

Synthesis of the mixed lithium–potassium–(bis)magnesium N-metallated/N, C-dimetallated amide $[\text{Li}_2\text{K}_2\text{Mg}_4\{\text{Bu}^t(\text{Me}_3\text{Si})\text{N}\}_4\{\text{Bu}^t[\text{Me}_2(\text{H}_2\text{C})\text{Si}\text{N}\}_4]$: an inverse crown molecule with an atomless cavity†

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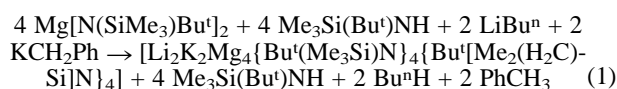
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Unlike previous members of the inverse crown family, which are heterobimetallic and have cationic rings surrounding anionic cores, the title compound is heterotrimetallic and its “guest” anion is intramolecularly stitched into the complex fused-ring structure of its cationic “host”.

Recent work in our laboratory has established that heterobimetallic (alkali metal–magnesium) amides, formally represented by “ $\text{MMg}(\text{NR}_2)_3$ ”, can function as specialist bases towards a range of protic acids.¹ The most interesting example to date has been the synergic sodium–magnesium diisopropylamide “ $\text{NaMg}(\text{NPr}_2)_3$ ”-promoted tetrametallation of ferrocene to an unprecedented 1,1',3,3'-tetrayl form.² Here, as in related cases, following the liberation of the amine (HNR_2) co-product, the residue of the synergic amide encapsulates the deprotonated entity to give the appearance of a cationic host ring–anionic guest molecule. Their general designation as “inverse crowns”¹ acknowledges a reversed topology (Lewis acidic host–Lewis basic guest) relative to that in conventional crown ether complexes. Hitherto, all known inverse crowns have involved pairs of metal atoms (Li/Mg; Na/Mg; or K/Mg) intimately linked through amido N bridges into 8-, 12-, 16- or 24-membered host rings, the cores of which are filled by H^- ,³ O^{2-} , O_2^{2-} , RO^- ,⁴ Ar^- , Ar^{2-} or $[(\text{C}_5\text{H}_3)_2\text{Fe}]^{4-}$ anionic guests. However, in this paper we show how the introduction of a third metal variable into the mixed-metal amide system can promote formation of a remarkable new type of inverse crown ring structure, the anionic core of which is “missing”. Looking further afield than inverse crown chemistry, this new colourless crystalline compound $[\text{Li}_2\text{K}_2\text{Mg}_4\{\text{Bu}^t(\text{Me}_3\text{Si})\text{N}\}_4\{\text{Bu}^t[\text{Me}_2(\text{H}_2\text{C})\text{Si}\text{N}\}_4](\text{hexane})_x$, **1**, also represents the first heterotrimetallic lithium–potassium–magnesium amide.

We first prepared **1** fortuitously by reacting a 1 : 1 mixture of impure butylpotassium and commercial dibutylmagnesium with three molar equivalents of *tert*-butyltrimethylsilylamine. Expecting the product to be the bimetallic tris(amide) “[$\text{KMg}\{\text{Me}_3\text{Si}(\text{Bu}^t\text{N})_3\}$ ”, the few crystals obtained from the reaction mixture were instead found to be **1** by an X-ray crystallographic study. The adventitious presence of lithium in **1** can be attributed to contamination of the butylpotassium as the metal–metal interchange reaction between butyllithium and the heavier alkali metal *tert*-butoxide used to generate it,⁵ is not generally quantitative. Deliberately adding lithium in a subsequent rational approach (eqn. 1) afforded **1** reproducibly in an improved yield.‡ The dual reactant–product character of the secondary amine (see eqn. 1) may appear odd, but it is needed initially to convert all of the metal alkyl molecules to amide, whereas the four molar equivalents later produced arise from amide deprotonation of a trimethylsilyl group (*i.e.*, $\text{Me}_3\text{Si} \rightarrow \text{Me}_2\text{SiCH}_2^-$). Benzylpotassium was chosen in preference to butylpotassium as the potassium source in the rational synthesis

due to its easier accessibility in a pure form, its milder basicity and its incapacity for β -hydride elimination.



The molecular structure of **1** (Fig. 1)§ is best viewed as a 16-membered (KNMgNLiNMgN)₂ primary ring with four 6-membered (MgCSiNLiN) appendant secondary rings, arranged in two transannular sets of two. Surrounding a vacant core [the shortest distance across the ring is the $\text{K}\cdots\text{K}$ separation of 6.145(1) Å], the primary ring appears crown-like when observed side-on (Fig. 2). Sharing a plane, the two Li atoms and the two K atoms engage in linear and near-linear N–M–N bonding respectively (mean bond angles, 179.15° and 170.61° respectively). Bound to 1C and 2N atoms, the Mg atoms occupy distorted trigonal planar geometries with wide N–Mg–N (mean, 135.80°), intermediate C–Mg–N(K) (mean,

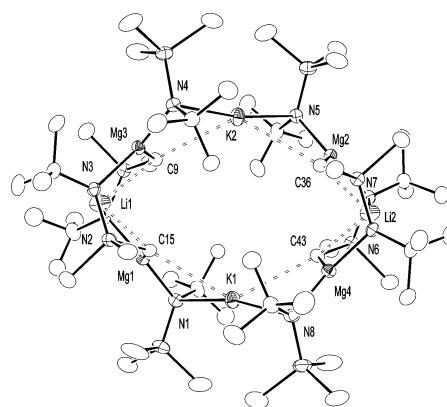


Fig. 1 Molecular structure of **1** with selective atom labelling. Hydrogen atoms and solvent molecules have been omitted for clarity.

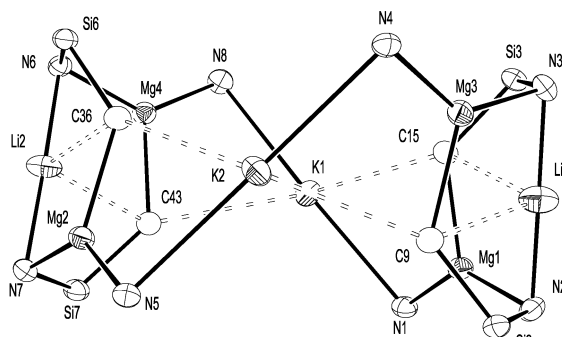
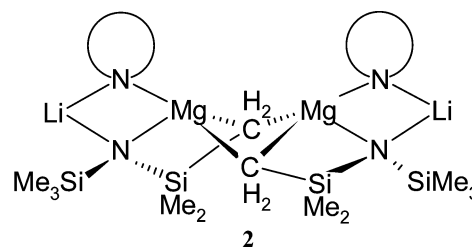


Fig. 2 Multi-fused ring core of **1** highlighting its pseudo-crown shape.

† Electronic supplementary information (ESI) available: NMR spectra. See <http://www.rsc.org/suppdata/cc/b3/b301374j/>

115.58°), and narrow C–Mg–N(Li) (mean, 108.15°) bond angles. Both types of N atom (N1/N8/N4/N5 and N2/N3/N6/N7) display four-coordinate geometries, highly distorted from tetrahedral [range of bond angles: 90.67(7)–121.73(15)° and 81.39(14)–123.63(15)°, respectively]. The largest angles involve the C–N–Si branches (mean values: first type, 120.96°; second type, 123.24°), while the smaller ones, which predictably show a greater difference between the types, are those associated with the metal-distinct M–N–Mg primary ring units (mean values: M=K, 91.25°; M=Li, 81.61°). To close the chelate (secondary) rings, the methylene C atoms must also deviate markedly from tetrahedral [mean Si–C(H)₂–Mg bond angle, 130.05°]. Turning to bond lengths, the Mg–N ones cover a narrow range [2.0292(19)–2.072(2) Å; mean, 2.051 Å]. A search of the Cambridge Crystallographic Database⁶ revealed no hits for the *tert*-butyltrimethylsilylamido ligand bound to Mg (or any alkali metal) thus ruling out a direct comparison with metal–N bond lengths in **1**. However, the homoleptic zinc amide [Zn{(Me₃Si)BuⁿN)}₂] is available⁷ and shows a considerable contraction in its mean Zn–N length (1.817 Å) compared to the Mg–N counterpart in **1**. While a lower coordination number (*i.e.*, 2 for Zn *vs.* 3 for Mg) exacerbates the margin of this difference (0.234 Å), the contraction is in keeping with the trend that Zn–N lengths are systematically 0.07–0.08 Å shorter than their Mg–N counterparts in the inverse crown ethers [M₂M'₂–{(Me₃Si)₂N}₄(O)_x(O₂)_y] (where M = Na or K; M' = Mg or Zn). Note that the crystal structures of transition metal (Ti,⁸ V⁹) and Group 16 (Se, Te)¹⁰ compounds containing *tert*-butyltrimethylsilylamide have also been documented. Returning to the dimensions of **1**, while both Li and K each bind to two N atoms (mean lengths, 1.995 Å and 2.951 Å respectively), they also each form two short contacts to anionic C(H)₂[–] atoms (range of lengths: Li–C, 2.449–2.494 Å; K–C, 3.289–3.315 Å). If these weaker M–C contacts (shown as dashed bonds in Figs. 1 and 2) are included, then in addition to the aforementioned primary and secondary rings, the structure also contains two transannular sets of four (LiCMgN) and two (KCMgN) tertiary rings. The significantly shorter Mg–C contacts (range: 2.203–2.214 Å signify that the precursor Si(CH₃) groups involved have been magnesiated (as opposed to lithiated or potassiated), a point reinforced by the equal numbers of Mg atoms and CH₂[–] anions (4:4) present. In that regard **1** represents a typical inverse crown, as it is characteristic that the Mg atom count in the host ring tallies exactly with the number of deprotonated centres within the core guest, though here the guest anion forms part of the loop arrangement within the host ring leaving the core vacant.

The directing influence of the third metal variable on the structure of **1** can be demonstrated indirectly by making a comparison with the markedly different arrangement of the lithium–magnesium hexamethyldisilazane derivative [(LiMg(TMP)(CH₂Si(Me)₂N(SiMe₃)))₂]¹¹ (TMP = 2,2,6,6-tetramethylpiperidide). Though this bimetallic structure **2** also possesses metallated Si(CH₃) units, its CH₂[–] anions function as dimerisation junctions through the central (MgC)₂ ring of a fivefold-fused ring system. In contrast, in **1** the dimerisation junctions involve, not the CH₂[–] anion, but the third metal (K) atom which, because of its long reach, can connect to a N atom of the neighbouring monomeric (trinuclear) fragment (mean N...N separation distance in N–K–N units, 5.873 Å). Were the K atom to be replaced by another Li atom, the significantly closer approach of these N atoms to each other (note that the mean N...N separation distance in the N–Li–N units of **1** is only 3.998 Å), would lead to greatly increased steric congestion, thus ruling it out as a viable structural option, *i.e.*, the structural motif of **1** is almost certainly unique to its special heterotrimetallic composition. Future prospects for expanding the inverse crown family appear brighter still in the light of this finding.



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Notes and references

† Rational synthesis. Under a protective argon atmosphere, a hexane solution of Mg[N(SiMe₃)Buⁿ]₂ (made from the 2:1 reaction of the parent amine and commercial dibutylmagnesium) (5 mmol) was treated with Me₃Si(Buⁿ)NH (5 mmol) then LiBuⁿ (2.5 mmol in hexane), was stirred for 30 min and then chilled to 0 °C. *Via* a solids addition tube, KCH₂Ph (2.5 mmol) was subsequently added and the resulting orange–brown mixture was allowed to warm to ambient temperature. After 10 min a homogeneous orange solution was obtained. On standing, the solution afforded colourless crystals of **1** (isolated yield, assuming hexane of crystallisation lost upon drying, 44%, 0.73 g). Mp 168–170 °C. Microanalysis (found C, 51.2; H, 10.6; K, 6.1; Li, 0.9; Mg, 7.0; N 8.0%. C₅₆H₁₄₀K₂Li₂Mg₄N₈Si₈ requires C, 50.3; H, 10.5; K, 5.8; Li, 1.0; Mg, 7.3; N, 8.4; Si, 16.7%). The room temperature ¹H NMR spectrum ([²H₈]-toluene, 400.13 MHz) is extremely complicated, suggesting dynamic exchange between two or more conformations. Lowering the temperature leads to a simplification such that at 280 K there appears to be one main conformation, the data for which fits well with the crystal structure: thus (theoretical integrals in square parentheses) δ 1.52 (Buⁿ, 37H [36H]), 1.43 (Buⁿ, 38H [36H]), 0.61 (Me₂Si, 13H [12H]), 0.48 (Me₂Si, 13H [12H]), 0.24 (Me₃Si, 35H [36H]), –1.86 (br, CH₂Mg, 8H [8H]). Additional minor resonances appear at 1.39, 1.33 (br), 0.45, 0.32, 0.30. NMR resonance assignments were verified by means of 2D [¹H, ¹³C] and 2D [¹H, ²⁹Si] HSQC NMR spectra acquired at 400 MHz. Variable temperature observation of 1D ¹H NMR spectra (220 to 370 K) and acquisition of 2D [¹H–¹H] EXSY NMR data verified the existence of a dynamic conformational exchange process. For further details see ESI.†

§ Crystal data for hexane solvate of **1**: C₆₂H₁₅₄K₂Li₂Mg₄N₈Si₈, *M_r* = 1425.97, monoclinic, space group C2/c, *a* = 29.5490(2), *b* = 14.6937(1), *c* = 43.9600(3) Å, β = 106.135(2)°, *V* = 18334.9(2) Å³, *Z* = 8, ρ_{calc} = 1.033 g cm^{–3}, Mo–Kα radiation, λ = 0.71073 Å, μ = 0.271 mm^{–1}, *T* = 123 K; 33036 reflections were collected, 19142 were unique, *R*_{int} 0.0298. The hexane solvate and the methyl C-atoms of two *tert*-butyl groups were each modelled as disordered over two sites. Final refinement (SHELXL-97; G. M. Sheldrick, University of Göttingen, Germany) to convergence on *F*² with all ordered, non-H atoms anisotropic gave *R* = 0.0505 (*F*, 15434 obs. data only) and *R_w* = 0.1213, all data), GOF = 1.051, 858 refined parameters, residual electron density max. and min. 0.653 and –0.589 e Å^{–3}. CCDC 203656. See <http://www.rsc.org/suppdata/cc/b3/b301374j/> for crystallographic data in .cif or other electronic format.

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