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Alkoxide binding in inverse crown chemistry: rational synthesis of a series of composite alkali metal–magnesium–alkoxide–diisopropylamides

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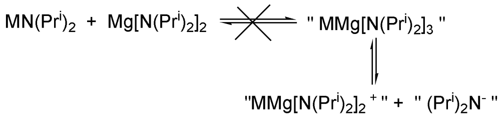
A series of composite lithium– or sodium–magnesium–alkoxide–diisopropylamides of general formula $[\{MMg[N(Pr^i)_2]_2OR\}_2]$ (where M = Li, R = Oct^n; M = Na, R = Bu^n or Oct^n), has been synthesised rationally by treating synergic amide mixtures with the appropriate alcohol.

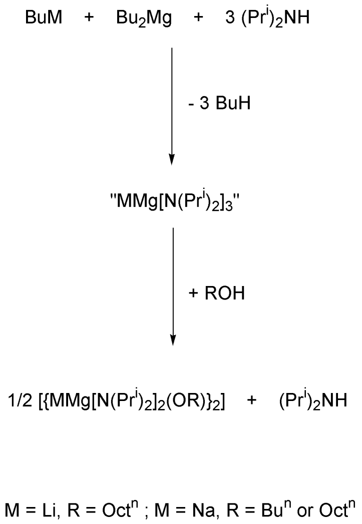
The synergic effects of mixing organolithium derivatives (*e.g.*, alkyls, amides or enolates) with heavier alkali metal (*e.g.*, sodium or potassium) alkoxides (*e.g.*, *tert*-butoxides or *tert*-pentoxides) have long been appreciated and exploited in synthetic organic chemistry.[1] Enhanced basicity is the primary benefit (hence the reason why such combinations are known generically as 'superbases'), but there can also be secondary benefits of higher chemo-, regio- or stereocontrol in comparison to that achievable with the pure homometallic organolithium compounds. Recently, we have uncovered a powerful new type of synergic chemistry, which can be activated by pairing together certain alkali metal amides with their congeneric magnesium bis-amides.[2] The term 'inverse crown chemistry' has been coined for this developing area as its first compounds exhibit a topological (anti) relationship to conventional crown ether complexes, *i.e.*, metal atoms belong to the host rings while oxygen components occupy guest positions. Matching a sodium amide with the corresponding magnesium bis-amide can promote *hyperbasic* properties, which can be used to convert a metallocene[3] to an unprecedented polymetallated form. Here we report the prototypal examples of alkoxide-based inverse crowns and thus establish a further important link between superbase and inverse crown chemistries.

The new inverse crowns $[\{NaMg[N(Pr^i)_2]_2OBu^n\}_2]$ **1**, $[\{NaMg[N(Pr^i)_2]_2OOct^n\}_2]$ **2** and $[\{LiMg[N(Pr^i)_2]_2OOct^n\}_2]$ **3**, can also be classified as composite alkali metal–magnesium–alkoxide–amides: in this description **1** and **2** can be regarded as novel variants of sodium diisopropylamide (NDA), and **3** of lithium diisopropylamide (LDA), both of which (particularly LDA) find widespread use in chemical synthesis. Scheme 1 outlines the general approach used in the synthesis of **1**–**3**.† Significantly the reactions were carried out exclusively in hydrocarbon solution. NDA on its own is essentially insoluble in such non-coordinating solvents, but is rendered soluble when combined with $Mg(DA)_2$. This is a critical aspect of the synergism and rules out the possibility of an equilibrium between the separated homometallic amides and the unified heterobimetallic tris-amide in the absence of a Lewis base cosolvent [eqn. (1)]. Formally, it is better to regard the



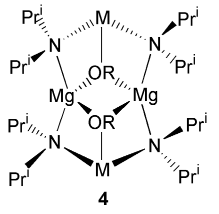
$$\begin{tikzcd} MN(Pr^i)_2 + Mg[N(Pr^i)_2]_2 \arrow[r, "\times" description, shift left] & \arrow[l, shift left] \text{"}MMg[N(Pr^i)_2]_3\text{"} \arrow[d, shift left] \\ & \text{"}MMg[N(Pr^i)_2]_2{}^+\text{"} + \text{"}(Pr^i)_2N^-\text{"} \arrow[u, shift left] \end{tikzcd} \quad (1)$$

ris-amides as sources of hyperbasic '$[(Pr^i)_2N^-]$' anions and cationic '$[(MNMgN)^+]$' complexing arcs, as this description fits the dual action of their reactivity towards Brønsted–Lowry acids: the former strip off hydrogen atoms, while in turn the latter complex to, and encapsulate, the deprotonated residue (in reality, it is possible that these events occur in a concerted manner through a ring-templating effect). The high steric bulk of the amido ligands is a major factor in the efficacy of the encapsulation process. Here the acid employed is *n*-butanol (in the case of **1**) or *n*-octanol (in the case of **2** or **3**).



Scheme 1

X-Ray crystallographic studies‡ have established that **1**, **2** and **3** belong to the same structural type, denoted by representation **4**. Detailed discussion is limited to the structures of **1** and **2** as the data obtained for **3** are of poorer quality due in part to mutual substitution disorder, which renders the Li and Mg atoms mutually indistinguishable (a common problem in Li–Mg based inverse crowns). The centrosymmetric structures of **1** and **2** consist of octagonal $(NaNMgN)_2$ inverse crown cationic rings, face-capped at the top and bottom by the O atom of an alkoxide anion. This is clearly evident from the view of **1** (in Fig. 1). The alternative side-on perspective shown for **2** (in Fig. 2) reveals that the octagonal ring is chair-shaped with the Na atoms displaced on either side of the plane defined by NMgN···NMgN. This distortion from planarity is more pronounced in the octoxide case with the angles between the NNaN chair-backs and the aforementioned planes being 154.64 and 140.33° for **1** and **2**, respectively. Toluene solvation of the Na atoms in the hydride-encapsulated inverse crown **5**[4] contributes to a similar chair-like distortion [corresponding fold angle, 153.5(2)°]. As there is no solvation in **1** or **2**, the displacement of their Na atoms can be attributed to an attraction for the alkoxide O atoms. Each Na atom interacts only with the O atom disposed *syn* to itself at distances of 2.5659(9) and 2.4721(17) for **1** and **2**, respectively [the corresponding non-bonding



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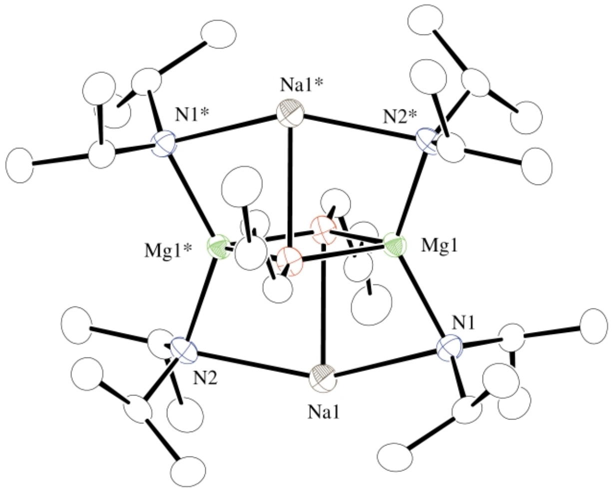


Fig. 1 Molecular structure of **1** (excluding hydrogen atoms).

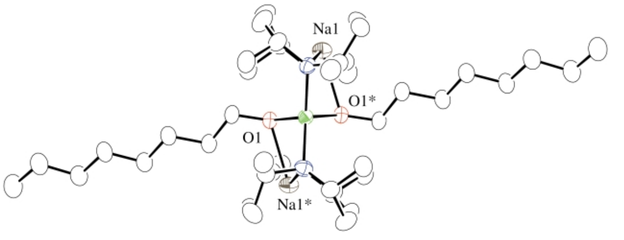
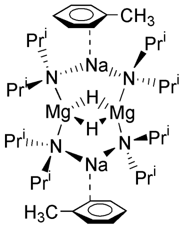


Fig. 2 Molecular structure of **2** (excluding hydrogen atoms) from an alternative perspective from that of **1** highlighting the chair conformation of the $(NaNMgN)_2$ ring.



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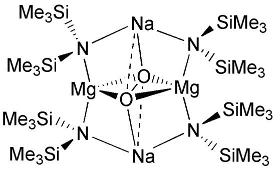

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distances to the *anti* O atoms are 3.104(1) and 3.204(2)]. This lop-sided μ_3-O bonding arrangement establishes an interesting pattern in the nature of the host–guest interactions within the $(NaNMgN)_2$-based inverse crowns: the number of Na–guest interactions increases sequentially from zero to 1 to 2 on changing the guest from hydride to alkoxide to peroxide (see **6**). While there is clearly a direct correlation here with the steric bulk of the guest, this pattern should not be interpreted in isolation without considering the influence of the Mg atoms. Significantly the number of Mg–guest interactions is 2 in every case with the aforementioned anions. Thus the stabilisation of the guests is due primarily to the stronger bonding characteristics of the smaller divalent Mg atom. In **1** and **2** this is manifested in short Mg–O bonds [2.0216(8)/2.0320(9) and 2.0270(15)/2.0304(15) Å, respectively] and in perfectly planar $(MgO)_2$ rings. Two amide N atoms complete the distorted tetrahedral geometry of the Mg atom at distances (mean: in **1**, 2.051 Å; in **2**, 2.046 Å) comparable to that in **5** (2.065 Å). Similarly, the Na–N bonds which complete the distorted trigonal pyramidal N/N/O coordination of the Na atoms, have distances (mean: in **1**, 2.469 Å; in **2**, 2.478 Å) comparable to that in **5** (2.4807 Å). Angular dimensions within the octagonal rings of **1** [NMgN, 133.44(4)°; NNaN, 147.07(4); NaNMg, mean 81.74°] and **2** [corresponding values: 134.10(8)°; 142.71(7)°; 81.78°] show little variance from each other, but comparison with those in **5** [corresponding values: 133.16(11)°; 132.08(10)°; 88.29(7)°] reveals that toluene solvation draws the Na atom from the octagonal ring thus greatly contracting the NNaN bond angle.

Though definite structural information on superbases remains scant, there is a general belief that their structures are dominated by Li–O bonding. One can draw a parallel with the structures of **1** and **2**, which are manifestly dominated by Mg–O bonding. This begs the interesting question, could Mg replace Li as the passive ‘hard’ metal in superbases with active ‘soft’ heavier alkali metal organyl components? On valency grounds alone, there are certain to be major structural differences on replacing Li by Mg; however, the effect of these differences on the reactivity and selectivity of the active anion within such composite species is not easy to predict.

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Notes and references

† *General preparative method* (on a 5 mmol scale in a Schlenk tube under argon gas): Bu^nM (M = Li or Na) in hexane is mixed with Bu_2Mg in heptane to form a brown congealed mass, which dissolves on addition of Pr^i_2NH (15 mmol). Next, 5 mmol of the alcohol (*n*-butanol or *n*-octanol) is added slowly to the mixture, resulting in an exothermic reaction. Cooling of the solution (after removing hydrocarbon solvent and replacing it with toluene in the case of **1**) affords colourless, air- and moisture-sensitive crystals of **1**, **2** or **3**. Yields (unrefined) 75, 71 and 26%, respectively. ^1H NMR (400.13 MHz, $C_6D_5CD_3$, 300 K): **1**, δ 3.97 (m, $OCHH'CH_2$), 3.35 (septet, $CHMe_2$), 1.71 (m, $CHH'CH_2CH_2$), 1.26 (sextet, $CH_2CH_2CH_3$), 1.21 (d, $CHMe_2$), 0.93 (t, CH_3CH_2); **2**, δ 3.99 (m, $OCHH'CH_2$), 3.37 (septet, $CHMe_2$), 1.76 (m, $CHH'CH_2CH_2$), 1.37–1.27 (overlapping m's, CH_2's of *n*-Oct), 1.24 (d, $CHMe_2$), 0.89 (t, CH_3); **3**, δ 4.08 (m, $OCHH'CH_2$), 3.40 (sep, $CHMe_2$), 1.93 (m, $CHH'CH_2$) 1.45–1.14 (overlapping m's, CH_2's of *n*-Oct), 1.30 (d, $CHMe_2$), 0.91 (t, CH_3). ^{13}C NMR (100.61 MHz, $C_6D_5CD_3$, 300 K): **1**, δ 66.2 ($OCHH'$), 47.3 ($CHMe_2$), 39.2 ($CHH'CH_2CH_2$), 29.0 ($CHMe_2$), 19.4 ($CH_2CH_2CH_3$), 14.3 (CH_3); **2**, δ 65.6 ($OCHH'$), 47.3 ($CHMe_2$), 37.0 ($CHH'CH_2CH_2$), 32.2 ($CH_2CH_2CH_2$), 30.0 ($CH_2CH_2CH_2$), 29.6 ($CH_2CH_2CH_2$), 29.0 ($CHMe_2$), 26.0 ($CH_2CH_2CH_2$), 23.1 (CH_2CH_3), 14.3 (CH_3); **3**, δ 66.0 ($OCHH'$), 46.8 ($CHMe_2$), 36.7 ($CHH'CH_2CH_2$), 32.2 ($CH_2CH_2CH_2$), 29.9 ($CH_2CH_2CH_2$), 29.6 ($CH_2CH_2CH_2$), 28.4 ($CHMe_2$), 26.2 ($CH_2CH_2CH_2$), 23.1 (CH_2CH_3), 14.3 (CH_3). ^7Li NMR (155.50 MHz, $C_6D_5CD_3$, 300 K): **3**, δ 1.07. ^7Li chemical shift is given relative to external LiCl in D_2O. Satisfactory microanalyses (C, H, N) were obtained for **1**, **2** and **3**.

‡ *Crystal data*: for **1**: $C_{32}H_{74}Mg_2N_4Na_2O_2$, M_r = 641.55, triclinic, space group $P1$, a = 9.6321(2), b = 10.3272(2), c = 11.4653(2) Å, α = 100.339(1), β = 108.296(1), γ = 108.270(1)°, V = 978.13(3) Å^3, Z = 1, D_c = 1.089 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, μ = 0.114 mm^{-1}, T = 123 K; 19701 reflections were collected, 4460 were unique, R_{int} 0.028; final refinement to convergence on F^2 with all non-H atoms anisotropic and all H atoms modeled isotropically gave R = 0.0450 (F, 3652 obs. data only) and R_w = 0.0848 (F^2, all data), GOF = 1.020, 338 refined parameters; max./min. residual electron density: 0.225/−0.159 e Å^{-3}.

For **2**: $C_{40}H_{90}Mg_2N_4Na_2O_2$, M_r = 753.76, monoclinic, space group $P2_1/c$, a = 10.7260(4), b = 13.8181(4), c = 16.5769(5) Å, β = 98.680(1)°, V = 2428.77(14) Å^3, Z = 2, D_c = 1.031 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, μ = 0.101 mm^{-1}, T = 123 K; 18646 reflections were collected, 4218 were unique, R_{int} 0.157; final refinement to convergence on F^2 with all non-H atoms anisotropic (except for the sixminor-occupancy C sites of the disordered NPr^i_2 group, which were treated isotropically) and all H atoms in calculated positions gave R = 0.0643 (F, 3614 obs. data only) and R_w = 0.1814 (F^2, all data), GOF = 1.060, 260 refined parameters; max./min. residual electron density: 0.418/−0.235 e Å^{-3}.

CCDC reference numbers 182083 and 182084. See http://www.rsc.org/suppdata/cc/b2/b202549c/ for crystallographic data in CIF or other electronic format.

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