# Identification of a Unimetal Complex of Bases by $^6$Li NMR Spectroscopy and Single-Crystal Analysis

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Much attention is now focused on the use of complex bases in organic synthesis, and many applications have been found for these versatile organometallic reagents.[1–3] It has long been thought that mixed bases exist as aggregates;[4] however, supporting evidence is generally derived from synthetic studies and more recently from model crystal structures.[5] Continuing our investigation of mixed-anion aggregates,[6] we now provide both crystallographic and NMR evidence for the existence of a new species consisting of a lithium alkoxide and an amidolithium both in solution and in the solid state. Related thermochemical studies of mixtures between lithium hexamethyldisilazide and potassium butoxide by Arnett and Moe also suggest some form of mixed aggregation in solution.[2]

Preparation of crystalline $[\{Pr^i_2NLi\}\cdot\{(Me_2NCH_2)_2CHOLi\}]_2$ (**1**) is achieved by separate lithiation of diisopropylamine (DPA) and 1,3-bis(dimethylamino)-2-propanol (DMP) with Bu$^n$Li in hexane at 0 °C. After mixing these two species and cooling the resultant mixture to −50 °C for 2 days, colorless crystals of **1** are deposited. These crystals are highly air sensitive and decompose upon removal of solvent but could be mounted directly from the reaction vessel to the diffractometer with care. The structure of **1**, shown in Figure 1,[7] consists of two four-membered LiNLiO rings connected through a four-membered LiOLiO ring giving rise to a four-rung ladder core (with two Li−O and two Li−N rungs).[8] Two five-membered LiOCCN rings edge share each of the terminal rings' Li−O bonds. The central ring LiOLiO also edge shares two such five-membered rings. Every terminal dimethylamine unit of the alkoxide chelates to an adjacent lithium atom. This structural motif presents two distinct lithium environments.

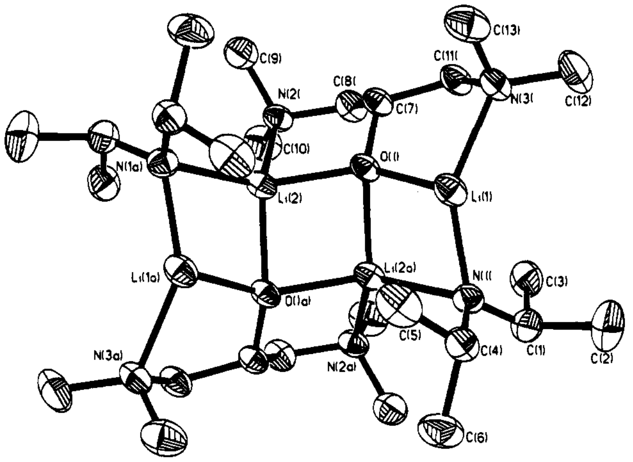

**Figure 1.** Computer-generated thermal ellipsoid plot of **1** at 30% probability (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Li(1)−O(1) 1.853(6), Li(1)−N(1) 1.936(6), Li(1)−N(3) 2.067(5), Li(2)−O(1) 1.944(6), Li(2)−O(1a) 2.000(5), Li(2)−N(2) 2.385(5), Li(2)−N(1a) 2.116(6), O(1)−Li(1)−N(1) 110.4(3), O(1)−Li(2)−O(1a) 96.3(3), N(1a)−Li(2)−O(1a) 98.2(2), O(1)−Li(2)−N(1a) 135.1(3), Li(1)−N(1)−Li(2a) 73.4(2), Li(1)−O(1)−Li(2a) 78.0(2), Li(2)−O(1)−Li(2a) 82.4(3), Li(1)−O(1)−Li(2) 143.3(2).

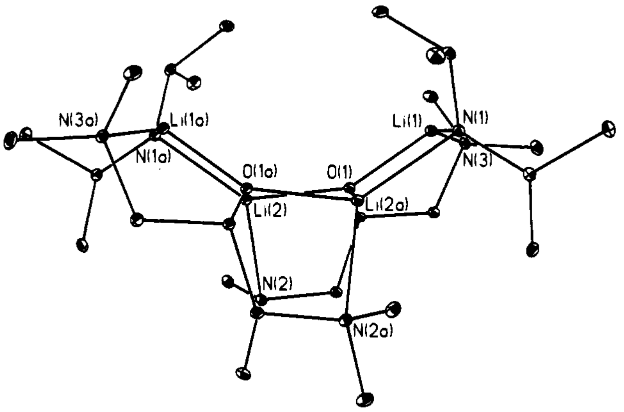

**Figure 2.** Computer-generated plot of **1** looking along the axis of the ladder core (thermal ellipsoids reduced to 3% probability for clarity).

The terminal lithiums, Li(1) and Li(1a), are three-coordinate, pseudo-trigonal-planar with the metal sitting 0.335 Å out of the O(1)N(1)N(3) plane. The angles at the three-coordinate lithium are very distorted from the ideal 120°, ranging between 92.7° and 148.4°. As expected, the Li(1)−O(1) bond is shorter than the Li(1)−N(1) amido bond, which in turn is shorter than the Li(1)−N(3) dative bond (1.853, 1.936, and 2.067 Å, respectively).

The central lithium atoms, Li(2) and Li(2a), display a rather different geometry, which is a distorted tetrahedral environment, achieved by chelation of one dimethylamine unit. The angles at Li(2) vary between 135.1° for O(1)Li(2)N(1a) and 83.9° for O(1)Li(2)N(2). For the tetracoordinate Li(2), the increase in coordination number at the metal leads to elongated Li−O and Li−N bonds relative to Li(1).

Four-rung ladders as found in **1** were previously considered to be formed by association of two dimers.[9] From an alternative perspective, the central lithium alkoxide dimer is complexed by two LDA monomers. This latter concept is consistent with the unusual solvation of the central lithium atoms. Heteroatom

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(7) Crystal data for **1**: $C_{26}H_{62}Li_4N_6O_2$, $M = 518.58$, monoclinic, $C2/c$, $a = 22.267(7)$ Å, $b = 10.420(4)$ Å, $c = 18.166(12)$ Å, $\beta = 121.94(3)°$, $V = 3577(3)$ Å$^3$, $Z = 8$, $d_{calc} = 0.963$ Mg/m$^3$, $\mu$(Mo K$_\alpha$) = 0.059 mm$^{-1}$, $F(000) = 1152$, $2\theta_{max} = 50°$, $T = 233$ K, 3840 measured reflections, 3161 independent reflections, 3160 reflections used in the refinement, structure solved by direct methods using SHELXTL, all non-hydrogen atoms anisotropic, $R(1) = 0.070$, $wR(1) = 0.167$, full matrix least squares refinement on $F^2$ using SHELXL-93.

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solvation of a central lithium atom in a four-rung ladder has not previously been noted, although agostic Li−H interactions were reported.[10,11] The central dimeric lithium alkoxide is stabilized by weak dimethylamine chelation in **1** with Li(2)−N(2) being 2.385 Å. This distance is expected to be shorter in a simple dimer. The distortion involved in LDA association is evident from the dihedral angle of 36.7° between the central and outer rings of the ladder, as seen in Figure 2.

Pure $^{6}$Li labeled lithium diisopropylamine ($^{6}$LDA) and the lithiated alcohol ($^{6}$LDMP) were prepared and their NMR spectra ($^{1}$H/$^{13}$C/$^{6}$Li) compared to that obtained from a 1:1 mixture of the bases.[12] $^{1}$H-, $^{13}$C-, and $^{6}$Li NMR spectra of the mixture $^{6}$LDA/$^{6}$LDMP exhibited appreciable differences compared to the spectra of the single bases (see supporting information). These spectra suggest that in solution a mixed-anion complex is formed between LDA and LDMP. The room temperature $^{6}$Li NMR spectrum of the mixture is seen in Figure 3 as four distinct signals.[13] The two largest peaks in a 1:1 ratio were identified as $^{6}$LDA and $^{6}$LDMP from their chemical shift values. Two smaller signals sit in between these peaks and represent approximately 17% of the sum of the integration. These latter peaks integrate into a 1:1 ratio, which is consistent with the crystal structure of **1**, *i.e.*, Li(1) and Li(2) in electronically inequivalent environments. In contrast, Bauer and Lochmann reported no observable mixed aggregate between lithium trityl and cesium 3-ethyl-3-heptoxide.[14]

Very recently the first spectroscopic evidence for complex base formation was reported as the $^{23}$Na MAS NMR spectrum of NaNH$_2$/Bu$^t$ONa (2:1).[15] To our knowledge, the $^{6}$Li NMR spectrum of **1** is the only evidence reported of a mixed aggregate between an amidolithium and a lithium alkoxide, although Collum notes the possibility of such a species.[13a] When the solution of our mixture of LDA/LDMP is cooled to −80 °C, a more complex spectrum is obtained in which $^{6}$LDA and $^{6}$LDMP are both still present but numerous new signals appear. These signals may arise by formation of new oligomers and by slowing of the on/off chelation of the dimethylamido side arm as well as by solvent attack.[3d] It is noteworthy that the most reactive species in solution may be present in relatively small amounts. Even though only 17% of mixed base is observed at room temperature, this component may be important in the reactivity of the mixture.

In conclusion, we have unambiguously assigned the structure of a unimetal complex of bases in the crystal and observed evidence of retention of this aggregate in solution. Since known superbases contain constituents similar to **1**, the structure described represents a model for future research.

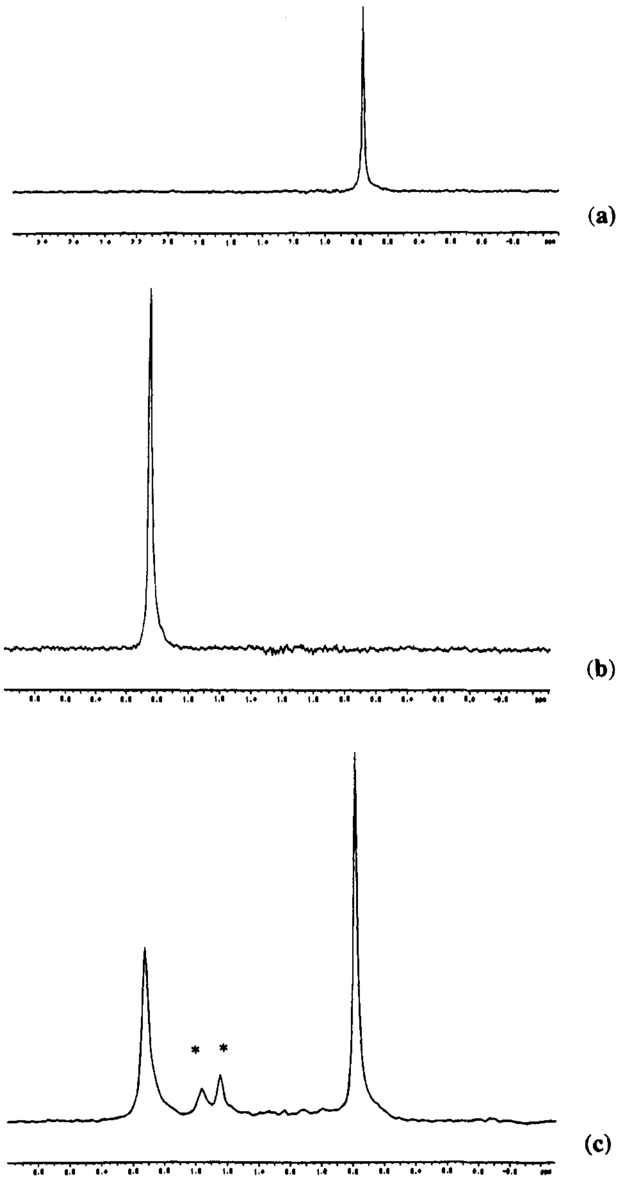

**Figure 3.** $^{6}$Li spectra of the solutions recorded at 20 °C in $d_8$-THF. (a) $^{6}$LDMP: The aggregate involved was not identified, although the crystal structure of the alkoxide has been elucidated as a cyclic hexamer. Henderson, K. W.; Walther, D. S.; Williard, P. G. Unpublished results. (b) $^{6}$LDA: This species has previously been assigned to a THF-solvated dimer. Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 6772. (c) Mixture of $^{6}$LDA and $^{6}$LDMP showing the presence of a 1:1 complex marked by asterisks in addition to the signals associated with the discrete bases.

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**Supporting Information Available:** $^{1}$H/$^{13}$C/$^{6}$Li NMR spectra for $^{6}$LDA, $^{6}$LDMP, and a $^{6}$LDA/$^{6}$LDMP mixture and full crystallographic details including atomic coordinates, thermal parameters, bond lengths and angles, and atomic displacement parameters (15 pages); listing of observed and calculated structure factors (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(12) The $^{6}$LDA and $^{6}$LDMP were prepared by direct reaction of $^{n}$Bu$^{6}$Li with the secondary amines in pentane solution. Crystallizations were accomplished at −20 °C after 12 h. Manipulation of the solids was carried out in an argon-filled glovebox. All spectra were recorded as solutions in $d_8$-THF on a Bruker AM400 spectrometer. Samples were referenced to a 0.3 M $^{6}$LiCl/$d_4$-MeOH solution ($\delta$ 0.0) at the temperature at which each spectrum was run.

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