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A polymeric solvent-free variant of a hydridomagnesium inverse crown

David V. Graham,[a] Alan R. Kennedy,[a]* Robert E. Mulvey[a] and Charles T. O'Hara[b]

[a]WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland, and [b]Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, England
Correspondence e-mail: a.r.kennedy@strath.ac.uk

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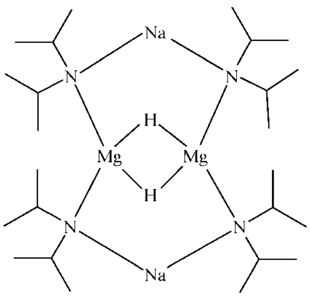
A solvent-free agostically propagated polymeric variant of a previously reported hydride-containing inverse crown molecule has been prepared, namely tetra-μ_2-diisopropylamido-di-μ_2-hydrido-dimagnesium(II)disodium(I), $[Mg_2Na_2H_2(C_6H_{14}N)_4]$. The asymmetric unit contains two crystallographically independent centrosymmetric molecules, each existing as a cationic eight-membered ring, with alternating metal and N atoms, which acts as a host towards two hydride anions. The metal amide rings are linked *via* Na$\cdots$C agostic interactions to produce one-dimensional polymeric chains propagating along the crystallographic *b* direction.

Comment

Recent work in our group has focused on the special synergic chemistry which can take place when an alkali metal amide is placed within the same molecular environment as its magnesium bis(amide) congener (Mulvey, 2006). A consequence of this work was the development of a new class of compounds which have become known as 'inverse crown ethers', due to their inverse topological relationship with conventional crown ether complexes (Mulvey, 2001). Further compounds were subsequently prepared which had a similar cationic 'host' ring, but the 'guests' were anions which did not contain oxygen. These oxygen-free compounds have become known as 'inverse crowns' (Mulvey, 2006).



(I)

As part of our study, the reaction of mixed sodium–magnesium tris(diisopropylamide), NaMg(DA)$_3$, with different substrates was probed. In the presence of ferrocene, ruthenocene or osmocene, a simultaneous regioselective fourfold deprotonation of the metallocene occurred to give a 16-membered inverse crown molecule (Clegg *et al.*, 2001; Andrikopoulos *et al.*, 2004). The title complex, (I), was serendipitously prepared by heating under reflux a hydrocarbon solution of NaMg(DA)$_3$ with the arene complex bis(benzene)chromium. The reaction was attempted in order to ascertain whether the arene complex could undergo deprotonation akin to the metallocenes. No deprotonation was detected by X-ray or NMR spectroscopic analyses, and the only compounds to precipitate from solution were (I) and unreacted bis(benzene)chromium. It is now known that bis-

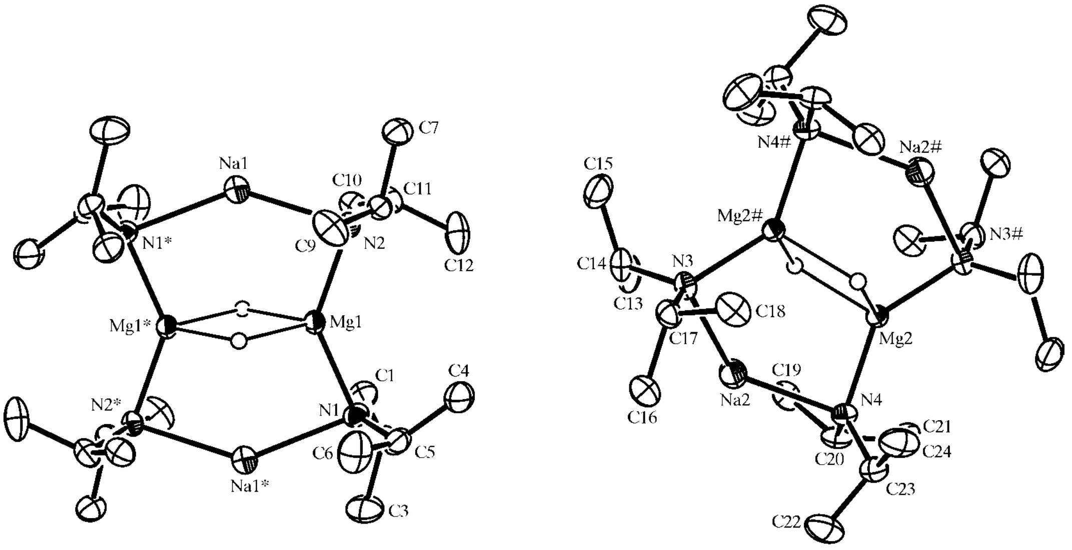


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Non-hydride H atoms have been omitted for clarity. Atoms labelled with an asterisk (*) or hash (#) are generated by the symmetry codes $(-x, -y + 1, -z + 2)$ and $(-x + 1, -y + 2, -z + 1)$, respectively.

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(benzene)chromium can be selectively monodeprotonated using a different base, [(TMEDA)·Na(μ-Bu)(μ-TMP)Mg(TMP)], where TMP is 2,2,6,6-tetramethylpiperidide and TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Hevia *et al.*, 2005).

The structure of (I) contains two crystallographically independent molecules, each residing on a centre of symmetry (Fig. 1). The internal geometric parameters of both molecules are essentially identical: Mg1—N2 = 2.078 (2) Å *versus* Mg2—N4 2.062 (2) Å is the largest difference between the two inverse-crown frames. Key geometric parameters can be found in Table 1. Compound (I) is a polymeric solvent-free variant of the previously prepared compound [Na_2Mg_2(μ-DA)$_4$(μ-H)$_2$.(toluene)$_2$], (II), which has the same connectivity as (I) but with the addition of a toluene molecule π-bonded to each Na atom (Gallagher *et al.*, 2002). This toluene-to-Na π–ion interaction causes a significant difference in the Na—N bond lengths, which are shorter in (I) [2.397 (2)–2.407 (2) Å] than in the solvated (II) [2.481 (2) Å]. The endocyclic N—Na—N angles are also different [136.1 (1)–137.5 (1)° for (I) and 132.1 (1)° for (II)]. The Na atoms of (I) compensate for the loss of bound toluene by forming a range of agostic interactions. Some of these are intramolecular [Na···C = 2.962 (4)–3.124 (4) Å], but each Na atom also forms one intermolecular agostic bond [Na···C = 3.014 (4) and 3.125 (4) Å], hence propagating one-dimensional polymeric chains along the crystallographic *b* direction (Fig. 2).

Metal hydrides are of interest as reducing agents, but magnesium hydrides are not as well known as their aluminium counterparts. In fact, in addition to (I) and (II), only two similar molecular magnesium hydrides have been structurally characterized to date, namely the K analogue of (II) (Andrikopoulos *et al.*, 2003) and a $TiMg_2$ species where the hydrides bridge all three metals (Mokuolu *et al.*, 2003). In (I), each hydride forms a slightly asymmetrical bridge between the two Mg atoms of a ring, with Mg—H distances in the range 1.91 (2)–1.94 (2) Å. Comparing small differences in *M*—H bond distances from X-ray data is of course dangerous. We note, however, that these distances are similar to those found for (II) [1.88 (2) Å] and for the K analogue of (II) [1.94 (2) Å], which has a larger metal amide ring than the Na species. More significance can be attached to the collective difference between these Mg—H distances and the longer distances [2.029 (15)–2.045 (15) Å] found in the μ_3-hydrido $TiMg_2$ complex.

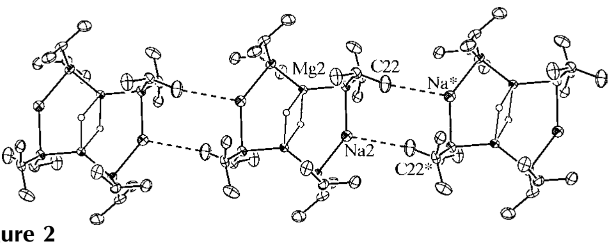

Figure 2
Part of the polymeric chain that extends along the *b* direction. Each chain is constructed of units from only one of the two crystallographically independent fragments shown in Fig. 1. Atoms labelled with an asterisk are generated by the symmetry code ($-x + 1, -y + 1, -z + 1$).

Experimental

All experimental manipulations were carried out using standard Schlenk techniques under an argon atmosphere. *n*-BuNa (5 mmol) (Lochmann *et al.*, 1966) was suspended in hexane (10 ml) and a heptane solution of dibutylmagnesium (5 mmol) was added to produce a congealed brown mass. Diisopropylamine (15 mmol) was then introduced slowly to give a yellow solution. Bis(benzene)chromium (1.25 mmol) (Fischer & Hafner, 1955) was added and the mixture was heated under reflux for 2 h. The resulting dark solution was left to cool to ambient temperature in a Dewar flask filled with hot water. Large colourless crystals of (I) and small black crystals of bis(benzene)chromium were isolated. ^{1}H NMR (400.13 MHz, $C_6D_5CD_3$, 300 K): δ 3.70 (2H, *s*, Mg—H), 3.17 (8H, *m*, CH), 1.19 (48H, *d*, CH_3); ^{13}C NMR (100.62 MHz, $C_6D_5CD_3$, 300 K): δ 49.5 (CH), 27.7 (CH_3).

Crystal data

[$Mg_2Na_2H_2(C_6H_{14}N)_4$]
$M_r = 497.34$
Triclinic, $P\overline{1}$
$a = 8.2448$ (4) Å
$b = 10.1118$ (5) Å
$c = 20.1990$ (9) Å
$\alpha = 82.419$ (3)°
$\beta = 83.897$ (3)°
$\gamma = 68.916$ (2)°

$V = 1554.36$ (13) Å^3
$Z = 2$
$D_x = 1.063$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 123$ (2) K
Cut tablet, colourless
0.40 × 0.38 × 0.30 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
27877 measured reflections

7078 independent reflections
3944 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\rm max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.140$
$S = 1.08$
7078 reflections
383 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.9833P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mg1—N1	2.051 (2)	Na1—N1^{ii}	2.405 (2)
Mg2—N3^{i}	2.051 (2)	Na2—N3	2.407 (2)
Mg1—N2	2.078 (2)	Na1—C7^{iii}	3.014 (3)
Mg2—N4	2.062 (2)	Na1—C6^{ii}	3.072 (5)
Mg1—H1*H*	1.92 (2)	Na1—C10	3.089 (3)
Mg1—H1*H*^{ii}	1.91 (2)	Na2—C13	2.962 (4)
Mg2—H2*H*	1.94 (2)	Na2—C19	2.980 (4)
Mg2—H2*H*^{i}	1.91 (2)	Na2—C20	3.124 (3)
Na1—N2	2.397 (2)	Na2—C22^{iv}	3.125 (4)
Na2—N4	2.399 (2)		
N1—Mg1—N2	136.48 (9)	N2—Na1—N1^{ii}	137.51 (9)
N3^{i}—Mg2—N4	137.00 (10)	N4—Na2—N3	136.06 (9)

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y + 1, -z + 2$; (iii) $-x, -y + 2, -z + 2$; (iv) $-x + 1, -y + 1, -z + 1$.

The hydride H atoms and those attached to agostic C atoms were found in a difference synthesis and refined isotropically. All other H atoms were constrained to geometrically idealized positions using a riding model; for CH atoms, C—H = 1.00 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C), and for CH_3 atoms, C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C).

Data collection: *COLLECT* (Nonius, 1988) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3015). Services for accessing these data are described at the back of the journal.

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