ligands is ignored. These assumptions are within the spirit of the "one-electron" theory of optical activity and the "crystal-field" theory of d-d transitions in transition metal complexes. Given this model, the interaction operator  $V'_{ML}$  (eq 2) is expressed as a power series in tesseral harmonic functions defined about an origin centered on the metal ion.<sup>44</sup> That is

$$V'_{ML} = \sum_l r^l \sum_{m=0}^l (4\pi/2l+1) \sum_p [C_l^m(\alpha_p, \beta_p) C_l^m(\theta, \phi) + S_l^m(\alpha_p, \beta_p) S_l^m(\theta, \phi)] Q_p R_p^{-(l+1)} \quad (3)$$

where  $C_l^m$  and  $S_l^m$  are normalized tesseral harmonic functions (as defined by Prather<sup>44</sup>),  $r$ ,  $\theta$ , and  $\phi$  are the spherical polar coordinates of the chromophoric electron localized on the metal ion,  $R_p$ ,  $\alpha_p$ , and  $\beta_p$  are the spherical polar coordinates of ligand perturber site  $p$ ,  $Q_p$  is the formal charge associated with perturber site  $p$ , and  $\sum_p$  is taken over all perturber sites in the ligand environment. The function  $V'_{ML}$  transforms as the totally symmetric irreducible representation of the

point group to which the overall metal complex belongs.

It was noted in section B that  $V'_{ML}$  can be partitioned into two parts,  $V'_g$  and  $V'_u$ , which differ with respect to their behavior upon inversion through the metal atom (the coordinate system origin for  $(r, \theta, \phi)$  and for  $(R, \alpha, \beta)$ ). Additionally, it is useful to classify the ligand perturber sites according to their chemical identities, spectroscopic properties, structural identities (ligand atoms, chelate ring bridging atoms, ring substituents, etc.), or electrostatic nature (e.g., charged or uncharged, polar or nonpolar). This classification permits further partitioning of  $V'_{ML}$  according to the signs and magnitudes of the parameters  $Q_p$  and specific stereochemical features of the complex.

**D. Rotatory Strengths.**—The rotatory strength of the perturbed  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition expressed to second-order in perturbation theory is given by

$$R_{01} = \text{Im}(\mathbf{P}_{01}^{(1)} \mathbf{M}_{10}^{(0)}) + \text{Im}(\mathbf{P}_{01}^{(2)} \mathbf{M}_{10}^{(0)} + \mathbf{P}_{01}^{(1)} \mathbf{M}_{10}^{(1)}) \quad (4)$$

where the subscripts 0 and 1 denote the ground state and the excited state, respectively, and the superscripts (0), (1), and (2) denote the zeroth, first, and second orders, respectively, of the electric dipole ( $\mathbf{P}$ ) and magnetic dipole ( $\mathbf{M}$ ) transition moments. The rotatory strength of the perturbed  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition is expressed to second order by

$$R_{02} = \text{Im}(\mathbf{P}_{02}^{(1)} \mathbf{M}_{20}^{(1)}) \quad (5)$$

Equations 4 and 5 can be reexpressed in terms of transition integrals, perturbation matrix elements, and energy differences between the octahedral basis states of our model. The new expressions are

$$R_{01} = \text{Im} \sum_{1(\gamma)} \sum_{b(\gamma)} \{ M_{10}^0 [P_{0b}^0 V_{1b} \Delta E_{1b}^{-1} + P_{0b}^1 V_{0b} \Delta E_{0b}^{-1}] + P_{0b}^0 [M_{10}^0 V_{b1} (V_{bb} - V_{11}) \Delta E_{1b}^{-2} - M_{10}^0 V_{b0} V_{01} \Delta E_{1b}^{-1} \Delta E_{01}^{-1} + M_{10}^0 V_{b0} V_{01} \Delta E_{0b}^{-1} \Delta E_{01}^{-1}] + P_{0b}^1 [M_{10}^0 V_{b1} V_{10} \Delta E_{0b}^{-1} \Delta E_{01}^{-1} + M_{10}^0 (V_{bb} - V_{00}) V_{b0} \Delta E_{0b}^{-2} + M_{10}^0 V_{10} V_{0b} \Delta E_{01}^{-1} \Delta E_{0b}^{-1} + M_{10}^0 V_{01} V_{1b} \Delta E_{01}^{-1} \Delta E_{1b}^{-1}] + \sum_{a(\gamma) \neq 0,1} P_{0b}^0 [M_{10}^0 V_{ba} V_{a1} \Delta E_{1b}^{-1} \Delta E_{1a}^{-1} + M_{1a}^0 V_{0a} V_{1b} \Delta E_{0a}^{-1} \Delta E_{1a}^{-1} + M_{10}^0 V_{a1} V_{1b} \Delta E_{1b}^{-1} \Delta E_{1a}^{-1}] + \sum_{a(\gamma) \neq 0,1} P_{0b}^1 [M_{10}^0 V_{ba} V_{a0} \Delta E_{0b}^{-1} \Delta E_{0a}^{-1} + M_{1a}^0 V_{0a} V_{0b} \Delta E_{0a}^{-1} \Delta E_{0b}^{-1}] + \sum_{a(\gamma) \neq 0,1} P_{0ab}^0 M_{10}^0 [V_{0a} V_{1b} \Delta E_{0a}^{-1} \Delta E_{1b}^{-1} + V_{0b} V_{1a} \Delta E_{0b}^{-1} \Delta E_{1a}^{-1}] \} \quad (6)$$

$$R_{02} = \text{Im} \sum_{2(\gamma)} \sum_{b(\gamma)} \{ P_{0b}^0 [M_{22}^0 V_{b2} V_{20} \Delta E_{02}^{-1} \Delta E_{2b}^{-1} + \sum_{a(\gamma) \neq 0,2} (M_{2a}^0 V_{0a} V_{2b} \Delta E_{0a}^{-1} \Delta E_{2a}^{-1} + M_{a0}^0 V_{a2} V_{2b} \Delta E_{2b}^{-1} \Delta E_{2a}^{-1})] + P_{0b}^1 [M_{22}^0 V_{20} V_{0b} \Delta E_{02}^{-1} \Delta E_{0b}^{-1} + \sum_{a(\gamma) \neq 0,2} M_{2a}^0 V_{a0} V_{0b} \Delta E_{0a}^{-1} \Delta E_{0b}^{-1}] \} \quad (7)$$

where, for example,  $P_{0b}^0 = \langle A_1 | \mathbf{p} | \Gamma_u^b(\gamma) \rangle^0$ ,  $M_{10}^0 =$

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$\langle T_1(\gamma) | m | A_1 \rangle^0$ ,  $V_{b1} = \langle \Gamma_u^b(\gamma) | V'_{ML} | T_1(\gamma) \rangle^0$ , and  $\Delta E_{1b} = (E^0_1 - E^0_b) = -\Delta E_{b1}$ . The summation  $\Sigma_{b(\gamma)}$  is taken over all orbital components  $\gamma$  (in the case of orbital degeneracy) of all ungerade states  $\Gamma_u^b$ , and  $\Sigma_{1(\gamma)}$  and  $\Sigma_{2(\gamma)}$  are threefold sums over the orbital components of the triply degenerate  $T_{1g}$  and  $T_{2g}$  octahedral basis states, respectively.

The first-order contribution to  $R_{01}$  is given by the first two terms inside the braces of (6). The signs and magnitudes of these terms are dependent upon the perturbation matrix elements  $V_{1b}$  and  $V_{0b}$ . In previous work<sup>4-6,17-20</sup> it has been shown that the net first-order contribution to  $R_{01}$  is zero unless the octahedral basis states,  $A_{1g}$  and  $T_{1g}$ , are subjected to a perturbation whose operator transforms as the pseudoscalar irreducible representation ( $A_{1u}$ ) of the  $O_h$  point group. The first term in the expansion of  $V'_{ML}$  (eq 3) which transforms as  $A_{1u}$  in the  $O_h$  point group is of order  $l = 9$  and exhibits an  $R_p^{-10}$  dependence on perturber-metal radial separation distances. Expressed in terms of the cartesian positional coordinates of the perturbing groups, this interaction operator has the following dependence on perturber site positions:  $\Sigma_p X_p Y_p Z_p \cdot (X_p^2 - Y_p^2)(Y_p^2 - Z_p^2)(Z_p^2 - X_p^2)R_p^{-10}$ . It is apparent that this function of perturber site positions can achieve significant values only when the perturber sites are exceedingly close to the metal ion due to the steep inverse dependence on  $R_p$ . In fact, it can only have significant magnitude in the domain where the electrodynamic and electron-exchange forces between the metal and ligand sites will surely dominate. This term is devoid of meaning in the context of a one-electron model which assumes that the optically active system can be partitioned into a chromophoric group and a set of perturbing groups which interact only *via* nonexchange mechanisms.

There is an additional undesirable feature of this  $V'_{ML}(A_{1u})$  operator in the present model. Since the zeroth-order spectroscopic basis states are constructed from metal 3d orbitals,  $V'_{ML}(A_{1u})$  can only mix in ungerade states constructed from metal atomic orbitals of  $l \geq 7$ . This necessity makes the use of  $V'_{ML}$  extremely unattractive and possibly absurd from a purely physical point of view. It should be pointed out, however, that a sector rule based on the perturber position dependence of  $V'_{ML}(A_{1u})$  has been used with some success in correlating the CD spectra and stereochemical features of a number of dissymmetric Co(III) complexes.<sup>10,42,45</sup> The possible utility of such a sector rule is not disputed in the present study; however, its theoretical validity and general applicability are called into question and an alternative set of rules are proposed based on the second-order terms displayed in eq 6 and 7.

Each of the second-order terms contributing to  $R_{01}$  and to  $R_{02}$  includes a product of interaction matrix elements. In each of these products one matrix element has a gerade perturbation operator ( $V'_g$ ), and the other matrix element has an ungerade perturbation operator ( $V'_u$ ). Making use of the Wigner-Eckart theorem and the irreducible tensor formalism, a term by term analysis of eq 6 and 7 reveals that  $R_{01}(\text{net})$  and  $R_{02}(\text{net})$  are nonvanishing only if the following symmetry condition is satisfied term by term:  $\Gamma_g^V(\gamma) \cdot \Gamma_u^V(\gamma) = A_{1u}$ . That is, the direct product of the

irreducible representations of  $V'_g$  and  $V'_u$  must contain the pseudoscalar representation,  $A_{1u}$ . The permissible pair combinations of  $\Gamma_g^V(\gamma)$  and  $\Gamma_u^V(\gamma)$  are

$$\begin{aligned} & [A_{1g}, A_{1u}] \\ & [A_{2g}, A_{2u}] \\ & [E_g(\theta), E_u(\theta)]; [E_g(\epsilon), E_u(\epsilon)] \\ & [T_{1g}(x), T_{1u}(x)]; [T_{1g}(y), T_{1u}(y)]; [T_{1g}(z), T_{1u}(z)] \\ & [T_{2g}(\xi), T_{2u}(\xi)]; [T_{2g}(\eta), T_{2u}(\eta)]; [T_{2g}(\zeta), T_{2u}(\zeta)] \end{aligned}$$

The leading terms in the tesseral harmonic expansion of  $V'_{ML}$  (eq 3) transform as follows under the symmetry operations of the  $O_h$  point group

$$\begin{aligned} l = 0; & A_{1g} \\ l = 1; & T_{1u} \\ l = 2; & E_g, T_{2g} \\ l = 3; & A_{2u}, T_{1u}, T_{2u} \\ l = 4; & A_{1g}, E_g, T_{1g}, T_{2g} \\ l = 5; & E_u, 2T_{1u}, T_{2u} \end{aligned}$$

The lowest "order" pair combinations of  $(\Gamma_g^V, \Gamma_u^V)$  are, therefore, the  $[T_{1g}, T_{1u}]$  and  $[T_{2g}, T_{2u}]$  combinations, which have  $[l = 4, l = 1]$  and  $[l = 2, l = 3]$  dependencies, respectively, on the  $l$  numbers.

The dependencies of the  $[T_{1g}, T_{1u}]$  and  $[T_{2g}, T_{2u}]$  pair combinations on the cartesian positional coordinates of the perturber sites and on the perturber-metal radial distances are given by

$$[T_{1g}(x), T_{1u}(x)]: \sum_p \sum_{p'} Y_p Z_p (Y_p^2 - Z_p^2) X_p R_p^{-9} R_{p'}^{-3} \quad (8a)$$

$$[T_{1g}(y), T_{1u}(y)]: \sum_p \sum_{p'} X_p Z_p (Z_p^2 - X_p^2) Y_p R_p^{-9} R_{p'}^{-3} \quad (8b)$$

$$[T_{1g}(z), T_{1u}(z)]: \sum_p \sum_{p'} X_p Y_p (X_p^2 - Y_p^2) Z_p R_p^{-9} R_{p'}^{-3} \quad (8c)$$

$$[T_{2g}(\xi), T_{2u}(\xi)]: \sum_p \sum_{p'} Y_p Z_p X_p (Y_p^2 - Z_p^2) R_p^{-6} R_{p'}^{-7} \quad (9a)$$

$$[T_{2g}(\eta), T_{2u}(\eta)]: \sum_p \sum_{p'} X_p Z_p Y_p (Z_p^2 - X_p^2) R_p^{-6} R_{p'}^{-7} \quad (9b)$$

$$[T_{2g}(\zeta), T_{2u}(\zeta)]: \sum_p \sum_{p'} X_p Y_p Z_p (X_p^2 - Y_p^2) R_p^{-6} R_{p'}^{-7} \quad (9c)$$

where  $\Sigma_p$  and  $\Sigma_{p'}$  are each taken over all perturber sites. The  $V'_g(T_{1g})$  operator has the same dependence on  $R_p$  as the lowest "order" term in the  $O_h$  crystal-field potential. The  $V'_g(T_{2g})$ ,  $V'_u(T_{2u})$ , and  $V'_u(T_{1u})$  operators all have a less severe dependence on  $R_p$ . The metal p orbitals transform as  $T_{1u}$  in  $O_h$  and the metal d orbitals transform as  $T_{2g}$  and  $E_g$ . The direct products  $T_{1u} \cdot T_{2g}$  and  $T_{1u} \cdot E_g$  each span both the  $T_{1u}$  and  $T_{2u}$  irreducible representations of  $O_h$ , and the direct product  $E_g \cdot T_{2g}$  spans both  $T_{1g}$  and  $T_{2g}$ . Consequently, the orbital basis set from which the  $\Gamma_g^a$  and  $\Gamma_u^b$  states are constructed need only include metal atomic orbitals with  $l \leq 2$  to ensure the nonvanishing of the perturbation matrix elements which appear in eq 6 and 7.

By carrying our one-electron model to second order in the crystal-field potential function  $V'_{ML}$ , we have

succeeded in obtaining sector rule expressions for the rotatory strength of a dissymmetrically perturbed cubic system which avoids the  $R_p^{-19}$  dependence and the  $l \geq 7$  basis orbitals required by the first-order results. However, it would appear that applications of these second-order sector rules are made somewhat difficult by the necessity of considering the positions of *two* perturber sites at a time with respect to the metal ion. Furthermore, before expressions 8 and 9 can be applied as sector rules, an assignment of sign must be made for each perturber charge parameter,  $Q_p$ . Applications of expressions 8 and 9 as sector rules are discussed in some detail in section IV.

The rotatory strength given by eq 6 represents the *total* or *net* rotatory strength associated with all components of the triply degenerate cubic  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition. Similarly, eq 7 gives the *total* or *net* rotatory strength associated with all components of the triply degenerate cubic  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition. The contributions made by the individual components of each transition can be obtained by evaluating each term in the summations  $\Sigma_{1(\gamma)}$  and  $\Sigma_{2(\gamma)}$  separately. The symmetry conditions  $\Gamma_u^V = A_{1u}$  (for the first-order terms) and  $\Gamma_u^V \Gamma_g^V = A_{1u}$  (for the second-order terms) and the resulting sector rules apply only to the *total* or *net* rotatory strengths,  $R_{01}$  and  $R_{02}$ . In general, any ungerade potential function which transforms as the totally symmetric irreducible representation of a dissymmetric subgroup of  $O_h$  can lead to nonvanishing first-order terms in eq 6. However, the sum  $\Sigma_{1(\gamma)} R_{01}(\gamma)$  vanishes unless  $\Gamma_u^V = A_{1u}$ . Additionally, any combination of ungerade and gerade perturbation potentials which are each invariant under the symmetry operation of a dissymmetric subgroup of  $O_h$  will, in general, lead to nonvanishing second-order terms in both eq 6 and eq 7. However, the sums  $\Sigma_{1(\gamma)} R_{01}(\gamma)$  and  $\Sigma_{2(\gamma)} R_{02}(\gamma)$  will vanish unless  $\Gamma_u^V \Gamma_g^V = A_{1u}$ .

In principle, it is possible to analyze the d-d CD spectra of the Co(III) complexes in terms of the six-component rotatory strength contributions  $R_{01}$  ( $\gamma = I, II, III$ ) and  $R_{02}$  ( $\gamma = I, II, III$ ). In practice, however, this analysis would be exceedingly difficult. We suggest that a more practical and perhaps more useful procedure for extracting stereochemical information from the CD spectra is to apply the sector rules expressed in (8) and (9) to the *net* rotatory strength (or *net* CD intensity) associated with all components of a particular cubic transition.

#### IV. Applications

**A. Tris Complexes with Symmetric Bidentate Ligands,  $M(AA)_3$ .**—This class of metal complexes is exemplified by  $Co(en)_3^{3+}$ ,  $Co((S)\text{-pn})_3^{3+}$ ,  $Co(\text{tn})_3^{3+}$ , and  $Co(\text{ox})_3^{3-}$ , where  $en \equiv$  ethylenediamine,  $(S)\text{-pn} \equiv$  propylenediamine with  $S$  absolute configuration,  $tn \equiv$  1,3-diaminopropane (trimethylenediamine), and  $ox \equiv$  oxalate anion. To display separately the various stereochemical features which can contribute to the optical rotatory properties of these complexes, we consider the ten structures shown in Figure 1. Clearly, these ten structures cannot represent all the stereochemical possibilities, but they are sufficient for examining the principal sources of dissymmetry in the tris complexes of Co(III) with symmetric bidentate ligands. Each of the structures in Figure 1 *except* 1g and 1h

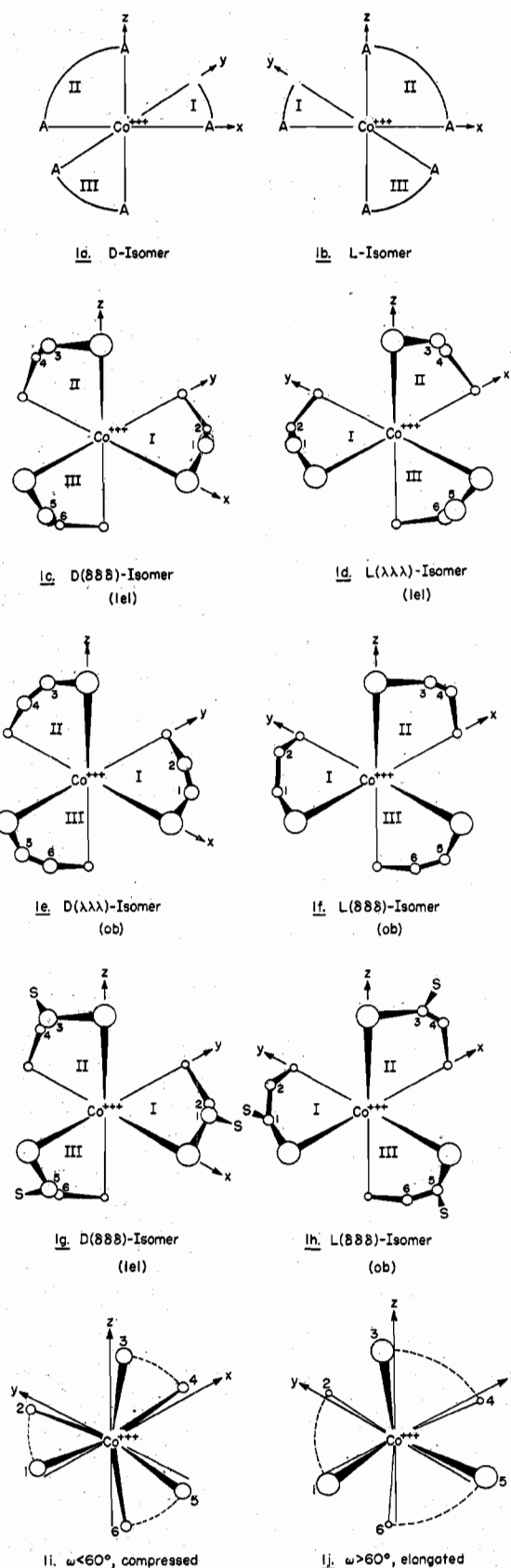


Figure 1.—(a and b) Tris complexes with *planar* symmetric bidentate ligands,  $M(AA)_3$ . (c and d) Tris complexes with *nonplanar* five-membered chelate rings,  $M(AA)_3$ , lel arrangement. (e and f) Tris complexes with *nonplanar* five-membered chelate rings,  $M(AA)_3$ , ob arrangement. (g and h) Tris complexes with *nonplanar* five-membered chelate rings,  $M(AA)_3$ , each chelate ring containing one asymmetric center with an  $S$  absolute configuration. (i and j) Trigonally distorted  $MA_6$  clusters.

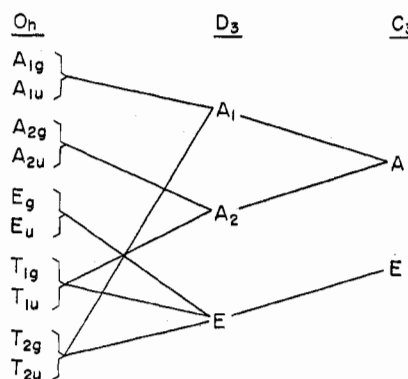


Figure 2.—Correlation diagram relating the irreducible representations of the  $O_h$ ,  $D_3$ , and  $C_3$  point groups.

possesses trigonal dihedral ( $D_3$ ) symmetry. Structures **1g** and **1h** have  $C_3$  symmetry.<sup>46</sup>

A correlation diagram relating the irreducible representations of the  $O_h$ ,  $D_3$ , and  $C_3$  point groups is given in Figure 2. The  $A_{1g}$ ,  $A_{1u}$ ,  $T_{2g}$ , and  $T_{2u}$  irreducible representations of the  $O_h$  group each contain a component which transforms as the totally symmetric  $A_1$  representation of the  $D_3$  group and the  $A$  representation of the  $C_3$  group. Additionally, the  $A_{2g}$ ,  $A_{2u}$ ,  $T_{1g}$ , and  $T_{2u}$   $O_h$  group representations each contain a component which transforms as the  $A$  representation of  $C_3$  group. To zeroth order on our model we assume that the  $M(AA)_3$  structures have "effective"  $O_h$  point group symmetry. The structural features responsible for the  $O_h \rightarrow D_3$  reduction in symmetry are treated by perturbation methods in our examination of the optical rotatory properties. We assert that the optical consequences of the  $D_3 \rightarrow C_3$  reduction of symmetry in structures **1g** and **1h** are negligible and shall assume "effective"  $D_3$  symmetry in each of the perturbed structures. The perturbation operator  $V'_{ML}$  must, therefore, transform as  $A_1$  under the symmetry operations of the  $D_3$  point group and as  $A_{1g}$ ,  $A_{1u}$ ,  $T_{2u}$ , or  $T_{2g}$  under the  $O_h$  group operations.

From these facts and the discussion in section III, it is apparent that the second-order contributions to the net rotatory strength of the d-d transitions in trigonally ( $D_3$ ) distorted six-coordinate Co(III) complexes will be governed by the  $[V'_g, V'_u]$  pair combinations  $[T_{2g}(\xi), T_{2u}(\xi)]$ ,  $[T_{2g}(\eta), T_{2u}(\eta)]$ , and  $[T_{2g}(\zeta), T_{2u}(\zeta)]$ . The functions  $3^{-1/2}(XY + XZ + YZ)$  and  $3^{-1/2}[X(Y^2 - Z^2) + Y(Z^2 - X^2) + Z(X^2 - Y^2)]$ , expressed in a tetragonal coordinate basis (*i.e.*, the  $x$ ,  $y$ , and  $z$  coordinates run through the vertices of the regular octahedron), transform as  $T_{2g}$  and  $T_{2u}$ , respectively, in the  $O_h$  point group and as  $A_1$  in  $D_3$ . The appropriate second-order sector rules for the trigonally distorted complexes are given, therefore, by expressions 9a-c.

To demonstrate the application of these rules to the structures displayed in Figure 1 we consider first the simplest case, structures **1a** and **1b**. For these structures the sole source of dissymmetry is the distribution of chelate bridging atoms about the metal ion chromophoric site. The signs of the functions found in expressions 9a-9c for the bridging atoms of chelate rings I-III are given in Table I. For the D isomer, the sign of each

(46) The stereoisomer symbols used throughout this paper are those adopted by C. J. Hawkins in "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971, Chapters 2 and 3.

TABLE I

	1a, D isomer			1b, L isomer		
	I	II	III	I	II	III
$XY$	+	0	0	-	0	0
$Z(X^2 - Y^2)$	0	+	+	0	+	+
$XZ$	0	-	0	0	+	0
$Y(Z^2 - X^2)$	-	0	-	-	0	-
$YZ$	0	0	+	0	0	+
$X(Y^2 - Z^2)$	+	+	0	-	-	0

pair combination  $[V'_g, V'_u]$  is positive, whereas for the L isomer the sign of each pair combination  $[V'_g, V'_u]$  is negative.

Consider next the structures displayed in **1c** and **1d**. There are two sources of dissymmetry in these structures: (1) the distribution of chelate bridging atoms about the metal ion (configurational dissymmetry) and (2) the inherent dissymmetry possessed by each chelate ring by virtue of its adopting a chiral conformational (conformational dissymmetry). For these structures the signs of the functions found in expressions 9a-9c for the bridging atoms of chelate rings I-III are given in Table II, where the Roman numerals I-III

TABLE II

	I		II		III	
	1	2	3	4	5	6
1c, D( $\delta\delta\delta$ ) ISOMER (1el)						
$XY$	+	+	$\oplus$ vs $\ominus$	$\ominus$	$\ominus$	$\oplus$ vs $\oplus$
$Z(X^2 - Y^2)$	$\ominus$	$\oplus$	+	+	+	+
$XZ$	$\oplus$	$\ominus$ vs $\oplus$	-	-	$\ominus$ vs $\oplus$	$\oplus$
$Y(Z^2 - X^2)$	-	-	$\ominus$	$\ominus$	-	-
$YZ$	$\oplus$ vs $\ominus$	$\ominus$	$\ominus$	$\oplus$ vs $\oplus$	+	+
$X(Y^2 - Z^2)$	+	+	+	+	$\oplus$	$\oplus$
1d, L( $\lambda\lambda\lambda$ ) ISOMER (1el)						
$XY$	-	-	$\ominus$ vs $\oplus$	$\oplus$	$\oplus$	$\ominus$ vs $\oplus$
$Z(X^2 - Y^2)$	$\oplus$	$\oplus$	+	+	+	+
$XZ$	$\ominus$	$\oplus$ vs $\oplus$	+	+	$\oplus$ vs $\ominus$	$\ominus$
$Y(Z^2 - X^2)$	-	-	$\ominus$	$\ominus$	-	-
$YZ$	$\oplus$ vs $\ominus$	$\ominus$	$\ominus$	$\oplus$ vs $\oplus$	+	+
$X(Y^2 - Z^2)$	-	-	-	-	$\ominus$	$\ominus$

denote chelate rings, the Arabic numerals designate ligand bridging atoms, the circles identify those quantities which are nonzero only by virtue of nonplanarity in the chelate rings, and vs next to an entry indicates that the absolute magnitude of the corresponding potential energy term is very small. The sum of contributions made to the allowed pair combinations  $[V'_g, V'_u]$  by the uncircled quantities represent the *pure configurational effect*. The sum of the contributions made by the circled quantities to the allowed  $[V'_g, V'_u]$  combinations represents the *pure conformational effect*. The contributions arising from the concerted influence of conformational and configurational variables constitute the *mixed configurational-conformational effect*. For structures **1c** and **1d**, the signs of these three effects are predicted to be

	1c	1d
Pure configurational	+	-
Pure conformational	-	+
Mixed configurational-conformational	-	+

Structures **1e** and **1f** also possess two sources of dissymmetry, configurational and conformational. For the bridging atoms in these structures the signs of the functions found in expressions 9a-9c are given in Table

III. For these structures, the signs predicted for the

TABLE III

	I		II		III	
	1	2	3	4	5	6
1e, D( $\lambda\lambda\lambda$ ) Isomer (ob)						
XY	+	+	$\ominus$ vs $\oplus$	$\oplus$	$\oplus$	$\ominus$ vs $\oplus$
Z( $X^2 - Y^2$ )	$\ominus$	$\ominus$	+	+	+	+
XZ	$\ominus$	$\oplus$ vs $\ominus$	-	-	$\ominus$ vs $\oplus$	$\oplus$
Y( $Z^2 - X^2$ )	-	-	$\oplus$	$\oplus$	-	-
YZ	$\ominus$ vs $\oplus$	$\oplus$	$\oplus$	$\ominus$ vs $\oplus$	+	+
X( $Y^2 - Z^2$ )	+	+	+	+	$\ominus$	$\ominus$
1f, L( $\delta\delta\delta$ ) Isomer (ob)						
XY	-	-	$\oplus$ vs $\ominus$	$\ominus$	$\ominus$	$\oplus$ vs $\ominus$
Z( $X^2 - Y^2$ )	$\oplus$	$\oplus$	+	+	+	+
XZ	$\oplus$	$\ominus$ vs $\oplus$	+	+	- vs $\oplus$	$\oplus$
Y( $Z^2 - X^2$ )	-	-	$\oplus$	$\oplus$	-	-
YZ	$\ominus$ vs $\oplus$	$\oplus$	$\oplus$	$\ominus$ vs $\oplus$	+	+
X( $Y^2 - Z^2$ )	-	-	-	-	$\oplus$	$\oplus$

various contributions to the net d-d rotatory strength are

	1e	1f
Pure configurational	+	-
Pure conformational	-	+
Mixed configurational-conformational	+	-

If we let  $M = \text{Co}^{3+}$  and  $AA = \text{en}$ , then the structures 1c, 1d, 1e, and 1f represent the D( $\delta\delta\delta$ ), L( $\lambda\lambda\lambda$ ), D( $\lambda\lambda\lambda$ ), and L( $\delta\delta\delta$ ) stereoisomers, respectively, of the  $\text{Co}(\text{en})_3^{3+}$  complex. In the D( $\delta\delta\delta$ ) and L( $\lambda\lambda\lambda$ ) isomers the C-C bond in each en ligand is approximately *parallel* to the  $C_3$  axis of the complex ion, while in the D( $\lambda\lambda\lambda$ ) and L( $\delta\delta\delta$ ) isomers the C-C bond in each en ligand is slanted or *oblique* to the  $C_3$  axis. Corey and Bailar<sup>47</sup> labeled these two kinds of isomers as the 1el and ob forms, respectively. According to the sector rules given by expressions 9a-9c, the pure configurational and mixed configurational-conformational contributions to the net rotatory strengths of the 1el isomers, D( $\delta\delta\delta$ ) and L( $\lambda\lambda\lambda$ ), should be of like sign. For the ob isomers, D( $\lambda\lambda\lambda$ ) and L( $\delta\delta\delta$ ), the pure configurational and mixed configurational-conformational contributions are of opposite sign. It is safe to assume that the pure configurational effect will dominate in all four isomers, so that the D( $\delta\delta\delta$ ) and D( $\lambda\lambda\lambda$ ) isomers should exhibit a net CD intensity of one sign while the L( $\delta\delta\delta$ ) and L( $\lambda\lambda\lambda$ ) isomers will exhibit a net CD intensity of opposite sign. However, based on our present analysis we can predict that the net CD intensity of the D( $\delta\delta\delta$ ) 1el isomer will be greater than that of the D( $\lambda\lambda\lambda$ ) ob isomer and that the net CD intensity of the L( $\lambda\lambda\lambda$ ) 1el isomer will be greater than that of the L( $\delta\delta\delta$ ) ob form. The D( $\delta\delta\delta$ ) and L( $\lambda\lambda\lambda$ ) isomers are enantiomers and will exhibit net CD intensities which are equal in magnitude but opposite in sign. The same is true for the enantiomeric pair D( $\lambda\lambda\lambda$ ) and L( $\delta\delta\delta$ ).

Structures 1g and 1h each possess three kinds of dissymmetry: configurational dissymmetry due to the chiral arrangement of the three chelate rings about the metal ion, conformational dissymmetry due to puckering in the five-membered chelate rings, and dissymmetry due to the presence of an asymmetric bridging atom in each ligand. The optical activity induced in the d-d

transitions by the substituents attached to the asymmetric centers constitutes the *vicinal effect*. In the present analysis, we take the asymmetric centers to be carbon atoms, each having a hydrogen atom substituent and an alkyl group substituent. The signs of functions 9a-9c for the bridging atoms and for the alkyl substituents in structures 1g and 1h are given in Table IV. The asymmetric centers in structures 1g and 1h are atoms 1, 3, and 5. The alkyl substituents are denoted by S. The signs predicted for the various contributions to the net rotatory strengths of structures 1g and 1h are listed as follows

	1g	1h
Pure configurational	+	-
Pure conformational	-	+
Mixed configurational-conformational	-	-
Pure vicinal	+	-

If  $AA \equiv (S)\text{-pn}$  and if the methyl substituent exhibits a strong preference for being equatorial to the chelate ring rather than axial, then the two most stable isomers of  $\text{Co}((S)\text{-pn})_3^{3+}$  are the D( $\delta\delta\delta$ ) and L( $\delta\delta\delta$ ) forms.<sup>46,47</sup> From our present analysis we predict that the optical activity exhibited by the d-d transitions in the L( $\delta\delta\delta$ ) isomer will be larger than that of the D( $\delta\delta\delta$ ) isomer. The configurational, mixed configurational-conformational, and vicinal contributions are all of the same sign for the L( $\delta\delta\delta$ ) isomer, whereas for the D( $\delta\delta\delta$ ) isomer the mixed configurational-conformational contribution has a sign opposite to the signs of the pure configurational and vicinal contributions.

A similar analysis of the L( $\lambda\lambda\lambda$ ) 1el and D( $\lambda\lambda\lambda$ ) ob isomers of  $\text{Co}((R)\text{-pn})_3^{3+}$  reveals that the signs of the various contributions to the net rotatory strengths are as follows

	L( $\lambda\lambda\lambda$ ) 1el	D( $\lambda\lambda\lambda$ ) ob
Pure configurational	-	+
Pure conformational	+	-
Mixed configurational-conformational	+	+
Pure vicinal	-	+

It is predicted that the largest net rotatory strength should be exhibited by the D( $\lambda\lambda\lambda$ ) ob isomer of  $\text{Co}((R)\text{-pn})_3^{3+}$ . This result is in agreement with the experimental CD data on the complex ions, *d*-[Co((R)-pn)<sub>3</sub>]<sup>3+</sup> and *l*-[Co((R)-pn)<sub>3</sub>]<sup>3+</sup>, which have the D( $\lambda\lambda\lambda$ ) and L( $\lambda\lambda\lambda$ ) isomeric forms, respectively.<sup>40,48,49</sup>

In all the tris complexes considered so far, the ligating atoms were assumed to be located at the vertices of a regular octahedron so that the MA<sub>6</sub> cluster possessed exact O<sub>h</sub> symmetry. The dissymmetry in these structures originates solely from the nonligating parts of the complexes. In structures 1i and 1j the ligating atoms are displaced from their octahedral positions and in both cases the MA<sub>6</sub> clusters are themselves dissymmetric, each possessing only trigonal-dihedral (D<sub>3</sub>) symmetry. To describe these deviations of MA<sub>6</sub> from the octahedral geometry it is not sufficient merely to specify the A-M-A angles in each chelate ring.<sup>50</sup> One must also characterize the distortions in terms of the polar angles  $\theta_A$  and azimuthal angles  $\phi_A$  of each ligator

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

(48) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

(49) Reference 35, Table 5-5.



TABLE IV

	I			II			III		
	1	2	S(I)	3	4	S(II)	5	6	S(III)
	<b>1g, D(<math>\delta\delta\delta</math>) Isomer (1el)</b>								
XY	+	+	+	$\oplus$ vs	$\ominus$	+ vs	$\ominus$	$\oplus$ vs	- vs
Z(X <sup>2</sup> - Y <sup>2</sup> )	$\oplus$	$\oplus$	+ vs	+	+	+	+	+	+
XZ	$\oplus$	$\ominus$ vs	+ vs	-	-	-	$\ominus$ vs	$\oplus$	- vs
Y(Z <sup>2</sup> - X <sup>2</sup> )	-	-	-	$\ominus$	$\oplus$	- vs	-	-	-
YZ	$\oplus$ vs	$\ominus$	+ vs	$\ominus$	$\oplus$ vs	+	+	+	+
X(Y <sup>2</sup> - Z <sup>2</sup> )	+	+	+	+	+	+	$\oplus$	$\oplus$	- vs
	<b>1h, L(<math>\delta\delta\delta</math>) Isomer (ob)</b>								
XY	-	-	-	$\oplus$ vs	$\ominus$	+ vs	$\ominus$	$\oplus$ vs	- vs
Z(X <sup>2</sup> - Y <sup>2</sup> )	$\oplus$	$\ominus$	- vs	+	+	+	+	+	+
XZ	$\oplus$	$\ominus$ vs	+ vs	+	+	+	$\ominus$ vs	$\oplus$	- vs
Y(Z <sup>2</sup> - X <sup>2</sup> )	-	-	-	$\oplus$	$\oplus$	+ vs	-	-	-
YZ	- vs	$\oplus$	- vs	$\oplus$	$\ominus$ vs	+ vs	+	+	+
X(Y <sup>2</sup> - Z <sup>2</sup> )	-	-	-	-	-	-	$\oplus$	$\oplus$	+ vs

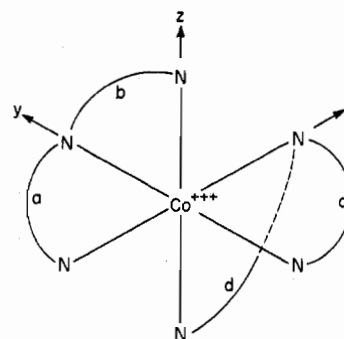
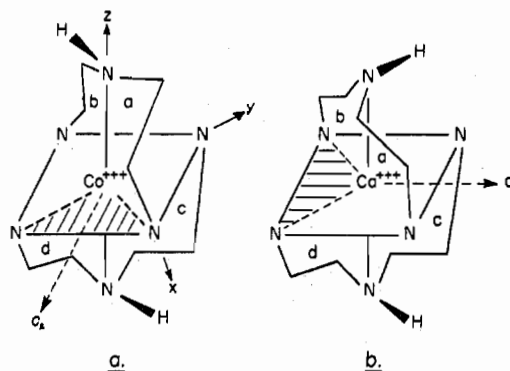
atom as measured with respect to a trigonal-coordinate system (in which the Z axis is coincident with the C<sub>3</sub> axis of the trigonally distorted MA<sub>6</sub> cluster).<sup>17</sup> In octahedral MA<sub>6</sub>, the polar angle is 54.7° for three of the ligator atoms and is 125.3° for the other three, and the six azimuthal angles are given by  $\phi_A = \pm(2n + 1)\pi/6$ ,  $n = 0, 1, 2$  (see ref 17 for a more detailed description). The difference ( $\phi_A - \phi_{A'}$ ), where A and A' label the two ligators of the same chelate ring, is referred to as the *twist* angle  $\omega$ .<sup>50</sup> If the polar angles are 125.3° >  $\theta_A > 54.7^\circ$ , the MA<sub>6</sub> cluster is said to be *compressed* along the trigonal axis. If 125.3° <  $\theta_A < 54.7^\circ$ , the MA<sub>6</sub> cluster is said to be *elongated* along the trigonal axis. In structure 1i,  $\omega < 60^\circ$  and the MA<sub>6</sub> cluster is compressed along the trigonal axis. Structure 1j is elongated along the trigonal axis and  $\omega > 60^\circ$ .

The signs of the functions 9a-9c for the ligating atoms of structures 1i and 1j are given in Table V. The signs

TABLE V

	I		II		III	
	1	2	3	4	5	6
	<b>1i, <math>\omega &lt; 60^\circ</math>, Compressed</b>					
XY	-	-	0	0	0	0
Z(X <sup>2</sup> - Y <sup>2</sup> )	0	0	+	+	+	+
XZ	0	0	+	+	0	0
Y(Z <sup>2</sup> - X <sup>2</sup> )	-	-	0	0	-	-
YZ	0	0	0	0	+	+
X(Y <sup>2</sup> - Z <sup>2</sup> )	-	-	-	-	0	0
	<b>1j, <math>\omega &gt; 60^\circ</math>, Elongated</b>					
XY	+	+	0	0	0	0
Z(X <sup>2</sup> - Y <sup>2</sup> )	0	0	+	-	-	-
XZ	0	0	-	-	0	0
Y(Z <sup>2</sup> - X <sup>2</sup> )	-	+	0	0	+	+
YZ	0	0	0	0	-	-
X(Y <sup>2</sup> - Z <sup>2</sup> )	-	+	+	-	0	0

of the allowed [ $V'_g, V'_u$ ] pair combinations suggest that the signs of the net CD observed for the d-d transitions in complexes with structures 1i and 1j should be identical. Furthermore, we note that all 24 nonzero pair combinations for structure 1i are negative in sign, whereas there are 16 negative and 8 positive pair combinations for structure 1j. The resulting partial cancellation of contributions to the net rotatory strength of structure 1j leads to the prediction that the net optical activity due to inherent configurational dissymmetry in the MA<sub>6</sub> cluster will be larger for trigonal complexes which are compressed along the trigonal axis and in

Figure 3.—Structure of *u-cis*-(+)-D-[Co(dien)<sub>2</sub>]<sup>3+</sup>.Figure 4.—Optical isomers of *trans*-[Co(dien)<sub>2</sub>]<sup>3+</sup>.

which  $\omega < 60^\circ$  than for trigonal complexes which are elongated along the C<sub>3</sub> axis and in which  $\omega > 60^\circ$ .

**B. Bis Complexes with Symmetric Tridentate Ligands, M(AAA)<sub>2</sub>.**—We shall only consider one coordination compound in this class: Co(dien)<sub>2</sub><sup>3+</sup>, where dien ≡ diethylenetriamine. Three geometric isomers of Co(dien)<sub>2</sub><sup>3+</sup> have been isolated.<sup>51</sup> Two of these isomers have C<sub>2</sub> symmetry—the unsymmetrical *cis* (*u-cis*) form and the *trans* form—and each has been resolved into its optical antipodes.<sup>51</sup> The one optical isomer of *u-cis*-[Co(dien)<sub>2</sub>]<sup>3+</sup> is shown in Figure 3, and both optical isomers of *trans*-[Co(dien)<sub>2</sub>]<sup>3+</sup> are shown in Figures 4a and 4b. Keene, Searle, and Mason<sup>52</sup> have reported the CD and absorption spectra of these complexes and have assigned a D( $\Delta$ ) configurational chirality to the *u-cis* isomer shown in Figure 3.

First, we consider the configurational optical activity

(51) F. R. Keene, G. H. Searle, Y. Yoshikawa, A. Imai, and K. Yamasaki, *Chem. Commun.*, 784 (1970).

(52) F. R. Keene, G. H. Searle, and S. F. Mason, *ibid.*, 893 (1970).

(50) K. R. Butler and M. R. Snow, *Inorg. Chem.*, **10**, 1838 (1971).

of the *u-cis*-[Co(dien)<sub>2</sub>]<sup>3+</sup> isomer shown in Figure 3. We shall assume that the CoN<sub>6</sub> cluster has regular *O<sub>h</sub>* symmetry so that the only source of dissymmetry is the distribution of chelate bridging atoms about the metal ion. The *C*<sub>2</sub> axis of the complex is defined by 2<sup>-1/2</sup>·(*X* + *Y*). The perturbation operators *V'*<sub>g</sub> and *V'*<sub>u</sub> must each be invariant to 180° rotation about this axis. We designate these operators by *V'*<sub>g</sub> = *V'*<sub>g</sub>(*t*) + 2<sup>-1/2</sup>[*V'*<sub>g</sub>(*η*) - *V'*<sub>g</sub>(*ξ*)] and *V'*<sub>u</sub> = *V'*<sub>u</sub>(*t*) + 2<sup>-1/2</sup>·[*V'*<sub>u</sub>(*η*) - *V'*<sub>u</sub>(*ξ*)], where the *V'*<sub>g</sub>(*t*), *V'*<sub>g</sub>(*η*), *V'*<sub>g</sub>(*ξ*), *V'*<sub>u</sub>(*t*), *V'*<sub>u</sub>(*η*), and *V'*<sub>u</sub>(*ξ*) functions transform as *xy*, *xz*, *yz*, *z(x<sup>2</sup> - y<sup>2</sup>)*, *y(z<sup>2</sup> - x<sup>2</sup>)*, and *x(y<sup>2</sup> - z<sup>2</sup>)*, respectively. The appropriate pair combinations for determining the sign of the net d-d rotatory strength are, therefore, [*V'*<sub>g</sub>(*t*), *V'*<sub>u</sub>(*t*)], [*V'*<sub>g</sub>(*η*), *V'*<sub>u</sub>(*η*)], and [*V'*<sub>g</sub>(*ξ*), *V'*<sub>u</sub>(*ξ*)]. The signs of these pair combinations for each chelate ring of the *u-cis*-[Co(dien)<sub>2</sub>]<sup>3+</sup> isomer shown in Figure 3 are given in Table VI. Six of the ten nonzero pair

TABLE VI

	Chelate rings			
	a	b	c	d
<i>XY</i>	-	0	-	0
<i>Z(X<sup>2</sup> - Y<sup>2</sup>)</i>	0	-	0	-
<i>XZ</i>	0	0	0	-
<i>Y(Z<sup>2</sup> - X<sup>2</sup>)</i>	-	+	+	0
<i>YZ</i>	0	+	0	0
<i>X(Y<sup>2</sup> - Z<sup>2</sup>)</i>	-	0	+	-

combinations are positive, and the net rotatory strength is predicted to be positive. The configurational effect in the *D* isomer of Co(en)<sub>3</sub><sup>3+</sup> was also predicted to contribute a positive net d-d rotatory strength. Based on our model, therefore, it would seem reasonable to assign a *D*(*Δ*) chirality to the structure shown in Figure 3. Keene, *et al.*,<sup>52</sup> based their assignment on ring-pairing relations. The positive sign of the net d-d rotatory strength predicted from our model is in agreement with the experimental CD spectrum reported by Keene, *et al.*<sup>52</sup>

In considering the two stereoisomers of *trans*-[Co(dien)<sub>2</sub>]<sup>3+</sup> which are shown in Figures 4a and 4b, we first note that if the CoN<sub>6</sub> cluster were regular octahedral, the chelate rings were planar, and the central nitrogen atom of each ligand were unsubstituted (*i.e.*, no hydrogen atom attached), then the overall symmetry of the complex would be *D*<sub>2d</sub> and it would be optically inactive. This suggests that there can be no configurational effect in the *trans*-[Co(dien)<sub>2</sub>]<sup>3+</sup>. However, because of the fact that the chelate rings are puckered (one in each ligand with a *δ* conformation and one in each ligand with a *λ* conformation) and because of the hydrogen substituents on the two central nitrogen atoms, the true symmetry of the complex is *C*<sub>2</sub>. The signs of the [*V'*<sub>g</sub>(*t*), *V'*<sub>u</sub>(*t*)], [*V'*<sub>g</sub>(*η*), *V'*<sub>u</sub>(*η*)], and [*V'*<sub>g</sub>(*ξ*), *V'*<sub>u</sub>(*ξ*)] pair combinations for the structure in Figure 4a are given in Table VII, where the signs for

TABLE VII

	Chelate rings and hydrogen substituents					
	a	H	b	c	H'	d
<i>XY</i>	0	0	0	0	0	0
<i>Z(X<sup>2</sup> - Y<sup>2</sup>)</i>	+	-	+	+	-	+
<i>XZ</i>	+	0	-	0	-	0
<i>Y(Z<sup>2</sup> - X<sup>2</sup>)</i>	+	-	+	+	0	-
<i>YZ</i>	0	-	0	-	0	+
<i>X(Y<sup>2</sup> - Z<sup>2</sup>)</i>	-	0	+	+	-	+

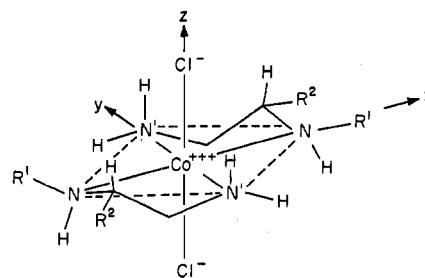


Figure 5.—Structure for complexes I (*R*<sup>1</sup> = methyl, *R*<sup>2</sup> = H), II (*R*<sup>1</sup> = H, *R*<sup>2</sup> = methyl), and III (*R*<sup>1</sup> = *R*<sup>2</sup> = methyl).

rings a-d were obtained by summing over both bridging atoms in each ring. We note that the central *N*-hydrogen substituents are responsible for the net *V'*<sub>g</sub>. However, both the ring bridging atoms and the central *N*-hydrogen contribute to *V'*<sub>u</sub>, but with opposite signs. If the magnitude of the product [*V'*<sub>g</sub>(hydrogens)]·[*V'*<sub>u</sub>(rings)] is larger than that of [*V'*<sub>g</sub>(hydrogens)]·[*V'*<sub>u</sub>(hydrogens)], then a negative net rotatory strength is predicted for the isomer shown in Figure 4a. If the relative magnitude of these products is reversed, then a positive net rotatory strength is predicted for this isomer. Due to the closer proximity of the ring bridging atoms to the metal ion than to the central *N*-hydrogen substituents, it might be expected that |*V'*<sub>u</sub>(rings)| > |*V'*<sub>u</sub>(hydrogens)| and that the isomer in Figure 4a will yield a negative net d-d rotatory strength. Keene, *et al.*,<sup>52</sup> call this the *trans-λ*-NH isomer of Co(dien)<sub>2</sub><sup>3+</sup>.

**C. Trans Bis Complexes with Symmetric Bidentate Ligands, *trans*-[M(AA)<sub>2</sub>X<sub>2</sub>].**—From this class of compounds we select three complex ions whose d-d circular dichroism spectra have been thoroughly studied by Mason,<sup>52</sup> by Hawkins,<sup>53</sup> and by Saburi, *et al.*<sup>54</sup> These complexes are as follows: *trans,trans*-dichlorobis(*N*-methyleneethylenediamine)cobalt(III), [Co(Meen)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (I); *trans*-dichlorobis(*S*)-propylenediamine)cobalt(III), [Co(*S*)-pn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (II); *trans*-dichlorobis(*N*-methyl(*S*)-propylenediamine)cobalt(III) (III). Structures for these complexes are displayed in Figure 5. Each of the structures shown in Figure 5 has *C*<sub>2</sub> symmetry, the symmetry axis being coincident with the *Z* axis. Of the six sector rules given in (8a-c) and (9a-c), only (8c) and (9c) are appropriate for this symmetry since only the functions which transform as *T*<sub>1g</sub>(*Z*), *T*<sub>1u</sub>(*Z*), *T*<sub>2g</sub>(*t*), or *T*<sub>2u</sub>(*t*) under the *O<sub>h</sub>* group operations are invariant to 180° rotation about the *Z* axis. In the following analysis only expression 9c will be used. It is easy to demonstrate that expression 8c leads to the same qualitative results but that the magnitudes of the associated crystal-field potential energy terms are much smaller.

The signs of the *XY* and *Z(X<sup>2</sup> - Y<sup>2</sup>)* functions for the perturber sites in compounds I-III (shown in Figure 5) are given in Table VIII, where only the principal perturber sites on ring 1 of each complex are included (since the signs for the corresponding perturber sites on ring 2 are the same). Note that only the hydrogen atoms which occupy positions axial to the ring are listed since the equatorial hydrogen atoms all lie very near to the nodal planes of the functions *XY*

(53) C. J. Hawkins, *Chem. Commun.*, 777 (1969).

(54) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, 9, 1476 (1970).

TABLE VIII

	I		II		III	
	$Z(X^2 - Y^2)$	$XY$	$Z(X^2 - Y^2)$	$XY$	$Z(X^2 - Y^2)$	$XY$
H <sub>a</sub> (N1)	0	-	0	-	0	-
CH <sub>3</sub> (N1)	-	+	0	0	-	+
CH(1)	+	+	+	+	+	+
CH <sub>3</sub> (C1)	0	0	+	-	+	-
CH <sub>2</sub> (1)	+	+	+	+	+	+
H <sub>a</sub> (N'1)	0	-	0	-	0	-

and  $Z(X^2 - Y^2)$ . If, in the Meen (I) and Mepn (III) complexes, the *N*-methyl groups are the principal perturber groups, then  $V'_g(\text{net}) < 0$ ,  $V'_u(\text{net}) > 0$ , and the net sign is -. For complex II,  $V'_g(\text{net}) > 0$ ,  $V'_u(\text{net}) < 0$ , and the net sign is again -. The net d-d rotatory strength is predicted, therefore, to be negative for all three complexes, I-III, shown in Figure 5. This result is in agreement with the experimental CD data reported by Mason<sup>32</sup> and by Saburi, *et al.*<sup>54</sup>

An additional feature of the CD spectra observed for complexes I-III needs to be explained, however. Whereas the sign pattern in the CD spectra (from 700 to 400 nm) of complexes I and III is + - + (net -) for the E(T<sub>1g</sub>), A(T<sub>1g</sub>), and E(T<sub>2g</sub>) bands, the sign pattern for complex II is - + + (net -). It is nearly certain that the relative energies of the A and E components of the T<sub>1g</sub> excited state are not altered. Instead, it appears that the first-order contribution to the rotatory strengths of the E band in complex II is opposite in sign to the first-order rotatory strength of the E band in complexes I and III. The same alteration in sign would also occur for the A band since the sum of the first-order rotatory strengths must vanish (or be vanishingly small) on our model. The sign of the first-order contribution is determined by the sign of  $V'_u$ , whereas the sign of the second-order rotatory strength and of the net d-d rotatory strength is determined by the sign of the product function  $V'_g V'_u$ . For complexes I and III,  $V'_u > 0$  and  $V'_g V'_u < 0$ ; for complex II,  $V'_u < 0$  and  $V'_g V'_u < 0$ .

Unlike the tris complexes of bidentate ligands and the bis complexes of tridentate ligands, the trans bis complexes of diamine ligands are somewhat more labile conformationally. For this reason, the application of sector rules for extracting stereochemical information from the sign pattern of CD spectra is subject to considerable ambiguity for the complexes considered in this section.

**D. Tris Complexes with Unsymmetric Bidentate Ligands, M(AB)<sub>3</sub>.**—From this class of compounds we consider the four isomeric tris complexes formed by Co(III) and  $\alpha$ -amino acids. Two of these isomers are commonly referred to as meridional or  $\alpha$  forms and the other two are called facial or  $\beta$  forms. The four stereoisomeric structures of the tris complex of *L*-alanine with Co(III) are shown in Figure 6. We consider first the  $\beta$  isomers shown in Figures 6c and 6d. For these structures, the obvious sector rule expressions to use are (8a-c) since the largest perturbations on the zeroth-order  $O_h$  crystal-field are expected to arise from the electrostatic or electrodynamic dissimilarities between the ligating amino groups and the ligating carboxylate anions. These perturbations will transform as  $X$ ,  $Y$ , or  $Z$  depending on which (O<sup>-</sup>, N) pairs are considered. In other words, the dissimilarities between the ligating N atoms and the ligating O<sup>-</sup> ions are expected to pro-

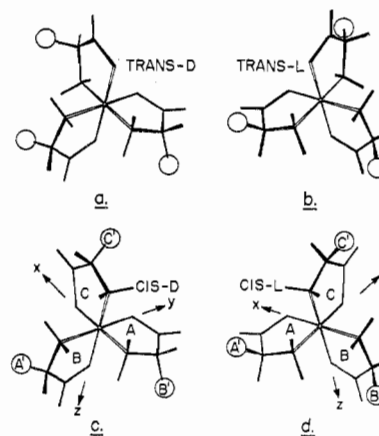


Figure 6.—Isomeric structures of tris(*L*-alaninato)cobalt (III): (a) trans-D or  $\alpha$  isomer; (b) trans-L or  $\alpha'$  isomer; (c) cis-D or  $\beta$  isomer; (d) cis-L or  $\beta'$  isomer.

vide the largest ungerade parts ( $V'_u$ ) of the perturbation, and these transform as  $X$ ,  $Y$ , or  $Z$ . Each  $\beta$  isomer of Co(*L*-ala)<sub>3</sub> is assumed to have exact  $C_3$  symmetry so that the lowest order term in  $V'_u$  transforms as  $3^{1/2}(X + Y + Z)$ . The lowest order term in  $V'_g$  which, when combined with  $V'_u$ , yields expressions 8a-c transforms as  $3^{1/2}[YZ(Y^2 - Z^2) + XZ(Z^2 - X^2) + XY(X^2 - Y^2)]$ .

To ascertain the signs of the net d-d rotatory strengths for the D-cis and L-cis isomers shown in Figures 6c and 6d, we first partition the ligand environment of the metal ion into nine principal perturber groups and then apply expressions 8a-c. The carboxylate groups are represented by A, B, and C, the amino groups by N<sub>A</sub>, N<sub>B</sub>, and N<sub>C</sub>, and the C <sub>$\alpha$</sub> HCH<sub>3</sub> groups by A', B', and C'. The signs of the terms in expressions 8a-c for these perturber groups can be determined from Table IX. The encircled signs indicate

TABLE IX

	X	YZ- (Y <sup>2</sup> - Z <sup>2</sup> )	Y	XZ- (Z <sup>2</sup> - X <sup>2</sup> )	Z	XZ- (X <sup>2</sup> - Y <sup>2</sup> )
D-Cis or $\beta$ Isomer						
A	⊖	0	+	0	0	+
N <sub>A</sub>	-	0	0	0	0	0
B	0	+	⊖	0	+	0
N <sub>B</sub>	0	0	-	0	0	0
C	+	0	0	+	⊖	0
N <sub>C</sub>	0	0	0	0	-	0
A'	-	⊖*	⊕	⊕*	⊕*	-
B'	⊕*	-	-	⊕*	⊕	⊕*
C'	⊕	⊕*	⊕*	-	-	⊕*
L-Cis or $\beta'$ Isomer						
A	+	0	⊖	0	0	-
N <sub>A</sub>	0	0	-	0	0	0
B	⊖	0	0	-	+	0
N <sub>B</sub>	-	0	0	0	0	0
C	0	-	+	0	⊖	0
N <sub>C</sub>	0	0	0	0	-	0
A'	⊕	⊕*	-	⊕*	⊕*	+
B'	-	⊕*	⊖*	+	⊕	⊕*
C'	⊖*	+	⊕	⊕*	-	⊕*

that the magnitudes of the corresponding terms in the potential energy expression are small due to the perturber sites being located very near a nodal plane. The signs marked with asterisks correspond to terms which would be zero if the  $\alpha$  carbons were not asymmetric centers (*i.e.*, these terms would be zero for Co(gly)<sub>3</sub>). We have assumed chelate ring planarity.

So far in our applications of expressions 8a-c and 9a-c to the net d-d rotatory strengths of chiral six-coordinate Co(III) complexes we have been able to ignore the signs of the charge parameters,  $Q_p$ , for the perturber sites  $p$  (see eq 3). In the present case, however, we must make explicit assumptions about the signs of these parameters. If the  $\text{CoO}_3\text{N}_3$  cluster of *cis*- $\text{Co}(\text{L-ala})_3$  contributes a term to  $V'_u$  which transforms as  $3^{1/2}(X + Y + Z)$ , and the O atoms are located along the positive  $X$ ,  $Y$ , and  $Z$  axes and the N atoms along the negative  $X$ ,  $Y$ , and  $Z$  axes, then the Co-O and Co-N interactions must be assigned charge parameters which are opposite in sign. If we assign  $Q < 0$  for all Co-A, -B, and -C interactions and  $Q > 0$  for all Co-A', -B', -C', -N<sub>A</sub>, -N<sub>B</sub>, and -N<sub>C</sub> interactions, then we must change the signs for all entries in the above tables for perturbers A, B, and C. Ignoring the encircled signs, we find that the net sign of the allowed pair combinations [ $V'_g$ ,  $V'_u$ ] for the D-*cis* isomer is +, and the net sign for the L-*cis* isomer is -. These results pertain only to the configurational contributions to the net d-d rotatory strength. To determine the signs of the vicinal effects, we must construct the pair combinations which include at least one asterisked quantity. The vicinal effect for both the D-*cis* and L-*cis* isomers is -.

In summary, the signs of the d-d rotatory strengths for the D-*cis* and L-*cis* isomers of  $\text{Co}(\text{L-ala})_3$  are predicted to be

	D-Cis ( $\beta$ )	L-Cis ( $\beta'$ )
Configurational	+	-
Vicinal	-	-

The net d-d rotatory strength is predicted to be negative for the L-*cis* isomer and positive for the D-*cis* isomer. Furthermore, the absolute magnitude of the net d-d rotatory strength of the L-*cis* isomer is predicted to be larger than that of the D-*cis* isomer, the difference between them being equal to 2 times the vicinal effect contribution. These results are in agreement with the experimentally observed CD spectra of the D-*cis* and L-*cis* isomers of  $\text{Co}(\text{L-ala})_3$ .<sup>55</sup> The L-*cis* isomer exhibits a net negative CD spectrum in the d-d region which is more intense than the net positive d-d spectrum exhibited by the D-*cis* isomer.<sup>55</sup> Additional experimental evidence that the vicinal and configurational contributions to the rotatory strength are of like sign for the L-*cis* isomers but of opposite sign for the D-*cis* isomers is presented in the work of Shibata, Nishikawa, and Nishida<sup>56</sup> on the complexes D- $[\text{Co}(\text{L-val})(\text{gly})_2]$ , L- $[\text{Co}(\text{L-val})(\text{gly})_2]$ , D- $[\text{Co}(\text{L-val})_2(\text{gly})]$ , and D- $[\text{Co}(\text{L-val})_2(\text{L-ala})]$ , where L-val  $\equiv$  L-valinato anion. Among these complexes, the L isomer exhibits the most intense d-d CD (negative in sign), and the net CD intensities (all positive in sign) of the D isomers decrease as the number of asymmetric centers increases. That is, D- $[\text{Co}(\text{L-val})_2(\text{L-ala})]$  exhibits the least intense and D- $[\text{Co}(\text{L-val})(\text{gly})_2]$  the most intense net positive CD among the D isomers. These results suggest that the vicinal and configurational effects have like signs in the L isomer but opposite signs in the D isomers.

Based on the sector rule expressions 8a-c, the vicinal effect contributions to the net d-d rotatory strength of  $\beta$

isomers by D-amino acids should be opposite in sign to those of L-amino acids; that is, the vicinal contribution should be positive in sign. There is no definitive experimental evidence that this is, indeed, the case. However, the CD spectra of L- $[\text{Co}(\text{L-val})_2(\text{D-ala})]$  and of D- $[\text{Co}(\text{L-ala})_2(\text{D-ala})]$  are suggestive of the accuracy of this prediction.<sup>56</sup>

The two meridional or  $\alpha$  forms of  $\text{Co}(\text{L-ala})_3$  are shown in Figures 6a and 6b. As in the  $\beta$  isomers, the  $\text{CoO}_3\text{N}_3$  cluster in the  $\alpha$  isomers is noncentrosymmetric. However, whereas the  $\text{CoO}_3\text{N}_3$  cluster in the  $\beta$  isomers is devoid of inversion symmetry at the metal ion in the  $X$ ,  $Y$ , and  $Z$  directions, the  $\text{CoO}_3\text{N}_3$  cluster of the  $\alpha$  isomers lacks inversion symmetry at Co in only one direction. One expects, therefore, that an ungerade "crystal field"  $V'_u$  which transforms as  $3^{1/2}(X + Y + Z)$  would be considerably weaker in the  $\alpha$  isomers than it is in the  $\beta$  isomers. Assuming this to be the case, the appropriate sector rule expressions for the  $\alpha$  isomers of  $\text{Co}(\text{L-ala})_3$  are expected to be (9a-c), rather than (8a-c). Application of (9a-c) to the trans-D (or  $\alpha$ ) and trans-L (or  $\alpha'$ ) isomers of  $\text{Co}(\text{L-ala})_3$  leads to the results

	Trans-D ( $\alpha$ )	Trans-L ( $\alpha'$ )
Configurational	+	-
Vicinal	+	+

For the  $\alpha$  forms of  $\text{Co}(\text{L-ala})_3$ , we predict that the trans-D ( $\alpha$ ) isomer will exhibit the more intense net d-d CD since for this structure the configurational and vicinal effects make contributions of the same sign. The trans-L ( $\alpha'$ ) isomer is expected to show a less intense net d-d CD. These results are in qualitative agreement with the experimental CD studies on the  $\alpha$  forms of  $\text{Co}(\text{L-ala})_3$  reported by Denning and Piper.<sup>55</sup>

## V. Discussion

The principal objective of this study was to develop a procedure by which the observables of the d-d circular dichroism spectra of chiral, six-coordinate Co(III) complexes could be correlated with specific stereochemical features of the ligand environment. The procedure which resulted from this study relates the sign of the *total* or *net* d-d rotatory strength (or the sign of the algebraic sum of the d-d CD band areas) to the distribution of ligand perturber sites (atoms or groups of atoms) about the metal ion. The theoretical underpinnings of the procedure are provided by the ligand-field theory of d-d spectroscopic states in metal complexes and by the one-electron theory of optical activity in symmetric chromophores. The unperturbed chromophoric group,  $\text{CoL}_6$ , is assumed to possess exact  $O_h$  symmetry so that any optical activity observed in the d-d transition must arise from chiral perturbations on the d-d states from extrachromophoric source.

Application of first-order perturbation theory to this problem yields a relationship between *net* d-d rotatory strengths and ligand geometry which exhibits an  $R_p^{-10}$  dependence on metal-perturber radial distances and which requires (on the ligand-field model) that the basis orbitals on the metal ion include a  $Y_7^m$  function. Taking the perturbation treatment to second order in the wave functions, the electric and magnetic transition dipoles, and the rotatory strengths, a relationship between the *net* d-d rotatory strength and ligand geometry was discovered which requires only s-, p-, and

(55) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).

(56) M. Shibata, H. Nishikawa, and Y. Nishida, *ibid.*, **7**, 9 (1968).

d-type orbitals on the metal ion and which exhibits only an  $R_p^{-3}R_{p'}^{-4}$  dependence on metal-perturber radial distances (where  $p$  and  $p'$  label perturber sites and  $p = p'$  or  $p \neq p'$ ). First-order contributions to the *net* d-d rotatory strength are negligible due to the steep inverse dependence on  $R_p$  and the necessity of including  $Y_r^m$  functions in the basis set for the spectroscopic states of the metal ion. Second-order contributions will completely determine the signs and magnitudes of *net* d-d rotatory strengths.

It must be pointed out that first-order contributions generally dominate the rotatory strength parameters of individual d-d transitions (or the components of degenerate d-d transitions), although their sum over the complete manifold of d-d transitions is vanishingly small. If it were always possible to resolve and correctly identify the individual d-d transitions in chiral complexes, then a spectra-structure relationship based on the sign and intensity of just one CD band would be preferred over a relationship based on the sign and magnitude of the *net* CD. It is generally the case, however, that band assignments cannot be made without serious ambiguities. With the exception of a few complexes in which the  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  and first charge-transfer bands overlap, it is usually a simple matter to determine the *net* CD associated with the d-d transitions of Co(III) compounds.

Complete neglect of the first-order contributions to the *net* rotatory strength of six-coordinate Co(III) complexes implies rejection of the so-called octahedral sector or regional rule,  $XYZ(X^2 - Y^2)(Z^2 - Y^2) \cdot (Z^2 - X^2)$ . We do not reject the utility or possible reliability of this rule in obtaining stereochemical information from CD spectra; rather, we assert that such a rule has no obvious theoretical basis in the one-electron, static-coupling theory of optical activity or in ligand-field theory. This octahedral regional rule has been used with some success in interpreting the CD spectra of several classes of Co(III) systems.<sup>10,31</sup> However, its generality is somewhat questionable due to its apparent failure when applied to tris complexes with planar, unsubstituted, symmetric bidentate ligands (e.g.,  $\text{Co}(\text{ox})_3^{3-}$ ).

The sector rules which apply to the second-order con-

tributions to the *net* d-d rotatory strengths appear to have general applicability, although their application is not as simple as that of the first-order octahedral rule. Use of expressions 8a-c and 9a-c as sector rules requires that the positional coordinates of pairs of perturber sites be considered rather than the coordinates of just one site at a time. When, for a given complex, there are pair combinations [ $V'_g, V'_u$ ] which have opposite signs, one must decide upon the relative magnitudes of the opposing contributions. This can be done either on the basis of relative metal-perturber radial distances or by estimating the relative magnitudes of the perturber charge parameters,  $Q_p$ .

The systems considered in section IV represent only a small number of the Co(III) complexes to which expressions 8a-c and 9a-c can be applied reliably as sector rules. Except for those systems in which there are strong ungerade distortions within the  $\text{CoL}_6$  cluster (such as there are in the  $\text{CoO}_3\text{N}_3$  cluster of  $\beta\text{-Co}(\text{L-ala})_3$ ), the rule given by expressions 9a-c is the preferred one and is most generally applicable. From the results given in section IV it appears that the second-order mixed sector rules can be used successfully to ascertain the signs of the rotatory strengths contributed by various "sources" or "kinds" of dissymmetry in the ligand environment. For example, the difference in the absolute magnitudes of the *net* CD observed for the  $\text{D}(\lambda\lambda\lambda)$  and  $\text{L}(\lambda\lambda\lambda)$  isomers of  $\text{Co}((R)\text{-pn})_3^{3+}$  can be explained in terms of the relative signs of the configurational, conformational, and vicinal effects in these complexes. A similar explanation is provided for the observed difference in *net* CD intensities of the  $\beta\text{-Co}(\text{L-ala})_3$  and  $\beta'\text{-Co}(\text{L-ala})_3$  complexes.

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