Registry No. CoTPP, 14172-90-8; CuTPP, 14172-91-9; ZnTPP, 14074-80-7; H_2TBMAP, 7125-37-3; CuTBMAP, 26568-91-2; H_2-TBTAP, 7125-35-1; CuTBTAP, 52647-45-7; H_2Pc, 574-93-6; TiOPc, 26201-32-1; VOPc, 13930-88-6; MnPc, 14325-24-7; FePc, 132-16-1; CoPc, 3317-67-7; NiPc, 14055-02-8; CuPc, 147-14-8; ZnPc, 14320-04-8.

Contribution from the Department of Chemistry,
York University, Downsview, Ontario, Canada M3J 1P3

Nuclear Magnetic Resonance Studies on the Structures of Some Substituted *N*-Alkylpyridinium Pentanitratolanthanate Ion Pairs in Solution

M. SALEEM QUERESHI and IAN M. WALKER*

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A series of paramagnetic pentanitratolanthanate(III) complexes containing the *N*-octyl-4-phenylpyridinium and 2,4,6-trimethylbenzyl-4-methylpyridinium cations have been prepared and studied by proton nmr in low-dielectric solvents. The observed isotropic shift ratios are used to establish a time-average structure for the ion-pair complex. Comparison of the observed shift ratios with those derived from model calculations reveals that the pyridine ring is in rapid rotation with respect to the anion, and the lanthanide ion sits at an angle of roughly 90° with respect to the C_2 axis of the pyridine ring. An interionic distance of 7 Å is obtained from the measurements, indicating that the nmr technique detects predominantly contact ion pairs.

Introduction

In a recent article,[1] we have shown that when tetra-*n*-butylammonium cations are associated with paramagnetic pentanitratolanthanate(III) anions in ion-pair complexes in low-dielectric solvents, isotropic shifts arise in the nuclear magnetic resonance spectrum of the cation protons. These shifts were used to obtain information on the interionic distance, defined as the separation between the central nitrogen atom of the cation and the central lanthanide ion of the anion.

In general, the isotropic shift ($\Delta\nu_{\text{iso}}$) of a nmr signal from its normal position in a diamagnetic complex can be written as the sum of three terms:[2,3] the Fermi contact term ($\Delta\nu_{\text{fc}}$) and the axial ($\Delta\nu_{\text{ax}}$) and rhombic ($\Delta\nu_{\text{rh}}$) dipolar terms (eq 1). It was shown[1] previously that the axial dipolar term is

$$\Delta\nu_{\text{iso}} = \Delta\nu_{\text{fc}} + \Delta\nu_{\text{ax}} + \Delta\nu_{\text{rh}} \qquad (1)$$

by far the predominant effect in $Ln(NO_3)_5{}^{2-}$ containing ion pairs. This term may be written

$$\Delta\nu_{\text{ax}} = f(\chi_1, \chi_2, \chi_3)(3\cos^2\alpha - 1)R^{-3} \qquad (2)$$

where R is the distance between the lanthanide ion and the resonant proton, while α is the angle between R and the principal susceptibility axis χ_3. The function $(3\cos^2\alpha - 1)R^{-3}$ is usually termed the geometric factor (GF). The function $f(\chi_1, \chi_2, \chi_3)$ cannot in general be evaluated for molecules in solution, since the principal susceptibilities $\chi_{1\text{-}3}$ are not known under these conditions. This term is usually eliminated by taking the isotropic shift of one proton on the cation as a reference $(\Delta\nu_j)_{\text{iso}}$, based on which ratios of the remaining cation proton shifts $(\Delta\nu_i/\Delta\nu_j)_{\text{iso}}$ are computed. These observed shift ratios are solely functions of the geometry of the ion-pair complex.

$$(\Delta\nu_i/\Delta\nu_j)_{\text{iso}} = (3\cos^2\alpha_i - 1)R_i^{-3}/(3\cos^2\alpha_j - 1)R_j^{-3} \qquad (3)$$

One may then, using known bond angles and distances in the cation, attempt to reproduce the observed shift ratios at suitable values of the interionic distance, by means of eq 3.

Obtaining geometrical information by this technique on tetraalkylammonium ions in ion pairs or on systems of similar flexibility is hindered by the difficulties inherent in calculating dipolar shift ratios from model structures in which the large number of different conformational possibilities for the alkyl chains must be taken into account. In other words, the structure of the cation in the ion-pair complex in solution is unknown, so that in general there are not enough nmr data available to establish both the cation structure and the structure of the ion-pair complex.

On the other hand, cations based on aromatic rings may be presumed to have structures in which the relative distance between the nuclei does not vary. Hence the cation structure is known in advance.

For this reason we have chosen to study dipolar shifts on cations of the *N*-alkyl- and *N*-benzylpyridinium class, at several concentrations and in several solvents. These are shown in Table I. Shift ratios have then been calculated from a variety of models for the ion-pair geometry, in which different degrees of mobility of the ions in the ion-pair complex have been assumed. These are then compared against the observed shift ratios in an attempt to establish the structure of the ion-pair complex on a time-average basis.

Experimental Section

Reagents. Rare earth oxides (99.9%, American Potash and Chemical Co.) were converted to the hydrated nitrates. 4-Phenylpyridine (Aldrich Chemical Co.) and γ-picoline (K & K Laboratories) were converted to the quaternary ammonium salts without further purification. All solvents used in this work were spectroscopic grade and were dried over molecular sieve for at least 24 hr before use.

Preparation of Complexes. 2,4,6-Trimethylbenzylpicolinium bromide, (TMBP)Br, prepared from γ-picoline and 2,4,6-trimethylbenzyl bromide,[4] was allowed to react with stoichiometric amounts of hydrated rare earth nitrate and silver nitrate, in acetonitrile as previously described.[1] The resulting $(TMBP)_2Ln(NO_3)_5$ complexes are insoluble in dichloromethane and only slightly soluble in acetone at ordinary temperatures. They were recrystallized from hot acetonitrile–ethyl acetate mixtures.

N-Octyl-4-phenylpyridinium iodide, (oct-py-Ph)I, was prepared by refluxing stoichiometric amounts of 4-phenylpyridine and 1-iodooctane in acetonitrile for 72 hr. After removal of the solvent, the crystals were precipitated with benzene and stirred with triethyl ortho-

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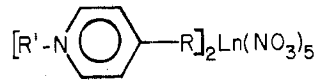
(1) I. M. Walker and D. H. Weeden, *Inorg. Chem.*, 12, 772 (1973).
(2) G. N. La Mar, *J. Chem. Phys.*, 43, 235 (1965).
(3) W. D. Horrocks, Jr., *Inorg. Chem.*, 9, 690 (1970).
(4) L. Rosenthal and I. M. Walker, *Inorg. Chem.*, 11, 2444 (1972).

Table I. Characterization of Pentanitratolanthanate(III) Complexes



R	R'	Ln	% Ln Calcd	% Ln Found
CH_3	2,4,6-$(CH_3)_3C_6H_2CH_2$	Er	17.98	18.07
		Yb	18.49	18.48
		Lu	18.66	18.55
C_6H_5	*n*-C_8H_{17}	Er	16.49	16.67
		Tm	16.63	16.90
		Yb	16.97	17.12
		Lu	17.12	17.15

formate for 1 hr. They were then washed six times with ether under suction under a flow of dry nitrogen. The salt is exceedingly hygroscopic when even slightly impure. The (oct-py-Ph)I was converted into the $Ln(NO_3)_5{}^{2-}$ salt as already described.

The complexes $(oct\text{-}py\text{-}Ph)_2Ln(NO_3)_5$ are soluble in acetone but only slightly so in dichloromethane at room temperature. The complexes were recrystallized as lustrous leaflets from hot dichloromethane, in which they are more soluble.

Metal analyses were obtained on all compounds by ignition to the oxide; the results are collected in Table I.

Nuclear Magnetic Resonance Spectra. These were obtained at 100 MHz on a Varian HA-100-D spectrometer at ambient probe temperature (29°). TMS was used as the internal reference in all cases.

Results

Isotropic Nmr Shifts. The isotropic shifts were obtained by subtracting the chemical shift relative to TMS observed in the paramagnetic complex from the corresponding chemical shift in the diamagnetic $Lu(NO_3)_5{}^{2-}$ complex. Definitive identification of the resonances in the fully paramagnetic solutions was made by the "mole fraction technique" developed previously.[1,4]

The experimental results, expressed as isotropic shift ratios $(\Delta\nu_i/\Delta\nu_{\alpha\text{-}CH_2})$ may be found in Table II. As noted for the tetrabutylammonium salts,[1] low-field shifts are found for complexes of Tb and Er, while high-field shifts are found for the Tm and Yb complexes. The shift ratios, on the other hand, are approximately independent of the metal ion, indicating that all four lanthanide ions form ion-pair complexes of very nearly the same structures, as we might expect from their similar ionic radii and chemical properties. The small variations which do occur may be attributed to a combination of experimental error (±5 Hz in the case of the pyridine ring proton shifts) and a small contribution from the other terms of eq 1, which vary from one metal complex to another.[1]

The phenyl protons of the oct-py-Ph cation were not clearly resolved in the lutetium salt. In the paramagnetic solutions, on the other hand, even meta and para phenyl protons are clearly resolved, appearing as somewhat broadened triplets in the expected total intensity ratio of 2:1. The potential use of the paramagnetic $Ln(NO_3)_5{}^{2-}$ anions as shift reagents for organic cations will be explored in a future paper.

Theoretical Models of Ion-Pair Structure. The geometrical details of the proposed ion-pair structure are as shown in Figure 1. The pseudo-C_2 axis of the pyridine ring was chosen as the left-handed molecular cartesian coordinate system. The $Ln(NO_3)_5{}^{2-}$ anion resides at coordinates (M_x, M_y, M_z), which are more conveniently written in terms of the spherical coordinates (A, θ, ϕ) where angle θ is measured down from the z axis and an angle ϕ is measured clockwise from the positive y axis to the projection of the metal ion on the xy plane. For reasons of mathematical simplicity, it is assumed that the principal susceptibility axis χ_3 of the complex points toward the origin of the coordinate system. The coordinates of the cation protons (x_i, y_i, z_i) were calculated on the assumption that the pyridine ring is a regular plane hexagon. Standard bond distances were assumed for all atoms. The bond angles in the alkyl-chain portions of the oct-py-Ph cation were all assumed to be tetrahedral.

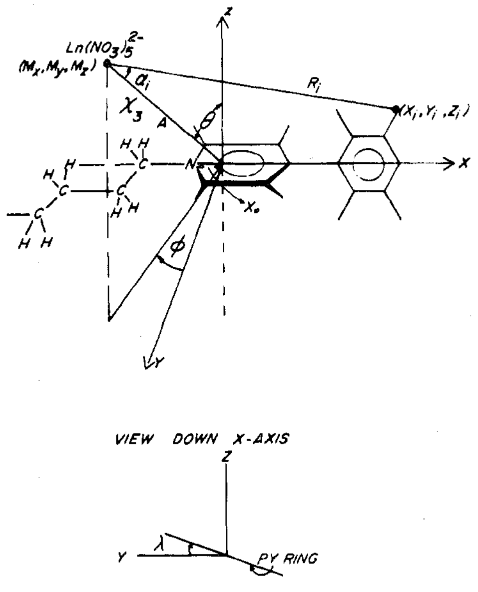


Figure 1. Coordinate system used in model calculations of ion-pair structure. For a description of parameters, see text.

In previous attempts[5] to establish ion-pair geometries it has been assumed that the principal susceptibility axis of the paramagnetic anion intersects the cation at the central (positively charged) atom. There is some justification for such a view in the case of ion pairs containing the pseudotetrahedral $Ph_3PCoI_3{}^-$ anion for instance, since the likely point of approach of the cation to the anion lies on the trigonal I_3 face of the anion suggesting that the principal magnetic (C_3) axis of the anion should pass through the cation's central atom on a time average.[5] The $Ln(NO_3)_5{}^{2-}$ anion, on the other hand, is a species of somewhat lower symmetry;[6] in addition, since all the ligands are identical, there is no obvious choice of a "close cation approach site" on the anion. We have therefore removed this restriction from our calculations by introducing a parameter x_0, which measures the distance between the coordinate origin and central nitrogen of the pyridine ring. The cation may thus be translated by an arbitrary amount along the x axis of the coordinate system. In summary, we use four parameters to specify the anion–cation orientation in the ion-pair complex; these are distances A and x_0 and angles θ and ϕ. The interionic distance will be, in general, a function of all four parameters.

Using the law of cosines, it is easily shown that the geometric factor for a given proton i can be written in terms of the above distances and angles in the ion-pair complex as

$$\frac{3\cos^2\alpha_i - 1}{R_i^3} = \frac{3(R_i^2 + A^2 - x_i^2 - y_i^2 - z_i^2)^2}{4R_i^5A^2} - \frac{1}{R_i^3} \tag{4}$$

where R_i, the distance between the lanthanide ion and the resonating cation proton i, is

$$R_i = [(A\sin\phi\sin\theta + x_i)^2 + (A\cos\phi\sin\theta - y_i)^2 + (A\cos\theta - z_i)^2]^{1/2} \tag{5}$$

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[5] R. H. Fischer and W. D. Horrocks, Jr., *Inorg. Chem.*, 7, 2659 (1968).

[6] A. R. Al-Karaghouli and J. S. Wood, *J. Chem. Soc. D*, 135 (1970).

Table II. Proton Isotropic Shifts in Substituted Pyridinium Pentanitratolanthanates

Cation	Anion	Solvent	Concn, *M*	$\Delta\nu_{\alpha\text{-CH}_2}$[a]	Pyridine ring proton ratios[b]		4-Phenyl proton ratios[b]			Corresponding no. in Fig 2 and 3
					Ortho	Meta	Ortho	Meta	Para	
TMBP	$Er(NO_3)_5^{2-}$	Acetone	Satd[c]	−272	1.11	0.625				1
TMBP	$Yb(NO_3)_5^{2-}$	Acetone	Satd[c]	144	1.15	0.694				2
oct-py-Ph	$Tb(NO_3)_5^{2-}$	H_2CCl_2	0.052	−860	1.55[d]	0.940	0.416	0.122	0.073	7
oct-py-Ph	$Er(NO_3)_5^{2-}$	H_2CCl_2	0.050	−650	1.37	0.807	0.366	0.128	0.075	4
oct-py-Ph	$Er(NO_3)_5^{2-}$	H_2CCl_2	0.026	−645	1.34	0.755	0.324	0.099	0.064	
oct-py-Ph	$Er(NO_3)_5^{2-}$	H_2CCl_2	0.010	−622	1.31	0.677	0.264	0.066	0.043	3
oct-py-Ph	$Er(NO_3)_5^{2-}$	Acetone	0.099	−333	1.44	0.918	0.465	0.174	*e*	
oct-py-Ph	$Er(NO_3)_5^{2-}$	Acetone	0.041	−283	1.42	0.851	0.402	0.138	*e*	
oct-py-Ph	$Tm(NO_3)_5^{2-}$	H_2CCl_2	0.050	593	1.53	0.949	0.443[d]	0.142	0.084	6
oct-py-Ph	$Yb(NO_3)_5^{2-}$	H_2CCl_2	0.050	275	1.49	0.960	0.458	0.171	0.098	5
oct-py-Ph	$Yb(NO_3)_5^{2-}$	Acetone	0.104	167[d]	1.57	1.02	0.395	0.246	*e*	
oct-py-Ph	$Yb(NO_3)_5^{2-}$	Acetone	0.049	149[d]	1.54	0.960	0.450	0.167	*e*	

[a] Shift in Hz at 100 MHz, with respect to corresponding resonance in $Ln(NO_3)_5^{2-}$ complex. [b] Shifts reported as ratios $\Delta\nu_i/\Delta\nu_{\alpha\text{-CH}_2}$. [c] ~0.05 *M*. [d] Isotropic shift value was extrapolated from a plot of observed shift *vs.* mole fraction of paramagnetic complex (see text). [e] Meta and para phenyl protons were not resolved in this solvent.

The question of how the ion pair behaves over the lifetime of the nmr experiment now arises. The following physical models were considered in an attempt to answer this question.

Static Model. In the static model, the anion is presumed to hold fixed values of A, θ, and ϕ relative to the cation during the lifetime of the nmr experiment; that is, there are no short-lived changes in the relative orientation between the counterions while the ion pair as a whole tumbles in the solution.

Rapidly Rotating Model. In this model, it is assumed that the cation rotates rapidly about the x axis of the molecular coordinate system, while the anion maintains fixed values of A, θ, and ϕ. For convenience, the $Ln(NO_3)_5^{2-}$ ion is placed in the xy plane ($\theta = 90°$), effectively removing one parameter from the calculation. The angle of rotation of the plane of the pyridine ring with respect to xy, the plane molecular coordinate system, is specified by dihedral angle λ (Figure 1). In this model, R_i and α_i are functions of the rotation angle λ and it is necessary to average the calculated geometric factors over all possible values of λ. This was accomplished by compiling cation coordinates for each value of λ in steps of 5° from $\lambda = 0°$ to $\lambda = 360°$. The new coordinates were then substituted into eq 4 and the resulting GF values were averaged. While this averaging technique is approximate, it should be noted that agreement between these results and those obtained by employing smaller increments of λ is virtually quantitative.

A distribution function $D(\lambda)$ may be introduced into the averaging process at this point to take account of preferred orientation of the cation with respect to the anion. The expression for the ratio of the averaged geometric factors then becomes

$$\left\langle \frac{GF_i}{GF_j} \right\rangle_\lambda = \frac{\Sigma_\lambda (GF_i)_\lambda D(\lambda)}{\Sigma_\lambda (GF_j)_\lambda D(\lambda)} \qquad (6)$$

If $D(\lambda) = 1.0$, then the cation rotation in the ion-pair complex is isotropic; *i.e.*, there is no preferred cation–anion orientation (unweighted rapid rotation). To allow for the possibility of preferred orientation of some kind during the ion-pairing process, the distribution functions $D(\lambda) = \cos^2 \lambda$ and $D(\lambda) = \sin^2 \lambda$ (*weighted rapid rotation*) were included in the model.

Comparison of Theoretical Models with Experiment. In order to test the agreement between theory and experiment a slight modification of the arithmetic R factor[7] appropriate to the comparison of shift ratios was used in the present case

$$R'(\%) = 100\,\frac{\Sigma_i\left|\left(\dfrac{\Delta\nu_i}{\Delta\nu_j}\right)_{\text{calcd}} - \left(\dfrac{\Delta\nu_i}{\Delta\nu_j}\right)_{\text{obsd}}\right|}{\Sigma_i|(\Delta\nu_i/\Delta\nu_j)_{\text{obsd}}|} \quad (j = \alpha\text{-CH}_2) \qquad (7)$$

where the sum runs over the independently determined shift ratios, of which there are five in the case of the oct-py-Ph cation. As a first approximation, we will regard that set of parameters giving a minimum value of R' as having the closest correspondence to the actual structure of the ion pair.

The only model which gave reasonable values of R' ($\leqslant 10\%$) at values of A, θ, ϕ, and x_0 which could be considered physically justifiable was the unweighted rapid rotation model. We shall consider two cases of this model: the assumption of $x_0 = 0$ used by previous workers and the assumption that x_0 may freely vary.

The results of the unweighted rapid rotation calculations are illustrated graphically in Figures 2 and 3. Figure 2 is a plot of calculated GF ratios $(GF)_i/(GF)_{\alpha\text{-CH}_2}$ for the phenyl and pyridine ring protons of the oct-py-Ph cation as a function of angle ϕ for different values of A. Parameter x_0 was set at zero for this particular calculation; thus the principal susceptibility axis passes through the pyridine nitrogen atom, and A represents the interionic distance. Only the range of ϕ giving reasonable agreement with experiment is shown. The pyridine ring proton ratios are seen to be enormously sensitive to changes in angle ϕ, varying by as much as a factor of 2 over a few degrees.

Data points taken from Table II are included for comparison; the numbers refer to the solution specified in the far left column of Table II. Figure 2 indicates clearly that of the possible A values correspondence between theory and experiment is best for $A = 7$ Å. The best fits are scattered over a small range of ϕ values. In this respect the shift ratio data for the $Er(NO_3)_5^{2-}$ complex fall somewhat out of line with those observed for the other complexes; this results in best-fit ϕ values which are considerably higher than found in the other cases.

It is possible that there may be a substantial rhombic dipolar shift in the case of erbium in this system although it was not apparent in our previous work.[1] There does not

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(7) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, p 158.

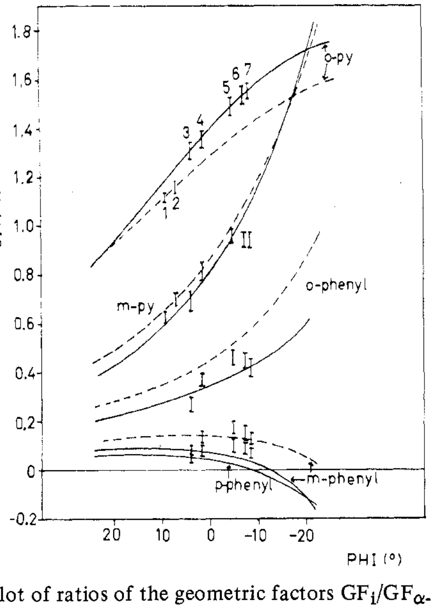

Figure 2. Plot of ratios of the geometric factors $GF_i/GF_{\alpha\text{-}CH_2}$ as a function of angle ϕ; $x_0 = 0$: solid curves, $A = 7.0$ Å; broken curves, $A = 8$ Å. The numbered data sets refer to Table II. The para phenyl curve for $A = 8$ Å has been omitted for the sake of clarity.

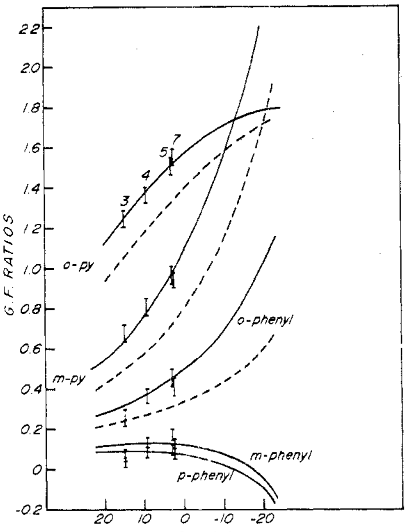

Figure 3. Plot of ratios of geometric factors *vs.* angle ϕ, showing the effect of changing x_0 on the ratios $GF_i/GF_{\alpha\text{-}CH_2}$; $A = 7$ Å: solid curves, $x_0 = -0.5$ Å; dotted curves, $x_0 = 0$. The meta and para phenyl curves for $x_0 = 0$ have been omitted for the sake of clarity.

appear to be any correlation of the best-fit ϕ values with any regularly varying property of the metal ions of this series such as size or polarizing power. We therefore conclude that the observed scatter reflects the experimental error and nonaxial shift contributions already alluded to.

The best-fit R factors and the corresponding values of ϕ are collected in Table III and can be seen to average a little under 10%.

The assumption of $x_0 = 0$ leads to considerable discrepancy between theory and experiment at the meta and para phenyl protons, however (Figure 2). These protons lie very close to the angular node in the function $(3 \cos^2 \alpha - 1)R^{-3}$ which occurs at $\alpha = 54.7°$. The calculated GF ratios for these protons are thus expected to be exceptionally sensitive to changes in distance A and can be seen to change sign at certain negative values of ϕ. Keeping A fixed at 7 Å it is found that, by varying ϕ and x_0, the R factors decrease to dramatically lower values in the vicinity of $x_0 = -0.5$ Å, with ϕ in the range 0-10°. These parameters represent a situation in which the principal susceptibility axis intersects the cation on the x axis at a point 0.5 Å within the pyridine ring. The final R factors are as shown in Table III and average around 3%.

Table III. Best-Fit Structural Parameters for $[\text{oct-py-Ph}]_2Ln(NO_3)_5$ Complexes[a]

Anion	Concn, M	ϕ, deg	x_0, Å	R', %
$Tb(NO_3)_5{}^{2-}$	0.052	−8.5	0.0	9.6
		2.5	−0.5	4.3
$Er(NO_3)_5{}^{2-}$	0.050	1.5	0.0	7.1
		9.5	−0.5	1.8
$Er(NO_3)_5{}^{2-}$	0.010	3.5	0.0	3.7
$Tm(NO_3)_5{}^{2-}$	0.050	−7.5	0.0	9.5
		2.5	−0.5	3.5
$Yb(NO_3)_5{}^{2-}$	0.050	−5.0	0.0	8.6
		3.0	−0.5	3.0

[a] $A = 7.0$ Å in all cases.

Table IV. Isotropic Shift Ratios in N-Octyl-Chain Proton Resonances[a]

$$N\text{-}\overset{1}{CH_2}\text{-}\overset{2}{CH_2}\text{-}\overset{3}{CH_2}\text{-}\overset{4}{CH_2}\text{-}\overset{5}{CH_2}\text{-}\overset{6}{CH_2}\text{-}\overset{7}{CH_2}\text{-}\overset{8}{CH_3}$$

Anion	Concn, M	Shift ratios[b]					
		H_2	H_3	H_4	H_5	$H_{6,7}$	H_8
$Tb(NO_3)_5{}^{2-}$	0.052	0.518	0.277	0.109	0.020	−0.04	−0.05
$Er(NO_3)_5{}^{2-}$	0.049	0.487	0.262	0.095	0.005	−0.04	−0.05
$Tm(NO_3)_5{}^{2-}$	0.050	0.521	0.323	0.130	0.0	−0.03	−0.03
$Yb(NO_3)_5{}^{2-}$	0.050	0.534	0.345	*c*	*c*	*c*	−0.02
Calcd[d]		1.118	0.448	0.272	0.068	−0.087	−0.096
Calcd[e]		0.451	0.335	0.212	0.128	0.072	0.04

[a] The solvent in all cases was H_2CCl_2. [b] The shift ratio is defined as $\Delta\nu_i/\Delta\nu_{\alpha\text{-}CH_2}$. [c] Resonance shifts masked by overlap. [d] Shift ratios calculated for $A = 7$ Å and $\phi = 5°$. The chain is permitted to rotate freely about the pyridine C_2 axis. The octyl chain is fully extended in the zigzag configuration. $x_0 = -0.5$ Å in this calculation. [e] Shift ratios calculated for $A = 7$ Å and $\theta = 5°$. The fully extended octyl chain does not rotate but remains fixed relative to the anion such that the carbon atoms lie in the $-x$, $-z$ plane ($\phi = 90°$). $x_0 = -0.5$ Å in this calculation.

The TMBP salts, on the basis of the very limited data available (Table II) appear to fit the theory best at $A = 8$ Å and $x_0 = 0$ in the range $\phi = 5$-10° (Figure 2).

Octyl-Chain Protons. The isotropic shift ratios observed for the octyl-chain protons may be found in Table IV. The resonances of all protons except H_6 and H_7 were fully resolved in the paramagnetic solutions, once again illustrating the potential usefulness of the $Ln(NO_3)_5{}^{2-}$ anion as a shift reagent. As previously observed for the tetrabutylammonium complexes, the shifts of the alkyl-chain protons attenuate with increasing distance from the central nitrogen atom. The shift ratios for the first four methylene groups are in fact nearly identical with those observed in $(n\text{-}C_4H_9)_4N$ salts, indicating that the time-average geometry is very similar in the two cases.[1]

It is exceptionally interesting that the protons H_6, H_7, and H_8 shift in the opposite direction to α-CH_2, indicating that these protons occupy, on a time average, a region of space where $3 \cos^2 \alpha - 1$ is negative [*i.e.*, $\alpha > \cos^{-1} (1/\sqrt{3})$]. The H_5 protons, which appear to be unshifted within experimental error, apparently lie on or quite near the nodal surface of the GF. Such behavior has not been noted in previous studies of systems possessing long alkyl chains.[8]

Calculations of the shift ratios for the n-octyl protons have

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(8) D. L. Rabenstein, *Anal. Chem.*, **43**, 1599 (1971); J. C. Fanning and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 3987 (1968).

been performed in an attempt to reproduce both the magnitude and sign of the observed shift ratios. Agreement was sought at the same A, ϕ, and x_0 which reproduced the ring proton shifts; however due to our lack of knowledge of the time-average geometry of the octyl chain, the quality of the agreement can hardly be expected to be superior. Hence these protons were omitted from the R factor calculations.

We assume the chain to be fully extended in solution, as shown in Figure 1. The results of an unweighted rapid-rotation calculation in which the chain rotates about the x axis are shown in Table IV. Agreement in both sign and order of magnitude for protons H_5–H_8 is good; however, for the protons H_2–H_4 the theoretical ratios exceed the experimental ratios by an unacceptable amount. This is presumably because, in the course of the rotation, these protons are brought unreasonably close to the anion. As can be seen from Table IV, a static-model calculation does a considerably better job for H_2–H_4; this calculation, however, fails to predict the correct sign for protons H_6–H_8. The most reasonable explanation for this behavior is that the outer portions of the chain are in rapid motion but that the inner portions of the chain tend to avoid close contact with the anion.

Discussion

Ion-Pair Structure. In 1958, on the basis of uv spectroscopy, Kosower[9] proposed a structure for ion pairs formed between *N*-alkylpyridinium cations and iodide anions. In the Kosower structure, the iodide ion was located directly above the central nitrogen atom of the pyridine ring ($\theta = 0°$), in a position which permits close approach of the centers of opposite charge, thereby minimizing the electrostatic potential energy.

On the basis of the results presented in this paper, this suggestion appears to be approximately true in the present case. It is obvious that a minimum potential energy structure will be adopted if the negatively charged oxygen atoms of the nitrate ions minimize their separation from the pyridine nitrogen atom; this can be achieved only by placing the Ln center at an angle of ~90° with respect to the C_2 axis of the pyridine ring. This type of interaction has also been observed by X-ray crystallography in the case of *N,N′*-dimethyl-4,4′-dipyridylium tetrachlorocobaltate[10] where the Cl^-–N^+ contacts occur at an angle of 80° with respect to the C_2 axis of the pyridine ring.

The observed A value, 7 Å, which may be roughly equated to the interionic distance Ln–N $\simeq$ 7.1 Å, is strikingly similar to what was observed for the tetrabutylammonium ion pairs.[1] Using an estimated hard-sphere radius for the $Ln(NO_3)_5^{2-}$ anion of 4.2 Å we thus obtain an effective pyridinium cation radius of ~3 Å. This is certainly reasonable, since it permits free rotation of the pyridine ring about the C_2 axis in the ion-pair complex. It also suggests that there is no intervening layer of solvent molecules between the anion and the cation.

As has been observed previously, both the shifts of the α-CH_2 protons and the shift ratios are very sensitive to changes in salt concentration. In the present case, the α-CH_2 shifts decrease as the concentration is reduced, as would be expected from simple ion-pair dissociation.[11] In the case of the tetrabutylammonium salts, on the other hand, an increase in the isotropic shift at all protons was observed as concentration decreased. Such behavior is believed to indicate the presence of micelles.[11]

The dramatic decrease in the shift ratios of the pyridine ring protons which accompanies lowering of concentration can be attributed to a small increase in angle ϕ, as can be seen from Table III and Figures 2 and 3. There is some evidence as well (Table IV) that the axis of χ_3 intersects the pyridine ring at positions increasingly close to the nitrogen atom as the concentration is lowered. One possible explanation for this behavior lies in a subtle change in the structure of the solvent shell surrounding the ion-pair complex. If, for example, solvation of the pyridine ring moiety became more pronounced at lower concentrations, this would have the effect of forcing the anion away from the pyridine ring to a slightly greater extent on a time average.

In a subsequent paper, we will explore several of the factors which influence the structures of ion pairs containing substituted pyridinium cations.

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Registry No. $(TMBP)_2[Er(NO_3)_5]$, 52540-68-8; $(TMBP)_2[Yb(NO_3)_5]$, 52540-69-9; $[oct\text{-}py\text{-}Ph]_2[Tb(NO_3)_5]$, 52540-72-4; $[oct\text{-}py\text{-}Ph]_2[Er(NO_3)_5]$, 52540-73-5; $[oct\text{-}py\text{-}Ph]_2[Tm(NO_3)_5]$, 52540-74-6; $[oct\text{-}py\text{-}Ph]_2[Yb(NO_3)_5]$, 52540-75-7.

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