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Registry No. $[Mn(NH_3)_6]^{2+}$, 15365-77-2; $[Fe(NH_3)_6]^{2+}$, 15365-76-1; $[Co(NH_3)_6]^{2+}$, 15365-75-0; $[Ni(NH_3)_6]^{2+}$, 15365-74-9; $[Zn(NH_3)_6]^{2+}$, 28074-39-7; $[Cd(NH_3)_6]^{2+}$, 29929-43-9; $[Cr(NH_3)_6]^{3+}$, 14695-96-6; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Ru(NH_3)_6]^{3+}$, 18943-33-4; $[Rh(NH_3)_6]^{3+}$, 16786-63-3; $[Os(NH_3)_6]^{3+}$, 48016-91-7; $[Ir(NH_3)_6]^{3+}$, 24669-15-6; $[Pt(NH_3)_6]^{4+}$, 18536-12-4; $[Co(NH_3)_4]^{2+}$, 22580-85-4; $[Zn(NH_3)_4]^{2+}$, 17095-57-7; $[Cd(NH_3)_4]^{2+}$, 18373-05-2; $[Cu(NH_3)_4]^{2+}$, 44001-04-9; $[Pd(NH_3)_4]^{2+}$, 15974-14-8; $[Pt(NH_3)_4]^{2+}$, 16455-68-8.

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Factors Influencing the Structures of Ion Pairs in Solution. Effect of Methyl Substitution in Alkylpyridinium Salts

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A series of paramagnetic anionic lanthanide–nitrato complexes containing *N*-alkyllutidinium cations have been prepared and characterized. The NMR spectra of these complexes in low-dielectric solvents reveal that 3,5 methyl substitution on the pyridine ring alters the structure of the ion pair compared to the previously studied 4-substituted cases, although the interionic distance (7 Å) appears to remain the same. Possible explanations for this phenomenon are considered. Methyl substitution in the 2 or 2,6 positions appears to result in an increase in the interionic distance; this is believed to be a steric effect.

Introduction

Since 1969, the ability of paramagnetic lanthanide ions to influence the NMR chemical shifts of ligand nuclei has found considerable practical application in organic chemistry.[1] In addition to the resolution of complex NMR spectra, lanthanide β-diketonate chelates (shift reagents) have been proven of value in distinguishing between different geometrical optical and conformational isomers of ligand molecules[2-6] and more recently in the extremely complex problem of establishing the conformations of biologically relevant molecules in solution.[7,8]

Applications of such a "shift reagent technique" to the study of the second coordination sphere antedates the development of the lanthanide chelate methods by several years.[9-11] The literature in this area, though not as extensive as in the shift reagent area, has been the subject of several critical reviews.[12]

We have been interested for some time in the use of NMR in elucidating ion-pair structure in low dielectric liquids.[13] The procedure consists of studying the chemical shifts of the cation protons in the presence of a paramagnetic counterion which possesses magnetic susceptibility anisotropy. In our most recent article,[14] we employed the *N*-octyl-4-phenylpyridinium (Oct(py)Ph) cation as a probe of cation orientation in the ion-pair complex with paramagnetic $Ln(NO_3)_5^{2-}$ anions.

As in the shift reagent technique, the $Ln(NO_3)_5^{2-}$ anion causes the cation NMR lines to shift from their normal positions. For salts of this anion, the induced shifts have been shown to lie predominantly in the axial dipolar shift term.[13,14] The axial dipolar shift is related to bond angles and bond distances in the ion pair by means of the equations[15]

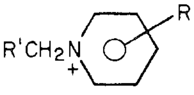
$$\Delta\nu = [F(\Delta\chi)](GF) \qquad (1)$$

$$GF = (3\cos^2\alpha_i - 1)R_i^{-3} \qquad (2)$$

where $F(\Delta\chi)$ represents a function of the magnetic susceptibility anisotropy. The geometric factor (GF) is a function of R_i, the distance between the unpaired electrons and the *i*th nucleus, and of α_i, the angle between R_i and the principal magnetic axis of the anion. By taking ratios of the observed dipolar shifts with respect to a reference proton, one obtains purely structural information which does not depend markedly on the magnetic properties of the complex.

In the pyridinium salts, the interionic distance *A*, defined as the distance between the trivalent lanthanide ion and the pyridine nitrogen, was measured to be ~7 Å, and the cation was shown to be oriented so that the metal sits perpendicular to the pyridine ring, resulting in a structure having the minimum electrostatic potential energy.[14] Comparison of the observed shift ratios with those calculated from model structures pointed to a considerable motional freedom on the part of the cation; best agreement was obtained if the cation was permitted to rotate freely about an axis perpendicular to the line connecting the Ln cation and the pyridine nitrogen.

In this article, we present evidence to show that the positioning of substituents around the pyridine ring has a substantial effect on the time average behavior of the cation in the ion pair. The cations chosen for study were of the lutidinium type, as shown, the 1 substituent being *n*-butyl or 2,4,6-trimethylbenzyl in all cases.



No.	R	R′	Abbreviation
I	$3,5\text{-}CH_3$	C_3H_7	3,5-BUL
II	$3,5\text{-}CH_3$	$2,4,6\text{-}(CH_3)_3C_6H_2$	3,5-TMBL
III	$3,4\text{-}CH_3$	$2,4,6\text{-}(CH_3)_3C_6H_2$	3,4-TMBL
IV	$2,6\text{-}CH_3$	C_3H_7	2,6-BUL
V	$2,4\text{-}CH_3$	$2,4,6\text{-}(CH_3)_3C_6H_2$	2,4-TMBL

Experimental Section

Preparation of 1-Butyl-2,6-dimethylpyridinium Iodide. Use of the literature method[16] in synthesizing this compound was found to result in poor yields (<20%). The salt was therefore prepared by refluxing 2,6-lutidine with an excess of 1-iodobutane in acetonitrile for 72 hr. The salt crystallizes in fair yield (60%) on addition of ethyl acetate.

The preparation of all other compounds proceeds very much as in our previous work on this series[14] and therefore will not be discussed further. All complexes were recrystallized from acetone–ethyl acetate mixtures. $(3,5\text{-TMBL})_2Pr(NO_3)_5$ is the only exception here; this complex, despite several attempts, could not be obtained crystalline. Lanthanide analyses performed in these laboratories were satisfactory for all other complexes.

Spectra were recorded in acetone-d_6 and H_2CCl_2 on Varian HA-100D (^1H) and Varian NV-14 (^{13}C) spectrometers operating at ambient temperature.

Assignment of the individual resonances is greatly assisted by the fact that the cations undergo fast exchange between diamagnetic and paramagnetic ion pairs. Thus one may correlate the shifts in the fully paramagnetic complexes with those in solutions containing mixtures of the diamagnetic and paramagnetic complexes.[13]

Results

Diamagnetic Salts. Identification of resonances in the diamagnetic lutetium compounds is relatively straightforward for the 3,5-BUL and 3,5-TMBL complexes. Two singlets (τ 1.96, 1.68) with the expected 1:2 intensity ratio were observed in the pyridine-ring region. In the 2,6-BUL salt, the AB_2 pattern was easily seen, with the para multiplet (τ 2.12) downfield from the meta (τ 2.67) as is the case in free 2,6-lutidine. Assignment of resonance signals in the methyl region for the TMBL salts was performed by comparison with the corresponding 1-butyl derivatives.

The pyridine ring proton spectrum of the 2,4-TMBL cation reveals the expected ABX pattern (J_{AB} = 5 Hz). The X nucleus (3-H) is discernibly coupled to the high-field component of the AB spectrum only (J_{BX} = 2 Hz). This coupling is reported[17] to be J_{36} in the free lutidine; this puts the 6-H resonance (τ 2.60) to high field of 5-H (τ 2.33) in the $Lu(NO_3)_5^{2-}$ complex. This assignment is in agreement with the expected isotropic shift pattern[14] (Table IV).

The pyridine ring pattern in the 3,4-TMBL salt shows no resolvable J_{25} or J_{26}. The 6-H, 5-H, and 2-H resonances are found, respectively, at τ 1.88, 2.34, and 1.80.

Paramagnetic Salts. 3,5- and 3,4-Lutidinium Complexes. The observed NMR isotropic shift ratios ($\Delta\nu_i/\Delta\nu_{\alpha\text{-}CH_2}$) in the paramagnetic complexes are presented in Tables I and II. It can be seen that the shift ratios for the 3,5-BUL and 3,5-TMBL series vary but little across the lanthanide series. This is a consequence of the axial dipolar origin[13,14] of the shift. The ion-pair structure appears to be independent of variations in the size of the lanthanide cation across the series, as has been noted on previous occasions.[13,14]

Several new facts are apparent from Table I. The shift ratio $\Delta\nu_o/\Delta\nu_{\alpha\text{-}CH_2}$ is very much smaller when methyl groups are present in the 3(5) position than when this position is unsubstituted, as was the case in the previously published 4-phenylpyridinium salts ($\Delta\nu_o/\Delta\nu_{\alpha\text{-}CH_2}$ = 1.3–1.5). Yet at the same time, the magnitude of the shift at the α-CH_2 protons (hertz) is comparable to that observed for the same metal ion in the Oct(py)Ph system (Table II, ref 14). Comparison of the pyridine ring shift ratios in 3,5-TMBL and 3,5-BUL complexes also indicates that the ratio $\Delta\nu_o/\Delta\nu_{\alpha\text{-}CH_2}$ does not appear to depend markedly on the nature of the *N*-alkyl substituent, although the ratio $\Delta\nu_p/\Delta\nu_{\alpha\text{-}CH_2}$ appears to be somewhat less in the 3,5-TMBL case.

In order to supplement the rather meager proton NMR data, ^{13}C NMR data were obtained for the $(3,5\text{-BUL})_2Yb(NO_3)_5$ and $(3,5\text{-BUL})_2Er(NO_3)_5$ complexes; these may be found in Table II.

2,6- and 2,4-Lutidinium Complexes. The shift data for these salts may be found in Table IV. It can be seen that when there are methyl groups at the 2(6) position, the α-CH_2 isotropic shift drops off quite markedly when compared to the 3,5- or 4-substituted cases.[14] The data on 2,4-TMBL salts indicate that only one methyl group at the 2 position is necessary to effect this decrease. It is also interesting to note that the pyridine ratios $\Delta\nu_m/\Delta\nu_{\alpha\text{-}CH_2}$ and $\Delta\nu_p/\Delta\nu_{\alpha\text{-}CH_2}$ are considerably greater than were observed in the 3,5-substituted complexes.

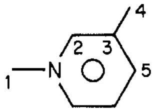
Calculations. The basic equations and method used in calculation of the geometric factors has already been reviewed in some detail.[14] The reader is therefore referred to our earlier work. In brief, we consider two distinctly different models of cation behavior. In the "frozen model", the cation nitrogen is placed in a fixed distance, *A*, from the central lanthanide cation, as shown in Figure 1. The orientation of the metal anion is specified by polar angle θ and azimuthal angle ϕ;

Table I. Proton Isotropic Shift Ratios[a,b] in Pentanitratolanthanate Complexes

Cation	Anion	Concn,[f] *M*	py proton ratios: Ortho	Meta	Para	$\Delta\nu_{\alpha\text{-CH}_2}$,[c] Hz
3,5-BUL	$Er(NO_3)_5{}^{2-}$	0.12	0.885	0.353	0.279	−634
		0.07	0.879	0.332	0.250	−628
		0.04	0.863	0.308	0.223	−642
3,5-BUL	$Yb(NO_3)_5{}^{2-}$	0.13	0.866	0.330	0.306	+261
3,5-TMBL	$Pr(NO_3)_5{}^{2-}$	~0.1	0.825	0.175	0.206	−63
3,5-TMBL	$Nd(NO_3)_5{}^{2-}$	0.11	0.838	0.257	0.238	−105
3,5-TMBL	$Nd(NO_3)_5{}^{2-}$	0.05	0.839	0.254	0.216	−106
3,5-TMBL	$Eu(NO_3)_5{}^{2-}$	0.10	0.822	0.258	0.201	+124
3,5-TMBL	$Sm(NO_3)_5{}^{2-}$	0.10	0.869	0.304	0.260	−20
3,5-TMBL	$Er(NO_3)_5{}^{2-}$	0.10	0.837	0.269	0.210	−646
3,5-TMBL	$Yb(NO_3)_5{}^{2-}$	0.10	0.833	0.256	0.219	+305
3,4-TMBL	$Er(NO_3)_5{}^{2-}$	0.10	0.905 (2)[e]	*d* (3)		
			0.952 (6)[e]	0.498 (5)[e]	*d*	−612
3,4-TMBL	$Tm(NO_3)_5{}^{2-}$	0.11	0.926 (2)	0.286 (3)	0.177	419
			1.01 (6)	*d* (5)		
3,4-TMBL	$Yb(NO_3)_5{}^{2-}$	0.11	0.938 (2)	0.301 (3)		
			1.01 (6)	0.555 (5)	0.193	259

[a] Defined as $\Delta\nu_i/\Delta\nu_{\alpha\text{-CH}_2}$. [b] The solvent in all cases was H_2CCl_2. [c] Shift at 100 MHz. An upfield shift is defined as positive. [d] Lines could not be unambiguously identified due to overlap. [e] The numbers in parentheses indicate position on py ring. [f] Concentration of complex.

Table II. Carbon-13 Isotropic Shift Ratios in 3,5-BUL Complexes



Observed

Anion	$\Delta\nu_1$,[a] ppm	$\Delta\nu_2/\Delta\nu_1$	$\Delta\nu_3/\Delta\nu_1$	$\Delta\nu_4/\Delta\nu_1$	$\Delta\nu_5/\Delta\nu_1$
$Er(NO_3)_5{}^{2-}$	−5.31	0.72[c]	0.55	0.42	0.38
$Yb(NO_3)_5{}^{2-}$	+2.30	0.87	0.59	0.45	0.53

Calculated[b]

ϕ, deg	$D(\lambda)$	$\Delta\nu_2/\Delta\nu_1$	$\Delta\nu_3/\Delta\nu_1$	$\Delta\nu_4/\Delta\nu_1$	$\Delta\nu_5/\Delta\nu_1$
20	1.0	0.82	0.55	0.38	0.45
15	$\sin^2\lambda$	0.85	0.60	0.40	0.51

[a] Shift at 15.16 MHz. Positive sign indicates an upfield shift. [b] $A = 7$ A in all cases. [c] Ortho-carbon resonance position uncertain due to low signal level.

values of the geometric factors are then calculated as outlined previously.[14]

Past experience[12,14] suggests that since the counterions are not chemically bonded, the observed isotropic shifts will be an average of the individual isotropic shifts of a very large number of orientations. In order to accommodate nature partially in our calculation, an average geometric factor must be computed by summing over a range of angles, with suitable weight being given to those orientations which are felt to be most likely to occur.

In the "rotating model",[14] the cation is permitted to rotate about the *x* axis of the coordinate system (Figure 1). Parameter θ is set at 90°; distance *A* and angle ϕ are varied until the calculated and observed shift ratios are in agreement. The rotation of the pyridine ring about the *x* axis is described[14] by a dihedral angle λ. We may introduce a distribution function $D(\lambda)$ to make the cation preferentially adopt (or avoid) certain orientations with respect to the anion. Since there is no a priori theoretical choice of distribution function appropriate to this problem, we have adopted the relatively simple functions $D(\lambda) = 1.0$ (isotropic rotation) and $D(\lambda) = \sin^2\lambda$ (weighted rotation) in attempting to fit theory to experiment.

A selection of results from these calculations may be found in Tables II–IV.

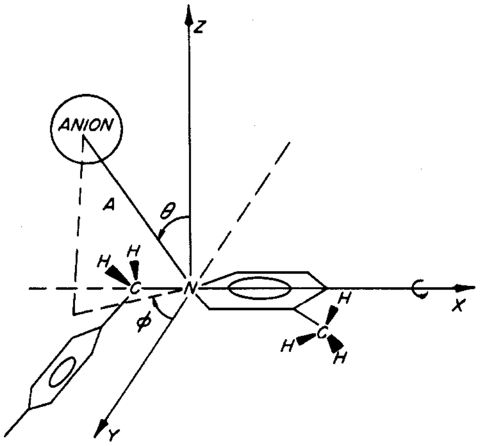


Figure 1. Cation-based coordinate system showing relative orientation of counterions in the ion-paired complex. The anion's principal susceptibility axis is assumed to lie along the vector Ln-N.

The GF ratios calculated for the methyl groups are averages of all three protons; these are in turn averaged over several different conformations. It was found that rotating this group by 60° induces at most a 5% change in the calculated ratios; thus it would appear that the choice of methyl rotamer makes very little difference to the calculated GF ratio.

Our interpretation of the shift ratio data will differ somewhat from the case of the Oct(py)Ph cation,[14] in which there were five experimentally determined shift ratios. A three-parameter model was found to be sufficient to account accurately for the shift ratios in the rotating model,[14] x_0 being the distance between the coordinate origin and the pyridine nitrogen atom. In the 3,5-BUL and 2,6-BUL cases, however, there are only three experimental proton shift ratios. Were we to adopt an identical procedure in this work, the number of model parameters would equal or surpass the number of observables. We have thus not included the parameter x_0 in our calculations. Thus, for the present work, the rotating model uses only two parameters (*A* and ϕ) while the frozen model uses three (*A*, θ, and ϕ).

A consequence of the systems chosen for study is that the protons all lie within 4 Å of the central nitrogen atom. For these protons, at values of ϕ near 0°, the calculated GF ratios are not very sensitive to the choice of parameter *A* (see Figures 2 and 3, ref 14).

A further consequence of the small number of observables is that one can obtain a fit to experiment at more than one set of model parameters. This implies that our final choice of model parameters will carry an inherent uncertainty of

Table III. Calculated GF Ratios for Pyridine Ring Protons in 3,5-Lutidinium Salts

				GF ratios[a]		
Case	A, Å	ϕ, deg	$D(\lambda)$	Ortho	Meta	Para
i	7.0	0	1.0	1.38	0.652	0.522
ii	6.0	20	1.0	0.839[b]	0.260[b]	0.220[b]
iii	7.0	20	1.0	0.812	0.286	0.270
iv	7.0	10	$\mathrm{Sin}^2\ \lambda$	0.830	0.350	0.349

[a] $(\mathrm{GF})_i/(\mathrm{GF})_{\alpha\text{-}\mathrm{CH}_2}$. [b] α-CH_2 group rotates isotropically; α-CH_2 group in all other cases frozen as illustrated in Figure 1 (see text).

several (~15) degrees in the choice of ϕ and presumably as much as 1 Å in the choice of A. Thus we cannot choose unambiguously between alternative structural hypotheses on the basis of shift ratios alone.

Discussion

Comparison of Theory with Experiment. If we are to attempt to overcome this last mentioned problem, it is necessary to make certain assumptions about the ions in solution. The α-CH_2 shift data strongly suggest that these protons all experience comparable magnetic anisotropy effects from the anion in Oct(py)Ph,[14] 3,5-TMBL, 3,4-TMBL, and 3,5-BUL (Table I). This suggests in turn that the α-CH_2 protons lie at comparable distances from the central Ln^{3+} cation. Underlying this hypothesis is our implicit assumption that the size and direction of the principal susceptibilities of the anion in solution are not influenced by changing the substituents on the cation. The hypothesis thus suggests that we should look for agreement between theory and experiment in the vicinity of $A = 7$ Å and $\phi = 0°$, our best fit parameters for the Oct(py)Ph salts. However, when the ring is permitted to rotate isotropically, the calculated shift ratios (case i, Table III) are clearly in disagreement with experiment.

In view of the predominant axial dipolar nature of the shifts observed in the proton spectra of this system[13,14] and in systems containing lanthanide β-diketonates,[18] we do not feel that the differences in behavior between the Oct(py)Ph and TMBL salts can be explained by recourse to either the rhombic dipolar or Fermi contact shift effects.[12]

The very low *o*-py:α-CH_2 ratio observed in the 3,5-dimethyl complexes thus indicates that the pyridine ring protons do not get as close to the anion on a time average as in the Oct(py)Ph case. We therefore attempt to fit the data at a larger value of ϕ. The parameters $A = 7$ Å and $\phi = 20°$ are the only acceptable solution yielded by the isotropic rotating model from the standpoint of shift ratios (case iii). The α-CH_2 GF is considerably less (4.83×10^{-3} Å^{-3}) at $\phi = 0°$ than at $\phi = 20°$ (6.7×10^{-3} Å^{-3}). This violates the hypothesis in that the susceptibility anisotropy would be forced to much lower values in the 3,5-BUL or 3,5-TMBL case in order to preserve comparable α-CH_2 shifts.

We may also fit the data by including the distribution function $D(\lambda) = \sin^2 \lambda$ in the calculation, since this reduces the edge-on contact (coplanarity) between anion and pyridine ring. As can be seen (case iv) agreement is reasonably good, though by no means perfect. This model gives us a reduced value of ϕ, which is desirable to maintaining the hypothesis.

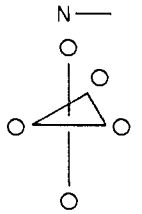
It is of interest that the isotropically rotating model gives an excellent fit to the data at $A = 6$ Å and $\phi = 20°$ (case ii); this solution is not viable, however, since at this distance, isotropic rotation is physically impossible.

There are certain additional problems in searching for agreement, in that Table I reveals slight differences between the shift ratios in 3,5-TMBL and 3,5-BUL complexes, but apparently only at the *m*-py and *p*-py positions. It is obvious that the same model structure does not apply to both types of salt. The same conclusion applies to solutions of the 3,5-BUL cation as a function of concentration (Table I). The origins of these subtle differences cannot be explained at present.

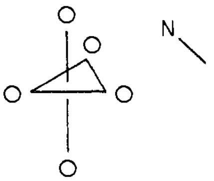
In sum, we are in the position of having at least two sets of parameters which satisfy the experimental data, for there are many ways in which the pyridine ring can avoid close approach to the anion.

Let us consider some possible physical reasons for the divergence in behavior between the 3,5-dimethyl and 4-phenyl salts. One possible explanation presumes the existence of a steric effect which prevents free rotation in the 3,5-dimethyl case. To test this idea, we have calculated contact distances between those atoms of the anion and cation most likely to be in contact with one another, namely, the noncoordinated terminal nitrate oxygen ($\mathrm{O_t}$) atoms and the *o*-H and *m*-CH_3 protons of the cation.

The $\mathrm{Ln(NO_3)_5}^{2-}$ anion is known from X-ray crystallography[19] to contain bidentate nitrate groups arranged in such a way that the nitrogen atoms form an approximate trigonal-bipyramidal arrangement about the central Ln cation. For the purposes of the calculations, the A vector of Figure 1 contains the nitrate nitrogen and $\mathrm{O_t}$ atoms. This configuration is referred to as the "apical attack model".



apical attack model[21]



facial attack model[21]

At $A = 7$ Å, with $\phi = 0°$, the closest approach distance recorded is $\mathrm{O_t}$ to pyridine *o*-H (0.89 Å), not to *m*-CH_3. This of course comes about when vector A and the pyridine ring are coplanar. The shortest corresponding $\mathrm{O_t}$–*m*-CH_3 proton contact recorded is 2.70 Å, which is in excess of the sum of the appropriate van der Waals radii (2.6 Å).[20] Thus, the apical attack model does not explain why the *o*-H protons in the 4-phenylpyridinium cation can approach the anion more closely than in the case of the 3,5-dimethyl compound, provided both types of salt are characterized by the same A and ϕ values.

An alternative placing of the cation involves attack on a face of the trigonal bipyramid (facial attack model). While this relieves the short contact at *o*-H, the methyl groups in the 3 and 5 positions would presumably encounter the $\mathrm{O_t}$ atoms of the basal nitrate ions, thus hindering the free rotation of the cation in the ion-pair complex. In the 4-phenyl salt, however, the *m*-H protons would not encounter the basal nitrate oxygens to the same extent, thus permitting freer rotation of the ring.

It must be remembered that the number of possible orientations of the cation with respect to the pseudo-C_3 axis of the anion is practically without limit and that with the limited data available no definite resolution of this question is possible. A knowledge of the principal values of the magnetic susceptibility of the anion would however help in distinguishing between these two attack models.

An alternate possibility that should not be overlooked is that the divergences in pyridine ring behavior are due to differences in solvation between the 3,5-dimethyl and 4-phenylpyridinium salts. There is not, however, sufficient experimental evidence of such solvation differences for this explanation to be considered seriously.

Shift Ratios in 3,4-TMBL Salts. Detailed calculations were not attempted on these compounds, since the simple model chosen is obviously inadequate to account for the observation of different shifts at the 2-H and 6-H positions on the pyridine ring without the inclusion of further distribution functions or coordinate shifts.[14] The shift ratio data do serve to reinforce

Table IV. Isotropic Shift Ratios for 2,4- and 2,6-Lutidinium Complexes[a]

Observed

			Shift ratios[b]			
Metal	Cation	Solvent	*o*-CH_3	*m*-H	*p*-H	$\Delta\nu_{\alpha\text{-}CH_2}$, Hz
Nd	2,6-BUL	Acetone-d_6	0.713	0.738	0.619	42
Er	2,6-BUL	H_2CCl_2	0.833	0.756	0.544	−390
Yb	2,6-BUL	H_2CCl_2	0.729	0.566	0.499	196
Yb	2,6-BUL	H_2CCl_2[c]	0.691	0.525	0.400	217
Yb	2,6-BUL	H_2CCl_2[d]	0.656	*e*	*e*	245
Yb	2,6-BUL	Acetone-d_6	0.714	0.699	0.556	133
Er	2,4-TMBL	H_2CCl_2	1.02 (2)[h] 0.711 (6)[h]	0.594 (3)[h] *e* (5)[h]	0.416	−377
Yb	2,4-TMBL	H_2CCl_2	0.933 (2) 0.904 (6)	0.733 (3) 0.844 (5)	0.556	135

Calculated

				GF ratios		
Case	*A*, Å	θ, deg	ϕ, deg	*o*-CH_3	*m*-H	*p*-H
i[f]	7	−5	90	0.744	0.715	0.618
ii[f]	9	0	90	0.747	0.661	0.589
iii[f]	9	5	90	0.710	0.590	0.517
iv[g]	9		0	1.05	0.822	0.670
v[g]	9		25	0.792	0.468	0.377

[a] Concentration is 0.12 *M* unless otherwise specified. [b] $\Delta\nu_i/\Delta\nu_{\alpha\text{-}CH_2}$. [c] Concentration 0.06 *M*. [d] Concentration 0.012 *M*. [e] Resonance could not be identified with certainty. [f] Frozen model. [g] Restricted rotating model. [h] Numbers in parentheses indicate position on pyridine ring.

our previous conclusion that a methyl group in the 3 position tends to block anion approach to the ring, ($\Delta\nu_2 < \Delta\nu_6$, Table I).

Orientation of the Benzyl Group. Observed shift ratios $\Delta\nu_i/\Delta\nu_{\alpha\text{-}CH_2}$ for this group are 0.19 ± 0.02 (*o*-CH_3), 0.06 ± 0.01 (*m*-H), and 0.03 ± 0.01 (*p*-CH_3) in the 3,5-TMBL complexes. Calculated GF ratios in either of the rapidly rotating models are in violent disagreement with the experiment (calcd for $A = 7$ Å, $\phi = 20°$: 1.31, *o*-CH_3; 2.31, *m*-H; 2.06, *p*-CH_3, isotropic model). This is probably due to the fact that the protons are brought very close to the anion in the course of the rotation. Order of magnitude agreement with experiment is only possible when the benzene ring is frozen as shown in Figure 1. (The parameter set ($\theta = 90°$, $\phi = 20°$, $A = 7$ Å) gives respectively 0.35, 0.16, 0.09.) Agreement can only be improved beyond the above numbers by reducing parameter *A* to impossibly small values.

The most likely conclusion is that the benzene ring tries to maximize its separation from the anion in the ion pair. Physically speaking, this is in keeping with minimizing the distance *A* and therefore with a minimum potential energy ion-pair structure. This requires, however, that the α-CH_2 protons are not free to rotate in the ion pair, i.e., that they tend to point permanently at the anion. The shift ratios in Table III were therefore calculated on this assumption.

^{13}C NMR Results. The calculated and experimental ^{13}C shift ratios are compared in Table II. It can be seen that the $Yb(NO_3)_5{}^{2-}$ data give a good fit to both the restricted and isotropic rotating models for the same range of *A* and for ϕ values that fit the proton spectra. The erbium data contain some minor divergences in the ratios $\Delta\nu_{C\text{-}2}/\Delta\nu_{C\text{-}1}$ and $\Delta\nu_{C\text{-}5}/\Delta\nu_{C\text{-}1}$; we nonetheless regard the fit as good at the remaining protons. A measure of internal consistency is provided by the ratio $\Delta\nu_{\alpha\text{-}CH_2}/\Delta\nu_{C\text{-}1}$; it can be seen that the agreement is satisfactory (calcd, 0.97; obsd, 1.15 ± 0.05).

2,6-BUL and 2,4-BUL Salts. The strongly reduced α-CH_2 shifts encountered here can be explained in several alternate ways: first, by a reduced ion-pair association constant compared to the 3,5- or 3,4-substituted salts, resulting in a greater fraction of free ions in solution, or, second, by virtually complete association as is believed to occur in all other cases studied[14] but with an increased interionic distance. This would presumably be a consequence of the 2-methyl group's blocking close approach of the anion to the pyridine nitrogen. The magnetic anisotropy, being a property of the anion, would be expected to remain comparable to that found in the preceding cases.

The data do not support the first explanation, since the values of the isotropic shifts *increase* with dilution at the α-CH_2 group, in H_2CCl_2, as has been found for similar systems in this solvent.[13,22]

A test of the second explanation is the comparison of GF values calculated for the α-CH_2 protons at 7 Å with those found at greater distances. At $\phi = 0°$, we calculate the ratio $(GF)_{9Å}/(GF)_{7Å}$ to be ~0.50; the result does not depend markedly on the model chosen. We may compare this number against the ratios of the observed α-CH_2 shifts in the 3,5- and 2,6-substituted cases, respectively. The numbers vary between 0.7 and 0.4, depending on the metal ion chosen (Tables I and IV). Thus the notion of an increase in the interionic distance by as much as 2 Å does not seem unreasonable.

Detailed calculations for these salts can be found in Table IV. The scatter in the observed ratios makes firm conclusions difficult here. It can be seen that the restricted rotation model (cases iv, v) fails to reproduce the shift at *o*-CH_3 in the 2,6-BUL salts satisfactorily at any angle except $\phi = 25°$; the fit is very poor at the meta and para protons at this angle, however. The only solution which minimizes the *o*-CH_3 shift ratio yet maintains the large meta:para shift ratios is the frozen model (Table IV, cases ii, iii). Thus, the evidence suggests that $A = 8$–9 Å and ϕ between 0 and 5° is the most likely fit to the data.

Summary and Conclusions

From the available data on *N*-alkylpyridinium complexes, we can identify three distinctly different sorts of cation behavior in the ion pair. These have been interpreted as due to (a) unrestricted cation motion in the ion-pair complex (4-phenylpyridinium cation), (b) restrictions on the motion of pyridine ring at distances comparable to those found in (a) (3,5- and 3,4-lutidinium cations), and (c) sterically induced increases in the interionic distance, coupled with an apparent loss of rotational freedom in the ion pair (2,6-BUL cation). The substituent on nitrogen does not appear to affect the behavior of the pyridine ring. The shifts cannot be unambiguously assigned to models at present since the experimental data can be fit by more than one set of geometrical parameters.

Nonetheless, the pyridine ring appears to be positioned such that its symmetry axis makes a roughly 90° angle with respect to the Ln–N^+ vector, as was found previously.[14] We plan to continue these investigations by studying cations in which the steric bulk in the vicinity of the nitrogen atom varies in a controlled fashion.

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Registry No. (3,5-BUL)$_2$Er(NO$_3$)$_5$, 55723-35-8; (3,5-BUL)$_2$Yb(NO$_3$)$_5$, 55723-36-9; (3,5-BUL)$_2$Pr(NO$_3$)$_5$, 55723-38-1; (3,5-BUL)$_2$Nd(NO$_3$)$_5$, 55723-39-2; (3,5-TMBL)$_2$Eu(NO$_3$)$_5$, 55723-41-6; (3,5-TMBL)$_2$Sm(NO$_3$)$_5$, 55723-43-8; (3,5-TMBL)$_2$Er(NO$_3$)$_5$, 55723-15-4; (3,5-TMBL)$_2$Yb(NO$_3$)$_5$, 55723-17-6; (3,4-TMBL)$_2$Er(NO$_3$)$_5$, 55723-19-8; (3,4-TMBL)$_2$Tm(NO$_3$)$_5$, 55723-21-2; (3,4-TMBL)$_2$Yb(NO$_3$)$_5$, 55723-22-3; (2,6-BUL)$_2$Nd(NO$_3$)$_5$, 55723-25-6; (2,6-BUL)$_2$Er(NO$_3$)$_5$, 55723-26-7; (2,6-BUL)$_2$Yb(NO$_3$)$_5$, 55723-27-8; (2,4-TMBL)$_2$Er(NO$_3$)$_5$, 55723-29-0; (2,4-TMBL)$_2$Yb(NO$_3$)$_5$, 55723-30-3.

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Synthesis and Structure of Some Bis(cyclopentadienyl)titanium(III) Metal Halides

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A series of air-sensitive Ti(III) complexes of the general formula (Cp$_2$TiX)$_2$MX$_2$ (X = Cl, Br; M = Zn, Be, Mn) have been prepared and characterized. Both solvent and the oxidation potential of the central metal atom are important in the synthesis of these materials. The crystal and molecular structure of (Cp$_2$Ti·DME)$_2$(Zn$_2$Cl$_6$)·C$_6$H$_6$ (I) (DME = dimethoxyethane) and (Cp$_2$TiCl)$_2$ZnCl$_2$·2C$_6$H$_6$ (II) have been determined from single-crystal three-dimensional X-ray (Mo Kα) diffraction data collected at room temperature. (Cp$_2$Ti·DME)$_2$(Zn$_2$Cl$_6$)·C$_6$H$_6$ crystallizes in the monoclinic space group $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14) with a = 11.810 (4) Å, b = 10.201 (5) Å, c = 17.284 (7) Å, and β = 93.20 (2)°; Z = 4, ρ_{calcd} = 1.527 g cm^{-3}, and ρ_{exptl} = 1.49 (3) g cm^{-3}. Full-matrix least-squares refinement of 2692 observations gave final agreement factors of R_1 = 0.084 and R_2 = 0.056. (Cp$_2$TiCl)$_2$ZnCl$_2$·2C$_6$H$_6$ crystallizes in the orthorhombic space group $Pbcn$ (No. 60) with lattice constants a = 18.236 (10) Å, b = 15.513 (8) Å, and c = 11.237 (6) Å; Z = 4 with ρ_{calcd} = 1.503 and ρ_{exptl} = 1.48 (3) g cm^{-3}. Least-squares refinement of 2074 observations gave final R factors of R_1 = 0.071 and R_2 = 0.049. Compound I is ionic. The DME coordinates to the titanium(III) atom as a bidentate ligand to form a cation and the zinc trichloride dimerizes to form a dianion with pseudotetrahedral geometry around each zinc atom. Compound II contains an approximately linear Ti–Zn–Ti arrangement with a Ti–Zn–Ti angle of 173.4 (1)°. The geometry around the zinc atom is pseudotetrahedral with chlorine atoms bridging to the titanium atoms. The benzene molecules in both structures reside in the crystal lattice.

Introduction

The reduction of Cp$_2$TiCl$_2$ to Cp$_2$TiCl (Cp = C$_5$H$_5$) by zinc was first investigated by Birmingham et al. in 1955[1a] and by other workers[1b] in the early 1960's as part of the early studies which were being made on Ziegler–Natta catalysis. The isolation and characterization by Saltzmann[2] in 1966 of these systems clearly indicated that complex formation had occurred. When this research was initiated, the exact nature of the organometallic complexes formed by titanium with reducing metals and metal complexes was unknown. A single-crystal X-ray study of one of the products formed, (Cp$_2$TiCl)$_2$ZnCl$_2$·2C$_6$H$_6$, by us and by Vonk[3] independently with film techniques revealed a trinuclear linear chain configuration.

As part of a broader program to study the structural, electronic, and chemical properties of exchange-coupled low-valent early transition metal complexes and as part of our earlier studies on electronic effects in one-dimensional systems,[4,5] we wish to report here the synthesis and structural properties of a number of mixed-metal complexes of bis(cyclopentadienyl)titanium(III).

Experimental Section

Syntheses. Starting materials were all commercially available. The solvents were dried and distilled from sodium ketyl and stored under