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Article

Multinuclear PGSE Diffusion and Overhauser NMR Studies on a Variety of Salts in THF Solution

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^{1}H, ^{19}F, and ^{7}Li pulsed gradient spin–echo (PGSE) NMR measurements for a series of salts are reported. The ^{7}Li is shown to complement the ^{1}H and ^{19}F measurements; however, the use of higher concentrations (for the less-sensitive ^{7}Li) can lead to aggregation. For all of the salts discussed {Li(BF$_4$); (n-Bu$_4$N)(BF$_4$), a trinuclear Ru cluster; [Ir(1,5-COD)(**4**)](BF$_4$), where **4** is a chiral P,N ligand; and the crown ether stabilized potassium salt, [K(18-crown-6)(NPh$_2$)], **6**}, the use of THF seems to promote strong ion pairing. In several cases, the degree of ion pairing approaches 100%. In THF solution, the potassium salt, **6**, prefers to exist as a more classical ion pair rather than as the π complex found in the solid state. In some cases, ^{1}H, ^{1}H NOESY and ^{1}H, ^{19}F HOESY spectra help to pinpoint the cation/anion spatial relationship.

Introduction

Determining the nature of cation−anion interactions still remains something of a problem. Conductivity measurements in relatively nonpolar solvents can be ambiguous, and often, the best polar solvents, for example, methanol, either do not dissolve, or react with, the salt in question.

Self-diffusion constants (*D* values) obtained via pulsed gradient spin−echo (PGSE) measurements are slowly gaining popularity[1] in that, for a suitable anion such as BF$_4^-$, one can measure the *D* values for the cation and anion separately, via ^{1}H and ^{19}F diffusion measurements, respectively. In a series of reports,[2−6] we have suggested that the individual *D* values for these ions can provide a useful alternative to conductivity data as the solvent of choice need not be very polar in nature. This is especially true when taken together with ^{1}H, ^{19}F HOESY measurements,[7−10] which often permit a relatively exact placement of the anion in three-dimensional space.

Generally, the PGSE NMR methodology is fairly rapid for both ^{1}H and ^{19}F (ca. 2 h) and requires only small quantities of material (usually 1−2 mM solutions). Several components of a mixture can be measured simultaneously (as long as they afford well-resolved NMR signals), which makes the technique especially valuable for solutions containing a number of compounds, for example, a mixture of diastereomeric compounds or perhaps several species in equilibrium. Low-temperature PGSE measurements are now routine, although the problem of convection must be surmounted.[11]

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PGSE data may also be presented as one component of a 2D spectrum in which the chemical shift is displayed in the first dimension and the diffusion coefficient in the second one. Such an experiment is called DOSY (diffusion ordered spectroscopy),[12,13] and has been referred to as "NMR chromatography", for its ability to facilitate and visualize the resolution and assignment of complex mixtures. DOSY has proven especially valuable where the molecules are relatively large.

We report, here, on an extension of our PGSE studies, with emphasis partially on ^{7}Li as the observed nucleus but also on THF as the solvent. ^{7}Li, as an NMR nucleus, is not as sensitive as either ^{1}H or ^{19}F, with the result that higher concentrations are necessary for good signal-to-noise ratios. There are only a few PGSE studies using ^{7}Li, and these often report[14] data from relatively concentrated solutions, which lead to questions with respect to aggregation effects;[15] nevertheless, we believe that, taken together with a suitable Overhauser measurement, there is much to be learned. THF is a frequently used solvent but has received relatively little attention as a solvent for diffusion measurements. We show, here, ^{1}H and ^{19}F diffusion data for a selection of small, medium, and large BF_4^- salts in THF solution and suggest that THF generally promotes strong ion pairing.

Results and Discussion

Lithium Salts. The trinuclear η^6 *p*-cymene ruthenium cluster, abbreviated as **1**, provides an illustrative example (See Chart 1). Severin and co-workers[16] have reported the synthesis of this material, and the various ^{1}H, ^{19}F, and ^{7}Li *D* values are shown in Table 1. In both dichloromethane and tetrahydrofuran solutions, one finds that the three nuclei afford identical values within the experimental error, indicating that not only is the lithium atom bound via the bridging oxygen atoms but the tetrafluoroborate anion is closely associated with the lithium cation. Often in THF solution, the $Li(THF)_4^+$ cation is quite stable, for example, as in the $Li(PPh_2)$ salt.[14a] Such a tetrakis THF Li cation would afford a ^{7}Li *D* value corresponding to a hydrodynamic radius, r_H[17] of ca. 4.8−5.0 Å;[14a,b] however, obviously, this is not the case for **1**.

Chart 1. Complex **1** (the Circle Represents an Abbreviation for the η^6 *p*-Cymene Ligand)

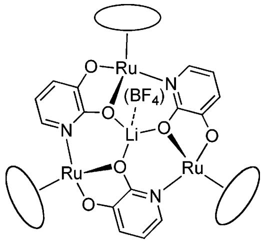

Table 1. *D* (10^{-10} m^2 s^{-1}) and r_H Values for Several Li$^+$ and BF_4^- Salts at Ambient Temperature

compound	solvent	concentration	nucleus	$D^{a,b}$	r_H (Å)
1	CD_2Cl_2	2	^{1}H	8.22	6.4
			^{19}F	8.22	6.4
			^{7}Li	8.26	6.4
1	THF-d_8	10	^{1}H	6.93	6.8
			^{19}F	7.06	6.7
			^{7}Li	7.08	6.7
$LiBF_4$	THF-d_8	10	^{19}F	11.68	4.2
			^{7}Li	11.90	4.1
$LiBF_4$	THF-d_8	60	^{19}F	10.95	4.4
			^{7}Li	10.90	4.4
$LiBF_4$	MeOH-d_4	60	^{19}F	16.3	2.5
			^{7}Li	9.96	4.1
$LiBF_4$	DMF-d_7	60	^{19}F	11.9	2.2
			^{7}Li	5.84	4.5
$Bu_4N(BF_4)^c$	THF-d_8	2	^{1}H	9.15	5.2
			^{19}F	9.36	5.1
$Bu_4N(BF_4)$	THF-d_8	60	^{1}H	7.37	6.4
			^{19}F	7.53	6.3
5 (as a BF_4 salt)	THF-d_8	2	^{1}H	7.78	6.1
			^{19}F	9.17	5.2
5	THF-d_8	20	^{1}H	7.18	6.6
			^{19}F	8.03	5.9
5	CD_2Cl_2	2	^{1}H	9.72	5.5
			^{19}F	13.79	3.9
5	MeOH-d_4	2	^{1}H	7.58	5.5
			^{19}F	16.62	2.5

[a] Experimental error is ±2%. [b] The viscosities (× 10^{-3} kg m^2 s^{-2}) η used in the Stokes−Einstein equation are (THF), 0.461; (CH_2Cl_2), 0.414, (MeOH), 0.533; (DMF), 0.834; ($CHCl_3$), 0.524. For $LiBF_4$, the lithium resonances are found between 0.98 and −0.58 ppm. [c] The ^{1}H and ^{19}F *D* (and r_H) values for a 2 mM solution of $Bu_4N(BF_4)$ in $CDCl_3$ are 8.23 (5.1) and 8.21 (5.1), respectively, thus supporting 100% ion pairing in this solvent.

The *D* and r_H values[17] for the salt $Li(BF_4)$, **2**, in three solvents are also shown in Table 1. On the basis of the almost identical *D* values for both the cation and anion in 10 and 60 mM THF solutions, we suggest that this salt is strongly ion paired in these solutions. The differences in *D* values between the two concentrations are likely to arise from aggregation effects.[18] The methanol and DMF measurements for **2** confirm that, in a relatively polar solvent, the ions can

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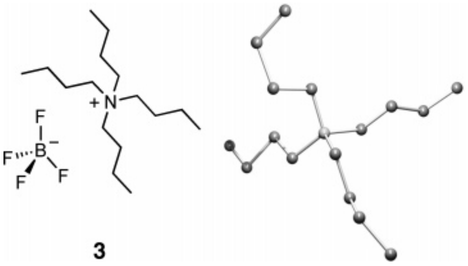
Chart 2. Complex **3**



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be well-separated, even at this relatively high concentration. The r_H value[17] for the BF_4^- anion in DMF is relatively small, ca. 2.2 Å, and that found in methanol solution, ca. 2.5 Å, is close to that found for a number of other BF_4^- anions in methanol solution.[2b,5a]

Salts in THF Solution. The diffusion results for the salt (n-Bu_4N)(BF_4), **3** (see Chart 2), in 2 mM and 60 mM THF solutions, also suggest strong—almost 100%—ion pairing. The calculated r_H values, ca. 6.3−6.4 Å, at 60 mM, seem rather large, suggesting aggregation. However, the 2 mM data afford r_H values around 5.1−5.2 Å, which are (a) in agreement with the estimated r_H of ca. 5.3 Å, from the reported solid-state structure[19] for the Bu_4N cation entrapped in a cationic host [made up of a tetrahedral coordination cage containing 24+ charges with $M_{12}L_6$ stoichiometry where M = (en)Pd^{2+} and L denotes a 1,4-bis(3,5-pyrimidyl)benzene], and (b) close to the r_H value, ca. 4.9 Å, calculated from the diffusion data of Pochapsky et al. for the Bu_4NCl in a 1.5 mM chloroform solution.[20a]

Having shown that THF promotes close to 100% ion pairing in several of our salts, we note that this need not be general. In their diffusion studies, Hayamizu et al.[14g] found ca. 64% association in THF solutions of $LiN(SO_2CF_3)_2$. In any case, this is still a very substantial amount.

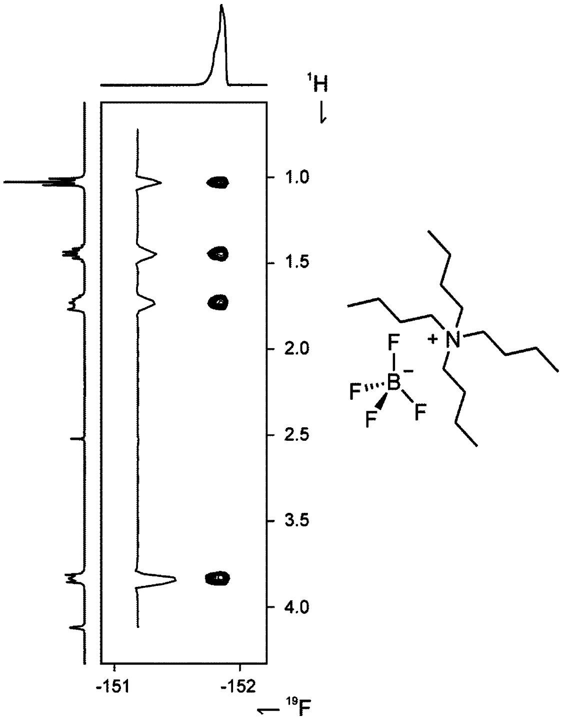
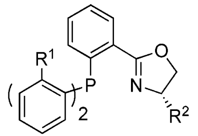


Figure 1. ^{1}H,^{19}F HOESY spectrum of **3** in THF solution showing the relatively strong cross-peaks to *all* of the n-butyl protons in keeping with the proposed strong ion pairing; however, the cross-peak to the NCH_2 resonance is the strongest. Note that the two isotopes of boron are not well-resolved in this solvent. See also Supporting Information Figure 1, which more clearly demonstrates the relative strengths of the cross-peaks in **3**.

Chart 3. Complex **4** (R^1 = CH_3 and R^2 = t-butyl)



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The ^{1}H, ^{19}F HOESY spectrum of **3** in THF solution is helpful (see Figure 1).[20c] One finds relatively strong cross-peaks to *all* of the n-butyl protons in keeping with the proposed strong ion pairing; however, the cross-peak to the NCH_2 resonance is the strongest, suggesting that the fluorine atom is nestled close to the *N* atom, although this is certainly not a static structure.

The NMR characteristics for the iridium-based cationic hydrogenation catalyst precursor, [Ir(1,5-COD)(**4**)](BF_4) (**5**; see Chart 3), have been studied in some detail[21] and have been recently subjected to PGSE measurements.[2b] In methanol, the ions of **5** are well separated; that is, the r_H value for the BF_4^- anion is ca. 2.5 Å; however, in dichloromethane, there is a significant amount of ion pairing, as indicated by the r_H value of 3.9 Å. However, on the basis of the observed *D* values (Table 1) for the anions in the two THF solutions, it seems that the ion pairing is even more pronounced. The r_H value of the cation increases from ca. 5.5 Å to ca. 6.1 Å (for the 2 mM solution), and the r_H value for the anion in THF is now relatively large at ca. 5.2 Å.

Diffusion data in THF solution for the crown ether stabilized potassium salt, [K(18-crown-6)(NPh_2)], **6**, are

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(17) The hydrodynamic radii, r_H, were calculated from the Stokes−Einstein equation $D = (k_BT)/(6\pi\eta r)$, where D is the diffusion coefficient, k_B is the Boltzman constant, T is the temperature in Kelvin, and η is the viscosity of the solution. It has been suggested that the factor c (= 6 in the equation) is not valid for small species whose van der Waals radii are <5 Å (Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261). This factor can be adjusted by using a semiempirical approach (see Chen, H.-C.; Chen, S.-H. *J. Phys. Chem.* **1984**, *88*, 5118. Espinosa, P. J.; de la Torre, J. G. *J. Phys. Chem.* **1987**, *91*, 3612) derived from the microfriction theory proposed by Wirtz and co-workers (Gierer, A.; Wirtz, K. *Z. Naturforsch. A* **1953**, *8*, 522. Spernol, A.; Wirtz, K. *Z. Naturforsch. A* **1953**, *8*, 532), in which the correction factor, c, is expressed as a function of the solute-to-solvent ratio of radii: $c = 6/\{1 + [0.695\ (r_{solv}/r_H)^{2.234}]\}$. To be consistent and facilitate comparisons with our earlier reports, we have used the Stokes−Einstein equation as shown ($c = 6$) in Tables 1 and 2. However, we recognize that for the organic compound aniline or for the salt Li(BF_4), **2**, a smaller c value would be better. Supplementary Table 1 (Supporting Information) shows two sets of r_H values calculated with (a) $c = 6$ and then (b) with the appropriate corrected c value (e.g., $c = 5.3$ for aniline in THF).

(18) Aggregation in fairly polar alcohol solvents is now well-recognized (see ref 15). A 60 mM solution is convenient for measuring ^{7}Li, as this is not a very sensitive nucleus; however, at this concentration, aggregation effects are likely to be significant.

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Table 2. D ($\times$ 10^{-10} m^2 s^{-1}) and r_H (Å) Values[a] for [K(18-crown-6)(NPh$_2$)] (**6**), Ph$_2$NH, and 18-crown-6, All in THF-d_8 at 299 K

	nucleus	D^b	r_H	R^c
6	^{1}H (Ph$_2$N$^-$)	8.54	5.6	
	^{1}H (K$^+$,18-crown-6)	8.44	5.6	
Ph$_2$NH	^{1}H	13.82	3.5	3.6
18-crown-6	^{1}H	12.69	3.7	4.3

[a] 43 mM. [b] Experimental error is ca. ±2%. η (THF, 299 K) = 0.461 $\times$ 10^{-3} kg s^{-1} m^{-1}. [c] Estimated by using Chem3D, averaging the distances between the centroid and the outer hydrogen.

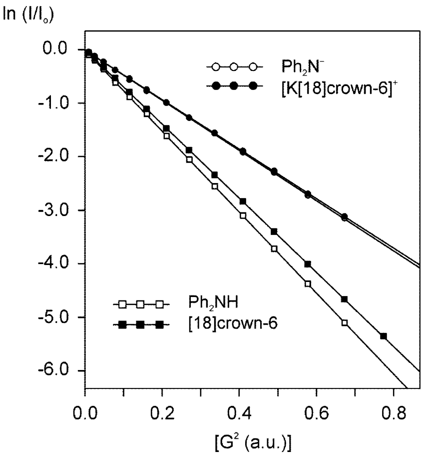
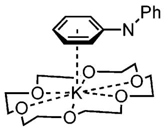


Figure 2. Plot of the ln(I/I_0) vs arbitrary units proportional to the square of the gradient amplitude for ^{1}H PGSE diffusion measurements on a 43 mM solution at 299 K in THF. ^{1}H (δ = 1.5 ms; Δ = 118 ms). Note that the lines, from the data for the complexed crown ether and the anion, have almost the same slope.

Chart 4. Complex 6 (Solid-State Structure)



given in Table 2. For comparison, D values for Ph$_2$NH and the free crown ether are also provided, and the measurements leading to all of these results are displayed in Figure 2. The solid-state structure for this salt has been determined (see Chart 4)[22] and reveals a π interaction between one of the aniline rings and the potassium atom, as indicated above. On the basis of the diffusion data, the anilide anion and crown ether are moving at about the same rate; that is, there is a strong interaction between these two species, leading to r_H values that are much larger than those of either of the two separate components. However, the ^{1}H spectrum for **6** shows that the two N-phenyl groups are equivalent on the NMR time scale. Further, the ^{1}H,^{1}H NOESY spectrum of **6** (Figure 3) reveals strong selective contacts from the crown ether methylene protons to the *ortho* and *meta* phenyl protons, with the former stronger than the latter. There are no contacts to the *para* protons, so that this position must be remote from the crown ether; that is, the structure shown above is not correct. Consequently, in THF solution, we favor an ion-paired structure in which the NPh$_2$ anion approaches the complexed potassium cation via the N atom, thus bringing the *ortho* and *meta*, but not the *para*, phenyl protons proximate to the crown ether ring. It is no longer unusual to find that the solid-state and solution structures are different.

Comments. The use of ^{7}Li as an additional diffusion probe nicely complements the now classical ^{1}H and ^{19}F measurements. Unfortunately, the need to work at higher concentrations can lead to aggregation, and the resulting D values require more care in interpretation. It is not always necessary to use 60 mM solutions for the ^{7}Li measurements; however, even 10 mM solutions are likely to suffer from aggregation effects.[15] Further, the ^{7}Li (2 mM) measurements require considerably more instrument time (i.e., overnight vs ca. 2h for ^{1}H or ^{19}F).

For all of the salts discussed here, and these range from the relatively simple Li(BF$_4$) to the fairly large iridium species, **5**, the use of THF seems to promote ion pairing. This is readily seen via the comparison of the D values for the BF$_4$ anion of **5** in the three solvents: methanol, dichloromethane, and THF. We note that the dielectric constants[23] for these solvents are 33.62, 9.08, and 7.54, respectively, so that the observed trend is not completely unexpected.

Finally, it would appear that, upon solution in THF, the potassium salt, **6**, prefers to exist as an a more classical ion pair rather than as the π complex found in the solid state. Once again, this emphasizes how important the solvent can be for the solution structure of salts.

Experimental Section

All PGSE experiments were carried out using standard sequences.[24,25]

Mathematically, the diffusion part of the echo amplitude can be expressed as shown:

$$\ln\left(\frac{I}{I_0}\right) = -(\gamma\delta)^2 G^2\left(\Delta - \frac{\delta}{3}\right)D$$

where G is the gradient strength, Δ is the delay between the midpoints of the gradients, D is the diffusion coefficient, and δ is the gradient length.

The diffusion coefficient D, which is proportional to the slope of the regression line, is obtained by plotting ln(I/I_0) (I/I_0 = observed spin−echo intensity/intensity without gradients) versus either Δ, δ^2 ($\Delta - \delta/3$), or G^2.

The measurements were performed on a 400 MHz Bruker AVANCE spectrometer equipped with a microprocessor-controlled gradient unit and an inverse multinuclear probe, with an actively shielded z-axis gradient coil. The shape of the gradient pulse was rectangular, and its strength varied automatically during the course of the experiments. The measurements were carried out without spinning. The ^{1}H spectra were referenced to TMS as an external standard. ^{7}Li and ^{19}F chemical shifts are referred to external LiCl for ^{7}Li (155.4 MHz) and CFCl$_3$ for ^{19}F (376.4 MHz). The sample temperature was calibrated, before the PGSE measurements, by introducing a thermocouple inside the bore of the magnet. The calibration of the gradients was carried out via a diffusion

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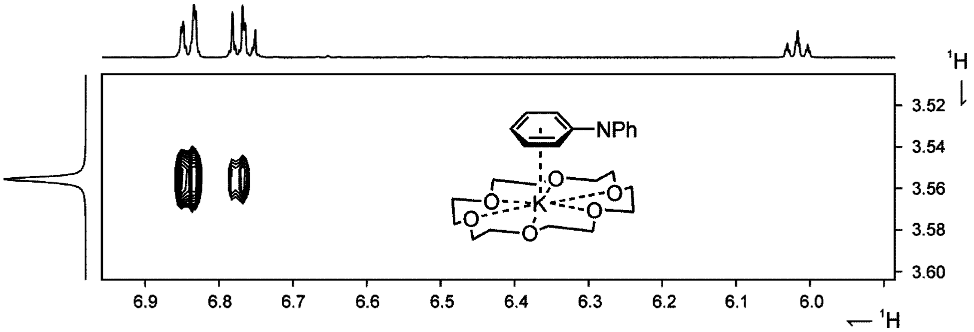

Figure 3. ^{1}H, ^{1}H NOESY spectrum of **6** (revealing the selective contacts from the crown ether methylene protons to the *ortho* and *meta* phenyl protons, with the former stronger than the latter). There are no contacts to the para protons. Note that the two phenyl rings are equivalent.

measurement of HDO in D_2O, which afforded a slope of 2.022×10^{-4}. We estimate the experimental error in the D values at ±2%. All of the data leading to the reported D values afforded lines whose correlation coefficients were >0.99, and 8−12 points have been used for regression analysis. To check reproducibility, three different measurements with different diffusion parameters (δ or Δ) were always carried out. The gradient strength was incremented in 8% steps from 10% to 98%. A measurement of ^{1}H, ^{19}F, and ^{7}Li T_1 was carried out before each diffusion experiment, and the recovery delay was set to 5 T_1.

In the ^{1}H−PGSE experiments, δ was set to 1.75 or 2 ms. The number of scans varied between 16 and 64 per increment with a recovery delay of 10−30 s. Typical experimental times were 2−3 h.

For ^{7}Li, the gradient lengths were typically $\delta = 2{-}4$ ms. The number of scans was usually between 64 and 256 with a recovery delay of 10−30 s and a total experimental time of ca. 3−10 h.

For ^{19}F in BF_4^-, δ was usually set to 1.75 or 2 ms. A total of 128−256 scans were taken with a recovery delay of 5−15 s and a total experimental time of ca. 2−4 h.

The ^{19}F, ^{1}H HOESY measurements were carried out with a doubly tuned (^{1}H, ^{19}F) TXI probe. A mixing time of 800 ms was used, and 32 scans were taken for each of the 512 T_1 increments recorded. The ^{19}F T_1 value for Bu_4NBF_4 was 1.3 s, and the delay between increments was set to 5 s.

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Supporting Information Available: Table 1 shows two sets of r_H values calculated with $c = 6$ and then with the appropriate corrected c value. Figure 1 more clearly demonstrates the relative strengths of the cross-peaks in **3**. This material is available via the Internet at http://pubs.acs.org.

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