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Model for a superbase: synthesis and crystal structure of the mixed-metal/mixed-anion aggregate $[NaLi_2\{N(H)R\}_2(OR')]_2$†

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The first structurally characterised example of a hetero-bis-s-block-metal amide–alkoxide complex, $[NaLi_2\{N(H)R\}_2(OR')]_2$ (1, R = 2-methoxyphenyl, R′ = *tert*-butyl), has been shown to be constructed from fusing four LiNNaO heterobimetallic rings with two Li_2N_2 rings through shared edges to form a cyclic ladder; the complex may serve as a model for "superbases" that are widely employed in organic synthesis.

Complexes containing mixed-anion aggregates and those containing hetero s-block-metal compositions have provoked considerable recent interest. This is due in part to the fact that both types of complex are known to modify the basicity of the parent lithium amide in a desirable fashion. Mixed-anion complexes have been shown to exhibit superior selectivity over parent amide bases in enolisation reactions, and mixed-metal complexes are known to have superior deprotonating ability (so called "superbases") over the parent lithium amide reagents.[1,2] Structural studies on such systems are, however, sparse because growing crystals suitable for study by single crystal techniques has proved a notoriously difficult task.[3–5] Of particular note have been the studies of Mulvey, who have succeeded in synthesising and structurally characterising a number of mixed s-block-metal and mixed anion complexes, displaying a rich assortment of stoichiometries and structures.[1] Herein, we report a new variant in this family of complexes, $[NaLi_2\{N(H)R\}_2(OR')]_2$ (R = 2-methoxyphenyl, R′ = *tert*-butyl) **1**,‡ the first example of a bi-s-block-metal/mixed amide–alkoxide complex. It was first isolated as part of our studies into amido and imido complexes of phosphorus, being formed from the reaction of P_2I_4 with 2-methoxyaniline (1 : 4 equiv.) in THF–NEt_3 followed by metallation with Bu^nNa {4 equiv., prepared *in situ* by the reaction of Bu^nLi and Bu^tONa (1 : 1 equiv.) in hexane}. The same complex (although not with X-ray quality crystals) can be prepared by direct combination of the lithiate of 2-methoxyaniline (prepared *in situ*) and sodium *tert*-butoxide (2 : 1 equiv.) in THF.

The low-temperature single crystal X-ray structure of **1** was determined (see Fig. 1).§ The quality of the crystallographic data is admittedly modest owing to the high air- and moisture-sensitivity of the product and small, weakly diffracting crystals. However, the data clearly illustrate that complex **1** is a dimeric ion-contacted complex formed around a hexagonal prismatic core resulting from the combination of the lithium, sodium, amide and alkoxide functionalities (in ratio 2 : 1 : 2 : 1) that exist in this complex solution.

Within complex **1**, each lithium centre binds to two amide groups, one alkoxide and one methoxy group (a sidearm of a 2-methoxyanilide group) in distorted tetrahedral geometries. By contrast, the larger sodium cations have distorted five coordinate geometries. The sodium atoms are bound to two amido nitrogen atoms and one alkoxide oxygen atom within the core, their coordination sphere being completed by the attachment of two THF solvent molecules. The amido nitrogen centres are five coordinate, being bound to two lithium atoms and one sodium atom in the core, and additionally being bound to the 2-methoxyphenyl group and the amido (N–H) proton. The existence of this proton could not be discerned from the electron difference map of the X-ray diffraction experiment, but its presence can be established from both IR and NMR spectroscopy where absorptions are seen at 3289 cm^{-1} in the infrared spectrum and a broad singlet at δ 4.07 in the ^1H NMR spectrum. The distortions of the coordination spheres of all the atoms that comprise the core reflect that the bonding within the core is principally ionic. Hence, the bonds formed are a result of electrostatic interactions rather than the directional requirements of covalent bonds. The bond lengths within the core show that the principal driving force dictating the structure of **1** is the formation of strong alkali metal–alkoxide bonds. Hence, the Bu^tO–Li and Bu^tO–Na distances (av. Li–O 1.90 Å; Na–O 2.30 Å) are comparable to those in their respective lithium and sodium alkoxides whereas the Li–N and Na–N distances (av.

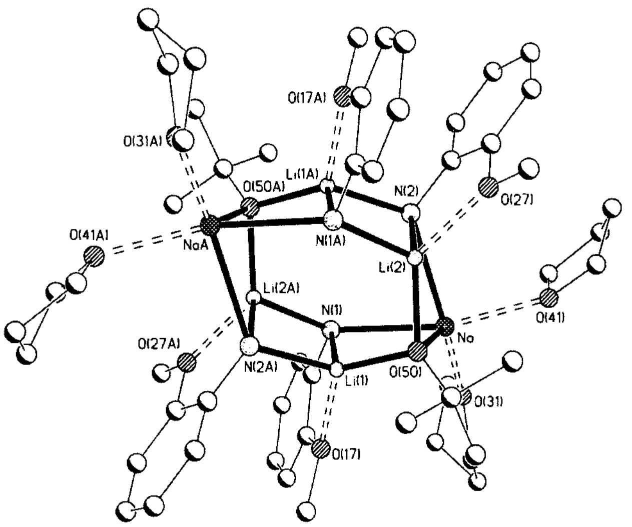

Fig. 1 The crystal structure of **1**. The molecule sits astride an inversion centre and symmetry equivalent atoms are denoted by the additional letter "A". All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Na–O(50) 2.303(7), Na–O(41) 2.402(8), Na–O(31) 2.409(8), Na–N(1) 2.576(8), Na–N(2) 2.595(8), N(1)–Li(1) 2.08(2), N(1)–Li(2A) 2.13(2), Li(1)–O(50) 1.90(2), Li(1)–O(17) 2.02(2), Li(1)–N(2A) 2.12(2), N(2)–Li(2) 2.06(2), N(2)–Li(1A) 2.12(2), Li(2)–O(50) 1.91(2), Li(2)–O(27) 2.06(2), Li(2)–N(1A) 2.13(2); O(50)–Na–O(41) 116.4(3), O(50)–Na–O(31) 127.3(3), O(41)–Na–O(31) 83.4(3), O(50)–Na–N(1) 85.0(3), O(41)–Na–N(1) 156.5(3), O(31)–Na–N(1) 91.2(3), O(50)–Na–N(2) 83.2(2), O(41)–Na–N(2) 94.1(3), O(31)–Na–N(2) 147.1(3), N(1)–Na–N(2) 78.2(2), O(50)–Li(1)–O(17) 123.0(8), O(50)–Li(1)–N(1) 112.1(8), O(17)–Li(1)–N(1) 81.1(6), O(50)–Li(1)–N(2A) 120.1(8), O(17)–Li(1)–N(2A) 106.8(7), N(1)–Li(1)–N(2A) 106.1(7), O(50)–Li(2)–N(2) 110.6(8), O(50)–Li(2)–O(27) 132.0(8), N(2)–Li(2)–O(27) 80.8(6), O(50)–Li(2)–N(1A) 115.5(8), N(2)–Li(2)–N(1A) 107.0(7), O(27)–Li(2)–N(1A) 104.0(7).

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3331/

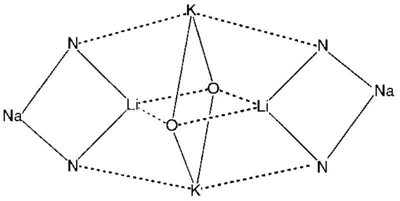

Fig. 2 The core of [{[PhN(H)]$_2$(Bu^{t}O)LiNaK·(TMEN)$_2$}$_2$].

Li–N 2.10 Å; Na–N 2.59 Å) are significantly longer.[1,6,7] This is a reflection of the stronger bonds formed between alkali metals and alkoxides, in comparison with alkali metals and amides, and presumably accounts for some of the distortion observed within the core of **1**.

The core of complex **1** is probably best viewed in terms of the ring stacking and ring laddering concepts that are widely used in the rationalisation of the organolithium structures.[8,9] Hence, the twelve-membered cage can be viewed as being constructed from fusing four LiNNaO heterobimetallic rings with two Li$_2$N$_2$ rings through shared edges, *i.e.*, ring stacking to form a cyclic ladder.

The structure of **1** is the first example of a bimetallic mixed sodium–lithium–amide–alkoxide complex, although Mulvey *et al.* have succeeded in isolating and characterising a more elaborate trimetallic (lithium–sodium–potassium) amide–alkoxide complex, [{[PhN(H)]$_2$(Bu^{t}O)LiNaK·(TMEN)$_2$}$_2$] from the reaction of lithium anilide with potassium *tert*-butoxide and sodium *tert*-butoxide (2 : 1 : 1 equiv.) in hexane.[7] The core of this molecule is also a twelve membered cage, but it adopts a very different structural arrangement compared to complex **1**. This trimetallic amide–alkoxide complex consists of a central K$_2$O$_2$ dimer ring lying approximately orthogonal to and sandwiched between two LiNNaN rings (see Fig. 2).

Both mixed-anion complexes and mixed-metal complexes have been widely heralded and used as superbases in organic synthesis.[10] Complex **1** exhibits both of these facets, and the bimetallic nature of the complex perhaps provides a more realistic model of the currently employed superbases than the trimetallic complex of Mulvey and co-workers.[7] The uses of complex **1** as a base in organic synthesis will form a central part of the further work originating from this result.

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Notes and references

‡ Preparation of **1**: To a stirred solution of THF (15 ml) and NEt$_3$ (5 ml) were added P$_2$I$_4$ (1 mmol, 0.57 g) and 2-methoxyaniline (4 mmol, 0.45 ml). The orange/brown opaque solution was filtered. The resulting clear yellow filtrate was added to the Bu^{n}Na solution {prepared *in situ* by the addition of Bu^{t}ONa (4 mmol, 0.384 g) to Bu^{n}Li (4 mmol, 2.5 ml) in hexane (25 ml)}, which instantly became a clear orange/yellow solution. Solvent was removed *in vacuo* until a precipitate formed. This redissolved on warming gently, and after storage at 25 °C, 0.498 g (25%, based on Na) of rectangular crystals formed, mp: 120 °C decomposed to black solid; IR (Nujol mull): ν/cm^{-1} = 3289 (N–H stretch); ^{1}H NMR (+25 °C, 300.4 MHz, [d$_5$]pyridine): δ 6.31–6.92 (8H, multiplet, aromatic), 4.07 (2H, br s, N–H), 3.64 (14H, multiplet, OMe, THF), 1.58 (8H, multiplet, THF), 1.32 (9H, singlet, ^{t}Bu); Anal.: C 62.6, H 7.8, N 5.4% (Calc.: C 62.9, H 7.8, N 5.6%).

Higher yields (*ca.* 60%), although not with crystals suitable for X-ray diffraction, can be obtained from the direct combination of the lithiate of 2-methoxyaniline and NaOBu^t (2 : 1 equiv.) in THF followed by recrystallisation at −30 °C.

§ Crystal data for **1**: C$_{52}$H$_{82}$Li$_4$N$_4$Na$_2$O$_{10}$, M = 996.96, monoclinic, space group $P2(1)/c$, a = 9.169(4) Å, b = 13.666(5) Å, c = 22.173(10) Å, β = 93.05(3)°, U = 2774(2) Å^3, Z = 2, T = 173(2) K, μ(Mo-Kα) = 0.093 mm^{-1}, 11443 reflections measured, 3624 unique [R(int) = 0.0839] which were used in all calculations. Data were collected on a Bruker SMART CCD area-detector diffractometer[11] using a crystal mounted on a glass fibre in a rapidly cooled perfluoropolyether.[12] The structure was solved by direct methods and refined by least squares on F^2 values for all reflections. Absorption corrections were applied, based on multiple and symmetry equivalent measurements.[13] Final $R1$ = 0.1347 [$I > 2\sigma(I)$] and $wR2$ = 0.3471 (all data).[14] CCDC reference number 186/1618. See http://www.rsc.org/suppdata/dt/1999/3331/ for crystallographic files in .cif format.

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