to those in reaction 8 have been proposed in the photolytic oxidation of $Cr(CO)_6$ cocondensed with O_2 in argon matrices, although no evolved $C^{18}O$ was detected in that study when the oxygen was $^{18}O^{18}O$.[28] The evolution of CO with as much as 50% $C^{18}O$ in this study requires, of course, that each step in (8) be reversible.

No experimental information is available that would permit a distinction between reactions 7 and 8 as the route to $C^{18}O$.

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Registry No. $Co_2(CO)_8$, 10210-68-1; $Co_4(CO)_{12}$, 17786-31-1.

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Empirical Intensity Parameters for the 4f → 4f Absorption Spectra of Nine-Coordinate Neodymium(III) and Holmium(III) Complexes in Aqueous Solution

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Absorption spectra are reported for five different 1:3 Ho^{3+}:ligand systems in aqueous solution under alkaline pH conditions, and these spectra are compared to that obtained for the $HoCl_3$ salt in aqueous solution (pH ~ 2). The transition intensities observed in these spectra are analyzed in terms of the Judd–Ofelt parameterization scheme for lanthanide 4f → 4f multiplet-to-multiplet transitions. A similar intensity analysis is reported for absorption results obtained previously on an analogous series of Nd(III) complexes. The values of the intensity parameters Ω_λ ($\lambda = 2, 4, 6$) determined for the various systems are compared, and variations in these values are discussed in terms of ligand structural properties.

Introduction

In two previous studies[1,2] we have reported absorption spectra and 4f → 4f oscillator strengths for a series of erbium(III)[1] and neodymium(III)[2] complexes in aqueous solution. The ligands included in those studies were oxydiacetate (ODA), dipicolinate (DPA), iminodiacetate (IDA), (methylimino)diacetate (MIDA), malate (MAL), and *N*,*N*′-ethylenebis(2-(*o*-hydroxyphenyl))glycinate (EHPG),[3] each of which has at least two donor moieties suitable for binding to a trivalent lanthanide ion in aqueous solution. The principal objectives were to examine the hypersensitivity of certain 4f → 4f transition intensities to ligand binding, to correlate the observed hypersensitive behavior to ligand structural properties, and to relate the pH dependence of the hypersensitive transition intensities to complex formation. Intensity calculations were also reported for a set of model systems whose structures were chosen to mimic those of the $Ln^{3+}(aq)$, $Ln(ODA)_3^{3-}$, $Ln(DPA)_3^{3-}$, $Ln(IDA)_3^{3-}$, and $Ln(MIDA)_3^{3-}$ complexes in solution.[1,2] These calculations were based on a 4f → 4f intensity model that includes both *static* point-charge crystal field effects and *dynamic* ligand-polarization effects.[4-7]

In our previous studies we reported oscillator strengths (calculated and empirically determined) for just a few of the observed 4f → 4f transitions in the Er(III)[1] and Nd(III)[2] complexes, with special emphasis on the "hypersensitive" transitions. No attempts were made to extract general intensity parameters from the data. In the present study we report absorption results for a series of Ho(III) complexes that are analogous to the Er(III) and Nd(III) complexes examined previously. The oscillator strengths obtained from the absorption intensity data are used to determine Judd–Ofelt intensity parameters Ω_λ ($\lambda = 2, 4, 6$)[8] for each system, employing standard "fitting" procedures. Using the results obtained in our previous study of Nd(III) complexes, we also carried out a parameterization of the Nd(III) intensity data within the general Judd–Ofelt Ω_λ parameter scheme for multiplet-multiplet transitions.

The Ω_λ parameterization of 4f → 4f (multiplet-to-multiplet) transition intensities has enormous utility for systematizing lanthanide intensity data. Excluding effects due to crystal field induced J-level mixings, the Ω_λ parameters in this scheme include *all* of the ligand-dependent effects contributing to 4f → 4f electric dipole intensity. For a given lanthanide ion, differences in the Ω_λ parameters determined for different complexes can be attributed to differential ligand field effects associated with, for example, coordination numbers, coordination geometries, and the respective lanthanide–ligand pairwise interaction mechanisms. Expressed in terms of the Ω_λ parameters, the oscillator strength of an A → B multiplet-to-multiplet transition is given by

$$f_{AB} = (8\pi^2 m_e c/3h)\chi\bar{\nu}_{AB}g_A^{-1}\sum_\lambda \Omega_\lambda \left|\sum_{\psi J}\sum_{\psi' J'} C_A^*(\psi J) \times C_B(\psi' J')\langle f^N\psi[SL]J\|U^\lambda\|f^N\psi'[S'L']J'\rangle\right|^2 \quad (1)$$

where $\lambda = 2$, 4, and 6, χ is the Lorentz field correction for the refractivity of the medium, $\bar{\nu}_{AB}$ is the A → B transition energy (expressed in wavenumbers), g_A is the degeneracy of state A, U^λ is an intraconfigurational unit tensor operator, and the coefficients $C_A(\psi J)$ and $C_B(\psi' J')$ give the compositions of states A and B in terms of the "free-ion" f^N intermediate-coupling wave functions. In eq 1, the radial-dependent parts of the A and B state functions have been absorbed into the Ω_λ parameters, so these parameters do contain properties in-

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herent to the lanthanide f^N electronic structure. Denoting the *nonradial* parts of $|A\rangle$ and $|B\rangle$ by $|\alpha\rangle$ and $|\beta\rangle$, respectively, we may rewrite eq 1 as

$$f_{AB} = 1.08 \times 10^{11} \chi \bar{\nu}_{AB} g_A^{-1} \sum_{\lambda} \Omega_\lambda \langle \alpha \| U^\lambda \| \beta \rangle^2 \qquad (2)$$

where $\bar{\nu}_{AB}$ is expressed in cm^{-1}, Ω_λ is expressed in cm^2, and the U^λ matrix elements contain the double summations over ψJ and $\psi' J'$ shown in eq 1.

In the present paper we restrict our attention to the *empirically* determined values of the Ω_λ intensity parameters obtained for $NdCl_3$ and $HoCl_3$ dissolved in water (under slightly acidic conditions) and for a series of 1:3 $NdCl_3$:ligand and 1:3 $HoCl_3$:ligand systems in aqueous solution at values of pH 8–10. The ligands included in this study are ODA, DPA, IDA, MIDA, and MAL. Calculations of the Ω_λ parameters, based on a specific 4f → 4f intensity model and the use of model structures for the ODA, DPA, IDA, and MIDA complexes, will be reported in a separate paper.[9] For the 1:3 Ln^{3+}:ODA and Ln^{3+}:DPA systems in aqueous solution under alkaline pH conditions, the major species are undoubtedly tris-terdentate complexes of the types, $Ln(ODA)_3^{3-}$ and $Ln(DPA)_3^{3-}$, each of which has effective D_3 point group symmetry.[10] The only difference between the coordination properties of the ODA and DPA ligands is in the nature of the respective *central* donor moieties—an ether oxygen in ODA and a pyridyl group in DPA. For the 1:3 Ln^{3+}:IDA and Ln^{3+}:MIDA systems in aqueous solution under alkaline conditions, the major species are also likely to be tris-terdentate complexes of the types $Ln(IDA)_3^{3-}$ and $Ln(MIDA)_3^{3-}$; but, for these complexes the effective point group symmetry will be C_{3h}.[10,11] The only difference between the IDA and MIDA ligands is the H vs. CH_3 substituent on the nitrogen donor atom. The structural species present in aqueous solutions of 1:3 Ln^{3+}/MAL under alkaline pH conditions are less well characterized, but there is some evidence that the major species are nine-coordinate $Ln(MAL)_3^{3-}$ complexes in which the hydroxyl groups of the malate ligands are acting as donor moieities (along with the carboxylate groups).[12]

Our primary interest here is to examine the sensitivity of the Ω_λ intensity parameters to structural differences in the coordination environments represented among the complexes discussed above. Characterization of this sensitivity and its correlation with structural details is an essential step in the development of accurate and reliable spectra–structure correlations for lanthanide 4f → 4f optical spectroscopy.

Experimental Section

$HoCl_3 \cdot 6H_2O$ (99.99%) was purchased from Aldrich and was used without further purification. Oxydiacetic acid ($ODAH_2$) and (methylimino)diacetic acid ($MIDAH_2$) were also purchased from Aldrich and used without further purification. Iminoacetic acid ($IDAH_2$) and disodium dipicolinate ($DPANa_2$) were purchased from Sigma. D,L-Malic acid was purchased from Aldrich.

All spectroscopic measurements reported here were carried out on aqueous solution samples in which $[Ho^{3+}] = 10$ mM. For $HoCl_3$ in water, the solution pH was fixed at ~2.0. A concentration ratio of 1:3 $[Ho^{3+}]$:[ligand] was used for each of the ligand studies, with a solution of pH ~8–10. Solution pH adjustments were made with NH_4OH. Absorption spectra were recorded on a Cary 17D spectrophotometer with the samples at room temperature. All absorption difference spectra were recorded with $HoCl_3$ (aq) in the reference beam and the $HoCl_3$/ligand/water system in the sample beam.

Table I. Transition Regions and U^λ Matrix Elements Used in the Nd(III) and Ho(III) Intensity Analyses

transition regions[a]					
label	transition	approx $\bar{\nu}_{max}$/ cm^{-1}	$\langle \| U^\lambda \| \rangle^2/10^{-3}$ $\lambda = 2$	$\lambda = 4$	$\lambda = 6$
Nd(a)	$^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$	13 500	0.95	45.7	660
Nd(b)	$^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	17 300	989	663	80.4
Nd(c)	$^4I_{9/2} \rightarrow {}^2K_{13/2}, {}^4G_{7/2}, {}^4G_{9/2}$	19 200	51.1	182	118
Nd(d)	$^4I_{9/2} \rightarrow {}^2K_{15/2}, {}^2G_{9/2}, {}^2D_{3/2}, {}^2P_{3/2}, {}^4G_{11/2}$	21 300	0.62	20.3	31.5
Nd(e)	$^4I_{9/2} \rightarrow {}^2P_{1/2}, {}^2D_{5/2}$	23 500	0.00	41.5	1.87
Nd(f)	$^4I_{9/2} \rightarrow {}^4D_{3/2}, {}^4D_{5/2}, {}^2I_{11/2}, {}^4D_{1/2}$	28 600	4.80	521	48.4
Ho(a)	$^5I_8 \rightarrow {}^5F_5$	15 500	0.00	446	572
Ho(b)	$^5I_8 \rightarrow {}^5S_2, {}^5F_4$	18 500	0.00	239	911
Ho(c)	$^5I_8 \rightarrow {}^5G_6$	22 100	1560	859	139
Ho(d)	$^5I_8 \rightarrow {}^5G_5, {}^3G_5$	23 900	0.00	539	3.20
Ho(e)	$^5I_8 \rightarrow {}^5G_5, {}^3H_5, {}^3H_6$	27 700	184	158	155

[a] Most of the labeled transition regions exhibit absorption bands comprised of several unresolved multiplet-to-multiplet transitions. The $\bar{\nu}_{max}$ values observed for these bands vary from system to system, so the values listed here are only meant to indicate the *approximate* locations of the bands.

Table II. Parameters Used in Calculating the Intermediate-Coupling Free-Ion States for Nd(III) and Ho(III)

parameter[a]/ cm^{-1}	Nd(III)	Ho(III)	parameter[a]/ cm^{-1}	Nd(III)	Ho(III)
F_2	321	419	β	−117.2	−621.0
F_4	46.3	65.0	γ	1321	2092
F_6	4.69	6.76	ζ_{so}	884.6	2141
α	0.5611	17.20			

[a] F_k denotes a Slater–Condon electrostatic radial parameter; α, β, and γ are configuration-interaction parameters; ζ_{so} denotes the radial spin–orbit coupling parameter.

Oscillator strengths, defined here by

$$f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu})\, d\bar{\nu} \qquad (3)$$

were obtained by evaluating $\int \epsilon(\bar{\nu})\, d\bar{\nu}$ over the transition region of interest. *Differential* oscillator strengths

$$\Delta f = f(\text{complex}) - f(HoCl_3(aq)) = 4.32 \times 10^{-9} \int \Delta\epsilon(\bar{\nu})\, d\bar{\nu} \qquad (4)$$

were determined directly from the $\Delta\epsilon(\bar{\nu})$ vs. $\bar{\nu}$ difference spectra.

Intensity Parameter Calculations

Intensity parameters (Ω_λ) were calculated by applying eq 2 to six different absorption regions of the Nd(III) systems and to five different absorption regions of the Ho(III) systems. The absorption regions and the transitions contributing to each of these regions are identified in Table I. For Nd(III), the ground-state multiplet in each case is $^4I_{9/2}$, so $g_A = 10$. For Ho(III), the ground-state multiplet in each case is $^5I_8$, so $g_A = 17$. In each case, χ was set equal to 1.19 and the $\bar{\nu}_{AB}$ values were set equal to the $\bar{\nu}_{max}$ frequencies observed within the respective absorption regions ($\bar{\nu}_{max}$ being the frequency at which a maximum in ϵ is observed). In evaluating the U^λ matrix elements in eq 2, we used free-ion intermediate-coupling wave functions calculated for the $4f^3$ configuration of Nd(III) and the $4f^{10}$ configuration of Ho(III). In each case, a seven-parameter free-ion electronic Hamiltonian was diagonalized within the appropriate $4f^N$ Russell–Saunders (SLJ) basis to obtain the intermediate-coupling (JM_J) states of interest. The parameters used in these calculations are listed in Table II.

Since empirical oscillator strengths were determined for transition *regions* rather than for individual multiplet-to-multiplet transitions, eq 2 was modified to the form

$$f_b = 1.08 \times 10^{11} \chi [\bar{\nu}_{max}(b)] g_J^{-1} \sum_{\lambda} \Omega_\lambda \sum_{\psi_b' J_b'} \langle \psi J \| U^\lambda \| \psi_b' J_b' \rangle^2 \qquad (5)$$

where b labels the transition *region* with an absorption maximum at $\bar{\nu}_{max}(b)$ ($J = {}^9/_2$ and $g_J = 10$ for Nd(III); $J = 8$ and $g_J = 17$ for Ho(III)) and the second summation is over all excited-state multiplet

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Table III. Experimental and Fitted Oscillator Strengths for the Nd(III) and Ho(III) Systems[a,b]

transition region[c]	aquo		ODA		DPA		IDA		MIDA		MAL	
	exptl	fit	exptl	fit	exptl	fit	exptl	fit	exptl	fit	exptl	fit
Nd(a)	7.84	8.01	8.94	8.01	16.73	16.90	12.41	12.46	9.11	9.26	9.22	9.31
Nd(b)	8.65	8.68	12.20	12.20	18.84	18.79	15.79	15.74	17.53	17.48	16.30	16.15
Nd(c)	6.20	4.01	6.72	4.44	9.71	6.67	8.21	6.36	7.29	5.21	7.29	5.86
Nd(d)	1.45	0.82	1.53	0.90	2.02	1.60	1.82	1.29	1.45	0.99	1.86	1.10
Nd(e)	0.35	0.60	0.35	0.59	0.35	0.62	0.35	0.91	0.35	0.74	0.36	0.99
Nd(f)	9.01	9.73	9.01	9.76	9.80	10.87	14.32	14.85	11.22	11.94	15.38	15.79
Ho(a)	3.35	3.58	3.70	4.08	5.19	5.14	4.94	5.17	3.41	3.62	4.07	4.57
Ho(b)	5.11	4.96	6.16	5.90	7.64	7.64	7.06	7.03			6.40	6.14
Ho(c)	5.64	5.66	20.51	20.51	26.61	26.59	16.29	16.43	17.96	18.10	18.22	18.32
Ho(d)	2.93	2.72	3.16	2.84	3.67	3.63	4.33	4.18	3.55	3.43	4.00	3.62
Ho(e)	2.33	2.05	4.68	4.44	8.45	6.84	5.61	4.81	5.54	3.82	5.36	4.52

[a] Except for Ln^{3+}(aq), all systems were 1:3 $[Ln^{3+}]/[\text{ligand}]$ in aqueous solution at pH ~8–10. [b] Oscillator strength values are given as $f/10^{-6}$. [c] See Table I.

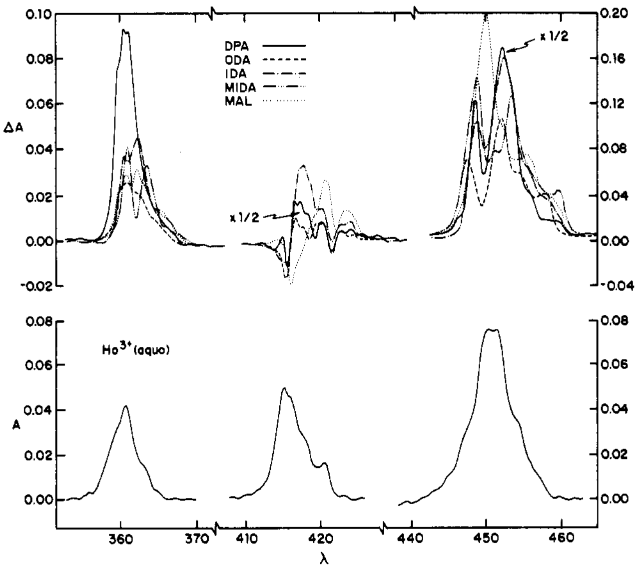

Figure 1. Top: Absorption difference spectra (ΔA) obtained in the Ho(e), Ho(d), and Ho(c) transition regions (as defined in Table I) for five different Ho^{3+}:ligand (1:3) vs. Ho^{3+}(aq) systems. The left-hand differential absorbance (ΔA) scale applies to the 350–430-nm spectral region, and the right-hand ΔA scale applies to the 440–460-nm region. Bottom: Absorption spectra for $HoCl_3$ in water.

levels included in the bth transition region. The $\langle \|U^\lambda\| \rangle^2$ values listed in Table I for the various transition regions were evaluated from

$$\langle \|U^\lambda\| \rangle^2 = \sum_{\psi_b' J_b'} \langle \psi J \| U^\lambda \| \psi_b' J_b' \rangle^2 \qquad (6)$$

using intermediate-coupling wave functions for the multiplet levels involved. Inserting the appropriate values for χ and g_J into eq 5, we have for Nd(III)

$$f_b(\text{Nd}) = 1.29 \times 10^{10} [\bar{\nu}_{\max}(b)] \sum_\lambda \Omega_\lambda (\Gamma_b^\lambda)^2 \qquad (7)$$

and for Ho(III)

$$f_b(\text{Ho}) = 7.56 \times 10^{9} [\bar{\nu}_{\max}(b)] \sum_\lambda \Omega_\lambda (\Gamma_b^\lambda)^2 \qquad (8)$$

where $\Gamma_b^\lambda = \langle \|U^\lambda\| \rangle$ for the bth absorption region. From empirical values for the $\bar{\nu}_{\max}(b)$ and calculated values for the $(\Gamma_b^\lambda)^2$ (the latter are listed in the last three columns of Table I), the values of the Ω_λ (λ = 2, 4, 6) parameters were varied to achieve optimal agreement between the f values calculated according to eq 7 or 8 and those determined from experiment. A standard least-squares fitting procedure was used in this parameter-optimization analysis. The experimental f values used in the fitting procedure are listed in Table III. The values listed for Nd(III) were taken from a previous study,[2] while the values listed for Ho(III) were determined from data obtained in the present study.

Table IV. Intensity Parameters Calculated from Experimental Data[a]

system[b]	$\Omega_\lambda/10^{-20}$ cm^2		
	$\lambda = 2$	$\lambda = 4$	$\lambda = 6$
Nd^{3+}(aq)	0.371 ± 0.88	4.55 ± 1.0	6.62 ± 0.83
Nd^{3+}/ODA (1:3)	2.00 ± 0.91	4.46 ± 1.1	7.57 ± 0.85
Nd^{3+}/DPA (1:3)	4.45 ± 1.2	4.40 ± 1.4	14.3 ± 1.1
Nd^{3+}/IDA (1:3)	1.70 ± 0.75	6.89 ± 0.87	10.5 ± 0.70
Nd^{3+}/MIDA (1:3)	3.60 ± 0.83	5.58 ± 0.97	7.78 ± 0.78
Nd^{3+}/MAL (1:3)	1.61 ± 0.63	7.65 ± 0.93	7.69 ± 0.59
Ho^{3+}(aq)	0.39 ± 0.21	2.74 ± 0.32	3.09 ± 0.22
Ho^{3+}/ODA (1:3)	5.86 ± 0.31	2.84 ± 0.49	3.77 ± 0.34
Ho^{3+}/DPA (1:3)	7.71 ± 0.93	3.62 ± 1.1	5.02 ± 0.98
Ho^{3+}/IDA (1:3)	3.48 ± 0.54	4.19 ± 0.85	4.33 ± 0.58
Ho^{3+}/MIDA (1:3)	4.68 ± 0.82	3.45 ± 1.3	2.62 ± 1.6
Ho^{3+}/MAL (1:3)	4.55 ± 0.55	3.65 ± 0.86	3.80 ± 0.59

[a] All values are given to within ±1σ as determined from the fitting procedure described in the text. [b] All 1:3 Ln^{3+}:ligand systems were in aqueous solution at pH ~8–10.

Table V. Ratios of Intensity Parameters[a]

Ln^{3+}	ligand	Ω_λ(complex)/Ω_λ(aquo)		
		$\lambda = 2$	$\lambda = 4$	$\lambda = 6$
Nd^{3+}	ODA	5.40	0.98	1.14
	DPA	12.0	0.97	2.16
	IDA	4.59	1.51	1.59
	MIDA	9.70	1.23	1.17
	MAL	4.35	1.68	1.16
Ho^{3+}	ODA	15.0	1.04	1.22
	DPA	19.8	1.32	1.62
	IDA	8.92	1.53	1.40
	MIDA	12.0	1.26	0.85
	MAL	11.7	1.33	1.22

[a] Calculated from the results given in Table IV.

Results

Holmium Absorption Spectra. Absorption difference spectra are shown in Figures 1 and 2 for five different Ho^{3+}:ligand (1:3) vs. Ho^{3+}(aq) systems, along with the absorption spectra of $HoCl_3$ in water. The Ho(e), Ho(d), and Ho(c) transition regions are shown in Figure 1, and the Ho(b) and Ho(a) transition regions are shown in Figure 2 (see Table I for a description of these transition regions). Of special note are the significantly larger values of ΔA observed within the Ho(c) region vs. those observed within the other four regions. This reflects the strongly *hypersensitive* behavior of the $^5I_8 \rightarrow {}^5G_6$ transition in Ho(III) systems.[8,13] We also note the generally

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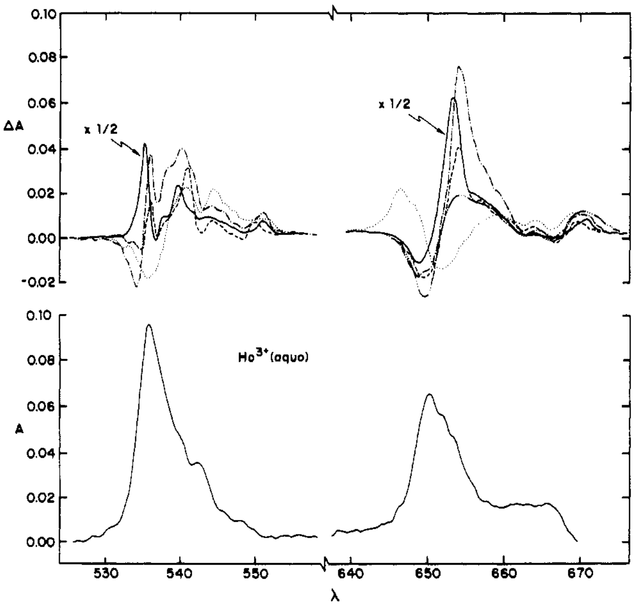

Figure 2. Top: Absorption difference spectra (ΔA) obtained in the Ho(**b**) and Ho(**a**) transition regions (as defined in Table I) for five different Ho^{3+}:ligand (1:3) vs. Ho^{3+}(aq) systems. The ΔA spectral traces are coded exactly as shown in Figure 1 (for the various ligands). Bottom: Absorption spectra for $HoCl_3$ in water.

larger ΔA values observed for the DPA system vs. those observed for the other ligand systems, indicating that the DPA ligand is especially effective in promoting 4f → 4f electric dipole intensity. This was also observed in our study of Nd(III) systems.[2]

Oscillator Strengths and Intensity Parameters. The Ω_λ values obtained from our fitting analysis of the empirical intensity data are listed in Table IV. Substituting these parameter values into eq 7 and 8 yielded the fitted oscillator strengths listed in Table III (alongside the corresponding experimentally determined oscillator strengths). Ratios of Ω_λ(complex)/Ω_λ(aquo) are given in Table V. We note that by far the largest ratios are for the $\lambda = 2$ parameters, indicating that the transitions with the largest U^2 matrix elements exhibit the greatest (intensity) sensitivity to ligand coordination. We also note that among the ligands examined in this study the DPA complexes give the largest Ω_2(complex)/Ω_2(aquo) ratios.

Discussion

Neodymium(III) Systems. Among the Nd(III) transitions examined here, the absorption intensity of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ pair exhibits the greatest sensitivity to the ligand environment. These transitions account for the Nd(**b**) absorption region centered around 580 nm (see Table I), and from Table I we see that they have large U^2 and U^4 matrix elements. These observations conform with previous studies in which this Nd(III) absorption region has been classified as being hypersensitive.[2,8,13] The results given in Table III show that the $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4S_{3/2}$ transition intensities (in the Nd(**a**) absorption region) also exhibit significant changes on going from the Nd^{3+}(aq) system to certain Nd^{3+}/ligand systems (especially for the DPA and IDA ligands). These transitions have small U^2 and U^4 matrix elements but a very large U^6 matrix element.

The results given in Tables IV and V identify Ω_2 as being the intensity parameter most sensitive to ligand effects. Most interesting are the DPA vs. ODA and MIDA vs. IDA comparisons. Recalling that $Nd(DPA)_3^{3-}$ and $Nd(ODA)_3^{3-}$ are expected to have identical coordination geometries (each with D_3 point group symmetry),[2,10] the rather large difference in Ω_2 values determined for these two systems must be attributable to differences in how pyridyl donor groups vs. ether oxygen donor groups interact with the f electrons of the lanthanide ion. Similarly, the $Nd(MIDA)_3^{3-}$ and $Nd(IDA)_3^{3-}$ systems are expected to have identical coordination geometries (each with C_{3h} point group symmetry).[2,10,11] In this case, the large difference in the Ω_2 values determined for the respective systems may be associated with effects due to methyl vs. hydrogen substitution at the central nitrogen donor atom of the ligands.

Holmium(III) Systems. Among the Ho(III) transitions examined in this study, the absorption intensity of $^5I_8 \rightarrow {}^5G_6$ exhibits the greatest sensitivity to the ligand environment. This transition produces the absorption band centered near 450 nm, and from Table I we see that it has a very large U^2 matrix element as well as a relatively large U^4 matrix element. The oscillator strength of this transition increases almost 5-fold on going from the Ho^{3+}(aq) system to the 1:3 Ho^{3+}:DPA system. Previous studies[8,13] have also shown the intensity of this transition to be hypersensitive to the ligand environment.

The Ho(**e**) absorption band centered near 360 nm also exhibits significant intensity enhancement in going from the Ho^{3+}(aq) system to the various Ho^{3+}/ligand systems (see Table III). The $^5I_8 \rightarrow {}^3H_6$ transition in this absorption region has a moderately large U^2 matrix element.

The results given in Tables IV and V identify Ω_2 as being the intensity parameter most sensitive to ligand effects. The DPA vs. ODA and MIDA vs. IDA comparisons for Ho(III) are qualitatively identical with those discussed above for Nd(III). Among the various Ho^{3+}/ligand systems examined here, the Ho^{3+}/malate system gives the most distinctively different spectral band shapes (in both the ΔA and A spectra). This possibly reflects the existence of multiple structural species in the 1:3 Ho^{3+}:MAL solutions, even at pH 9, or a major species having a coordination geometry significantly different from those characteristic of the ODA, DPA, IDA, and MIDA complexes. The latter is certainly a likely possibility since the backbone of the malate ligand and the disposition of its middle donor moiety (hydroxyl group) are significantly different from those found in the other ligands.

Conclusions

The principal objectives of this study were to (1) obtain empirical intensity parameters for a series of structurally related Nd(III) and Ho(III) complexes in aqueous solution and (2) demonstrate the sensitivity of these intensity parameters to structural differences between the ligands in the various complexes. The results obtained for both the Nd(III) and Ho(III) systems clearly show that among the Ω_λ (λ = 2, 4, 6) parameters Ω_2 is by far the most sensitive to ligand effects. Among the ligands examined in this study, the Ω_2(complex)/Ω_2(aquo) ratios were found to vary by as much as a factor of 2.8. The multiplet-to-multiplet transitions exhibiting the largest intensity variations among the complexes were those calculated to have the largest U^2 matrix elements. For the Nd(III) systems, the largest intensity variations were observed in the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition region (centered at ~580 nm), and for the Ho(III) systems, the largest intensity variations were observed in the $^5I_8 \rightarrow {}^5G_6$ transition region (centered at ~450 nm). We note that both the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ and $^5I_8 \rightarrow {}^5G_6$ transitions obey electric quadrupolar selection rules on ΔJ, ΔL, and ΔS. Conformity to these selection rules is often cited as the main criterion for hypersensitive behavior in a lanthanide 4f → 4f multiplet–multiplet transition.[8,13]

The next step in developing spectra–structure correlations for the types of systems examined in this study is to relate the variations in the empirically determined Ω_λ parameters to specific aspects of coordination geometry, ligand structure, and lanthanide electronic properties. This requires the adoption of detailed structural models for the complexes and some assumptions regarding the mechanisms responsible for 4f →

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 ($\lambda = 2, 4, 6$), 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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