The First Trimetallic Lithium−Sodium−Potassium Complex: Synthesis and Crystal Structure of a Twelve-Vertex Li$_2$Na$_2$K$_2$N$_4$O$_2$ Cage Molecule Containing an Amide−Alkoxide Combination

Fiona M. Mackenzie and Robert E. Mulvey*

Department of Pure and Applied Chemistry
Strathclyde University, Glasgow, G1 1XL, UK

William Clegg and Lynne Horsburgh

Department of Chemistry, University of Newcastle
Newcastle-upon-Tyne, NE1 7RU, UK

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Several molecular complexes containing a mixture of two alkali metals (e.g., lithium−sodium and lithium−potassium) have been characterised by X-ray crystallographic studies over the past decade.[1] Here, in this paper, we break new ground in this important area of intermetallic chemistry by reporting the successful synthesis and X-ray crystallographic characterization of an unprecedented trimetallic (lithium−sodium−potassium) formulation. Furthermore, the new complex, [{[PhN(H)]$_2$(*t*-BuO)LiNaK·(TMEDA)$_2$}$_2$], (**1**), is closely related to the co-compositions currently employed as "superbases",[2] reagents of boosted deprotonating ability, in organic synthesis. Two recently reported crystal structures regarded to be architectural models for superbases, a carbanion−alkoxide[3a] and a carbanion−amide[3b] combination, both contain their two anionic functionalities (C^-/RO^- and C^-/R_2N^-, respectively) within one ligand. On the other hand, more realistically, **1** contains two distinct types of anionic ligand [amide−alkoxide (R_2N^-/RO^-)][4] as is the case in superbase reagents.[2]

Our intention in the synthesis producing **1** was to grow crystals of a representative mixed metal/mixed amide−alkoxide cocomposition; in solution, such mixtures have proved to be highly efficient, nonnucleophilic bases in applications [e.g., the deprotonation of 1-(phenylseleno)alkenes][5] where conventional lithium amide or potassium amide reagents have failed. Knowing that superbases in their mixed state are notoriously difficult to crystallize (normally only microcrystalline monometallic solids are accessible[3a,6]) in seeking this breakthrough, we tested various permutations of reagents in various stoichiometries. Success came with a golden solution prepared under argon consisting of lithium anilide (20 mmol, freshly made by combining *n*-butyllithium and aniline in a 1:1 molar ratio), sodium *tert*-butoxide (10 mmol), potassium *tert*-butoxide (10 mmol), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (20 mmol) in hexane. Prior to adding the diamine, a pale yellow suspension was present, and the mixture was stirred in an ultrasonic bath. Cooling the solution to *ca.* −25 °C afforded a large crop of colorless, rhombic crystals of **1**,[7] whose surfaces are prone to blackening, indicating decomposition to aniline black. This synthetic procedure was repeated and found to be reproducible.

When metal cations and attached heteroatoms are included (excluding those of TMEDA), the crystal structure[8] (Figure 1) can be described as a centrosymmetric, twelve-vertex cage molecule. When contacts to C and H atoms are disregarded, which is a necessary consequence of ligand geometry, four of the six cations in the dimer [2Li$^+$and 2Na$^+$] are four-coordinate (distorted tetrahedral geometry), while the larger K$^+$ cations attain six-coordination (distorted octahedral geometry). Na$^+$ cations bind only to N atoms, whereas both Li$^+$ and K$^+$ contact a mixture of N/O atoms (i.e., 2/2 and 4/2, respectively). Embedded within the core, Li$^+$ cations are sterically shielded from possible solvation, in contrast to the edge-located Na$^+$ and K$^+$ cations which single TMEDA molecules chelate. When interactions are allowed with four and two anions respectively, the relative positions of the Li$^+$ and Na$^+$ cations are consistent with the former's superior attracting powers. Occupying a core site, the O atom of the *tert*-butoxo anion bridges a heterobimetallic LiKLiK rectangular face, while the edge-placed (anilino) N atoms bridge heterotrimetallic LiNaK triangular faces. There is no precedent in alkali metal chemistry for the latter type of bridge bonding.[9]

Though disorder in two anilino rings and all four TMEDA ligands complicates analysis of the cage dimensions, in general, the regular design of the structure leads to bond distances in accord with cation size. For example, those involving (anilino) N atoms follow the pattern K−N > Na−N > Li−N. Considering the orientations of the PhN(H) planes, it appears that the Li−N bonds arise from the interaction of Li with the amide sp^2 lone pair, whereas those involving Na and K arise from interaction with the amide p lone pair. A comparison of M−O and corresponding M−N bond distances confirms the maxim that the smaller cation prefers the smaller anion [e.g., Li(1)−O(1), 1.949(5) Å, is shorter than Li(1)−N(21), 2.148(5) Å] and

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(1) (a) Clegg, W.; Mulvey, R. E.; Snaith, R.; Toogood, G. E.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1740. (b) Schümann, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 584. (c) Williard, P. G.; MacEwan, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 7671. (d) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1989**, 57. (e) Williard, P. G.; Nichols, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 9671. (f) Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *Polyhedron* **1992**, *11*, 2809. (g) Freitag, S.; Kolodziejski, W.; Pauer, F.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1993**, 3479. (h) Gornitzka, H.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 693. (i) Baker, D. R.; Clegg, W.; Horsburgh, L.; Mulvey, R. E. *Organometallics* **1994**, *13*, 4170. (j) Henderson, K. W.; Williard, P. G.; Bernstein, P. R *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1117.

(2) Mordini, A. In *Advances in Carbanion Chemistry*; Snieckus, V., Ed.; JAI Press: London, 1992; Vol. 1, pp 1−42.

(3) (a) Harder, S.; Streitwieser, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1066. (b) Harder, S.; Lutz, M.; Kremer, T. *Organometallics* **1995**, *14*, 2133.

(4) (a) A unimetal amide−alkoxide complex is known, see: Henderson, K. W.; Walther, D. S.; Williard, P. G. *J. Am. Chem. Soc.* **1995**, *117*, 8680. (b) Compare the unimetal carbanion−alkoxide: Marsch, M.; Harms, K.; Lochmann, L.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 308.

(5) Raucher, S.; Koolpe, G. A. *J. Org. Chem* **1978**, *43*, 3794.

(6) (a) Lochmann, L.; Lim, D. *J. Organomet. Chem.* **1971**, *28*, 153. (b) Pi, R.; Bauer, W.; Schleyer. P.v.R. *J. Organomet. Chem.* **1986**, *306*, C1.

(7) Yield (based on consumption of sodium *tert*-butoxide) 78%; mp 137−139 °C. Anal. ($C_{28}H_{53}KLiN_5NaO$)C,H,K,Li,N,Na. From the stoichiometry within **1** it can be assumed that lithium *tert*-butoxide (10 mmol) remained in solution.

(8) Crystal data for **1**: $C_{56}H_{106}K_2Li_2N_{12}Na_2O_2$, $M = 1117.6$, triclinic, $P1$, $a = 10.6247(14)$ Å, $b = 13.329(2)$ Å, $c = 14.070$ (2) Å, $\alpha = 115.515$-(3)°, $\beta = 101.446(3)$°, $\gamma = 93.331(3)$°, $V = 1739.0(4)$ Å^3, $Z = 1$, $D_{\mathrm{calcd}} = 1.067$ g cm^{-3}, $\mu = 0.19$ mm^{-1} (Mo Kα, $\lambda = 0.71073$ Å), $F(000) = 608$, $T = 160$ K. Siemens SMART CCD area-detector diffractometer, crystal size 0.80 × 0.58 × 0.52 mm, $\theta_{\max} = 28.27$°, 10 469 reflections measured, 7365 unique ($R_{\mathrm{int}} = 0.0383$). Structure solution by direct methods, full-matrix least-squares refinement on F^2 with weighing $W^{-1} = \sigma^2(F_o^2) + (0.0589P)^2 + (1.3383P)$, where $P = (2F_c^2 + F_o^2)/3$, two-fold disorder for all TMEDA and half the anilino ligands, anisotropic displacement parameters, riding hydrogen atoms, no absorption or extinction corrections, restraints on geometry and displacement parameters of disordered groups. Final $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1959$ for all data, conventional $R = 0.0701$ on F values of 5501 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.190$ on F^2 for all data, 526 parameters and 1101 restraints. Final difference map between +0.62 and −0.41 e Å^{-3}. Programs: Siemens SMART and SAINT control and integration software, SHELXTL (G.M. Sheldrick, University of Göttingen, Germany), and local programs. Selected dimensions (Å and deg): K(1)−N(11) 2.955(4), K(1)−N(21′) 2.882(3), K(1)−O(1) 2.925(2), K(1)−O(1′) 2.932(2), K(1)−N(41) 2.974(3), K(1)−N(42) 2.917(3), Na(1)−N(11) 2.380(4), Na(1)−N(21) 2.438(3), Na(1)−N(31) 2.471(3), Na(1)−N(32) 2.541(3), Li(1)−N(11) 2.151(6), Li(1)−N(21) 2.148(5), Li(1)−O(1) 1.949(5), Li(1)−O(1′) 1.947(6), O(1)−K(1)−O(1′) 54.42(7), N(11)−K(1)−N(21′) 138.61(9), N(41)−K(1)−N(42) 63.45(10), N(11)−Na(1)−N(21) 89.73(11), N(31)−Na(1)−N(32) 74.46(9), N(11)−Li(1)−N(21) 104.5(2), O(1)−Li(1)−O(1′) 86.8(2).

(9) For reviews of X-ray structures, see (for lithium): Setzer, W.; Schleyer, P.v.R. *Adv. Organomet. Chem.* **1985**, *24*, 353. For heavier alkali metals see: Schade, C.; Schleyer, P.v.R. *Adv. Organomet. Chem.* **1987**, *27*, 169. For amides see: Gregory, K.; Schleyer, P.v.R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. Mulvey, R. E. *Chem. Soc. Rev.* **1991**, *20*, 167.

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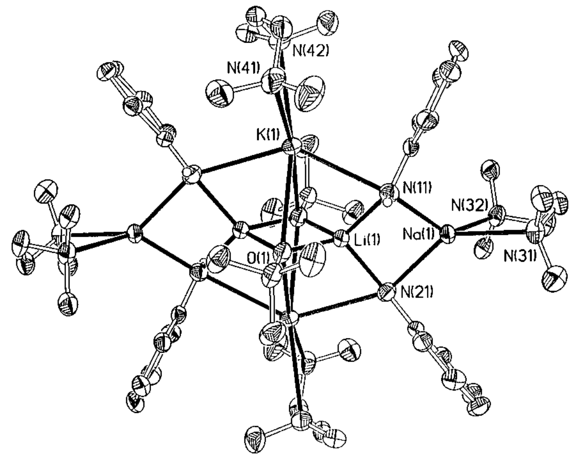

Figure 1. Thermal ellipsoid plot of **1** at 30% probability, showing the labeling scheme for key atoms. Hydrogen atoms, except for those in N(H) units, and minor disorder components are omitted for clarity. The molecule has crystallographic inversion symmetry.

the larger cation prefers the larger anion [e.g., conversely, K(1)−N(21a), 2.882(3) Å, is shorter than K(1)−O(1), 2.925(2) Å].[3b] At the cage center, the homometallic, fused $(Li-O)_2$ and $(K-O)_2$ rings are both planar, but while the former approaches a square [bond angles: Li, 86.8(2)°; O, 93.2(2)°] the latter, due to greater ion size inequality, is much more rhomboidal [K, 54.42(7)°; O, 125.58(7)°]. Possessing different cation types, the (LiNNaN) rings located nearer to the cage periphery are considerably less symmetrical. A selection of key dimensions is given in ref 8.

Certain features of **1** bear resemblance to those found in classical lithium magnesate structures. Specifically, the $[(TMEDA)\cdot Na(\mu\text{-}N)_2Li(\mu\text{-}O)_2Li(\mu\text{-}N)_2Na\cdot(TMEDA)]$ section can be compared with the structure of $[(TMEDA)\cdot Li(\mu\text{-}Ph)_2Mg(\mu\text{-}Ph)_2Mg(\mu\text{-}Ph)_2Li\cdot(TMEDA)]$:[10] both have four pseudotetrahedral metal centers linked by bridging anions, near-linear M−M−M−M units (in **1**, the Na−Li−Li angles are 169.5°), the stronger Lewis acidic cation occupying an inner position, and outer cations complexed by TMEDA molecules. However, due to different valency considerations, the magnesate is neutral, whereas the sodium lithate entity carries a 2^- charge. It is this charge differential which is critical to the formation of **1**, as two additional cations must be incorporated into the structure to attain neutrality. In this description, these K^+ cations cap the central $(LiO)_2$ rectangular face and simultaneously interact with a π-orbital on two (anilino) N atoms lying on opposite sides of this face.

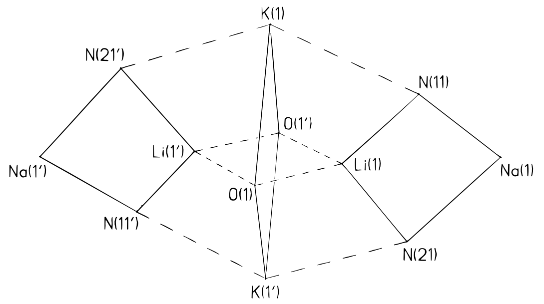

Figure 2. Line drawing of the main body of the structure illustrating that it originates from the fusing of three (metal−heteroatom)$_2$ dinuclear rings, the central one of which is unique.

While this is an interesting analogy, the structure of **1** is best regarded as being constructed from a central, strictly planar $(KO)_2$ dimeric ring, lying approximately orthogonal to (dihedral angle, 101.2°) and sandwiched between a pair of heterometallic (LiNNaN) rings (each approximately planar; rms deviation 0.154 Å), as illustrated in Figure 2. Both component parts have precedents in the literature. Potassium *tert*-butoxide, in the form of a six-membered $(KO)_3$ ring, was recently observed in the cage structure of the novel mixed group 1/group 15 cocomplex $[\{(cyNLi)_3Sb\}_2(t\text{-}BuOK)_3\cdot xC_6H_5CH_3]$.[11] The smaller four-membered variation in **1** must be dictated by the bidentate TMEDA solvation. A discrete, heterometallic (LiNNaN) ring structure derived from hexamethyldisilazane, which like **1** contains a four-coordinate Na^+ cation complexed by two donor atoms, has also been described.[1e]

The fact that this latter component can exist even with bulky secondary amides (*cf.* the primary amide in **1**), coupled with the orderly architectural design of **1**, gives every encouragement that a new family of trimetallic Li−Na−K structures with different amide−alkoxide combinations, of which **1** is the prototype, will be accessible.

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Supporting Information Available: Details of the X-ray analysis and tables of atomic coordinates, bond lengths and angles, and atomic displacement parameters (10 pages). Ordering information is given on any current masthead page.

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(10) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726.

(11) Barr, D.; Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Rennie, M. A.; Russell, C. A.; Wright, D. S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1012.