'Inverse crown ether' complexes extended to group 12 through the syntheses of $[Na_2Zn_2(HMDS)_4(O)]$ and $[\{K_2Zn_2(HMDS)_4(O_2)_x(O)_y\}_\infty]$

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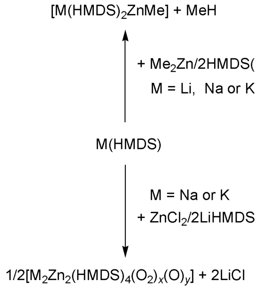
Received (in Cambridge, UK) 29th June 2000, Accepted 9th August 2000

The first sodium–zinc and potassium–zinc members of the inverse crown ether family, an emerging class of heterometallic macrocyclic amides previously limited to alkali metal–magnesium combinations, have been synthesised and crystallographically characterised.

The use of sterically hindered lithium amide bases, such as LDA, as selective deprotonating agents is widespread throughout organic chemistry.[1] Although these and other homometallic amides have been extensively studied, the possibility of fine-tuning the reactivity profiles of lithium amides by introducing a second metal centre has only recently been explored and has resulted in the characterisation of new structural types. We have described the formation of a new form of heterometallic macrocyclic amide, the inverse crown ether, which can be subdivided into two types. The first group consists of eight-membered $[MgNMN]_2$ rings (M = Li, N = HMDS or TMP;[†] M = Na or K, N = HMDS) which balance their 2+ charge by acting as oxygen scavengers and encapsulating oxide or peroxide dianions.[2–4] The second group consists of larger twelve-membered, $[NaNMgNNaN]_2$, and twenty-four-membered, $[MgNKN]_6$, rings (N = TMP) which encapsulate one dideprotonated or six monodeprotonated arene molecules, respectively, derived from the solvents used during the reaction.[5] This previous work encompasses a range of M^+ metals, of amide ligands and of guest anions, only the Mg^{2+} centre has remained constant. Substituting metals outside the s-block for magnesium would open new avenues for exploration. One intriguing possibility is that of performing redox chemistry on the guest anions by taking advantage of the range of easily accessible oxidation states displayed by many d-block metals. As a first step towards such compounds we sought to form mixed group 1 metal/zinc analogues. Zinc was chosen for these initial investigations owing to its similar size to magnesium, for its readiness to assume a trigonal-planar coordination geometry and for its stability in the +2 oxidation state, all of which fit the design criteria for inverse crown ether formation. As reported herein, this aim has been realised through the synthesis and crystallographic characterisation of the first sodium–zinc, $[Na_2Zn_2(HMDS)_4(O)]$ **1**, and potassium–zinc, $[\{K_2Zn_2(HMDS)_4(O_2)_x(O)_y\}_\infty]$ **2**, inverse crown ether complexes.

The magnesium containing macrocycles were formed on reacting mixtures of alkyl metal reagents with the appropriate amine;[2–4] however, following the same synthetic procedure with dimethylzinc and *n*-butyllithium did not give the expected macrocyclic product (Scheme 1). Instead one methyl group was retained and $[\{Li(\mu\text{-}HMDS)_2ZnMe\}_\infty]$ **3a**, was the only product isolated, forming in 39% yield as long, colourless needle crystals. The molecular structure of **3a**[‡] was found to be based on planar four-membered ZnNLiN rings (Fig. 1) with the methyl group occupying a third (terminal) coordination site on Zn. The molecule has crystallographically imposed two-fold symmetry with Zn, Li and C1 lying on a rotation axis. The coordinatively unsaturated (with respect to N) Li attains a higher coordination number by forming a short, linear, intermolecular bridging contact with a neighbouring methyl group (Li···C1 2.435(12) Å, Zn–C1···Li 180°) thus giving rise to a relatively insoluble and structurally robust (*vide infra*) polymer. This is in marked contrast to $[Li(\mu\text{-}HMDS)_2Mg(HMDS)]^2$ **4**, where lithium attains a tetrahedral geometry by forming two intramolecular Li···C contacts [of length 2.294(10) and 2.320(9) Å] with methyl groups from the HMDS ligands. Despite the methyl group being shared between the two metal centres the Zn–C1 distance in **3a** of 1.957(7) Å is similar to those in comparable, but molecularly discrete, compounds.[6] The linear, CH_3 face-capping[7] nature of the methyl to lithium interaction in **1a** is unusual and contrasts strongly with the bent motifs found both in **4** and in other mixed Zn/Li species.[8]



Scheme 1

Varying the reaction conditions by including a 4 h reflux or by initially preparing a separate '$Zn(HMDS)_2$' solution from $ZnMe_2$ and amine prior to addition of Li(HMDS) failed to dislodge the second methyl group and produced only **3a** as identified by ^1H NMR spectral data [C_5D_5N, δ 0.58 (s 12H, $SiMe_3$), −0.05 (s 1H, Me)]. Repeating the reaction with Bu^nNa or Bu^nK in place of Bu^nLi gave the equivalent sodium and potassium compounds, **3b** and **3c**, respectively, as assigned by comparison of their NMR spectra. To circumvent the retention of the methyl group, $Zn(HMDS)_2$ was prepared by a literature method[9] from $ZnCl_2$ and 2 equivalents of Li(HMDS), and subsequently purified by filtration and vacuum distillation. The pure zinc amide was then added to Na(HMDS) (in a 1 : 1 molar

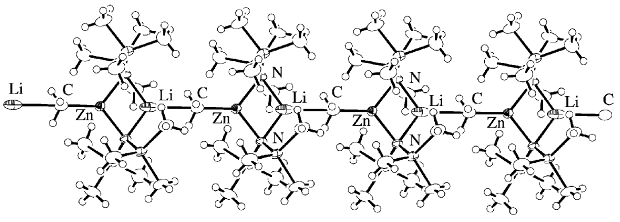


Fig. 1 Polymeric structure of **3a**. Selected geometric parameters (Å,°): Li–N 1.959(7); N–Zn–N* 102.0(2), C–Zn–N 129.0(1), Zn–N–Li 76.1(3), N–Li–C** 127.1(2), N–Li–N* 105.7(5). * = 1 − *x*, *y*, 1.5 − *z*, ** = *x*, 1 + *y*, *z*.

DOI: 10.1039/b005233g

ratio) in an arene solvent (which had previously had dry oxygen bubbled through it) and heated to reflux for 2 h. On cooling to room temperature, large colourless crystals were formed. These were found to be the desired product **1**.‡ Note that when 12-crown-4 is present during this reaction only the zincate $[Na(12\text{-crown-}4)_2][Zn(HMDS)_3]$ is obtained.[10] Repeating our reaction using K(HMDS) in place of Na(HMDS) gave crystals of peroxide rich **2** ($x = 0.82, y = 0.18$, for the crystal examined by X-ray diffraction). **2** is the first organoamido-group 12 metal peroxide to be crystallographically characterised, although relevant zinc oxides are known.[11] Compounds **1** and **2** are isomorphous with each other and with their magnesium containing analogues, **1a**[3] and **2a**.[4] Each consists of a near planar octagonal ring containing alternate metal and nitrogen centres (Figs. 2 and 3). Like metal atoms occupy transannular positions and all of them form a third attachment to the central oxide or peroxide guest. The Zn–N distances in **1** and **2** are essentially identical within each compound [mean 1.984(2) and 1.963(1) Å, respectively] and are shorter than that found for **3a** (2.010 Å), seemingly in line with the increasing electronegativity of the group 1 metal. Each Na or K atom forms one short and one long bond to an amide [Na–N 2.541(3), 2.597(2), K–N 2.797(1, 2.838(1) Å] and, unlike the smaller zinc atoms, are displaced both away from the centre of the ring and from the plane of the ring. This leaves both sodium and, more especially, potassium in relatively unfavoured low coordination states and with all their formal bonds on the same side of the coordination sphere. **2** compensates for this by forming short $K\cdots CH_3(SiMe_2)$ contacts. Each potassium forms one intermolecular contact [K··C 3.324(2) Å, K··C–Si 155.6(1)°], to give the linear polymer shown in Fig. 3, as well as several intramolecular contacts [range 3.309(2)–3.362(2) Å]. Note that, in contrast to **2a**, the intermolecular contact is no longer the shortest. It is of interest that the Na compounds display similar carbon contact distances but that these are normally disregarded due to the smaller size of Na. Preliminary results from a single crystal neutron diffraction study of **1** gave longer Na··H distances than those obtained from X-ray diffraction, which reinforces this view. Although the Zn–N distances are systematically 0.07–0.08 Å shorter than the Mg–N distances in **1a** and **2a**, the remaining ring bond lengths and angles are similar, giving essentially isostructural species and hence further encouragement for the future synthesis of larger heterometallic zinc macrocycles of the $[NaNZnNNaN]_2$ and $[KNZnN]_6$ types.

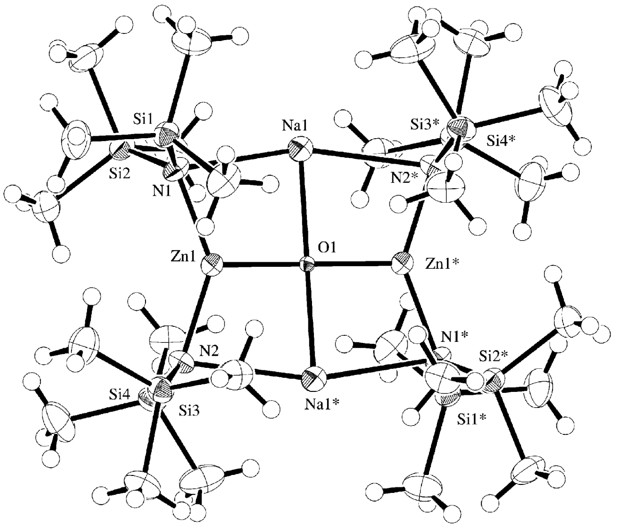


Fig. 2 Molecular structure of **1**. Selected geometric parameters (Å,°): Na1–O1 2.265(2), Zn1–N1 1.986(2), Zn1–N2 1.983(2), Zn1–O1 1.873(1); N1–Na1–N2* 158.96(8), N1–Zn1–N2 141.58(9), Na1–N1–Zn1 78.72(8), Na1*–N2–Zn1 79.78(8). * = $-x, -y, -z$.

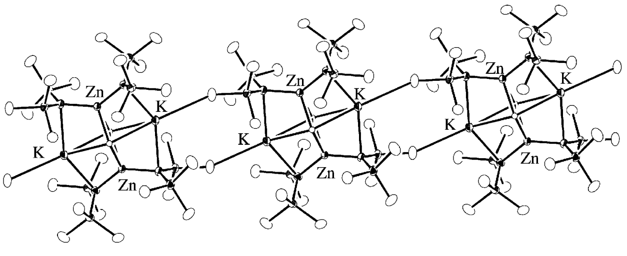


Fig. 3 Extended structure of **2** with H-atoms and the minor disorder component omitted for clarity. Selected geometric parameters (Å,°): Zn–N1 1.961(1), Zn–N2 1.965(1), O–O* 1.579(4), N1–K–N2* 143.75(3), N1–Zn–N2 135.32(4), K–N1–Zn 83.07(4), K*–N2–Zn 84.14(4). * = $1 + x, 1 + y, 1 + z$.

We thank the EPSRC for a grant (award no. GR/M78113) to fund G. C. F. and R. B. R., for partial funding for a diffractometer (W. C.) and also for a beamtime award (R. B. 11126) at the Rutherford Appleton Laboratory.

Notes and references

† TMP(H) = 2,2,6,6-tetramethylpiperidine; HMDS(H) = 1,1,1,3,3,3-hexamethyldisilazane.

Reported yields are for the first crystalline crop of materials obtained and have not been optimised. **1**: yield 40%, mp 172–173 °C; satisfactory C, H, N, Na, Zn analyses; δ_H(400 MHz, C_6D_6), 0.31 (s). δ_C(100.61 MHz, C_6D_6) 7.09. **2**: yield 18%, mp 165–166 °C; satisfactory C, H, N, K, Zn analyses. δ_H(400 MHz, C_6D_6), 0.30 (s), 0.29 (s) ratio 4:1, tentatively assigned to peroxo and oxo species respectively; δ_C(100.61 MHz, C_6D_6) δ 7.01. **3a**: yield 39%; satisfactory C, H, N, Li, Zn analyses; δ_H(400 MHz, C_5D_5N), 0.58 (s, 12H, $SiMe_3$), −0.05 (s, 1H, Me). **3b**: yield 14%. δ_H (400 MHz, C_6D_6), δ 0.21 (s, 12H, $SiMe_3$), −0.10 (s, 1H, Me). **3c**: yield 12%, δ_H(400 MHz, C_6D_6), 0.24 (s, 12H, $SiMe_3$), −0.48 (s, 1H, Me).

‡ *Crystal data*: **3a**: $C_{13}H_{39}LiN_2Si_4Zn$, $M = 408.13$, monoclinic, $C2/c$, $a = 17.040(10)$, $b = 6.840(8)$, $c = 21.558(10)$ Å, $\beta = 108.47(4)°$, $U = 2383(3)$ Å^3, $Z = 4$, $\lambda = 0.71069$ Å, $\mu = 1.228$ mm^{-1}, $T = 123$ K, $R = 0.0593$ for 2047 observed reflections with $I > 2\sigma(I)$, $wR2 = 0.1441$ for 2442 unique reflections (4689 measured, $R_{int} = 0.0654$).

1: $C_{24}H_{72}N_4Na_2OSi_8Zn_2$, $M = 834.30$, triclinic, $P\bar{1}$, $a = 10.711(6)$, $b = 12.810(6)$, $c = 8.970(4)$ Å, $\alpha = 108.96(3)$, $\beta = 99.77(4)$, $\gamma = 96.13(4)°$, $U = 1129.6(9)$ Å^3, $Z = 1$, $\lambda = 0.71069$ Å, $\mu = 1.316$ mm^{-1}, $T = 183$ K, $R = 0.0546$ for 5530 observed reflections, $wR2 = 0.1305$ for 6590 unique reflections (6914 measured, $R_{int} = 0.0134$).

2: $C_{24}H_{72}K_2N_4O_{1.82}Si_8Zn_2$, $M = 879.64$, triclinic, $P\bar{1}$, $a = 8.9898(4)$, $b = 10.9763(5)$, $c = 12.9529(6)$ Å, $\alpha = 97.322(2)$, $\beta = 108.154(2)$, $\gamma = 101.162(2)°$, $U = 1167.11(10)$ Å^3, $Z = 1$, $\lambda = 0.71073$ Å, $\mu = 1.436$ mm^{-1}, $T = 160$ K, $R = 0.0188$ for 4753 observed reflections, $wR2 = 0.0549$ for 5263 unique reflections (10058 measured, $R_{int} = 0.0112$). All structures solved and refined on F^2 using programs of the SHELX family (G. M. Sheldrick, University of Göttingen, Göttingen, Germany).

CCDC 182/1740. See http://www.rsc.org/suppdata/cc/b0/b005233g/ for crystallographic files in .cif format.

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