Hypersensitivity in the 4f—4f Absorption Spectra of Lanthanide(III) Complexes

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Abstract

Praseodymium, neodymium, holmium and erbium complexes of bis(acetylacetone)ethylenediamine (ac$_2$en) and bis(acetylacetone)benzidine (ac$_2$bz) have been spectrophotometrically investigated in DMSO solution and in the solid state. The observed spectra in the visible region have been analysed to calculate oscillator strength and covalency parameters ($\bar{\beta}$, $b^{1/2}$ and δ). The covalency parameters reflect that ac$_2$bz complexes are more covalent and ac$_2$bz is a stronger ligand in a nephelauxetic sense. It is found that ac$_2$bz is especially effective in promoting 4f—4f spectral intensity. The larger values of the oscillator strengths for ac$_2$bz complexes are correlated to the low molecular symmetry of these complexes compared to ac$_2$en complexes.

Introduction

Most of the sharp lines like 4f—4f transitions originating within the 4f configuration of the lanthanide(III) ions are little affected by the environment of the lanthanide ions. A few, however, are very sensitive to the environment and are more intense when the ion is complexed than they are in the corresponding aqua-ions. Such transitions have been called hypersensitive transitions by Jørgensen and Judd [1]. The oscillator strengths of such 4f—4f transitions exhibit an especially strong sensitivity to the structural details and chemical nature of the ligand environment. This phenomenon is generally referred to as hypersensitivity and has been the subject of considerable experimental and theoretical investigations [2–18]. The oscillator strengths and band shapes of the hypersensitive transitions in the absorption spectra of the lanthanides have been correlated with the coordination numbers and symmetries of the lanthanide ions [7, 8, 11–20]. In this paper absorption results obtained on lanthanide (praseodymium, neodymium, holmium and erbium) complexes of bis(acetylacetone)ethylenediamine [21] (ac$_2$en) and bis(acetylacetone)benzidine [22] (ac$_2$bz) are reported. Each of the ligands included in this study contains two acetylacetone units. In

ac$_2$en the ligand forms complexes in its keto form, whereas ac$_2$bz interacts in the enol form. But these ligands differ from one another with respect to the remainder of the molecule. The ac$_2$en system contains an aliphatic diamine, whereas ac$_2$bz contains an aromatic diamine. The main objectives of the study were to determine if, and by how much, the 4f—4f absorption spectra reflect differences in ligand coordination properties and structure and to correlate any observed spectral differences with specific structural parameters.

Experimental

The ligands ac$_2$en and ac$_2$bz and their complexes with Pr(III), Nd(III), Ho(III) and Er(III) were synthesized by the literature methods [21, 22].

The electronic spectra were recorded on a Cary 17 D spectrophotometer in DMSO in the concentration range 10^{-2} to 10^{-3} M and in the solid state. Covalency parameters were calculated using previously reported methods [11]. The intensity of an absorption band is measured by its oscillator strength. The oscillator strengths (P), defined by:

$$P = 4.32 \times 10^{-9} \left[\frac{9\eta}{(\eta^2 + 2)^2} \right] \int \epsilon(\nu)\, d\nu \qquad (1)$$

(where η is the refractive index of the solvent, ϵ is the molar extinction coefficient and ν is the energy of the transition in cm^{-1}) were obtained by evaluating $\int \epsilon(\nu)\, d\nu$ over the transition region of interest.

Results and Discussion

The energies of the transition and oscillator strengths are given in Table I. The bands of Pr(III) in the visible region are known to originate from symmetry-forbidden transitions from the ground $^3H_4$ level to excited J levels. The P_j bands of Pr(III) complexes show only a slight increase in intensity compared to the praseodymium aqua-ion. The oscillator strengths of ac$_2$en and ac$_2$bz praseodymium complexes show larger P values for the ac$_2$bz complex,

TABLE I. Transition Energy Range and Oscillator Strengths of the Complexes[a]

Metal ions/transitions	Spectral range (cm^{-1})	Oscillator strength $10^6 \times P$		
		aqua	ac$_2$en	ac$_2$bz
Praseodymium (ground state $^3H_4$)				
$^1D_2$	16000–17500	3.12	3.25	4.23
$^3P_0$	20200–21000	2.52	2.76	3.95
$^3P_1$	21000–22100	6.60	7.50	6.83
$^3P_2$	22100–23500	14.60	10.25	11.05
Neodymium (ground state $^4I_{9/2}$)				
$^4F_{5/2}$	12000–13000	5.80	6.35	7.00
$^4(F_{7/2}, S_{3/2})$	13000–14200	7.84	8.90	9.22
$[^4G_{5/2}, {}^2G_{7/2}]$	16600–18200	8.60	48.68	56.39
$(^2K_{13/2}, {}^4G_{7/2}, {}^4G_{9/2})$	18600–20200	6.20	7.29	8.21
$^2K_{15/2}$	21000–21600	1.45	1.86	2.02
$(^2P_{1/2}, {}^2D_{5/2})$	23100–24200	0.35	1.38	1.92
Holmium (ground state $^5I_8$)				
$^5F_5$	15000–16000	3.35	3.78	5.19
$^5(S_2, F_4)$	18000–19200	5.11	6.16	7.64
$^5F_3$	20100–20900	3.09	3.68	4.83
$[^5G_6]$	21600–23200	5.64	47.49	53.08
$(^5G, {}^3G)_5$	23400–24600	2.93	3.67	4.81
$(^5G, {}^3H)_5, {}^3H_6$	27200–28500	2.33	4.68	8.54
Erbium (ground state $^4I_{15/2}$)				
$^4F_{9/2}$	14800–15800	2.37	2.47	2.51
$^4S_{3/2}$	18000–18700	0.83	0.68	1.06
$[^2H_{11/2}]$	18700–19800	2.91	48.01	51.88
$^4F_{7/2}$	20000–21100	2.22	2.82	3.12
$^4F_{5/2}, {}^4F_{3/2}$	21800–23000	1.31	1.48	1.83
$(^2G, {}^4F, {}^2H)_{9/2}$	24100–25100	0.74	1.14	1.49
$[^4G_{11/2}]$	25100–26900	5.90	113.20	128.43

[a]ac$_2$en is bis(acetylacetone)ethylenediamine; ac$_2$bz is bis(acetylacetone)benzidine. Hypersensitive transitions are enclosed in square parentheses.

indicating that the ac$_2$bz ligand is especially effective in promoting 4f–4f intensity.

Six multiple-to-multiple transitions occur within the 400–800 nm spectral region for the neodymium complexes. These are given in Table I. Among these transitions the most intense are $(^2K_{13/2}, {}^4G_{7/2}, {}^4G_{9/2})$, $(^4G_{5/2}, {}^4G_{7/2})$, $(^4F_{7/2}, {}^4S_{3/2})$ and $^4F_{5/2}$, with oscillator strengths of 6.20×10^{-6}, 8.65×10^{-6}, 7.84×10^{-6} and 5.84×10^{-6}, respectively, for the neodymium aqua-ion. For the systems examined in this study only the oscillator strength of the $I_{9/2} \rightarrow (^4G_{5/2}, {}^2G_{7/2})$ transition exhibits hypersensitivity to changes in ligand environment. This transition is six and seven times more intense than the neodymium aqua-ion for ac$_2$en and ac$_2$bz systems, respectively.

For holium systems, the largest intensity variation was observed in the $^5I_8 \rightarrow {}^5G_6$ (21 600–23 200 cm^{-1}) region. It is eight and nine times more intense than the holium aqua-ion for ac$_2$en and ac$_2$bz systems, respectively. A significantly larger value of oscillator strength in the 21 600–23 200 cm^{-1} region *versus* those observed in five regions reflects the strongly hypersensitive behaviour of the $^5I_8 \rightarrow {}^5G_6$ transition in Ho(III) systems [6, 7].

Seven multiple-to-multiple transitions are observed within the 400–700 nm spectral region for Er(III) systems. These are $^4I_{15/2} \rightarrow {}^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4(F_{5/2}, F_{3/2})$, $(^2G, {}^4F, {}^2H)_{9/2}$ and $^4G_{11/2}$. Among these transitions the most intense are $^4G_{11/2}$ (5.9×10^{-6}), $^2H_{11/2}$ (2.91×10^{-6}), $^4F_{9/2}$ $(2.37 \times$

TABLE II. Covalency Parameters[a]

Metal ions	$\bar{\beta}$		$b^{1/2}$		δ	
	ac$_2$en	ac$_2$bz	ac$_2$en	ac$_2$bz	ac$_2$en	ac$_2$bz
Pr	0.997	0.996	0.039	0.045	0.30	0.40
Nd	0.995	0.992	0.050	0.063	0.50	0.81
Ho	0.995	0.991	0.050	0.067	0.50	0.91
Er	0.997	0.994	0.038	0.055	0.30	0.60

[a]ac$_2$en = bis(acetylacetone)ethylenediamine; ac$_2$bz = bis(acetylacetone)benzidine.

10^{-6}) and $^4F_{7/2}$ (2.20×10^{-6}), where the numbers in parentheses are the oscillator strengths determined for ErCl$_3$ in aqueous solutions. For the systems examined only the intensities of the $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4G_{11/2}$ transitions exhibited hypersensitivity to changes in ligand environment. In all other transitions changes in the oscillator strength were less than 20% of the values obtained for the Er(III) aqua-ion. However, these changes for $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4G_{11/2}$ were found to be as large as 17 and 22 times more than the Er(III) aqua-ion in the case of ac$_2$en and ac$_2$bz systems, respectively. Both the transitions obey electric quadrupolar selection rules on $\Delta J \leqslant 2$, $\Delta L \leqslant 2$ and $\Delta S = 0$ and are classified as hypersensitive [6, 7].

It is interesting to note that for any given metal ion the oscillator strengths are larger for the ac$_2$bz system than the ac$_2$en system, indicating that the ac$_2$bz ligand is especially effective in promoting 4f–4f intensity. The larger values observed for the ac$_2$bz system can most likely be attributed to interaction of this ligand with the lanthanides in the enol form, which leads to greater covalency in bonding and results in higher oscillator strength [6, 7, 19]. The oscillator strengths of the hypersensitive transitions depend upon the symmetry of the molecules. The larger values of oscillator strengths for ac$_2$bz complexes reflect that ac$_2$bz complexes have lower molecular symmetry than ac$_2$en complexes [20].

Attempts have been made to relate the band shape of the hypersensitive transitions to the coordination environment of the lanthanide ion [19, 20]. The complexes of both the ligands, ac$_2$bz and ac$_2$en, give distinctively different band shapes in the solid and solution spectra, which demonstrate a change in the environment about the lanthanide ion in the two states. This possibly reflects that the solvent molecule is entering the coordination sphere [13, 18, 20] which changes the coordination geometry. An adduct formation with DMSO in solution was proposed [21] which is supported by this observation.

Nephelauxetic ratio has long been regarded as a measure of covalency [23] and this ratio has been correlated with the intensity of hypersensitive transitions [24]. The nephelauxetic effect in the spectra of these complexes is revealed by the red-shift of the spectral bands compared to those of the respective aqua-ions. The nephelauxetic ($\bar{\beta}$) [23], bonding ($b^{1/2}$) [24] and covalency (δ) [25] parameters for the systems are given in Table II. Less than one value of $\bar{\beta}$ and positive values of $b^{1/2}$ and δ show covalent nature of bonding between the metals and the ligands. The $b^{1/2}$ and δ values are larger for ac$_2$bz systems than ac$_2$en systems. It follows that ac$_2$bz complexes are more covalent than ac$_2$en, and that ac$_2$bz is a stronger ligand in a nephelauxetic sense.

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