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^{6}Li and ^{15}N Nuclear Magnetic Resonance Studies of Mixed Alkali Metal Cation Hexamethyldisilazide Bases

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We report the results of NMR studies on the solution structure of the mixed, lithium potassium hexamethyldisilazide dimer **1**, which we isolated and characterized by X-ray diffraction analysis.[2] Related mixed alkali metal cation aggregates are proposed as reactive superbases by both Lochmann and Schlosser.[3] The ^{6}Li- and ^{15}N-enriched alkali metal bases used in the NMR studies[4] were prepared by the deprotonation of [^{15}N]hexamethyldisilazane (HMDS)[5] using [^{6}Li]-*n*-BuLi[6] and potassium hydride, and purified by published procedures.

Detailed NMR solution and theoretical studies of various aggregates of LiHMDS were recently reported by Collum and co-workers.[7] Previous work by this group suggests that mixed *anion* amide base aggregates form in solution, in particular mixed amide/halide aggregates, and that these differ in reactivity from the pure amide anion aggregates.[8] To the best of our knowledge, no NMR work to date addresses the existence and/or integrity in solution of simple mixed alkali metal *cation* HMDS aggregates such as **1**.[9] The first unambiguous evidence for the existence of the mixed cation HMDS dimer **1** in solution is presented in Figure 1.[10]

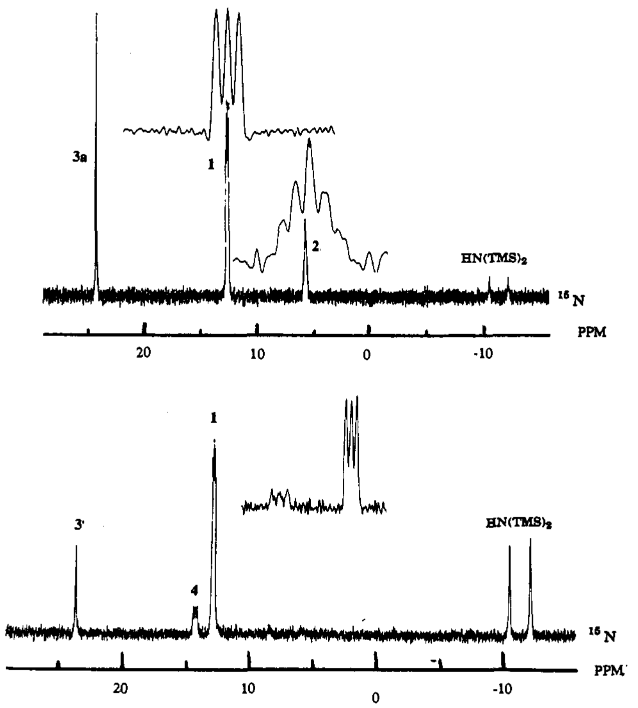

Figure 1. ^{15}N NMR spectra for the [^{6}Li,^{15}N]LiHMDS·[^{15}N]KHMDS mixture in toluene-d_8 at −80 °C. Spectrum I (top) was recorded in the presence of 4 equiv of THF. Labeled resonances correspond to the LiHMDS·KHMDS·3THF dimer complex **1**; (LiHMDS·THF)$_2$ dimer complex **2**; and KHMDS dimer **3a**. The ratio of the ^{15}N NMR resonances is 1:2:1 (**3a**:**1**:**2**). Spectrum II (bottom) was recorded in the presence of 4.4 equiv of TMEDA and 1.1 equiv of THF. Labeled resonances correspond to the LiHMDS·KHMDS·3THF dimer complex **1**; a KHMDS dimer complex (**3a** or **3b**); and LiHMDS·TMEDA monomer **4**. The ratio of the ^{15}N resonances is 1:1:5 (**3**:**4**:**1**). The inset expansions of resonances were calculated using Gaussian multiplication.

Spectrum I in Figure 1 is the ^{15}N NMR spectrum of an equimolar LiHMDS (0.150 M) and KHMDS (0.150 M) solution in toluene-d_8 in the presence of 4 equiv of THF recorded at −80 °C and clearly depicts three cleanly resolved species with an integration ratio of roughly 1:2:1. On the basis of the multiplicity of the ^{15}N resonances,[11] the quintet (δ 5.7) is the previously observed bis-THF solvated LiHMDS dimer **2**;[6,7,12] the triplet (δ 12.7) is the mixed LiHMDS·KHMDS dimer **1**, most likely tris-THF solvated as in the X-ray crystal structure;[2] and the singlet (δ 24.3) is the pure KHMDS dimer **3a**.[13] The ^{6}Li NMR spectrum of this solution is consistent with these assignments. These spectra represent entry A in Table 1.

We undertook a series of NMR experiments to probe the effect of ligand or cosolvent on the formation of the mixed alkali metal HMDS dimer **1**. In the presence of only TMEDA (entry B), the LiHMDS·TMEDA monomer **4** (a doublet and triplet in the ^{6}Li and ^{15}N NMR spectra, respectively) and the KHMDS·TMEDA dimer **3b** (a triplet in both the ^{6}Li and ^{15}N NMR spectra) were observed. *No mixed alkali metal HMDS* aggregates were observed. Spectrum II in Figure 1 is the ^{15}N NMR spectrum recorded after addition of 1.1 equiv of THF (entry C in Table

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[5] Prepared directly from [^{15}N]NH$_3$ (99% from Cambridge Isotope Laboratories) and trimethylsilyl chloride in the presence of ethylenediamine. The procedure was adapted from the following: Boersma, R. P.; Mendicino, F. D.; Omietanski, G. M. Union Carbide Corp., U.S. Pat. 3,809,713 issued 7 May 1974.

[6] ^{6}Li metal was purchased from Martin Marietta Energy Systems, Inc., operating contractor for the Oak Ridge National Laboratory. The synthesis of [^{6}Li]-*n*-BuLi and the purifications of the bases are given in the following: Nichols, M. A.; McPhail, A. T.; Arnett, E. M. *J. Am. Chem. Soc.* **1991**, *113*, 6222–33.

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[10] In contrast, mixed cation species were not observed in THF solution with cesium alkoxides and alkyl lithium reagents. See: Bauer, W.; Lochmann, L. *J. Am. Chem. Soc.* **1992**, *114*, 7482–9.

[11] The splitting of the ^{6}Li and ^{15}N resonances is governed by the equation $2nI + 1$, where n is the number of attached nuclei and I is the spin number of the attached nuclei. ($I = 1$ for ^{6}Li and $^{1}/_{2}$ for ^{15}N, respectively.) ^{39}K does not couple with ^{15}N. Note that the chemical shift of the ^{15}N nucleus is dependent upon the cation attached: Li, $\delta = 6.0$ ppm; K, $\delta = 24$ ppm; Cs, $\delta = 47$ ppm; Nichols, M. A.; Williard, P. G. Unpublished results.

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[13] These NMR experiments do not allow us to distinguish unambiguously the KHMDS complexes **3**. Therefore, we will identify only the KHMDS complex and not the coordinating solvent, although we also have obtained the crystal structures of both bis-THF solvated and tetra-THF solvated dimeric KHMDS **3a** and chelated, bis-TMEDA solvated KHMDS **3b**; Nichols, M. A.; Williard, P. G. Unpublished results.

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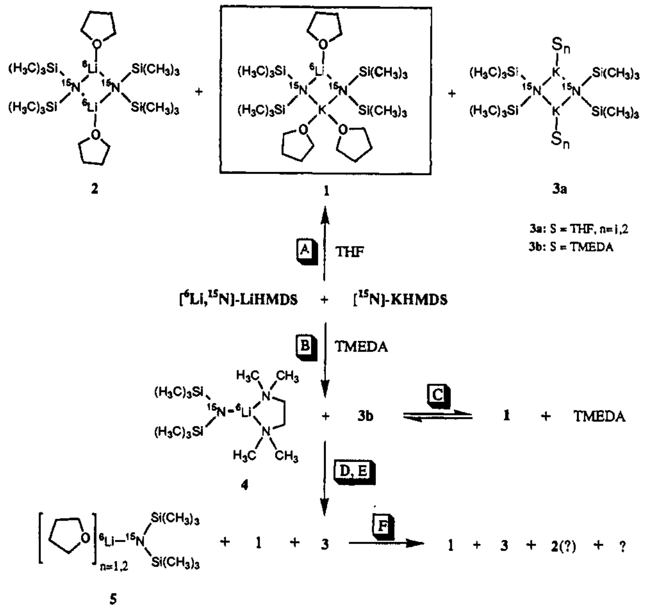
Table 1. Relative Ratios of Aggregates[a] by ^{15}N and ^{6}Li NMR Integration

	equiv[b] of added ligand		relative ratio of complexes					
entry	THF	TMEDA	**1**	**2**	**3**	**4**	**5**	other
A	4.0		2	1	1[c]			
B		4.4			1[d]	2		
C	1.1	4.4	5		1	2		
D	2.2	4.4	5		1		2	
E	3.3	4.4	5		1		2[e]	
F	6.6	4.4	5	[f]	1		[f]	[f]

[a] All solutions are in toluene-d_8. [b] Equivalents/HMDS base. [c] Only **3a** formed. [d] Only **3b** formed. [e] The NMR resonances broadened, probably due to increased THF exchange. [f] The concentrations were not determined.

Scheme 1 [a]



[a] Lettered solvent and reagent conditions correspond to entries in Table 1.

1). Three different HMDS aggregates were observed: (a) the LiHMDS·KHMDS dimer **1**, the triplet at δ 12.6; (b) a homonuclear KHMDS aggregate (probably a TMEDA solvated dimer), the singlet at δ 23.5; and (c) a LiHMDS monomer, the triplet at δ 14.0 in the ^{15}N NMR spectrum and a doublet in the ^{6}Li NMR spectrum. Mixed dimer **1** is clearly the major species in solution, and virtually all the THF can be accounted for if a tris-solvated aggregate is assumed. The addition of even small amounts of THF to the solution ($^{1}/_{4}$ equiv relative to TMEDA) effects formation of mixed alkali metal dimer.

As increasing amounts of THF are added to this solution, changes in the solvation and aggregation state of LiHMDS occur although the ratio of the mixed cation dimer **1** and the KHMDS dimer do not change substantially (see Table 1). After addition of 2.2 equiv (per amide base) of THF (entry D), the ^{6}Li and ^{15}N NMR resonances corresponding to the LiHMDS monomer **4** are shifted upfield, whereas the chemical shifts of the mixed cation dimer **1** remain unchanged, indicating that the LiHMDS·TMEDA monomer **4** is now solvated (probably bis-solvated)[7] by THF (i.e., complex **5**). As more THF is added (entries E and F), the LiHMDS monomer resonances in both the ^{6}Li and ^{15}N NMR spectra broaden, indicating increased THF ligand exchange. When an excess of THF is present (entry F), several small ^{15}N NMR resonances are observed, one of which appears to be the bis-THF solvated LiHMDS dimer **2**. These results mirror Collum's observations of pure LiHMDS solutions[7] and also support his recent conclusion that THF competes favorably and perhaps even binds more strongly to the lithium cations in LiHMDS complexes than the chelating ligand TMEDA.[14]

Scheme 1 summarizes the results of these NMR experiments. In the presence of only THF, a statistical mixture (1:2:1) of the LiHMDS·THF dimer **2**, mixed LiHMDS·KHMDS·THF dimer **1**, and KHMDS·THF dimer **3a** is observed. In the presence of only TMEDA, the LiHMDS·TMEDA monomer **4** and KHMDS·TMEDA dimer **3b** are observed, with no NMR evidence of formation of mixed alkali metal HMDS aggregates. In the presence of both THF and TMEDA, the maximum amount of mixed dimer **1** formed approaches 82%. At this point, the addition of more THF leads to ligand substitution of THF for TMEDA on the LiHMDS monomer **4** forming the THF bis-solvated LiHMDS monomer **5**. Further addition of THF leads only to broadening of the ^{6}Li and ^{15}N NMR signals of the monomeric species, attributable to faster THF ligand exchange, and in the presence of a several equivalent excess of THF, only the THF solvated dimers **1** and **5** are identifiable along with several minor LiHMDS aggregates.

These results represent the first comparative NMR data for mixed alkali metal HMDS aggregates in solution. Presently we are unable to resolve unambiguously the issues of ligand coordination and the aggregation states of KHMDS (i.e., complex **3a** or **3b**), although correlation with our X-ray crystal structures suggests that dimers are formed. We anticipate that these results will provide the basis on which to continue structure–reactivity studies of this highly important and synthetically useful class of reactive intermediates.

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Supplementary Material Available: ^{6}Li and ^{15}N NMR spectra for entries in Table 1 (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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