

78-6; selenium dioxide, 7446-08-4; fluorine, 7782-41-4; bis(pentafluoroselenium) oxide, 27218-15-1; pentafluoro-selenium fluorosulfate, 37988-80-0; peroxydisulfuryl di-fluoride, 13709-32-5; bis(trifluoromethyl) peroxide, 927-84-4; carbonyl fluoride, 353-50-4; SO<sub>3</sub>, 7446-11-9.

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## Isotropic Nuclear Magnetic Resonance Shifts in Ion-Paired Systems. A Study of Some Penta- and Hexanitratolanthanate (III) Complexes

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A series of complexes of the formulas [R<sub>n</sub>N]<sub>2</sub>Ln(NO<sub>3</sub>)<sub>5</sub> and [R<sub>n</sub>N]<sub>3</sub>Ln(NO<sub>3</sub>)<sub>6</sub> have been prepared and characterized. The proton nmr spectra of the organic cations in solution reveal shifts which can be ascribed to a dipolar mechanism. On the basis of these data an anion-cation distance of between 6 and 7 Å is calculated. Factors affecting the shape of the cation in solution in this as well as in other systems are discussed.

### Introduction

Recent proton nmr studies of organic cations ion paired to paramagnetic anions in solvents of low dielectric constant have given rise to the possibility of ascertaining the nature and structure of ion aggregates in solution.<sup>1-12</sup> The basis of the method lies in the fact that protons on an organic ion in solution experience shifts from their normal resonance frequencies in diamagnetic solutions when the ion is in contact with a paramagnetic counterion.

In general, the isotropic nmr shift in solution,  $\Delta\nu$ , is a sum of two terms: the Fermi contact term,  $\Delta\nu_f$ , which depends for its magnitude on the presence of unpaired spin density at the nucleus,<sup>13</sup> and the dipolar term,  $\Delta\nu_{\text{dip}}$ , which occurs in complexes where the metal ion experiences fields of less than cubic symmetry. Thus

$$\Delta\nu = \Delta\nu_f + \Delta\nu_{\text{dip}} \quad (1)$$

The dipolar shift is of interest to the solution chemist because of its dependence on bond distances and angles. In general we have<sup>13,14</sup>

$$\Delta\nu_{\text{dip}} = \nu[F_1 G_1(R, \theta) + F_2 G_2(R, \theta, \Omega)] \quad (2)$$

where  $F_1$  and  $F_2$  are functions of the principal susceptibilities of the metal complex. In axial symmetry,  $F_2 = 0$  and we are

left with an expression containing the first term only, for which

$$G_1(R, \theta) = \frac{3 \cos^2 \theta - 1}{R^3} \quad (3)$$

where  $R$  is the distance between the proton and the unpaired electron, assumed to be at the center of the metal atom, while  $\theta$  is the angle between vector  $R$  and the major susceptibility axis ( $\chi_{\parallel} = \chi_z$ ) of the molecule.

It is therefore possible, provided no Fermi contact shift is present, to use the observed shifts to obtain anion-cation distances and to obtain information on the structure of the cation in the ion pair.

In this paper, we report the results of a study on ion pairing between tetraalkylammonium cations and hexanitrate- and pentanitratolanthanate(III) anions. These complexes have the advantage of being soluble to a marked degree in a wide variety of solvents, making the study of ion association possible under a considerable range of conditions. Most important, the nitrate complexes, unlike the previously studied hexachloro complexes,<sup>11</sup> will be shown to give shifts which are less complicated by either the rhombic dipolar or Fermi contact effects. This frees us from the unwholesome burden of factoring the isotropic shift into its constituent parts, for which there is at present no simple or unambiguous method.

### Experimental Section

**Reagents.** Rare earth oxides (99.9%) were obtained from American Potash and Chemical Co., West Chicago, Ill., and were converted to the nitrates with concentrated nitric acid. Tetrapropylammonium iodide and tetrabutylammonium iodide (Eastman) were used as received. All solvents used in this work, with the exception of pyridine, were dried at least 24 hr before use over BDH Type 3A molecular sieve. Dichloromethane (Anachemia, Toronto) was fractionally distilled, and the fraction boiling between 40 and 41°C was collected and stored over molecular sieve.

**Preparation of Complexes.** The basic technique used follows closely that employed by Straub, Drago, and Donoghue<sup>15</sup> in preparing the nitrate complexes of the first transition series. Stoichiometric amounts of hydrated rare earth nitrate, finely powdered silver nitrate, and tetraalkylammonium iodide were allowed to react in refluxing acetonitrile for several hours, with complete exclusion of light. An excess of triethyl orthoformate was added during reflux to remove co-

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Table I. Analytical and Conductivity Data for the Nitrate Complexes

Complex <sup>a</sup>	% calcd			% found			$\Lambda$ , ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	
	C	H	M	C	H	M	$c = 1 \times 10^{-3}$	$c = 6 \times 10^{-5}$
(Bu <sub>4</sub> N) <sub>3</sub> La(NO <sub>3</sub> ) <sub>6</sub>	46.56	8.79	11.22	46.84	8.48	11.27	72.2	122.8
(Bu <sub>4</sub> N) <sub>3</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	46.51	8.78		46.85	8.68		65.6	124.7
(Bu <sub>4</sub> N) <sub>3</sub> Pr(NO <sub>3</sub> ) <sub>6</sub>	46.48	8.78		46.53	8.58		70.1	129.4
(Bu <sub>4</sub> N) <sub>3</sub> Nd(NO <sub>3</sub> ) <sub>6</sub>	46.36	8.75	11.60	46.54	8.59	11.52	71.3	142.0
(Bu <sub>4</sub> N) <sub>3</sub> Sm(NO <sub>3</sub> ) <sub>6</sub>	46.13	8.71	12.03	46.25	8.50	11.96	70.5	122.6
(Pr <sub>4</sub> N) <sub>2</sub> Nd(NO <sub>3</sub> ) <sub>5</sub>			17.44			17.52		
(Pr <sub>4</sub> N) <sub>2</sub> Ho(NO <sub>3</sub> ) <sub>5</sub>	34.01	6.66	19.46	34.30	6.62	19.18	46.9	115.9
(Pr <sub>4</sub> N) <sub>2</sub> Tm(NO <sub>3</sub> ) <sub>5</sub>	33.84	6.63	19.83	34.07	6.41	19.81	51.7	157.2
(Pr <sub>4</sub> N) <sub>2</sub> Yb(NO <sub>3</sub> ) <sub>5</sub>	33.68	6.60	20.22	33.82	6.42	20.17	56.8	100.6
(Bu <sub>4</sub> N) <sub>2</sub> Ho(NO <sub>3</sub> ) <sub>5</sub>	40.04	7.56	17.18	40.18	7.60	16.90		
(Bu <sub>4</sub> N) <sub>2</sub> Er(NO <sub>3</sub> ) <sub>5</sub>			17.38			17.30		
(Bu <sub>4</sub> N) <sub>2</sub> Tm(NO <sub>3</sub> ) <sub>5</sub>			17.52			17.54		
(Bu <sub>4</sub> N) <sub>2</sub> Yb(NO <sub>3</sub> ) <sub>5</sub>	39.70	7.50	17.88	39.44	7.26	17.98	45.7	93.0
(Bu <sub>4</sub> N) <sub>2</sub> Lu(NO <sub>3</sub> ) <sub>5</sub>			18.04			17.90		

<sup>a</sup> Bu<sub>4</sub>N = tetra-*n*-butylammonium ion; Pr<sub>4</sub>N = tetra-*n*-propylammonium ion.

ordinated water. After cooling to room temperature, followed by stirring for several hours, the solid silver iodide was filtered off, and the filtrate was concentrated on a water bath. The resulting crude solid was recrystallized from dichloromethane by filtration of the solution, followed by concentration and dropwise addition of ethyl acetate. It has been found that three such recrystallizations are usually necessary in order to free the complex completely of the last traces of silver halide.

Analyses for carbon and hydrogen were performed by Chemalytics, Inc., Tempe, Ariz. Analyses for lanthanide metal were performed in triplicate in these laboratories by igniting the complex to the oxide. The analytical data may be found in Table I.

Nuclear magnetic resonance spectra were obtained on the Varian HA-100 spectrometer at ambient temperatures (34°) in the solvents dichloromethane, nitrobenzene, pyridine, acetone, and dimethyl sulfoxide-*d*<sub>6</sub>. Conductivity measurements were made in nitrobenzene at 25° on the Wayne-Kerr universal bridge, Model B221A. Visible-uv spectra were recorded on the Cary 14 spectrophotometer.

## Results

**Characterization of the Complexes.** In addition to the well-known compounds of the type M<sup>III</sup><sub>3</sub>Ln<sub>2</sub>(NO<sub>3</sub>)<sub>12</sub>·24H<sub>2</sub>O, which contain the hexanitratolanthanate(III) anion,<sup>16</sup> several compounds of the type M<sup>I</sup><sub>2</sub>Ln(NO<sub>3</sub>)<sub>5</sub> have been prepared by Medoks, *et al.*<sup>17</sup> (M<sup>I</sup>, M<sup>II</sup> represent respectively uni- and divalent cations.) The structures of both the hexanitrate<sup>16</sup> and pentanitratocerate(III)<sup>18</sup> ions are known on the basis of X-ray crystallography and approximate to distorted octahedral and trigonal-bipyramidal geometries, respectively, if the nitrate is viewed as a unidentate ligand.<sup>18</sup>

The present series of compounds reveal several interesting properties which appear to depend both on the lanthanide metal and the organic cation chosen. First, attempts to prepare compounds of the type (Bu<sub>4</sub>N)<sub>3</sub>Ln(NO<sub>3</sub>)<sub>6</sub> for Ln = Ho, Er, Tm, Yb, or Lu have consistently met with failure on our part. Elemental analyses on the gummy solids which result from the reaction mixture are in agreement with no definite stoichiometry. Similarly, attempts to produce compounds of the type (Pr<sub>4</sub>N)<sub>3</sub>Ln(NO<sub>3</sub>)<sub>6</sub> have met with failure for all members of the series. The fact that in the present series hexanitrate complexes can be prepared only for the first (and largest) of the lanthanide cations suggests that both ionic radius and cation size effects play a role in determining the ability of the metal ion to coordinate more than five nitrate groups.

It is also of interest that crystals of (Bu<sub>4</sub>N)<sub>2</sub>Yb(NO<sub>3</sub>)<sub>5</sub>

grown in the presence of a small amount of copper(II) nitrate in dichloromethane have a distinct blue color. The blue color is not removed by repeated recrystallizations, suggesting that substitution of Cu(NO<sub>3</sub>)<sub>4</sub><sup>2-</sup> for Yb(NO<sub>3</sub>)<sub>5</sub><sup>2-</sup> readily occurs in the lattice. This is consistent with the findings of Wood,<sup>18</sup> *et al.*, who have commented on the isodimensionality of the unit cells of [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As]<sub>2</sub>Co(NO<sub>3</sub>)<sub>4</sub> and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PC<sub>2</sub>H<sub>5</sub>]<sub>2</sub>Ce(NO<sub>3</sub>)<sub>5</sub>, only a small change in nitrate positions in the former compound being necessary in order to accommodate a fifth nitrate ion.

The molar conductance results in nitrobenzene may be found in Table I. The values of  $\Lambda_m$  for the pentanitrate series are seen to be consistent with their formulation as 2:1 electrolytes ( $\Lambda_m = 40$ –60).<sup>19</sup> The hexanitrate ions have molar conductance values in the range found for the previously studied LnCl<sub>6</sub><sup>3-</sup> complexes, which were characterized as 3:1 electrolytes in nitrobenzene.<sup>11,20</sup>

**Visible-Uv Spectra.** We have examined solution spectra of (Bu<sub>4</sub>N)<sub>3</sub>Nd(NO<sub>3</sub>)<sub>6</sub> and (Pr<sub>4</sub>N)<sub>2</sub>Nd(NO<sub>3</sub>)<sub>5</sub> in nitrobenzene and dichloromethane. The principal feature in the visible region is the hypersensitive transition<sup>21</sup> <sup>4</sup>I<sub>9/2</sub> → <sup>4</sup>G<sub>5/2</sub> at 17,000–17,500 cm<sup>-1</sup>. The spectra in both solvents in this region are identical for the two salts above and are not affected by addition of excess tetrabutylammonium nitrate. This perhaps indicates that Nd(NO<sub>3</sub>)<sub>6</sub><sup>3-</sup> is unstable, losing one nitrate ion to become the pentanitrate species.

The spectra of Er(NO<sub>3</sub>)<sub>5</sub><sup>2-</sup> reveal two hypersensitive transitions in the visible-near-uv region. The band at 19,000–19,400 cm<sup>-1</sup> is usually assigned<sup>21</sup> to the transition <sup>4</sup>I<sub>15/2</sub> → <sup>2</sup>H<sub>11/2</sub>, and has been found to be exceptionally useful in monitoring changes in the composition of the coordination sphere about erbium.<sup>22</sup>

A more intense band at 26,000–26,600 cm<sup>-1</sup> is assigned to the transition <sup>4</sup>I<sub>15/2</sub> → <sup>4</sup>G<sub>11/2</sub> (see Figure 1). The energies of the principal band features in Er(NO<sub>3</sub>)<sub>5</sub><sup>2-</sup>, along with their extinction coefficients, are collected in Table II.

The band envelopes of both transitions are identical in acetone, dichloromethane, and nitrobenzene and differ only marginally from the Nujol mull spectrum. In addition, the extinction coefficients are identical in all three solvents. Table II and Figure 1 reveal, however, that on passing to pyridine and dimethyl sulfoxide, there is a general loss of resolution and in the case of dimethyl sulfoxide, a considerable drop in extinction coefficient.

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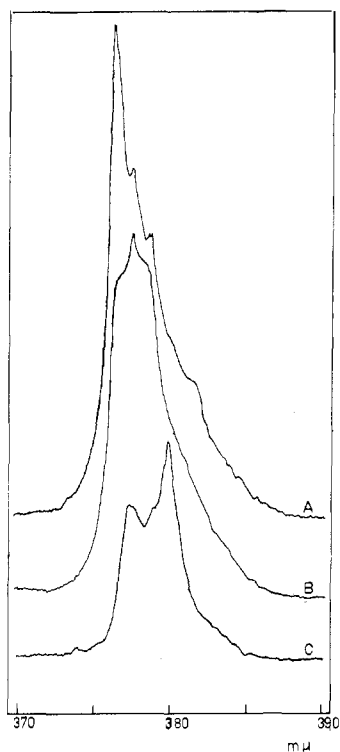
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**Table II.** Electronic Spectral Data for the Pentanitrateoerbate Complex in Various Solvents<sup>a</sup>

Solvent	Energy, cm <sup>-1</sup>
Acetone	19,391 sh
	19,320 (14.1)
	19,297 (13.9)
	19,179 (12.0)
	19,093 sh
	18,984 sh
(CH <sub>3</sub> ) <sub>2</sub> SO	26,546 (35.1)
	26,198 sh
	19,227 (6.22)
	19,102 (7.59)
C <sub>5</sub> H <sub>5</sub> N	26,578 (10.51)
	26,402 (14.86)
	19,186 (12.16)

<sup>a</sup> sh = shoulder. Numbers in parentheses are extinction coefficients.



**Figure 1.** A plot of absorbance vs. wavelength for the  ${}^4I_{15/2} \rightarrow {}^4G_{11/2}$  transition of erbium(III) in  $(\text{Bu}_4\text{N})_2\text{Er}(\text{NO}_3)_5$ : A, spectrum in acetone; B, pyridine; C, dimethyl sulfoxide.

As one might expect from the poor ligating properties of acetone,  $\text{H}_2\text{CCl}_2$ , and nitrobenzene, the anion appears to be unaffected by dissolution in these solvents. On the other hand, coordination by the solvent is strongly suggested from the pyridine and dimethyl sulfoxide spectra. These results will be of interest in the interpretation of the nmr spectra which follow.

**Nmr Data. Spectra of the Diamagnetic Complexes.** The proton resonance spectrum of the tetrabutylammonium ion under diamagnetic conditions has received some attention in the past.<sup>6,11</sup> In the present series of compounds the  $\alpha$  and  $\delta$  resonances of the tetrabutylammonium ion are clearly resolved at 100 MHz in all solvents, while the  $\beta$  and  $\gamma$  resonances usually overlap appreciably. In the case of  $(\text{Bu}_4\text{N})_2\text{Lu}(\text{NO}_3)_5$  in nitrobenzene and pyridine it is possible to distinguish a broad septet ( $\tau$  8.2–8.3), assigned to the  $\beta$  resonance, with a sharper septet to high field ( $\gamma$  resonance) with an apparent chemical shift separation of 0.40 ppm. In dichloromethane, these resonances overlap strongly, so that the chemical shift values quoted in Table III are only approxi-

**Table III.** Proton Nmr Data for the Tetrabutylammonium Ion in Different Environments

Anion	Solvent	Concn, <i>M</i>	Shifts <sup>a</sup>			
			$\alpha$	$\beta$	$\gamma$	$\delta$
$\text{Ce}(\text{NO}_3)_6^{3-}$	$\text{H}_2\text{CCl}_2$	0.107	3.40	1.77	1.45	0.98
$\text{Pr}(\text{NO}_3)_6^{3-}$	$\text{H}_2\text{CCl}_2$	0.098	3.58	1.84	1.47	0.95
$\text{Nd}(\text{NO}_3)_6^{3-}$	$\text{H}_2\text{CCl}_2$	0.115	3.65	1.89	1.55	1.00
$\text{Sm}(\text{NO}_3)_6^{3-}$	$\text{H}_2\text{CCl}_2$	0.103	3.29	1.69	1.43	0.99
$\text{Lu}(\text{NO}_3)_5^{2-}$	$\text{H}_2\text{CCl}_2$	0.100	3.14	1.63	1.37	0.98
	Acetone	0.109	3.41	1.70	1.46	0.98
	$\text{C}_6\text{H}_5\text{NO}_2$	0.108	3.48	1.91	1.57	1.06
	$\text{C}_5\text{H}_5\text{N}$	0.104	3.42	1.77	1.41	0.93
	$\text{C}_5\text{H}_5\text{N}$	0.048	3.44	1.77	1.38	0.90
	$\text{C}_5\text{H}_5\text{N}$	0.012	3.47	1.77	1.36	0.88

<sup>a</sup> All shifts in ppm, downfield relative to internal TMS.

mate. They are consistent, however, with those obtained at 220 MHz for the same protons in  $(\text{Bu}_4\text{N})_3\text{LaCl}_6$  ( $\tau_\beta$  8.36,  $\tau_\gamma$  8.54).<sup>11</sup> The data for the diamagnetic lutetium complex in a variety of solvents may be found in Table III.

In only one solvent, pyridine, was it found that the diamagnetic resonance frequencies were concentration dependent. Thus, in pyridine, isotropic shifts were determined by subtracting the  $\text{Lu}(\text{NO}_3)_5^{2-}$  cation frequencies from the resonance frequencies in the paramagnetic solutions of the same concentration.

**Spectra of the Paramagnetic Complexes.** The cation nmr spectra of the light rare earth–hexanitrate complexes in dichloromethane can be found in Table III. All resonances are shifted to low field, with the exception of the  $\delta$  protons, which show shifts equal to zero, within experimental error ( $\pm 2$  Hz). Compared to the heavy rare earths, the shifts at the beginning of the series are very small, a feature which precludes any extensive discussion of their origin. This in turn is presumably due to the small magnetic susceptibility values which characterize the first members of the rare earth series.

The nmr data for the pentanitrate complexes of holmium, erbium, thulium, and ytterbium are reported as isotropic shifts with respect to the corresponding frequencies in the  $\text{Lu}(\text{NO}_3)_5^{2-}$  complex in Table IV. The holmium and erbium complexes have been studied in greatest detail because the shifts are largest and, since they are uniformly to low field, are well resolved (see Figure 2).

The  $\text{Tm}(\text{NO}_3)_5^{2-}$  and  $\text{Yb}(\text{NO}_3)_5^{2-}$  complexes, on the other hand, show strong upfield shifts, which result in a complicated spectrum. With the exception of the terminal methyl resonances, we cannot use intensities as a guide to identification, nor are the differences in line widths sufficient to enable us to identify the resonances on the basis of the inverse sixth-power law.<sup>6</sup>

The problem is particularly severe with  $\text{Yb}(\text{NO}_3)_5^{2-}$ , where cation resonances are observed at 46, 80, and 97 Hz downfield from TMS, in  $\text{H}_2\text{CCl}_2$  with intensity ratios 2:5:2, respectively (Figure 3). In order to assign the spectrum, use is made of the fact that the cations in this system, as in all systems studied to date, exhibit fast exchange between ion pairs with paramagnetic and diamagnetic anions. Thus the “fast exchange equation” (eq 4) applies. Here,  $f_{\text{para}}$  and  $f_{\text{dia}}$  are the mole

$$\Delta\nu_{\text{obsd}} = f_{\text{para}}\Delta\nu_{\text{para}} + f_{\text{dia}}\Delta\nu_{\text{dia}} \quad (4)$$

fractions of cation associated with paramagnetic and diamagnetic anions, respectively.  $\Delta\nu_{\text{para}}$  is the cation resonance frequency, relative to TMS, in the solution of paramagnetic complex, and  $\Delta\nu_{\text{dia}}$  represents the resonance frequency in the diamagnetic lutetium complex. A plot of observed shift,  $\Delta\nu_{\text{obsd}}$ , vs. mole fraction for the Yb complex is shown in Figure 4. This allows us to assign the resonance at 97 Hz

Table IV. Isotropic Shifts<sup>a</sup> in Pentanitratolanthanate(III) Complexes

Ln	Concn, <i>M</i>	Solvent	Isotropic shift				Shift ratios			
			$\alpha$	$\beta$	$\gamma$	$\delta$	$Q_{\alpha/\beta}$	$Q_{\beta/\delta}$	$Q_{\gamma/\delta}$	$Q_{\beta/\alpha}$
Ho	0.178	$H_2CCl_2$	-8.98	-4.81	<i>b</i>	-0.69	13.01	6.97		0.535
	0.122		-8.86	-4.83	-2.79	-0.65	13.63	7.43	4.29	0.546
	0.054		-9.49	-5.21	-2.93	-0.73	13.00	7.13	4.01	0.549
	0.026		-9.75	-5.43	-3.01	-0.79	12.34	6.87	3.81	0.556
	0.010	-10.00	-5.62	<i>b</i>	-0.84	11.90	6.69		0.562	
	0.186	Acetone	-7.05	-4.15	-2.29	<i>b</i>				0.588
	0.119		-6.35	-3.78	-2.07	<i>b</i>				0.595
	0.057		-5.36	-3.18	-1.64	<i>b</i>				0.592
	0.024		-5.01	-3.06	-1.59	<i>b</i>				0.610
	0.098	$C_6H_5NO_2$	<i>b</i>	-3.23	-1.86	-0.460		7.02	4.04	
	0.048		<i>b</i>	-2.34	-1.36	-0.345		6.81	3.94	
	0.016		-2.82	-1.62	-0.94	-0.250	11.30	6.48	3.78	0.575
	0.058	Pyridine ( $CH_3$ ) <sub>2</sub> SO	<i>b</i>	-3.27	-1.66	-0.365		8.93	4.53	
	0.211		0.0	0.0	0.0	0.0				
Er	0.110	$H_2CCl_2$	-4.30	-2.22	-1.43	-0.345	12.46	6.43	4.14	0.515
	0.116	$C_6H_5N$	-2.90	-1.59	-0.91	-0.20	14.50	7.95	4.55	0.549
	0.018		-1.09	-0.60	-0.36	-0.08	13.62	7.50	4.50	0.549
	0.093	Acetone	-2.70	-1.65	<i>b</i>	-0.24	11.25	6.88	<i>b</i>	0.610
	0.100	$C_6H_5NO_2$	-2.63	-1.41	-0.86	-0.23	11.44	6.09	3.74	0.536
	0.0446		-1.96	-1.06	-0.66	-0.16	12.25	6.62	4.12	0.541
	0.0166		-1.30	-0.72	-0.43	-0.11	11.81	6.54	3.91	0.552
Tm	0.137	$H_2CCl_2$	4.57	2.58	1.28	0.31	14.72	8.32	4.13	0.565
	0.028		5.05	2.90	1.37 <sup>c</sup>	0.40	12.62	7.25	<i>b</i>	0.575
Yb	0.130	$H_2CCl_2$	2.18	1.18	0.62	0.18	12.11	6.56	3.44	0.541

<sup>a</sup> All values in ppm with respect to the corresponding resonance positions in the diamagnetic  $Lu(NO_3)_5^{2-}$  complex, in the solvents indicated. A negative sign indicates a low-field shift. <sup>b</sup> Resonance masked by solvent. <sup>c</sup> Resonance uncertain due to overlapping with TMS.

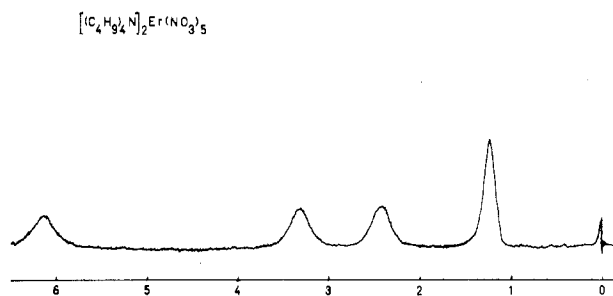


Figure 2. The 100-MHz proton nmr spectrum of  $(Bu_4N)_2Er(NO_3)_5$  in nitrobenzene (0.10 *M*). Resonance assignments, from left to right, are to  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  protons, respectively. Horizontal scale in ppm.

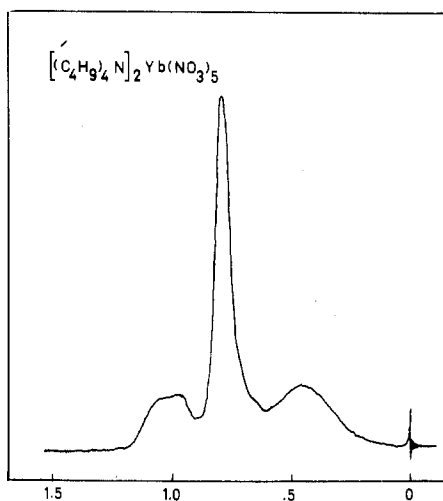


Figure 3. The 100-MHz proton nmr spectrum of  $(Bu_4N)_2Yb(NO_3)_5$  in  $H_2CCl_2$  (0.13 *M*). Horizontal scale in ppm. Resonance assignments, from left to right, are to  $\alpha$ ,  $\delta$ , and  $\beta$  protons, respectively. The  $\gamma$  resonance is hidden beneath the sharp  $\delta$  resonance.

downfield from TMS to the  $\alpha$  protons. The resonance at 46 Hz is assigned to the  $\beta$ - $CH_2$  protons, while the resonance at 80 Hz contains contributions from both the  $\gamma$ - $CH_2$  and the  $\delta$ - $CH_3$  protons. The  $\gamma$  protons appear to lie to slightly higher

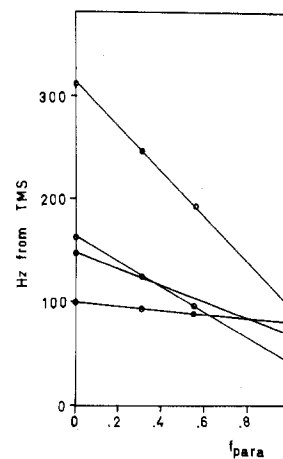


Figure 4. A plot of observed resonance frequency vs. mole fraction of paramagnetic complex,  $f_{para}$ , for mixtures of  $Lu(NO_3)_5^{2-}$  and  $Yb(NO_3)_5^{2-}$ .

field than the  $\delta$  protons, thus accounting for the high-field tail on the  $\delta$  resonance and the somewhat greater apparent intensity of the  $\beta$  resonance. A similar plot for the thulium complex has confirmed the assignments in Table IV.

In view of the basicity of pyridine and its known tendency to coordinate to lanthanide cations,<sup>23</sup> the pyridine solvent resonances were studied as a function of added  $Er(NO_3)_5^{2-}$  complex. A shift of 0.30 ppm to low field was noted for the ortho resonance in the most concentrated solution (0.12 *M*) relative to neat pyridine, pointing once again to the interaction between solvent and metal ion. Similarly, the single-resonance line of  $CD_3SOCD_2H$  in dimethyl sulfoxide-*d*<sub>6</sub> undergoes a 0.25-ppm shift to low field in the presence of  $Ho(NO_3)_5^{2-}$  ion, suggesting solvent coordination in agreement with the results of the visible spectral study.

## Discussion

**Interpretation of the Nmr Shifts.** As we have already point-

ed out, in order to interpret the observed nmr shifts in a purely geometrical sense, the contact term must be completely absent from eq 1. For any two protons,  $i$  and  $j$ , on a given axially symmetric complex for which this situation pertains, we obtain, using eq 2 and 3

$$\frac{(\Delta\nu_{\text{dip}})_i}{(\Delta\nu_{\text{dip}})_j} = \frac{\left(\frac{3 \cos^2 \theta_i - 1}{R_i^3}\right)}{\left(\frac{3 \cos^2 \theta_j - 1}{R_j^3}\right)} = Q_{i/j} \quad (5)$$

*i.e.*, the ratios of the dipolar shifts are independent of the electronic structure of the metal ion. When we extend this idea to series of complexes where the ligands remain constant, but only the central metal ion changes, then the ratios of the dipolar shifts  $Q_{i/j}$  should also be independent of the metal ion, *i.e.*

$$[Q_{i/j}]_{M_1} = [Q_{i/j}]_{M_2} \quad (6)$$

This identity will hold exactly only if the substitution of metal  $M_2$  for  $M_1$  does not alter the bond angles and distances or stoichiometry of the complex. These two assumptions have been used successfully in the past<sup>24</sup> in factoring the isotropic shift into its contact and dipolar components in complexes of tetrahedral cobalt and nickel.

The trivalent lanthanide cations display a considerable reduction in ionic radii on passing from the light to the heavy end of the series (0.2 Å, or about 20%). We therefore might not expect eq 6 to hold over the entire series. For the metals holmium through ytterbium on the other hand, the variation in ionic radius is only 0.04 Å; hence comparisons within this group of metal ions should come closer to the requirements of theory. We therefore believe that not only will ion aggregates formed between anions and cations of similar chemical properties and ionic radii be isostructural but also the dipolar shift ratios of organic cations in the ion aggregates will be virtually identical.

Table IV indicates that the ratios of the observed isotropic shifts in the pentanitratolanthanate(III) complexes are only slightly dependent on the metal ion. As has been discussed elsewhere,<sup>11</sup> changes in sign such as those observed on passing from erbium(III) to thulium(III) in the present series are not consistent with a dominant Fermi contact mechanism, since the contact effect is predicted to have the same sign for all rare earth ions lying between gadolinium and lutetium.<sup>25</sup> On the other hand, the sign of the dipolar shift is under no such constraint; the sign of the magnetic anisotropy may vary from complex to complex in an isostructural series, as is apparent from the shifts of pyridine ligands coordinated to lanthanide dipivaloylmethanide complexes.<sup>26</sup> The dipolar nature of these shifts has been confirmed recently by comparison of the nmr data with the results of single-crystal magnetic anisotropy studies.<sup>27</sup>

The behavior observed in the pentanitrate complexes thus contrasts strongly with that observed in the series  $(\text{Bu}_4\text{N})_3\text{-LnCl}_6$  where the shift ratios were found to vary in both sign and magnitude on changing the metal ion. It is believed that both dipolar and contact terms of comparable size contribute to the total isotropic shift in this case, the contact term being

upfield for the light rare earths and downfield for the heavy rare earths.<sup>11</sup>

The relative invariance of the shift ratios in the nitrate series also indicates that the second (rhombic) term of eq 2 is not a major contributor to the shifts. This may seem surprising at first glance, since strictly speaking the nitrate ions would be expected on the basis of X-ray evidence<sup>18</sup> to provide at any instant a crystalline field of at most  $C_2$  point symmetry at the rare earth ion. Since, however, the coordination polyhedron of the anion is in rapid motion on the nmr time scale, the instantaneous rhombic component of the susceptibility sensed by the proton attenuates strongly in a time short compared with the proton relaxation time. Thus we may conclude that the axial dipolar term dominates the observed shifts. It should be obvious, however, that since a slight dependence of shift ratio on metal ion is observed in the present case (Table IV), one should not overlook the possibility of a small contact or rhombic term, representing between 5 and 10% of the total isotropic shift.

**Solvent and Concentration Effects.** The observed shifts in the pentanitratolanthanate complexes reveal two types of variation with concentration, depending on the solvent chosen. In the higher dielectric constant solvents acetone ( $\epsilon$  20.7), nitrobenzene ( $\epsilon$  33.7), and pyridine ( $\epsilon$  12.3) it is found that the shifts increase in magnitude as the concentration is increased (Table IV). On the other hand, the shifts in  $\text{H}_2\text{CCl}_2$  ( $\epsilon$  9.08) decrease somewhat with increasing concentration, as can be seen from our data for holmium and thulium. This anomalous behavior has been noted in several previous investigations.<sup>10,28</sup> The current explanation is that decreasing shift with increasing concentration can be attributed to micelle formation.<sup>5,28</sup> Cations in the micelle are considered to be less shifted than in the single 1:1 ion pair found in very dilute solutions, due to an environment which is on the average more magnetically isotropic than in the simple ion pair.

Comparison of our shift data in pyridine and dichloromethane suggests that the transition between the two types of concentration dependence occurs over an extremely narrow range of dielectric constants, the critical value being  $\epsilon$  10-11.

The shift ratios  $Q_{i/j}$  in the pentanitratolanthanates also appear to be somewhat sensitive to solvent and concentration, suggesting that the structure of the cation varies somewhat in solution. The effect is apparently largest with the  $Q_{\alpha/\delta}$  ratios, although the amount of scatter in the data makes any firm conclusions unreliable. This ratio is particularly susceptible to small measurement errors, due to the relatively small size of the  $\delta$ -proton shift. Due to the large size of the  $\alpha$  and  $\beta$  shifts, the data for  $Q_{\beta/\alpha}$  are less subject to this uncertainty, and we will use these data to derive several conclusions about the ion aggregate structure, subject to the cautions at the close of the preceding section.

**Ion Aggregate Structure.** The theoretical problem of calculating the geometric factors for cations in ion pairs has received some attention in the past.<sup>2,9,11</sup> It has been demonstrated that for a cation tumbling completely freely at a fixed distance,  $A$ , from a paramagnetic anion such that each proton describes a spherical shell centered on the central atom of the cation ("isotropic tumbling") the geometric factor averages to<sup>11</sup>

$$\left(\frac{3 \cos^2 \theta - 1}{R_i^3}\right)_{\text{av}} = \frac{2}{A^3} \quad (7)$$

Since  $A$  is defined as the metal-nitrogen distance in this

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model, it follows that all cation protons should show the same dipolar shift. This is never observed in practice, however. The dipolar portion of the shift is always observed to attenuate with increasing distance from the central charged atom,<sup>4,8,12</sup> indicating that in these flexible systems the outer organic portions of the cation tend to avoid close contact with the anion. In other words, the cation is "crushed" by the ion-pairing process, presumably due to the electrostatic attraction between the positively charged center on the cation and the negative ligands of the anion. A "restricted tumbling" model has been designed by Larsen<sup>9</sup> to take account of this situation. The amount of freedom allowed to the cation in the ion aggregate is governed by a "boundary angle,"  $\alpha$ , such that at any given interionic distance, an increase in  $\alpha$  results in isotropic shift ratios which approach unity. Calculated values of  $Q_{\beta/\alpha}$  vs. ion-pair distance for different values of  $\alpha$  have been plotted in Figure 3 of ref 9. For a given experimentally determined  $Q_{\beta/\alpha}$ , this plot gives an upper limit to the interionic distance, corresponding to  $\alpha = 0$  (rigid orientation). Thus for  $Q_{\beta/\alpha}$  in the range 0.52-0.59 found in this work, we predict that  $A$  would be at least 6.2 and at most 7.2 Å.

We may also obtain an estimate of the interionic distance from crystallography. Using the available data for anionic nitrate complexes,<sup>16,18</sup> we calculate that the distance between the central rare earth ion and the outer (uncoordinated) oxygen of the nitrate ligand is  $\approx 4.2$  Å. We may take this to be the effective "hard-sphere radius" of the anion. La Mar<sup>2</sup> has shown that flexible cations, such as tetrabutylammonium, may adopt a configuration which allows for a relatively close approach of the anion to the central nitrogen atom. This leads to a smaller cation "radius" (3.1 Å in this case<sup>2</sup>) than might otherwise be expected. The interionic distance so obtained (7.3 Å) certainly compares well with that obtained from the nmr data and suggests that an appreciable fraction of the ion aggregates in these solvents are of the unsolvated (intimate) variety.

The shift ratios  $Q_{\beta/\alpha}$  in the present compounds are very similar to those obtained for the system  $[\text{Bu}_4\text{N}][\text{Co}(\text{acac})_3]$  studied by La Mar,<sup>4</sup> indicating similar ion-pairing distances in both cases.

The small variations in  $Q_{\beta/\alpha}$  with concentration and solvent, which are evident in Table IV, need not be interpreted in terms of a change in the interionic distance. In fact, the

"sphere in continuum model"<sup>29,30</sup> of ion association predicts that the interionic distance should be independent of the dielectric constant of the solvent. This being the case, we would interpret these variations as being due to changes in the amount of motional freedom available to the cation in the ion aggregate. On this basis, the cation appears to possess greater motional freedom at lower concentrations in any given solvent.

Our main conclusion based on this work is that the time-average structures of the cations in the present series of compounds are relatively insensitive to the differences in solvating power of the solvents used. This may appear surprising when we consider that the paramagnetic anion in pyridine solutions is undoubtedly of the type  $[\text{Ln}(\text{NO}_3)_5\text{Py}_x]^{2-}$ . The presence of pyridine in the first coordination sphere might have been expected to result in an increase in the "hard-sphere radius" of the anion.

The results obtained in dimethyl sulfoxide represent the only exception to the above generalization. The absence of any detectable nmr shift coupled with the dramatic spectral changes in the visible region suggests that complete dissociation of the pentanitrate anion takes place. This indicates to us that the rare earth ion occurs as either an electrically neutral or cationic species in dimethyl sulfoxide. This is certainly in keeping with the high dielectric constant and excellent ligating properties of this solvent.

**Registry No.**  $(\text{Bu}_4\text{N})_3\text{La}(\text{NO}_3)_6$ , 37843-70-2;  $(\text{Bu}_4\text{N})_3\text{Ce}(\text{NO}_3)_6$ , 37233-55-9;  $(\text{Bu}_4\text{N})_3\text{Pr}(\text{NO}_3)_6$ , 37843-71-3;  $(\text{Bu}_4\text{N})_3\text{Nd}(\text{NO}_3)_6$ , 37843-72-4;  $(\text{Bu}_4\text{N})_3\text{Sm}(\text{NO}_3)_6$ , 37843-73-5;  $(\text{Pr}_4\text{N})_2\text{Nd}(\text{NO}_3)_5$ , 37871-69-5;  $(\text{Pr}_4\text{N})_2\text{Ho}(\text{NO}_3)_5$ , 37871-70-8;  $(\text{Pr}_4\text{N})_2\text{Tm}(\text{NO}_3)_5$ , 37871-71-9;  $(\text{Pr}_4\text{N})_2\text{Yb}(\text{NO}_3)_5$ , 37871-72-0;  $(\text{Bu}_4\text{N})_2\text{Ho}(\text{NO}_3)_5$ , 37871-73-1;  $(\text{Bu}_4\text{N})_2\text{Er}(\text{NO}_3)_5$ , 37871-74-2;  $(\text{Bu}_4\text{N})_2\text{Tm}(\text{NO}_3)_5$ , 37871-75-3;  $(\text{Bu}_4\text{N})_2\text{Yb}(\text{NO}_3)_5$ , 37871-76-4;  $(\text{Bu}_4\text{N})_2\text{Lu}(\text{NO}_3)_5$ , 37871-77-5;  $\text{H}_2\text{CCl}_2$ , 75-09-2;  $\text{C}_6\text{H}_5\text{NO}_2$ , 98-95-3;  $\text{C}_5\text{H}_5\text{N}$ , 110-86-1;  $\text{CH}_3\text{COCH}_3$ , 67-64-1;  $\text{CD}_3\text{SOCD}_3$ , 2206-27-1.

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