A new polymeric alkyl/alkoxide magnesium–sodium inverse crown complex

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Poly[bis(μ_3-trimethylsilylmethanolato)tetrakis(μ_2-trimethylsilylmethyl)dimagnesiumdisodium], [$Na_2Mg_2(C_4H_{11}OSi)_2$-$(C_4H_{11}Si)_4$]$_n$, was obtained from the controlled exposure to oxygen of the unsolvated sodium magnesate [$NaMg(CH_2SiMe)_3$]$_n$. Exhibiting a centrosymmetric ($Z' = \frac{1}{2}$) dimeric core of a heterobimetallic eight-membered cationic ring, hosting two alkoxide ligands at its core, the title compound forms a two-dimensional coordination polymer in the crystallographic bc plane through Na$\cdots$Me contacts. These contacts from Na to formally uncharged groups are only 0.06 Å longer than those between Na and the formally charged CH_2R anions. The coordination polymers stack along the a direction to give a layer structure with alternating hydrophobic and hydrophilic regions.

Comment

Alkali metal organometallic compounds can react violently with moisture and oxygen, hence the exclusion of air during the preparation and employment of these complexes is mandatory, with manipulations carried out under a dry inert atmosphere (Wardell, 1982, and references therein). Having stated that, regulated exposure of metal alkyls to dry oxygen can lead to an interesting array of structures, with oxygen inserting into the metal–carbon bond (Barron, 1993; Kennedy *et al.*, 1999; Forbes *et al.*, 2000; Mulvey, 2001; Bailey *et al.*, 2003). Here, we report an example of controlled oxygen insertion into the homoleptic trialkyl sodium magnesate [{$NaMgR_3$}]$_\infty$ ($R = CH_2SiMe_3$), a compound which itself has recently been structurally authenticated as a unique two-dimensional supramolecular network in the solid state (Baillie *et al.*, 2011). A drying tube (containing $CaCl_2$) was fitted to a Schlenk tube containing a solution of the starting magnesate complex, to allow oxygen but not water to enter the system. Slow cooling of the resulting colourless solution led to the deposition of colourless crystals of [{$NaMgR_2(OR)$}]$_\infty$, (I),

where the alkoxide ligand OR is formed as a result of oxygen insertion into the polar metal–carbon bond of an alkyl group.

(I)
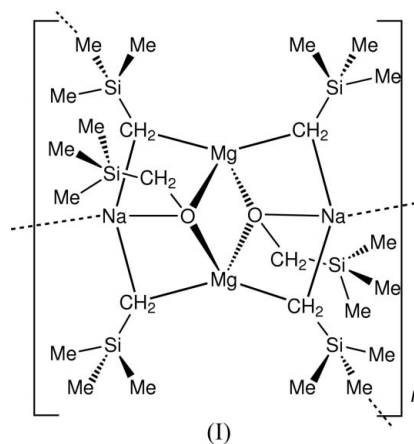
Looking at its empirical formulation, (I) can be envisaged as the co-complexation product of the bis-alkyl $Mg(CH_2SiMe_3)_2$ and the alkoxide $NaOCH_2SiMe_3$ and, as such, may be considered an alkaline earth metal relation of the Lochmann–Schlosser reagent, LiC–KOR, which pairs *n*-butyllithium with the heavier alkali metal potassium *tert*-butoxide (Lochmann, 2000). LiC–KOR can be described as a superbase, due to its dramatic enhancement in reactivity in deprotonation reactions compared with a mixture of an alkyllithium with lithium butoxide. Despite the wide applications of the superbase in synthesis, definitive structural information on the Lochmann–Schlosser reagent has not been forthcoming. However, elucidation of the structure of (I) may provide indirect insight into the structural make-up of the alkali metal-rich superbase.
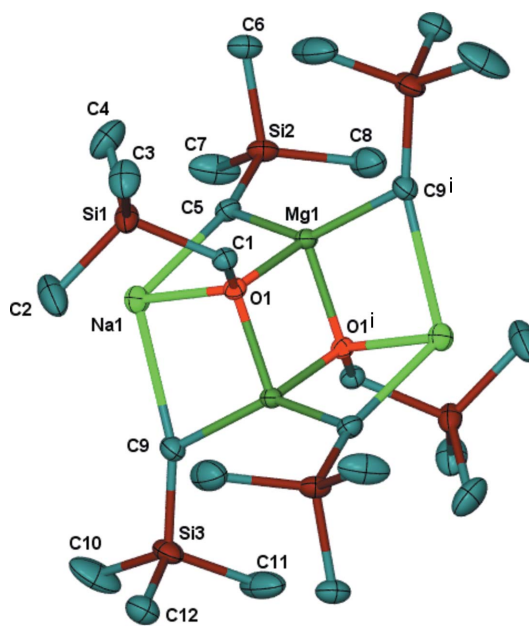
Figure 1
The molecular structure of (I), showing the dimeric unit generated by a centre of symmetry. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $-x$, $-y$, $-z$.]
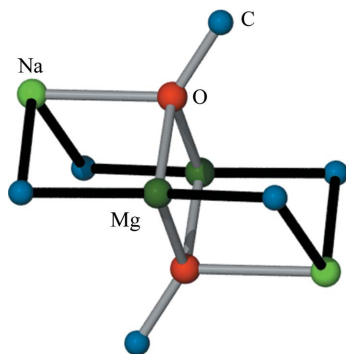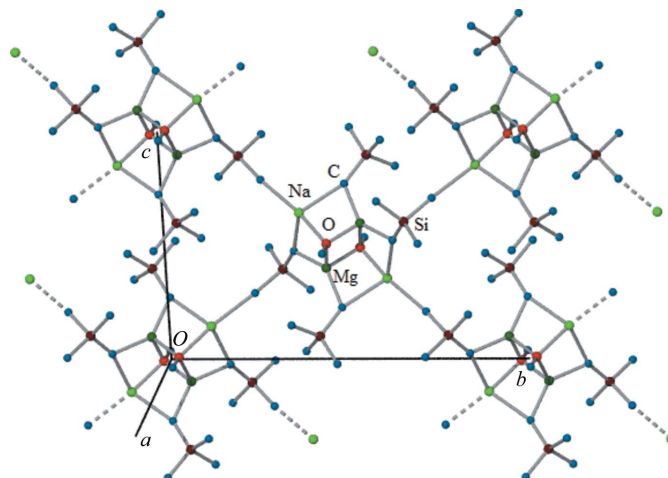
Figure 2
Detail of the central core of (I), with its pseudo-chair motif.

Compound (I) features a dimeric arrangement comprising two {NaMgR_2(OR)} units, giving rise to a face-fused double heterocubane structure with two missing corners. The OR groups face-cap the 'top' and 'bottom' of the structure, acting as a bridge between two Mg centres and an Na centre (Fig. 1). Alternatively, the compound can be described as an inverse crown complex consisting of a cationic eight-atom {NaCMgC}$_2$ heterobimetallic ring hosting two alkoxide ligands at its core (Mulvey, 2001). This cationic ring adopts a pseudo-chair structure, with the Na centres constituting the 'head' and 'footrest' of the chair (see the alternative view in Fig. 2).

The Mg centre resides in a four-coordinate environment, with widely varying bond angles [84.77 (5)–138.14 (7)°] and bonds to two alkyl groups and two alkoxide ligands; see Table 1 for more details and for a definition of the symmetry operators. Each Na centre bonds to two bridging alkyl groups within the dimeric unit and also to one alkoxide OCH$_2$SiMe$_3$ ligand. In addition, Na also forms a secondary intermolecular interaction with a neighbouring methyl group [Na1···C6^{ii} = 2.7448 (18) Å]. Note that this interaction with a neutral methyl group is only about 0.06 Å longer than the interactions with the formally charged CH$_2$$R$ anions. The Na centre is thus tetracoordinate, with a wide range of angles observed from 82.79 (5) to 171.69 (6)°.

Unlike related inverse crown structures, where Lewis basic donors such as N,N,N',N'-tetramethylethylenediamine (TMEDA) coordinate to the alkali metal (Barnett et al., 2005) or alternatively where the alkali metal is coordinatively supported through metal–arene contacts from aromatic solvents (Gallagher et al., 2002; Andrikopoulos et al., 2003), no such stabilization is observed in (I). This lack of externally added solvating molecules around Na is compensated for by the additional secondary electrostatic interactions with the methyl groups of SiMe$_3$ fragments from neighbouring molecules. Of the four alkyl groups present in the ring scaffold of (I), only two alkyl units, diagonally opposite each other and inversion related, interact with the neighbouring dimeric units. This leads to polymerization of the eight-membered rings and results in a two-dimensional coordination sheet propagating in the crystallographic bc plane (Fig. 3). Each plane has a core of polar elements surrounded by organic groups and thus a structure with alternating hydrophilic and hydrophobic layers results.

Figure 3
Na···Me interactions (shown as dashed lines) give a two-dimensional polymeric sheet structure in the bc plane of (I). The SiMe$_3$ groups of the alkoxide and all H atoms have been omitted for clarity.

In the oxygen-free parent compound [{NaMgR_3}]$_\infty$ (Baillie et al., 2011), a very different structure is observed, made up of 12-atom {(NaCMgC)$_3$} fused rings. However, as in (I), each alkyl group acts as a bridge between an Na and an Mg centre, and similar distances are found in the Na—C bond lengths [2.6708 (19) Å]. In addition, the Mg—O distance in (I) is almost identical to those reported in the closely related inverse crown ether {NaMg(Bu)$_2$(O^{t}Bu)·(TMEDA)}$_2$ (Barnett et al., 2005) [compare Mg—O1 and Mg—O1^i in Table 1 with Mg—O distances of 2.028 (4) and 2.033 (4) Å in the TMEDA-solvated structure]. To the best of our knowledge, this analogous structure is the only other inverse crown ether with an eight-membered scaffold constructed exclusively with metal–carbon bonds. In contrast with (I), {NaMg(Bu)$_2$-(O^{t}Bu)·(TMEDA)}$_2$ was formed using a different synthetic approach by the co-complexation of the monometallic components NaO^{t}Bu and MgBu$_2$ in the presence of TMEDA, which coordinates the alkali metal and removes the opportunity for polymeric propagation.

Experimental

To a stirred suspension of NaCH$_2$SiMe$_3$ (0.11 g, 1.0 mmol) in hexane (15 ml) was added Mg(CH$_2$SiMe$_3$)$_2$ (0.20 g, 1.0 mmol), and the resulting white suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by approximately half under reduced pressure. Benzene (3 ml) was then introduced and the mixture was gently heated. A CaCl$_2$ drying tube was fitted and the reaction mixture was exposed to air through this tube for 1 h, after which the tube was resealed and the mixture stirred overnight. The solvent was removed in vacuo and hexane (5 ml) was added with gentle heating. After being allowed to cool slowly to room temperature, the resulting colourless solution afforded a crop of colourless crystals of (I) (yield 0.03 g, 15%). ^{1}H NMR (400.03 MHz, 298 K, C$_6$D$_6$): δ −2.12 (4H, s, SiCH_2), −0.04 [9H, s, Si(CH_3)$_3$], −0.35 [18H, s, OSi(CH_3)$_3$], 3.43 (2H, s, OCH_2); ^{13}C {^{1}H} NMR (100.62 MHz, 298 K, C$_6$D$_6$): δ −6.00 (MCH_2), −2.61 [OCH$_2$Si(CH_3)$_3$], 4.65 [MCH$_2$Si(CH_3)$_3$], 55.37 (OCH_2).

Table 1
Selected geometric parameters (Å, °).

Mg1—O1	2.0274 (12)	Na1—O1	2.2716 (12)
Mg1—O1^i	2.0347 (11)	Na1—C5	2.6850 (18)
Mg1—C5	2.1915 (17)	Na1—C9	2.6706 (18)
Mg1—C9^i	2.1890 (17)	Na1—C6^{ii}	2.7448 (18)
O1—Mg1—O1^i	84.77 (5)	O1—Na1—C9	83.19 (5)
O1—Mg1—C9^i	110.06 (6)	O1—Na1—C5	82.79 (5)
O1^i—Mg1—C9^i	102.46 (6)	C9—Na1—C5	116.83 (6)
O1—Mg1—C5	102.52 (6)	O1—Na1—C6^{ii}	171.69 (6)
O1^i—Mg1—C5	106.08 (6)	C9—Na1—C6^{ii}	104.77 (6)
C9^i—Mg1—C5	138.14 (7)	C5—Na1—C6^{ii}	95.46 (6)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Crystal data

[Na₂Mg₂(C₄H₁₁OSi)₂(C₄H₁₁Si)₄]
$M_r = 649.91$
Monoclinic, $P2_1/c$
$a = 9.8057$ (3) Å
$b = 18.1602$ (5) Å
$c = 11.8234$ (3) Å
$\beta = 95.482$ (3)°

$V = 2095.80$ (10) Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.27$ mm⁻¹
$T = 123$ K
$0.23 \times 0.18 \times 0.15$ mm

Data collection

Oxford Gemini S diffractometer
Absorption correction: multi-scan
(*CrysAlis PRO*; Oxford
Diffraction, 2010)
$T_{min} = 0.804$, $T_{max} = 1.000$

17871 measured reflections
5052 independent reflections
3663 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.100$
$S = 0.96$
5052 reflections
196 parameters

H atoms treated by a mixture of
independent and constrained
refinement
$\Delta\rho_{max} = 0.46$ e Å⁻³
$\Delta\rho_{min} = -0.28$ e Å⁻³

The H atoms of the CH₂ groups were found through difference synthesis and were refined isotropically [C—H = 0.89 (2)–1.041 (17) Å]. Methyl H-atom positions were found by allowing the torsion angle about the Si—C bond to refine but with an idealized geometry, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

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