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Sector Rules and the Circular Dichroism of Ligand Field Bands in Transition Metal Complexes[1]

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The circular dichroic properties of the ligand field bands in transition metal complexes are examined within the framework of the one-electron theory of optical activity. Special emphasis is placed on the sector rules which can be used to correlate the stereochemical features of the metal complexes with the circular dichroism spectra associated with their ligand field transitions. Expressions for the rotatory strength are developed to second order in perturbation theory. The zeroth-order basis states in the perturbation expansion are assumed to be eigenstates of either an octahedral (O_h) or tetragonal (D_{4h}) ligand field Hamiltonian operator. The sector rules, therefore, are applicable to dissymmetric complexes which have "nearly" D_{4h} or O_h symmetry.

I. Introduction

Sector or regional rules, which relate the signs of the observed Cotton effects and circular dichroism (CD) bands to specific structural features in optically active systems, have played an essential role in the use of optical rotatory dispersion (ORD) and CD for elucidating the stereochemistry of organic compounds. These rules have been most successfully applied to the CD spectrum associated with the n → π^* transition in the carbonyl chromophore of organic ketones and aldehydes.[2] Their applications to the CD spectra of other transitions in the carbonyl group and to other chromophores of organic systems have been extensively studied but with considerably less success than was achieved in the n → π^* carbonyl case. The primary limitation to their utility is that the transitions responsible for the observed CD bands must be well characterized with respect to their electronic origins and symmetries. For example, the 300-nm band in the absorption and CD spectra of carbonyl compounds is known to be an n → π^* transition localized in the carbonyl chromophore which is magnetic dipole allowed and electric dipole forbidden with respect to the C_{2v} local symmetry of the carbonyl group. The electronic transitions in most other organic chromophores are less well characterized and unambiguous applications of sector rules are somewhat more difficult. Sector rules are based on theoretical models which assume some *a priori* knowledge about the electronic distributions in the ground and excited states involved in the absorption processes giving rise to circular dichroism.[3] In the absence of accurate electronic wave functions or without a detailed characterization of the electronic absorption spectrum of an optically active system, this knowledge does not exist and sector rules are of little use.

Sector rules for making correlations between the CD spectra and structural features of optically active transition metal complexes have been of particular interest to inorganic chemists in recent years.[4-13] The ligand field (d → d) transitions in these systems are of special interest for developing viable theoretical models of optical activity because (a) their absorption bands lie in the experimentally accessible near-infrared, visible, and near-ultraviolet regions of the spectrum, (b) they are localized in a group with high inherent symmetry, and (c) their optical absorption properties indicate that they are only weakly influenced by the ligand environment beyond the ML_n cluster (M = metal atom, L = ligating atoms). Furthermore, the ligand field bands are, in general, well separated from those which arise from charge-transfer processes and intraligand transitions in complex ions of the first transition series. In most systems of interest, the extinction coefficients for the d → d bands are usually <100 and seldom >400. Furthermore, they gain most of their intensity by the Herzberg–Teller vibronic mechanism and only 5 or 10%, in most instances, from static ungerade components of the ligand field. These results suggest that the "effective" symmetry of the ML_n chromophore deviates only slightly from octahedral O_h ($n = 6$) or tetragonal D_{4h} ($n = 4$) in most systems of interest here. If we accept this to be the case, then in any quantum mechanical description of the overall complex we can represent interactions between the ML_n cluster and other parts (nonligating) of the complex as small perturbation terms in the total Hamiltonian of the system. Additionally, small distortions of the ML_n cluster from strict O_h or D_{4h} symmetry can be treated as perturbations.

It would appear that in transition metal complexes all the conditions necessary for deriving a set of sector rules for the d → d CD spectra are satisfied. These conditions are (a) a set of transitions whose electronic origins are well characterized and whose intensity-gaining mechanism is identified, (b) chromophoric groups that have well-defined "effective" symmetries, and (c) weak interactions between the chromophoric group and the ligand environment. There are, however, several complications in these systems which make the development of simple sector rules somewhat

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[1] This work was supported in part by the Petroleum Research Fund (PRF No. 2022-G2) and the National Science Foundation (NSF Institutional Grant to the University of Virginia).

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difficult. In high-symmetry environments (*e.g.*, O_h or D_{4h}), many of the excited states and, in some cases, the ground state of the d^n electronic configurations in transition metal ions are orbitally degenerate. These orbital degeneracies make the system subject to Jahn–Teller distortions. The orbital triplets occurring in a ML_6 octahedral cluster can couple to a t_{2g} vibrational mode or an e_g vibrational mode or to both the t_{2g} and e_g vibrational modes simultaneously. The orbital doublets in ML_6 can only couple to the e_g vibrational mode to produce a Jahn–Teller distortion. In a tetragonal ML_4 cluster, both Jahn–Teller distortions (in the orbital doublet states) and pseudo Jahn–Teller interactions (interactions between two nearly degenerate states) are likely to occur. In the discussion that follows, we shall ignore these vibronic interactions. Our justification for neglecting them is twofold: (a) we are primarily interested in the total or net CD associated with a particular transition and not in the detailed band shapes or vibrational structure in the CD spectra; (b) the perturbations arising from the low-symmetry components of the ligand fields are likely to be stronger than any Jahn–Teller interactions in the systems of interest. A detailed account of how vibronic interactions can influence the CD spectra of metal complexes will be given elsewhere.[14] Their neglect has no effect on the results presented in the present study.

II. Theory

Detailed theoretical studies of sector rules for pseudotetragonal and for trigonal dihedral metal complexes have recently been reported.[15,16] In these studies it was concluded that sector rules based on the static one-electron model of optical activity are identical with those derived from the dynamic electric dipole–magnetic dipole coupled oscillator model. In this paper we adopt a static one-electron model in which the chromophoric electron is localized on the metal atom. The dynamical behavior of this electron is determined to zeroth order by the total potential field of the undistorted ML_n cluster and to higher orders by the potential field of the nonligating parts of the complex and by static distortions (nonvibronic) within the ML_n cluster. Spin–orbit interactions are neglected in our model.

The ligands in the systems of interest here are either bidentate or tridentate, and the nonligating environment can, therefore, be separated into chelate ring atoms (bridging atoms) and ring substituent groups or atoms. We shall designate the ring perturber sites by t and the substituent perturber sites by s. The total Hamiltonian for the complex is partitioned as

$$H = H_0 + H_t + H_s + V_t + V_s + V_{ts} + V_L \quad (1)$$

where H_0 is the Hamiltonian for an isolated, undistorted ML_n cluster of O_h or D_{4h} symmetry; H_t and H_s are the Hamiltonians for the isolated t and s groups, respectively; V_t and V_s are interaction potentials between the metal chromophore and the t and s groups, respectively; V_{ts} is an interaction between the t and s groups; and V_L represents a distortion potential in the ML_n cluster due to any distortions of the ML_n framework from O_h or D_{4h} symmetry. The total Hamiltonian which determines the behavior of the chromophoric d electrons on the metal atom is given by

$$H_m = H_0 + V_t + V_s + V_L \quad (2)$$

H_0 is taken as our zeroth-order Hamiltonian and V_t, V_s, and V_L are treated as small perturbations. We shall represent the gerade eigenstates of H_0 by F_{gi} and the ungerade eigenstates by F_{uj}.

Suppose that we are interested in calculating the rotatory strength of the transition $F_{g0} \rightarrow F_{g1}$. If this transition is magnetic dipole allowed, then the first-order rotatory strength is expressed on the one-electron model as

$$R'_{0,1} = \mathrm{Im}\Big[\sum_j \langle F_{g0}|\vec{\mu}|F_{uj}\rangle \cdot \langle F_{g1}|\vec{m}|F_{g0}\rangle\langle F_{uj}|V|F_{g1}\rangle / \Delta E_{1j} + \sum_j \langle F_{uj}|\vec{\mu}|F_{g1}\rangle \cdot \langle F_{g1}|\vec{m}|F_{g0}\rangle\langle F_{uj}|V|F_{g0}\rangle / \Delta E_{0j}\Big] \quad (3)$$

where $\vec{\mu}$ is the electric dipole moment operator, $\vec{m}$ is the magnetic dipole moment operator, ΔE_{1j} and ΔE_{0j} are the energy differences between the F_{uj} state and the F_{g1} and F_{g0} states, respectively, and

$$V = \sum_t V_t + \sum_s V_s + V_L \quad (4)$$

In order for the electric dipole and magnetic dipole transition moments in (3) to have parallel components (*i.e.*, to ensure that their scalar product is nonvanishing) the direct product of their irreducible representations in the group of H_0 must contain the pseudoscalar irreducible representation Γ_{ps}. That is, $\Gamma_\mu \cdot \Gamma_m$ must include Γ_{ps}. In order for the first term of (3) to be nonvanishing it is further required that $\Gamma_{g1} \cdot \Gamma_{uj} = \Gamma_{ps}$ and that $\Gamma_V = \Gamma_{ps}$. In order for the second term in (3) to be nonvanishing, it is necessary that $\Gamma_{g0} \cdot \Gamma_{uj} = \Gamma_{ps}$ and that $\Gamma_V = \Gamma_{ps}$.

If we assume that the undistorted ML_n cluster has D_{4h} symmetry, then $\Gamma_V = \Gamma_{ps} = A_{1u}$ of the D_{4h} point group. Now it is necessary to find the components of V that transform as A_{1u} under the symmetry operations of the D_{4h} point group. If we express each potential energy function in (4) as an expansion in spherical harmonic functions about an origin located at the metal atom, then the first terms in the expansions that transform as A_{1u} in D_{4h} are given by

$$V' = r^5 \sum_t K_t X_t Y_t Z_t (X_t^2 - Y_t^2)/R_t^{11} + r^5 \sum_s K_s X_s Y_s Z_s (X_s^2 - Y_s^2)/R_s^{11} + r^5 \sum_L K_L X_L Y_L Z_L (X_L^2 - Y_L^2)/R_L^{11} \quad (5)$$

where r is the radial coordinate of the chromophoric electron; K_t, K_s, and K_L are functions of the electron angular coordinates and of the static charge distributions on the perturber sites; X_t, Y_t, and Z_t are the Cartesian positional coordinates of the t^th^ perturber site in a coordinate system whose origin is at the metal atom, and R_t is the radial distance between the t^th^ site and the metal atom. The sum Σ_L is taken over all ligating atoms which are distorted from the tetragonal geometry.

Equation 5 is an expression of the hexadecant rule which has been applied to the CD spectra of pseudotetragonal complexes by several workers.[4–13,15] The functions of electron angular coordinates in V' can be

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expressed in terms of the spherical harmonics, $2^{-1/2}\cdot(Y_5^{-4} - Y_5^{4})$. Since the basis states F_{g0} and F_{g1} are constructed from d orbitals ($l = 2$) and the perturbation operator V' is a function of $(Y_5^{-4} - Y_5^{4})$, it is clear that the mixed-in states F_{uj} must be constructed from basis orbitals with $l \geqslant 3$. In order for the matrix elements $\langle F_{uj}|V'|F_{g1}\rangle$ and $\langle F_{uj}|V'|F_{g0}\rangle$ to be nonvanishing, $l(F_{uj}) + l(F_{g1}) \geqslant l(V')$ and $l(F_{uj}) + l(F_{g0}) \geqslant l(V')$, respectively. This means that V' cannot promote d–p mixing in the metal chromophore, but it can promote d–f mixing.

If we assume that the undistorted ML_n cluster has octahedral symmetry, then $\Gamma_V = \Gamma_{ps} = A_{1u}$ of the octahedral point group. In this case if we expand V in a spherical harmonic basis about the metal atom, the first term to transform as A_{1u} in O_h has $l = 9$. The mixed-in oribtals must now be of the order $l \geqslant 7$. At this point, our model carried to first order becomes absurd. It is necessary, therefore, to carry our perturbation treatment to second order.[17]

We approximate the eigenstates of H_m by expanding them in a perturbation series in which the eigenstates of H_0 form the expansion basis set and V is the perturbation operator. If we take this perturbation treatment to second order in the wave functions, then both the electric and magnetic dipole transition moments can be obtained to second order. Furthermore, the rotatory strength can be obtained to second order completely. Third- and fourth-order terms for the rotatory strength can also be obtained but these are incomplete unless the wave functions are developed up to fourth order. The second-order contributions to the rotatory strength are given by

$$R''_{0,1} = \mathrm{Im}\sum_i\sum_j [\mathbf{P}_{0j}\cdot\mathbf{M}_{i0}V_{uj1}V_{gi1}/\Delta E_{1j}\Delta E_{1i} \quad (6a)$$

$$+\mathbf{P}_{j1}\cdot\mathbf{M}_{1i}V_{uj0}V_{gi0}/\Delta E_{0j}\Delta E_{0i} \quad (6b)$$

$$+\mathbf{P}_{j1}\cdot\mathbf{M}_{i0}V_{uj0}V_{gi1}/\Delta E_{0j}\Delta E_{1i} \quad (6c)$$

$$+\mathbf{P}_{0j}\cdot\mathbf{M}_{1i}V_{uj1}V_{gi0}/\Delta E_{1j}\Delta E_{0i} \quad (6d)$$

$$+\mathbf{P}_{ij}\cdot\mathbf{M}_{10}V_{uj1}V_{gi0}/\Delta E_{1j}\Delta E_{0i} \quad (6e)$$

$$+\mathbf{P}_{ji}\cdot\mathbf{M}_{10}V_{uj0}V_{gi1}/\Delta E_{0j}\Delta E_{1i} \quad (6f)$$

$$+\mathbf{P}_{j1}\cdot\mathbf{M}_{10}V_{uji}V_{gi0}/\Delta E_{0i}\Delta E_{0j} \quad (6g)$$

$$+\mathbf{P}_{0j}\cdot\mathbf{M}_{10}V_{uji}V_{gi1}/\Delta E_{1i}\Delta E_{1j} \quad (6h)$$

$$-\mathbf{P}_{j1}\cdot\mathbf{M}_{10}V_{uj0}V_{g00}/\Delta E_{0j}^2 \quad (6i)$$

$$-\mathbf{P}_{0j}\cdot\mathbf{M}_{10}V_{uj1}V_{g11}/\Delta E_{1j}^2] \quad (6j)$$

P and **M** are, respectively, the electric and magnetic dipole transition moments between the basis states (F_{gi}, F_{uj}); V_u and V_g are, respectively, the ungerade and gerade components of the potential energy function V, and the perturbation matrix elements are defined according to the following examples: $V_{g0i} = \langle F_{g0}|V_g|F_{gi}\rangle$ and $V_{u0j} = \langle F_{g0}|V_u|F_{uj}\rangle$. Terms 6a–d are obtained from the products between first-order electric dipole and first-order magnetic dipole transition moments. Terms 6e–j result from products between second-order electric dipole transition moments and the zeroth-order magnetic dipole transition moment. Terms 6a–f are obtained with first-order wave functions, and terms 6g–j require second-order wave functions.

If the summations in eq 6 are taken over a complete set of states (i, j), then the vanishing or nonvanishing nature of each term in (6) can be determined by a simple "selection rule" derived from the symmetry properties of the operators $\vec{\mu}$, $\vec{m}$, V_g, and V_u. The "selection rule" is $\Gamma(V_u)\cdot\Gamma(V_g) = \Gamma_{ps}$. The direct product between the irreducible representations of V_u and V_g in the point group of H_0 must include the pseudoscalar representation of this group. The general proof for this selection rule will not be given here. One is referred to ref 15 for this proof. The group theoretical basis for the selection rule can be most easily demonstrated by consideration of (6a). First, we know that $\Gamma_0\cdot\Gamma_u\cdot\Gamma_j = \Gamma_i\cdot\Gamma_m\cdot\Gamma_0 = \Gamma_{ps}$ (totally symmetric representation) must be satisfied to ensure that the integrals $\mathbf{P}_{0j}$ and $\mathbf{M}_{i0}$ not vanish on symmetry grounds. Second, in order that the scalar product $\mathbf{P}_{0j}\cdot\mathbf{M}_{i0}$ not vanish, $\Gamma_\mu\cdot\Gamma_m = \Gamma_{ps}$. It follows, therefore, that $\Gamma_j\cdot\Gamma_i = \Gamma_{ps}$. For the perturbation matrix elements we require that $\Gamma_j\cdot\Gamma_1\cdot\Gamma(V_u) = \Gamma_i\cdot\Gamma_1\cdot\Gamma(V_g) = \Gamma_{ts}$ and $\Gamma_j\cdot\Gamma_i = \Gamma_{ps}$. It follows that $\Gamma(V_u)\cdot\Gamma(V_g) = \Gamma_{ps}$. We now have a "selection rule" from which second-order sector rules can be derived.

First we shall consider an undistorted ML_n cluster with D_{4h} symmetry. We expand both V_g and V_u in terms of the normalized tesseral harmonic functions (as defined by Prather[18]) and retain only those terms in the expansion for which $l \leqslant 5$. The potential energy function V, expressed in terms of tesseral harmonics, is given by

$$V = \sum_{l=0}^{5} r^l \sum_{m=0}^{l} \frac{4\pi}{2l+1}\sum_\alpha [C_l^m(x, y, z)C_l^m(X_\alpha, Y_\alpha, Z_\alpha) + S_l^m(x, y, z)S_l^m(X_\alpha, Y_\alpha, Z_\alpha)]Q_\alpha R_\alpha^{-(l+1)} \quad (7)$$

where r is the radial coordinate of the chromophoric electron, x, y, and z are the Cartesian coordinates of the electron, R_α is the radial distance between perturber site α and the metal atom, and X_α, Y_α, and Z_α are the Cartesian coordinates of the perturber site α. The summation Σ_α is taken over all perturber sites α = s, t, and L, and Q_α is the classical charge assigned to the perturber site α. The terms in which l = 1, 3, and 5 belong to V_u, and the terms in which l = 2 and 4 belong to V_g. The tesseral harmonics, C_l^m and S_l^m, which appear in V_u and V_g are listed in Table I along with the irreducible representation to which they belong in the D_{4h} point group.

To derive sector rules for the second-order contributions to the rotatory strength, we must first identify the pair combinations of V_g and V_u for which $\Gamma(V_u)\cdot\Gamma(V_g)$ includes Γ_{ps}. These combinations, expressed in terms of the tesseral harmonics of Table I, are given in Table II. The first ten product functions in Table II come from (V_u, V_g) pair combinations that can cause d–d and d–p mixings. The remaining four product functions appear in (V_u, V_g) combinations which promote d–d and d–f mixings. If the product functions in Table II are expressed in terms of the perturber Cartesian coordinates, the first five products (1–5 in Table II) have an R^{-5} dependence on the radial distances between perturber sites and the metal atom, and the last nine products (6–14 in Table II) have an R^{-7} dependence on perturber radial distances. The $V_u\cdot V_g$ products ob-

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[17] Schellman[3] was the first to suggest the possible necessity of developing the one-electron model to a higher order of perturbation theory when deriving sector rules for "high-symmetry" systems.

[18] J. Prather, "Atomic Energy Levels in Crystals," National Bureau of Standards Monograph No. 19, U. S. Government Printing Office, Washington, D. C., 1961.

TABLE I

TESSERAL HARMONIC FUNCTIONS IN THE EXPANSIONS OF V_g AND V_u[a]

V_g		V_u	
C_2^0 (A_{1g})	S_4^1 (E_g)	C_1^0 (A_{2u})	C_5^0 (A_{2u})
C_2^1 (E_g)	C_4^2 (B_{1g})	C_1^1 (E_u)	C_5^1 (E_u)
S_2^1 (E_g)	S_4^2 (B_{2g})	S_1^1 (E_u)	S_5^1 (E_u)
C_2^2 (B_{1g})	C_4^3 (E_g)	C_3^0 (A_{2u})	C_5^2 (B_{2u})
S_2^2 (B_{2g})	S_4^3 (E_g)	C_3^1 (E_u)	S_5^2 (B_{1u})
C_4^0 (A_{1g})	C_4^4 (A_{1g})	S_3^1 (E_u)	C_5^3 (E_u)
C_4^1 (E_g)	S_4^4 (A_{2g})	C_3^2 (B_{2u})	S_5^3 (E_u)
		S_3^2 (B_{1u})	C_5^4 (A_{2u})
		C_3^3 (E_u)	S_5^4 (A_{1u})
		S_3^3 (E_u)	C_5^5 (E_u)
			S_5^5 (E_u)

$$C_l^m = \pi^{-1/2}\theta_l^m \cos m\phi; \quad C_l^0 = (2\pi)^{-1/2}\theta_l^0$$
$$S_l^m = \pi^{-1/2}\theta_l^m \sin m\phi; \quad S_l^0 = 0$$

[a] The functions θ_l^m are the normalized Legendre functions.

TABLE II

PRODUCTS OF TESSERAL HARMONICS TRANSFORMING AS A_{1u} IN THE D_{4h} POINT GROUP

1. $C_1^0 \cdot S_4^4$
2. $(C_1^1 + S_1^1) \cdot (C_4^3 \pm S_4^3)^a$
3. $(C_2^1 + S_2^1) \cdot (C_3^3 \pm S_3^3)^a$
4. $C_2^2 \cdot S_3^2$
5. $S_2^2 \cdot C_3^2$
6. $C_3^2 \cdot S_4^2$
7. $S_3^2 \cdot C_4^2$
8. $C_3^0 \cdot S_4^4$
9. $(C_3^1 + S_3^1) \cdot (C_4^3 \pm S_4^3)^a$
10. $(C_3^3 + S_3^3) \cdot (C_4^1 \pm S_4^1)^a$
11. $C_2^2 \cdot S_5^2$
12. $S_2^2 \cdot C_5^2$
13. $C_2^0 \cdot S_5^4$
14. $(C_2^1 + S_2^1) \cdot (C_5^3 \pm S_5^3)^a$

[a] These products contain components which transform as A_{1u}.

tained from the first five terms in Table II have an R^{-12} dependence on R, and the $V_u \cdot V_g$ products obtained from the remaining nine terms in Table II have an R^{-16} dependence on R. Sector rules based on the first five products of Table II should, therefore, be predominant in the second-order contribution to the rotatory strength. We shall only consider these sector rules in detail here.

Considering only the first five product functions in Table II, the sector rules for R'' are given by

$$\sum_\alpha\sum_\beta Z_\alpha[X_\beta Y_\beta(X_\beta^2 - Y_\beta^2)]Q_\alpha Q_\beta \tag{8a}$$

$$\sum_\alpha\sum_\beta X_\alpha[Y_\beta Z_\beta(Y_\beta^2 - Z_\beta^2)]Q_\alpha Q_\beta \tag{8b}$$

$$\sum_\alpha\sum_\beta Y_\alpha[X_\beta Z_\beta(Z_\beta^2 - X_\beta^2)]Q_\alpha Q_\beta \tag{8c}$$

$$\sum_\alpha\sum_\beta [Y_\alpha(Z_\alpha^2 - X_\alpha^2)]X_\beta Z_\beta Q_\alpha Q_\beta \tag{8d}$$

$$\sum_\alpha\sum_\beta [X_\alpha(Y_\alpha^2 - Z_\alpha^2)]Y_\beta Z_\beta Q_\alpha Q_\beta \tag{8e}$$

$$\sum_\alpha\sum_\beta [Z_\alpha(X_\alpha^2 - Y_\alpha^2)]X_\beta Y_\beta Q_\alpha Q_\beta \tag{8f}$$

$$\sum_\alpha\sum_\beta X_\alpha Y_\alpha Z_\alpha(X_\beta^2 - Y_\beta^2)Q_\alpha Q_\beta \tag{8g}$$

where Σ_α and Σ_β are taken over all perturber sites α and β, and (α, β) = (r, s, L). For those terms in which $\alpha = \beta$, the sector rule is hexadecal and the contributions of the individual perturber sites are obtained separately. The terms in which $\alpha \neq \beta$ lead to "mixed sector rules" and, in these cases, the contributions to R'' must be obtained by considering pairs of perturber sites. As written in terms 8a–g, the α perturbers produce ungerade perturbations on the D_{4h} ML_n cluster and the β perturbers exert gerade perturbations on the undistorted ML_n cluster. The interaction potential produced by the combined influence of an (α, β) pair is dissymmetric with respect to ML_n and can promote optical activity. The gerade perturbation potential from which the terms in (8) were derived is only effective in mixing the d-like oribtals on ML_n among themselves. The ungerade perturbation potential which leads to the various terms in (8) can only promote mixing between the d- and p-like orbitals on ML_n. It is safe to assume that the effects of d–d and d–p mxing on the spectral properties of the complex will predominate over any effects caused by d–s, d–g, d–f, and higher order mixings. It is important, however, to note that the sector rules presented in (8) were derived on a perturbation model in which the expansion of V_g was truncated after the $l = 4$ term, and the expansion of V_u was truncated after the $l = 5$ term. Furthermore, all second-order terms in which $l(V_g) + l(V_u) > 5$ were dropped.

The validity of using expressions 8a–g as sector rules also depends upon the formal or classical charges which are assigned to each of the perturber sites. If Q_α and Q_β are of like sign for each (α, β) pair, then a sector rule based only on the positional coordinates of α and β is sufficient. In fact, when Q_α and Q_β are of like sign, the second-order rotatory strength is completely independent of the signs of the perturbing charges. However, when Q_α and Q_β have opposite signs, these signs must be incorporated into the sector rules.

In many six-coordinate, dissymmetric metal complexes the ML_6 cluster has a regular octahedral geometry. In these cases, the "effective" ligand field in which the metal d electrons move is represented by a large octahedral (O_h) component and a sum of smaller, low-symmetry (hemihedric and holohedric) components. A perturbation treatment of these systems makes use of zeroth-order electronic states which form bases for the irreducible representations of O_h. The first term in a general spherical harmonic expansion of the ligand field potential function which transforms as A_{1u} in O_h (the pseudoscalar representation in O_h) is of order $l = 9$. The sector rule which applies to this potential function is $XYZ(X^2 - Y^2)(Z^2 - Y^2)(Z^2 - X^2)$. This rule has been successfully applied to the stereochemical interpretation of CD spectra for several dissymmetrically distorted cubic (O_h) systems[19] and should, in principle, be applicable to the signs of CD bands associated with transitions in any essentially octahedral chromophore. However, if one's objective is to relate the observed CD spectra to the orbital descriptions of the responsible electronic transitions, then a dissymmetric perturbation potential with $l = 9$ dependence is of little use.

If the perturbation model for the zeroth-order octahedral system is carried to second order (in the wave functions) and three-way interactions are admitted (two different perturber groups and the chromophore), then products of perturbing potentials which have l(odd) $\geqslant 3$ and l(even) $\geqslant 2$ dependence are effective in producing nonvanishing rotatory strengths in the d → d ligand field transitions. In this second-order representation therefore, the orbital description of the optical rotatory properties can be given in terms of an s, p, d, and f atomic orbital basis set centered on the central metal ion. This description allows maximum use of the powerful concepts of crystal field and ligand field theories in interpreting the CD spectra in terms of other spectroscopic properties of the ligand field transitions.

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(19) B. Bosnich, private communication.

Using procedures similar to those applied in the D_{4h} ML_n case, a set of sector rules for R''_{net} in dissymmetrically distorted octahedral systems can be derived. The six lowest order terms in this case are identical with those given in (8a)–(8f). Term 8g does not apply since the direct product $\Gamma(XYZ)\cdot\Gamma(X^2 - Y^2)$ transforms as E_u in O_h. The following are the next higher order terms which apply to the distorted O_h case

$$\sum_\alpha\sum_\beta [X_\alpha Y_\alpha Z_\alpha(X_\alpha^2 - Y_\alpha^2)(3Z_\beta^2 - R_\beta^2)]Q_\alpha Q_\beta \tag{9a}$$

$$\sum_\alpha\sum_\beta [X_\alpha Y_\alpha Z_\alpha(3Z_\alpha^2 - R_\alpha^2)(X_\beta^2 - Y_\beta^2)]Q_\alpha Q_\beta \tag{9b}$$

$$\sum_\alpha\sum_\beta [X_\alpha(Y_\alpha^2 - Z_\alpha^2)Y_\beta Z_\beta(7X_\beta^2 - R_\beta^2)]Q_\alpha Q_\beta \tag{9c}$$

$$\sum_\alpha\sum_\beta [Y_\alpha(Z_\alpha^2 - X_\alpha^2)X_\beta Z_\beta(7Y_\beta^2 - R_\beta^2)]Q_\alpha Q_\beta \tag{9d}$$

$$\sum_\alpha\sum_\beta [Z_\alpha(X_\alpha^2 - Y_\alpha^2)X_\beta Y_\beta(7Z_\beta^2 - R_\beta^2)]Q_\alpha Q_\beta \tag{9e}$$

$$\sum_\alpha\sum_\beta [X_\alpha(Y_\alpha^2 - Z_\alpha^2)(3X_\alpha^2 - R_\alpha^2)Y_\beta Z_\beta]Q_\alpha Q_\beta \tag{9f}$$

$$\sum_\alpha\sum_\beta [Y_\alpha(Z_\alpha^2 - X_\alpha^2)(3Y_\alpha^2 - R_\alpha^2)X_\beta Z_\beta]Q_\alpha Q_\beta \tag{9g}$$

$$\sum_\alpha\sum_\beta [Z_\alpha(X_\alpha^2 - Y_\alpha^2)(3Z_\alpha^2 - R_\alpha^2)X_\beta Y_\beta]Q_\alpha Q_\beta \tag{9h}$$

where the perturbers α provide an ungerade distortion (V_u) and the β perturbers provide a gerade distortion (V_g). The perturbation terms from which (9a)–(9h) were derived can mix s, p, d, and f metal orbitals, whereas those from which (8a)–(8g) were derived can only mix s, p, and d metal orbitals. Only when the true symmetry of the total system is C_1 (*i.e.*, asymmetric), will all the expressions (8a)–(8f) and (9a)–(9h) apply. For example, if the true symmetry of the complex is C_2 and the twofold rotational axis coincides with the octahedral C_2 (Z) axis, then only (8a), (8f), (9a), (9b), (9e), and (9f) have both gerade and ungerade components which transform as the A irreducible representation in the C_2 point group.

III. First- and Second-Order Contributions to CD Spectrum

In this section the general theory developed in section II is used to assess the qualitative features of the CD spectra associated with the ligand field (d → d) transitions of optically active complexes with a tetragonal (D_{4h}) ML_n cluster. Primary attention is given to how the sector rules derived in section II can be used to interpret the CD spectra in terms of specific structural features of the metal complexes.

A. First Order.—The d → d transitions are magnetic dipole allowed and electric dipole forbidden, and their rotatory strengths can be obtained to first order in perturbation theory from eq 3. If we represent the perturbation potential by V' (eq 5), then the orbital basis set for the ungerade functions F_{uj} must include at least f orbitals. As was pointed out in section II, V' will not mix d and p orbitals. In the first-order treatment, we shall construct the functions F_{gi} from a d-orbital basis and the functions F_{uj} from an f-orbital basis. To evaluate the $R'_{i,i'}$ matrix for the complete manifold of $i \rightarrow i'$ (d → d) transitions, we need the magnetic transition dipole matrix $\mathbf{M}_{i,i'}$, the electric transition dipole matrix $\mathbf{P}_{i,j}$, and the perturbation matrix $V'_{i,j}$. The one-electron basis functions used in evaluating these matrices are represented as

$$|\text{da}_1\rangle\text{:}\quad (3z^2 - r^2)\ \text{a}_{1g};\quad |\text{fb}_1\rangle\text{:}\quad (xyz)\ \text{b}_{1u}$$

$$|\text{db}_1\rangle\text{:}\quad (x^2 - y^2)\ \text{b}_{1g};\quad |\text{fe}x\rangle\text{:}\quad x(5x^2 - 3r^2)\ \text{e}_u$$

$$|\text{de}\xi\rangle\text{:}\quad (yz)\ \text{e}_g;\quad |\text{fe}y\rangle\text{:}\quad y(5y^2 - 3r^2)\ \text{e}_u$$

$$|\text{de}\eta\rangle\text{:}\quad (xz)\ \text{e}_g;\quad |\text{fa}_2\rangle\text{:}\quad z(5z^2 - 3r^2)\ \text{a}_{2u}$$

$$|\text{db}_2\rangle\text{:}\quad (xy)\ \text{b}_{2g};\quad |\text{fe}\xi\rangle\text{:}\quad x(y^2 - z^2)\ \text{e}_u$$

$$|\text{fe}\eta\rangle\text{:}\quad y(z^2 - x^2)\ \text{e}_u$$

$$|\text{fb}_2\rangle\text{:}\quad z(x^2 - y^2)\ \text{b}_{2u}$$

The symbols on the right side of the functions indicate the irreducible representations under which they transform in the D_{4h} point group.

Since we are primarily concerned with sector rules and the symmetry-controlled aspects of optical activity rather than with quantitative calculations of R', we shall take the d and f wave functions to be pure metal orbitals. This approximation simplifies our evaluation of the elements of the $\mathbf{M}_{i,i'}$, $\mathbf{P}_{i,j}$, and $V'_{i,j}$ matrices which are given in Tables III–V, respectively. The functions R_d and R_f which appear in the quantities q_{df} and v'_{df} are the radial functions of the d and f orbitals, respectively. To specify the first-order rotatory strengths we further require the energy differences between the d and f orbitals which are mixed by V'. These energy differences are denoted as

TABLE III

MAGNETIC DIPOLE TRANSITION MOMENTS,[a] d → d TRANSITIONS

$M_{i,i'}$	$\|\text{da}_1\rangle$	$\|\text{db}_1\rangle$	$\|\text{de}\xi\rangle$	$\|\text{de}\eta\rangle$	$\|\text{db}_2\rangle$
$\langle\text{da}_1\|$	0	0	$+(3^{1/2})i$	$-(3^{1/2})j$	0
$\langle\text{db}_1\|$	0	0	$+i$	$+j$	$-2k$
$\langle\text{de}\xi\|$	$-(3^{1/2})i$	$-i$	0	$+k$	$-j$
$\langle\text{de}\eta\|$	$+(3^{1/2})j$	$-j$	$-k$	0	$+i$
$\langle\text{db}_2\|$	0	$+2k$	$+j$	$-i$	0

[a] In the units: $(-1)^{1/2}e\hbar/2mc = (-1)^{1/2}\beta$ (Bohr magneton).

TABLE IV

ELECTRIC DIPOLE TRANSITION MOMENTS,[a] d → f TRANSITIONS

$\mathbf{P}_{j,i}$	$\|\text{da}_2\rangle$	$\|\text{db}_1\rangle$	$\|\text{de}\xi\rangle$	$\|\text{de}\eta\rangle$	$\|\text{db}_2\rangle$
$\langle\text{fb}_1\|$	0	0	$+i$	$+j$	$+k$
$\langle\text{fe}x\|$	$-{}^3/_2({}^1/_5)^{1/2}i$	$+{}^3/_2({}^3/_5)^{1/2}i$	0	$-({}^3/_5)^{1/2}k$	$-({}^3/_5)^{1/2}j$
$\langle\text{fe}y\|$	$-{}^3/_2({}^1/_5)^{1/2}j$	$-{}^3/_2({}^3/_5)^{1/2}j$	$+({}^3/_5)^{1/2}k$	0	$-({}^3/_5)^{1/2}i$
$\langle\text{fa}_2\|$	$+({}^9/_5)^{1/2}k$	0	$-({}^3/_5)^{1/2}j$	$-({}^3/_5)^{1/2}i$	0
$\langle\text{fe}\xi\|$	$-({}^3/_4)^{1/2}i$	$-{}^1/_2i$	0	$-k$	$+j$
$\langle\text{fe}\eta\|$	$+({}^3/_4)^{1/2}j$	$-{}^1/_2j$	$-k$	0	$-i$
$\langle\text{fb}_2\|$	0	$+k$	$-j$	$+i$	0

[a] In the units: $q_{df} = -({}^1/_7)^{1/2}e\int R_d R_f r^3\,dr$.

TABLE V

FIRST-ORDER d–f INTERACTION MATRIX[a]

$V'_{i,j}$	$\|\text{fb}_1\rangle$	$\|\text{fe}x\rangle$	$\|\text{fe}y\rangle$	$\|\text{fa}_2\rangle$	$\|\text{fe}\xi\rangle$	$\|\text{fe}\eta\rangle$	$\|\text{fb}_2\rangle$
$\langle\text{da}_1\|$	0	0	0	0	0	0	0
$\langle\text{db}_1\|$	-1	0	0	0	0	0	0
$\langle\text{de}\xi\|$	0	$-({}^5/_{12})^{1/2}$	0	0	$+{}^1/_2$	0	0
$\langle\text{de}\eta\|$	0	0	$+({}^5/_{12})^{1/2}$	0	0	$+{}^1/_2$	0
$\langle\text{db}_2\|$	0	0	0	0	0	0	-1

[a] In the units: $v'_{df} = -3(217.8)^{1/2}A_5^4\int R_d R_f r^7\,dr$, where $A_5^4 = {}^3/_{11}(385\pi)^{1/2}\Sigma_\alpha(X_\alpha Y_\alpha Z_\alpha)(X_\alpha^2 - Y_\alpha^2)Q_\alpha/R_\alpha^{11}$; α = all perturber sites s, t, and L.

$$\epsilon_k = \Delta E_{ij} = \langle i|H_0|i\rangle - \langle j|H_0|j\rangle$$

ϵ_k	i	j
ϵ_1	$\|\text{db}_1\rangle$	$\|\text{fb}_1\rangle$
ϵ_2	$\|\text{db}_2\rangle$	$\|\text{fb}_2\rangle$
ϵ_3	$\|\text{de}\xi\rangle$ $\|\text{de}\eta\rangle$	$\|\text{fe}\xi\rangle$ $\|\text{fe}\eta\rangle$
ϵ_4	$\|\text{de}\xi\rangle$ $\|\text{de}\eta\rangle$	$\|\text{fe}x\rangle$ $\|\text{fe}y\rangle$

TABLE VI

FIRST-ORDER ROTATORY STRENGTHS, d–f MIXING[a]

$R'_{i,i'}$	$\mathrm{da}_1\rangle$	$\lvert\mathrm{db}_1\rangle$	$\lvert\mathrm{de}\xi\rangle$	$\lvert\mathrm{de}\eta\rangle$	$\lvert\mathrm{db}_2\rangle$
$\langle\mathrm{da}_1\rvert$	0	0	$-{}^3/_4(\epsilon_3^{-1} - \epsilon_4^{-1})$	$-{}^3/_4(\epsilon_3^{-1} - \epsilon_4^{-1})$	0
$\langle\mathrm{db}_1\rvert$	0	0	$-{}^1/_4(4\epsilon_1^{-1} + 3\epsilon_4^{-1} + \epsilon_3^{-1})$	$-{}^1/_4(4\epsilon_1^{-1} + 3\epsilon_4^{-1} + \epsilon_3^{-1})$	$+2(\epsilon_1^{-1} + \epsilon_2^{-1})$
$\langle\mathrm{de}\xi\rvert$	$+{}^3/_4(\epsilon_3^{-1} - \epsilon_4^{-1})$	${}^1/_4(4\epsilon_1^{-1} + 3\epsilon_4^{-1} + \epsilon_3^{-1})$	0	$+(\epsilon_3^{-1} - \epsilon_4^{-1})$	$-{}^1/_2(2\epsilon_2^{-1} + \epsilon_3^{-1} + \epsilon_4^{-1})$
$\langle\mathrm{de}\eta\rvert$	$+{}^3/_4(\epsilon_3^{-1} - \epsilon_4^{-1})$	${}^1/_4(4\epsilon_1^{-1} + 3\epsilon_4^{-1} + \epsilon_3^{-1})$	$-(\epsilon_3^{-1} - \epsilon_4^{-1})$	0	$-{}^1/_2(2\epsilon_2^{-1} + \epsilon_3^{-1} + \epsilon_4^{-1})$
$\langle\mathrm{db}_2\rvert$	0	$-2(\epsilon_1^{-1} + \epsilon_2^{-1})$	$+{}^1/_2(2\epsilon_2^{-1} + \epsilon_3^{-1} + \epsilon_4^{-1})$	$+{}^1/_2(2\epsilon_2^{-1} + \epsilon_3^{-1} + \epsilon_3^{-1})$	0

[a] In the units: $\beta q_{\mathrm{df}} v'_{\mathrm{df}}$.

The first-order rotatory strength matrix for d → d transitions is given in Table VI. The elements of the matrix are expressed in terms of β (Bohr magneton), q_{fd}, v'_{fd}, and the four energy differences ϵ_1, ϵ_2, ϵ_3, and ϵ_4.

If we assume that the strongest parts of the ligand field originate with the ligating atoms L and if these atoms are located on the x, y, and z axes of the system, then the relative magnitudes of the energy differences ϵ_k are given by: $\epsilon_4 > \epsilon_3 > \epsilon_2 > \epsilon_1$. In general, the energy interval between the d- and f-orbital manifolds is much larger than the energy splittings within the two manifolds. For this reason, it is a good approximation in any crude analysis to set $\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_{\mathrm{df}}$, where ϵ_{df} is the difference between the mean energies of the d- and f-orbital manifolds. Using this approximation, we see from Table VI that the total rotatory strength associated with all one-electron excitations to $\lvert\mathrm{db}_1\rangle$ is zero. Similarly, the rotatory strength associated with one-electron excitations to $\lvert\mathrm{da}_1\rangle$ is zero. For example, if we consider a Cu(II) complex in which the only unoccupied d orbital in the ground state is $\lvert\mathrm{db}_1\rangle$ and in which the splitting between $\lvert\mathrm{de}\eta\rangle$ and $\lvert\mathrm{de}\xi\rangle$ is very small, then to first order in V' the CD spectrum due to ligand field transitions should exhibit two bands which are nearly equal in magnitude but which have opposite signs. The one band is associated with the $\mathrm{db}_2 \rightarrow \mathrm{db}_1$ transition and has a rotatory strength approximately equal to $4\beta q_{\mathrm{df}} v'_{\mathrm{df}} \epsilon_{\mathrm{df}}$. The second band arises from the two transitions $\mathrm{de}\xi \rightarrow \mathrm{db}_1$ and $\mathrm{de}\eta \rightarrow \mathrm{db}_1$ and has a rotatory strength approximately equal to $-4\beta q_{\mathrm{df}} v'_{\mathrm{df}} \epsilon_{\mathrm{df}}$. In order that the net rotatory strength of the overall d → d spectrum not vanish to first order in V', the energy splittings within the d- and f-orbital manifolds must be included explicitly. If we consider these splittings, the net first-order rotatory strength is given by ${}^1/_2(4\epsilon_2^{-1} - 3\epsilon_4^{-1} - \epsilon_3^{-1})\beta q_{\mathrm{df}} v'_{\mathrm{df}}$ for the Cu(II) complex.

So far it has been assumed that the deη and deξ orbitals are sufficiently close in energy that their individual CD components cannot be resolved. If the energy difference between these orbitals is >500 cm^{-1}, it becomes questionable whether a perturbation model, in which a tetragonal (D_{4h}) ML$_n$ cluster is assumed to zeroth order, is valid. In this case, a rhombic or orthorhombic zeroth-order representation of ML$_n$ is to be preferred. The intermediate case in which the splitting is between 0 and 500 cm^{-1} is of special interest in the interpretation of CD data since, in this case, the isotropic absorption spectrum should show no evidence of the splitting, whereas the CD spectrum can show two overlapping but resolvable bands.

The deη and deξ functions are the orbital components of a doubly degenerate tetragonal state belonging to the E$_g$ irreducible representation. From the group theoretical analysis given in section II it was deduced that, to first-order in perturbation theory, the optical activity associated with any transition between tetragonal states is zero unless a perturbation potential transforming as A$_{1u}$ (in D_{4h}) is present. Note that this result applies only to transitions between perturbed tetragonal states. In the case of the E$_g$ state, it applies to the combinations of one-electron transitions to or from the deη and deξ orbitals. If the E$_g$ state is split, it is necessary to evaluate the rotatory strengths of the individual deη and deξ orbital components which are induced by the ungerade parts of V which are of lower order than $V'(l = 5)$. Both the $V(l = 1)$ and $V(l = 3)$ parts of the total ligand field potential will mix the deη and deξ orbitals with pe$x$, pe$y$, and pe$z$ orbitals to first order in perturbation theory. Furthermore, these d–p mixings lead to induced rotatory strengths for one-electron transitions to deη and deξ which are equal in magnitude but opposite in sign. Since the average energy difference, ϵ_{dp}, between the d and p orbitals is somewhat smaller than ϵ_{df}, these rotatory strengths will be larger than those due to d–f mixing (*i.e.*, those given in Table VI) by at least a factor of $\epsilon_{\mathrm{dp}}/\epsilon_{\mathrm{df}}$. The net rotatory strength associated with transitions to the E$_g$ state is still given by the sum of the deη and deξ rotatory strengths given in Table VI. However, when the splitting between these components is resolvable in the CD spectrum, it is possible that two distinct bands of opposite signs and unequal magnitudes will be observed. The qualitative features of the component CD bands due to transitions to the E$_g$ state are depicted in Figure 1. For very small splittings, of course, only one band should be observed and its intensity is derived solely from d–f mixing to first order.

B. Second Order.—To obtain complete expressions for the second-order contributions to the rotatory strength of each d → d transition, each term in eq 6 must be evaluated. The resulting expressions are long and complex even on a quasi crystal field model and are of limited value for interpreting the experimental CD spectra. A more practical approach for making use of the second-order rotatory strengths is to determine how they influence the overall (net) rotatory strength associated with all d → d transitions. The signs and relative magnitudes of the rotatory strengths associated with the individual d → d transitions depend upon the ordering of d-orbital energies as well as upon the stereochemical properties of the complex. The sign and magnitude of the net rotatory strength also depends upon the relative energies of the d orbitals; however, for this quantity the analysis can be conveniently broken down into two separate cases: (1) the weak tetragonal field case; (2) the strong tetragonal field case. In the first case, it is assumed that Δ_o (octahedral crystal field splitting energy, $10Dq$) $> \Delta_t$ (tetragonal crystal field splitting energy). In the second case, it is assumed that $\Delta_o \leqslant \Delta_t$. Only the weak tetragonal field case will be considered in the following discussion.

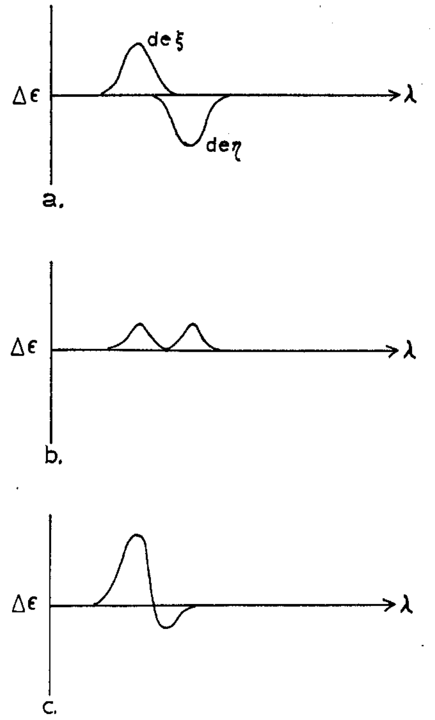

Figure 1.—Features of the CD bands associated with transitions to the split orbital components of the tetragonal E_g state: (a) first-order contributions due to d–p mixing; $V(l = 1, 3)$; (b) first-order contributions due to d–f mixing, $V(l = 5)$; (c) sum of first-order contributions.

The net second-order rotatory strength associated with all d → d transitions is given by $R''_{\text{net}} = \Sigma_i R''_{0,i}$, where Σ_i is taken over all the one-electron d → d transitions and $R''_{0,i}$ is given by eq 6. Complete evaluation of eq 6 is unmanageable because of the many unknown intermediate states F_{uj} with odd parity. The main contributions will, however, come from the ungerade states in which one of the five 3d orbitals is promoted to a 4p orbital owing to the large overlap of the wave functions. It is, therefore, a good approximation to replace the energy differences ΔE_{ij} by the mean energy separation between the 3d and 4p orbital manifolds and then sum over the ungerade intermediate states using the closure properties of the F_{uj} eigenfunctions. Summing over the complete set of F_{uj} states and applying the average energy approximation and closure theorem, we obtain

$$\begin{aligned} R''_{\text{net}} = 2 \operatorname{Im} \sum_{i' \neq 0} \sum_{i \neq 0, i'} \epsilon_{\text{dp}}^{-1} \{ \langle F_{g0} | \vec{\mu} \cdot V_u | F_{gi'} \rangle \times \\ [\mathbf{M}_{i0} V_{gii'} \cdot \Delta E_{i'i}^{-1} + \mathbf{M}_{i'i} V_{gi0} \Delta E_{0i}^{-1}] + \\ \langle F_{gi} | \vec{\mu} \cdot V_u | F_{gi'} \rangle \mathbf{M}_{i'0} V_{gi0} \Delta E_{0i}^{-1} + \\ \langle F_{g0} | \vec{\mu} \cdot V_u | F_{gi} \rangle \mathbf{M}_{i'0} V_{gii'} \Delta E_{i'i}^{-1} - \\ \langle F_{gi'} | \vec{\mu} \cdot V_u | F_{g0} \rangle \epsilon_{\text{dp}}^{-1} \mathbf{M}_{i'0} [V_{g00} + V_{gi'i'}] \} \quad (10) \end{aligned}$$

where $\Sigma_{i'}$ and Σ_i are taken over only the d → d excited states. If we separate the perturbation operators V_u and V_g into two parts, those that depend only upon the coordinates of the chromophoric electrons and those that are independent of these electron coordinates, then eq 10 can be rewritten as

$$\begin{aligned} R''_{\text{net}} = 2 \operatorname{Im} \tilde{V}_u \tilde{V}_g \epsilon_{\text{dp}}^{-1} \sum_{i' \neq 0} \sum_{i \neq 0, i'} \{ v_{gii'} \Delta E_{i'i}^{-1} \times \\ [\mathbf{M}_{i0} \langle F_{g0} | \vec{\mu} \cdot v_u | F_{gi'} \rangle + \mathbf{M}_{i'0} \langle F_{gi} | \vec{\mu} \cdot v_u | F_{g0} \rangle] + v_{gi0} \Delta E_{0i}^{-1} \times \\ [\mathbf{M}_{i'i} \langle F_{g0} | \vec{\mu} \cdot v_u | F_{gi'} \rangle + \mathbf{M}_{i'0} \langle F_{gi} | \vec{\mu} \cdot v_u | F_{gi'} \rangle] \} \quad (11) \end{aligned}$$

$\tilde{V}_u$ and $\tilde{V}_g$ are those parts of V_u and V_g, respectively, which are independent of electron coordinatees, v_u and v_g are the electron-dependent parts of the V_u and V_g operators, and v_{gi0} and $v_{gii'}$ are matrix elements of the electronic operator v_g. $\tilde{V}_u$ and $\tilde{V}_g$, of course, represent sums over the nuclear positional coordinates and the charges of the perturbing sites. The sector rules which govern R''_{net} are derived from $\tilde{V}_u$ and $\tilde{V}_g$.

To derive sector rules for R''_{net}, we must identify those parts of eq 11 whose signs are sensitive to the stereochemical characteristics of the perturbing ligand environment. Certainly the signs of $\tilde{V}_u$ and $\tilde{V}_g$ are dependent upon the geometrical disposition of the atoms in the ligand environment. However, the relative ordering of the d → d excited states is also sensitive to the geometrical arrangement of the ligands and this ordering determines the signs of the energy differences $\Delta E_{i'i}$ and ΔE_{0i}, which appear in eq 11. We shall restrict our discussion to the class of complex ions in which the tetragonal component of the ligand field is smaller than the octahedral field and in which the axial part of the tetragonal perturbation is smaller than the in-plane part (*i.e.*, the complexes are axially elongated rather than axially compressed). This class encompasses most of the amino acid, di- and tripeptide, and diamino complexes formed by the first-row transition metal ions in aqueous solution. Within this class of complex ions, the ΔE_{0i} and $\Delta E_{i'i}$ quantities will always have the same sign and the electronic matrix elements in eq 11 will, of course, always have the same signs. Sector rules for R''_{net} can, therefore, be completely based on $\tilde{V}_u$ and $\tilde{V}_g$.

In the optically active complexes of the second-row Pd(II) and third-row Pt(II) transition metal ions, the tetragonal component of the ligand field is, in many cases, comparable in magnitude to the octahedral splitting energy. In these cases, eq 11 cannot be used without explicit information about the relative energies of the d → d excited states.

The sector rules based on $\tilde{V}_u$ and $\tilde{V}_g$ in (11) are given by the seven expressions (8a)–(8g). That is, the sign dependence of R''_{net} on the positional coordinates and charges of the perturbing ligand groups is determined by the signs and relative magnitudes of (8a)–(8g).

IV. Discussion

In the theoretical analyses presented in sections II and III it was assumed that the spectroscopic states involved in the ligand field transitions of chiral metal coordination compounds could be adequately described in terms of a quasi crystal field model. That is, it was assumed that these states could be described entirely in terms of metal atomic orbitals and that the ligand environment could be represented by an array of "static" charge distributions. Differential overlap between the metal and ligand electron orbitals was neglected and the dynamical behavior of the electronic distributions on the ligands was ignored. These assumptions are within the spirit of the "one-electron" theory of optical activity and the ligand field theory of d → d transitions in transition metal complexes. They cannot support a quantitative analysis of the optical rotatory properties of the ligand field bands, but, on the other hand, they should provide a valid and reliable basis for analyzing the symmetry-controlled, qualitative aspects of these properties. The recent use of sector rules in correlating the signs of the ligand field CD bands with stereochemical features of the ligand environment in transition metal compounds[4-13] has been entirely based on the general concepts of the "one-electron" model of optical rotatory power.[3] This latter fact makes necessary a more detailed scrutiny of the quantum mechanical basis for sector rules in transition metal complexes treated on a crystal field model. The theory presented in sections II and III provides the basis for such a study.

The crystal field one-electron model is most appropriately applied to the ligand field CD spectra of metal complexes in which the ligands exhibit no strong absorption bands in the spectral region $\lambda > 200$ nm (*e.g.*, diamines with saturated hydrocarbon bridging and substituent groups). In these cases the dynamical behavior of the ligand electron distributions probably have little influence on the d → d spectroscopic states. For metal complexes in which the ligands are amino acids, di- or tripeptides, or oxalate anions, it is likely that the one-electron model provides an incomplete description of the optical rotatory properties of the ligand field transitions. In these cases, there are electronic transitions localized in the ligand chromophoric groups which occur at wavelengths >200 nm and which have moderately large electronic transition dipoles. Under these conditions it is expected that dynamical coupling between the magnetic transition dipoles associated with the metal d → d transitions and the electric transition dipoles associated with the chiral ligand environment will provide an additional mechanism for optical activity. However, in a previous theoretical study[15] it was shown that the electric–magnetic coupled oscillator mechanism and the one-electron mechanism should lead to identical sector rules with respect to the stereochemical arrangement of the ligands about the metal atom. The sector rules given in section II, therefore, should be applicable to the class of ligands which includes amino acids, di- and tripeptides, and oxalate anions.

Examples of mixed-sector rules for various types of pseudotetragonal transition metal complexes are given in the Appendix. In each case it is assumed that the σ-bond structure of the ML_4Z_2 cluster has tetragonal (D_{4h}) symmetry and that the spectroscopic states responsible for the ligand field spectra can be described to zeroth-order as eigenstates of a Hamiltonian which has D_{4h} symmetry. The perturbed spectroscopic states are sensitive to (a) dissimilarities between the four in-plane ligating atoms due, for example, to their varying abilities to form π bonds with the metal atom, (b) the presence of the bridging atoms in the chelate rings, and (c) the presence of substituents attached to the ligating or bridging groups. In other words, to zeroth order we partition each complex into four independent subsystems: the ML_4Z_2 σ-bond structure, the metal–ligator π-bond structure, the bridging atoms, and the substituent groups. The mixed-sector rules originate with the three-way interactions which occur between the ML_4Z_2 chromophoric electrons and any two of the remaining three subsystems. For example, in the complex Cu(L-alaninato)$_2$ we assume to zeroth order that the CuO_2N_2 cluster has full D_{4h} symmetry. Perturbations on this zeroth-order representation are then assumed to originate from dissimilarities between the O^- and N ligator atoms, from the carbon and carbonyl bridging groups, and from the methyl and hydrogen substituents. In this case, the ligating atoms provide a rhombic distortion which transforms as $(X^2 - Y^2)$ and the substituents provide a distortion which transforms as (XYZ). Taken together, these distortions provide a dissymmetric potential in which the metal d electrons must move. The hexadecant rule for this compound (based on a first-order perturbation treatment of rotatory strength) has as its basis a $XYZ(X^2 - Y^2)$ distortion provided by the substituent methyl groups. The potential energy function representing the d-electron–substituent interaction in this case has R^{-11} dependence on the radial distance between the metal atom and the substituent group. For the mixed-sector rule (based on a second-order treatment of rotatory strength) the potential energy expression has $R_\gamma^{-7} \cdot R_\alpha^{-5}$ dependence on the radial distances R_γ (substituents–metal) and R_α (ligators–metal).

The search for sector rules which are applicable to the CD spectra of dissymmetric transition metal complexes is closely related to another problem of current interest in inorganic CD spectroscopy. This problem arises from attempts to correlate the signs and magnitudes of the observed CD bands with three general "kinds" of stereochemical features in the ligand environment. These three "kinds" of stereochemical features are defined as follows: (1) the geometrical distribution, or *configuration*, of chelate rings about the central metal atom, (2) the *conformations* of the individual chelate rings, and (3) the presence of asymmetric centers in the ligand environment—asymmetric centers *vicinal* to the metal chromophore. It has been proposed that the CD spectrum associated with the ligand field bands of a transition metal complex can be represented as a sum of three independent contributions which are attributable to these three "kinds" of stereochemical features.[20-25] The contribution orginating with configurational dissymmetry is called the *configurational effect*, the contribution due to dissymmetry in the chelate rings is termed the *conformational effect*, and the contributions attributable to asymmetric centers in the ligands are referred to as *vicinal effects*. It has been recognized, of course, that the configurational and conformational stereochemical features of a complex are, in general, interdependent and that they are also influenced by the number and structural details of the asymmetric centers in the ligands. However, given a particular configurational isomer of a complex comprised of optically active ligands which form chelate rings with prescribed conformations, it is assumed possible to separate the observed CD spectrum into configurational, conformational, and vicinal contributions.

The model presented in section II of this paper does not explicitly distinguish between the configurational, conformational, and vicinal effects. The ligand environment is represented as a constellation of nonoverlapping charge distributions which are centered on the ligand atoms. The chromophoric electrons are assumed

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to be localized on the metal atom, but their dynamical behavior reflects the geometrical disposition of the ligand atoms. If the total potential energy function representing the interactions between the chromophoric electron and the ligand atoms includes a dissymmetric part, then optical activity is observed in the transitions involving this electron. The space occupied by the complex is partitioned into sectors whose boundaries are defined by the nodal surfaces of the ligand field potential function. The distribution of ligand perturber sites among these sectors then determines the overall chirality of the complex and, consequently, the signs and magnitudes of the CD bands. The physical bases of our model are two-way (in the first-order perturbation terms) or three-way (in the second-order perturbation terms) electrostatic interactions between two or three nonoverlapping charge distributions, respectively.

In the context of this one-electron model, the configurational, conformational, and vicinal "effects" are related to our description of the perturber site distribution among the sectors. Configurational isomerization generally leads to rather large changes in the perturber site distribution of a complex, whereas conformational changes in the individual chelate rings lead to relatively small changes in the spatial distribution of perturber sites. In general, therefore, configurational effects should be considerably larger than conformational effects. Vicinal effects, as defined here, originate with the substituents attached to asymmetric ring atoms. Their magnitude is partly dependent upon ring conformation (since a change in ring conformation will in general alter the ring substituents, positions in space) and partly dependent upon the size and electrical properties of the substituent groups.

Further examination of how configurational, conformational, and vicinal effects can be interpreted on the basis of our model will not be given here. The primary objective of the present study was to derive sector rules for ligand field transitions on a one-electron model which displays the symmetry-controlled aspects of the dissymmetric metal–ligand interactions and which provides an orbital description of the optically active electronic transitions within the framework of crystal field theory.

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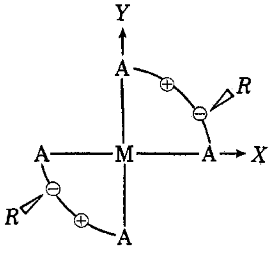
Appendix

Examples of Mixed-Sector Rules for Pseudo-Tetragonal Systems

1. **MA_4**

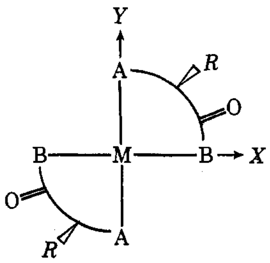


nonplanar chelate rings

Group	Symmetry	Perturbation
MA_4	D_{4h}	
Bridging atoms (β)	D_2	$\sum_\beta Q_\beta[(X_\beta Y_\beta)R_\beta^{-5} + Z_\beta(X_\beta^2 - Y_\beta^2)R_\beta^{-7}]$
Substituents (γ)	C_2	$\sum_\gamma Q_\gamma[Z_\gamma R_\gamma^{-3} + (X_\gamma^2 - Y_\gamma^2) \times R_\gamma^{-5} + (X_\gamma Y_\gamma)R_\gamma^{-5} + Z_\gamma(X_\gamma^2 - Y_\gamma^2)R_\gamma^{-7} + (X_\gamma Y_\gamma Z_\gamma)R_\gamma^{-7}]$

Sector rule: $\sum_\beta \sum_\gamma Q_\beta Q_\gamma [X_\beta X_\beta Z_\gamma (X_\gamma^2 - Y_\gamma^2)R_\beta^{-5}R_\gamma^{-7} + X_\gamma Y_\gamma Z_\beta (X_\beta^2 - Y_\beta^2)R_\beta^{-7}R_\gamma^{-5}]$

2. *trans*-**MA_2B_2**

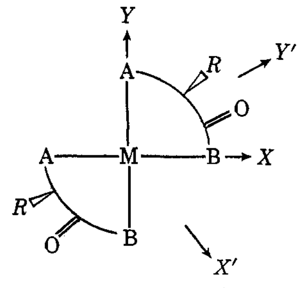


planar chelate rings

Group	Symmetry	Perturbation
MA_2B_2 (α)	D_{2h}	$\sum_\alpha Q_\alpha(X_\alpha^2 - Y_\alpha^2)R_\alpha^{-5}$
Bridging atoms (β)	C_{2h}	$\sum_\beta Q_\beta[(X_\beta Y_\beta)R_\beta^{-5} + (X_\beta^2 - Y_\beta^2)R_\beta^{-5} + X_\beta Y_\beta(X_\beta^2 - Y_\beta^2)R_\beta^{-9}]$
Substituents (γ)	C_2	$\sum_\gamma Q_\gamma[Z_\gamma R_\gamma^{-3} + (X_\gamma Y_\gamma)R_\gamma^{-5} + (X_\gamma^2 - Y_\gamma^2))R_\gamma^{-5} + (X_\gamma X_\gamma Z_\gamma) \times R_\gamma^{-7} + Z_\gamma(X_\gamma^2 - Y_\gamma^2)R_\gamma^{-7}]$

Sector rule: $\sum_\alpha \sum_\gamma Q_\alpha Q_\gamma (X_\alpha^2 - Y_\alpha^2)X_\gamma Y_\gamma Z_\gamma R_\alpha^{-5}R_\gamma^{-7} + \sum_\beta \sum_\gamma Q_\beta Q_\gamma [X_\beta Y_\beta Z_\gamma (X_\gamma^2 - Y_\gamma^2)R_\beta^{-5}R_\gamma^{-7} + (X_\beta^2 - Y_\beta^2)X_\gamma Y_\gamma Z_\gamma R_\beta^{-5}R_\gamma^{-7} + (X_\beta^2 - Y_\beta^2)X_\beta Y_\beta Z_\gamma R_\beta^{-9}R_\gamma^{-3}]$

3. *cis*-**MA_2B_2**



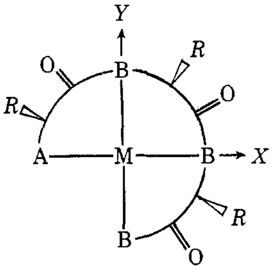
planar chelate rings

Group	Symmetry	Perturbation
MA_2B_2 (α)	C_{2v} (X′)	$\sum_\alpha Q_\alpha \left[\frac{1}{\sqrt{2}}(X_\alpha - Y_\alpha)R_\alpha^{-3} + (X_\alpha Y_\alpha)R_\alpha^{-5}\right]$

Group	Symmetry	Perturbation
Bridging atoms (β)	C_{2v} (X′)	$\sum_\beta Q_\beta\left[\frac{1}{\sqrt{2}}(X_\beta - Y_\beta)R_\beta^{-3} + (X_\beta Y_\beta)R_\beta^{-5}\right]$
Substituents (γ)	C_2 (X′)	$\sum_\gamma Q_\gamma\left[\frac{1}{\sqrt{2}}(X_\gamma - Y_\gamma)R_\gamma^{-3} + (X_\gamma Y_\gamma)R_\gamma^{-5} + Z_\gamma(X_\gamma^2 - Y_\gamma^2) \times R_\gamma^{-7} + \frac{1}{\sqrt{2}}(X_\gamma Z_\gamma + Y_\gamma Z_\gamma)R_\gamma^{-5}\right]$

Sector rule: $$\sum_\alpha\sum_\gamma Q_\alpha Q_\gamma X_\alpha Y_\alpha Z_\gamma(X_\gamma^2 - Y_\gamma^2)R_\alpha^{-5}R_\gamma^{-7} + \sum_\beta\sum_\gamma Q_\beta Q_\gamma X_\beta Y_\beta Z_\gamma(X_\gamma^2 - Y_\gamma^2)R_\beta^{-5}R_\gamma^{-7}$$

4. MAB$_3$



planar chelate rings

Group	Symmetry	Perturbation
MAB$_3$ (α)	C_{2v} (X)	$\sum_\alpha Q_\alpha[X_\alpha R_\alpha^{-3} + (X_\alpha^2 - Y_\alpha^2) \times R_\alpha^{-5} + X_\alpha(Y_\alpha^2 - Z_\alpha^2)R_\alpha^{-7}]$
Bridging atoms (β)	C_s (σ_{xy})	$\sum_\beta Q_\beta[X_\beta R_\beta^{-3} + Y_\beta R_\beta^{-3} + (X_\beta Y_\beta)R_\beta^{-5} + (X_\beta^2 - Y_\beta^2) \times R_\beta^{-5} + X_\beta(Y_\beta^2 - Z_\beta^2)R_\beta^{-7} + Y_\beta(Z_\beta^2 - X_\beta^2)R_\beta^{-7}]$
Substituents (γ)	C_1	All terms in expansion

Sector rule: $$\sum_\alpha\sum_\gamma Q_\alpha Q_\gamma[Y_\gamma Z_\gamma X_\alpha(Y_\alpha^2 - Z_\alpha^2)R_\alpha^{-7} \times R_\gamma^{-5} + X_\gamma Y_\gamma Z_\gamma(X_\alpha^2 - Y_\alpha^2)R_\alpha^{-5}R_\gamma^{-7} + X_\alpha Y_\gamma Z_\gamma(Y_\gamma^2 - Z_\gamma^2)R_\alpha^{-3}R_\gamma^{-9}] + \sum_\beta\sum_\gamma[X_\gamma Z_\gamma Y_\beta \times (Z_\beta^2 - X_\beta^2)R_\beta^{-7}R_\gamma^{-5} + Y_\gamma Z_\gamma X_\beta(Y_\beta^2 - Z_\beta^2) \times R_\beta^{-7}R_\gamma^{-5} + X_\gamma Y_\gamma Z_\gamma(X_\beta^2 - Y_\beta^2)R_\beta^{-5}R_\gamma^{-7} + X_\beta Y_\beta Z_\gamma(X_\gamma^2 - Y_\gamma^2)R_\beta^{-5}R_\gamma^{-7} + Y_\beta X_\gamma Z_\gamma \times (Z_\gamma^2 - X_\gamma^2)R_\beta^{-3}R_\gamma^{-9} + X_\beta Y_\gamma Z_\gamma \times (Y_\gamma^2 - Z_\gamma^2)R_\beta^{-3}R_\gamma^{-9}]$$

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Sulfur Dioxide Insertion. XV. Transition Metal–Vinyl Complexes Containing a Sultine Ring[1,2]

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Transition metal–2-alkynyl complexes react with liquid sulfur dioxide or with SO_2 in solution to form the corresponding vinyl derivatives containing a sultine ring, $\mathrm{M\overline{C{=}C(R)S(O)OC}H_2}$. Prepared in this manner were $\mathrm{Mn(CO)_5(C_3H_2RSO_2)}$ (R = H, CH_3), π-$\mathrm{C_5H_5Fe(CO)_2(C_3H_2RSO_2)}$ (R = H, CH_3, C_6H_5), π-$\mathrm{C_5H_5Mo(CO)_3(C_3H_2RSO_2)}$ (R = H, CH_3, C_6H_5), π-$\mathrm{C_5H_5Mo(CO)_2[P(OC_6H_5)_3](C_4H_5SO_2)}$, and the bimetallic π-$\mathrm{C_5H_5M(CO)_x(C_3H_2SO_2)CH_2M(CO)_x(\pi\text{-}C_5H_5)}$ (M = Fe, $x = 2$; M = Mo, $x = 3$). The infrared and ^{1}H nmr spectra of these compounds are presented and compared with those of the organic sultines. The manganese and iron complexes $\mathrm{Mn(CO)_5(C_3H_3SO_2)}$ and π-$\mathrm{C_5H_5Fe(CO)_2(C_4H_5SO_2)}$ lose SO_2 when heated *in vacuo* or treated with alumina, respectively, and revert to the parent alkynyls. Although 2-alkynyl-*S*-sulfinates are not accessible from the corresponding metal alkynyls and SO_2, one representative of this classs, π-$\mathrm{C_5H_5Fe(CO)_2(SO_2CH_2C{\equiv}CCH_3)}$, was synthesized by reaction of π-$\mathrm{C_5H_5Fe(CO)_2^-}$ with SO_2, followed by addition of $\mathrm{BrCH_2C{\equiv}CCH_3}$. Plausible mechanisms of these and related reactions of SO_2 are considered.

Introduction

Reactions between sulfur dioxide and transition metal–2-alkenyl complexes proceed with the formation of the corresponding *S*-sulfinates which often contain a rearranged allylic moiety[3] (eq 1). In order to ascertain

$$\mathrm{MCH_2CH{=}C(R)(R') + SO_2 \longrightarrow MSO_2C(R)(R')CH{=}CH_2} \quad (1)$$

whether a similar rearrangement to give allenylsulfinato complexes occurs with 2-alkynylmetal derivatives, we examined reactions of the latter with SO_2. Preliminary results of these studies have already been communicated;[4] at that time the products were formulated as possessing an allenyl(oxy)sulfinyl linkage, $\mathrm{MS(O)OC(R){=}C{=}CH_2}$. Later, investigations on such reactions were extended to other 2-alkynyls by Roustan and Charrier,[5] who designated the products as allenyl-*O*-sulfinates, $\mathrm{MOS(O)C(R){=}C{=}CH_2}$. As our studies on these systems expanded in scope, it became evident

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