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Trimagnesium-bridged trinuclear ferrocenophanes cocomplexed with solvated mononuclear alkali metal amide molecules†

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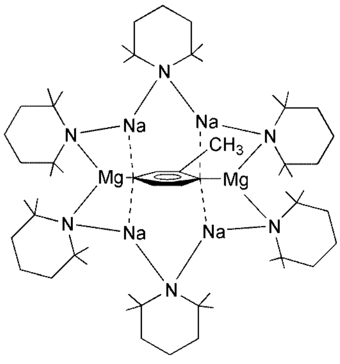
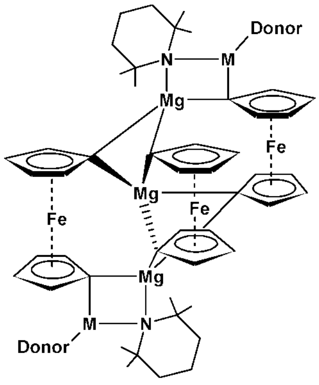
Three prototypes of the remarkable new class of compound referred to in the title have been synthesised by treating ferrocene with the same mixed lithium (or sodium)–magnesium amide recipes as those used previously to make s-block metal inverse crowns.

A recent feature article[1] highlighted the special synergistically driven chemistry that can be activated by pairing two distinct metal atom types (Li, Na or K from Group 1 with Mg or Zn from Group 2 or 12) within the same molecular amide environment. Arene molecules such as toluene can undergo selective dideprotonation at thermodynamically unfavourable ring sites to generate dianions which are locked within the central cavities of these so-called 's-block metal inverse crowns'. A representative example germane to the new work described herein is **1**.[2]



1

Derived from the sterically demanding amine 2,2,6,6-tetramethylpiperidine (TMPH) and formulated as $[\mathrm{Na_4Mg_2(TMP)_6\{C_6H_3(CH_3)\}}]$, **1** displays a twelve-membered polymetallic ring, comprising alternate NaNMg and NNaN units, which stabilises the encapsulated arenediide through a combination of Mg–C σ bonds and Na–C π bonds (aligned parallel and perpendicular, respectively, to the arene ring plane). This interplay of σ and π bonding prompted the possibility of introducing cyclopentadienyl-based ligands into this developing area of heterometallic chemistry. Here, as a first attempt towards this goal we have subjected ferrocene to the same mixed sodium–magnesium amide recipe as that used to prepare **1**. The surprising product of this reaction is the trinuclear ferrocenophane disodium trimagnesium amide $[\{\mathrm{Fe(C_5H_4)_2}\}_3\{\mathrm{Na_2Mg_3(TMP)_2\cdot(TMPH)_2}\}]$ **2**. We have also been successful in synthesising two lithium analogues $[\{\mathrm{Fe(C_5H_4)_2}\}_3\{\mathrm{Li_2Mg_3(TMP)_2\cdot(TMPH)_2}\}]$, **3** and $[\{\mathrm{Fe(C_5H_4)_2}\}_3\{\mathrm{Li_2Mg_3(TMP)_2\cdot(pyridine)_2}\}]$ **4**, and so herein report the prototypes of a remarkable new class of structure.



2/3/4

In the preparation of **2**, freshly prepared Bu^{n}Na and commercial Bu$_2$Mg (10 mmol of each) were stirred together in a hexane–heptane mixture in an argon-filled Schlenk tube. The congealed brown mass obtained was then treated with TMPH (30 mmol) and the mixture was stirred until complete dissolution had occurred. Next, ferrocene (5 mmol) was introduced and the mixture was heated to reflux for 90 min. This produced a red powder which only partially dissolved on addition of hot toluene (40 ml), so what remained was collected by filtration. Left to cool overnight in a Dewar flask of hot water, the filtrate deposited a crop of red crystals. Both the powder and crystals were identified as **2**.‡ Substituting Bu^{n}Li for Bu^{n}Na in a similar procedure afforded the lithium analogue **3**.‡ Note that TMPH is available as a ligand here because it is the byproduct of ferrocene deprotonation by amido anions (TMP). Isolated **3** can be smoothly converted to **4**‡ by re-dissolving it in toluene solution and adding several molar equivalents of the stronger donor pyridine.

Each Mg atom independently stitches together the three ferrocene-1,1′-diyl units of **2** (Fig. 1). The distorted tetrahedral coordination sphere of centric Mg(1) comprises four C atoms, belonging to the 'top', 'bottom', and 'top' and 'bottom' C$_5$H$_4$ rings attached to Fe(1A), Fe(1) and Fe(2), respectively. This unique third ferrocenyl unit is disordered over two sites. Unfortunately this disorder would prejudice any discussion of dimensions pertaining to **2**, though it has no bearing on the connectivities within the structure which are unambiguous. A crystallographic C_2 axis runs through Mg(1) and Fe(2). The fourth coordination site of symmetry partners Mg(2)/Mg(2A) is filled by an amido N atom [N(1)/N(1A)]. Essentially planar (CMgNNa) rings, solvated at Na by TMPH molecules, complete the architecture. Of special significance therein is the Na(1)–C(1) bond [length 2.526(4) Å] as, to the best of our knowledge, it represents the first direct contact between Na and a ferrocenyl unit.

Detailed discussion of the structure is confined to that of **4** (Fig. 2) because there is no disorder within its molecular structure though there are disordered solvent molecules in the extended structure. Its connectivity pattern follows that of **2**, though the C_2 symmetry about the Mg(2)$\cdots$Fe(2) axis is only approximate in this case. Mimicking the role of the TMPH

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† Dedicated to Professor P. L. Pauson on the 50th anniversary of the landmark discovery of ferrocene.

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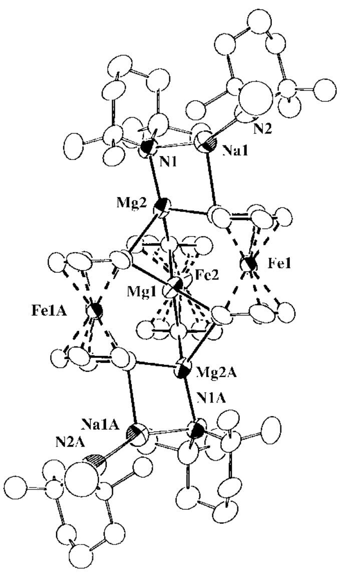

Fig. 1 Molecular structure of **2** without H atoms and disorder component.

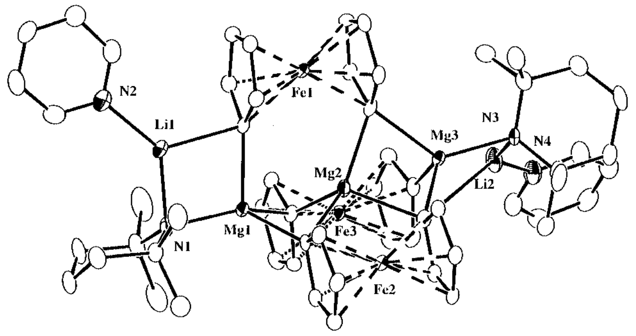

Fig. 2 Molecular structure of **4** from an alternative view to that given for **2** in Fig. 1. H atoms and solvent molecules of crystallisation have been omitted. Key dimensions (Å): Li1–N1 2.031(8), Li1–N2 2.050(8), Li1–C1 2.279(8), Li2–N3 2.027(8), Li2–N4 2.049(8), Li2–C26 2.243(8), Mg1–N1 2.072(3), Mg1–C1 2.187(4), Mg1–C11 2.224(4), Mg1–C21 2.344(4), Mg3–N3 2.094(3), Mg3–C6 2.304(4), Mg3–C16 2.221(4), Mg3–C26 2.194(4), Mg2–C6 2.224(4), Mg2–C11 2.352(4), Mg2–C16 2.307(4), Mg2–C21 2.219(4).

molecules in **2**, pyridine molecules bind terminally to Li at the periphery of the structure. Centric Mg(2) bonds asymmetrically to the ferrocenyl units: the pair of Mg–C bridging bonds to the Fe(2) unit are longer than their single terminal counterparts to the Fe(1) and Fe(3) units (mean lengths, 2.339 and 2.234 Å respectively). Significantly the shortest such bonds in the structure [Mg(1)–C(1) 2.187(4) Å, Mg(3)–C(26) 2.194(4) Å] lie almost parallel with their attached C$_5$H$_4$ ring [torsion angles: Mg(1)–C(1)–C(2)–C(3) 176.6(3)°, Mg(3)–C(26)–C(27)–C(28) −176.3(3)°] implying a high degree of σ character. All three Mg atoms deviate substantially from a tetrahedral geometry, with distortion most pronounced for the exclusively ferrocenyl-bound Mg(2) [range of bond angles 90.04(14)–140.42(15)°]. Another salient feature is the near-planarity of the four-element (CMgNLi) rings (sum of endocyclic bond angles, 359.05 or 360.05°). The quasi perpendicular approach of the Li atoms towards the C$_5$H$_4$ ring [*e.g.* Li1–C1–C2–C3, 103.6(3)°] signifies a large π contribution to the Li–C bonding. Finally it should be noted that each ferrocenyl unit has essentially eclipsed C$_5$H$_4$ rings, and that the staggered positioning of the three ferrocenyl ligands with respect to the Mg···Mg axis gives each molecule a chiral nature.

No precedent exists for this extraordinary class of heterotrimetallic complex, either in terms of composition or structure. The closest analogy, also reported in 2001,[3] is the homo-main group-metallic gallium-bridged species [{Fe(C$_5$H$_4$)$_2$}$_3${Ga·(pyridine)}$_2$]. Made by a condensation reaction from a methylgallium precursor as opposed to the novel synergic metallation approach used here, it possesses a similar chiral ‘carousel’ arrangement of ferrocenyl units linked by two end-positioned Ga atoms [*à la* Mg(1) and Mg(3) in **4**], but is ‘missing’ a centric metal atom and metal amide component. A trinuclear ferrocenyl unit was first observed in the homometallic lithium-bridged species [{Fe(C$_5$H$_4$)$_2$}$_3$Li$_6$·(TMEDA)$_2$],[4] but the bridges are exclusively μ$_2$-Li–C in this case. While no other trinuclear examples are known, there has been a recent report[5] of a dinuclear ferrocenyl complex containing both lithium and magnesium; however, [(FcN)$_2$Li$_2$Mg(Br)$_2$·(OEt$_2$)] (where FcN is a dimethylaminomethylferrocenyl unit) bears little structural resemblance to **4**.

Returning to the original theme of the work, while **2**, **3** and **4** are clearly not inverse crown ring systems (*à la* **1**) they do nonetheless contain component parts thereof. In particular, their bimetallic MNMg (where M is an alkali metal) fragments are essential building blocks of all the known 8-, 12- and 24-membered inverse crown ring systems. Furthermore the ferrocene-diyl units can be likened to the arene-diyl units encountered in the 12-membered inverse crown **1**. Where **2**, **3** and **4** are truly unique in the context of heterometallic s-block chemistry, is in having a (centric) Mg atom stripped naked of amido ligands. With this atom acting as a fulcrum for supporting the three ferrocenyl units, it should be possible to build supramolecular assemblies of multiple trinuclear ferrocenophane molecules by exploiting the metathetical reactivity of the peripheral alkali metal amide fragments. Such redox-active assemblies could possess a range of interesting electrochemical, electronic and magnetic properties.

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Notes and references

‡ **2**: Yield (based on ferrocene consumption) 49%; mp decomp. from 200 °C; pyrophoric; satisfactory C, H, N analyses; δ_H (400 MHz, C$_5$D$_5$N), 4.83/4.77 (α- or β-H, C$_5$H$_4$), 1.58 (γ-H, TMP/H), 1.30 (β-H, TMP/H), 1.12 (α-Me, TMP/H), NH resonance was not observed. **3**: Yield, 68%; mp 174–176 °C; non-pyrophoric, satisfactory C, H, N analyses; δ_H (400 MHz, C$_5$D$_5$N). 4.85/4.80 (α- or β-H, C$_5$H$_4$), 1.57 (γ-H, TMP/H), 1.29 (β-H, TMP/H), 1.12 (α-Me, TMP/H), NH resonance was not observed. **4**: Yield, 63%; mp 166–168 °C; non-pyrophoric, satisfactory C, H, N analyses; δ_H (400 MHz, C$_5$D$_5$N), 8.74 (α-H, pyr), 7.59 (γ-H, pyr), 7.23 (β-H, pyr), 4.84/4.80 (α- or β-H, C$_5$H$_4$), 1.58 (γ-H, TMP), 1.29 (β-H, TMP), 1.12 (α-Me, TMP). All samples are extremely sensitive to hydrolysis as shown by trace amounts of ferrocene at δ 4.20. Note that solubility problems were encountered when the reactions were repeated using the stoichiometry consistent with the formulas of **2**, **3** and **4**. However, in all cases the same products were again observed.

Crystal data: for **2**: C$_{66}$H$_{98}$Fe$_3$Mg$_3$N$_4$Na$_2$, M = 1233.94, monoclinic, space group $P2/c$, a = 16.6871(3), b = 10.3932(2), c = 18.5237(4) Å, β = 102.392(1)°, U = 3137.8(1) Å^3, Z = 2, λ = 0.71073 Å, μ = 0.77 mm^{-1}, T = 150 K, R = 0.062 for 4553 observed reflections, $wR2$ = 0.1705 for 6166 unique reflections for 355 parameters refined to convergence on F^2.

For **4**·C$_6$H$_5$CH$_3$: C$_{65}$H$_{78}$Fe$_3$Li$_2$Mg$_3$N$_4$, M = 1169.66, triclinic, space group $P\bar{1}$, a = 15.402(5), b = 16.552(2), c = 11.622(3) Å, α = 98.651(11), β = 100.01(2), γ = 94.796(14)°, U = 2866.2(11) Å^3, Z = 2, λ = 0.71069 Å, μ = 0.83 mm^{-1}, T = 123 K, R = 0.0499 for 6837 observed reflections, $wR2$ = 0.1350 for 8991 unique reflections and 696 parameters refined to convergence on F^2.

CCDC reference numbers 165404 and 165405. See http://www.rsc.org/suppdata/cc/b1/b105009p/ for crystallographic data in CIF or other electronic format.

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