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Mixed-Metal Sodium – Magnesium Macrocyclic Amide Chemistry: A Template Reaction for the Site Selective Dideprotonation of Arene Molecules

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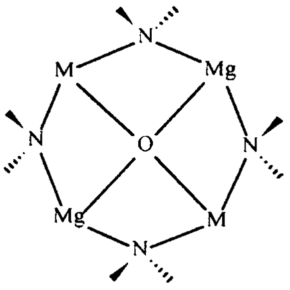

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In a new development in s block chemistry, we recently reported the first examples of mixed-metal (Group 1/Group 2) cationic ring systems with anionic oxo or peroxo cores.[1] Eight-membered macrocyclic amides, their basic motif, **1** (shown with an oxo core), consists of alternating nitrogen and metal atoms, two lithium or two sodium atoms combined with two magnesium atoms. The nitrogen atoms belong to sterically encumbered hexamethyldisilazide (HMDS) or 2,2,6,6-tetramethylpiperidide (TMP) ligands. This new class of compound can be regarded as antithetical "crown ether" complexes, where the host–guest (Lewis acid/Lewis base) positions have been reversed relative to those in conventional crown ether complexes: as such, they can be likened to the mercuracarborands pioneered by Hawthorne et al.[2] Here, in another link to crown ether chemistry, we reveal that a larger twelve-membered ($N_6Na_4Mg_2$) cationic ring system can be prepared. From the perspective of the number of metal centers in the ring, if the former macrocyclic amides prompt comparisons with [12]crown-4, then this new type can be compared to [18]crown-6. Most interestingly of all, the hexanuclear metallic ring acts as a host to the selectively dideprotonated arene molecules $[C_6H_3(CH_3)]^{2-}$ (from toluene) or $C_6H_4^{2-}$ (from benzene). The formation of these dianions suggests a template reaction is in operation.

Complexes **2** and **3** can be prepared easily and reproducibly from a 1:1:3 molar ratio of *n*BuNa, Bu_2Mg, and TMPH in

$[(tmp)_6Na_4Mg_2\{C_6H_3(CH_3)\}]$ **2**

$[(tmp)_6Na_4Mg_2(C_6H_4)]$ **3**

hydrocarbon media, to which the appropriate arene is added in excess. Attempts to prepare them from a 2:1:3 molar ratio of reactants matching the stoichiometry in the crystalline products, are hampered by solubility problems at the amine addition step.

Disregarding the methyl substituent of the dimetalated toluene, the molecular structures of **2** and **3** are essentially equivalent.[3] Figure 1 shows **2** viewed from above the macrocycle, while Figure 2 shows an alternative side view of **3**. Notable features include: a) the severely puckered $N_6Na_4Mg_2$ ring possesses crystallographic inversion symmetry; b) the arene molecules lie almost orthogonal to the mean plane of this ring; c) the metalation sites of the toluene dianion (2,5-

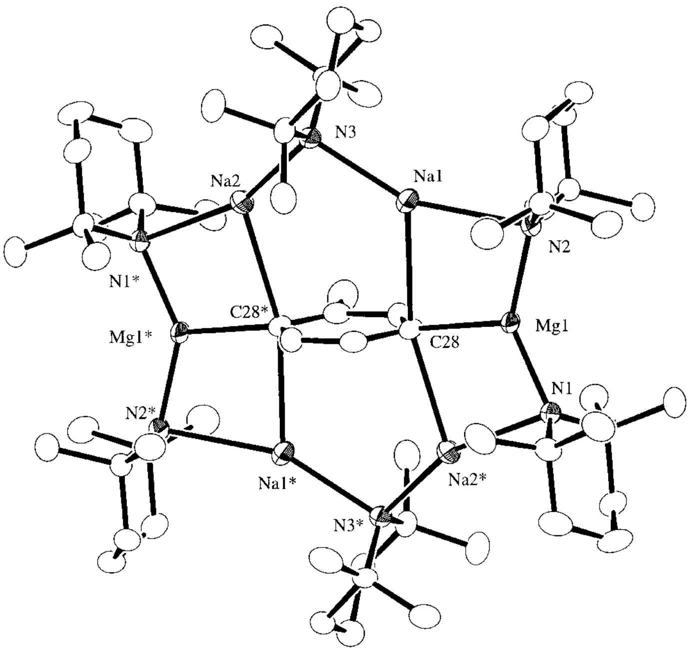

Figure 1. Molecular structure of **2** without hydrogen atoms and disorder component. Selected bond lengths [Å] and angles [°]: Na1–N2 2.626(2), Na1–N3 2.393(2), Na1–C28 2.691(2), Na2–N3 2.350(2), Na2–N1* 2.596(2), Na2–C28* 2.682(2), Mg1–N1 2.048(2), Mg1–N2 2.051(2), Mg1–C28 2.200(2); N2-Na1-N3 156.25(6), N2-Na1-C28 80.18(6), N3-Na1-C28 123.31(7), N3-Na2-N1* 160.54(6), N3-Na2-C28* 116.54(7), N1*-Na2-C28* 82.36(6), N1-Mg1-N2 142.85(7), N1-Mg1-C28 109.75(7), N2-Mg1-C28 107.32(7), Na1-C28-Na2* 164.17(9), Na1-C28-Mg1 83.38(7), Na2*-C28-Mg1 80.93(7), C29-C28-C30* 113.3(2). * = 1 − *x*, 1 − *y*, 1 − *z*.

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[**] This work was supported by the UK Engineering and Physical Science Research Council.

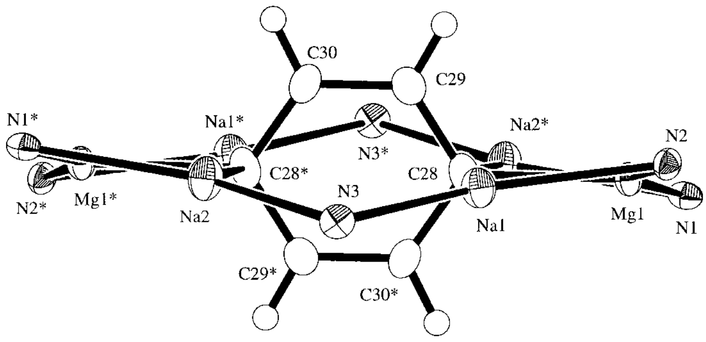
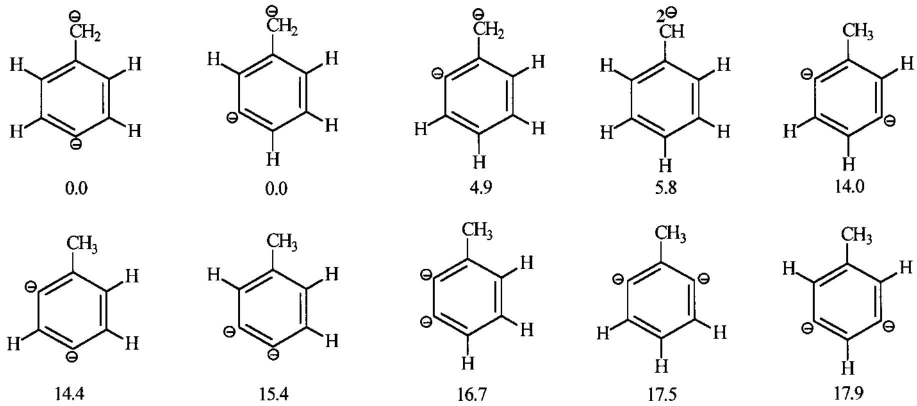


Figure 2. Side view of the molecular structure of **3** without amide carbon and hydrogen atoms. Selected bond lengths [Å] and angles [°]: Na1–N2 2.603(4), Na1–N3 2.387(4), Na1–C28 2.689(5), Na2–N3 2.350(4), Na2–N1* 2.591(4), Na2–C28* 2.676(5), Mg1–N1 2.049(4), Mg1–N2 2.037(4), Mg1–C28 2.192(5); N2-Na1-N3 157.4(1), N2-Na1-C28 80.2(1), N3-Na1-C28 122.1(1), N3-Na2-N1* 159.9(1), N3-Na2-C28* 117.6(1), N1*-Na2-C28* 81.8(1), N1-Mg1-N2 143.8(2), N1-Mg1-C28 108.8(2), N2-Mg1-C28 107.4(2), Na1-C28-Na2* 164.6(2), Na1-C28-Mg1 82.9(1), Na2*-C28-Mg1 81.7(1), C29-C28-C30* 112.7(4). $* = 1 - x, 1 - y, 1 - z$.

positions) are the same as those of the benzene dianion (1,4-positions); d) the two missing C–H σ bonds of each arene have been replaced by two C–Mg σ bonds; and e) these same C atoms each engage in π interactions with two Na^+ ions that lie above and below the aromatic ring. The similarity between **2** and **3** extends to their respective dimensions. Significantly, the N–Na bond lengths within the NaNNa units (mean over the two structures, 2.370 Å) are on average 0.234 Å shorter than those in the NaNMg units (mean 2.604 Å). This is primarily a consequence of the large difference in the endocyclic bond angles at N (that is, mean 101.5° for N3 and 87.1° for N1/N2). The former bond lengths lie in the range of those found in the cyclic trimeric polymorph of $[\{(Me_3Si)_2NNa\}_3]$ (2.358–2.394 Å),[4] while the latter compare well with those in $[(hmds)_4Na_2Mg_2(O_2)_x(O)_y]$ (mean 2.572 Å). There is also good agreement between the N–Mg bond lengths (mean 2.046 Å) and exocyclic N-Mg-N bond angles (mean 143.3°) with corresponding values in $[(hmds)_4Na_2Mg_2(O_2)_x(O)_y]$ (2.051 Å and 141.6°). The C–Mg bonds are slightly shorter (mean 2.196 Å) than those in polymeric $[(Ph_2Mg)_\infty]$ (2.261 Å),[5] which has four-coordinate Mg centers (cf. three-coordinate here). These complete the distorted trigonal-planar Mg geometry. The same geometry is apparent at the Na center (range of summed bond angles 359.3–359.7°), confirming that the N-Na-N units are coplanar with the metalated C atoms to maximize C–Na π interactions. This is reflected by a mean distance of 2.684 Å, which places them toward the lower limit of interactions of this type (approximate range 2.6–3.2 Å) as presently recorded in the Cambridge Structural Database.[6]

Metalation of toluene by reagents such as BuLi/TMEDA[7] or BuNa[8] predominantly yields the resonance-stabilized benzyl carbanion, the thermodynamically favored product. Kinetic control can bring about ring metalation, though generally only to a minor extent. It is therefore noteworthy that the toluene ring fragment in **2** is deprotonated at the diagonal *ortho–meta* positions and that the methyl group remains intact. While it is known that a complex mixture of polylithiated species is generated on treating toluene with excess BuLi/TMEDA,[9] significantly an *ortho–meta* dilithiated species is not among them. As a normal metalation would produce a benzyl group, the novel *ortho–meta*-directed metalation in **2** can be attributed to a special ring template effect. To give an estimation of the power of this effect, we have performed geometry-optimized ab initio MO calculations[10] (at the B3LYP/6-311G (d,p) level)[11] on the ten possible isomers formed when toluene is deprotonated twice (Scheme 1). These reveal that an energy deficit of 14.0 $kcal\,mol^{-1}$ has to be overcome if the experimentally observed isomer is to be preferred to the most stable one (methyl-*para* or methyl-*meta* deprotonated) in a thermodynamically controlled reaction.

Clearly, on this evidence, the cationic ring of **2** or **3**, or more precisely its immediate precursor of unknown structure, must possess exceptional proton abstraction capabilities, well beyond that of conventional magnesium amides. Presumably the precursor is $(tmp)_8Na_4Mg_2$, which must lose two ligands on reaction with the arene to give amine as a by-product [Eq. (a)].



Scheme 1. Relative energies of toluene-based dianions in $kcal\,mol^{-1}$.

$$[(tmp)_8Na_4Mg_2] + C_6H_5CH_3 \longrightarrow [(tmp)_6Na_4Mg_2\{C_6H_3(CH_3)\}] + 2\,TMPH \qquad (a)$$

Studies are in hand to examine whether the ring template effect[12] can overturn the normal reactivity patterns of other core guest molecules. Anion-exchange possibilities are also under investigation.

Experimental Section

2 and **3**: Preparations were performed in Schlenk tubes under dry argon. To a mixture of *n*-butylsodium (10 mmol) and dibutylmagnesium (10 mmol) in hydrocarbon media, was added 2,2,6,6-tetramethylpiperidine (30 mmol). The cloudy solution produced was filtered through Celite. Addition of the appropriate arene in excess (5 mL) caused an immediate precipitation of a solid. This crude product was recrystallized from the same arene (50 mL), in which it is only partially soluble. Colorless crystals of **2** or **3** were obtained by leaving the hot filtrates to cool on the bench. Yield of crystalline material (first batches) 26% and 27%, respectively; m.p. 180°C (decomp) and 175°C (decomp), respectively. Satisfactory C,H,Mg,N,Na analyses were obtained for both compounds.

Received: August 11, 1998 [Z12273IE]
German version: *Angew. Chem.* **1999**, *111*, 231–233

Keywords: alkali metals · alkaline earth metals · amides · arenes · macrocycles · template synthesis

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A New and Simple Route to Alkali Metal Oxometalates[**]

Dieter Trinschek and Martin Jansen[*]

Dedicated to Professor Edgar Niecke
on the occasion of his 60th birthday

The alkali metal oxides are the strongest oxide bases available; the basicity increases from Li_2O to Cs_2O. Accordingly these exhibit pronounced reactivity in solid-state reactions to give ternary oxides. In particular, systematic research by Hoppe et al. has revealed that the cations in such ternary alkali metal oxometalates exhibit an extraordinarily wide variety of valence, structural chemistry, and physical properties. Insulators as well as ionic or metallic conductors, maximum (e.g. K_2FeO_4,[1] $K_6Co_2O_7$[2]) or minimum oxidation states (K_3FeO_2,[3] Cs_3AuO[4]), unusually low (K_2NiO_2[5]) or high (Na_3NO_4[6]) coordination numbers, and last but not least special coordination geometries (Na_4FeO_3,[7] $KCoO_2$[8]) are found in this class of compounds. However, the synthesis of these materials can be a rather tedious and difficult task. In particular, for the heavier alkali metals the procedure includes preparation and purification of the metals, their oxidation with molecular oxygen to oxides, peroxides, or hyperoxides with a well-defined composition. All preparative work including weighing and homogenizing the starting components must be performed under strictly inert conditions. Additional problems arise from the fact that the commonly used crucibles are attacked by the alkali metal oxides more or less severely. Finally, the reaction parameters must be chosen very carefully. In this paper we present a considerably simplified and generally applicable new route to multinary alkali metal oxometalates, which circumvents most of the difficulties noted above. The approach is based on the reaction of sodium azide with sodium nitrite or sodium nitrate, first described by Zintl and Baumbach[9] [Eq. (1) and (2)]:

$$3\,NaN_3 + NaNO_2 \longrightarrow 2\,Na_2O + 5\,N_2 \qquad (1)$$

$$5\,NaN_3 + NaNO_3 \longrightarrow 3\,Na_2O + 8\,N_2 \qquad (2)$$

This particular method has not been generally accepted for the preparation of sodium oxide itself, because the components often react in an unforeseeable way, with a tendency to explode, which agrees with our own experiences. However, the reaction always proceeds in a controlled manner, if the starting materials already contain the particular oxide for the synthesis of the alkali metal oxometalate thus diluting the azide/nitrate mixture, and if the reaction is conducted in a closed container. Under these conditions the evolving N_2 can

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[**] This work was funded by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.