of cations per anion respectively; the potassium fluorotungstate crystallizes in a system similar to that of a 2–18 compound such as $P_2W_{17}MnO_{61}(H_2O)K_8$.

The fact that the two X-ray powder patterns are very similar leads us to believe that this similarity stems from a structural similarity.

By using $P_2W_{18}O_{62}{}^{6-}$, Dawson was the first to establish the structure of the 2–18 series:[6] he showed that the molecule consists of two PW_9O_{34} units derived from the Keggin structure and joined together by six oxygen atoms (Figure 7).[21]

A glance at the model representation of the molecule (Figure 8) reveals that every XW_9O_{34} unit consists of a compact group W_3O_{13} of three octahedra joined together by three edges and the remaining six octahedra, ordered at the base of the XO_4 tetrahedron, forming a ring joined alternately by edges and corners.

It is reasonable to assume that in $H_2W_{18}F_6O_{56}{}^{8-}$ the fluorines are assigned to the corners of the tetrahedron, the center of which is occupied by a proton. NMR spectra show that, in the molecule which contains two tetrahedra, the fluorines are coupled in groups of three with a central proton; the J_{H-F} is very similar to that of the 1–12 series, in which the fluorines are clearly located on the central tetrahedron. Among the oxygens of the tetrahedron, we distinguish the one belonging to the compact group W_3O_{13} from the three others belonging to the ring: the first is bound to three W and the second only to two W. Also, on the basis of the NMR properties, we can assert that the fluorines are identical and that they replace the oxygens of the ring. It is noteworthy that the fluorines all occupy the same type of site, so that the overall symmetry of the molecule X_2W_{18} is preserved.[22]

Conclusion

We characterized by use of NMR data a new metatungstic species belonging to the 2–18 series and having the formula $H_2W_{18}O_{56}F_6{}^{8-}$.

Its essential properties, which differ from those of the fluorotungstates of the 1–12 series, are very similar to those of the previously examined heteropolyanions of the 2–18 series: stability with respect to OH^-, polarogram, molecular weight, and X-ray powder patterns. Hence the compound exhibits a number of remarkable NMR properties which support the hypothesis that it belongs to the 2–18 series.

It can be classified in the heteropolyanion category with the metatungstic structural model, since the two constitutive heteroelements of the 2–18 series molecule are replaced here by a proton. However, no unfluorinated equivalent compound has been observed up to the present. Fluorine probably has a stabilizing effect on such molecules. As in the fluorotungstates of the 1–12 series, the fluorine atoms are located at the center of the molecule and the structure retains a high degree of symmetry.

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Registry No. $[H_2W_{18}O_{56}F_6]H_8$, 74185-24-3; $[H_2W_{18}O_{56}F_6]K_8$, 74185-25-4; $[H_2W_{18}O_{56}F_6](N(CH_3)_4)_8$, 74331-35-4.

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Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

Selection Rules for Lanthanide Optical Activity

FREDERICK S. RICHARDSON

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Selection rules are developed for the electronic factors which govern the *magnitudes* of the chiroptical properties associated with the 4f–4f transitions in optically active lanthanide(III) complexes. These selection rules are based on the *S*, *L*, and *J* angular momentum quantum numbers of lanthanide 4f-electron states perturbed by spin–orbit coupling and 4f-electron/crystal field interactions. The lanthanide term-to-term transitions are classified according to their predicted (relative) electric dipole strengths, rotatory strengths, and dissymmetry factors in a chiral ligand environment. Several types of these transitions are predicted to be particularly favorable for optical activity studies (large rotatory strengths and dissymmetry factors). These transitions are designated as "CD-sensitive" transitions. Comparisons are made between available experimental data and the predictions derived from the selection rules and classification schemes developed in this study.

I. Introduction

The natural optical activity of lanthanide ions in chiral coordination environments has been the subject of a number of experimental studies.[1-17] Generally, the object of these studies has been to relate the spectroscopic observables of optical activity to specific structural features of the lanthanide

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coordination species present in the sample. These structural features include coordination geometry and stereochemistry, as well as the electronic structural properties of the lanthanide ion chromophore. Success in making these spectra–structure relationships is essential to establishing chiroptical spectroscopy as a useful probe of lanthanide complex structure. By analogy, chiroptical techniques have proved to be of enormous value in structural studies of transition-metal complexes.[1,18] Not only has optical activity been useful in elucidating the coordination geometries and ligand stereochemistry of transition-metal complexes, but it also has proved valuable in characterizing the electronic spectroscopic states of these systems.

The theory of natural optical activity in transition-metal complexes and its applications in the interpretation of chiroptical spectra are relatively well developed. Although the *quantitative* success of the prevailing theories and models in this field may be judged to be inadequate for detailed interpretation of spectra, it is generally agreed that they provide spectra–structure correlations which are qualitatively, and in some cases semiquantitatively, useful and reliable. In contrast, very little theoretical work has been done on the optical activity of chiral lanthanide complexes and the interpretation of lanthanide chiroptical spectra remains rather primitive. The dearth of theoretical studies on lanthanide optical activity can be attributed, in part, to the complexity of lanthanide ion electronic structure (especially in low-symmetry ligand fields) and to the general absence of chiral lanthanide complexes whose structural properties are well-defined and known. The latter situation hinders attempts to "calibrate" theoretical models on the basis of data obtained on *known* structures. In solution media (fluid phase), lanthanide complexes are generally assumed to be labile both with respect to lanthanide–ligand binding *and* with respect to coordination geometry.

Although certain lanthanide term-to-term 4f-electron transitions will remain relatively uncomplicated in low-symmetry coordination environments (such as, for example, the ${}^7F_0 \rightarrow {}^5D_{0,1,2}$ transitions of Eu^{3+}), most such transitions will exhibit very complex crystal field induced splittings and mixings (consider, for example, the ${}^3H_4 \rightarrow {}^1I_6$ transition of Pr^{3+}). The complexity of the lanthanide ion 4f-electron spectroscopic states and the relatively weak 4f-electron/crystal field interactions (that is, relative to the free-ion electrostatic and spin–orbit interactions) make development of a lanthanide optical activity theory especially difficult. There are, however, certain aspects of the lanthanide optical activity problem which are amenable to straightforward analysis without requiring a "full-blown" computational study. In the present study we shall restrict our attention to these aspects of the problem.

In a number of experimental studies on lanthanide optical activity, it has been noted that certain transitions (term-to-term) exhibit considerably greater dissymmetry factors than those of others. Dissymmetry factors are measures of the "degree of chirality" sensed by an electronic transition and are defined by

$$g_{\mathrm{abs}} = \Delta\epsilon/\epsilon \qquad (1)$$

in circular dichroism/absorption measurements, and by

$$g_{\mathrm{lum}} = \Delta I/I \qquad (2)$$

in circularly polarized luminescence/emission measurements. In these expressions

$$\Delta\epsilon = \epsilon_L - \epsilon_R \qquad \epsilon = (\epsilon_L + \epsilon_R)/2$$

$$\Delta I = I_L - I_R \qquad I = (I_L + I_R)/2$$

where $\epsilon_{L(R)}$ is the molar decadic extinction coefficient for left (right) circularly polarized light and $I_{L(R)}$ is the intensity of the left (right) circularly polarized component of the luminescence. The magnitudes of g_{abs} and g_{lum} may be taken as measures of the degree of optical activity in electronic absorption or emissive transitions. Lanthanide 4f–4f transitions exhibiting particularly large dissymmetry factors have been referred to in the literature as "CD-sensitive" transitions (in absorption)[4,5] or "CPL-sensitive" transitions (in emission).[19] CPL, here, refers to circularly polarized luminescence.[19]

In the present study we address the question of what electronic selection rules are operative in determining the CD- or CPL-sensitivity of lanthanide 4f–4f transitions. At present we are most interested in selection rules based on free-ion electronic quantum numbers (and applications to term-to-term transitions), rather than selection rules based on crystal field quantum numbers. The latter cannot be dealt with in the absence of extensive computational studies. The electronic selection rules considered here will not find direct application in making spectra–structure correlations since the details of the crystal (or ligand) fields will be ignored. Instead, they will help identify those lanthanide transitions which are most optically active and which will be most useful as diagnostic chiroptical probes. Additionally, they will also play a central role in more refined lanthanide optical activity models based on detailed crystal field analyses.

II. Theory

Considering an isotropic sample comprised of randomly oriented absorbing (or emitting) systems, the magnitude and sign of the optical activity associated with a transition a → b are gauged by the rotatory strength quantity

$$R_{ab} = \mathrm{Im}(\mathbf{P}_{ab}\cdot\mathbf{M}_{ba}) \qquad (3)$$

where $\mathbf{P}_{ab}$ is the electric dipole transition vector defined by eq 4 and $\mathbf{M}_{ba}$ is the magnetic dipole transition vector defined

$$\mathbf{P}_{ab} = \langle A_a|\hat{\mu}|A_b\rangle \qquad (4)$$

by eq 5. The electric dipole and magnetic dipole operators

$$\mathbf{M}_{ba} = \langle A_b|\hat{\mathbf{m}}|A_a\rangle \qquad (5)$$

are denoted, respectively, by $\hat{\mu}$ and $\hat{\mathbf{m}}$, and $|A_a\rangle$ and $|A_b\rangle$ denote the appropriate spectroscopic state functions involved in the a → b transition. To calculate the rotatory strength of a transition, we must first calculate the electric and magnetic dipole transition moment vectors and then evaluate the scalar product of these vectors. Equation 3 can be written alternatively as eq 6, where τ_{ab} is the angle between the $\mathbf{P}_{ab}$ and $\mathbf{M}_{ba}$ vectors.

$$R_{ab} = |\mathbf{P}_{ab}||\mathbf{M}_{ba}| \cos \tau_{ab} \qquad (6)$$

Since the 4f–4f lanthanide transitions are parity allowed in magnetic dipole radiation, the magnetic dipole transition moments $\mathbf{M}_{ba}$ can to a good approximation be evaluated within a spectroscopic basis set comprised entirely of 4f-electron configurational states. That is, the $|A_a\rangle$ and $|A_b\rangle$ state functions appearing in eq 5 may be assumed localized on the lanthanide ion and may be constructed as linear combinations of "free-ion" intermediate-coupling 4f-electron wave functions. In this approximation

$$|A_a\rangle = \sum_m C_{am}|A_m\rangle = \sum_{\psi J M_J} C(a|\psi J M_J)|\psi[SL]JM_J\rangle \qquad (7)$$

$$|A_b\rangle = \sum_n C_{bn}|A_n\rangle = \sum_{\psi' J' M'_J} C(b|\psi' J' M'_J)|\psi'[S'L']J'M'_J\rangle \qquad (8)$$

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where the $|A_m)$ and $|A_n)$ denote free-ion intermediate-coupling wave functions and the C_{am} and C_{bn} expansion coefficients are determined by the details of the crystal field acting on the lanthanide 4f electrons. Substituting eq 7 and 8 into eq 5 yields eq 9, where the magnetic dipole matrix elements are now

$$\mathbf{M}_{\mathrm{ba}} = \sum_{\psi JM_J} \sum_{\psi' J'M'_J} C^*(\mathrm{b}|\psi' J'M'_J) \times C(\mathrm{a}|\psi JM_J)(\psi'[S'L']J'M'_J|\hat{\mathbf{m}}|\psi[SL]JM_J) \quad (9)$$

expressed in the 4f-electron intermediate-coupling basis of the free ion. The rigorous selection rules governing these matrix elements are $\Delta J = 0$ or ± 1 (excluding $J = J' = 0$). Weaker, but still important, selection rules operative for these matrix elements are $\Delta L = 0$ and $\Delta S = 0$.

Since the 4f–4f lanthanide transitions are parity forbidden in electric dipole radiation, the state functions appearing in eq 4 must be expressed in a basis which includes states outside the $4f^N$ configurational manifold and, more specifically, these additional states must be of odd parity. In the so-called "static-coupling" mechanism for 4f–4f electric dipole intensity,[20–23] the odd-parity states included in the spectroscopic basis are taken from lanthanide $4f^{N-1}5d$ and $4f^{N-1}ng$ configurations, and the *interconfigurational* interactions are assumed to be due to odd-parity multipole (lanthanide)–point charge (ligand) interactions. In the "dynamic-coupling", or ligand polarization, mechanism for 4f–4f electric dipole intensity, the spectroscopic basis set is expanded to include (electric) dipolar excitations localized on the ligands.[22–25] In this latter case, the lanthanide–ligand interactions are described in terms of multipole (lanthanide)–dipole (ligand) couplings. These two mechanisms make separate contributions to the 4f–4f electric dipole transition moments and we may, therefore, write eq 10, where the superscripts (s) and (d) refer to the static- and dynamic-coupling contributions, respectively.

$$\mathbf{P}_{\mathrm{ab}} = \mathbf{P}_{\mathrm{ab}}^{(\mathrm{s})} + \mathbf{P}_{\mathrm{ab}}^{(\mathrm{d})} \quad (10)$$

The physical bases and formal treatment of the "static-coupling (SC)" and "dynamic-coupling (DC)" mechanisms for 4f–4f electric dipole intensity have been given elsewhere[22–26] and will not be recited again here. Referring to these previous treatments, the final expressions for $\mathbf{P}_{\mathrm{ab}}^{(\mathrm{s})}$ and $\mathbf{P}_{\mathrm{ab}}^{(\mathrm{d})}$ may be written as eq 11 and 12, where q denotes the qth spherical

$$\mathbf{P}_{\mathrm{ab}}^{(\mathrm{s})} = \sum_q P_{\mathrm{ab};q}^{(\mathrm{s})} = \sum_q \sum_{l_{\mathrm{A}}(\mathrm{odd})} \sum_{m_{\mathrm{A}}} (A(l_{\mathrm{A}},m_{\mathrm{A}}))(Z_{\mathrm{ab};q}^{(\mathrm{s})}(l_{\mathrm{A}},m_{\mathrm{A}})) \quad (11)$$

$$\mathbf{P}_{\mathrm{ab}}^{(\mathrm{d})} = \sum_q P_{\mathrm{ab};q}^{(\mathrm{d})} = \sum_q \sum_{l_{\mathrm{A}}(\mathrm{even})} \sum_{m_{\mathrm{A}}} (B(l_{\mathrm{A}},m_{\mathrm{A}};q))(Z_{\mathrm{ab}}^{(\mathrm{d})}(l_{\mathrm{A}},m_{\mathrm{A}})) \quad (12)$$

component ($q = 0, \pm 1$) of the vector quantities. The $A(l_{\mathrm{A}},m_{\mathrm{A}})$ coefficients depend upon ligand charges and ligand positional coordinates, and the $B(l_{\mathrm{A}},m_{\mathrm{A}};q)$ coefficients depend upon ligand dipolar polarizabilities and ligand positional coordinates. The electronic factors $Z_{\mathrm{ab};q}^{(\mathrm{s})}$ may be expressed as eq 13, where

$$Z_{\mathrm{ab};q}^{(\mathrm{s})}(l_{\mathrm{A}},m_{\mathrm{A}}) = e^2(-1)^{m_{\mathrm{A}}+q} \sum_{\lambda} (2\lambda+1) \begin{pmatrix} 1 & \lambda & l_{\mathrm{A}} \\ q & -m_{\mathrm{A}}-q & m_{\mathrm{A}} \end{pmatrix} \times (\Xi(l_{\mathrm{A}},\lambda))\Big[\sum_{\psi JM_J} \sum_{\psi' J'M'_J} C^*(\mathrm{a}|\psi JM_J) C(\mathrm{b}|\psi' J'M'_J) \times \begin{pmatrix} J & \lambda & J' \\ -M_J & m_{\mathrm{A}}+q & M'_J \end{pmatrix} (\psi J \| U^{(\lambda)} \| \psi' J')\Big] \quad (13)$$

$C(\mathrm{a}|\psi JM_J)$ and $C(\mathrm{b}|\psi' J'M'_J)$ are crystal field coupling coefficients as defined in eq 7 and 8, and the $\Xi(l_{\mathrm{A}},\lambda)$ factors are defined exactly as given by Krupke.[27] In eq 13, $\lambda = 2, 4$, or 6 and $l_{\mathrm{A}} = 1, 3, 5$, or 7.

The electronic factors $Z_{\mathrm{ab}}^{(\mathrm{d})}(l_{\mathrm{A}},m_{\mathrm{A}})$ in eq 12 are given in eq 14, where $l_{\mathrm{A}} = 2, 4$, or 6.

$$Z_{\mathrm{ab}}^{(\mathrm{d})}(l_{\mathrm{A}},m_{\mathrm{A}}) = -(7)^{1/2} e \sum_{\psi JM_J} \sum_{\psi' J'M'_J} (-1)^{J-M_J+3} \times C^*(\mathrm{a}|\psi JM_J) C(\mathrm{b}|\psi' J'M'_J) \times \begin{pmatrix} J & l_{\mathrm{A}} & J' \\ -M_J & m_{\mathrm{A}} & M'_J \end{pmatrix} \begin{pmatrix} 3 & l_{\mathrm{A}} & 3 \\ 0 & 0 & 0 \end{pmatrix} (\psi J \| U^{(l_{\mathrm{A}})} \| \psi' J')(4\mathrm{f} \| r^{l_{\mathrm{A}}} \| 4\mathrm{f}) \quad (14)$$

The electronic selection rules operative in eq 10 are entirely determined by the selection rules governing $Z_{\mathrm{ab}}^{(\mathrm{s})}$ and $Z_{\mathrm{ab}}^{(\mathrm{d})}$. The matrix elements over Russell–Saunders wave functions obey the selection rules (a) $\Delta S = 0$ for all values of λ and l_{A} in eq 13 and 14, (b) $|\Delta L| \leq \lambda$ in eq 13 and $|\Delta L| \leq l_{\mathrm{A}}$ in eq 14, and (c) $|\Delta J| \leq \lambda$ in eq 13 and $|\Delta J| \leq l_{\mathrm{A}}$ in eq 14, *except* when either J or $J' = 0$ in which case $|\Delta J| = 2, 4$, or 6. Only the latter selection rules on $|\Delta J|$ remain good in the intermediate-coupling approximation.

III. Selection Rules

A. General Aspects. The selection rules examined in this section are based on the magnetic dipole and electric dipole intensity models discussed in section II. Of principal interest are the *electronic* selection rules which play the dominant role in determining the optical activity of lanthanide term-to-term transitions. In this context, selection rules for ΔJ in electric and magnetic dipole transition matrix elements over intermediate-coupling states are of primary importance, while selection rules for ΔS and ΔL in matrix elements over Russell–Saunders states are of secondary importance. More general (and rigorous) selection rules based on crystal field effects will be left to a future, more detailed, computational study.

The dissymmetry factors given by eq 1 and 2 are defined in terms of the observables $\Delta\epsilon$, ϵ, ΔI, and I, each of which is frequency dependent. If we assume identical line shapes in circular dichroism and absorption, then g_{abs} will be a constant for a given absorptive transition, g → e, equal to[19] eq 15, where

$$f_{\mathrm{abs}}(\mathrm{g} \rightarrow \mathrm{e}) = 4R_{\mathrm{ge}}/D_{\mathrm{ge}} \quad (15)$$

R_{ge} is the rotatory strength of the transition and D_{ge} is the dipole strength of the transition. If we assume identical line shapes in the circularly polarized luminescence and total luminescence spectra, then g_{lum} will be a constant for a given emissive transition, g ← e, equal to[19] eq 16. In writing eq

$$g_{\mathrm{lum}}(\mathrm{g} \leftarrow \mathrm{e}) = 4R_{\mathrm{ge}}/D_{\mathrm{ge}} \quad (16)$$

15 and 16 we have assumed that all of the absorptive and emissive intensity is attributable to radiation–molecule *dipole* interaction mechanisms. If we further assume that the total absorption and emission intensities can be attributed predominantly to *electric dipole* interaction mechanisms, then we may write, for the dissymmetry factor of a transition a → b, eq 17

$$g(\mathrm{a} \rightarrow \mathrm{b}) = 4R_{\mathrm{ab}}/D_{\mathrm{ab}} = \frac{4|\mathbf{M}_{\mathrm{ba}}|}{|\mathbf{P}_{\mathrm{ab}}|} \cos \tau_{\mathrm{ab}} \quad (17)$$

from eq 6 and from eq 18, where a → b may be either ab-

$$D_{\mathrm{ab}} \simeq |\mathbf{P}_{\mathrm{ab}}|^2 \quad (18)$$

sorptive or emissive. For a given value of $\cos \tau_{\mathrm{ab}}$ (determined by the geometry of the overall system), the magnitude of $g(\mathrm{a} \rightarrow \mathrm{b})$ will be determined by the relative magnetic dipole allowedness vs. electric dipole allowedness of the transition.

The CD or CPL intensity of a transition a → b will be determined by R_{ab} as defined in eq 3 and 6. This rotatory

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Table I. Selection Rules Governing Electric and Magnetic Dipole Transitions between Perturbed 4f-Electron States

	magnetic dipole	electric dipole
		Weak[a]
ΔS	0	0
$\|\Delta L\|$	0	$\leqslant 6$
		Strong[b]
$\|\Delta J\|$	0, 1 (except $0 \longleftrightarrow 0$)	$\leqslant 6$ (except when either J or $J' = 0$, in which case $\|\Delta J\| = 2, 4$, or 6)

[a] Broken by spin–orbit interactions within the free ion. [b] Broken by lanthanide–crystal field interactions.

Table II. Spin–Orbit and Crystal Field Perturbations Required to Produce Nonvanishing Magnetic and Electric Dipole Transition Moments between Term Levels

transition properties				perturbation terms[b]	
type	$\|\Delta S\|$	$\|\Delta L\|$[a]	$\|\Delta J\|$	magnetic dipole	electric dipole
1	0	0	0, 1 ($J \neq 0 \neq J'$)	(0)	V_u
2	0	0	1 (J or $J' = 0$)	(0)	$V_g + V_u$
3	0	>0	0, 1 ($J \neq 0 \neq J'$)	V_g	V_u
4	0	>0	1 (J or $J' = 0$)	V_g	$V_g + V_u$
5	0	$\geqslant 0$	$2 \leqslant \|\Delta J\| \leqslant 6$ ($J \neq 0 \neq J'$)	V_g	V_u
6	0	$\geqslant 0$	2, 4, or 6 (J or $J' = 0$)	V_g	V_u
7	0	$\geqslant 0$	3 or 5 (J or $J' = 0$)	V_g	$V_g + V_u$
8	0	$\geqslant 0$	0 ($J = J' = 0$)	V_g	$V_g + V_u$
9	>0	$\geqslant 0$	0, 1 ($J \neq 0 \neq J'$)	H_{so}	$H_{so} + V_u$
10	>0	$\geqslant 0$	1 (J or $J' = 0$)	H_{so}	$H_{so} + V_g + V_u$
11	>0	$\geqslant 0$	$2 \leqslant \|\Delta J\| \leqslant 6$ ($J \neq 0 \neq J'$)	$H_{so} + V_g$	$H_{so} + V_u$
12	>0	$\geqslant 0$	2, 4, or 6 (J or $J' = 0$)	$H_{so} + V_g$	$H_{so} + V_u$
13	>0	$\geqslant 0$	3 or 5 (J or $J' = 0$)	$H_{so} + V_g$	$H_{so} + V_g + V_u$
14	>0	$\geqslant 0$	0 ($J = J' = 0$)	$H_{so} + V_g$	$H_{so} + V_g + V_u$

[a] Upper limit on $|\Delta L|$ is 6. [b] See section IIIA of text for definitions of H_{so}, V_g, and V_u.

Table III. Dependence of Electric Dipole Strengths, Rotatory Strengths, and Dissymmetry Factors on Spin–Orbit and Crystal Field Perturbation Terms

transition types[a]	electric dipole strengths[b]	rotatory strengths[c]	dissymmetry factors[d]
1	$(V_u)^2$	V_u	$(V_u)^{-1}$
2	$(V_g V_u)^2$	$V_g V_u$	$(V_g V_u)^{-1}$
3, 5, 6	$(V_u)^2$	$V_g V_u$	(V_g / V_u)
4, 7, 8	$(V_g V_u)^2$	$V_g^2 V_u$	$(V_u)^{-1}$
9	$(H_{so} V_u)^2$	$H_{so}^2 V_u$	$(V_u)^{-1}$
10	$(H_{so} V_g V_u)^2$	$H_{so}^2 V_g V_u$	$(V_g V_u)^{-1}$
11, 12	$(H_{so} V_u)^2$	$H_{so}^2 V_g V_u$	(V_g / V_u)
13, 14	$(H_{so} V_g V_u)^2$	$H_{so}^2 V_g^2 V_u$	$(V_u)^{-1}$

[a] See Table II for definitions and properties of the transition types. [b] Defined according to eq 18. [c] Defined according to eq 3. [d] Defined according to eq 17.

strength quantity, for a given value of cos τ_{ab}, will be dependent upon the electric *and* magnetic dipole strengths of the transition. It is evident at this point that the selection rules for large dissymmetry factors vs. large CD or CPL intensities are not the same. The largest dissymmetry factors will be exhibited by transitions which are magnetic dipole allowed and electric dipole forbidden. The largest CD or CPL intensities will be exhibited by transitions which are *both* electric dipole allowed and magnetic dipole allowed. These general statements apply, of course, only to situations where cos τ_{ab} can be considered constant. Given the electric dipole and magnetic dipole intensity mechanisms discussed in section II (vide supra), selection rules for transitions between *perturbed* intermediate-coupling states of the lanthanide ion may be readily deduced. These selection rules are summarized in Table I. To see how these selection rules may be applied to the *relative* dipole strengths, rotatory strengths, and dissymmetry factors of lanthanide term-to-term transitions, it is instructive to first examine the "effective" 4f-electron Hamiltonian operator for an optically active lanthanide complex. This operator may be written as in eq 19, where the free-ion Hamiltonian may

$$H_{4f} = H_{4f}(\text{free ion}) + H_{4f}(\text{cf}) \tag{19}$$

be expressed as in eq 20. In eq 20, the index i runs over all

$$H_{4f}(\text{free ion}) = \sum_i T_i - \sum_i (Z^* e^2/r_i) + \sum_{i<j} (e^2/r_{ij}) + \sum_i \zeta(r_i) \hat{s}_i \cdot \hat{l}_i \tag{20}$$

4f electrons ($i = 1$–N), Z^*e is the screened charge of the nucleus, $\zeta(r_i)$ is the radial spin–orbit coupling constant, and $\hat{s}_i$ and $\hat{l}_i$ are one-electron spin and orbital angular momentum operators, respectively. The kinetic energy operators are denoted by T_i. For our purposes, it will be useful to rewrite eq 20 as eq 21, where H_{so} is defined as just the last term in eq

$$H_{4f}(\text{free ion}) = H_{4f}(SLJ) + H_{so} \tag{21}$$

20. Although both $H_{4f}(SLJ)$ and H_{so} are diagonal in J, only $H_{4f}(SLJ)$ is diagonal in S and L.

The H_{4f}(cf) part of eq 19 is the crystal field interaction term, and it may be partitioned as in eq 22, where V_g and V_u are

$$H_{4f}(\text{cf}) = V_g + V_u \tag{22}$$

the components of H_{4f}(cf) which transform *gerade* and *ungerade*, respectively, under an inversion operation. The V_g operator is defined to operate only *within* the 4f-electron manifold of states, leading to J–J mixings and to J-level (crystal field) splittings. The V_u operator is an *interconfigurational* operator effective in mixing 4f-electron configurational states with states of opposite parity. The V_u operator plays the essential role in effecting electric dipole intensity in the lanthanide 4f–4f transitions.

Now we rewrite H_{4f} as eq 23. The operator, $H_{4f}(SLJ)$ +

$$H_{4f} = H_{4f}(SLJ) + H_{so} + V_g + V_u \tag{23}$$

H_{so}, determines the energy levels of the free ion, and its eigenstates are the so-called free-ion intermediate-coupling states, $|4f^N\psi[SL]JM_J\rangle$. The operator H_{so} mixes states of different S and L quantum numbers (so that S and L are no longer "good" quantum numbers). The intraconfigurational operator V_g splits J levels *and* mixes different J levels. The interconfigurational operator V_u mixes odd-parity states into the 4f-electron even-parity configurational states. To a very good approximation it may be assumed that $H_{so} \gg V_g > V_u$. Considering H_{so}, V_g, and V_u as perturbation operators in our analysis of the spectroscopic properties associated with the lanthanide 4f–4f transitions, we have constructed Table II to show which of these operators are essential to producing nonvanishing magnetic dipole and electric dipole transition moments for various types of transitions. Each transition type is characterized by changes in $S(\Delta S)$, $L(\Delta L)$, and $J(\Delta J)$. No explicit consideration is given to the details of the crystal field (as expressed by $V_g + V_u$), so crystal field quantum numbers have been ignored. Note that V_u is required for electric dipole strength in every transition (to break the Laporte forbiddeness of the 4f–4f transitions), and H_{so} is required for each transition type for which $|\Delta S| \neq 0$.

Using the results presented in Table II and the defining equations for electric dipole strength (eq 18), rotatory strength (eq 3), and dissymmetry factors (eq 17), we have constructed Table III. This table shows the qualitative dependence of each of these spectroscopic properties on the perturbative interactions H_{so}, V_g, and V_u. (The exponents on the terms appearing

Table IV. Classification Schemes for Electric Dipole Strengths, Rotatory Strengths, and Dissymmetry Factors

class	transition types[a]	class	transition types[a]
A. Electric Dipole Strength (Absorption and Emission Intensities)			
EI	1, 3, 5, 6	EIII	2, 4, 7, 8
EII	9, 11, 12	EIV	10, 13, 14
Relative Dipole Strengths: EI > EII > EIII > EIV			
B. Rotatory Strength (CD and CPL Intensities)			
RI	1	RIII	4, 7, 8, 10, 11, 12
RII	2, 3, 5, 6, 9	RIV	13, 14
Relative Rotatory Strengths: RI > RII > RIII > RIV			
C. Dissymmetry Factors			
DI	2, 10	DIII	3, 5, 6, 11, 12
DII	1, 4, 7, 8, 9, 13, 14		
Relative Dissymmetry Factors: DI > DII > DIII			

[a] See Table II for definitions of transition types.

in this table reflect our taking products of perturbed transition matrix elements and do not necessarily relate to *orders* of the perturbation expansions of the wave functions.) With use of the results shown in Table III and the assumption that $H_{so} \gg V_g > V_u$, the qualitative classification schemes of Table IV have been developed. These schemes classify the various term-to-term transition types according to their predicted *relative* electric dipole strengths, rotatory strengths, and dissymmetry factors. Taking H_{so} to be much larger than $H_{4f}(\mathrm{cf}) = V_g + V_u$ leads to very weak ΔS and ΔL selection rules (certainly a valid approximation for lanthanide systems). Taking $V_g > V_u$ assumes that *intraconfigurational* interactions are more important than *interconfigurational* interactions. A more detailed discussion of the classification schemes of Table IV will be given in sections IIIB and IIIC (vide infra).

The selection rules presented and used in Tables I–IV are based entirely on considerations of angular momentum quantum numbers (S, L, J) and parity. In this sense, they are equally applicable to all members of the lanthanide series. However, great caution must be exercised in using the classification schemes of Table IV when the spectroscopic results obtained for different lanthanide ions are compared. This is due to the fact that the radial parts of H_{so}, V_g, and V_u and the electric dipole transition amplitudes exhibit significant variations across the lanthanide series. For example, the radial spin–orbit coupling constant (ζ) increases across the series with the value for $\mathrm{Pr}^{3+}(4\mathrm{f}^2)$ being less than one-third the value for $\mathrm{Er}^{3+}(4\mathrm{f}^{11})$. On the other hand, the values of $\langle r^k \rangle_{4f}$ generally decrease on going from the beginning of the series ($4\mathrm{f}^1$) to the end ($4\mathrm{f}^{14}$). Variations in energy spacings between term levels can also influence the extent to which V_g can cause J-level mixing. Clearly, the term (energy) structure and the radial dependence of H_{so}, V_g, and V_u must be taken into account when the classification schemes of Table IV are applied to *different* lanthanide ions.

In constructing Tables II–IV, details of the lanthanide–crystal field interactions (V_g, V_u) have been ignored. Therefore, neither the signs nor the magnitudes of the cos τ_{ab} factors of eq 17 are taken into account. These factors will depend upon the geometrical and symmetry properties of the ligand environment and, ultimately, upon the polarizations of the electric and magnetic dipole transition vectors. A detailed consideration of these factors is beyond the scope of the present study. However, one simple and qualitative consideration of the lanthanide–crystal field interactions allows breaking transition types 5, 6, 11, and 12 (see Table II) down into additional subsets. Computational studies[28] show that J–J' mixing for $|J' - J| = |\Delta J| \leq 2$ is very much larger than for $|\Delta J| > 2$. Thus, transitions requiring $|\Delta J| > 2$ are predicted to be much less intense than transitions involving $|\Delta J| \leq 2$. This prediction is in agreement with empirical observation.[22–25]

B. Rotatory Strengths and Dissymmetry Factors. A problem arises as to what is meant by "term-to-term" rotatory strengths and dissymmetry factors. Since term-to-term transitions are generally comprised of a set of crystal field transitions, a term-to-term rotatory strength may in some cases refer to the algebraic sum of component crystal field rotatory strengths (recall that rotatory strength is a signed quantity). In this case we may write eq 24, where A → B denotes a

$$R_{\mathrm{AB}} = \sum_{\mathrm{a}}\sum_{\mathrm{b}}(B_{\mathrm{a}}(T))R_{\mathrm{ab}} \tag{24}$$

term-to-term transition comprised of a set of a → b crystal field component transitions and where $B_a(T)$ is an appropriate Boltzmann weighting factor for initial state a. Similarly for the term-to-term dissymmetry factor

$$G_{\mathrm{AB}} = \sum_{\mathrm{a}}\sum_{\mathrm{b}}(B_{\mathrm{a}}(T))(4R_{\mathrm{ab}}/D_{\mathrm{ab}}) \tag{25}$$

In the treatment of lanthanide optical activity presented here, we have ignored the details of the lanthanide–crystal field interactions. Therefore, we have no information regarding the relative signs and orientations of the $\mathbf{P}_{ab}$ and $\mathbf{M}_{ba}$ transition vectors and consequently no information regarding the relative signs of the a → b crystal field rotatory strengths within a term-to-term transition. Our treatment is appropriate only to the *magnitudes* of R_{ab} and g_{ab} as determined by the parentages of states a and b to various (SLJ) levels. The results shown in Tables II–IV apply, then, to crystal field components of the term-to-term transitions. It is possible that even though the magnitudes of the component R_{ab} values within a particular term-to-term manifold of crystal field transitions are predicted to be large, the value of R_{AB} may be vanishingly small.

It is clear from Table IV that what is meant by a "CD-sensitive" or "CPL-sensitive" transition depends upon whether one is using CD (or CPL) intensities or dissymmetry factors as the diagnostic criteria. With regard to dissymmetry factors, one set of easily observable transitions stand out as uniquely suitable for chiroptical measurements. These transitions are the ${}^7\mathrm{F}_0 \rightarrow {}^5\mathrm{D}_1$ and ${}^7\mathrm{F}_1 \rightarrow {}^5\mathrm{D}_0$ excitations in Eu^{3+} and the ${}^7\mathrm{F}_1 \leftarrow {}^5\mathrm{D}_0$ emission of Eu^{3+}. Each of these transitions is of type 10 and belongs to the dissymmetry factor DI class. The Eu^{3+} ${}^7\mathrm{F}_0 \rightarrow {}^7\mathrm{F}_1$ transition (type 2) also falls in the DI class, but the excitation frequency of this transition is the far-infrared region (~ 350 cm^{-1}). The ${}^7\mathrm{F}_0 \rightarrow {}^5\mathrm{D}_1$ and ${}^7\mathrm{F}_1 \rightleftarrows {}^5\mathrm{D}_0$ Eu^{3+} transitions are, in fact, the *only* lanthanide transitions which are in class DI and which are accessible to absorption/CD or emission/CPL measurements. From Table III we note that both the rotatory strengths and dissymmetry factors of type 10 transitions depend upon the V_g *and* V_u components of the crystal field. This suggests that the chiroptical properties of these transitions should be especially sensitive to the detailed structural features of the ligand environment. For the Eu^{3+} ${}^7\mathrm{F}_0 \rightarrow {}^5\mathrm{D}_1$ and ${}^7\mathrm{F}_1 \rightleftarrows {}^5\mathrm{D}_0$ transitions, $|\Delta J| = |\Delta L| = |\Delta S| = 1$, so that these transitions are magnetic dipole allowed to *first order* in the H_{so} operator.

With regard to rotatory strength, all of the absorptive transitions belonging to the RI class (type 1 transitions) have excitation frequencies falling in the infrared spectral region. These transitions are magnetic dipole allowed to zeroth order and gain electric dipole strength to first order in V_u. They each belong to the DII dissymmetry factor class. A listing of these transitions is given in Table V. The RII class of transitions includes five different transition types (2, 3, 5, 6, 9). A selection of transitions falling in this class is given in Table VI. These transitions are predicted to exhibit relatively large rotatory strengths, but they vary with respect to the predicted dissymmetry factors.

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(28) Faulkner, T. R.; Saxe, J. D.; Richardson, F. S., unpublished results.

Table V. Transitions Belonging to the RI Class

ion	transition	transition freq (approx),[a] cm^{-1}
Ce^{3+}	$^2F_{5/2} \rightarrow ^2F_{7/2}$	2100
Pr^{3+}	$^3H_4 \rightarrow ^3H_5$	2150
Nd^{3+}	$^4I_{9/2} \rightarrow ^4I_{11/2}$	2000
Pm^{3+}	$^5I_4 \rightarrow ^5I_5$	1600
Sm^{3+}	$^6H_{5/2} \rightarrow ^6H_{7/2}$	1400
Eu^{3+}	$^7F_1 \rightarrow ^7F_2$	1100
Tb^{3+}	$^7F_6 \rightarrow ^7F_5$	2100
Dy^{3+}	$^6H_{15/2} \rightarrow ^6H_{13/2}$	3500
Ho^{3+}	$^5I_8 \rightarrow ^5I_7$	5000
Er^{3+}	$^4I_{15/2} \rightarrow ^4I_{13/2}$	6400
Tm^{3+}	$^3H_6 \rightarrow ^3H_5$	5800
Yb^{3+}	$^2F_{7/2} \rightarrow ^2F_{5/2}$	10000

[a] Approximate barycenter locations.

Table VI. A Selection of Transitions Belonging to the RII Class[a]

ion	transition	type	dissymmetry class	transition freq (approx),[b] cm^{-1}
Pr^{3+}	$^3H_4 \rightarrow ^3P_2$	5	DIII	23 150
	$\rightarrow ^3P_1$	5	DIII	22 000
	$\rightarrow ^3P_0$	5	DIII	21 400
	$\rightarrow ^1G_4$	9	DII	9 950
Nd^{3+}	$^4I_{9/2} \rightarrow ^2H_{9/2}$	9	DII	12 600
	$\rightarrow ^4F_{7/2}$	3	DIII	13 500
	$\rightarrow ^4G_{5/2}$	5	DIII	17 300
	$\rightarrow ^4G_{7/2}$	3	DIII	17 500
Eu^{3+}	$^7F_1 \rightarrow ^5D_1$	9	DII	18 700
	$\rightarrow ^5D_2$	9	DII	21 200
Tb^{3+}	$^7F_6 \rightarrow ^5G_6$	9	DII	26 200
	$\rightarrow ^5G_5$	9	DII	27 800
Dy^{3+}	$^6H_{15/2} \rightarrow ^4I_{15/2}$	9	DII	21 900
Ho^{3+}	$^5I_8 \rightarrow ^3K_8$	9	DII	21 300
	$\rightarrow ^5G_6$	5	DIII	22 100
	$\rightarrow ^5G_5$	5	DIII	23 900
	$\rightarrow ^3K_7$	9	DII	26 100
Tm^{3+}	$^3H_6 \rightarrow ^3F_4$	5	DIII	12 700

[a] All of the transitions listed here have transition frequencies in the visible or near-infrared region of the spectrum. [b] Approximate barycenter locations.

Table VII. Classifications for Emissive Transitions in Eu^{3+} and Tb^{3+} Complexes

ion	transition	type	classification		
Eu^{3+}	$^7F_0 \leftarrow ^5D_0$	14	EIV	RIV	DII
	$^7F_1 \leftarrow$	10	EIV	RIII	DI
	$^7F_2 \leftarrow$	11	EII	RIII	DIII
	$^7F_3 \leftarrow$	13	EIV	RIV	DII
	$^7F_4 \leftarrow$	12	EII	RIII	DIII
Tb^{3+}	$^7F_6 \leftarrow ^5D_4$	11	EII	RIII	DIII
	$^7F_5 \leftarrow$	9	EII	RII	DII
	$^7F_4 \leftarrow$	9	EII	RII	DII
	$^7F_3 \leftarrow$	9	EII	RII	DII
	$^7F_2 \leftarrow$	11	EII	RIII	DIII
	$^7F_1 \leftarrow$	11	EII	RIII	DIII
	$^7F_0 \leftarrow$	12	EII	RIII	DIII

In aqueous solution at room temperature only Eu^{3+} and Tb^{3+} complexes exhibit significant luminescence. The Eu^{3+} emitting level is $^5D_0$ and the Tb^{3+} emitting level is $^5D_4$. The luminescence quantum yields of Tb^{3+} complexes are generally somewhat higher than those of the corresponding Eu^{3+} complexes. CPL spectra have been reported for a wide variety of optically active Eu^{3+} and Tb^{3+} complexes in solution.[9-17] The luminescent transitions observed in these spectra are listed and classified in Table VII according to the classification schemes presented in Table IV. Among the Tb^{3+} transitions, the $^7F_5$, $^7F_4$, and $^7F_3 \leftarrow ^5D_4$ emissions are predicted to exhibit the greatest optical activity (the largest rotatory strengths and g_{lum} values). This prediction is in complete agreement with experimental observation.[19] Among the Eu^{3+} transitions, the most remarkable is the $^7F_1 \leftarrow ^5D_0$ emission which is predicted to exhibit very large g_{lum} values. Again, this is in complete agreement with experimental observation. The largest g_{lum} values reported to date in the literature have been associated with the Eu^{3+} $^7F_1 \leftarrow ^5D_0$ emissive transitions.[12]

Only three transition types (1, 2, 9) span the (RI + RII) *and* (DI + DII) classes of Table IV. These transition types should prove to be the most suitable for chiroptical studies. In absorption these transitions should exhibit relatively large values for both $\Delta\epsilon$ and g_{abs}, which is essential to obtaining good experimental spectra. Although transitions of type 10 are predicted to exhibit relatively weak CD intensities (low rotatory strength, RIII class), their (predicted) large dissymmetry factors may also make them favorable candidates for CD/absorption studies. Among the transition types 1, 2, 9, and 10, types 2 and 10 should exhibit the greatest sensitivity to details of the ligand environment since their electric dipole strength and rotatory strength depend upon *both* the V_g and V_u components of the lanthanide–crystal field interaction. The one common characteristic of the 1, 2, 9, and 10 *favored* set of transition types is that in each case the transitions are magnetic dipole allowed in the free-ion intermediate-coupling approximation (that is, $\Delta J = 0$ or ± 1, excluding $J = J' = 0$).

C. Electric Dipole Strengths. The electric dipole transition moments of the transitions classified as EI in Table IV share two characteristics in common. First, they are each first order in V_u, and, second, they obey the selection rules $|\Delta S| = 0$, $|\Delta L| \leq 6$, and $|\Delta J| \leq 6$. The transition types classified as EII obey these same selection rules with the one exception that for these transitions $|\Delta S| \neq 0$. A *subset* of the transition types falling in the EI and EII classes of Table IV constitutes a class of transitions which are referred to as "hypersensitive" or "potentially hypersensitive" transitions. These transitions conform to the selection rules $|\Delta J| \leq 2$ and $|\Delta L| \leq 2$. In an operational (empirical) context, a hypersensitive 4f–4f transition is one whose absorption and/or emission intensity exhibits very strong sensitivity to the ligand environment (especially to the nature of the donor ligand groups). Empirically, it has been found that the hypersensitive transitions conform to the $|\Delta J| \leq 2$ and $|\Delta L| \leq 2$ selection rules.[22,29] Ignoring the weaker $\Delta S = 0$ condition, these selection rules are just those of an electric quadrupole transition. Two of the prevailing theories of hypersensitivity identify electric quadrupole allowedness as a precondition for a transition to exhibit hypersensitivity.[22,29] In the present study, we are concerned with the electric dipole strength of a transition only insofar as it influences the chiroptical properties, rotatory strength and dissymmetry factors.

IV. Discussion

The selection rules and transition classifications developed in this study were based entirely on the angular momentum quantum numbers S, L, and J appropriate to the 4f-electron states in an intermediate-coupling representation. As such, they are directly applicable to the chiroptical properties of lanthanide term-to-term transitions, but they reveal little about the crystal-field structure within these transitions. Their validity and utility of application rest largely on the assumption that the purely electronic factors governing the chiroptical properties of lanthanide 4f–4f transitions will be dominated by the free-ion parentage of the transitions. Except for parity, details of crystal field structure have been ignored so that our selection rules apply only to relative *magnitudes* of rotatory strengths and dissymmetry factors, and not to relative signs. A full crystal field treatment must be carried out to account

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(29) Henrie, D. E.; Fellows, R. L.; Choppin, G. R. *Coord. Chem. Rev.* **1976**, *18*, 199.

for the detailed band structures observed in 4f–4f chiroptical spectra. Despite the qualitative nature of the treatment given here, the selection rules and classification schemes given in Tables II–IV should prove useful in identifying those lanthanide transitions most suitable as diagnostic chiroptical probes.

How easily a transition may be studied by absorption/CD measurements is determined by two criteria: (1) the magnitude of the rotatory strength of the transition; and (2) the dissymmetry factor of the transition. In section IIIB, we identified three transition types which are predicted to satisfy these dual criteria. These transition types are 1, 2, and 9, with each satisfying the selection rule $|\Delta J| \leq 1$ (excluding $J = J' = 0$). We designate transitions belonging to any one of these three types as "CD-sensitive" transitions. Another transition type of special interest is type 10. Although the rotatory strengths of transitions belonging to type 10 are predicted to be relatively small in magnitude, the dissymmetry factors associated with these transitions are predicted to be very large. Additionally, type 10 transitions are predicted to be very sensitive to crystal field effects (via V_g and V_u). We shall also designate the type 10 transitions as "CD-sensitive".

All of the transitions listed in Table V are of type 1 and are categorized, therefore, as "CD-sensitive". No CD measurements have been reported for any of these transitions, although they are predicted to have large rotatory strengths and reasonably large dissymmetry factors. Many of these transitions are accessible to study by existing infrared CD spectrophotometers. Some additional examples of transitions predicted to be "CD-sensitive" are given in Table VI (type 9) and in Table VII (types 9, 10).

In our CPL studies of Eu^{3+} complexes in solution,[9–14] the CPL (ΔI) intensities of the $^7F_1 \leftarrow {}^5D_0$ and $^7F_2 \leftarrow {}^5D_0$ transitions are invariably found to be roughly comparable, with the $^7F_1 \leftarrow {}^5D_0$ CPL showing the greater sensitivity to changes in the ligand environment. On the other hand, $g_{lum}({}^7F_1 \leftarrow {}^5D_0)$ is always observed to be about an order-of-magnitude larger (in absolute magnitude) than $g_{lum}({}^7F_2 \leftarrow {}^5D_0)$. Similarly in absorption/CD studies, the $^7F_0 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_2$ transitions exhibit comparable CD intensities ($\Delta\epsilon$) while $g_{abs}({}^7F_0 \rightarrow {}^5D_1)$ is generally found to be about 10 times larger than $g_{abs}({}^7F_0 \rightarrow {}^5D_2)$. It is quite common to observe dissymmetry factors $|g| > 0.3$ for the Eu^{3+} $^7F_0 \rightarrow {}^5D_1$ and $^7F_1 \leftarrow {}^5D_0$ transitions—values which are *extraordinarily* large for *any* optically active system. These results are in complete agreement with our classification of the $^7F_{0(1)} \rightleftarrows {}^5D_{1(0)}$ transitions as (RIII, DI) and our classification of the $^7F_{0(2)} \leftrightarrow {}^5D_{2(0)}$ transitions as (RIII, DIII).

CPL results on Tb^{3+} complexes in solution[9,10,14–17] are also in complete qualitative agreement with predictions based on the classifications of Table VII. The largest dissymmetry factors are observed within the predicted "CD-sensitive" transitions, $^7F_5$, $^7F_4$, and $^7F_3 \leftarrow {}^5D_4$. More quantitatively, the $^7F_5 \leftarrow {}^5D_4$, dissymmetry factors (and CPL intensities) are generally observed to be 3–10 times greater than those observed for the $^7F_4$ and $^7F_3 \leftarrow {}^5D_4$ transitions. These quantitative differences cannot be explained on the basis of the selection rules developed in the present study. However, they *are* explicable in a rather straightforward way when the details of crystal field induced *J*-level mixings are taken into account.[28]

Sen, Bera, and Chowdhury[3] have reported rotatory strengths and dissymmetry factors for the $^3H_4 \rightarrow {}^3P_2$, $^3P_1$, and $^3P_0$ transitions of Pr^{3+} in crystalline $Na_3[Pr(oxydiacetate)_3]\cdot 2NaClO_4\cdot 6H_2O$. The rotatory strengths are moderately large ($(\sim 1–3) \times 10^{-42}$ esu^2 cm^2), but the dissymmetry factors are relatively small ($(\sim 1–25) \times 10^{-3}$ esu^2 cm^2). Each of these transitions belongs to our classes RII and DIII (see Table VI). For Eu^{3+} in the same crystalline host, we have obtained the results[30]

transitions	$^7F_0 \rightarrow {}^5D_1$	$^7F_0 \rightarrow {}^5D_2$
rotatory strength	0.17×10^{-42} esu^2 cm^2	0.12×10^{-42} esu^2 cm^2
dissymmetry factor	0.38	0.061
classifications	RIII, DI	RIII, DIII

These results further support the qualitative correctness of the classification schemes given in Table IV.

The transition types most commonly found to be hypersensitive in absorption are 5, 6, 11, and 12, with the restriction that $|\Delta J| = 2$. We note from Table IV that each of these transition types falls in the dissymmetry factor DIII class and in either the RII or RIII rotatory strength class. From this it may be concluded that the 4f–4f hypersensitive transitions will not, in general, be the most favorable chiroptical probe transitions.

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(30) Morley, J.; Banerjee, A.; Schwartz, R. W.; Richardson, F. S., unpublished results.

Contribution from the Chemistry Department,
Colorado State University, Fort Collins, Colorado 80523

Additivity of d–d Circular Dichroism in Discrimination between the Cis-α and Cis-β Modes of Wrapping of Substituted Triethylenetetramines in Cobalt(III) Complexes

ROBERT JOB* and PATRICK J. KELLEHER

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When solutions of *cis*-α and *cis*-β-(carbonato) and *cis*-α- and *cis*-β-dinitro complexes of (triethylenetetramine)cobalt(III) in 3 M *d*-tartaric acid were heated for a 2-h period, intense CD spectra developed in the visible region. The CD spectra of the β complexes were nearly identical with each other but were dramatically different from those of the α complexes. The same results extended to vicinal effects (calculated from a CD additivity rule) obtained for Λ-α- and Δ-β-(carbonato)- and Λ-α- and Δ-β-dinitrocobalt(III) complexes of the substituted tetraamines (2*S*,9*S*)-2,9-diamino-4,7-diazadecane and (3*S*,10*S*)-3,10-diamino-5,8-diaza-2,11-dimethyldodecane in *d*- and *l*-tartaric acids.

Introduction

The recent work of Schipper has provided a firm theoretical foundation for additivity in circular dichroism of the d–d transitions of chiral complexes.[1] The simplest example of an additivity rule is as follows: consider a complex, AB_1B_2 (composite complex), with two chiral centers, B_1 and B_2, and

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(1) Schipper, P. E. *J. Am. Chem. Soc.* **1978**, *100*, 1433.

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