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[17] For details of X-ray crystallography on **7**, **12**, and **17** see the Supporting Information. Crystal data for **7**: $C_{51}H_{37}Co$, $M_r = 708.74$, triclinic, P-1, $a = 10.9507(8)$, $b = 12.1458(8)$, $c = 15.4401(11)$ Å, $\alpha = 86.981(1)$, $\beta = 79.657(1)$, $\gamma = 65.458(1)^\circ$, $V = 1837.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.281$ g cm^{-3}. $2\theta_{max} = 50.2^\circ$; 15359 reflections collected, 6532 independent, 5052 with $I > 2\sigma(I)$. No absorption correction ($\mu = 0.50$ mm^{-1}). $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0416, 0.814, respectively.

[18] Crystal data for **12**: $C_{51}H_{36}Fe \cdot 0.25\,CH_2Cl_2$, $M_r = 725.88$, hexagonal, $P6_3$, $a = 27.174(2)$, $c = 9.1170(7)$ Å, $V = 5830.4(7)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.240$ g cm^{-3}. $2\theta_{max} = 48.2^\circ$; 22326 reflections collected, 5788 independent, 4316 with $I > 2\sigma(I)$. No absorption correction applied ($\mu = 0.46$ mm^{-1}). $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0623, 0.1231, respectively; GOF = 1.013. 509 parameters refined, 4 restraints (disordered CH_2Cl_2 solvent).

[19] Crystal data for **17**: $C_{69}H_{59}Co$, $M_r = 939.03$, monoclinic, $P2_1/n$, $a = 10.568(1)$, $b = 35.490(4)$, $c = 15.132(2)$ Å, $\beta = 102.215(3)^\circ$, $V = 5547.0(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.124$ g cm^{-3}. $2\theta_{max} = 45.1^\circ$; 21290 reflections collected, 7278 independent, 3104 with $I > 2\sigma(I)$. No absorption correction ($\mu = 0.35$ mm^{-1}). $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.1098, 0.2544, repectively; GOF = 1.008. 605 parameters refined. Molecular disorder corresponding to a 90° rotation around the $Co \cdots Cp_{centroid}$ vector is present, but could not be modeled as a result of the small fraction (< 10 %).

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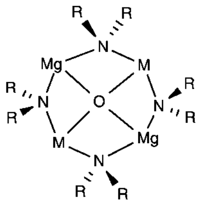
Hexameric Mg–O Stacks with Six THF-Solvated Sodium Amide Appendages: "Super" Variants of Inverse Crown Ethers Generated by Cleavage of THF[**]

Allison M. Drummond, Lorraine T. Gibson,
Alan R. Kennedy, Robert E. Mulvey,[*]
Charles T. O'Hara, René B. Rowlings, and
Tracy Weightman

s-Block organometallic compounds are known to be thermodynamically unstable with respect to oxidation or hydrolysis (giving oxides or hydroxides). However, under certain kinetic conditions such reactions may not reach completion but instead stop at intermediate composite structures containing metal cations, oxygen-based anions (usually O^{2-} or OH^-), and organic skeletons. This "oxygen encapsulation" phenomenon[1] has probably existed since these air- and moisture-sensitive compounds first appeared about a century ago, but it is only relatively recently that its detection has become routine (in suitably crystalline samples) through X-ray crystallographic study. Inevitably the proliferation of such studies has meant more structures of this type (mainly formed fortuitously rather than intentionally) coming to light, though the complex factors controlling their formation remain largely in the dark. We are interested in a special class of oxygen-encapsulated compound: inverse crown ethers[2] are mixed alkali-metal magnesium (or zinc) amides, the amido component of which is derived from the exceptionally bulky amines (2,2,6,6-tetramethylpiperidine (tmpH) or 1,1,1,3,3,3-hexamethyldisilazane (hmds(H))). Their common structure is characterized by octagonal $(NM^1NM^2)_2$ rings (e.g. **1**) which act as square-planar tetrametallic hosts for the encapsulation of a *single* anion (either O^{2-} or $(O_2)^{2-}$). Herein we describe a "super" variant to these simple, two-dimensional inverse crown ethers in a new class of heterobimetallic amide, the novel three-dimensional cage construction of which includes *multiple* O^{2-} encapsulation. Moreover we have traced the source of encapsulated O^{2-} ions, often a matter of puzzlement in examples reported previously, to the cleavage of THF solvent molecules used in the reaction.



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Originally we set out to synthesize hypothetical $[Na_2Mg_2(tmp)_4(O)_x(O_2)_y]$, the missing entry in the series of

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[*] Prof. R. E. Mulvey, A. M. Drummond, Dr. L. T. Gibson,
Dr. A. R. Kennedy, C. T. O'Hara, Dr. R. B. Rowlings, T. Weightman
Department of Pure and Applied Chemistry
University of Strathclyde
Glasgow, G1 1XL (UK)
Fax: (+44) 141-552-0876
E-mail: r.e.mulvey@strath.ac.uk

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known inverse crown ethers $[Li_2Mg_2(hmds)_4(O)_x(O_2)_y]$, $[Li_2Mg_2(tmp)_4O]$, and $[Na_2Mg_2(hmds)_4(O)_x(O_2)_y]$.[2] This was approached using the standard "synergic" metal amide mixture (3 tmpH:1 *n*BuNa:1 Bu_2Mg) in a hydrocarbon solution). When the solution was exposed to dry oxygen (a proven method of generating inverse crown ethers), no solid product could be obtained from it. This failure prompted us to introduce THF to a fresh reaction mixture, not exposed to oxygen, in anticipation of a solvated inverse crown ether. A vivid change in the color of the solution (yellow to brown) accompanied this addition, as a sign that THF was intimately involved (in a dual role, intact as a ligand and cleaved; see later) in the ensuing reactions. While a THF solvate was produced, it proved to be much more unique in composition and structure than expected, having the formula $[\{NaMg(tmp)(O)(thf)\}_6]$ (**2**). To test the generality of this new found reaction, we carried out the same procedure but replaced TMPH by the bulky amine diisopropylamine, HN(*i*Pr)$_2$. By yielding $[\{NaMg(N\textit{i}Pr_2)(O)(thf)\}_6]$ (**3**), this second reaction confirmed that a new class of mixed sodium–magnesium amide, sixfold oxygen-encapsulated, had been discovered.

X-ray crystallographic studies established that **2** and **3** are isostructural, so only the data for one structure need to be discussed here. Exhibiting crystallographically imposed S_6 symmetry, the molecular structure of **3**[3] (Figure 1) is hexameric. Its $(MgO)_6$ core (Figure 2) comprises two stacked $(MgO)_3$ trimeric rings. Appended to each of these rings is a set of three *exo*-oriented four-membered Mg-O-Na-N rings, positioned in a staggered fashion with regard to the opposing set. Dative Na–O(thf) bonds complete the structure. To effect ring stacking, the distorted tetrahedral Mg atoms form highly strained (inter-trimer) O-Mg-O′ connectivities (mean angle, 92.78°). For the distorted trigonal-planar Na atom, strain is most pronounced at the O-Na-N corner (angle, 88.68(6)°) of the heterometallic–heteroanionic ring. To the best of our knowledge no precedent exists for a simple molecular $(MgO)_6$ cage. While tetrameric $(MgO)_4$ cubanes exist (e.g., in the alkoxide $[(CpMgOEt)_4]$[4]), hitherto hexameric cages have only been identified with organoelement ligands isoelectronic to O^{2-} such as imides (e.g., in $[\{(thf)MgN(Ph)\}_6]$[5]) or phosphanediides (e.g., in $[\{MgP(Si\textit{t}Bu_3)\}_6]$[6]). There is also a recent report of an odd hexanuclear magnesium diisopropylcarbamato structure with a single encapsulated μ_4-bonding O^{2-} ion in $[Mg_6(O_2CN\textit{i}Pr_2)_{10}(O)]$.[7] The structure of **3** follows the pattern running through the whole inverse crown family: the encapsulated "guest" (here O^{2-} : elsewhere, O_2^{2-};[2] H^-;[8] Ar^-;[2] Ar^{2-};[2] $[(C_5H_3)_2Fe]^{4-}$[9]) is stabilized predominantly by interaction with Mg, as opposed to M, centers (where M = Li, Na, or K). Covering a narrow range (1.9473(13)–2.0020(14) Å), the Mg–O bond lengths in **3** cannot be compared with their counterparts in $[Na_2Mg_2(hmds)_4(O_2)_x(O)_y]$[2] due to the latter's contamination with peroxide. The metal–N(diisopropylamide) bond lengths in **3** (for Mg, 2.1324(16) Å; for Na, 2.4040(18) Å) are similar with those in the hydride-encapsulated inverse crown **4** (2.0651(18) and 2.4807(18) Å respectively).[8] As expected there is a substantial difference in the Na–O bond lengths in **3** reflecting the anionic/dative distinction between the O centers involved (i.e., for O^{2-}, 2.1402(15) Å; for THF, 2.2689(18) Å).

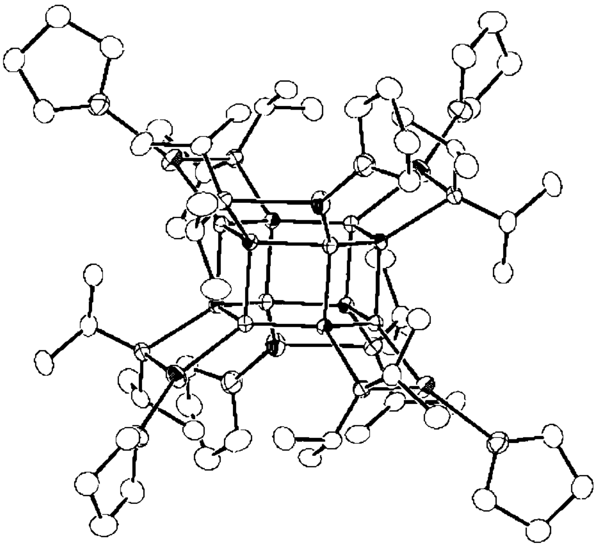


Figure 1. Molecular structure of **3** (atoms drawn as 35% probability ellipsoids; hydrogen atoms omitted for clarity).

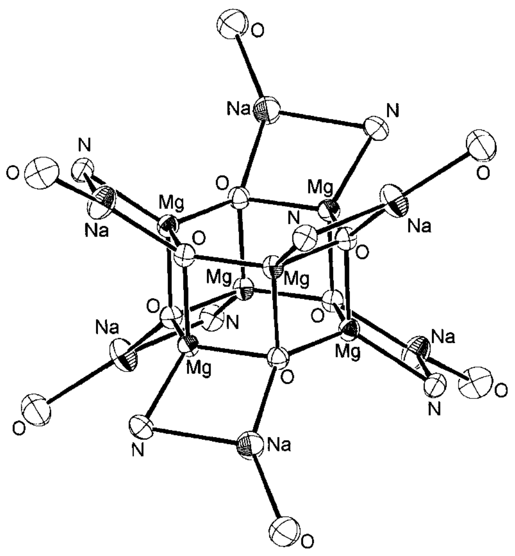
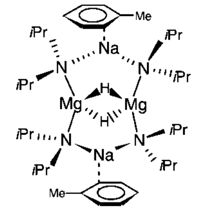


Figure 2. Inorganic core of **3** (atoms drawn as 40% probability ellipsoids).



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In view of the nature of the cages of the structures of **2** and **3**, strictly they should not be classed themselves as inverse crown ethers. Originally the name was coined to describe host–guest *ring* systems, which topologically display an inverse relationship to conventional crown ether complexes, that is, the metal-based host rings are Lewis acidic (cationic), while their oxygen-based guests are Lewis basic (anionic). However, the fact that **2** and **3** are built up of heterobimetallic–amido–oxo "NaMg[N(R$_2$)]O" monomeric subunits, clearly places them within the developing framework of inverse crown chemistry.

In an attempt to pinpoint the source of the oxide in the hexameric structures, we repeated the preparation of **2** in a vial connected through a heated capillary to a Hiden Analytical Quadrupole mass spectrometer (Warrington, England). After the addition of THF, the reaction mixture was heated and the volatile products blown into the mass spectrometer were subjected to selective ion mass (SIM) analysis. This confirmed the presence of ethylene (parent peak at 28 amu; daughter fragments at 27, 26, and 25 amu). Ethylene is commonly extruded during THF-cleavage processes,[10] so the origin of the O^{2-} ions in **2** is almost certainly from THF. Fragmentation of THF is a complex matter, the outcome of which can differ depending on many variables such as the metal and the nature of the organyl assailant. Hard organolithium bases are known to deprotonate THF at the α-position, before undergoing a $[\pi 4s+\pi 2s]$ cycloreversion to afford enolate “$CH_2{=}CH{-}O^-$” and ethylene.[11] There are also precedents for THF fragmentation leading to M-O-M bridges in organolanthanide chemistry,[12] and to O^{2-} in other metal[13] and metalloidal[14] systems. Here the heterobimetallic nature of the inverse crown ether system exacerbates the complexity of the THF fragmentation process, a sign of which is that the filtrates left following the isolation of **2** and **3** darken and degrade to viscous oils in a matter of days. However the salient point is that both new compounds can be prepared reproducibly in a pure crystalline form, and isolated for future synthetic exploration, before the onset of this degradation.

Experimental Section

2 and **3**: In a typical preparation, BuNa, Bu_2Mg, and the relevant amine (5:5:15 mmol) were mixed together in a hydrocarbon solution under a protective argon atmosphere. Dry, distilled THF (5 mL, 62 mmol) was then added and the solution warmed for 30 min. Cooling the solution on the bench (for **2**) or in the refrigerator at $-26\,^{\circ}C$ (for **3**) afforded colorless crystals of **2** or **3**. Yields of first batches isolated were typically 18 or 11 %, respectively. No further solids could be isolated due to degradation of the filtrate solutions. M.p. 330 °C (decomp) and 258 °C (decomp), respectively. Satisfactory analyses (C, H, N) were obtained for both compounds. ^1H NMR (400.13 MHz, $[D_6]$DMSO, 300 K): **2**: $\delta = 3.60$ (m, 4H; CH_2O-THF), 1.76 (m, 4H; CH_2-THF), 1.57 (m, 2H; γ-CH_2), 1.23 (m, 4H; β-CH_2), 1.02 ppm (s, 12H; CH_3); ^1H NMR (400.13 MHz, $[D_8]$toluene, 300 K) **3**: $\delta = 3.35$ (m, 4H; CH_2O-THF), 3.26 (septet, 2H; CH), 1.33 (m, 4H; CH_2-THF), 1.20 ppm (d, 12H; CH_3).

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[3] Crystal data for **3**: $C_{60}H_{132}Mg_6N_6Na_6O_{12}$; a colorless needle of approximate dimensions $0.55 \times 0.10 \times 0.10$ mm gave a trigonal space group $R\bar{3}h$, $a = b = 23.8599(6)$, $c = 12.1274(4)$ Å, $V = 5979.1(3)$ Å^3, $T = 123$ K, $Z = 3$, $\rho_{calcd} = 1.178\ \mathrm{Mg\,m^{-3}}$, $2\theta_{max} = 52^{\circ}$, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å. The structure was solved, and refined on F^2, using programs of the Shelx family to convergence at $R1 = 0.0419$ (for 2019 reflections with $I > 2\sigma(I)$), $wR2 = 0.1177$, and $S = 1.022$ for 140 parameters and 2602 unique reflections. Highest residual electron density 0.437 e Å^{-3}. Hydrogen atoms were placed in calculated positions and in a riding mode. Compound **2** was found to be isostructural with **3** but contained highly disordered groups at the THF positions which adversely affected the quality of the solution. CCDC-1790244 (**2**) and CCDC-1790245 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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A Unique Bismuth–Iron Chain Polymer Containing the $\cdots$-Bi-Fe-$\cdots$ Link: Formation and Structure of $[n\mathrm{BuBiFe(CO)_4}]_\infty$**

Minghuey Shieh,* Yeantarn Liou, Miao-Hsing Hsu, Rung-Tsang Chen, Shiow-Jane Yeh, Shie-Ming Peng, and Gene-Hsiang Lee

The construction of supramolecules or extended frameworks based on coordination and organometallic complexes is one of the major areas of current research in inorganic and organometallic chemistry.[1] Nevertheless, this approach has received little attention in the field of organobismuth–transition-metal complexes;[2] such complexes are of great importance mainly due to their potential applications as catalysts in olefin oxidation and ammoxidation[3] and as precursors to a variety of electronic materials.[4] Bismuth has been shown to form the polymer $[Et_2Bi(OAr)]_\infty$ in which the alkoxide ligand bridges the Et_2Bi groups giving a helical chain with no direct Bi–Bi interaction.[5] For the Bi-Fe-CO system, the polymer $[\{PhCH_2NMe_3\}\{(\mu\text{-}H)Fe_2(CO)_6Bi_2(\mu\text{-}Cl)_2\}]_\infty$ was

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[*] Prof. Dr. M. Shieh, Y. Liou, M.-H. Hsu, R.-T. Chen, S.-J. Yeh
Department of Chemistry
National Taiwan Normal University
Taipei, Taiwan, 116 (Republic of China)
Fax: (+886) 2-2932-4249
E-mail: mshieh@scc.ntnu.edu.tw

Prof. Dr. S.-M. Peng, G.-H. Lee
Department of Chemistry
National Taiwan University
Taipei, Taiwan, 117 (Republic of China)

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