Synthesis and structure of the novel octanuclear lithium aryloxide cluster [(hmqLi)₈(THF)₄] (hmq⁻ = 2-hydroxy-4-methylquinoline monoanion): formation of a rare four-rung intercepted Li–O ladder

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The title complex, readily prepared by the facile deprotonation of 2-hydroxy-4-methylquinoline by *n*-butyllithium in ethereal solvent, crystallises as a novel octanuclear cluster constructed around a rare intercepted four-rung Li–O ladder.

Metal alkoxides, as a result of their applications as precursors to ceramics and electronic materials by sol–gel and MOCVD processes, have been the subject of intense interest.[1–3] These processes often utilise mixed-metal alkoxides and it is thus necessary to control reaction stoichiometries tightly in order to produce high quality materials. These "single-source" precursors are frequently generated through the introduction of a cation such as an alkali metal,[4,5] which can subsequently be exchanged by metathesis, although their applications are often hindered by partial retention of the alkali metal in the target compounds. In order to gain a better understanding of the chemistry and formation of such "single-source" precursors it is necessary to garner structural information about the homometallic components themselves. Structural studies of organolithium complexes such as alkyls, alkoxides and amides have been investigated in great detail and have revealed a number of common structural motifs.[6] Within preparative chemistry, Group 1 alkoxides may also find additional applications in two-component superbases, as typified by 'Bu^nLi·Bu^tOK'.[7] Recently, as part of an on-going study of Group 1 derivatives of hydroxymethylpyridine (Hhmp), we reported the mixed anion–dianion cage [(6-LiCH₂Py-2-OLi)₄(6-CH₃Py-2-OLi)₂-(THF)₉] 1.[8] As a ligand, hmp⁻ has been employed extensively in transition metal chemistry, where its similarity to the carboxylate group has been exploited to probe the nature of multiple metal–metal bonds in dinuclear transition metal complexes.[9] However, examples of Group 1 complexes of hmp⁻ are limited to a handful of examples. As already realised by the characterisation of 1, the solid state structures adopted by Group 1 complexes of hmp⁻ promise to be more diverse than 'pure' alkoxides or aryloxides, due to the additional coordination possibilities provided by the pyridyl nitrogen, although in 1 the facile deprotonation of the methyl group complicates the resulting structure. In order to assess the structural impact of different functionalities on the pyridyl ring, we have sought to investigate Group 1 complexes of 2-hydroxy-4-methylquinoline (Hhmq). A further incentive to pursue this avenue of research is that, to the best of our knowledge, there are only four crystallographic examples of the hmq⁻ anion, all as phosphine-stabilised rhenium hydride complexes.[10,11] Herein, we report the synthesis and solid state structure of the title compound 2.

In a Schlenk tube under dry nitrogen, a slurry of Hhmq in dry THF, when treated with one equivalent of Bu^nLi, affords a deep red solution. Standing the solution overnight yields a pale yellow solution, and colourless air- and moisture-sensitive crystals of 2 are deposited as the sole isolated product.† Washing with *n*-hexane and drying *in vacuo* results in loss of all uncoordinated THF solvent (see below) to give pure 2 (as evidenced by CHN microanalysis), as a white powder, which is insoluble in arene solvents and sparingly soluble in THF. In contrast to 1, we find no evidence for subsequent deprotonation at the methyl site, even with excess Bu^nLi.

The molecular structure of 2 (Fig. 1)‡ consists of an octanuclear cluster constructed around an intercepted four-rung (LiO)₄ ladder core (Fig. 2), which lies on a crystallographic inversion centre. Four molecules of THF per cluster crystallise uncoordinated in the crystal structure. The complex is not fully solvated, in that only four of the eight lithium centres are coordinated by THF. This is attributed to a combination of the steric bulk of the hmq⁻ anion and the presence of the N donor centres. All eight lithium centres are four-coordinate, exhibiting distorted tetrahedral environments, with four distinct pairs in the centrosymmetric structure. Li(4) is coordinated by four hmq⁻ oxygens, Li(3) by three hmq⁻ oxygens and a molecule of THF, Li(2) by two hmq⁻ oxygens, an hmq⁻ nitrogen and one THF, and Li(1) by three nitrogens and one oxygen of hmq⁻ ligands. The hmq⁻ anions display a variety of coordination modes, with μ₂ and μ₃ bridging oxygens, and two lithium centres are internally coordinated by the hmq⁻ nitrogen donor centres. As also demonstrated by 1, the consequence of an additional donor site is realised by the formation of a cluster more complicated than that observed in classical cubane or hexamer architectures. Although the ring laddering principle for lithium amides is well established,[6c] it is a comparatively rare occurrence for aryloxides or alkoxides. Indeed, there are few reports of such homometallic ladders;[12] the vast majority of Li–O-containing metalloorganic species display cubane,[13] hexamer[14] or higher aggregates[15] in the solid state. However, Wheatley and co-workers recently reported a mixed-anion lithium aluminate species;[16] although this is the product of a reaction with dioxygen, the (LiO)₄ core displays a strikingly similar architecture to that of 2.
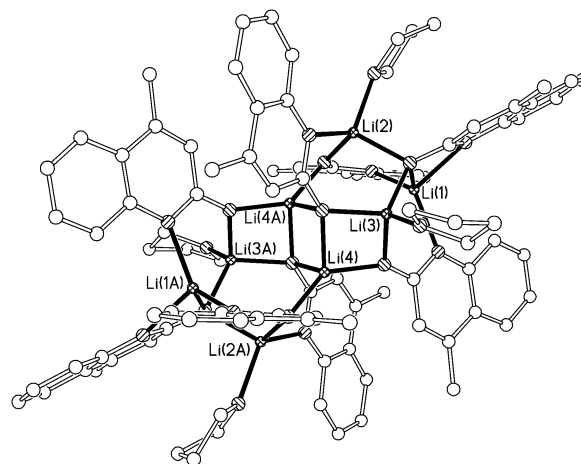

Fig. 1 Molecular structure of 2; hydrogen atoms are omitted for clarity. Only Li atoms are labelled.
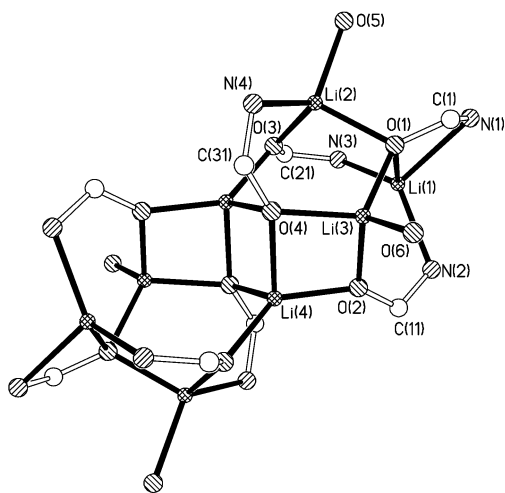
Fig. 2 View of **2**, highlighting the intercepted ladder core. *ipso* carbons of hmq⁻ anions are shown; others are omitted for clarity. Selected bond lengths (Å): Li(1)–O(1) 2.020(10), Li(1)–N(1) 2.205(10), Li(1)–N(2) 2.086(10), Li(1)–N(3) 2.090(10), Li(2)–O(1) 1.955(10), Li(2)–O(3) 1.915(9), Li(2)–N(4) 2.087(9), Li(2)–O(5) 2.013(9), Li(3)–O(1) 1.894(10), Li(3)–O(3) 1.883(10), Li(3)–O(4) 1.916(10), Li(3)–O(6) 1.938(10), Li(4)–O(2) 1.889(10), Li(4)–O(4) 1.990(10), Li(4)–O(3A) 1.888(9), Li(4)–O(4A) 2.046(10); atoms with suffix A are related to the originals by inversion symmetry.

The Li–O$_{hmq}$ bond lengths in **2** span the range 1.883(10)–2.046(10) Å, reflecting the various coordination modes of the hmq⁻ ligands, and this is similar to the range observed in **1**. The Li–O$_{THF}$ bond lengths [mean 1.976(9) Å] are in accord with such distances previously reported.[6f] The Li–N bond lengths span the range 2.086(10)–2.205(10) Å, reflecting the varied coordination modes exhibited by hmq⁻, and agree well with the range observed in **1**. The O–C$_{ipso}$ bond lengths span the range 1.291(6)–1.317(6) Å, indicating a bond order greater than one, due to resonance delocalisation of the anionic charge in the aromatic π system.

Recorded in [²H]$_8$ THF solution at 298 K, the ¹H NMR (200 MHz) and ¹³C NMR (50 MHz) spectra each exhibit a single set of resonances attributable to the hmq⁻ anion and THF, and the ⁷Li NMR spectrum consists of a single peak at 1.31 ppm (relative to a 1 M solution of LiCl in D₂O at 0.00 ppm). Among the possible scenarios that could explain this are the following: (i) the solid state structure deaggregates in polar solvents to give a species with one lithium environment; (ii) the structure is retained in solution and the chemical shifts are accidentally equivalent; or (iii) the structure is retained in solution and the ligands and lithium atoms are exchanging in a fast process (on the NMR timescale) with a low energy barrier. Indeed, dynamic exchange in solution is well known for metal alkoxides. Unfortunately, variable-temperature NMR studies of **2** were precluded, due to the poor solubility of this complex once formed, even in THF, implying that a large cluster of some kind is actually retained in solution; even at room temperature, the complex precipitates from solution in a few hours.

In conclusion, we have demonstrated that structurally diverse and complicated lithium aryloxides can be generated by anions such as hmp⁻ and hmq⁻. Further studies will investigate higher Group 1 metal complexes and related anions.

Notes and references

† A slurry of 2-hydroxy-4-methylquinoline (0.79 g, 5.00 mmol) in THF (50 mL) was treated with Bu^{n}Li (2.0 mL, 5.00 mmol) to afford a red solution. Standing overnight at ambient temperature resulted in a pale yellow solution and a crop of colourless crystals of **2** suitable for an X-ray study (0.68 g, 67.6%). Spectroscopic data for **2**: ¹H NMR (298 K, 200.1 MHz, [²H]$_8$ THF) δ = 1.63 (16 H, m, CH₂ of THF), 2.12 (24 H, s, Me), 3.47 (16 H, m, OCH₂ of THF), 6.40 (8 H, s, β-H-aryl), 6.90 (8 H, t, aryl), 7.22 (8 H, t, aryl), 7.48 (8 H, d, aryl) and 7.67 (8 H, d, aryl). ¹³C NMR (298 K, 50.3 MHz, [²H]$_8$ THF) δ = 18.31 (Me), 25.11 (CH₂ of THF), 67.19 (OCH₂ of THF), 119.78, 120.24, 123.76, 125.34, 128.42, 129.46, 145.23, 149.17 and 171.95 (aryl). ⁷Li NMR (298 K, 116.6 MHz, [²H]$_8$ THF) δ = 1.31. Anal. Found: C, 70.20; H, 5.87; N, 6.66%. Calc for C$_{96}$H$_{96}$N$_8$O$_{12}$Li$_8$ (no uncoordinated THF): C, 71.64; H, 6.01; N, 6.96%.

‡ Crystal data for **2**·4THF: C$_{96}$H$_{96}$N$_8$O$_{12}$Li$_8$·4C$_4$H$_8$O, M = 1897.7, triclinic, space group $P\bar{1}$, a = 12.5281(14), b = 13.7330(15), c = 16.4814(18) Å, α = 77.117(2), β = 68.609(2), γ = 83.432(2)°, U = 2572.1(5) Å³, Z = 1, D_c = 1.225 g cm⁻³, μ = 0.08 mm⁻¹ (MoKα, λ = 0.71073 Å), T = 160 K, R ($F^2 > 2\sigma$) = 0.0784, R_w (F^2, all data) = 0.2221, goodness-of-fit = 0.910 for all 8406 unique data (11076 measured, R_{int} = 0.0612, $2\theta < 50°$, CCD diffractometer) and 654 refined parameters. Programs: standard Bruker AXS control and integration software and SHELXTL.[17] CCDC reference number 189782. See http://www.rsc.org/suppdata/dt/b2/b206894j/ for crystallographic data in CIF or other electronic format.

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