4f electric dipole intensity in lanthanide systems. We pursue these matters in the paper that follows.[9]

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Registry No. Nd(ODA)$_3^{3-}$, 43030-80-4; Nd(DPA)$_3^{3-}$, 38721-35-6; Nd(IDA)$_3^{3-}$, 12561-55-6; Nd(MIDA)$_3^{3-}$, 89746-87-2; Nd(MAL)$_3^{3-}$, 89773-17-1; Ho(ODA)$_3^{3-}$, 58855-74-6; Ho(DPA)$_3^{3-}$, 38785-79-4; Ho(IDA)$_3^{3-}$, 83233-72-1; Ho(MIDA)$_3^{3-}$, 83233-73-2; Ho(MAL)$_3^{3-}$, 92816-65-4.

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

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Model calculations of 4f–4f intensity parameters are reported for a series of Nd(III) and Ho(III) complexes. These complexes were chosen to mimic the principal coordination species known (or assumed) to be present in aqueous solutions of a series of 1:3 Ln^{3+}:ligand systems under alkaline pH conditions. The ligands included in the study are oxydiacetate (ODA), dipicolinate (DPA), 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 different intensity parameters, Ω_λ (λ = 2, 4, 6), and it is shown that both mechanisms must be included in the model calculations in order to achieve satisfactory agreement between theory and experiment. In most cases, this agreement is at best semiquantitative, although it is also shown that modest adjustments to the *input* parameters of the theoretical model can lead to nearly quantitative agreement for several of the systems studied.

Introduction

In this paper we attempt to rationalize the 4f → 4f electric dipole intensity parameters of several nine-coordinate Nd(III) and Ho(III) complexes in terms of two specific theoretical models. Each of these models is based on the so-called "electrostatic" theory of lanthanide 4f → 4f electric dipole intensity, in which all effects due to lanthanide–ligand orbital overlaps (and covalency) are neglected. In the one model, referred to as the *static-coupling* (or SC) model, the ligand environment is represented in terms of static point charges (located on atoms or groups of atoms). In the other model, referred to as the *dynamic-coupling* (or DC) model, the ligand environment is represented in terms of atoms, groups of atoms, and chemical bonds with charge distributions that are (dynamically) polarized by the electric dipole components of a radiation field. In the latter model, the ligand properties of special interest are the "dynamic" polarizabilities of the constituent atoms and chemical bonds. The formal aspects of the SC and DC intensity models within the context of the general electrostatic theory of 4f → 4f electric dipole intensity have been discussed in several recent publications.[1-3]

Our main interest here is in calculating the Ω_λ intensity parameters associated with the isotropic absorption spectra of multiplet-to-multiplet transitions in the tris-terdentate complexes of Nd(III) and Ho(III) with the ligands oxydiacetate (ODA), dipicolinate (DPA), imiodiacetate (IDA), and (methylimino)diacetate (MIDA). Empirically determined values for these parameters have been reported in a previous paper.[4] Rationalizing the relative values of these parameters for the respective complexes in terms of specific ligand structural properties is an important step toward developing general spectra–structure relationships applicable to lanthanide 4f → 4f optical spectra. Each of the complexes considered here is nine-coordinate, and each has a LnL$_6$L$'_3$ coordination polyhedron with a tricapped-trigonal-prism structure in which the L donor groups are situated at the vertices of the trigonal prism and the L$'$ donor groups occupy the "capping" positions (located on normals to the rectangular faces of the prism). Furthermore, in each system the L donors are carboxylate oxygen atoms. The structural differences between the complexes are associated with (1) differences in the nature of the L$'$ donor atoms (or groups) and (2) differences in the spatial dispositions of the chelate rings and their substituent groups. Two of the complexes, Ln(ODA)$_3^{3-}$ and Ln(DPA)$_3^{3-}$, have D_3 point group symmetry, and the other two complexes, Ln(IDA)$_3^{3-}$ and Ln(MIDA)$_3^{3-}$, are assumed to have C_{3h} point group symmetry.

Given the relatively minor structural differences between the systems examined here, it is perhaps surprising that the 4f → 4f optical properties associated with these systems are so strikingly different. This has been observed in the absorption studies carried out on the Nd(III),[4,5] Ho(III),[4] and Er(III)[6] systems, and in the emission studies carried out on the Eu(III) systems.[7] Accounting for these differences in optical properties in terms of structural differences between the coordinated ligands provides a rather difficult challenge (and stringent test) for theory. The Ω_λ parameterization scheme for 4f → 4f electric dipole intensity is perfectly general within the one-electron, one-photon approximation for lan-

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(1) Richardson, F. S. *Chem. Phys. Lett.* **1982**, *86*, 47.
(2) Reid, M. F.; Richardson, F. S. *J. Chem. Phys.* **1983**, *79*, 5735.
(3) Reid, M. F.; Richardson, F. S. *J. Phys. Chem.*, **1984**, *88*, 3579.
(4) Stephens, E. M.; Davis, S. A.; Reid, M. F.; Richardson, F. S. *Inorg. Chem.*, preceding paper in this issue.
(5) Stephens, E. M.; Schoene, K.; Richardson, F. S. *Inorg. Chem.* **1984**, *23*, 1641.
(6) Davis, S. A.; Richardson, F. S. *Inorg. Chem.* **1984**, *23*, 184.
(7) Foster, D. R.; Richardson, F. S. *Inorg. Chem.* **1983**, *22*, 3996.

0020-1669/84/1323-4611$01.50/0

thanide–ligand–radiation field (Ln–L–$h\nu$) interactions.[2,3,8-10] However, to relate these parameters to specific aspects of ligand structure and coordination requires explicit consideration of the mechanistic details involved in the Ln–L–$h\nu$ interactions. These mechanistic details are not yet well understood, especially with respect to the relative importance of overlap- vs. nonoverlap-dependent effects involving the lanthanide and ligand electronic charge distributions. However, a number of recent studies have shown that intensity models based on nonoverlaping mechanisms can lead to at least semiquantitatively useful correlations between structure and 4f → 4f spectral intensities.[11-18] The static-coupling and dynamic-coupling electrostatic models employed in the present study (and described briefly in the opening paragraph of this paper) each involve the neglect of overlap effects. The possible importance of overlap and covalency effects in producing 4f → 4f electric dipole intensity has been considered by Poon and Newman,[19] but detailed calculations of such effects have not yet been done.

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,[1-3] so we restrict our discussion here to the final expressions required to carry out actual calculations of the Ω_λ intensity parameters and transition oscillator strengths.

For a $\psi J \rightarrow \psi' J'$ multiplet-to-multiplet transition occurring within a f^N configuration, the transition oscillator strength may be expressed as

$$f_{JJ'} = 1.08 \times 10^{11} \chi \bar{\nu}_{JJ'} (2J + 1)^{-1} \sum_{\lambda} \Omega_\lambda \langle f^N \psi J \| U^\lambda \| f^N \Psi' J' \rangle^2 \tag{1}$$

where $\lambda = 2, 4, 6$, χ is the Lorentz field correction for the refractivity of the medium, $\bar{\nu}_{JJ'}$ is the $\psi J \rightarrow \psi' J'$ transition energy (expressed in cm^{-1} units), U^λ is an intraconfigurational unit tensor operator, and the Ω_λ intensity parameters are expressed in cm^2 units. Within the one-electron, one-photon approximation for the Ln–L–$h\nu$ interactions, eq 1 is independent of mechanism (for electric dipole processes). All of the mechanism-dependent aspects of the electric dipole transition oscillator strength have been folded into the Ω_λ parameters. Assuming that the static-coupling and dynamic-coupling intensity mechanisms make *independent* contributions to the $\psi J \rightarrow \psi' J'$ electric dipole transition moments[1-3] and neglecting contributions from all other mechanisms, the Ω_λ parameters may each be partitioned as

$$\Omega_\lambda = \Omega_\lambda[\mathrm{SC}] + \Omega_\lambda[\mathrm{DC}] + \Omega_\lambda[\mathrm{SC,DC}] \tag{2}$$

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 a contribution arising from *interferences* between transition moments induced by the SC and DC mechanisms. 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 central 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 4. When the various contributions to the Ω_λ parameters are discussed, it will be convenient to define each Ω_λ in terms of yet another set of parameters:

$$\Omega_\lambda = (2\lambda + 1)^{-1} \sum_{t,p} |A_{tp}^{\lambda}|^2 \tag{3}$$

where the A_{tp}^{λ} parameters have been defined previously[2,3] to parameterize 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

$$A_{tp}^{\lambda} = A_{tp}^{\lambda}[\mathrm{SC}] + A_{tp}^{\lambda}[\mathrm{DC}] \tag{4}$$

In the static-coupling model employed here, the ligand field is represented as an array of point charges, and the $A_{tp}[\mathrm{SC}]$ parameters may be expressed as[2,3]

$$A_{tp}^{\lambda}[\mathrm{SC}] = -A_{tp} \Xi(t,\lambda) [(2\lambda + 1)/(2t + 1)^{1/2}] \tag{5}$$

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

$$A_{tp} = -(-1)^p e^2 \sum_{\mathrm{L}} q_{\mathrm{L}} [\mathrm{C}_{-p}^{t}(\theta_{\mathrm{L}}, \phi_{\mathrm{L}})] R_{\mathrm{L}}^{-(t+1)} \tag{6}$$

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 an spherical tensor. The $\Xi(t,\lambda)$ quantity in eq 5 depends entirely on the electronic properties of the lanthanide ion, and it is defined here exactly as in eq 14 of Judd.[8]

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 distributions, each $A_{tp}^{\lambda}[\mathrm{DC}]$ parameter may be expressed as a sum of two contributions[2,3]

$$A_{tp}^{\lambda}[\mathrm{DC}] = A_{tp}^{\lambda}[\mathrm{DC},\bar{\alpha}] + A_{tp}^{\lambda}[\mathrm{DC},\beta] \tag{7}$$

where $A_{tp}[\mathrm{DC},\bar{\alpha}]$ represents the contributions from the spherically symmetric (isotropic) components of the ligand polarizabilities and $A_{tp}[\mathrm{DC},\beta]$ includes all contributions arising from ligand polarizability anisotropy. The latter is especially important in representing the influence of chemical bonds in promoting 4f → 4f electric dipole intensity via the dynamic-coupling mechanism.[14-20] From our previous work,[2,3] the $A_{tp}^{\lambda}[\mathrm{DC},\bar{\alpha}]$ parameters may be expressed as

$$A_{tp}^{\lambda}[\mathrm{DC},\bar{\alpha}] = 7\begin{pmatrix} 3 & \lambda & 3 \\ 0 & 0 & 0 \end{pmatrix} [(\lambda + 1)(2\lambda + 1)]^{1/2} \langle r^\lambda \rangle (-1)^p \times \sum_{\mathrm{L}} \mathrm{C}_{-p}^{t}(\theta_{\mathrm{L}}, \phi_{\mathrm{L}}) R_{\mathrm{L}}^{-(t+1)} \bar{\alpha}_{\mathrm{L}} \tag{8}$$

with t now restricted to values of $\lambda + 1$ and where $\langle r^\lambda \rangle$ is a radial expectation value for the lanthanide 4f orbitals, $\bar{\alpha}_{\mathrm{L}}$ is the "mean" isotropic polarizability of the Lth ligand perturber

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(8) Judd, B. R. *Phys. Rev.* **1962**, *127*, 750.
(9) Ofelt, G. S. *J. Chem. Phys.* **1962**, *37*, 511.
(10) Newman, D. J.; Balasubramanian, G. *J. Phys. C.* **1975**, *8*, 37.
(11) Reid, M. F.; Richardson, F. S. *J. Less-Common Metals* **1983**, *93*, 113.
(12) Reid, M. F.; Dallara, J. J.; Richardson, F. S. *J. Chem. Phys.* **1983**, *79*, 5743.
(13) Reid, M. F.; Richardson, F. S. *J. Chem. Phys.* **1984**, *80*, 3507.
(14) Dallara, J. J.; Reid, M. F.; Richardson, F. S. *J. Phys. Chem.* **1984**, *88*, 3587.
(15) Malta, O. L.; deSa, G. F. *Chem. Phys. Lett.* **1980**, *74*, 101.
(16) Malta, O. L.; deSa, G. F. *Phys. Rev. Lett.* **1980**, *45*, 890.
(17) Mason, S. F.; Peacock, R. D.; Stewart, B. *Mol. Phys.* **1975**, *30*, 1829.
(18) Mason, S. F.; Tranter, G. E. *Chem. Phys. Lett.* **1983**, *94*, 29.
(19) Poon, Y. M.; Newman, D. J. *J. Phys. C*, in press.
(20) Kuroda, R.; Mason, S. F.; Rosini, C. *Chem. Phys. Lett.* **1980**, *70*, 11.

Table I. Number of $A_{tp}{}^{\lambda}$ Intensity Parameters That May Contribute in the D_{3h}, D_3, and C_{3h} Point Group Symmetries[a,b]

parameter	point group D_{3n}	D_3	C_{3h}
$A_{1p}{}^2$	0	0	0
$A_{2p}{}^2$	0	1	0
$A_{3p}{}^2$	1	1	2
$A_{3p}{}^4$	1	1	2
$A_{4p}{}^4$	1	2	2
$A_{5p}{}^4$	1	1	2
$A_{5p}{}^6$	1	1	2
$A_{6p}{}^6$	1	3	2
$A_{7p}{}^6$	1	2	2

[a] The numbers in this table represent the occurrences of the totally symmetric irreducible representation in t for each of the point groups.[2] [b] The [SC] mechanism contributes only to the $t = \lambda \pm 1$ parameters, the [DC,$\bar{\alpha}$] mechanism contributes only to the $t = \lambda + 1$ parameters, and the [DC,β] mechanism may contribute to each of the $t = \lambda, \lambda \pm 1$ parameters.

site located at (R_L,θ_L,ϕ_L), and $C_{-p}{}^t$ is a spherical tensor.

Assuming cylindrically symmetric perturber groups (L) with S-type electronic ground states, the $A_{tp}{}^{\lambda}$[DC,β] parameters may be expressed as[2,3]

$$A_{tp}{}^{\lambda}[\mathrm{DC},\beta] = -7(10/3)^{1/2}\begin{pmatrix} 3 & \lambda & 3 \\ 0 & 0 & 0 \end{pmatrix} \times$$

$$[(\lambda + 1)(2\lambda + 1)(2\lambda + 3)]^{1/2}\langle r^{\lambda}\rangle(-1)^{p}\begin{Bmatrix} \lambda & \lambda + 1 & 1 \\ 2 & 1 & 1 \end{Bmatrix} \times$$

$$\sum_{L} \{C^{\lambda+1}(\theta_L,\phi_L)C^{2}(\theta_L',\phi_L')\}^{t}_{-p} R_L{}^{-(\lambda+2)}\beta_L \quad (9)$$

where $t = \lambda, \lambda \pm 1$ and $\langle r^{\lambda}\rangle$ and (R_L,θ_L,ϕ_L) are defined as in eq 8. The β_L parameter defines the *polarizability anisotropy* of the Lth perturber

$$\beta_L = \alpha_{\parallel}'(L) - \alpha_{\perp}'(L) \quad (10)$$

where $\alpha_{\parallel}'(L)$ and $\alpha_{\perp}'(L)$ denote polarizability components defined parallel ($\parallel$) and perpendicular ($\perp$) to the symmetry axis of the Lth group. The spherical tensor $C_m{}^2(\theta_L',\phi_L')$ in eq 9 rotates the local coordinate system on L (defined such that Z_L' coincides with the symmetry axis of the group) to one parallel with that defined for the overall complex.

Equations 3–9 provide the basis for the intensity calculations carried out in this study. For the static-coupling calculations we need values for the $\Xi(t,\lambda)$ electronic parameters, as well as ligand charges (eq_L) and ligand positional coordinates (R_L,θ_L,ϕ_L). For the dynamic-coupling calculations we need values for the electronic radial integrals $\langle r^{\lambda}\rangle$, the ligand polarizability parameters $\bar{\alpha}_L$ and β_L, the ligand positional coordinates (R_L,θ_L,ϕ_L), and the ligand orientational functions $C_m{}^2(\theta_L',\phi_L')$.

Three different point group symmetries are represented among the model structures examined in this study: D_{3h}, D_3, and C_{3h}. The numers of $A_{tp}{}^{\lambda}$ parameters that are nonvanishing by symmetry in each of these point groups are given in Table I. The static-coupling model employed here is identical in every respect with the point-charge crystal field intensity theory originally proposed by Judd[8] and Ofelt,[9] and our $A_{tp}{}^{\lambda}$[SC] parameters are related to the $A_{tp}\Xi(t,\lambda)$ parameters of that theory according to eq 5. The dynamic-coupling model used here is equivalent to the ligand-polarization intensity model first introduced by Mason and co-workers[17,18,20–23] and elaborated upon by Judd,[24] and Stewart,[25] and Reid and Richardson.[2,3,26]

Table II. Ligand Perturber Site Properties for the Nd(**1**) Model Structure

perturber site (L)[a,b]	positional coord R_L/Å	θ_L/deg	ϕ_L/deg	q_L/e	$\bar{\alpha}_L$/Å^3
H_2O(ax)	2.49	54.04	30.00	−0.3	1.49
H_2O(eq)	2.54	90.00	90.00	−0.3	1.49

[a] The six H_2O(ax) sites are located at the vertices of a regular trigonal prism polyhedron. The coordinates of only one of these sites are given. [b] The three H_2O(eq) sites are located on normals to the rectangular faces of a regular trigonal prism polyhedron. These sites are related by C_3 and C_3^2 symmetry operations about the trigonal axis of the system.

Model Structures

Five model structures are considered here for both Nd(III) and Ho(III). We denote these structures as Ln(**1**), Ln(**2**), Ln(**3**), Ln(**4**), and Ln(**5**), where Ln = Nd or Ho. The Ln(**1**) structures are intended to model the Ln^{3+}(aq) complexes, the Ln(**2**) and Ln(**3**) structures are intended to model the tris-terdentate (D_3 symmetry) $Ln(ODA)_3{}^{3-}$ and $Ln(DPA)_3{}^{3-}$ complexes, respectively, and the Ln(**4**) and Ln(**5**) structures are intended to model the tris-terdentate (C_{3h} symmetry) $Ln(IDA)_3{}^{3-}$ and $Ln(MIDA)_3{}^{3-}$ complexes, respectively. Each model structure is nine-coordinate, and each has trigonal symmetry—D_{3h} for Ln(**1**), D_3 for Ln(**2**) and Ln(**3**), and C_{3h} for Ln(**4**) and Ln(**5**). The Ln(**1**) structures have just nine ligand perturber sites, each representing a water molecule with a point charge and an isotropic polarizability. In structures Ln(**2**)–Ln(**5**), the ligand environment is represented in terms of atomic charges and (isotropic) polarizabilities, functional group charges and polarizabilities (which are sometimes considered to be anisotropic), and chemical bond polarizabilities (always considered to be anisotropic). In each case, the Nd and Ho structures are identical with each other *except* that all Ho–L radial distances are assigned values smaller than the corresponding Nd–L radial distances according to the relation $R_L(\mathrm{Ho}) = 0.97R_L(\mathrm{Nd})$. [Note that L labels the ligand perturber sites, which may be atoms, groups of atoms, *or* chemical bonds in the ligand environment.]

The ligand perturber site properties for Nd(**1**) are given in Table II. This structure is used to model the $Nd(H_2O)_9{}^{3+}$ complexes presumed to be the major species present in $NdCl_3$/water solutions under acidic pH conditions.[27] The structure has exact D_{3h} symmetry, and each water molecule is represented as a single site having an isotropic polarizability ($\bar{\alpha}_L$) and an "effective" charge (q_Le). Our Ho(**1**) structure is identical with that of Nd(**1**) *except* for the $R_L(\mathrm{Ho}) = 0.97R_L(\mathrm{Nd})$ scalings. It has been conjectured that the dominant Ho^{3+}(aq) species are eight-coordinate $Ho(H_2O)_8{}^{3+}$ complexes,[28] so our Ho(**1**) may not be an accurate model structure for the major complexes present in $HoCl_3$/water solutions.

The ligand perturber site properties for our Nd(**2**) and Nd(**3**) structures are listed in Table III. Each of these structures has exact D_3 symmetry with respect to both the NdL_9 coordination cluster *and* the chelate-ring dispositions. These structures are used to model the tris-terdentate Nd-

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

(22) Peacock, R. D. *Struct. Bonding (Berlin)* **1975**, *22*, 83.

(23) Mason, S. F. *Struct. Bonding (Berlin)* **1980**, *39*, 43.

(24) Judd, B. R. *J. Chem. Phys.* **1979**, *70*, 4830.

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

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

(27) Rajnak, K.; Couture, L. *Chem. Phys.* **1981**, *55*, 331.

(28) Habenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1979**, *70*, 3758; **1980**, *73*, 442.

Table III. Ligand Perturber Site Properties for the Nd(**2**) and Nd(**3**) Model Structures[a]

perturber site (L)[b,c]	positional coord[d]						orientation[e]	
	R_L/A	θ_L/deg	ϕ_L/deg	q_L/e	$\bar{\alpha}_L/A^3$	β_L/A^3	θ_L'/deg	ϕ_L'/deg
$O_{1a}(1)^*$	2.406	45.69	142.00	−1.15	0.206	0		
$O_{1b}(2)^*$	2.406	134.31	38.00	−1.15	0.206	0		
$O_{2a}(3)$	4.473	52.24	128.70	−0.44	0.434	0		
$O_{2b}(4)$	4.473	127.76	51.30	−0.44	0.434	0		
$C_{1a}(5)$	3.310	55.98	123.02	0.57	0.062	0		
$C_{1b}(6)$	3.310	124.02	56.98	0.57	0.062	0		
C_{1a}-$O_{1a}(7)$	2.824	51.28	130.32	0	0.603	0.430	97.76	83.56
C_{1b}-$O_{1b}(8)$	2.824	128.72	49.68	0	0.603	0.430	82.24	96.44
$O_3(9)^*$	2.490	90.00	90.00	−0.20	0.212	0		
$C_{2a}(10)$	3.442	74.39	103.03	−0.04	0.401	0		
$C_{2b}(11)$	3.442	105.61	76.97	−0.04	0.401	0		
$H_{1a}(12)$	4.136	84.58	110.75	0.08	0.135	0		
$H_{2a}(13)$	4.136	68.61	91.10	0.08	0.135	0		
$H_{1b}(14)$	4.136	111.39	88.90	0.08	0.135	0		
$H_{2b}(15)$	4.136	95.42	69.25	0.08	0.135	0		
C_{2a}-$O_3(16)$	2.921	80.88	103.00	0	0.603	0.430	48.63	135.27
C_{2b}-$O_3(17)$	2.921	99.12	76.98	0	0.603	0.430	131.37	44.73
N(18)*	2.490	90.00	90.00	−0.15	0.470	0		
py(19)	3.870	90.00	90.00	0	9.47	−5.24	50.56	0.00

[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. The ligands are chemically identical and are structurally related (in each complex) by C_3 and C_3^2 symmetry operations. [b] Sites 1–8 are common to both the Nd(**2**) and Nd(**3**) structures. Sites 9–17 are found only in Nd(**2**). Sites 18 and 19 are found only in Nd(**3**). Asterisks denote atoms coordinated to the Nd(III) ion. [c] The atoms $C_{1a(b)}$, $O_{1a(b)}$, and $O_{2a(b)}$ comprise the ligand carboxylate groups; the atoms $C_{2a(b)}$, $H_{1a(b)}$, and $H_{2a(b)}$ comprise the methylene (CH_2) groups (in structure **2**); O_3 is the ether oxygen atom (in structure **2**); N is the pyridinium nitrogen atom (in structure **3**); py denotes the centroid of the pyridyl group in structure **3**. [d] The coordinate system is defined so 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 (dihedral) symmetry axes. For the chemical bond perturber sites 7, 8, 16, and 17, 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. These angles are required in evaluating eq 9 (see Theory section in text).

Table IV. Ligand Perturber Site Properties for the Nd(**4**) and Nd(**5**) Model Structures[a]

perturber site (L)[b,c]	positional coord[d]						orientation[e]	
	R_L/A	θ_L/deg	ϕ_L/deg	q_L/e	$\bar{\alpha}_L/A^3$	β_L/A^3	θ_L'/deg	ϕ_L'/deg
$O_{1a}(1)^*$	2.471	31.37	30.35	−1.15	0.206	0		
$O_{1b}(2)^*$	2.471	148.63	30.35	−1.15	0.206	0		
$O_{2a}(3)$	4.281	34.45	79.29	−0.44	0.434	0		
$O_{2b}(4)$	4.281	145.54	79.29	−0.44	0.434	0		
$C_{1a}(5)$	3.388	42.45	70.06	0.57	0.272	0		
$C_{1b}(6)$	3.388	137.55	70.06	0.57	0.272	0		
$C_{2a}(7)$	3.363	66.63	113.37	−0.04	0.359	0		
$C_{2b}(8)$	3.363	75.47	75.47	−0.04	0.359	0		
$H_{1a}(9)$	3.830	75.63	67.25	0.08	0.135	0		
$H_{2a}(10)$	4.265	65.26	85.66	0.08	0.135	0		
$H_{1b}(11)$	3.830	104.37	67.25	0.08	0.135	0		
$H_{2b}(12)$	4.265	114.74	85.66	0.08	0.135	0		
N(13)*	2.490	90.00	90.00	−0.16	0.253	0		
C_{1a}-$O_{1a}(14)$	2.857	36.23	55.98	0	0.603	0.430	75.75	−77.59
C_{1b}-$O_{1b}(15)$	2.857	143.77	55.98	0	0.603	0.430	104.25	−77.59
C_{2a}-N(16)	2.850	77.02	81.93	0	0.720	1.02	36.22	33.69
C_{2b}-N(17)	2.850	102.98	81.93	0	0.720	1.02	143.78	33.69
$H_N(18)$	2.937	90.00	106.88	0.04	0.135	0		
Me(19)	3.376	90.00	116.56	0.33	0.523	0		
Me-N(20)	2.855	90.00	105.23	0	0.720	1.02	0.00	−19.43

[a] Each structure has exact C_{3h} point group symmetry. Properties are given for just one of the three ligands in each tris-terdentate structure. The ligands are structurally related (in each complex) by C_3 and C_3^2 symmetry operations. [b] Sites 1–17 are common to both Nd(**4**) and Nd(**5**). Site 18 is found only in Nd(**4**), and sites 19 and 20 are found only in Nd(**5**). [c] Atomic sites 1–12 are defined as given in footnote *c* of Table III. The N(13) site is an amino donor group nitrogen atom, $H_N(18)$ is the hydrogen atom substituent on N(13) in the Nd(**4**) structure, Me(19) is the methyl group substituent on N(13) in the Nd(**5**) structure and Me-N(20) represents the methyl-N chemical bond in Nd(**5**). [d] The coordinate system is defined so that the *z*-axis coincides with the C_3 symmetry axis of each structure. For the chemical bond perturber sites 14–17 and 20, the coordinates locate the bond midpoints. [e] See footnote *e* of Table III.

$(ODA)_3^{3-}$ [Nd(**2**)] and $Nd(DPA)_3^{3-}$ [Nd(**3**)] complexes. The geometry-dependent parameters for these structures were derived from x-ray crystallographic data,[29,30] and our methods for assigning q_L, $\bar{\alpha}_L$, and β_L values have been discussed elsewhere.[5,6,14,31,32] Each atomic site listed in Table III is assigned a fractional charge (q_Le) and an isotropic polarizability ($\bar{\alpha}_L$), and each chemical bond perturber site (7, 8, 16, and 17) is represented as a source of anisotropic polarizability (with values for $\bar{\alpha}_L$ *and* β_L). The centroid of the pyridyl group in the Nd(**3**) structure is also assigned values for both $\bar{\alpha}_L$ and β_L. Our Ho(**2**) and Ho(**3**) structures were taken to be identical

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(29) Albertsson, J. *Acta Chem. Scand.* **1968**, *22*, 1563; **1970**, *24*, 3527.

(30) Albertsson, J. *Acta Chem. Scand.* **1970**, *24*, 1213; **1972**, *26*, 985, 1005, 1023.

(31) Kirby, A. F.; Richardson, F. S. *J. Phys. Chem.* **1983**, *87*, 2544, 2557.

(32) Dallara, J. J. M.S. Thesis, University of Virginia, 1983.

Table V. Lanthanide Electronic Parameters Used in the Ω_λ Calculations

parameter	source[a,b]	Nd(III)	Ho(III)
$\Xi(1,2)/\text{cm}^2\ \text{erg}^{-1}$	Krupke	-1.58×10^{-6}	-0.63×10^{-6}
	L-M	-1.01×10^{-6}	-0.79×10^{-6}
$\Xi(3,2)/\text{cm}^4\ \text{erg}^{-1}$	Krupke	1.35×10^{-22}	0.46×10^{-22}
	L-M	1.56×10^{-22}	0.89×10^{-22}
$\Xi(3,4)/\text{cm}^4\ \text{erg}^{-1}$	Krupke	1.50×10^{-22}	0.46×10^{-22}
	L-M	1.39×10^{-22}	0.90×10^{-22}
$\Xi(5,4)/\text{cm}^6\ \text{erg}^{-1}$	Krupke	-1.98×10^{-38}	-0.58×10^{-38}
	L-M	-3.90×10^{-38}	-1.10×10^{-38}
$\Xi(5,6)/\text{cm}^6\ \text{erg}^{-1}$	Krupke	-1.62×10^{-38}	-1.20×10^{-38}
	L-M	-4.27×10^{-38}	-2.49×10^{-38}
$\Xi(7,6)/\text{cm}^8\ \text{erg}^{-1}$	Krupke	3.96×10^{-54}	1.08×10^{-54}
	L-M	6.83×10^{-54}	3.34×10^{-54}
$\langle r^2 \rangle/\text{Å}^2$	F-W	0.2803	0.1949
$\rho_2/\text{Å}^2$	M-L	0.1706	0.1692
$\langle r^4 \rangle/\text{Å}^4$	F-W	0.1883	0.0960
$\rho_4/\text{Å}^4$	M-L	0.5776	0.4217
$\langle r^6 \rangle/\text{Å}^6$	F-W	0.2722	0.0997
$\rho_6/\text{Å}^6$	M-L	1.5897	1.0119

[a] The $\Xi(t,\lambda)$ values were taken from either Krupke[35] or Leavitt and Morrison (L-M).[36] See text for a discussion of these parameter choices. [b] The $\langle r^\lambda \rangle$ values were taken from Freeman and Watson,[37] and the ρ_λ values were taken from Morrison and Leavitt.[38] See text for a discussion of the relationship between the $\langle r^\lambda \rangle$ and ρ_λ parameters.

with those of Nd(**2**) and Nd(**3**), *except* for the $R_L(\text{Ho}) = 0.97R_L(\text{Nd})$ scalings in each case.

The ligand perturber site properties for our Nd(**4**) and Nd(**5**) structures are listed in Table IV. In each of these structures the NdL_9 coordination cluster has exact D_{3h} symmetry, but addition of the chelate rings and the N-substituent groups reduce their overall symmetry to C_{3h}.[5-7] These structures are used to model the tris-terdentate $\text{Nd(IDA)}_3{}^{3-}$ [Nd(**4**)] and $\text{Nd(MIDA)}_3{}^{3-}$ [Nd(**5**)] complexes. The geometry-dependent parameters for these structures were derived by the procedures described in ref 5. These structures provide rather tenuous representations of the real complexes, since X-ray crystallographic data on the latter are not available. However, our model structures are compatible with the structural evidence that has been deduced from solution-phase luminescence studies on the corresponding Tb(III)[33] and Eu(III)[7] systems. Note that the only difference between our Nd(**4**) and Nd(**5**) structures is the replacement of the $\text{H}_\text{N}(18)$ perturber site (in **4**) with the Me(19) and Me–N(20) perturber sites (in **5**). This replacement of a hydrogen atom with a methyl group gives Nd(**5**) a substantially larger ligand polarizability. Our Ho(**4**) and Ho(**5**) structures are identical with those of Nd(**4**) and Nd(**5**), *except* for the $R_L(\text{Ho}) = 0.97R_L(\text{Nd})$ scaling factors.

Our structures **2**–**5** have the following in common: (1) nine-fold coordination; (2) tricapped-trigonal-prism structures for the LnL_9 coordination clusters; (3) carboxylate donor groups defining the top and bottom triangles of the trigonal prisms; (4) "nearly" D_{3h} symmetry for the coordination polyhedra. Their differences are (1) in how the chelate rings are arranged about the lanthanide ion (**2** and **3** differ from **4** and **5** in this respect), (2) in chelate-ring conformations, and (3) in the substituent groups attached to the middle (equatorial) donor atoms of the ligands.

Most of the results reported in this study are from calculations based on the complete ligand perturber sets listed in Tables II–IV. A detailed account of contributions made by selected subsets of the perturber sites will be reported in a separate paper.[34]

Table VI. Intensity Parameters Calculated for the Nd(III) Model Structures by Using Krupke's $\Xi(t,\lambda)$ Parameters[35]

		$\Omega_\lambda/10^{-21}\ \text{cm}^2$				
structure	λ	[SC]	[DC][a]	[SC,DC][a]	[total][a]	[total][b]
Nd(**1**)	2	0.05	7.80	−1.25	6.60	2.18
	4	0.76	21.16	−7.41	14.51	176.6
	6	5.12	0.48	−0.18	5.42	20.44
Nd(**2**)	2	12.20	44.04	42.75	98.99	54.56
	4	35.60	1.96	−7.34	30.22	31.27
	6	66.96	0.01	−1.11	65.86	60.82
Nd(**3**)	2	13.62	622.2	186.9	822.7	357.8
	4	38.51	2.70	−8.58	32.63	58.66
	6	64.98	0.06	−0.78	64.26	62.47
Nd(**4**)	2	1.57	202.6	33.53	237.7	96.98
	4	6.82	1.01	−2.47	5.36	8.65
	6	26.87	0.04	−0.83	26.08	23.38
Nd(**5**)	2	1.49	206.0	32.11	239.6	97.30
	4	6.66	1.69	−3.15	5.20	12.78
	6	26.94	0.02	−0.53	26.43	24.52

[a] Calculated by using the Freeman and Watson values for $\langle r^\lambda \rangle$.[37] [b] Calculated by using the Morrison and Leavitt ρ_λ parameters[38] in place of $\langle r^\lambda \rangle$.

Table VII. Intensity Parameters Calculated for the Nd(III) Model Structures by Using $\Xi(t,\lambda)$ Parameters Adapted from Leavitt and Morrison[36]

		$\Omega_\lambda/10^{-21}\ \text{cm}^2$				
structure	λ	[SC]	[DC][a]	[SC,DC][a]	[total][a]	[total][b]
Nd(**1**)	2	0.07	7.80	−1.45	6.42	2.08
	4	2.62	21.16	−14.61	9.17	156.2
	6	4.42	0.48	−0.31	4.59	18.98
Nd(**2**)	2	16.29	44.04	49.37	109.7	62.70
	4	56.59	1.96	−15.31	43.24	27.55
	6	57.68	0.01	−1.04	56.65	51.95
Nd(**3**)	2	18.19	622.2	215.1	855.5	379.6
	4	58.36	2.70	−17.79	43.27	28.59
	6	56.00	0.06	−0.66	55.40	54.20
Nd(**4**)	2	2.09	202.6	38.71	243.4	100.7
	4	15.99	1.01	−5.44	11.56	8.62
	6	24.36	0.04	−0.92	23.48	20.35
Nd(**5**)	2	1.99	206.0	37.11	245.1	100.8
	4	15.88	1.69	−6.79	10.78	10.72
	6	24.42	0.02	−0.59	23.85	21.65

[a] Calculated by using the Freeman and Watson values for $\langle r^\lambda \rangle$.[37] [b] Calculated by substituting the Morrison and Leavitt ρ_λ parameters[38] for $\langle r^\lambda \rangle$.

Model Calculations

Electronic Parameters. Given the structural properties specified in the preceding section (and in Tables II–IV), it remains only to specify the lanthanide $\Xi(t,\lambda)$ and $\langle r^\lambda \rangle$ electronic parameters in order to characterize our calculations of the Ω_λ intensity parameters (see eq 2–9). Two different sets of $\Xi(t,\lambda)$ values were used in our static-coupling (SC) intensity calculations, on both the Nd(III) and Ho(III) systems. The one set was taken (directly or by interpolation) from a study of Krupke,[35] and the other set was taken from a study by Leavitt and Morrison.[36] In each case, contributions from both $4f^N$–$4f^{N-1}\,5d$ and $4f^N$–$4f^{N-1}\,ng$ *interconfigurational* interactions were included. In all of our previously reported intensity calculations,[5,6,11,12,14,31] only the Krupke $\Xi(t,\lambda)$ values were used. Values for the Krupke[35] and the Leavitt and Morrison (L-M)[36] $\Xi(t,\lambda)$ parameters are listed in Table V.

Two different sets of 4f-electron $\langle r^\lambda \rangle$ radial integrals were used in our dynamic-coupling (DC) intensity calculations. The one set is comprised of the Freeman and Watson (F-W)[37] Hartree-Fock values, and the other set is comprised of the latter *corrected* for "screening" and "antiscreening" effects as described by Morrison and Leavitt (M-L).[38] The Freeman and Watson $\langle r^\lambda \rangle$ values are listed in Table V, along with the Morrison and Leavitt ρ_λ values (which

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(33) Salama, S.; Richardson, F. S. *J. Phys. Chem.* **1980**, *84*, 512.
(34) Stephens, E. M.; Reid, M. F.; Richardson, F. S., unpublished work.
(35) Krupke, W. F. *Phys. Rev.* **1966**, *145*, 325.
(36) Leavitt, R. P.; Morrison, C. A. *J. Chem. Phys.* **1980**, *73*, 749.
(37) Freeman, A. J.; Watson, R. E. *Phys. Rev.* **1962**, *127*, 2058.
(38) Morrison, C. A.; Leavitt, R. P. *J. Chem. Phys.* **1979**, *71*, 2366.

Table VIII. Ratios of Calculated vs. Experimental Ω_λ Values for the Nd(III) Model Structures[a]

structure	λ	Ω_λ(exptl)/ 10^{-21} cm^2	Ω_λ(calcd)/Ω_λ(exptl) (K, F-W)[b]	(L-M, M-L)[c]	(SC, L-M)[d]
Nd(**1**)	2	3.71 ± 8.8	1.8	0.56	0.02
	4	45.5 ± 10	0.32	3.4	0.06
	6	66.2 ± 8.3	0.08	0.29	0.07
Nd(**2**)	2	20.0 ± 9.1	4.9	3.1	0.82
	4	44.6 ± 11	0.68	0.62	1.3
	6	75.7 ± 8.5	0.87	0.69	0.76
Nd(**3**)	2	44.5 ± 12	18	8.5	0.46
	4	44.0 ± 14	0.74	0.65	1.3
	6	143 ± 11	0.45	0.38	0.40
Nd(**4**)	2	17.0 ± 7.5	14	5.9	0.13
	4	68.9 ± 8.7	0.08	0.13	0.34
	6	105 ± 7.0	0.25	0.20	0.23
Nd(**5**)	2	36.0 ± 8.3	6.6	2.8	0.06
	4	55.8 ± 9.7	0.10	0.20	0.29
	6	77.8 ± 7.8	0.34	0.28	0.32

[a] Experimental Ω_λ values from ref 4. [b] From calculations using $\Xi(t,\lambda)$ values from Krupke[35] and $\langle r^\lambda \rangle$ values from Freeman and Watson.[37] [c] From calculations using $\Xi(t,\lambda)$ parameters adapted from Leavitt and Morrison[36] and ρ_λ values as given by Morrison and Leavitt.[38] [d] From calculations that included *only* the static-coupling [SC] contributions to the Ω_λ and made use of the Leavitt and Morrison $\Xi(t,\lambda)$ values.

Table IX. Comparisons of Calculated and Experimentally Determined Ω_2:Ω_4:Ω_6 Ratios for the Ln(**2**)-Ln(**5**) Structures

structure	Ω_2:Ω_4:Ω_6 exptl	calcd[a]	calcd[b]	calcd[c]
Nd(**2**)	4.6:10:17	23:10:19	2.9:10:11	12:10:2.4
Nd(**3**)	10:10:32	130:10:19	3.0:10:9.6	117:10:5.1
Nd(**4**)	2.5:10:15	110:10:24	1.3:10:16	106:10:8.5
Nd(**5**)	6.2:10:13	93:10:20	1.3:10:15	64:10:2.7
Ho(**2**)	21:10:13	27:10:14	4.2:10:17	14:10:0.17
Ho(**3**)	22:10:14	170:10:13	4.3:10:15	140:10:0.65
Ho(**4**)	8.4:10:11	180:10:16	2.8:10:38	120:10:1.4
Ho(**5**)	14:10:8.0	110:10:10	2.7:10:39	70:10:0.50

[a] Calculations including *all* [SC], [DC], and [SC,DC] contributions, using Leavitt and Morrison $\Xi(t,\lambda)$ parameters[36] and Morrison and Leavitt ρ_λ parameters.[38] [b] Calculations including *only* [SC] contributions, using Leavitt and Morrison $\Xi(t,\lambda)$ parameters.[36] [c] Calculations including *only* [DC] contributions, using Morrison and Leavitt ρ_λ parameters.[38]

Table X. Intensity Parameters Calculated for the Ho(III) Model Structures by Using Krupke's $\Xi(t,\lambda)$ Parameters[35]

structure	λ	$\Omega_\lambda/10^{-21}$ cm^2 [SC]	[DC][a]	[SC,DC][a]	[total][a]	[total][b]
Ho(**1**)	2	0.01	4.81	−0.38	4.44	3.11
	4	0.09	7.93	−1.59	6.43	146.1
	6	0.50	0.10	−0.03	0.57	10.92
Ho(**2**)	2	1.81	27.17	12.92	41.90	31.98
	4	4.30	0.73	−1.57	3.46	11.52
	6	6.52	0.01	−0.17	6.36	5.12
Ho(**3**)	2	2.02	387.1	54.88	444.0	323.0
	4	4.65	1.01	−1.85	3.81	16.07
	6	6.32	0.01	−0.11	6.22	6.47
Ho(**4**)	2	0.23	124.9	10.17	135.3	97.47
	4	0.83	0.38	−0.53	0.68	5.78
	6	2.63	0.01	−0.13	2.51	2.37
Ho(**5**)	2	0.22	127.1	9.68	137.0	98.61
	4	0.81	0.63	−0.68	0.76	10.02
	6	2.64	0.01	−0.09	2.56	2.34

[a] Calculated by using the Freeman and Watson values for $\langle r^\lambda \rangle$.[37] [b] Calculated by using the Morrison and Leavitt ρ_λ parameters[38] in place of $\langle r^\lambda \rangle$.

Table XI. Intensity Parameters Calculated for the Ho(III) Model Structures by Using $\Xi(t,\lambda)$ Parameters Adapted from Leavitt and Morrison[36]

structure	λ	$\Omega_\lambda/10^{-21}$ cm^2 [SC]	[DC][a]	[SC,DC][a]	[total][a]	[total][b]
Ho(**1**)	2	0.03	3.41	−0.61	2.83	4.11
	4	0.34	153.0	−13.34	140.0	5.24
	6	2.16	10.71	−0.91	11.96	2.17
Ho(**2**)	2	6.81	19.28	21.14	47.23	59.06
	4	16.25	14.17	−13.14	17.28	14.00
	6	28.17	0.24	−3.42	24.99	27.84
Ho(**3**)	2	7.60	274.8	89.70	372.1	501.2
	4	17.59	19.55	−15.36	21.78	15.11
	6	27.35	1.28	−2.23	26.40	27.14
Ho(**4**)	2	0.88	88.71	16.61	106.2	145.5
	4	3.09	7.29	−4.41	5.97	2.46
	6	11.73	1.01	−2.95	9.79	11.45
Ho(**5**)	2	0.83	90.22	15.85	106.9	146.8
	4	3.01	12.20	−5.63	9.58	2.36
	6	11.76	0.52	−1.90	10.38	11.58

[a] Calculated by substituting the Morrison and Leavitt ρ_λ parameters[38] for $\langle r^\lambda \rangle$. [b] Calculated by using the Freeman and Watson values for $\langle r^\lambda \rangle$.[37]

Table XII. Ratios of Calculated vs. Experimental Ω_λ Values for the Ho(III) Model Structures[a]

structure	λ	Ω_λ(exptl)/ 10^{-21} cm^2	Ω_λ(calcd)/Ω_λ(exptl) (K, F-W)[b]	(L-M, M-L)[c]
Ho(**1**)	2	3.9 ± 2.1	1.1	0.73
	4	27.4 ± 3.2	0.24	5.1
	6	30.9 ± 2.2	0.02	0.39
Ho(**2**)	2	58.6 ± 3.1	0.72	0.81
	4	28.4 ± 4.9	0.12	0.61
	6	37.7 ± 3.4	0.17	0.67
Ho(**3**)	2	77.1 ± 9.3	5.7	4.8
	4	36.2 ± 11	0.11	0.61
	6	50.2 ± 9.8	0.13	0.53
Ho(**4**)	2	34.8 ± 5.4	3.9	3.0
	4	41.9 ± 8.5	0.02	0.15
	6	43.3 ± 5.8	0.06	0.23
Ho(**5**)	2	46.8 ± 8.2	2.9	2.3
	4	34.5 ± 13	0.03	0.28
	6	26.2 ± 16	0.10	0.40

[a] The experimental Ω_λ values are from ref 4. [b] From calculations using $\Xi(t,\lambda)$ parameters adapted from Krupke[35] and $\langle r^\lambda \rangle$ values from Freeman and Watson.[37] [c] From calculations using $\Xi(t,\lambda)$ parameters adapted from Leavitt and Morrison[36] and ρ_λ values as given by Morrison and Leavitt.[38]

are effective $\langle r^\lambda \rangle$ parameters).[38] Note that for both Nd(III) and Ho(III), ρ_2 is smaller than $\langle r^2 \rangle$, whereas ρ_4 and ρ_6 are substantially larger than $\langle r^4 \rangle$ and $\langle r^6 \rangle$, respectively. In all of our previously reported intensity calculations, only the F-W $\langle r^\lambda \rangle$ values were used.

Calculated Results. Intensity parameters calculated for the Nd(III) model structures (as they are described in Tables II–IV) are given in Tables VI and VII. The Ω_λ[SC] values are calculated according to eq 3, 5, and 6, the Ω_λ[DC] values were calculated according to eq 3 and 7–9, and the Ω_λ[SC,DC] values were calculated from

$$\Omega_\lambda[\mathrm{SC,DC}] = (2\lambda + 1)^{-1}\sum_{t,p}|A_{tp}^{\lambda}[\mathrm{SC}] + A_{tp}^{\lambda}[\mathrm{DC}]|^2 - \Omega_\lambda[\mathrm{SC}] - \Omega_\lambda[\mathrm{DC}] \quad (11)$$

and eq 5–9. The Ω_λ[total] values were calculated according to eq 2. The $\Xi(t,\lambda)$ electronic parameters *only* enter into the static-coupling calculations, whereas the $\langle r^\lambda \rangle$ (or ρ_λ) electronic parameters only enter into the dynamic-coupling calculations.

A comparison of the calculated vs. empirically determined Ω_λ values is given in Table VIII for the Nd(III) systems. The empirical Ω_λ values listed in this table are from ref 4. In Table IX, the empirical and several calculated Ω_2:Ω_4:Ω_6 ratios are given for structures Ln(**2**)–Ln(**5**). In each case, the ratio is normalized to Ω_4 = 10. Among the Ω_λ (λ = 2, 4, 6) parameters, Ω_4 exhibits the least sensitivity to the ligand environment.[4]

Intensity parameters calculated for the Ho(III) model structures are given in Tables X and XI. The model structures used in these calculations are identical with those described in Tables II–IV, *except* for the R_L(Ho) = 0.97R_L(Nd) isotropic scalings. A comparison of the calculated vs. empirically determined Ω_λ values is given in Table

Table XIII. Sensitivity of Calculated Intensity Parameters to R_L Radial Distances[a]

structure	λ	$\Omega_\lambda/10^{-21}$ cm^2		$\Omega_\lambda(A)/\Omega_\lambda(B)$
		A[b]	B[b]	
Ho(1)	2	4.11	3.22	1.28
	4	5.24	3.64	1.44
	6	2.17	1.50	1.45
Ho(2)	2	59.06	46.30	1.28
	4	14.00	10.80	1.30
	6	27.84	19.30	1.44
Ho(3)	2	501.2	393.0	1.28
	4	15.11	11.80	1.28
	6	27.14	18.80	1.44
Ho(4)	2	145.5	114.1	1.28
	4	2.46	1.86	1.32
	6	11.45	7.90	1.45
Ho(5)	2	146.8	115.0	1.28
	4	2.36	1.79	1.32
	6	11.58	7.98	1.45

[a] Intensity parameters calculated by using the Leavitt and Morrison $\Xi(t,\lambda)$ values[36] and Freeman and Watson $\langle r^\lambda\rangle$ values.[37] [b] The relationship between the R_L values used in the A and B calculations is $R_L(A) = 0.97R_L(B)$, for *all* ligand perturber sites (L).

XII for the Ho(III) systems, and Ω_2:Ω_4:Ω_6 ratios (each normalized to $\Omega_4 = 10$) are presented in Table IX.

The results given in Table XIII demonstrate the R_L dependence of the Ho(III) intensity parameters. The $\Omega_\lambda(A)$ parameters listed in this table were calculated by using $R_L(\text{Ho}) = 0.97R_L(\text{Nd})$ scaling, with the $R_L(\text{Nd})$ values taken from Tables II–IV. The $\Omega_\lambda(B)$ parameters were calculated by using $R_L(\text{Ho}) = R_L(\text{Nd})$; i.e., in the latter case the Ho(III) and Nd(III) systems were assumed to be entirely isostructural. From eq 8 and 9, we see that both the $A_{tp}^\lambda[\text{DC},\bar{\alpha}]$ and $A_{tp}^\lambda[\text{DC},\beta]$ parameters have an $R_L^{-(\lambda+2)}$ dependence and, therefore, the $\Omega_\lambda[\text{DC}]$ parameters will exhibit a simple $R_L^{-(2\lambda+4)}$ radial dependence. On the other hand, eq 5 and 6 show that the $A_{tp}^\lambda[\text{SC}]$ parameters have an $R_L^{-(t+1)}$ ($t = \lambda \pm 1$) dependence, so that each $\Omega_\lambda[\text{SC}]$ parameter may include both $R_L^{-(2\lambda+4)}$- and $R_L^{-2\lambda}$-dependent terms (for $t = \lambda + 1$ and $t = \lambda - 1$, respectively). One may expect, therefore, that the $\Omega_\lambda(A)/\Omega_\lambda(B)$ ratios calculated for the five structures Ho(**1**)–Ho(**5**) will differ, reflecting the relative importance of the [SC], [DC], and [SC,DC] contributions to the Ω_λ[total] values of each system. This is seen to be the case for $\lambda = 4$ and 6, where some variations in the $\Omega_\lambda(A)/\Omega_\lambda(B)$ ratios calculated for the different structures are exhibited (see Table XIII). The constant value of 1.28 calculated for the $\Omega_2(A)/\Omega_2(B)$ ratio of *all* the systems is dictated by the condition that no $A_{1p}^2[\text{SC}]$ parameters are allowed for structures **1**–**5** (see Table I). Therefore, each of the $\Omega_2[\text{SC}]$, $\Omega_2[\text{DC}]$, and $\Omega_2[\text{SC,DC}]$ parameters will exhibit the same $R_L^{-(2\lambda+4)} = R_L^{-8}$ dependence, and $\Omega_2(A)/\Omega_2(B) = 0.97^{-8} = 1.28$ for all the structures.

All of the calculated results presented in Tables VI–XIII were obtained by using the ligand perturber sets and properties specified in Tables II–IV. Other calculations, based on the use of selected *subsets* of perturber sites and properties, were carried out, and these proved useful in sorting out the major ligand contributors to the Ω_λ intensity parameters. The results of these calculations will not be described here except for the following general comments: (1) The noncoordinated O_2, C_1, C_2, H_1, and H_2 atoms contribute very little to the intensity parameters. (2) The $\Omega_\lambda[\text{SC}]$ parameters are dominated by contributions from the O_1(carboxylate) sites and are diminished in magnitude when equatorially disposed ligand sites are added (reflecting interference effects between the transition moments induced by the axial and equatorial ligand sites). (3) Inclusion of polarizability anisotropy (β) at the chemical bond perturber sites (and on the pyridyl groups of structure **3**) has a significant (but not dominant) influence on the Ω_2 parameters. The percent *increases* in the calculated Ω_2[total] values due to the inclusion of polarizability anisotropy are ~15–20% for structures **1** and **4**, and ~25–30% for structures **3** and **5**.

Discussion

Electronic Parameter Dependence. Among the electronic parameter sets employed in this study, the Leavitt and Morrison (L-M)[36] $\Xi(t,\lambda)$ and Morrison and Leavitt (M-L)[38] ρ_λ combinations give calculated results in best "overall" agreement with experiment. However, calculations based on these parameters tend to give $\Omega_2(\text{calcd})/\Omega_2(\text{exptl})$ ratios >1 and $\Omega_\lambda(\text{calcd})/\Omega_\lambda(\text{exptl})$ ($\lambda = 4, 6$) ratios <1. The only exceptions to this are encountered for Nd(**1**) and Ho(**1**) where the Ω_2 intensity parameters are *underestimated* and the Ω_4 parameters are *overestimated* by the calculations and for Ho(**2**) where the Ω_2 parameter is slightly underestimated by the model calculations. No systematic attempts were made in the present study to find and "optimal" set of values for the $\Xi(t,\lambda)$ and ρ_λ electronic parameters. Considering the relative dynamic-coupling vs. static-coupling contributions to each of the Ω_λ intensity parameters, however, it is clear that the Ω_2(calcd) values will be most sensitive to adjustments in the ρ_2 parameters, while the Ω_6(calcd) values will be most sensitive to adjustments in the $\Xi(t,6)$ parameters. These conclusions follow from the observation that the dominant contributions to the Ω_2(calcd) parameters are from the dynamic-coupling mechanism, whereas the dominant contributions to the Ω_6(calcd) parameters are from the static-coupling mechanism. The relative contributions of the dynamic-coupling vs. static-coupling mechanisms to the Ω_4(calcd) parameters vary significantly from system to system, so adjustments to both ρ_4 and $\Xi(t,4)$ would have to be considered in any Ω_4(calcd) optimization study.

Static Coupling vs. Dynamic Coupling. For all of the structures examined here, the Ω_2(calcd) parameters are dominated by [DC] and [SC,DC] contributions, and the Ω_6(calcd) parameters are dominated by [SC] contributions. The relative [SC], [DC], and [SC,DC] contributions to the Ω_4(calcd) parameters vary considerably from system to system and are quite sensitive to the choice of $\Xi(t,4)$ and $\langle r^4\rangle$ (or ρ_4) parameters. It is interesting to note that $\Omega_4[\text{SC,DC}]$ and $\Omega_6[\text{SC,DC}]$ are calculated to be *negative* in sign for all of the structures, whereas $\Omega_2[\text{SC,DC}]$ is calculated to be *negative* for Nd(**1**) and Ho(**1**), but *positive* for all the remaining structures. Given the complexities of the structures considered here, it is not possible to give a simple explanation for these latter results. It is clear, however, that the [SC,DC] cross-term contributions to the Ω_2 and Ω_4 intensity parameters cannot be ignored in the context of the electrostatic f–f intensity model used in the present study.

For all the Nd(III) systems except Nd(**3**), the relative magnitudes of the Ω_2, Ω_4, and Ω_6 parameters can be at least *qualitatively* accounted for by considering *only* the pure [SC] contributions, using *either* the Krupke[35] *or* the Leavitt and Morrison[36] $\Xi(t,\lambda)$ values. This correlation may be extended to the Nd(**3**) system as well, if only Krupke's $\Xi(t,\lambda)$ parameters are used *and* if the uncertainties in the Ω_2(exptl) value for Nd(**3**) are taken into account. For the Ho(III) systems, on the other hand, the relative magnitudes of the Ω_2, Ω_4, and Ω_6 parameters can be qualitatively accounted for *only* by considering *all* of the model contributions: [SC], [DC], [SC,DC]. For all except the Nd(**1**), Ho(**1**), and Ho(**2**) systems, inclusion of dynamic-coupling effects in the model calculations leads to overestimates of the Ω_2 parameters. However, these overestimates are somewhat more serious for the Nd(III) systems than they are for the Ho(III) systems, despite the fact that our calculated $\Omega_2[\text{DC}]/\Omega_2[\text{SC}]$ ratios for the Nd(III) systems are generally 2–3 times smaller than those for the Ho(III) systems. Within the context of our model, this suggests that the values we used for $\rho_2(\text{Nd})/\rho_2(\text{Ho})$, as well as for $\rho_2(\text{Nd})$ and $\rho_2(\text{Ho})$, are all too big for the systems considered here. Of course, it is also possile that our overestimates of the [DC] contributions to the Ω_2 parameters arise from overestimates of the ligand polarizability parameters used as input to our dynamic-coupling calculations.

Ligand Sensitivity. Among the Ω_λ(exptl) parameters determined for both the Nd(III) and Ho(III) systems, Ω_2 exhibits

Table XIV. Calculated vs. Experimental Ω_λ(complex)/Ω_λ(aquo) Ratios

	$\lambda = 2$		$\lambda = 4$		$\lambda = 6$	
complex	calcd[a]	exptl	calcd[b]	exptl	calcd[a]	exptl
Nd(2)	30	5.4	2.1	0.98	2.7	1.2
Nd(3)	180	12	2.2	0.97	2.8	2.2
Nd(4)	48	4.6	0.37	1.5	1.1	1.5
Nd(5)	48	9.7	0.36	1.2	1.2	1.2
Ho(2)	16	15	2.6	1.0	2.1	1.2
Ho(3)	130	20	2.8	1.3	2.2	1.6
Ho(4)	37	8.9	0.47	1.5	0.82	1.4
Ho(5)	38	12	0.45	1.3	0.87	0.85

[a] From calculations based on the Leavitt and Morrison[36] $\Xi(t,\lambda)$ and the Morrison and Leavitt[38] ρ_λ electronic parameters. [b] From calculations based on the Leavitt and Morrison[36] $\Xi(t,\lambda)$ and the Freeman and Watson[37] $\langle r^\lambda \rangle$ electronic parameters.

the greatest sensitivity to the ligand environment.[4,5] This result is clearly reproduced by all of our model calculations if we exclude from consideration the anomalously large Ω_4 values calculated for Nd(**1**) and Ho(**1**) from the Morrison and Leavitt[38] ρ_4 electronic parameters. Table XIV gives a comparison of calculated vs. experimental Ω_λ(complex)/Ω_λ(aquo) ratios.

In the case of both Nd(III) and Ho(III), the Ln(**1**) system is calculated and observed to have the smallest Ω_2 value, while the Ln(**3**) system is calculated and observed to have the largest Ω_2 value. In each case, however, the Ω_2(**3**)/Ω_2(**1**) ratio is overestimated by our model calculations: by a factor of ~15 for Nd(III) and by a factor of ~6 for Ho(III). The most influential ligand parameters in our Ω_2(**3**) calculations are the $\bar{\alpha}_L$ and β_L polarizability parameters associated with the pyridyl moieties in the DPA ligands. Scaling down either, or both, of these parameters by a factor of 2 or more (from the values listed in Table III) yields calculated Ω_2(**3**)/Ω_2(**1**) ratios in substantially better agreement with experiment. However, it is important to point out that the pyridyl moieties cannot be entirely eliminated as perturber sites in our model calculations on the Ln(**3**) systems since they play the crucial role of making the Ω_2(**3**) values larger than the Ω_2(**2**), Ω_2(**4**), and Ω_2(**5**) values, a result that conforms to experimental observations.

Our model calculations tend to overestimate the Ω_2 values for the Ln(**4**) and Ln(**5**) systems *relative* to those for the Ln(**2**) systems. This problem can be rectified to a large extent by judicious adjustments of the N(13), C–N(16,17), H_N(18), Me(19), Me–N(20) perturber site parameters of structures Ln(**4**) and Ln(**5**) (see Table IV for a description of these structures). However, a more likely source of the problems encountered with these systems is the inadequacy of structures **4** and **5** for representing the real complexes present in 1:3 Ln^{3+}:IDA and Ln^{3+}:MIDA aqueous solutions. The major species present in these solutions under alkaline pH conditions are probably modeled reasonably well by our structures **4** and **5**. However, it is quite likely that a number of minority species with structures somewhat different from those of **4** and **5** are also present. Good candidate structures for these minority species would be bidentate with respect to IDA (or MIDA) coordination, with the amino group nitrogen atom of the ligand being replaced in the inner-coordination sphere by OH^- ions (from the alkaline solution).

Among the model structures used in this study, Nd(**2**) and Ho(**2**) probably provide the most accurate representations of the real complexes they were chosen to mimic, $Nd(ODA)_3{}^{3-}$ and $Ho(ODA)_3{}^{3-}$. This may account for the significantly better agreement between theory and experiment achieved for these systems compared to the other systems we examined. The agreement for Ho(**2**) is especially good: Ω_λ(calcd)/Ω_λ(exptl) = 0.77–0.86 (λ = 2), 0.54–0.75 (λ = 4), 0.61–0.74 (λ = 6), for calculations based on the L–M[36] and M–L[38] electronic parameter sets.

Conclusion

One of the primary objectives of this study was to rationalize the 4f → 4f electric dipole intensity parameters of a series of Nd(III) and Ho(III) complexes in terms of an electrostatic intensity model that includes both static-coupling (point-charge crystal field) and dynamic-coupling (ligand-polarization) effects. Central to this objective was identifying specific correlations between the observed spectral intensities and the ligand properties associated with the respective complexes. Intensity calculations, based on the electrostatic intensity model, were carried out for a series of model structures constructed to mimic the real complexes presumed to be present in aqueous solution. These model calculations reproduced certain aspects of the empirical intensity data quite well, but in general they failed to account for the intensity variations observed among systems having only small structural differences. In most cases, however, the calculated intensity parameters could be brought into at least semiquantitative agreement with experiment by making small (and physically reasonable) adjustments to the input parameters of the computational model (e.g., the q_L, $\bar{\alpha}_L$, and β_L ligand parameters and the $\Xi(t,\lambda)$, $\langle r^\lambda \rangle$, and ρ_λ lanthanide parameters).

The model calculations reported here clearly demonstrate that within the context of the electrostatic f–f intensity theory it is important to consider both the static-coupling and the dynamic-coupling mechanisms. Contributions from the static-coupling mechanism dominate the Ω_6 intensity parameter, while contributions from the dynamic-coupling mechanism dominate Ω_2. The relative contributions of the two mechanisms to Ω_4 were shown to be very sensitive to the detailed nature of the ligand environment about the lanthanide ion.

Our model calculations on the Ln(**4**) and Ln(**5**) structures were the most difficult to reconcile with experimental data. As was noted in the Discussion section (vide supra), this may be due to these structures providing only approximate representations of the real complexes present in 1:3 Ln^{3+}:IDA and 1:3 Ln^{3+}:MIDA solutions. However, it is also possible that the sp^3-hybridized valence orbitals on the nitrogen donor atoms in IDA and MIDA lead to Ln–L interaction effects distinctly different from those associated with the sp^2-hybridized valence orbitals presented by the middle donor atoms of ODA and DPA. These types of effects cannot be properly treated within the framework of the electrostatic intensity model employed in the present study. One would expect, however, that they would play a prominant role in any model that includes Ln–L orbital overlap effects.

Finally, we note the need for single-crystal, variable-temperature, polarized absorption spectra on at least one of the complexes examined in this study. Such spectra would yield intensity data on individual crystal field transitions and would permit evaluation of the $A_{tp}{}^\lambda$ intensity parameters. These intensity parameters carry significantly more information than the Ω_λ parameters,[2,3,11–14,39] and their availability would be enormously useful to calibrating and refining the types of model calculations reported in this paper. An excellent candidate for study is $Nd(ODA)_3{}^{3-}$ in the trigonal crystal $Na_3[Nd(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$.

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Registry No. Nd(**2**), 43030-80-4; Ho(**2**), 58855-74-6; Nd(**3**), 38721-35-6; Ho(**3**), 38785-79-4; Nd(**4**), 12561-55-6; Ho(**4**), 83233-72-1; Nd(**5**), 89746-87-2; Ho(**5**), 83233-73-2.

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(39) Kirby, A. F.; Palmer, R. A. *Inorg. Chem.* **1981**, *20*, 4219.