Crystallographic characterisation of binary alkali metal alkoxide–magnesium bis(alkyl) mixtures: differential binding of Na$^+$ and K$^+$ to a common dinuclear diorganomagnesiate

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Relevant to mixtures studied in solution and utilised in styrene polymerisation but hitherto not characterised in the solid, two crystal structures of alkali metal alkoxide–magnesium bis(alkyl) co-complexes have been determined, revealing that in binding to the C$_2$O tripodal face of a common organomagnesiate anion, Na$^+$ prefers O-coordination, whereas K$^+$ prefers C-coordination.

Recently we described a series of composite alkali metal–magnesium–alkoxide–diisopropylamides of general formula [{MMg[N(Pr^i)$_2$]$_2$OR}$_2$] (where M = Li, R = Oct^n; M = Na, R = Bu^n or Oct^n) and general structure **1**.[1] This octagonal (MNMgN)$_2$ cyclic arrangement coupled with the pseudo-encapsulated OR groups, fitted into our developing theme of inverse crown complexes (macrocyclic heterometallic amides, where, opposite to that in conventional crown ether complexes, host rings are Lewis acidic and their guests Lewis basic), an idea conceived originally through singly-occupied host, oxide-guest molecules like **2**.[2]
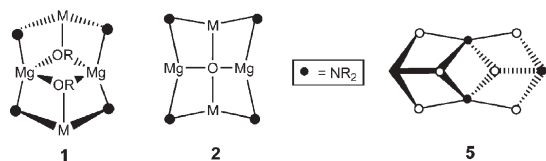
Since **1** could be viewed alternatively as a co-complex between an alkali metal alkoxide (MOR) and a magnesium bis(amide) [Mg(NR$_2$)$_2$], we pondered whether it would be possible to substitute the latter component for a magnesium bis(alkyl) (MgR$_2$) to generate the first alkyl inverse crown, as hitherto s-block inverse crowns have been exclusively amide based. Binary alkali metal alkoxide–magnesium bis(alkyl) mixtures have recently been investigated *in situ* as initiators for the stereospecific anionic polymerisation of styrene with potassium systems noted for producing isotactic-rich polystyrene.[3] Richey has also studied their solution behaviour by NMR spectroscopy.[4] Here, in an intersection of these two distinct research lines, we reveal that attempts to synthesise alkyl inverse crowns have been successful and thus we are able to report coincidentally the first crystallographically characterised mixed sodium alkoxide– and potassium alkoxide–magnesium bis(alkyl) complexes in [{NaMg(Bu)$_2$(OBu^t).(TMEDA)}$_2$] **3** and [{KMg(Bu)$_2$(OBu^t).(TMEDA)}$_2$] **4**, respectively (TMEDA is *N,N,N',N'*-tetramethylethylenediamine).

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Whereas the amide–alkoxide inverse crowns **1** were synthesised by deprotonation of an alcohol ROH with the synergic tris(amide) "MMg[N(Pr^i)$_2$]$_3$", the best method for preparing **3** and **4** is *via* a direct addition (co-complexation) procedure. Mixing the alkali metal *tert*-butoxide with *n, sec*-dibutylmagnesium in hydrocarbon media and adding TMEDA stoichiometrically affords the new alkyl inverse crowns in crystalline form.† While the use of the isomeric alkyl magnesium reagent leads unavoidably to incorporation of both Bu^n and Bu^s ligands, the crystalline products tend to be much richer in the former, though ratios vary, as determined by NMR spectroscopic studies on several different batches.

The centrosymmetric molecular structures of **3** and **4** are identical in terms of connectivity.‡ Fig. 1 shows that of **3** from a view emphasising its host [(NaCMgC)$_2$] ring and guest [2 × OBu^t] inverse crown appearance. Fig. 2 shows that of **4** from an alternative side-on perspective. Principal dimensions within **3** and **4** (see figure legends) reveal that the five-coordinate M$^+$ interact with two α-C atoms of distinct Bu bridges, two TMEDA N atoms, but only one O atom [that disposed *syn* to M$^+$ at distances of 2.533(5) and 2.995(3) Å in **3** and **4**, respectively]. Though a similar endo connectivity pattern distinguishes the amide–alkoxide structures **1**,
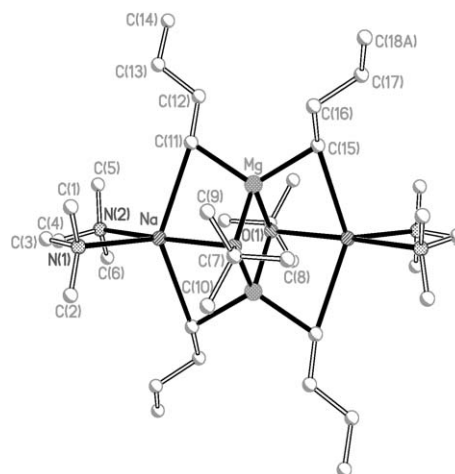

Fig. 1 Molecular structure of **3** with atom labelling. Minor disorder components and hydrogen atoms are omitted for clarity. Selected dimensions (Å and °): Mg–O(1) 2.033(4), Mg–O(1A) 2.028(4), Mg–C(11) 2.190(6), Na–N(1) 2.556(8), Na–N(2) 2.596(7), Na–O(1) 2.533(5), Na–C(11) 2.852(7); O(1)–Mg–O(1A) 82.47(19), O(1)–Mg–C(11) 106.9(2), O(1A)–Mg–C(11) 119.0(2), N(1)–Na–N(2) 73.3(3), N(1)–Na–O(1) 119.9(2), N(1)–Na–C(11) 111.0(3), N(2)–Na–O(1) 166.8(2). O(1A) is centrosymmetrically related to O(1).
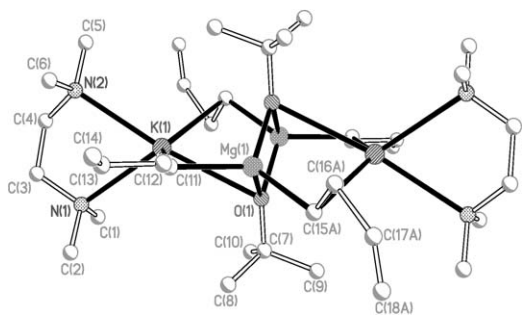
Fig. 2 Molecular structure of **4** viewed through the edge of the $K_2Mg_2C_4$ chair-shaped ring, with atom labelling. Disorder components and hydrogen atoms are omitted for clarity. Selected dimensions (Å and °): Mg–O(1) 2.012(3), Mg–O(1A) 2.016(3), Mg–C(11) 2.197(5), K–N(1) 2.831(4), K–N(2) 2.835(4), K–O(1) 2.995(3), K–C(11) 2.974(5); O(1)–Mg–O(1A) 78.87(13), O(1)–Mg–C(11) 114.90(17), O(1A)–Mg–C(11) 115.18(18), N(1)–K–N(2) 65.03(12), N(1)–K–O(1) 121.08(10), N(1)–K–C(11) 107.23(14), N(2)–K–O(1) 173.62(11). O(1A) is centrosymmetrically related to O(1).

they diverge from **3** and **4** in having vacant exo M^+ (Li or Na) sites. This divergence can be attributed in the main to the attenuation in steric strain on substituting Bu bridges for bulkier secondary amides (though there may also be an electronic influence), which allows attachment of didentate TMEDA ligands to Na^+ or K^+.

The close similarity between corresponding dimensions within the common $[\{Bu_2Mg(\mu\text{-}OBu^t)_2MgBu_2\}^{2-}]$ substructure of **3** and **4** supports the idea that these structures are also dinuclear organomagnesiates. Richey previously proposed such a substructure for related 1:1, R_2Mg–MOR solution species.[4] In this interpretation the alkali metals could be considered unimportant, mere counter-ions. However, Deffieux's aforementioned study unequivocally establishes that the identity of the cation is a critical factor in controlling the stereochemistry of the growing polymer chain with Li and Na behaving profoundly differently from K in producing substantially less isotactic polystyrene. Moreover, Deffieux envisages a mechanism whereby styrene monomer inserts directly into a M–Bu bond [albeit in a mononuclear $BuMg(\mu\text{-}OBu^t)(\mu\text{-}Bu)M$ system as opposed to the dinuclear version seen here]. Thus the structures of **3** and **4** provide unique insight into the nature of, and the similarities/differences between, such Na^+– and K^+–organomagnesiate interactions. In both, the 'ate offers two diametrically opposed M^+ cations the same tripodal ($2 \times C$; $1 \times O$) connectivity. Facilitated by the electron richness of the μ_3-Bu^tO^- group ('guest' in inverse crown notation), this heteroanionic η^3-chelation contrasts with the more common η^2 variation seen in 'ates such as $[\{LiMg(Ph)_3.(TMEDA)\}_2]$.[5] Significantly, however, the relative affinity of M^+ for the distinct coordinating atoms of the ligand differs in **3** and **4**. To elaborate, little discrimination exists between the K–C and K–O bond lengths (the former are actually shorter by 0.021 Å, though this is statistically insignificant) in contrast, the Na–O bond is substantially shorter (by 0.319 Å) than its C analogues. Moreover, comparison of K–O/Na–O, K–N/Na–N and K–C/Na–C bond lengths reveals that the expected reduction in size (taking into account the relative sizes of K^+ and Na^+) is not uniform, but shows a diminishing trend of 0.462, 0.257 and 0.122 Å, respectively. It can

therefore be concluded that, when bonding to the C_2O ligand face, K^+ displays a bias towards C-coordination, whereas Na^+ has a bias towards O-coordination. This divergence may be a contributory factor to the different results obtained for K^+ and Na^+ in the aforementioned polystyrene study. The implication is that K^+ is more likely to remain in the vicinity of alkyl groups in the active site of the propagating end of the polymer chain, leading to a higher degree of isotacticity. However, it should be noted that TMEDA was absent in the polymerisation study, so it is possible that oligomers of higher nuclearity than that of **3** and **4** may be involved.

Searching for related non-magnesium MOR–$M'R'_2$ structures, one notes that of $[\{[KZn(Et)_2(OBu^t)]_2\}_\infty]$:[6] this solvent-free 'ate displays basically the same $(KM'C_2O)_2$ motif as **4** (but with $M' = Zn$), though its intramolecular K–C(Et) bonds (mean length, 3.065 Å, *cf.* 2.974 Å in **4**) were not mentioned in the report of this structure and neither was the plethora of intermolecular K–C(Et) contacts (spanning 3.3–3.5 Å) that marks this structure as a polymer of linked dimers, not a discrete dimer as **4** (caused by TMEDA chelation). While this maintains the affinity of K^+ for C-coordination, the comparison is complicated by the fact that the K–O bond is unusually short in this case (2.626 Å). Searching further afield, it is clear that this structural motif (sometimes described as two cuboidal arrays, each 'missing' a corner, and sharing a common face – depicted in **5**) is fast becoming a general structural type in inorganic chemistry. Representative heterometallic examples include the sodium–iron all-alkoxide $[\{NaFe(OBu^t)_3.(THF)\}_2]$,[7] the potassium–calcium all-enolate $[\{KCa(R)_3.(THF)\}_2]$[8] [R = OC(Mes)=CH_2], and the potassium–zinc all-siloxide $[\{KZn(OSiMe_3)_3.(TMEDA)\}_2]$,[9] but the type extends also to homometallic systems such as the alkylmagnesium amide $[\{Bu^nMg_2[N(H)Dipp]_2(OBu^n)\}_2]$,[10] the zinc relation $[\{EtZn_2[N(H)Dipp]_2(OEt)\}_2]$[11] and the Grignard reagent $[\{(PhCH_2)Mg_2Cl_3.(THF)_3\}_2]$.[12]

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Notes and references

† Standard inert-atmosphere Schlenk techniques were used throughout. General preparative method: $MOBu^t$ (M = Na **3** or K **4**) (10 mmol) was suspended in hexane (10 ml) and $^{n,s}Bu_2Mg$ (10 mmol, 10 ml of a 1.0 M solution in heptane) added dropwise to give a sticky pale yellow solid. TMEDA (10 mmol, 1.5 ml) was added dropwise to slowly dissolve the solid, resulting in a colourless oil. Storage of the oil at -28 °C yielded a crop of colourless needle-like crystals in both cases. **3**: Yield = 1.94 g, 55.3%, mp 116–117 °C (decomp.). ^1H NMR (400.13 MHz, C_6D_6, 300 K): δ 2.08 (s, 12H, CH_3, TMEDA), 2.01–2.09 (m, 4H, CH$_2$CH_2CH$_2$), 1.96 (s, 4H, CH_2, TMEDA), 1.74 (sextet, 4H, CH$_2$CH_2CH$_3$, J = 7.16 Hz), 1.44 (s, 9H, OCMe_3), 1.24 (t, 6H, CH_3CH$_2$, J = 7.30 Hz), -0.56 (m, 4H, Mg–CH_2). The presence of Bu^s groups was established by a broad multiplet between 0.01 and 0.09 ppm. Other Bu^s resonances were obscured by other signals. ^{13}C NMR (100.61 MHz, C_6D_6, 300 K): δ 67.1 (OCMe$_3$), 58.2 (CH_2, TMEDA), 46.8 (CH_3, TMEDA), 35.4 (OCMe_3), 34.3 (CH$_2$CH_3), 33.6 (CH_2CH$_2$CH$_3$), 15.1 (CH_3CH$_2$), 12.2 (MgCH_2). **4**: Yield 0.91 g, 24.8%, mp 117–118 °C (decomp.). ^1H NMR (400.13 MHz, C_6D_6, 300 K): δ

2.00 (s, 12H, CH_3, TMEDA), 1.98 (s, 4H, CH_2, TMEDA), 1.91–1.96 (m, 4H, CH$_2$CH_2CH$_2$), 1.76 (sextet, 4H, CH$_2$CH_2CH$_3$, J = 7.36 Hz), 1.40 (s, 9H, OCMe_3), 1.26 (t, 6H, CH_3CH$_2$, J = 7.32 Hz), −0.53 (m, 4H, MgCH_2). All Bu^s signals were broad and weak. ^{13}C NMR (100.61 MHz, C$_6$D$_6$, 300 K); δ 67.4 (OCMe$_3$), 56.1 (CH_2, TMEDA), 46.2 (CH_3, TMEDA), 35.5 (OCMe_3), 35.1 (CH_2CH$_2$CH$_2$), 33.8 (CH_2CH$_3$), 16.3 (MgCH_2), 15.2 (CH_3CH$_2$). Satisfactory microanalyses (C, H and N) were obtained for **3** and **4**.

‡ *Crystal data*: for **3**: C$_{36}$H$_{86}$Mg$_2$N$_4$Na$_2$O$_2$, M = 701.7, monoclinic, space group $P2_1/n$, a = 11.710(3), b = 14.312(3), c = 14.520(4) Å, β = 101.787(15)°, V = 2382.1(10) Å^3, Z = 2, T = 293 K, μ(Cu-Kα) = 0.85 mm^{-1}. 3805 data, 2497 unique (R_{int} = 0.0439). $wR(F^2)$ = 0.2511 for all data, conventional R = 0.0723 for F values of 1472 reflections with $F_o^2 > 2\sigma(F_o^2)$. Minor disorder modelled for substitution of 30% Bu^s for Bu^n; H atoms constrained with a riding model. For **4**: C$_{36}$H$_{86}$K$_2$Mg$_2$N$_4$O$_2$, M = 733.91, monoclinic, space group $P2_1/n$, a = 11.4984(6), b = 14.7210(11), c = 14.4940(10) Å, β = 103.391(4)°, V = 2386.7(3) Å^3, Z = 2, T = 123 K, μ(Mo-Kα) = 0.255 mm^{-1}. 22825 data, 4156 unique (R_{int} = 0.088). $wR(F^2)$ = 0.1964 for all data, conventional R = 0.0762 for F values of 2212 reflections with $F_o^2 > 2\sigma(F_o^2)$. One of the Bu groups was modelled as disordered over two sites. CCDC 249271 and 249272. See http://www.rsc.org/suppdata/cc/b4/b413191f/ for crystallographic data in .cif or other electronic format.

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