CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY,
E. I. DU PONT DE NEMOURS AND COMPANY, AIKEN, SOUTH CAROLINA 29801

Hypersensitive Transitions of Six-, Seven-, and Eight-Coordinate Neodymium, Holmium, and Erbium Chelates[1]

BY D. G. KARRAKER

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The hypersensitive transitions in absorption spectra of solutions of lanthanide β-diketonates show differences that are characteristic of the coordination and the symmetry of the lanthanide ion. This conclusion is based on: (1) comparison of a hypersensitive transition in the absorption spectra for neodymium, holmium, and erbium six-, seven-, and eight-coordinate β-diketonates, (2) a demonstration that the spectra of six-coordinate chelates complexed with 1 and 2 additional moles of the coordinating ligand hexafluoroacetylacetone (HFAA) closely resemble the spectra of seven- and eight-coordinate chelates, (3) a demonstration that dehydration of benzene solutions of $Ln(CF_3COCHCOCF_3)_3 \cdot 2H_2O$ (Ln = Nd, Ho, or Er) is accompanied by changes in the absorption spectra that can be correlated with a change from an eight-coordinate to a six- or seven-coordinate chelate, and (4) a correlation of the oscillator strengths of hypersensitive transitions with the coordination number of the lanthanide chelate. Changes in the absorption spectra with changes in coordination of the lanthanide ion were also observed for praseodymium, samarium, europium, dysprosium, thulium, and ytterbium chelates.

Introduction

The absorption spectra of several of the trivalent lanthanide ions have been found[2-6] to have certain bands that change in intensity between aqueous and nonaqueous solutions and between aqueous solutions containing varying concentrations of chelating ligands. These effects are most pronounced for Nd(III) and Er(III), but attempts[2-4] to correlate these changes with the ratio of lanthanide ion to complexing ligand were unsuccessful. Changes in the coordination number of lanthanide ions have been suggested[2] as a possible cause for intensity and fine-structure differences.

The intensity of the absorption bands in Ln^{3+} spectra has been studied both theoretically and experimentally.[7-13] The theory proposed independently by Judd[7] and by Ofelt[8] has been reasonably successful in accounting for the intensity for most transitions on the basis of crystal-field-induced electric dipole transitions between individual Stark components.

The absorption bands that show abnormal variations in intensity and fine structure are classed as "hypersensitive." These variations are attributed[10] to the action of an inhomogeneous electromagnetic field from the medium. The intensities of normally weak quadrupole transitions increase as a result of the inhomogeneous field. Judd[12] has also suggested that the hypersensitive lines are strongly affected by changes in the symmetry of the field on the lanthanide ion.

In the present work, the hypersensitive transitions in the absorption spectra of six-, seven-, and eight-coordinated Nd, Ho, and Er β-diketonates in nonaqueous solvents were studied to assess the effect of the coordination number on the intensity and fine structure of the absorption spectra. Lanthanide β-diketonates were selected for investigation since all ligands are bonded to the lanthanide ion through oxygen atoms, and the effects of asymmetric bonding can be minimized. The organic liquids used as solvents were of low polarity to avoid solvent contributions to the crystal field of the lanthanide ions.

Experimental Section

Compounds.—The lanthanide β-diketonates were prepared using published methods or minor modifications of published methods. The compounds, their abbreviations, and references[14-17] to their preparation and characterization are listed in Table I.

TABLE I

LANTHANIDE β-DIKETONATES

Compound	Abbreviation	Ref
$Ln[(CH_3)_3CCOCHCOC(CH_3)_3]_3$	$Ln(thd)_3$	14
$Ln(CF_3COCHCOCH_3)_3 \cdot xH_2O^a$	$Ln(tfaa)_3 \cdot xH_2O$	15
$Ln(CF_3COCHCOCF_3)_3 \cdot xH_2O^a$	$Ln(hfaa)_3 \cdot xH_2O$	15
$(CH_3)_3NHLn(CF_3COCHCOCF_3)_4$	$(CH_3)_3NHLn(hfaa)_4$	16
$Ln(C_6H_5COCHCOC_6H_5)_3$	$Ln(DPPD)_3$	16, 17

^{a} $x = 1$ or 2.

Chelates of praseodymium, neodymium, samarium, europium, dysprosium, holmium, erbium, thulium, and ytterbium were prepared for most of the compounds listed in Table I. The lanthanide nitrates were purchased as 99.9% grade from commercial vendors. Some compounds of each type were completely analyzed; metal analyses of the analogs were assumed to be sufficient to assure proper identification. For $Ln(DPPD)_3$ compounds, the absence of water was verified by infrared absorption. Analyses of the compounds used were in reasonable agreement with the formula composition. Solvents used were

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[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

[2] L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, **68**, 3779 (1964).

[3] T. Moeller and W. F. Ulrich, *J. Inorg. Nucl. Chem.*, **2**, 164 (1956).

[4] T. Moeller and E. P. Horowitz, *ibid.*, **12**, 49 (1959).

[5] T. Moeller and D. E. Jackson, *Anal. Chem.*, **22**, 1393 (1950).

[6] T. Moeller and J. C. Brantley, *J. Am. Chem. Soc.*, **72**, 5447 (1950).

[7] B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).

[8] G. S. Ofelt, *J. Chem. Phys.*, **37**, 511 (1962).

[9] C. K. Jørgensen and B. R. Judd, *Mol. Phys.*, **8**, 281 (1964).

[10] W. F. Krupke and J. B. Gruber, *Phys. Rev.*, **139**, A2008 (1965).

[11] W. T. Carnall, P. R. Fields, and B. G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).

[12] B. R. Judd, *ibid.*, **44**, 839 (1966).

[13] W. F. Krupke, *Phys. Rev.*, **145**, 325 (1966).

[14] K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc.*, **87**, 5254 (1965).

[15] F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **40**, 2790 (1964).

[16] L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **68**, 5117 (1964).

[17] R. G. Charles and A. Perrotto, *J. Inorg. Nucl. Chem.*, **26**, 373 (1964).

of chemically pure grade and were further purified by drying in a column of 4A molecular sieve. Anhydrous hexafluoroacetylacetone (HFAA)[17a] was prepared by drying the commercially available monohydrate with concentrated sulfuric acid and distilling.[18]

Absorption spectra were measured with Cary Models 11 and 14 spectrophotometers, with solutions contained in stoppered quartz cells.

Absorption intensities were determined by planimeter measurement of the area under the absorption curve and are presented as oscillator strengths calculated from the reduced expression[11]

$$P = 4.31 \times 10^{-9}\left[\frac{9\eta}{(\eta^2 + 2)^2}\right]\int \epsilon(\nu)\mathrm{d}\nu$$

where η is the refractive index of the solution and $\epsilon(\nu)$ is the molar extinction coefficient at wavelength ν. Handbook values for the refractive indices of the solvents were used in calculations.

The linear dependence of absorption intensity on concentration was demonstrated over a concentration range of (2–4) × 10^{-2} M to (5–10) × 10^{-4} M for all chelates investigated.

Results

General Material.—The β-diketonates investigated were considered to provide either six-, seven-, or eight-coordination for the lanthanide ion. Ln(thd)$_3$ and Ln(DPPD)$_3$ have been classified as six-coordinate,[14,17] based on their composition and properties. Ln(thd)$_3$ compounds are reported to be monomeric in benzene;[14] Ln(DPPD)$_3$ has not been investigated in solution, so the possibility of a polymeric species cannot be ignored.

Ln(tfaa)$_3$ and Ln(hfaa)$_3$ may be either anhydrous, monohydrate, or dihydrate;[15,19] only hydrated compounds were prepared. Analytical data, infrared absorption, and internal evidence of absorption band shape were used to distinguish between seven- and eight-coordinated chelates.

The eight-coordination of the yttrium in the Y(hfaa)$_4^-$ ion has been established crystallographically,[20] and the assumption of the same coordination for lanthanide derivatives is supported by emission spectroscopy[21,22] and molecular weight measurements in CH_2Cl_2 solution. Absorption shapes and intensities were identical for Nd(hfaa)$_4^-$, Ho(hfaa)$_4^-$, and Er(hfaa)$_4^-$ anions in ethanol, CH_2Cl_2, and $CHCl_3$, but were normally measured in ethanol because of higher solubility.

The solvents are considered noncoordinating or coordinating, depending upon their effects on the spectra of the lanthanide β-diketonates. No coordination by CH_2Cl_2, $CHCl_3$, benzene, or petroleum ether (bp 20–40°) was either exhibited or expected; ethanol is a noncoordinating solvent to Ln(hfaa)$_4^-$ species and to Ln(thd)$_3$, but on the basis of spectral data it coordinates with Ln(hfaa)$_3$. HFAA has been shown to be 100% in the enol form and was found in this work to function as a unidentate ligand in nonionizing solvents.

Neodymium.—The absorption spectrum of Nd^{3+} due to the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions[22] exhibits[3,23,24] striking changes in intensity in different environments. The absorption spectra for four β-diketonates are shown in Figure 1: the eight-coordinate Nd(hfaa)$_4^-$ ion, the seven-coordinate Nd(tfaa)$_3 \cdot H_2O$, and the six-coordinate chelates Nd(thd)$_3$ and Nd(DPPD)$_3$.

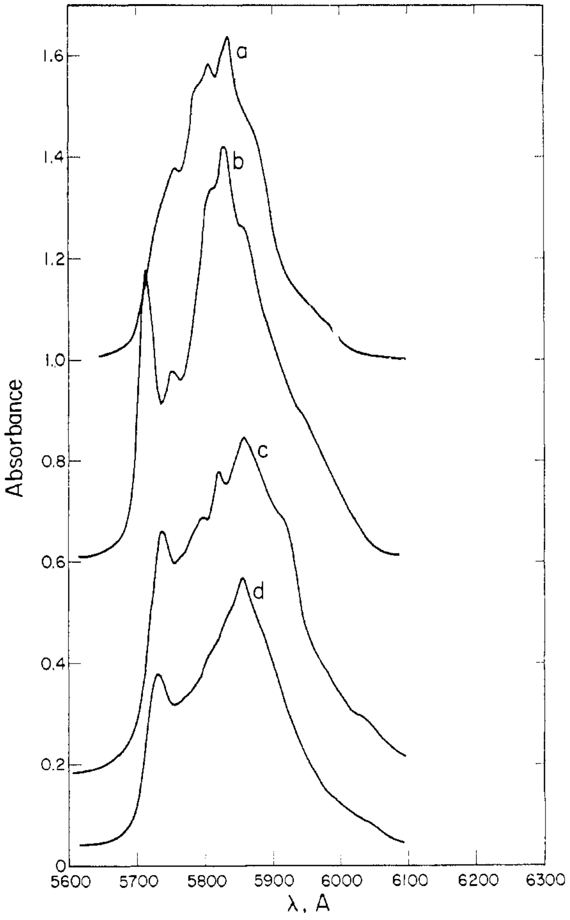

Figure 1.—Spectra of Nd chelates: (a) $(CH_3)_3NHNd(hfaa)_4$ in C_2H_5OH; (b) Nd(tfaa)$_3 \cdot H_2O$ in C_2H_5OH; (c) Nd(thd)$_3$ in $CHCl_3$; (d) Nd(DPPD)$_3$ in C_6H_6.

The intensity of absorption and the appearance of the absorption bands of Nd^{3+} are both altered by the addition of HFAA to solutions of Nd(DPPD)$_2$ and Nd(thd)$_3$. The absorption bands for HFAA:Nd chelate mole ratios of 0, 1, and 2 are shown for Nd(thd)$_3$ in Figure 2; those for Nd(DPPD)$_3$ are similar. The changes in spectral shape and inflections in a graph of oscillator strength *vs.* HFAA : Nd chelate ratio (Figure 3a and b) coincide with the stoichiometry required for a stepwise addition of two molecules of HFAA to the coordination sphere of the Nd^{3+} ion. The spectral shape after addition of 2 mole equiv of HFAA to both chelates is nearly identical with the spectral shape of the eight-coordinate Nd(hfaa)$_4^-$ ion (Figure 1a).

A spectral change due to a reduction in coordination

[17a] Note Added in Proof.—The β-diketone is indicated by capital letters as HFAA; combined as a ligand, it is represented by lower case letters as in Ln(hfaa)$_3 \cdot H_2O$; in addition compounds, it appears as in Ln(thd)$_3 \cdot$HFAA.

[18] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

[19] M. L. Bhaumik, *ibid.*, **27**, 261 (1965).

[20] S. J. Lippard, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **88**, 5930 (1966).

[21] H. Bauer, J. Blanc, and D. L. Ross, *ibid.*, **86**, 5125 (1964).

[22] C. Brecher, A. Lempicki, and H. Samelson, *J. Chem. Phys.*, **41**, 279 (1964).

[23] B. G. Wybourne, *ibid.*, **32**, 639 (1960).

[24] E. A. Boudreaux and A. K. Mukherji, *Inorg. Chem.*, **5**, 1280 (1966).

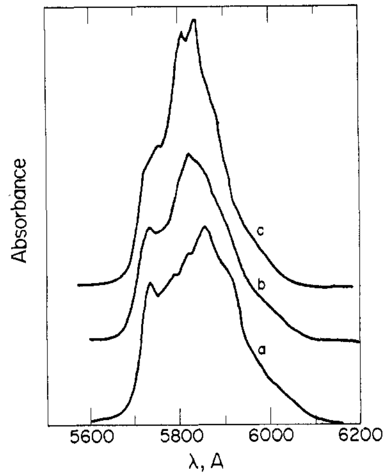

Figure 2.—Spectra of Nd(thd)$_3$–HFAA in CHCl$_3$: (a) no HFAA; (b) HFAA:Nd(thd)$_3$ = 1; (c) HFAA:Nd(thd)$_3$ = 2.

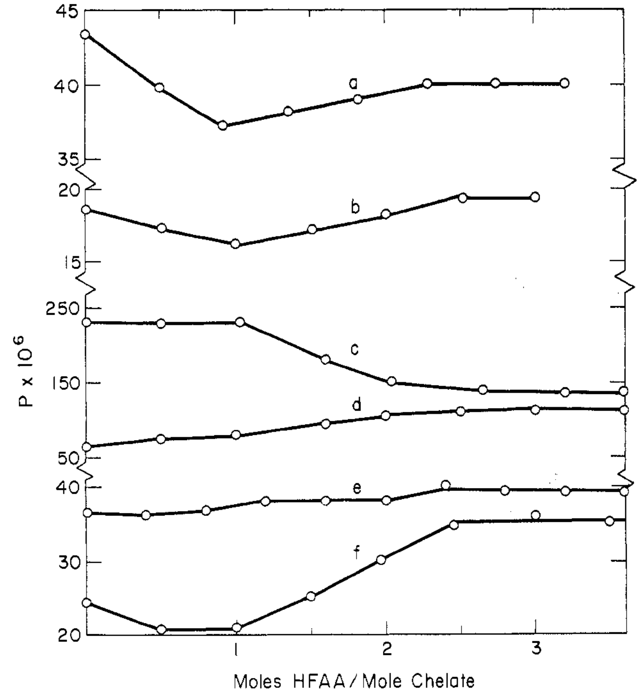

Figure 3.—Oscillator strengths for Ln chelates–HFAA: (a) Nd(DPPD)$_3$; (b) Nd(thd)$_3$; (c) Ho(DPPD)$_3$; (d) Ho(thd)$_3$; (e) Er(DPPD)$_3$; (f) Er(thd)$_3$.

number of Nd^{3+} was shown by removing coordinated water from a benzene solution of the Nd(hfaa)$_3$·2H$_2$O chelates with a column of 4A molecular sieve. The spectrum of Nd(hfaa)$_3$·2H$_2$O (Figure 4a) is identified as similar to that of the eight-coordinate Nd^{3+} chelate; after the solution was passed through the molecular sieve column, the spectrum corresponded to that of a seven-coordinate Nd^{3+} chelate (Figure 4b). The addition of a small amount of water to the spectrometer cell and agitation restored the eight-coordinate Nd^{3+} spectrum (Figure 4c). Attempts to remove water from Nd(hfaa)$_3$·H$_2$O with a molecular sieve column were unsuccessful; apparently Nd(hfaa)$_3$ absorbs on the molecular sieve and could be removed by ethanol, but not by benzene. The spectrum of this ethanol solution was that of seven-coordinate Nd^{3+}; ethanol apparently acted as coordinating solvent toward Nd(hfaa)$_3$.

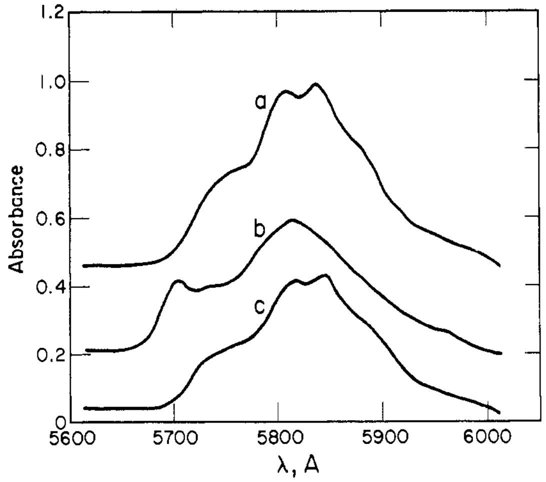

Figure 4.—Spectra of Nd(hfaa)$_3$·2H$_2$O and Nd(hfaa)$_3$·H$_2$O: (a) Nd(hfaa)$_3$·2H$_2$O in benzene; (b) Nd(hfaa)$_3$·H$_2$O—solution of (a) after drying with 4A molecular sieve column; (c) solution from (b) shaken with H$_2$O.

The measured oscillator strengths for Nd^{3+} chelates are listed in Table II. This table includes values obtained from the additions of HFAA to solutions of the six-coordinate chelates and for HFAA addition to Nd(tfaa)$_3$·H$_2$O (assuming that one HFAA replaces the water molecule without changing the coordination and the second HFAA increases the coordination).

TABLE II

OSCILLATOR STRENGTHS FOR THE Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ TRANSITION AT 16,949–17,606 CM^{-1}

Compound (complex)	Solvent	10^6P
Six-coordinate		
Nd(thd)$_3$	C$_6$H$_6$	18.7
Nd(DPPD)$_3$	C$_6$H$_6$	43.5
Seven-coordinate		
Nd(thd)$_3$·HFAA	CHCl$_3$	16.3
Nd(DPPD)$_3$·HFAA	C$_6$H$_6$	37.0
Nd(tfaa)$_3$·H$_2$O	C$_2$H$_5$OH	17.3
Eight-coordinate		
(CH$_3$)$_3$NHNd(hfaa)$_4$	C$_2$H$_5$OH	24.0
Nd(thd)$_3$·2HFAA	CHCl$_3$	18.5
Nd(DPPD)$_3$·2HFAA	C$_6$H$_6$	40.0
Nd(tfaa)$_3$·2HFAA	C$_2$H$_5$OH	19.4

Holmium.—The absorption spectra of Ho^{3+} due to the hypersensitive $^5I_8 \rightarrow {}^5G_6, {}^5F_1$ transitions[25] for the six-, seven-, and eight-coordinated Ho^{3+} chelates are shown in Figure 5. A suggested cause for the difference in band shape between the six-coordinate compounds Ho(thd)$_3$ and Ho(DPPD)$_3$ is a different geometrical arrangement of the ligands about the Ho^{3+} ion.

Incremental additions of HFAA to solutions of six-coordinate Ho^{3+} chelates altered both the shape of the absorption bands and their intensity. Figure 3c and d shows the effect of HFAA on the oscillator strength, and Figure 6 shows the changes in the appearance of the absorption band for the addition of HFAA to Ho(thd)$_3$.

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(25) M. H. Crozier and W. A. Runciman, *J. Chem. Phys.*, **35**, 1392 (1961.)

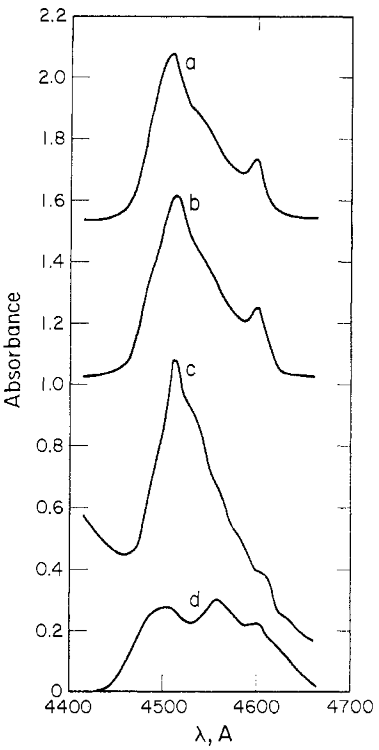

Figure 5.—Absorption spectra of Ho chelates: (a) $(CH_3)_3NHHo(hfaa)_4$ in C_2H_5OH; (b) $Ho(tfaa)_3 \cdot H_2O$ in C_2H_5OH; (c) $Ho(DPPD)_3$ in C_6H_6; (d) $Ho(thd)_3$ in petroleum ether.

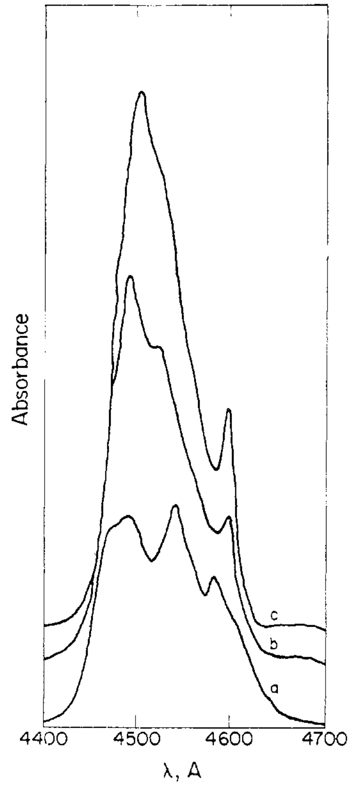

Figure 6.—Spectra of $Ho(thd)_3$–HFAA in petroleum ether: (a) no HFAA; (b) HFAA:$Ho(thd)_3$ = 1; (c) HFAA:$Ho(thd)_3$ = 2.

TABLE III

OSCILLATOR STRENGTHS FOR THE Ho^{3+} $^5I_8 \rightarrow {}^5G_8, {}^5F_1$ TRANSITION AT 22,727–21,505 CM^{-1}

Compound (complex)	Solvent	10^6P
Six-coordinate		
$Ho(thd)_3$	Pet. ether	65
$Ho(thd)_3$	C_6H_6	61
$Ho(DPPD)_3$	C_6H_6	228
$Ho(DPPD)_3 \cdot H_2O$	C_6H_6	132
Seven-coordinate		
$Ho(thd)_3 \cdot HFAA$	Pet. ether	79
$Ho(DPPD)_3 \cdot DMSO$	DMSO	80
$Ho(tfaa)_3 \cdot H_2O$	C_2H_5OH	75
$Ho(DPPD)_3 \cdot HFAA$	C_6H_6	228
Eight-coordinate		
$Ho(thd)_3 \cdot 2HFAA$	Pet. ether	110
$Ho(DPPD)_3 \cdot 2HFAA$	C_6H_6	136
$(CH_3)_3NHHo(hfaa)_4$	C_2H_5OH	138

The measured oscillator strengths for Ho chelates are listed in Table III. Aside from DPPD complexes, the intensities agreed with species of the same coordination; the combination of band shape and oscillator strength may distinguish between seven- and eight-coordinated Ho^{3+}.

A benzene solution of $Ho(hfaa)_3 \cdot 2H_2O$ was dehydrated by passage through a column of 4A molecular sieve. The absorption spectra (Figure 7) show the conversion of most of the $Ho(hfaa)_3 \cdot 2H_2O$ to the anhydrous $Ho(hfaa)_3$. The addition of excess water to the dehydrated benzene solution of $Ho(hfaa)_3$ resulted in a solution whose absorption spectrum was identical with that of $Ho(hfaa)_3 \cdot 2H_2O$. $Ho(hfaa)_3$ and $Ho(thd)_3$ have similar appearances for their absorption bands, implying a similarity of structure.

Erbium.—The absorption band investigated for Er^{3+} chelates is due to the $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition.[26] The spectra of Er^{3+} in the eight-coordinate $Er(hfaa)_4^-$ anion, seven-coordinate $Er(thd)_3 \cdot HFAA$, and two six-coordinate chelates, $Er(thd)_3$ and $Er(DPPD)_3$, are displayed in Figure 8. As with the six-coordinate Ho^{3+} chelates, there is a pronounced difference between the two six-coordinate Er^{3+} chelates, possibly because of different structures.

Incremental additions of HFAA to solutions of $Er(thd)_3$ and $Er(DPPD)_3$ altered the appearance and intensities of the Er^{3+} absorption band. Figure 3e and f shows the effect of HFAA on the band intensities. The appearance of the absorption band is similar for $Er(thd)_3 \cdot HFAA$ and $Er(DPPD)_3 \cdot HFAA$, which are seven-coordinate, and for $Er(thd)_3 \cdot 2HFAA$, $Er(DPPD)_3 \cdot 2HFAA$, and the $Er(hfaa)_4^-$ ion, which are eight-coordinate.

The measured oscillator strengths for Er^{3+} chelates are listed in Table IV. Except for DPPD compounds, the oscillator strengths are consistently in the same range for compounds (or complexes) of the same coordination number.

A benzene solution of $Er(hfaa)_3 \cdot 2H_2O$ that was dehydrated by passage through a column of 4A molecular sieve gave a spectrum that corresponded to that of seven-coordinated Er^{3+}. Addition of water to the partially dehydrated solution restored the original spectrum; ethanol eluted the absorbed chelate from the molecular sieve column.

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(26) G. H. Dieke and S. Singh, *J. Chem. Phys.*, **35**, 555 (1961).

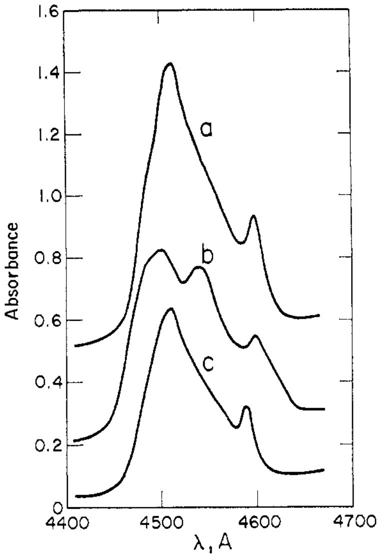

Figure 7.—Spectra of $Ho(hfaa)_3 \cdot 2H_2O$ and $Ho(hfaa)_3$: (a) $Ho(hfaa)_3 \cdot 2H_2O$ in benzene; (b) $Ho(hfaa)_3$—solution of (a) after drying with 4A molecular sieve column; (c) solution of (b) after addition of H_2O.

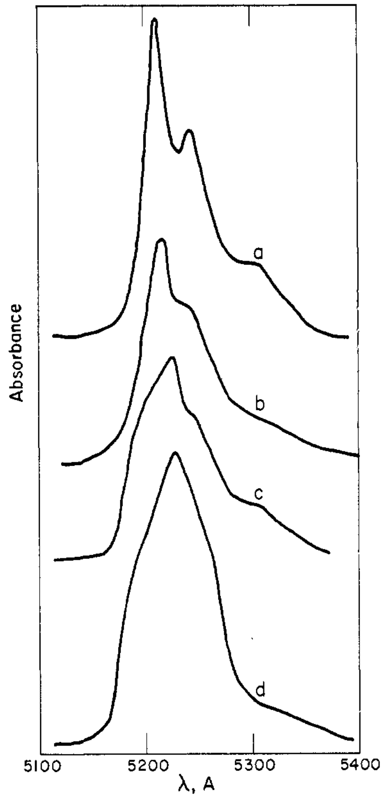

Figure 8.—Spectra of Er^{3+} chelates: (a) $(CH_3)_3NHEr(hfaa)_4$ in ethanol; (b) $Er(thd)_3 \cdot HFAA$ in benzene; (c) $Er(DPPD)_3$ in benzene; (d) $Er(thd)_3$ in petroleum ether.

TABLE IV

OSCILLATOR STRENGTHS FOR THE Er^{3+} $^4I_{15/2} \rightarrow {}^2H_{11/2}$ TRANSITION AT 18,605–19,572 CM^{-1}

Compound (complex)	Solvent	10^6P
Six-coordinate		
$Er(thd)_3$	Pet. ether, C_6H_6	24.5
$Er(DPPD)_3$	C_6H_6	37.4
Seven-coordinate		
$Er(thd)_3.HFAA$	Pet. ether, C_6H_6	20.9
$Er(DPPD)_3 \cdot HFAA$	C_6H_6	37.4
$Er(hfaa)_3 \cdot H_2O$	C_2H_5OH	27.4
$Er(DPPD)_3 \cdot DMSO$	DMSO	25.9
Eight-coordinate		
$Er(thd)_3 \cdot 2HFAA$	Pet. ether, C_6H_6	34.4
$Er(DPPD)_3 \cdot 2HFAA$	C_6H_6	39.0
$(CH_3)_3NHEr(hfaa)_4$	C_2H_5OH	33.6
$Er(hfaa)_3 \cdot 2H_2O$	C_2H_5OH	31.7

Other Lanthanide Chelates.—A comparison of the absorption spectra of solutions of $Ln(thd)_3$ and $(CH_3)_3NHLn(hfaa)_4$, where Ln is praseodymium, samarium, europium, dysprosium, thulium, or ytterbium, showed differences in the appearance of at least one absorption band for each lanthanide ion that were attributed to differences in the coordination of the lanthanide ion in six- and eight-coordinated chelates. The absorption spectra of $Ln(thd)_3$ solutions in pure HFAA were similar in band shape to the spectra of the eight-coordinate $Ln(hfaa)_4^-$ ion. The transitions and the regions of the spectra where these effects were observed are listed in Table V. The transitions investigated are not always hypersensitive, indicating that other transitions of lanthanide ions also show changes in shape with differences in coordination.

TABLE V

COORDINATION EFFECTS ON LANTHANIDE SPECTRA

Lanthanide	Transitions	Wavelength, A
Praseodymium	$^3H_4 \rightarrow {}^3P_1$	4,730
Samarium	$^6H_{5/2} \rightarrow {}^6P_{3/2}{}^a$	3,950, 4,100
Europium	$^7F_0 \rightarrow {}^5D_2$	4,650
Dysprosium	$^6H_{15/2} \rightarrow {}^6H_{9/2}$	13,000
Thulium	$^3H_6 \rightarrow {}^3F_2$	7,900
Ytterbium	$^2F_{7/2} \rightarrow {}^2F_{5/2}$	9,510

[a] W. T. Carnall and K. Rajnak, unpublished work; private communication from K. Rajnak.

A striking qualitative effect is the bright fluorescence of eight-coordinate Eu^{3+} chelates—$Eu(hfaa)_3 \cdot 2H_2O$ and $(CH_3)_3NHEu(hfaa)_4$—under irradiation from a simple ultraviolet light. Similar observations have been reported for solutions of Eu^{3+} chelates.[27] Under similar conditions, no fluorescence could be detected from the six-coordinated $Eu(thd)_3$ and $Eu(DPPD)_3$ chelates. The six-coordinate $Tb(thd)_3$ fluoresces brightly under these conditions, but no fluorescence is observed from the eight-coordinate $(CH_3)_3NHTb(hfaa)_4$.

Discussion

The experimental results can be summarized as demonstrating the following effects: (1) there is a difference between the appearance of the absorption bands for hypersensitive transitions between six-, seven-, and eight-coordinate lanthanide ions; (2) addition of HFAA to solutions of six- and seven-coordinate chelates results in changing the spectra of these chelates to spectra resembling those of seven- and eight-coordinate chelates; (3) the removal of water from solutions of hydrated chelates results in changing their spectra to spectra resembling chelates of lower coordination; (4)

[27] C. Brecker, A. Lempicki, and H. Samelson, *J. Chem. Phys.*, **41**, 279 (1964).

oscillator strengths for chelates of the same coordination are approximately the same value, except for Ln(DPPD)$_3$ compounds.

The explanation proposed to explain these results is that the appearance of the absorption bands is indicative of the coordination number and symmetry of the lanthanide ion. Generally, a difference in absorption spectra demonstrates a difference in the environment of an ion; for these compounds, all groups are attached to the lanthanide ion through oxygen atoms, leaving the number and geometry of the bonding groups as the major experimental variable. The evidence is essentially circumstantial, but the variety and consistency of the effects observed are considered to provide a strong basis for the proposed explanation.

The experimental results and the explanation proposed for them conform to Judd's theoretical prediction.[12] Given a symmetry effect on the hypersensitive transitions, the occurrence of similar spectra for similar symmetries is a predictable result. The effect of media on the intensity of hypersensitive transitions is well known, and hypersensitive bands have been predicted theoretically.[7,8] Again, for a similar environment, a similar intensity is a reasonable result. It is tempting to speculate that the occurrence of hypersensitive transitions implies an extension of the f orbitals in the higher state, compared to the ground state of the ion.

Consistent with the hypothesis proposed in this paper, the differences in the appearance of the spectral bands between two compounds of the same coordination are considered to be due to differences in symmetry of the field on the ion. The DPPD and thd chelates of Nd^{3+} have similar spectral bands, but the Ho^{3+} and Er^{3+} analogs show marked differences; different intensity effects result from the addition of HFAA to Nd chelates, on one hand, and Ho and Er chelates, on the other. A consistent explanation is that both Nd^{3+} six-coordinate chelates have the same structure, but that the Ho^{3+} and Er^{3+} chelates do not. The ionic radii of Ho^{3+} and Er^{3+} are 0.894 and 0.881 A, respectively, compared to 0.995 A for Nd^{3+}.[28] It is quite probable that the decrease in ionic radius in the lanthanide series results in an adjustment in the structure of one or both chelates to accommodate the ligands sterically, and structures that are similar for Nd^{3+} become dissimilar for Ho^{3+}, Er^{3+}, and smaller lanthanide ions.

The shape of the absorption bands of these lanthanide ions in seven-coordinate chelates shows a general resemblance to the shape of the bands of either six- or eight-coordinate chelates of the same ion. For example, the spectrum of seven-coordinate Nd^{3+} in Nd(tfaa)$_3\cdot H_2O$ resembles that of eight-coordinate Nd^{3+}; the spectrum of seven-coordinate Nd^{3+} in Nd(thd)$_3\cdot$HFAA is not greatly different from six-coordinate Nd^{3+}. Seven-coordinate structures are often the result of addition of a monodentate ligand to a six-coordinate structure or a coordination vacancy in an eight-coordinate structure.[29] The observed resemblances of the spectra of seven-coordinate chelates to the spectra of six- or eight-coordinate chelates might thus be expected.

Solid addition compounds could not be isolated either from addition of a stoichiometric ratio of HFAA per six- or seven-coordinate chelate or by treating the chelate with a large excess of HFAA. In the first case, HFAA was removed during vacuum drying. In the second case, HFAA apparently exchanged[30] with the chelating ligand to yield a chelate with mixed ligands. The addition of HFAA to six-coordinate chelates in solution probably involves an equilibrium that strongly favors complex formation.

This report shows that, under restricted conditions, the symmetry of the chelate is indicated by its absorption spectrum. Several examples can be found in the published literature—Moeller and Ulrich studied the spectra[3] for several lanthanide acetylacetonates [Ln(acac)$_3$] in benzene solution, with the assumption that the chelates were anhydrous. Their data indicate that the Nd(acac)$_3$ product is seven-coordinate, and the Ho(acac)$_3$ and Er(acac)$_3$ compounds are either seven- or eight-coordinate. Subsequent work by Pope, Steinbach, and Wagner[31] has demonstrated that all acetylacetonates of the lanthanides include coordinated water bound so tightly that its removal leads to decomposition of the chelate. Properly applied, the effect of coordination on spectral shape should be a useful tool for investigations of lanthanide chelates; an obvious area for further study is the spectra of solid lanthanide chelates.

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