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A Spectroscopic Study of Erbium(III) Acetate and Haloacetates Utilizing Judd–Ofelt Intensity Parameters and NMR Chemical Shifts

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Spectroscopic studies of lanthanide ion complexes over the past five decades have provided as many questions as they have answered. Theories developed to explain the electronic transitions of the lanthanide ions still lack a full explanation for the occurrence of intensity-sensitive transitions known as 'hypersensitive' transitions. Such transitions are observed in the electronic spectra of the ultraviolet and visible (UV–Vis) region. The selection rules assigned to these transitions are $\Delta J \leqslant 2$, $\Delta L \leqslant 2$ and $\Delta S = 0$ which are the selection rules for quadrupole radiation. The observed intensities are greater than those due to quadrupole radiation and are therefore referred to as hypersensitive pseudoquadrupole transitions. Many of the theories proposed for the phenomenon of hypersensitivity take into account a perturbation in the electronic configuration of the lanthanide ions and their $4f \rightarrow 4f$ transitions. Popular theories range from oscillations in the electric dipole moment of the lanthanide complex in the case of the inhomogeneous dielectric theory [1], to covalency through mixing of the $4f^n$ configuration with the ligands $\phi^{m-1}\ 4f^{n+1}$ [2]. These theories, which consider the hypersensitive transitions to be dipolar in nature, approach a spectroscopic study of lanthanide complexes from a viewpoint dealing mainly with the lanthanide ion and do not fully consider the ligands.

In NMR studies, chemical shifts are attributed to the effect of the lanthanide ions on the electron-charge distribution of the ligands. Lanthanide shift reagents (LSR, bare ions and complexes) are used as perturbing agents. These chemical shifts which are generally quite large, are related to the hyperfine interactions between the electron spin of the paramagnetic lanthanide ion and the ligand nuclei. The hyperfine interactions can be related to two shifting mechanisms: the contact shift and dipolar shift [3, 4]. When considering bare lanthanide ions as shift reagents, the contact shift which has been attributed to covalency [5], is predominant in the nuclei nearest to the lanthanide ion. Whereas, when dealing with highly complexed LSR so that only through-space perturbations are considered, the dipolar shift makes the largest contribution.

Since both areas of spectroscopy (the hypersensitive pseudoquadrupole transitions in UV–Vis studies and ^{13}C, ^{17}O and ^{1}H chemical shifts induced by LSR in NMR studies) supply information regarding the interactions between the lanthanide ion and its ligands, it is believed that a correlation between these two phenomena can be established. At this time, there is only one interdisciplinary reference in the literature [6]. Much experimental and theoretical work is needed in this correlative area of research.

Experimental

Preparations of the stock solutions (Er^{3+}, CH_3COOD, $CH_2ClCOOD$, $CH_2BrCOOD$ and CH_2ICOOD) were carried out in a glove bag under dry nitrogen. Deuterochloric acid and sodium deuterooxide were used to regulate the pH of the solutions. For UV–Vis studies, samples were prepared with constant erbium concentration whereas those for NMR studies were prepared with constant ligand concentration.

An IBM 9430 spectrophotometer was used to collect absorbance data in the range of 9000 to 2000 Å using 1.0 cm quartz cells. A blank was prepared using lanthanum and the corresponding ligand in the same concentrations as the sample. The data were analyzed on a VMS/VAX computer system where the erbium concentration was confirmed with a least-squares fitting routine using molar absorptivity values [7] for 10 transitions. Deconvolution of the spectral data was then carried out using an algorithm by Mardquardt [8] in order to determine the oscillator strenghts for the $4f \rightarrow 4f$ transitions. After making assignments according to Carnall [9], the transition intensity parameters Ω_2, Ω_4 and Ω_6 were calculated utilizing the equation of Judd and Ofelt [10, 11].

NMR data were obtained using a JEOL model FX90Q in the Fourier-transition mode with the following nuclei and observation frequencies: ^{1}H at 89.55 MHz; ^{13}C at 22.49 MHz; ^{17}O at 12.11 MHz. Acetone was used as an external reference for all three nuclei. The temperature was held constant at 300 ± 2 K. Lanthanum was used as a blank for each ligand in order to determine the isotropic shift. The data sets were analyzed after baseline correction and deconvolution of the spectra were carried out.

Discussion

The experimental oscillator strengths (f_{exp}) for the two hypersensitive transitions of erbium(III), $^{4}I_{15/2} \rightarrow {}^{2}H_{11/2}$ and $^{4}I_{15/2} \rightarrow {}^{4}G_{11/2}$, are presented

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TABLE 1. Judd–Ofelt parameters $(\Omega_\lambda)^a$ and experimental oscillator strengths $(f_{exp})^b$ calculated from spectrosocopic data for $M(ligand)_3$ in D_2O (where M = Er^{3+}; ligand = CH_3COOD, $CH_2ClCOOD$ and $CH_2BrCOOD$)

Ligand	f_{exp}		Ω_2	Ω_4	Ω_6	r.m.s.^{c}
	$\langle ^2H_{11/2} \rangle$	$\langle ^4G_{11/2} \rangle$				
CH_3COOD	2.42	4.26	0.7(1)	2.4(1)	0.7(1)	2.1
$CH_2ClCOOD$	2.45	4.30	0.9(1)	2.3(1)	0.7(1)	2.2
$CH_2BrCOOD$	2.66	4.39	1.1(1)	2.3(1)	0.7(1)	1.5

^{a}Parameters reported as $\Omega_\lambda \times 10^{20}$ (λ = 2,4,6). ^{b}Oscillator strength $\times 10^6$. ^{c}Root mean square $\times 10^7$.

in Table 1. The experimental oscillator strength values were used in the calculation of the phenomenological parameters (Ω_λ) of the Judd–Ofelt equation [10, 11] which are also presented in Table 1, along with their root mean square (r.m.s.) values. The Judd–Ofelt parameters are least-squares fitted values that can be related to pure electrostatic crystal field effects, vibronic effects or a combination of both effects. This implies that the Ω_λ parameters are good guiding indices with respect to the intensity of the 4f → 4f transitions, especially in regard to the hypersensitive transitions. The model [2] employed in this work suggests that the transition intensity parameters are implicitly influenced by the ligand field and that the Ω_2 parameter is affected by the polarization and the basicity of the ligands. The popular theories used in explaining the phenomenon of hypersensitivity show an emphasis on the modification of the Ω_2 parameter, which is dependent on the large square matrix elements associated with hypersensitive transitions [1, 2, 9, 10]. The parameter Ω_2 in Table 1 is observed to increase in the order $CH_3COOD < CH_2ClCOOD < CH_2BrCOOD$ which is the order of polarizability for the ligands. The spectra for $Er(CH_2ICOOD)_3$ did not provide usable transition data. This was due to interference by a broad intense band which began at 21 000 cm^{-1} resulting from the presence of free iodine.

The isotropic shifts, $\Delta\nu^{iso}$, for each ligand are presented in Table 2. Isotropic shift values have been determined as the difference between La^{3+} and Er^{3+} shift values (in Hz). The ^1H and $^{13}C_\alpha$ frequency shifts $(\Delta\nu^{iso})$ follow the haloacetate order of $CH_2ClCOOD > CH_2BrCOOD > CH_2ICOOD$. This order is in reverse when compared to a similar investigation using Nd^{3+} as the lanthanide ion [6]. Since the contact hyperfine interactions (contact shifts) are related to bonding effects within a complex, interactions (shifts) result from the formation of bonds between the lanthanide ion and the ligands and from a redistribution of electron charge through orbital overlapping [12–14]. The contact shift is a product of the hyperfine coupling constant (in Hz) and the projection of the total electron spin magnetization, $\langle S_z \rangle$, of the Ln(III) ion [14]. The calculated values for erbium and neodymium are +15.0 and −5.0, respectively. This explains the inversion in order for the haloacetate series in this work as compared to that of the neodymium investigation [6].

TABLE 2. NMR shift data and coordination numbers (*CN*) for Er^{3+} complexes of acetic acid, chloroacetic acid, bromoacetic acid and iodoacetic acid in D_2O at 300 K

Nucleus	Ligand	*CN*	$\Delta\nu^{iso\ a}$
^1H	CH_3COOD	3.3(8)	201.6(4)
	$CH_2ClCOOD$	3.7(6)	286.0(6)
	$CH_2BrCOOD$	3.6(9)	198.2(4)
	CH_2ICOOD	3.2(8)	85.0(5)
$^{13}C_\alpha$	CH_3COOD	3.8(9)	40.9(5)
	$CH_2ClCOOD$	4.1(9)	63.0(7)
	$CH_2BrCOOD$	3.7(7)	59.9(8)
	CH_2ICOOD	3.3(8)	24.6(4)
$^{13}C_{COO}$	CH_3COOD	3.2(9)	22.7(4)
	$CH_2ClCOOD$	3.5(8)	22.7(6)
	$CH_2BrCOOD$	3.6(7)	34.6(5)
	CH_2ICOOD	2.8(9)	11.5(4)
$^{17}O_{Solv}$	CH_3COOD^b	4.3(9)	−1725(6)
	$CH_2ClCOOD^b$	4.8(9)	−1731(6)
	$CH_2BrCOOD^b$	4.4(9)	−2639(9)
	CH_2ICOOD	4.5(8)	−770(2)

^{a}Isotropic shift values (in Hz) are expressed as the difference of frequencies for Er^{3+} and La^{3+} complexes. ^{b}Shift data for solvent peak of the indicated complex.

The two phenomena, hypersensitive pseudoquadrupole transitions in the electronic spectra of the ultraviolet and visible region, and the induced chemical shift of lanthanide shift reagents in nuclear magentic resonance studies, have been treated independently of one another until now. Developing a direct correlation between these two major areas of research is the goal of this study. The extension of this study to other members of the lanthanide series will provide the data necessary for the determination of the contact shift contribution which is a measure of covalent bonding between the lanthanide and the ligand. A relationship between this and the phenomenological parameter for hypersensitivity, Ω_2, should bring about a sharper focus in the understanding of the role of covalency and polarizability in the interaction between the lanthanide ions and their ligands.

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