additional hardware needed is a miniaturized compartmented sample container suitable for NMR spectroscopy. For a typical small molecular weight substance, 30 µg dissolved in a capillary is enough to provide a spectrum of sufficient quality to deduce the structural integrity of the substance and impurities in the 10% range.

As the achievable signal-to-noise ratio is determined only by the sensitivity of the NMR probe and the number of spins in the detection volume, the method presented here by no means generates an improvement in the sensitivity of the NMR equipment. The gain in throughput is based solely on the reduction of the lengthy time required for frequent change of samples. This is only possible at the relatively high concentration of samples available in all fields mentioned in the introduction. Automation of the manually difficult filling of the capillary bundles is currently in progress in our workshop.[11] Further miniaturization of the diameters of the capillaries is due to limitations of available technology for automated liquid handling is not advisable.

The application of large diameter (7–10 mm) probes to increase the number of capillaries included in the detection volume is hampered by the lower intrinsic sensitivity of these probes, which reduces the quality of the spectra. This limitation might change in the near future if cryogenic technology[12] becomes available for larger diameter probes. A simple geometry for positioning 19 capillaries in a standard detection volume is described in the technical section. A bundle of flow-through capillaries measured by use of the CSI technique might also help to further increase the throughput of samples.

Experimental Section

For the experiments presented here each capillary tube was filled with 10 µL by using a syringe. The nine substances dissolved at concentrations below 10 mM in deuterated dimethyl sulfoxide ([D$_6$]DMSO) were arbitrarily obtained from our routine NMR laboratory. The solvent served as an internal lock. All data presented were taken on a DMX 600 Bruker spectrometer equipped with a standard triple-axis gradient TXI probe housing all the gradient coils. The temperature was set to 300 K. The NMR experimental parameters were set as follows: Proton pulse 8 µs; interscan delay 1 s; eddy current compensation δ 2 ms. FIDs of $4K$ complex time points were acquired in the digital filtering and quadrature detection mode of DMX spectrometers. The x- and y-gradient pulses ($t_g = 1$ ms) were ramped in 16 steps from -5 to $+5$ G cm^{-1} to obtain the needed spatial resolution of 300 µm. The 3 G cm^{-1} G_z gradient was used to remove 180° pulse imperfections.

This acquisition gave a data matrix of $(16 \times 16)_{\text{spatial}} \times 4K_{\text{complex,time}}$ data points. Eight dummy scans were allowed for thermal equilibration of the spin system prior to acquisition of the data. The data were processed using a matched exponential filtering along the chemical shift dimension and time-centered sine functions along both spatial dimensions together with first order phase correction (as needed) in all dimensions. Small truncation artifacts seen for multiplets are due to evolution of J-coupling during the spin-echo delays δ of the pulse sequence. A final data matrix of $(64 \times 64)_{\text{spatial}} \times 8K_{\text{chemical shift}}$ data points was obtained after zero filling. A bundle of capillaries (and interstice) filled with a 90% H$_2$O/D$_2$O mixture was used for a standard two-step z-gradient shimming protocol for the determination of initial shim settings. Low order off-axis shims were adjusted manually. The intercapillary space was originally filled with the same solvent as used in the capillaries to improve the homogeneity of the magnetic field over the bundle. Our highly symmetric arrangement comprises one central capillary surrounded by a second layer with eight capillary tubes. In the course of the experiments it turned out that the distortion of the magnetic field homogeneity introduced by the removal of the intercapillary liquid is negligible (Figure 4.). If the bundle is included in a standard NMR tube with a glass wall of 0.4 mm the active detection volume of the spectrometer cannot be filled completely with capillaries. The outer NMR tube is not necessary as the intercapillary liquid can be removed. Therefore, a bundle of 19 capillaries consisting of a central capillary surrounded by a second layer of 6 and a third layer of 12 capillaries will perfectly fill the available detection volume. Currently work is in progress in our laboratory to build such an improved geometry.

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Landmark Crystal Structure of an Experimentally Utilized Tetralithium–Tetrapotassium Amide–Alkoxide Superbase**

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Robert E. Mulvey*

It has long been known that mixtures of organolithium derivatives (e.g., alkyls, amides, or enolates) and heavier alkali metal alkoxides (e.g. *tert*-butoxides or *tert*-pentoxides) can exhibit special proton-abstracting powers well beyond the capability of the lithium compounds on their own.[1] A forest of literature has grown around this superbasicity focussing mainly on its exploitation in organic synthesis[2] and, to a lesser extent in polymerization.[3] Yet for all this accumulated knowledge, there is still much uncertainty about the precise

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identities and structures of these superbasic reagents, which seems remarkable given that in general their two separate components (e.g. *n*BuLi[4] and *t*BuOK[5]) have themselves been fully characterized both in solution and in the solid state. But the situation is complicated by the vast number of structural permutations possible when the two components are mixed together in solution. To summarize, each separate component can autoaggregate and may exist in several oligomeric forms, or combine with the other component to generate mixed oligomers, and in theory all of these distinct species could form adducts with the substrate to be metallated or with the solvent employed in the reaction, or even with both.[6] Hence the reason why structural studies[7] are deemed to be so important if the secrets of superbasicity are to be finally revealed. Several research groups have already made significant progress along this path by reporting the structures of "model superbases": these compounds contain a combination of anions, and in some cases a combination of metals, representative of those found in superbasic mixtures though they differ in one or more ways from the actual combinations used in practice (thus the need for the qualification "model"). Model structures of this type are known for a variety of classes of superbase.[8] Our approach to this problem has been more direct in that we have reinvestigated authentic, experimentally utilized superbasic mixtures and endeavored to grow crystals from them. Most attempts have predictably ended in failure for reasons all too familiar to researchers in the field: solids isolated from such mixtures tend to be microcrystalline or single-component (homometallic) species. However, a breakthrough came in revisiting a reaction first studied by Lochmann and Trekoval in 1979 in their pioneering work on the reactions of substituted N-lithium amides with heavier alkali metal alkoxides; specifically they reported[9] that mixtures of lithium *tert*-butylamide and potassium *tert*-butoxide in solution in benzene exhibited increased metalation properties toward toluene, yielding mainly benzylpotassium. We have now been successful in isolating and crystallographically characterizing a mixed-metal mixed-anion complex from this mixture and confirmed that it readily metalates toluene. We therefore report herein the first crystal structure of a bona fide superbase.

Lochmann and Trekoval highlighted the said reaction as atypical because unlike the other amide systems studied by them, no precipitate separated from it upon mixing the two components together. As this implied the superbase remained in solution, we decided to use a much more concentrated benzene solution of the alkoxide/amide mixture (2 M) than that employed originally (0.2–0.4 M). Furthermore we amended the alkoxide:amide stoichiometry from that used by Lochmann and Trekoval (1.3:1) to 1:1. This adapted reaction [Eq. (1)] afforded colorless crystals of **1**, a benzene solvate.

$$t\mathrm{BuN(H)Li} + t\mathrm{BuOK} + x\,\mathrm{s}\mathrm{C_6H_6} \longrightarrow [\{[t\mathrm{BuN(H)}]_4(t\mathrm{BuO})_4\mathrm{Li_4K_4}\cdot(\mathrm{C_6H_6})_3\}(\mathrm{C_6H_6})] \quad (1)$$

1

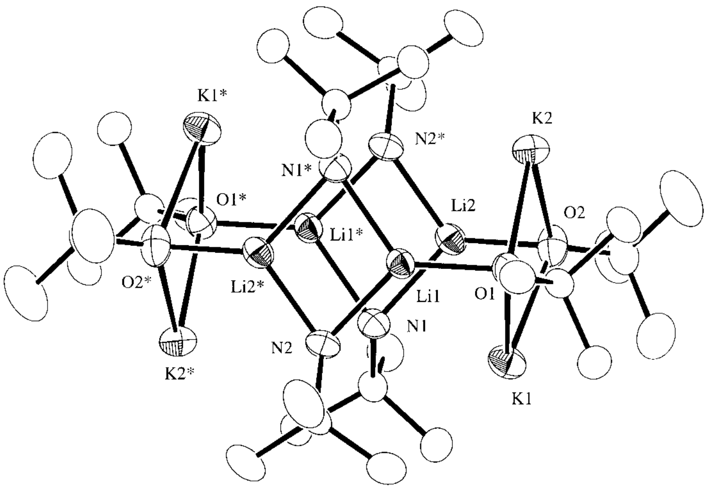

Figure 1. Core structure of **1** without hydrogen atoms and benzene ligands. Selected bond lengths [Å]: K1-O1 2.6106(17), K1-O2 2.658(2), K1-N1 3.192(2), K2-O1 2.6312(17), K2-O2 2.6334, K2*-N2 3.325(2), O1-Li1 1.879(4), O2-Li2 1.865(4), N1-Li2 2.007(4), N1*-Li1 2.040(4), N2*-Li2 2.006(5), N2-Li1 2.046(4). * denotes the symmetry operation $1-x$, $-y$, $-1-z$.

Four (metal–heteroatom)$_2$ dimeric rings arranged in two pairs provide the building blocks of the centrosymmetric molecular structure of **1** (Figure 1).[10] Symmetry dictates that the two equivalent rings within each pair lie strictly parallel to each other, while the distinct sets (e.g., K1-O1-K2-O2 and Li1-N2-Li2*-N1*) lie essentially perpendicular (e.g., angle between least-squares planes of rings, 82.92°) to each other. The rings join together in a carousel arrangement through strong Li–O bonds, which collectively make up a $\mathrm{Li_4O_4}$ plane ("seat") running through the center of the structure. Bent away from the $\mathrm{(LiN)_2}$ or $\mathrm{(KO)_2}$ ring planes to which they are attached, the two distinct types of *tert*-butyl substituent adopt exocyclic positions with respect to the hexadecanuclear inorganic core, while the symmetry-equivalent types eclipse each other. Furthest from the core lie benzene solvent ligands which complete the coordination spheres of the K atoms. Those attached to K2/K2* bind terminally and symmetrically (η^6) with six K–C distances under 4 Å in length (range, 3.71–3.83 Å). In contrast, those attached to K1/K1* adopt a "slipped" asymmetrical (η^3) arrangement which enables them to bridge between neighboring $\mathrm{Li_4K_4N_4O_4}$ units using either side of the arene π system (range of K–C distances, 3.67–4.00 Å) to generate an extended structure of one-dimensional zigzag chains (Figure 2). An additional benzene molecule of crystallization (one per $\mathrm{Li_4K_4N_4O_4}$ unit) occupies a gap between the chains.

What information can be gleaned about the structures of superbases using the architecture of **1** as an exemplar? One point to note is that the structure organizes around Li–O

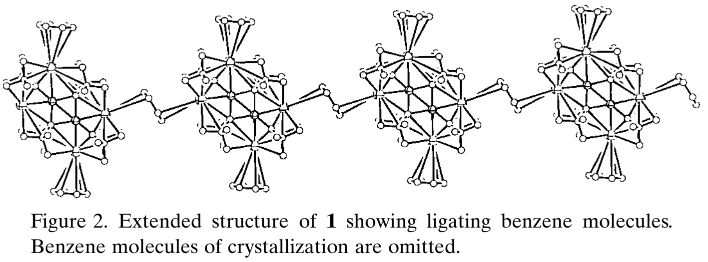

Figure 2. Extended structure of **1** showing ligating benzene molecules. Benzene molecules of crystallization are omitted.

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bonding. Thus the $(LiN)_2$ rings align themselves almost perfectly with the $(KO)_2$ rings to create the Li_4O_4 plane (root mean square (RMS) deviation from planarity, 0.016 Å) which maximizes the overlap between the small cation and small anion centers. Short Li–O bond lengths (mean, 1.872 Å) are formed as a result (cf. 1.916 Å in $(tBuOLi)_6$.[11] That said, it is perhaps surprising that the number of Li–O bonds is not maximized (i.e., there is only one per Li). This contrasts with the two such bonds per Li center in $[\{[PhN(H)]_2(tBuO)LiNaK \cdot 2TMEDA\}_2]$ (TMEDA = tetramethylethylenediamine[8] (mean length, 1.948 Å) reflecting the different bridging role of its heteronuclear (N-Na-N-Li) ring towards the $(KO)_2$ ring. A further surprise is the absence of any significant K–N bonding in **1** as the mean contact distance is 3.259 Å (some 0.34 Å longer than the mean K–N(amido) bond length in the aforementioned trimetallic complex) and the K1 ⋯ K2* and N1 ⋯ N2 vectors are poorly aligned (RMS deviation from planarity, 0.159 Å). Therefore the amido ligands are held in place mainly by two Li–N bonds (mean length, 2.025 Å). Contrast this with the situation in the known homometallic analogue $[\{tBuN(H)Li\}_8]$,[12] a cyclic ladder molecule, in which three such bonds (mean length, 2.050 Å) hold the amido anions much more tightly within the aggregate. It would appear that this weakening of the Li–N bonding is an important factor in the enhanced basicity of **1** versus its parent lithium amide, which significantly cannot deprotonate toluene under the conditions studied here. The presence of the heavier alkali metal gives **1** another possible advantage, a potential binding site for the arene substrate (here demonstrated by the K–π interactions with benzene). It is well established in enolate chemistry that carbonyl substrates can take the place of conventional donor solvent ligands by coordinating to a metal atom as a prerequisite to undergoing deprotonation.[13] In the case of **1** the benzene ligands could similarly be replaced by toluene molecules prior to the deprotonation step. The absence of a heavier alkali metal coupled with the steric crowding (comprising three bulky amido ligands) about the smaller lithium cations, negate this possibility in $[\{tBuN(H)Li\}_8]$. This prebinding of the toluene molecules would lower the entropy of the subsequent deprotonation reaction (see Schlosser's article in reference [1] for an illuminating discussion of such proximity effects).

To verify that **1** is indeed a superbase, we isolated it, redissolved it in benzene, then added toluene. The presence of benzylpotassium was subsequently confirmed by ^1H NMR spectroscopic studies.[14] However, note that **1** is only superbasic in the sense that it has superior proton-abstracting powers to its parent lithium amide. It should not be measured against classical alkyl (carbanion) superbases which are inherently more basic.

Experimental Section

1: Under a protective dry oxygen-free argon atmosphere in a Schlenk tube, $tBuNH_2$ (10 mmol) was added dropwise to a solution of *n*BuLi (10 mmol) in hexane. Butane was evolved as the primary amide *t*BuN(H)Li formed in solution. This was subsequently isolated and the dry solid and solid *t*BuOK (10 mmol) were placed together in another Schlenk tube and covered with benzene (5 mL) to give a dark brown suspension which required gentle heating for complete dissolution. Cooling the solution on the bench afforded a crop of colorless crystals of **1**. Yield (disregarding benzene molecules most of which are lost upon isolation), 75 %. Elemental (C, H, N) analysis was hampered by the loss of solvent immediately upon isolation of the crystals. During the analysis itself the sample lost weight too rapidly for reliable results to be obtained. M.p. 102–103 °C; ^1H NMR (400 MHz, $[D_6]$benzene, 25 °C): $\delta = 3.87$ (s, 1 H, NH), 1.24 (s, 9 H, *t*BuO/*t*BuN), 1.21 (s, 9 H, *t*BuO/*t*BuN).

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[10] Crystal structure data for **1**: $C_{56}H_{100}K_4Li_4N_4O_4$, $M_r = 1077.56$, colorless chip, approximately 0.35 × 0.20 × 0.20 mm. $Mo_{K\alpha}$ graphite-monochromated radiation ($\lambda = 0.71073$ Å), $T = 150$ K; triclinic, space group $P\bar{1}$; $a = 12.4570(5)$, $b = 12.6523(5)$, $c = 13.1390(5)$ Å; $\alpha = 93.621(2)$, $\beta = 116.846(2)$, $\gamma = 109.314(2)°$; $V = 1687.21(11)$ Å^3; $Z = 1$, $\mu = 0.304$ mm^{-1}, $\rho_{calcd} = 1.061$ Mg m^{-3}, $2\theta_{max} = 54.96°$, 12560 reflections collected, 7712 unique used ($R_m = 0.0270$). The structure was solved and refined to convergence on F^2 using published programs and techniques (G. M. Sheldrick, SHELXS and SHELXL-97, University of Göttingen, Germany **1997**). $R1 = 0.0595$ (for 5070 reflections with $I > 2\sigma(I)$), $wR2 = 0.1649$ and $S = 1.021$ for 343 parameters. Maximum residual electron density 0.701 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162484. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[14] Recorded in $[D_5]$pyridine at 400 MHz, the ^1H NMR spectrum of the reaction mixture most characteristically reveals a CH_2 resonance at $\delta = 3.04$, identical to that found for an authentic sample of pure benzylpotassium. Free amine is also observed in the spectrum at $\delta = 1.13$ (*t*Bu), confirming that it is a by-product of the arene deprotonation process, that is, $tBuN(H)^-$ is the active base unit within the superbase molecule.