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A new Na/Mg inverse crown ether

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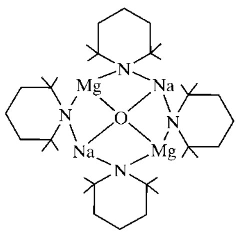
A 'missing' member of the inverse crown ether family, namely μ_4-oxo-tetrakis(μ-2,2,6,6-tetramethylpiperidinido)dimagnesium(II)disodium(I), $[Na_2Mg_2O(C_9H_{18}N)_4]$, has been synthesized by blocking the alternative aromatic metallation route *via* the use of sterically hindered 1,3,5-mesitylene as a solvent. $[Na_2Mg_2O(NR_2)_4]$ (NR_2 is 2,2,6,6-tetramethylpiperidinide) is shown to form a cationic planar eight-membered ring with alternating metal and N atoms, which captures at its core an oxide guest that lies on an inversion centre [principal dimensions: Na—O = 2.2405 (11) Å, Na—N = 2.445 (3) and 2.572 (3) Å, Mg—O = 1.8673 (9) Å, and Mg—N = 2.032 (2) and 2.063 (2) Å].

Comment

Lithium (and to a lesser extent sodium and potassium) amides find a wide range of uses in synthetic chemistry, and the literature on these compounds is vast [for pertinent examples, see Gregory *et al.* (1991) and Mulvey (1991)]. In contrast, magnesium bis(amides) have been largely neglected to date, although recent studies have demonstrated their effectiveness in the fields of aldehyde/ketone addition (Allan *et al.*, 1997, 1999) and asymmetric synthesis (Henderson *et al.*, 2000). Recently, our group has attempted to combine the properties of the two distinct reagents, namely the relatively low nucleophilicity and strong Brønsted basicity of lithium amides and the selectivity and moderated reactivity of the magnesium bis(amides), into a single compound by preparing mixed alkali-metal–magnesium amides. We have been largely successful in producing a series of mixed-metal synergic amide bases involving three different bulky secondary amides in diisopropyl amide, hexamethyldisilazide (HMDS) and 2,2,6,6-tetramethylpiperidinide (TMP), and have isolated a number of unique products from the subsequent reactions of these bases with various substrates. For a review of this work, see Mulvey (2001). In the absence of a suitable substrate, the bases act as highly efficient oxygen scavengers, thus producing compounds known as 'inverse crown ethers', which contain oxo and/or peroxo dianions as 'guests' in their eight-membered cationic 'host' ring cores. These compounds have the general formula $[M_2M'_2(NR_2)_4(O_2)_xO_{1-x}]$. When NR_2 is HMDS, the series in which M is Li, Na or K and M' is Mg, and that in which M is Na or K and M' is Zn, have been crystallographically characterized (Mulvey, 2001). When the amide is TMP, the analogous compound involving Li and Mg can be made easily, but with Na (and indeed K), a novel alternative reaction involving the reaction solvent takes place. This reaction affords larger 12-membered host rings, which contain solvent-derived benzene ($C_6H_4^{2-}$) or toluene $[C_6H_3(CH_3)^{2-}]$ dianions (in the case of Na) and 24-membered rings hosting six benzene-based ($C_6H_5^-$) or six toluene-based $[C_6H_4(CH_3)^-]$ monoanions (in the case of K) (Kennedy *et al.*, 1998; Andrews *et al.*, 2000). Surprisingly, in the toluene cases, the most acidic methyl H atom, which would normally be deprotonated with conventional bases (Schlosser, 2001, and references therein) under thermodynamic conditions (Broaddus, 1966), is left untouched and only ring deprotonation occurs. With a judicious shift to a different aromatic solvent (1,3,5-mesitylene), whereby ring metallation is highly sterically unfavoured, we were successful in synthesizing, for the first time, the title compound, $[Na_2Mg_2O(TMP)_4]$, (I). No arene metallation was detected.



(I)

As with the other eight-membered cationic rings mentioned above, the molecular structure of (I) is based on alternating metal and N atoms, with a guest oxide anion on the inversion centre at the centre of the ring (Fig 1). The ring and its guest

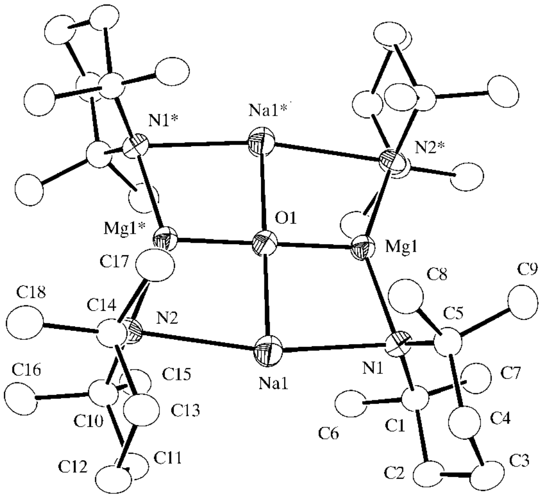


Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 50% probability level and H atoms omitted for clarity. Atoms marked with an asterisk (*) are at the symmetry position $(2 - x, -y, -z)$.

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are coplanar, while the TMP rings adopt chair conformations, with the Mg atoms in equatorial positions and the Na atoms in axial positions. This conformation leads to the organic ring systems lying perpendicular to the inorganic ring. In general, the structural detail of these species seems to be controlled by the coordination needs of the Mg atoms (Mulvey, 2001). There is some evidence here to support this hypothesis, in that the geometry about the Mg atom in (I) is similar to that in the HMDS analogue (Kennedy *et al.*, 1998), while the Na-atom geometry is relatively flexible. The Mg—N distances are 2.032 (2) and 2.063 (2) Å in (I) (Table 1), compared with 2.049 (1) and 2.055 (1) Å in the HMDS analogue, while the respective N—Mg—N angles are 144.48 (11) and 141.60 (5)°. The corresponding distances and angles at the Na atom are 2.445 (3) Å, 2.572 (3) Å and 166.57 (9)° for (I), and 2.549 (1) Å, 2.595 (1) Å and 159.84 (2)° for the HMDS analogue. Little detailed geometrical comparison can be made with the lithium relative, $[Li_2Mg_2O(TMP)_4]$, as this structure has disordered metal sites (Kennedy *et al.*, 1998). However, we do note that substituting the larger Na atoms for Li atoms moves the metal further from the oxide core and gives a reflex exocyclic N—Na—N angle. This change, together with the inherent coordinative unsaturation of the three-coordinate Na atoms, allows several short Na···Me contacts to form [the closest is Na···C6 at 3.105 (3) Å].

Experimental

n-BuNa was synthesized according to the method described by Lochmann *et al.* (1966) and was then suspended (5 mmol) in hexane (10 ml). A solution (0.875 *M*) of dibutylmagnesium (5 mmol) in heptane was added dropwise, giving a congealed brown mass. Tetramethylpiperidine (15 mmol) was then introduced, causing an exothermic reaction that produced an orange solution. When this solution was stirred overnight, it gradually darkened and a white precipitate was formed. The mixture was filtered through Celite and then all solvents were removed under a vacuum, leaving an orange oil. Mesitylene (5 ml) was added and the mixture was stirred at ambient temperature until all the oil had dissolved and a red solution had formed. Colourless crystals suitable for X-ray analysis formed after a few days from this solution, which had darkened to a near-black colour.

Crystal data

$[Na_2Mg_2O(C_9H_{18}N)_4]$	$D_x = 1.117$ Mg m^{-3}
$M_r = 671.58$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6087 reflections
$a = 11.7971$ (6) Å	$\theta = 1.9$–24.2°
$b = 11.5539$ (7) Å	$\mu = 0.11$ mm^{-1}
$c = 15.313$ (1) Å	$T = 123$ (2) K
$\beta = 106.956$ (2)°	Cube, colourless
$V = 1996.5$ (2) Å^3	0.35 × 0.12 × 0.10 mm
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	$R_{\rm int} = 0.046$
φ and ω scans	$\theta_{\rm max} = 24.2°$
6087 measured reflections	$h = -13 \rightarrow 13$
3178 independent reflections	$k = -13 \rightarrow 13$
2228 reflections with $I > 2\sigma(I)$	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 1.6466P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$(\Delta/\sigma)_{\rm max} < 0.001$
$wR(F^2) = 0.141$	$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}
3178 reflections	
212 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Na1—O1	2.2405 (11)	Mg1—O1	1.8673 (9)
Na1—N1	2.445 (3)	Mg1—N2$^{\rm i}$	2.032 (2)
Na1—N2	2.572 (3)	Mg1—N1	2.063 (2)
O1—Na1—N1	84.24 (6)	N2$^{\rm i}$—Mg1—N1	144.48 (11)
O1—Na1—N2	82.45 (6)	Mg1$^{\rm i}$—O1—Na1	90.35 (4)
N1—Na1—N2	166.57 (9)	Mg1—O1—Na1	89.65 (4)
O1—Mg1—N2$^{\rm i}$	109.26 (8)	Mg1—N1—Na1	79.84 (9)
O1—Mg1—N1	106.25 (8)	Mg1$^{\rm i}$—N2—Na1	77.93 (8)

Symmetry code: (i) $2 - x, -y, -z$.

H atoms were refined as riding atoms, with C—H distances in the range 0.98–0.99 Å.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1696). Services for accessing these data are described at the back of the journal.

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