‘Inverse crown ether’ complexes: extension to potassium through the synthesis of $[\{[(Me_3Si)_2N]_4K_2Mg_2(O_2)\}_\infty]$, a peroxo-centred macrocycle linked into infinite chains by intermolecular $K\cdots CH_3(SiMe_2)$ interactions

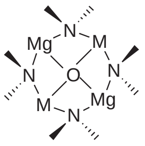
Alan R. Kennedy,[a] Robert E. Mulvey,*[a] Colin L. Raston,[b] Brett A. Roberts[a] and René B. Rowlings[a]

[a] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL.*
E-mail: r.e.mulvey@strath.ac.uk
[b] *Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia*

Received (in Cambridge, UK) 11th December 1998, Accepted 18th January 1999

The title compound represents the first potassium example of a novel class of amide-supported heterobimetallic macrocycle having a dicationic $(N_4K_2Mg_2)^{2+}$ octagonal ring framework surrounding a dianionic $(O_2)^{2-}$ core.

In the conventional host–guest chemistry of crown ether complexes,[1] the series of oxygen centres within the macrocyclic ligand host provide an electron-rich cavity tailor-made for the entertainment of electron-poor metal cation guests. Recently, however, we have described a remarkable new type of macrocyclic complex which conversely has a series of metal cations within its cyclic ring framework and an oxygen anion within the cavity of the ring.[2] Their generalised structural formula is depicted in **1**. Best regarded as ‘inverse crown ether’ complexes, their ring motifs in containing four Lewis acidic metal sites can be thought of in effect as the inverse of [12]crown-4 with its four Lewis basic ligand sites. Preceding this work, the collection of [12]mercuracarborand-4 complexes developed by Hawthorne and coworkers[3] have been similarly interpreted as ‘anti-crown’, charge-reversed analogues of [12]crown-4, but, in this case, no oxygen anions are involved; instead the softer acid Hg centres bind anions such as Cl^-, Br^-, I^- or *closo*-$B_{10}H_{10}^{2-}$. Returning to the inverse crown ether complexes, three have been reported previously. Two are dilithium-dimagnesium amides, $[\{(Me_3Si)_2N\}_4Li_2Mg_2(O_2)_x(O)_y]^4$ **2** and $[(Me_2CCH_2CH_2CH_2Me_2CN)_4Li_2Mg_2(O)]^2$ **3**; while the third is a disodium analogue $[\{(Me_3Si)_2N\}_4Na_2Mg_2(O_2)_x(O)_y]^2$ **4**. Here, in this paper, we extend this novel class of heterobimetallic macrocyclic complex to the next member of the alkali metal family, potassium, through the synthesis and structural characterisation of the dipotassium-dimagnesium amide $[\{[(Me_3Si)_2N]_4K_2Mg_2(O_2)\}_\infty]$ **5**. Though also based on an eight-membered $(N_4M_2Mg_2)$ ring system, the crystal structure of **5** differs in two major respects from those of its lithium and sodium congeners: first, the $(N_4K_2Mg_2)$ ring is not molecular, but polymerises through intermolecular $K\cdots CH_3(SiMe_2)$ interactions; second, throughout the bulk polymer the cavities of the 2+ charged rings are filled exclusively by peroxo (O_2^{2-}) dianions, *i.e.* no oxide (O^{2-}) ions are present.



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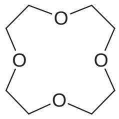

[12]crown-4

In the fortuitous preparation of the first inverse crown ether complex, we concluded that mixtures of butyllithium, dibutylmagnesium and the sterically demanding amine hexamethyldisilazane were highly efficient oxygen scavengers.[4] Thus, any oxygen contaminant available in solution would be readily sequestered by the reaction system and then precipitated in the form of the stable peroxo–oxo centred mixed-metal macrocycle **2**. With this insight we subsequently deliberately added molecular oxygen to other reaction solutions of this type. This strategy was used in the preparations of **3** and **4**. The preparation of **5** essentially mimicked that of its lighter alkali metal counterparts. Like **2**, it was initially obtained unexpectedly (in a low yield of 2%) by the reaction shown in eqn. (1): here, oxygen

$$\text{'BuK'} + Bu_2Mg + 3(Me_3Si)_2NH \xrightarrow{\text{trace of } O_2} {}^1\!/_x[\{(Me_3Si)_2N\}_4K_2Mg_2(O_2)] + \text{other products} \qquad (1)$$

was not deliberately added to the solution; though, significantly, neither the amine reactant nor the solvents (hexane, heptane, *p*-xylene) were deoxygenated beforehand. Note also that the potassium reagent used was not pure butylpotassium, but rather the unrefined solid isolated from the metal–metal exchange reaction between butyllithium and potassium *tert*-butoxide.[5] Repeating the preparation in a Schlenk tube adapted with a calcium chloride drying tube at its inlet, gave substantially larger amounts of colourless, crystalline **5** (best yield to date, 23%).† While we attribute this improvement to the intentional introduction of atmospheric oxygen, the possibility that minute traces of moisture are involved cannot be completely dismissed. However, in a control experiment, following the same procedure carried out in eqn. (1), a stoichiometric amount of deoxygenated H_2O was additionally introduced to the reaction solution. A white solid precipitated out within a few minutes and would not redissolve on warming. The isolated solid exhibited distinct melting point characteristics from those of **5**;† even more significantly, its IR spectrum revealed the presence of a strong O–H band at 3695 cm^{-1} [characteristic of $Mg(OH)_2$] before the mull was exposed to air. Clearly this solid is not **5**.

The octagonal ring structure of **5** (Fig. 1)‡ consists of alternating nitrogen and metal atoms. Like metal atoms occupy transannular positions, and each one coordinates (side-on) to the O_2^{2-} ion in the core of the ring. These ring molecules are not discrete, but link through intermolecular $K\cdots CH_3(SiMe_2)$ interactions (one per K centre) to form one-dimensional infinite chains (Fig. 2) which propagate along the *a* direction. Selected bond lengths and bond angles are given in the legend to Fig. 1. The O–O bond length [1.583(1) Å] is close to that [1.541(9) Å] in the heptalithium-tetrarubidium mixed alkoxide peroxide $[\{(Bu^tOLi)_5(Bu^tORb)_4(Li_2O_2)\cdot 2TMEDA\}_\infty]$.[6] While the Mg centre engages this dianion in a symmetrical manner (Mg–O: mean, 2.012 Å; difference, 0.005 Å), the interaction with the K centre is lopsided (K–O: mean, 2.843 Å; difference, 0.121 Å). The extra atoms (from Me_3Si groups, see below) in the coordination sphere of the K centre may be a factor in this asymmetry. One might be inclined to explain the 100% peroxide incorporation within the ring cavity in terms of the ‘soft’ nature of potassium; but, the true explanation must be more profound as there is no regular pattern to the peroxide:

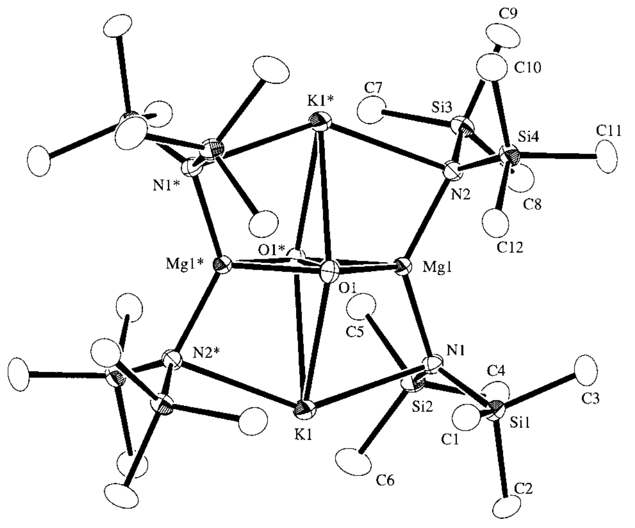

Fig. 1 Double asymmetric unit of **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): K1–O1 2.782(1), K1–O1* 2.903(1), K1–N1 2.855(1), K1–N2* 2.804(1), Mg1–O1 2.015(1), Mg1–O1* 2.010(1), Mg1–N1 2.044(1), Mg1–N2 2.043(1), K1–N1–Mg1 83.95(3), K1*–N2–Mg1 83.11(4). * $1 - x, y, z$.

oxide ratios found in **2**, **3** and **4** (*i.e.* 72 : 28, 0 : 100, 32 : 68 respectively). Clearly, the hard/moderately hard/soft demarcation normally associated with the Li/Na/K series is not the sole factor here. Kinetic influences must also be at work. The ($N_4K_2Mg_2$) ring in **5** is essentially planar [sum of endocyclic bond angles, 1074.6 *cf.* 1073.7° for the ($N_4Na_2Mg_2$) ring in **4**]. A salient feature running through the series of inverse crown ether complexes is that the Mg atoms are always displaced towards the centre of the ring as a result of strong Mg–O bonding. The magnitude of this displacement increases with increasing size of the alkali metal partner in the ring, as evidenced by the *endo*cyclic N–Mg–N bond angles in **2** [193.3° (approximate value owing to Li/Mg substitutional disorder in crystal)], **4** (218.4°) and **5** (227.8°). Likewise, the small Li cation in **2** and **3** is pulled towards the centre of the ring through strong Li–O bonding, resulting in endocyclic N–Li–N bond angles > 180°. Conversely, the heavier alkali metal cations in **4** and **5** occupy peripheral ring sites with endocyclic N–M–N bond angles significantly < 180° [159.84(2)° in **4**, 142.44(3)° in **5**], reflecting longer, weaker Na–O/K–O bonding. In contrast, there is considerably less variation in the endocyclic M–N–Mg bond angles throughout the series [range: 76.58(7)–83.95(3)°]. The final feature of note in **5** is the short $K\cdots CH_3(SiMe_2)$ contacts. Measuring 3.246(2) Å, the shortest of these are intermolecular ones ($K1\cdots C2^*$) which link the ($N_4K_2Mg_2$) rings together through near-linear K···C–Si units [angle, 157.29(7)°]. Interestingly, intermolecular Na···C–Si contacts of a similar length [3.275(2) Å] appear in **4**,[2] but these are normally accorded less significance when the smaller size of Na is taken into account (ionic radii: Na^+, 1.02 Å; K^+, 1.38 Å). However, the similar intermolecular contacts seen in **4** and **5** raises the question as to whether the former truly consists of discrete molecules. Intramolecular K···C–Si contacts [lengths: 3.317(2), 3.359(1) and 3.397(2) to C7, C1 and C6, respectively] also contribute to the bonding in **5**. These agostic-type interactions[7] are comparable to those in other recently reported potassium structures,[8] most pertinently in $[\{(Me_3Si)_2NK\}_2]$ (shortest, 3.34 Å).[9]

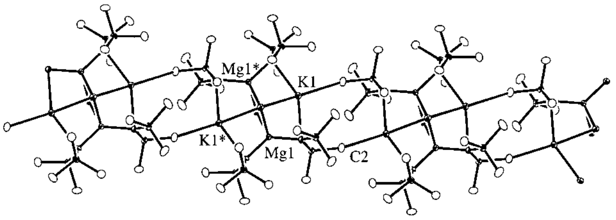

Fig. 2 View showing extended chain arrangement of **5**. Intermolecular $K\cdots CH_3(SiMe_2)$ interactions are shown; intramolecular ones are omitted for clarity.

We thank the EPSRC (for studentship to R. B. R.) and Monash University (for providing B. A. R. with a travel grant to allow him to work at Strathclyde).

Notes and references

† Satisfactory microanalyses have been obtained. **5** proved to be too insoluble in arene solvents for a useful, diagnostic ^1H NMR spectrum to be obtained. It starts to decompose at 80 °C and gradually darkens to a black solid at 140 °C. On the other hand, the white solid from the control reaction fails to melt below 300 °C and does not change colour.

‡ *Crystal data* for **5**: $C_{24}H_{72}K_2Mg_2N_4O_2Si_8$, M = 800.34, triclinic, space group $P\bar{1}$, a = 11.102(4), b = 12.907(6), c = 8.906(3) Å, α = 107.63(3), β = 100.47(3), γ = 96.34(4)°, U = 1177.3(9) Å^3, Z = 1, λ = 0.71069 Å, μ = 0.457 mm^{-1}, T = 123 K, R = 0.0229, R_w = 0.0404 for 5156 reflections with $I > 2\sigma(I)$. 5673 reflections measured with $2\theta < 55°$. Refinement on F, to convergence, with isotropic H atoms gave a maximum residual electron density of 0.323 e Å^{-3} . Program used Texsan. CCDC 182/1145. See http://www.rsc.org/suppdata/cc/1999/353/ for crystallographic files in .cif format.

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Communication 8/09681C