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Model Calculations for the Intensity Parameters of Nine-Coordinate Erbium(III) Complexes of Trigonal Symmetry

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Model calculations of 4f–4f intensity parameters are reported for a series of tris(terdentate) Er(III) complexes. Four of these complexes are assumed to have trigonal dihedral (D_3) symmetry, and two are assumed to have C_{3h} symmetry. The ligands in the D_3 complexes are oxydiacetate (ODA), dipicolinate (DPA), chelidonate (CDO), and chelidamate (CDA). The ligands in the C_{3h} complexes are iminodiacetate (IDA) and (methylimino)diacetate (MIDA). The intensity calculations are based on an electrostatic intensity model for lanthanide 4f → 4f electric-dipole transitions, which includes consideration of both the static-coupling (point-charge crystal field) and dynamic-coupling (ligand-polarization) intensity mechanisms. The intensity parameters obtained from the model calculations are compared to those derived from empirical intensity data, and correlations are made between the relative intensity properties exhibited by the various systems and their respective structural features (including properties inherent to their constituent ligands). Conclusions are drawn regarding the relative contributions made by the static-coupling vs. dynamic-coupling mechanisms to the Ω_λ (λ = 2, 4, 6) intensity parameters.

Introduction

In this paper we attempt to rationalize the relative values of the electric-dipole intensity parameters reported in the preceding paper[1] for a series of erbium(III) complexes. We consider just one structure type (and coordination geometry) for each complex, and we employ a theoretical model identical with that applied previously in our studies of neodymium(III) and holmium(III) complexes.[2] This model includes explicit consideration of both the *static-coupling* (or static-charge) and *dynamic-coupling* (or ligand-polarization) mechanisms of 4f → 4f electric-dipole intensity,[3-5] but it neglects all intensity contributions that require lanthanide–ligand orbital overlap. According to this model, the ligand dependence of the Ω_λ intensity parameters can be rationalized (and calculated) in terms of the spatial distribution of atomic charges, atomic polarizabilities, and chemical-bond polarizabilities in the ligand environment of a lanthanide ion. The ligand environment is represented as an array of atomic and chemical-bond perturber sites (each with a characteristic electric charge and/or polarizability), and each site is presumed to perturb the $4f^N$ electronic configuration of the lanthanide ion via purely electrostatic interactions.[4,5]

The systems of primary interest in this study are the tris(terdentate) complexes $Er(ODA)_3^{3-}$ (**1**), $Er(DPA)_3^{3-}$ (**2**), $Er(CDO)_3^{6-}$ (**3**), $Er(CDA)_3^{6-}$ (**4**), $Er(IDA)_3^{3-}$ (**5**), and $Er(MIDA)_3^{3-}$ (**6**), where ODA = oxydiacetate, DPA = dipicolinate, CDO = chelidonate,[6] CDA = chelidamate,[7] IDA = iminodiacetate, and MIDA = (methylimino)diacetate. Systems **1**–**4** are assumed to have trigonal dihedral (D_3) symmetry (as was described in ref 1), and systems **5** and **6** are assumed to have C_{3h} symmetry (see ref 1).

Theory

The formal theory and mechanistic bases for the static-coupling (SC) and dynamic-coupling (DC) electrostatic models of 4f → 4f electric-dipole intensity have been presented and discussed elsewhere,[2-5] so we restrict our discussion here to the final expressions required to carry out actual calculations of the Ω_λ intensity parameters. Equation 2 in ref 1 shows how these parameters are related to the oscillator strengths of multiplet-to-multiplet ($\psi J \rightarrow \psi' J'$) transitions.

Assuming that the static-coupling and dynamic-coupling intensity mechanisms make *independent* contributions to the electric-dipole transition moments, and neglecting contributions from all other mechanisms, the Ω_λ parameters may be partitioned as

$$\Omega_\lambda = \Omega_\lambda[\mathrm{SC}] + \Omega_\lambda[\mathrm{DC}] + \Omega_\lambda[\mathrm{SC, DC}] \qquad (1)$$

where $\Omega_\lambda[\mathrm{SC}]$ denotes the contribution made by the static-coupling mechanism alone, $\Omega_\lambda[\mathrm{DC}]$ denotes the contribution made by the dynamic-coupling mechanism alone, and $\Omega_\lambda[\mathrm{SC, DC}]$ represents contributions arising from ***interferences*** between transition moments induced by the SC and DC mechanisms.[2-5] The $\Omega_\lambda[\mathrm{SC}]$ and $\Omega_\lambda[\mathrm{DC}]$ terms are, of course, always positive in sign, whereas the $\Omega_\lambda[\mathrm{SC, DC}]$ term may be either positive or negative in sign, depending on the relative phases of the SC and DC electric-dipole transition moments. The phase relationships between these transition moments are dependent on the geometrical distributions of ligand charge and polarizability about the lanthanide ion.

The main objectives of the present study are to assess the relative importance of the [SC], [DC], and [SC, DC] contributions to the Ω_λ intensity parameters for the systems described in the Introduction and to compare the calculated $\Omega_\lambda[\mathrm{total}]$ values to the empirically determined values reported in ref 1. In a consideration of the various contributions to the Ω_λ parameters, it will be useful to define each Ω_λ in terms of yet another set of parameters:

$$\Omega_\lambda = (2\lambda + 1)^{-1} \sum_{t,p} |A_{tp}^{\lambda}|^2 \qquad (2)$$

where the A_{tp}^{λ} parameters have been defined previously[2,4,5] to parametrize the electric-dipole transition moments associated with transitions between individual crystal field (Stark) levels. Each A_{tp}^{λ} parameter may be partitioned into a SC part and a DC part, so that

$$A_{tp}^{\lambda} = A_{tp}^{\lambda}[\mathrm{SC}] + A_{tp}^{\lambda}[\mathrm{DC}] \qquad (3)$$

Substituting eq 3 into eq 2 yields an expression for Ω_λ that may be rearranged to a form reflecting the three terms appearing in eq 1.

In the static-coupling model the ligand field is represented as an array of point charges, and the $A_{tp}^{\lambda}[\mathrm{SC}]$ parameters may be expressed as[4,5]

$$A_{tp}^{\lambda}[\mathrm{SC}] = -A_{tp}[\Xi(t, \lambda)][(2\lambda + 1)/(2t + 1)^{1/2}] \qquad (4)$$

with t restricted to values of $\lambda \pm 1$ and with A_{tp} being an odd-parity crystal field parameter defined by

$$A_{tp} = -(-1)^p e^2 \sum_L q_L [C_{-p}^{t}(\theta_L, \phi_L)] R_L^{-(t+1)} \qquad (5)$$

where eq_L represents the charge on the Lth ligand perturber site, (R_L, θ_L, ϕ_L) are the positional coordinates of the Lth site, and C_{-p}^{t} is a spherical tensor. The $\Xi(t, \lambda)$ quantity in eq 4 depends entirely on the electronic properties of the lanthanide ion, and it is defined here exactly as in eq 14 of Judd.[8]

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[1] Devlin, M. T.; Stephens, E. M.; Richardson, F. S.; Van Cott, T.; Davis, S. A. *Inorg. Chem.*, preceding paper in this issue.

[2] Stephens, E. M.; Reid, M. F.; Richardson, F. S. *Inorg. Chem.* **1984**, *23*, 4611.

[3] Richardson, F. S. *Chem. Phys. Lett.* **1982**, *86*, 47.

[4] Reid, M. F.; Richardson, F. S. *J. Chem. Phys.* **1983**, *79*, 5735.

[5] Reid, M. F.; Richardson, F. S. *J. Phys. Chem.* **1984**, *88*, 3579.

[6] Chelidonate (CDO) refers here to the deprotonated form of chelidonic acid (4-hydroxypyran-2,6-dicarboxylic acid) in aqueous solution under alkaline pH conditions.

[7] Chelidamate (CDA) refers here to the deprotonated form of chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid) in aqueous solution under alkaline pH conditions.

[8] Judd, B. R. *Phys. Rev.* **1962**, *127*, 750.

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Table I. Lanthanide Electronic Parameters Used in the Ω_λ Calculations[a]

parameter	value	parameter	value
$\Xi(1, 2)$	-9.61×10^{-7} cm^2/erg	$\langle r^2 \rangle$	1.706×10^{-17} cm^2
$\Xi(3, 2)$	8.74×10^{-23} cm^4/erg	$\langle r^4 \rangle$	4.126×10^{-33} cm^4
$\Xi(3, 4)$	8.84×10^{-23} cm^4/erg	$\langle r^6 \rangle$	9.826×10^{-49} cm^6
$\Xi(5, 4)$	-1.14×10^{-38} cm^6/erg		
$\Xi(5, 6)$	-2.43×10^{-38} cm^6/erg		
$\Xi(7, 6)$	3.16×10^{-54} cm^8/erg		

[a] The $\Xi(t, \lambda)$ values were taken from Leavitt and Morrison,[9] and the $\langle r^\lambda \rangle$ values were taken from Morrison and Leavitt.[10]

In the dynamic-coupling model employed here, the ligand field is represented as an array of polarizable charge distributions associated with atoms, groups of atoms, and chemical bonds. Allowing for polarizability *anisotropy* in each of the perturbing charge distributions, each $A_{tp}{}^{\lambda}$[DC] parameter may be expressed as a sum of two contributions[4,5]

$$A_{tp}{}^{\lambda}[\mathrm{DC}] = A_{tp}{}^{\lambda}[\mathrm{DC}, \bar{\alpha}] + A_{tp}{}^{\lambda}[\mathrm{DC}, \beta] \qquad (6)$$

where $A_{tp}{}^{\lambda}[\mathrm{DC}, \bar{\alpha}]$ represents the contributions from the spherically symmetric (isotropic) components of the ligand polarizabilities and $A_{tp}{}^{\lambda}[\mathrm{DC}, \beta]$ includes all contributions arising from ligand polarizability anisotropy. Expressions for the $A_{tp}{}^{\lambda}[\mathrm{DC}, \bar{\alpha}]$ and $A_{tp}{}^{\lambda}[\mathrm{DC}, \beta]$ parameters, appropriate for the model calculations reported here, are given by eq 8 and 9 in ref 2. These expressions assume that each ligand perturber entity (which may be an atom, a group of atoms, or a chemical bond) has a polarizability ellipsoid that is at least cylindrically symmetric.[2,4,5] Therefore, only two numbers are needed to characterize the polarizability of each ligand perturber. These numbers are the values of $\alpha_{\parallel}'(L)$ and $\alpha_{\perp}'(L)$, which represent polarizability components defined parallel ($\parallel$) and perpendicular ($\perp$) to the principal axis of the ligand's polarizability ellipsoid. The mean (isotropic) polarizability, $\bar{\alpha}$, and the polarizability anisotropy, β, of the Lth ligand perturber are defined by

$$\bar{\alpha}_L = \tfrac{1}{3}(\alpha_{\parallel}' + 2\alpha_{\perp}') \qquad (7)$$

$$\beta_L = \alpha_{\parallel}' - \alpha_{\perp}' \qquad (8)$$

For the dynamic-coupling calculations carried out in this study, the following input data were required: (1) values for the 4f-electron radial integrals, $\langle r^\lambda \rangle$; (2) values for the $\bar{\alpha}_L$ and β_L polarizability parameters (for each ligand perturber); (3) positional coordinates (R_L, θ_L, ϕ_L) for each perturber site; (4) a set of angles (θ_L', ϕ_L') for each anisotropic perturber to describe the orientation of its polarizability ellipsoid (the principal axis) *relative* to the coordinate system defined for the overall system.[2,4,5] For the static-coupling calculations, the required input data were (1) values for the $\Xi(t,\lambda)$ electronic parameters, (2) values for the ligand charges, eq_L, and (3) positional coordinates (R_L, θ_L, ϕ_L) for each ligand perturber site.

Calculations

Erbium Electronic Parameters. Values for the $\Xi(t, \lambda)$ and $\langle r^\lambda \rangle$ electronic parameters used in this study are listed in Table I. The $\Xi(t, \lambda)$ parameter values were taken from a study by Leavitt and Morrison,[9] and the $\langle r^\lambda \rangle$ values were taken from a study by Morrison and Leavitt.[10] Note that our $\langle r^\lambda \rangle$ values correspond to the ρ_λ values given by Morrison and Leavitt[10] for erbium.

Ligand Parameters. The parameters (or properties) required for each perturber site in the ligand environment are q_L, $\bar{\alpha}_L$, β_L, (R_L, θ_L, ϕ_L), and (θ_L', ϕ_L'). The (θ_L', ϕ_L') angles are needed only when $\beta_L \neq 0$. For the model structures considered in this study, the perturbers were either atoms or chemical bonds. Each chemical-bond perturber was assigned $\bar{\alpha}_L$ and β_L values but no net charge (i.e., $q_L = 0$), and (R_L, θ_L, ϕ_L) for each bond located the bond midpoint. The principal axis of each bond polarizability ellipsoid was defined to be coincident with the diatom axis of the bond. Each atomic perturber was assigned a value for $\bar{\alpha}_L$ and, in most cases, a value for q_L. The model structures assumed for Er(ODA)$_3^{3-}$ (**1**), Er(DPA)$_3^{3-}$ (**2**), Er(CDO)$_3^{6-}$ (**3**), and Er(CDA)$_3^{6-}$ (**4**) each had exact trigonal-dihedral (D_3) symmetry with respect to both the ErL$_6$L$'_3$ coordination polyhedron *and* the overall complex.[1] The model structures assumed for Er(IDA)$_3^{3-}$ (**5**) and Er(MIDA)$_3^{3-}$ (**6**) each had exact C_{3h} symmetry.

The ligand structural (geometrical), charge, and polarizability parameters used in the present study for the Er(ODA)$_3^{3-}$ (**1**), Er(IDA)$_3^{3-}$ (**5**), and Er(MIDA)$_3^{3-}$ (**6**) model systems were identical with those employed in our previous study[2] of the analogous holmium(III) systems. Except for the pyridyl ring atoms and bonds, the Er(DPA)$_3^{3-}$ (**2**) model system was also parametrized similarly to the analogous holmium complex.[2] However, whereas previously we used only two perturber sites to represent the pyridyl moiety (one located at the nitrogen atom and the other located at the centroid of the pyridyl ring), in the present study we included *each* ring atom *and* bond as a separate perturber. The ligand perturber site properties used in our calculations for the Er(DPA)$_3^{3-}$ (**2**) and Er(CDA)$_3^{6-}$ (**4**) systems are listed in Table II. Note that the model structures for these two systems are differentiated by just one perturber site (19). The model structure used for Er(CDO)$_3^{6-}$ (**3**) is identical with that of **4** *except* that an oxygen atom is inserted in place of N(14)*. This oxygen atom was assigned a q_L value of -0.20 and an $\bar{\alpha}_L$ value of 0.21 Å^3.

All of the calculated results reported in this paper were obtained by using the model structures and ligand parameters described (or referenced) above. Additional calculations were carried out in which certain ligand parameter values and perturber site distributions were varied. The results of these calculations will not be tabulated here, but they will be cited, where appropriate, in the text.

Results and Discussion

The Ω_λ intensity parameters calculated for structures **1**–**6** are listed in Table III along with the empirically determined values for these parameters (as reported in ref 1). The mechanistic contributions to each Ω_λ parameter (as calculated according to the intensity model described in Theory) are also listed in Table III. Note that the [DC] and [SC, DC] contributions dominate the Ω_2(calcd) values, whereas the [SC] contributions dominate the Ω_6(calcd) values. The [SC], [DC], and [SC, DC] contributions to the Ω_4(calcd) parameters are comparable in *magnitude*, although we note that in each case the [SC, DC] contribution is *negative* in sign.

Ratios of the calculated vs. empirically determined Ω_λ parameters are given in Table IV, and in Table V we list *relative* Ω_λ values using the **1** (ODA) complex as our reference system. These data show that our model calculations were *least* successful in treating the intensity properties of the **5** (IDA) and **6** (MIDA) complexes. Note from Table III, however, that the Ω_4 and Ω_6 empirical values for both **5** and **6** have large uncertainties associated with them.

The best overall agreement between calculated and experimental intensity results was achieved for the **1** (ODA) and **4** (CDA) systems. In Table VI we list the $A_{tp}{}^{\lambda}$ parameter values calculated for these systems. Note that the [SC] contributions are restricted to the $t = \lambda \pm 1$ parameters, the $[\mathrm{DC}, \bar{\alpha}]$ contributions are restricted to the $t = \lambda + 1$ parameters, and $[\mathrm{DC}, \beta]$ contributions may be found in *all* the $t = \lambda, \lambda \pm 1$ parameters.[4,5] Inclusion of the $[\mathrm{DC}, \beta]$ contributions, which arise from perturber site polarizability anisotropies, was found to be quite important for calculating Ω_2 parameters in reasonable agreement with experiment.

From the ligand parameters described in Calculations (vide supra) and listed in Table II, our model calculations overestimate the Ω_2 value for the **2** (DPA) system and they underestimate the Ω_2 value for the **3** (CDO) system. In each case, the disparity between the calculated and empirical Ω_2 values can be eliminated by modest adjustments in the $\bar{\alpha}$ value assigned to the central donor atom of each ligand (N for DPA and O for CDO) *or* by adjustment of the bond polarizability parameters associated with the pyridyl and pyran rings of DPA and CDO, respectively. More specifically, *decreasing* these polarizability parameters by ~40% for DPA and *increasing* them by ~50% for CDO lead to calculated Ω_2 values in quite good agreement with the empirically determined values.

Our model calculations tend to overestimate the Ω_2 values for the **5** (IDA) and **6** (MIDA) systems (see Tables III and IV), and reasonable adjustments of the ligand input parameters do not fully

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(9) Leavitt, R. P.; Morrison, C. A. *J. Chem. Phys.* **1980**, *73*, 749.
(10) Morrison, C. A.; Leavitt, R. P. *J. Chem. Phys.* **1979**, *71*, 2366.

Table II. Ligand Perturber Site Properties for the $Er(DPA)_3^{3-}$ (**2**) and $Er(CDA)_3^{6-}$ (**4**) Model Structures[a]

perturber site (L)[b]	positional coordinates[c,d]						orientation[e]	
	R_L/Å	θ_L/deg	ϕ_L/deg	q_L	$\bar{\alpha}_L/Å^3$	$\beta_L/Å^3$	θ_L'/deg	ϕ_L'/deg
O_{1a}(1)*	2.33	45.7	142.0	-1.15	0.21	0		
O_{1b}(2)*	2.33	134.3	38.0	-1.15	0.21	0		
O_{2a}(3)	4.34	52.2	128.7	-0.44	0.43	0		
O_{2b}(4)	4.34	127.8	51.3	-0.44	0.43	0		
C_{1a}(5)	3.21	56.0	123.0	0.57	0.06	0		
C_{1b}(6)	3.21	124.0	57.0	0.57	0.06	0		
C_{1a}-O_{1a}(7)	2.74	51.3	130.3	0	0.60	0.43	82.2	96.4
C_{1b}-O_{1b}(8)	2.74	128.7	49.7	0	0.60	0.43	97.8	83.6
C_{2a}(9)	3.34	74.4	103.0	0	0.40	0		
C_{2b}(10)	3.34	105.6	77.0	0	0.40	0		
C_{3a}(11)	4.71	79.0	99.0	0	0.40	0		
C_{3b}(12)	4.71	101.0	81.0	0	0.40	0		
C_4(13)	5.26	90.0	90.0	0	0.40	0		
N(14)*	2.42	90.0	90.0	-0.15	0.47	0		
N-C_{2a}(15)	2.83	80.9	103.0	0	0.65	-0.12	131.4	44.7
N-C_{2b}(16)	2.83	99.1	77.0	0	0.65	-0.12	48.6	135.3
C_{2a}-C_{3a}(17)	4.00	76.8	100.7	0	0.97	1.38	0	90.0
C_{2b}-C_{3b}(18)	4.00	103.2	79.3	0	0.97	1.38	0	90.0
C_4-O(19)	4.87	90.0	90.0	0	0.60	0.43	0	90.0

[a] Each structure has exact D_3 point-group symmetry. Properties are given for just one of the three ligands in each tris(terdentate) structure. [b] Sites 1-8 are located in the two carboxylate moieties of the ligand. Sites 9-18 are located on atoms and bonds of the pyridyl ring. Site 19 exists only for the CDA ligand. Asterisks identify atoms coordinated to the metal ion. [c] The coordinate system is defined such that the z axis coincides with the C_3 symmetry axis of each structure and the y axis coincides with one of the three C_2 symmetry axes. [d] For the chemical bond perturber sites 7, 8, and 15-19, the coordinates locate the bond midpoints. [e] The angles θ_L' and ϕ_L' define the orientation of the principal axis of the cylindrically symmetric polarizability ellipsoid associated with perturber L (see Theory in text).

Table III. Calculated and Empirically Determined Values for Ω_λ Intensity Parameters[a]

complex ligand	λ	Ω_λ(calcd)/10^{-20} cm^2				Ω_λ(empirical)/ 10^{-20} cm^2
		[SC]	[DC]	[SC, DC]	[total]	
1 (ODA)	2	0.64	2.10	2.14	4.88	5.26 ± 0.48
	4	1.60	1.35	-1.34	1.61	1.61 ± 0.64
	6	2.73	0.02	-0.27	2.48	3.23 ± 0.74
2 (DPA)	2	0.72	6.81	4.27	11.80	7.81 ± 0.69
	4	1.72	2.09	-2.05	1.76	1.67 ± 0.92
	6	2.67	0.03	-0.11	2.59	3.23 ± 1.05
3 (CDO)	2	0.66	3.77	3.19	7.62	10.45 ± 0.26
	4	1.64	1.46	-1.42	1.68	2.06 ± 0.29
	6	2.72	0.02	-0.26	2.48	3.41 ± 0.34
4 (CDA)	2	0.68	7.01	4.41	12.10	12.03 ± 0.18
	4	1.81	2.15	-2.09	1.87	2.55 ± 0.20
	6	2.67	0.03	-0.11	2.59	3.56 ± 0.23
5 (IDA)	2	0.09	10.10	1.81	12.00	5.33 ± 0.77
	4	0.36	0.87	-0.46	0.77	2.17 ± 1.03
	6	1.11	0.08	-0.27	0.92	2.44 ± 1.18
6 (MIDA)	2	0.08	9.74	1.58	11.40	7.20 ± 0.88
	4	0.34	1.19	-0.54	0.99	1.99 ± 1.17
	6	1.19	0.06	-0.16	1.09	2.90 ± 1.33

[a] Empirical values are from ref 1.

Table IV. Ratios of Calculated vs. Empirically Determined Ω_λ Parameters

complex (ligand)	Ω_λ(calcd)/Ω_λ(empirical)		
	λ = 2	λ = 4	λ = 6
1 (ODA)	0.93	1.00	0.77
2 (DPA)	1.51	1.05	0.80
3 (CDO)	0.73	0.82	0.73
4 (CDA)	1.00	0.73	0.73
5 (IDA)	2.25	0.36	0.38
6 (MIDA)	1.58	0.50	0.38

Table V. Relative Values of Ω_λ Parameters[a]

complex (ligand)	λ = 2		λ = 4		λ = 6	
	calcd	exptl	calcd	exptl	calcd	exptl
1 (ODA)	*1.00*	*1.00*	*1.00*	*1.00*	*1.00*	*1.00*
2 (DPA)	2.41	1.49	1.09	1.04	1.04	1.00
3 (CDO)	1.56	1.99	1.04	1.28	1.00	1.05
4 (CDA)	2.48	2.29	1.16	1.58	1.04	1.10
5 (IDA)	2.46	1.01	0.48	1.35	0.37	0.75
6 (MIDA)	2.33	1.37	0.62	1.24	0.44	0.89

[a] The numbers in this table are Ω_λ values calculated *relative* to those listed in Table III for the **1** (ODA) complex.

correct the disparities between the calculated and experimental results for these systems. A possible source of the problems encountered with these systems might be the existence of significant concentrations of species having structures somewhat different from our model structures. The *major* species present in solution (under the conditions used in ref 1) are probably well-represented by our model structures for $Er(IDA)_3^{3-}$ and $Er(MIDA)_3^{3-}$. However, it is quite likely that a number of minority species with somewhat different structures are also present. Candidate structures for these minority species would be tris(bidentate) or bis(terdentate) with respect to the IDA (or MIDA) ligand, with OH^- ions occupying another two or three sites within the inner coordination sphere of the Er^{3+} ion. These structures would have symmetries *and* perturber site properties somewhat different from those of our tris(terdentate) model structures, and no attempts were made to model them in the study reported here.

All of the calculated results reported in Tables III-VI for systems **1**-**4** were obtained by using model structures that are identical with respect to their carboxylate parameters (charges,

Table VI. Contributions to the A_{tp}^{λ} Parameters Calculated for the $Er(ODA)_3^{3-}$ (**1**) and $Er(CDA)_3^{6-}$ (**4**) Model Structures[a]

parameter	structure	$A_{tp}^{\lambda}/10^{-11}$ cm[b]			
		[SC]	[DC, $\bar{\alpha}$]	[DC, β]	[total]
A_{20}^{2}	**1**	0	0	12.48	12.48
	4	0	0	12.00	12.00
A_{33}^{2}	**1**	−12.71	−23.41	2.37	−33.75
	4	−13.43	−47.16	6.17	−54.42
A_{33}^{4}	**1**	−23.14	0	−1.36	−24.51
	4	−24.46	0	2.21	−22.24
A_{40}^{4}	**1**	0	0	−0.98	−0.98
	4	0	0	−0.57	−0.57
A_{43}^{4}	**1**	0	0	0.46	0.46
	4	0	0	0.45	0.45
A_{53}^{4}	**1**	13.51	−25.38	0.72	−11.14
	4	13.31	−31.12	0.44	−17.37
A_{53}^{6}	**1**	41.59	0	−2.48	39.11
	4	40.98	0	−1.29	39.69
A_{60}^{6}	**1**	0	0	−1.69	−1.69
	4	0	0	−1.31	−1.31
A_{63}^{6}	**1**	0	0	−0.98	−0.98
	4	0	0	−0.83	−0.83
A_{66}^{6}	**1**	0	0	1.29	1.29
	4	0	0	0.24	0.24
A_{73}^{6}	**1**	−2.79	−0.55	−0.28	−3.62
	4	−2.88	−3.11	−0.41	−6.40
A_{76}^{6}	**1**	2.22	−1.78	−0.25	0.19
	4	2.23	−1.25	−0.43	0.55

[a] See Theory in the text for a discussion of the various contributions to the A_{tp}^{λ} intensity parameters. [b] All values listed in the table must be multiplied by the imaginary number *i*.

polarizabilities, *and* geometry). *Except* for geometry,[2] these same carboxylate parameters were also used in the model calculations for systems **5** and **6**. This clearly provides only a very crude representation of reality since the Er^{3+}–carboxylate interactive strengths for the various systems are most certainly different. These differences will, of course, be reflected in the relative binding strengths of the various ligands, and they are likely to be reflected in the *even-parity* components of the crystal field potential sensed by the 4f electrons of the Er^{3+} ion. However, it is much less likely that these differences will be reflected very strongly in the *odd-parity* crystal field interactions responsible for generating 4f → 4f electric-dipole intensity. In fact, changing the carboxylate charge and polarizability parameters by ±25% in any one of the model structures (**1**–**6**) produces negligible changes in the calculated Ω_2 intensity parameters and only modest changes (5–10%) in the Ω_4 and Ω_6 intensity parameters. According to our model calculations, the Ω_λ parameters (especially Ω_2) are much more sensitive to the geometry and properties associated with the ligand perturber sites (atoms and bonds) lying near the equatorial plane of the $ErL_6L'_3$ coordination polyhedron. Except for the equatorial *donor* atoms (L′), these sites make the major contributions to the *noncentrosymmetric* 4f-electron crystal field potential and, therefore, they contribute most strongly to the 4f → 4f electric-dipole intensities. For each of the systems examined in this study, model intensity calculations were carried out by using several sets of ligand charge and polarizability parameters. These calculations produced results that were qualitatively similar with respect to the *relative* intensity parameters for the respective systems. The results shown in Tables III and VI may be considered as generally representative of these model calculations.

Conclusion

The calculations performed in this study were based on a theoretical model that includes consideration of two different 4f → 4f electric-dipole intensity mechanisms. These two mechanisms are the ones most commonly used to interpret and rationalize the electric-dipole intensities of 4f → 4f transitions in lanthanide complexes, although it is by no means certain that they will *always* make the dominant contributions. Therefore, only qualitative rather than quantitative significance should be attached to the results obtained in this study, even though near-quantitative agreement between calculated and experimental results is achieved in a number of cases (see Table IV).

Among the more interesting results obtained in this study are those showing that (1) the Ω_2(calcd) parameters are dominated by [DC] and [SC, DC] mechanistic contributions, (2) the Ω_6(calcd) parameters are dominated by [SC] contributions, (3) the Ω_2[SC, DC] contributions are positive in sign, whereas the Ω_4[SC, DC] and Ω_6[SC, DC] contributions are negative in sign (see Table III), and (4) both the [DC, $\bar{\alpha}$] and [DC, β] components of the A_{tp}^{λ}[DC] parameters may contribute significantly to the calculated Ω_λ values (especially for $\lambda = 2$). These results suggest that *both* the static-coupling *and* dynamic-coupling mechanisms are essential to intensity calculations carried out within the framework of the intensity model employed in this study and that the so-called [SC, DC] interference (or cross-term) contributions should not be ignored. Furthermore, in modeling the ligand environment with respect to perturber site polarizabilities, it is important to take into account polarizability anisotropy. The importance of the latter has been demonstrated in several previous studies of lanthanide 4f → 4f transition intensities (considered within the context of the dynamic-coupling intensity mechanism).[11-15] Among the A_{tp}^{λ} intensity parameters, those for which $t = \lambda$ *vanish* in the absence of [DC, β] contributions.[4,5,16,17]

Among the D_3 complexes (**1**–**4**) examined in this study, the empirical Ω_2 values exhibit somewhat greater variations than do the Ω_4 and Ω_6 values. This greater sensitivity of the Ω_2 intensity parameter to the ligand environment is also reflected in the results from our model calculations (see Table V). Judicious (and physically reasonable) adjustments to the ligand parameters used in our model calculations would lead to nearly quantitative agreement between theory and experiment for the Ω_2, Ω_4, and Ω_6 variations among the **1**–**4** systems. Although such agreement is gratifying, its significance is unclear given the approximations inherent to our theoretical model and our representations of the ligand environment. Our major objective in this study was to assess the relative importance of the [SC], [DC], and [SC, DC] contributions to the Ω_λ parameters of the various systems, and our *qualitative* findings in this regard would not be altered by small changes in how we represented the ligand environment.

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(11) Kuroda, R.; Mason, S. F.; Rosini, C. *Chem. Phys. Lett.* **1980**, *70*, 11.

(12) Kuroda, R.; Mason, S. F.; Rosini, C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 2125.

(13) Dallara, J. J.; Reid, M. F.; Richardson, F. S. *J. Phys. Chem.* **1984**, *88*, 3587.

(14) May, P. S. M.S. Thesis, University of Virginia, 1986.

(15) Mason, S. F. *J. Less-Common Met.* **1983**, *93*, 45.

(16) Reid, M. F.; Richardson, F. S. *Chem. Phys. Lett.* **1983**, *95*, 501.

(17) Stewart, B. *Mol. Phys.* **1983**, *50*, 161.