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An Investigation of the Hypersensitive Pseudoquadrupole Transitions of Neodymium(III) Complexes and their Induced NMR Chemical Shifts

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Two phenomena, the hypersensitive pseudoquadrupole transition in the electronic spectra of the ultraviolet and visible (UV–Vis) region, and the induced chemical shift of lanthanide shift reagents (LSR) in nuclear magnetic resonance (NMR) studies, are well known in the chemistry and physics of the lanthanides.

As early as the 1930s Selwood [1] and Van Vleck [2] observed a sensitivity of the optical absorption spectra for the lanthanide ions to their environment. These highly sensitive absorption bands, referred to as hypersensitive, were later assigned to transitions within the f-orbitals of the lanthanides. For these hypersensitive transitions, the selection rules on J, the total angular momentum, are the same as those for quadrupole radiation: $|\Delta J| \leqslant 2$; $|\Delta L| \leqslant 2$; $|\Delta S| = 0$. Hence, these transitions are appropriately referred to as hypersensitive pseudoquadrupole transitions.

The mechanism for the hypersensitive $4f \rightarrow 4f$ transitions is considered to be dipolar in nature. Theories that have been proposed for these transitions range from oscillations in the electric dipole moment (the inhomogeneous dielectric theory of Jorgensen and Judd [3]) to dipoles induced by ligand polarization (the dynamic coupling theory of Mason *et al.* [4]), as well as to the mixing of $4f^n$ with $\phi^{m-1}4f^{n+1}$ states (the covalency theory of Henrie *et al.* [5]).

Induced NMR chemical shifts originate from the effect of the lanthanide ions on the electron-charge distribution of the ligand. These shifts have been attributed to the hyperfine interaction between the electron spin of the central paramagnetic lanthanide ion and the nuclei of the ligands in the complex. These shifts are usually quite large and can be related to two independent mechanisms of hyperfine interaction, the contact and dipolar shift contributions [6, 7].

Both phenomena, the hypersensitive pseudoquadrupole transition in UV–Vis spectroscopic studies and the carbon-13 (^{13}C), oxygen-17 (^{17}O) and proton (^{1}H) chemical shifts induced by LSR (bare ions and complexes) in NMR studies, are related to the interactions between lanthanide ions and the ligands. A link between these two phenomena has not been established since interdisciplinal work has not been reported. This is the first study directed towards ascertaining a correlation between hypersensitive pseudoquadrupole transitions and LSR-induced chemical shifts.

Experimental

Stock solutions of Nd^{3+}, CH_3COOD, $CH_2ClCOOD$ and $CH_2BrCOOD$ were prepared under dry nitrogen in a glove bag. Acidity was regulated by the addition of deuterochloric acid. Solutions for study by UV–Vis spectroscopy were prepared with constant neodymium ion concentration, while those for NMR studies were prepared with constant ligand concentration.

UV–Vis absorbance data were collected on an IBM 9430 spectrophotometer from 9000 to 2000 Å using 1.0-cm quartz cells and a corresponding lanthanum blank. The data were analyzed on a VMS/VAX computer system where the concentrations were confirmed using molar absorptivity values [8] for 16 transitions with a least-squares fitting routine. The spectral data were then deconvoluted by employing an algorithm by Maquardt [9] in order to calculate the oscillator strengths. The transition intensity parameters (Ω_2, Ω_4 and Ω_6) were determined using the assignments of Judd [10] and Carnall *et al.* [11].

NMR data for the nuclei ^{1}H, ^{13}C and ^{17}O were obtained on an FX90Q model in the Fourier-transform mode at 300 ± 3 K using observation frequencies of 89.55, 22.49 and 12.11 MHz, respectively. Acetone was used as an external reference for all three nuclei. The data sets were analyzed after being transferred to a computer where baseline corrections and deconvolution of spectra were performed.

Discussion

The calculated parameters Ω_2, Ω_4 and Ω_6 with their root-mean-squares (RMS) for the neodymium complexes are given in Table 1, along with the oscillator strengths and molar absorptivities for the hypersensitive transitions $^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^4G_{5/2}$ (the $^2G_{7/2}$ transition showing the largest increase in its molar absorptivity). The employed model [5] suggests that the Ω_λ parameters ($\lambda = 2, 4, 6$) are implicitly influenced by the ligand field and that Ω_2 is strongly affected by the polarization and

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TABLE 1. Judd–Ofelt Parameters[a], Oscillator Strengths $(f)^b$ and Molar Absorptivities (ϵ) Calculated from Spectroscopic Data for $M(Lig)_3$ (where $M = Nd^{3+}$; Lig = CH_3COOD, $CH_2ClCOOD$ and $CH_2BrCOOD$) in Solution

Ligand	ϵ	f	Ω_2	Ω_4	Ω_6	RMS
CH_3COOD $^2G_{7/2}$	3.882	5.463				
$^4G_{5/2}$	4.174	2.022				
			0.9(5)	0.6(3)	14(3)	11.1
$CH_2ClCOOD$ $^2G_{7/2}$	3.964	5.586				
$^4G_{5/2}$	4.191	2.069				
			2.0(2)	0.4(2)	14(3)	12.3
$CH_2BrCOOD$ $^2G_{7/2}$	4.217	5.953				
$^4G_{5/2}$	4.478	2.173				
			4.9(8)	0.3(2)	12(3)	13.5

[a]Parameters reported as $\Omega_\lambda \times 10^{20}$ ($\lambda = 2, 4, 6$). [b]Oscillator strength $\times 10^6$.

TABLE 2. NMR Shift Data and Coordination Numbers (CN) for Nd^{3+} Complexes of Acetic Acid, Chloroacetic Acid and Bromoacetic Acid

Nucleus	Ligand	CN	ν^a (Hz)	$\Delta\nu^b$ (Hz)
^1H	CH_3COOD	3.0(9)	−387.8(1)	−611.6(3)
	$CH_2ClCOOD$	3.8(9)	400.5(3)	−29.8(2)
	$CH_2BrCOOD$	3.8(9)	491.5(3)	4.5(6)
$^{13}C_\alpha$	CH_3COOD	4.0(9)	347.8(1)	−805.3(3)
	$CH_2ClCOOD$	4.0(9)	966.2(3)	31.6(7)
	$CH_2BrCOOD$	3.8(9)	658.1(3)	10.5(9)
$^{13}C_{COO}$	CH_3COOD	4.0(9)	3868.5(5)	−148.7(4)
	$CH_2ClCOOD$	3.5(9)	3945.1(6)	31.6(6)
	$CH_2BrCOOD$	3.6(9)	3903.9(6)	−2.5(5)
$^{17}O_{solv}$	CH_3COOD^c	5.0(9)	334.6(6)	368.5(9)
	$CH_2ClCOOD^c$	4.8(9)	547.6(4)	558.8(8)
	$CH_2BrCOOD^c$	4.9(9)	414.4(6)	429.1(8)
$^{17}O_{COO}$	CH_3COOD^d		a) 3086(1) b) 3117(1)	
	$CH_2ClCOOD^d$		a) 3044(1) b) 3127(1)	

[a]Values in addition to observation frequency (ν) of the indicated nuclei. [b]Frequency values are expressed as difference between Nd^{3+} and La^{3+} complexes ($\Delta\nu$). [c]Shift data for solvent peak for the indicated complex. [d]Data of carboxylate group for stock solution of indicated ligand.

the basicity of the ligands. The parameter Ω_2 is observed to increase in the order $CH_3COOD < CH_2ClCOOD < CH_2BrCOOD$ for the same coordination number. This order is in agreement with the polarizability of the ligand. The ^1H frequency shift values ($\Delta\nu$) in Table 2 follow this same order. However, the ^{13}C $\Delta\nu$ values are reversed with respect to chloro- and bromoacetic acid. The remaining coordination sights around the metal ion are occupied by solvent molecules, as indicated by the ^{17}O NMR data.

These two fields of research, which have been treated as independent of one another until now, can provide information about the interaction between the lanthanide ion and its ligands. This study will be extended to other members of the lanthanide series in order to obtain the hyperfine coupling constants which are related to covalent bonding effects of complexed ligands. A thorough analysis of factors related to polarizability and covalency will allow for a better understanding of these interactions and clarify the origin of hypersensitivity, the objective of an on-going project.

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