Table IV. Nmr Chemical Shifts[a] for Complexes of Glymes with Fluorenyl$^-$,Na^+ and Fluorenyl$^-$,K^+ in THF at 40°

System	Glyme peaks[b] CH_3	CH_2 (ext)	CH_2 (int)
Glyme-4, -5, -6, and -7	6.73	6.51	6.47
F^-,Li^+-glyme-5 (1:1)	7.23	7.13	7.05
F^-,Na^+-glyme-7 (1:1)	6.98	6.96	6.95
F^-,Na^+-glyme-6 (1:1)	7.03	6.97	6.95
F^-,Na^+-glyme-5 (1:1)	6.98	6.97	
F^-,Na^+-glyme-4 (1:1)	7.00	6.97	
F^-,Na^+-glyme-4 (1:2)	6.94	6.90	
F^-,K^+-glyme-4 (1:1)	6.95	6.93	
F^-,K^+-glyme-7 (1:1)	7.01	6.95	

[a] In τ scale downfield from TMS. [b] Assignments of glyme proton peaks is only certain in the pure glymes, but not in the complexes. Some of the peaks also move considerably more upfield at lower temperatures.

One expects therefore two glyme-4 molecules coordinated to a glyme-4-separated F^-,Na^+ ion pair.

To check this point further, we looked at the nmr spectrum of glyme-4 in a mixture of 0.2 *M* of F^-,Na^+ and 0.44 *M* of glyme-4 in THF. The optical absorption spectrum shows approximately 75% glyme-separated ion pairs (peak overlap makes calculation of ion pair fractions from the visible region of the optical absorption spectrum less reliable). More important, the chemical shifts of the glyme protons are still very close to those of an equimolar solution of glyme-4 and F^-,Na^+ in THF.

This is an another strong indication that the glyme-4-separated F^-,Na^+ ion pairs actually contain two glyme-4 molecules (the slightly larger than 2:1 ratio of glyme-4 to F^-,Na^+ should of course bring the peaks somewhat downfield because of the free ether which is present, and even at an exact 2:1 ratio there is still some free glyme present). On the other hand, the nmr spectrum of a THF solution containing a 2:1 ratio of *glyme-5* over F^-,Na^+ was close to the weighted average of the spectra for pure glyme-5 and that of a 1:1 ratio of glyme-5 to F^-,Na^+. In this case the glyme-separated ion pair contains only one glyme-5 molecule, and the noncoordinated glyme will rapidly exchange with the coordinated glyme. No nmr measurements were done for systems containing glyme-3, but it is not unlikely that the separated ion pairs with both F^-,Li^+ and F^-,Na^+ also contain two glyme-3 molecules.

Nmr data for F^-,K^+ and glymes in THF show that a mixture of 0.25 mol of F^-,K^+ and 0.25 mol of glyme-4 yields essentially the same upfield shift for the glyme protons as a mixture of 0.3 mol of F^-,K^+ and 0.3 mol of glyme-7 (see Table IV). However, one determines from the visible region of the optical absorption spectrum that the former mixture contains only 20% glyme-separated ion pairs in THF at 25° and the latter mixture close to 80%. From a calculation of the known K_2 values (see Table III) the respective percentages are expected to be 20 and 70%, which is indeed close to the experimental values. The almost identical chemical shifts for the glymes in the two systems suggests, therefore, that practically all the glyme-4 is bound to the potassium salt, but mainly in the form of a glymated contact ion pair. This observation supports therefore the conclusions arrived at from our optical absorption data, namely that the glyme-4 coordinates first externally to F^-,K^+ and that a second glyme-4 molecule is needed to convert these ion pairs to glyme-separated ones.

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A Corrected Primary Solvation Number of Magnesium(II) in Liquid Ammonia

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Abstract: The primary solvation number of magnesium(II) in anhydrous liquid ammonia has been redetermined and been found to be six. The redetermination incorporates an improved procedure for obtaining anhydrous solutions and the use of a proton nmr complete line-shape analysis.

Magnesium(II) represents one of the few metallic cations for which solvation numbers in solution can be obtained by straightforward proton magnetic resonance signal integration.[1-4] In three of the solvents studied, methanol,[1] water,[3] and aqueous acetone,[4] the primary solvation number is six while in the third, ammonia, it was measured as five.[2] Because of the biochemical inportance of Mg(II)–nitrogen coordination such five-coordination should be investigated further to

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[1] S. Nakamura and S. Meiboom, *J. Amer. Chem. Soc.*, **89**, 1765 (1967).

[2] T. J. Swift and H. H. Lo, *ibid.*, **89**, 3988 (1967).

[3] N. A. Matwiyoff and H. Taube, *ibid.*, **90**, 2796 (1968).

[4] A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *Chem. Commun.*, 173 (1968).

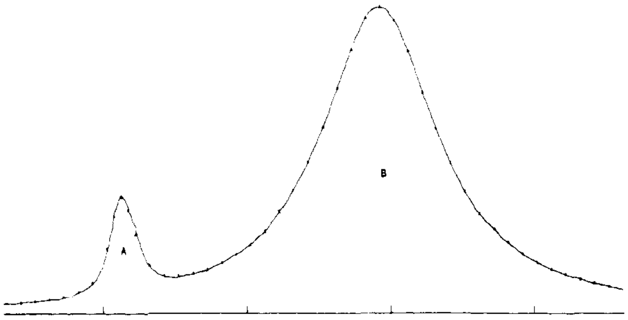

Figure 1. The pmr spectrum of a $Mg(ClO_4)_2$–liquid ammonia solution of $[Mg]/[NH_3] = 1.03 \times 10^{-2}$ and 0.01 M in $Cu(ClO_4)_2$, at a temperature of −75°. Peak A is due to the primary solvation-sphere ammonia and peak B is from the bulk ammonia. The continuous line is the experimental spectrum, and the X's are from the computer calculated spectrum. The markers are drawn 50-Hz apart.

see if it arises for instance from contact ion pairing. In addition, the recent paper of Dewald and Tsina[5] leads us to believe that the previously[2] studied "anhydrous" ammonia solutions could have contained significant amounts of water. In that study "anhydrous" solutions were prepared from aquated magnesium salts with drying involving repeated distillation of the solvent ammonia in and out of a potassium–ammonia solution. The recent observation by Dewald and Tsina that water could coexist with potassium in liquid ammonia makes it imperative that the solutions be prepared in such a way that it is impossible for water to be present. We have found in this laboratory that relatively stable solutions of potassium in liquid ammonia can be prepared containing nearly 1 M water. Ammonia is now dried in this laboratory by repeated distillation in and out of a potassium amide solution prepared by the decomposition of a potassium–ammonia solution over platinum black.

Another possible source of error can be eliminated by going over to complete line-shape analysis of the proton spectra. This was not done originally because of phasing problems arising from the large ratio of bulk to bound solvent, a consequence of the limited solubility of Mg(II) salts in liquid ammonia.

The first of the two problems was solved by reacting magnesium metal with the appropriate ammonium ion salt in anhydrous ammonia. Hydrogen is rapidly evolved and the solution is easily prepared.

The second problem was surmounted by adding a small concentration of Cu(II) to the solution in order to broaden the bulk peak. This effectively worsens the resolution, but it also considerably lessens the phasing problem and a good line-shape analysis can be performed.

Experimental Section

All solutions were prepared under anhydrous conditions using high-vacuum-line techniques. Reagent grade magnesium shavings were treated with an excess of dried NH_4BF_4 or NH_4ClO_4 in liquid ammonia which had been previously dried by the amide technique. The nearly saturated solutions were approximately 0.35 M in Mg(II) and 0.1 M in NH_4^+. The magnesium(II) solution was then passed through a fritted-glass filter on the vacuum line into a compartment containing enough dried $Cu(NH_3)_4(BF_4)_2$ or $Cu(NH_3)_4(ClO_4)_2$ to make the resulting solution *ca.* 0.01 M in Cu(II). The nmr sample tube was then filled and sealed and proton spectra were recorded on a Varian A-60A spectrometer equipped with a V-6040 temperature control unit.

The solutions were analyzed for free NH_3 by distilling onto concentrated H_2SO_4. The remaining ammonia was analyzed by acid–base back-titrations and the Mg^{2+} by EDTA titration.

Results

The proton spectrum of a typical $Mg(ClO_4)_2$–ammonia solution is shown in Figure 1. Complete line-shape analysis of this and the other spectra were accomplished through use of the equation and techniques employed by Wawro and Swift.[6] In all cases the spectra could be fit extremely well, as is illustrated in Figure 1. With both the perchlorate and the fluoroborate salts the measured solvation number was 5.9 ± 0.1. Hence the ammonia result is completely in agreement with those for water and methanol as indicating a solvation number of six.

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[5] R. R. Dewald and R. V. Tsina, *J. Phys. Chem.*, 72, 4520 (1968).

[6] R. G. Wawro and T. J. Swift, *J. Amer. Chem. Soc.*, **90**, 2792 (1968).