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Synthesis and structure of the novel mixed anion–dianion lithium cage compound [(6-LiCH$_2$Py-2-OLi)$_4$(6-CH$_3$Py-2-OLi)$_2$(THF)$_9$]

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The title compound crystallises as a novel homometallic mixed anion–dianion cage incorporating two four-coordinate diorgano lithiate centres, in addition to eight lithium centres coordinated only by oxygen and nitrogen atoms.

The past two decades have witnessed considerable interest in organolithium chemistry. Within this realm the formation of complexes containing ‘ate’ centres is still comparatively rare, despite the overwhelming number of organolithium complexes reported to date. The first example was reported by Eaborn *et al.*,[1] and some closely related complexes subsequently followed.[2] There are only a handful of other examples,[3] including the recently reported dibenzyl lithiate complex by Bildmann and Müller, which contains the first example of a four-coordinate diorganolithiate.[3c] Examples of ate complexes with nitrogen donors have also been reported.[4]

We are currently interested in aspects of the structural chemistry of 2-hydroxy-6-methylpyridine (Hhmp) and other substituted 2-pyridones. Hhmp has been employed extensively in transition metal chemistry where the similarity of its anion hmp$^-$ to the carboxylate group has been exploited to probe the nature of multiple metal–metal bonds in dinuclear complexes.[5] Such complexes are frequently synthesised *via* an alkali metal salt; these are notable by their relative lack of structural characterisation. Indeed, a search of the Cambridge Structural Database[6] reveals, with the exception of some heterobimetallic alkali metal–transition metal complexes,[7] only two related compounds, both produced in aqueous media, namely the monohydrated potassium salt of 2-pyridone [2-KOPy·H$_2$O][8] and the caesium salt of the more highly substituted 2-pyridone [2-CsO-3-CN-4-CF$_3$-6-Ph-Py·H$_2$O].[9] Consequently we have sought to characterise alkali metal complexes of hmp, as they promise to be more structurally diverse than ‘pure’ alkoxides or aryloxides due to the additional coordination possibilities provided by the pyridyl nitrogen. Although our principal goal has been to synthesise monometallated complexes, we find that subsequent lithiation at the methyl site occurs readily, thus allowing facile access to the synthesis of mixed anion–dianion complexes. Indeed, it is possible to control precisely the extent of metallation from monometallated through to dimetallated by addition of the appropriate amount of butyllithium. It is consequently possible to synthesise aggregates with varying degrees of anion/dianion character and we have synthesised a range of such complexes, which will be elaborated on in a full account of this work. As revealed herein, we describe the synthesis and solid state structure of the title compound **1**, which is notable for being a rare example of a Group I mixed anion–dianion complex containing two four-coordinate organolithiate centres.

In a Schlenk tube under dry nitrogen, Hhmp (10 mmol) in dry THF (50 mL) was lithiated by Bu^{n}Li (10 mmol) to afford a dark orange solution. Addition of an additional 2/3 equivalent of Bu^{n}Li (6.67 mmol) affords a dark red solution with evolution of gas clearly visible [eqn. (1)]. Concentration and layering with *n*-hexane at −30 °C affords highly air-sensitive orange crystals of

$$\begin{aligned}&\text{6-CH}_3\text{Py-2-OH} + 10\ \text{Bu}^n\text{Li} \xrightarrow{\text{THF}} \\ &[(\text{6-LiCH}_2\text{Py-2-OLi})_4(\text{6-MePy-2-OLi})_2(\text{THF})_9] + \\ &\qquad\qquad\qquad\qquad 10\ \text{Bu}^n\text{H}\end{aligned} \tag{1}$$

the title compound **1** in 82.4% isolated yield, which rapidly degrade to a yellow powder when removed from solvent or exposed to vacuum. Despite repeated attempts, it was not possible to obtain satisfactory microanalysis for **1**, due to the extremely air- and moisture-sensitive nature of this complex and loss of coordinated THF. Analyses obtained were consistent with variable loss of non-integral amounts of coordinated THF (typically between two and four molecules).

The structure of **1** (Fig. 1)† consists of an alkoxo cage with two diorgano lithiate centres. There are ten lithium centres, two anionic and four dianionic hmp ligands (deprotonated at the hydroxy *and* methyl sites), and nine THF molecules. Each lithium centre, with the exception of the three-coordinate Li(2), which is distinctly pyramidal [sum of angles 343.5(6)°], displays a distorted tetrahedral environment. Setting aside the C–Li bonds, four of the hmp ligands are tetra-coordinating [N(1), N(2), N(4) and N(6)] (with μ_3-oxygen atoms) and two [N(3) and N(5)] are penta-coordinating (with μ_4-oxygen atoms).

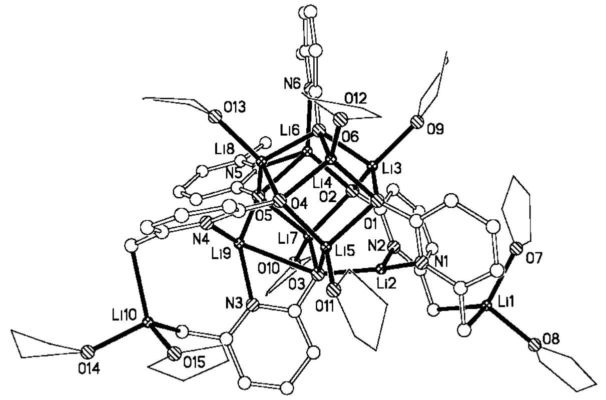

Fig. 1 Molecular structure of **1**. Hydrogen atoms and parentheses in atom labels have been omitted for clarity. Selected bond lengths (Å): Li(1)–O(7) 1.998(15), Li(1)–O(8) 1.994(15), Li(1)–C(6) 2.198(16), Li(1)–C(12) 2.230(16), Li(2)–N(1) 1.996(15), Li(2)–N(2) 2.015(15), Li(2)–O(3) 1.957(14), Li(3)–O(1) 1.937(13), Li(3)–O(2) 1.898(15), Li(3)–O(6) 2.034(16), Li(3)–O(9) 1.961(16), Li(4)–O(1) 1.959(15), Li(4)–O(4) 1.916(15), Li(4)–O(6) 1.982(14), Li(4)–O(12) 1.991(15), Li(5)–O(1) 2.036(15), Li(5)–O(3) 1.938(15), Li(5)–O(4) 1.948(15), Li(5)–O(11) 1.937(14), Li(6)–O(2) 1.907(15), Li(6)–O(5) 2.267(15), Li(6)–N(5) 2.043(15), Li(6)–N(6) 2.070(17), Li(7)–O(2) 1.979(14), Li(7)–O(3) 1.927(14), Li(7)–O(5) 2.063(15), Li(7)–O(10) 2.010(15), Li(8)–O(4) 1.956(15), Li(8)–O(5) 2.004(15), Li(8)–O(6) 1.974(16), Li(8)–O(13) 1.933(16), Li(9)–O(3) 2.580(16), Li(9)–O(5) 1.970(16), Li(9)–N(3) 1.984(18), Li(9)–N(4) 1.996(18), Li(10)–O(14) 1.994(16), Li(10)–O(15) 1.934(16), Li(10)–C(18) 2.243(18), Li(10)–C(24) 2.300(20).

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Both these bonding modes are, to the best of our knowledge, unprecedented with this ligand; only mono-, di- and tri-coordination modes are known. The core of the cage may be thought of as a stack of two six-membered $(LiO)_3$ rings [ring 1: Li(3)–O(1)–Li(5)–O(3)–Li(7)–O(2); ring 2: O(6)–Li(4)–O(4)–Li(9)–O(5)–Li(6)], of similar architecture to the hexameric complex $[\{Li(OPh)(THF)\}_6]$,[10] which has been distorted by the presence of the four extra lithium centres [Li(1), Li(2), Li(8) and Li(10)]. The chiral cage crystallises in the non-centrosymmetric space group *P*1.

Turning to bond lengths, excluding the four long Li–O contacts of 2.267(15), 2.580(16), 2.613(15) and 2.655(17) Å [Li(6)–O(5), Li(9)–O(3), Li(6)–O(6) and Li(9)–O(4) respectively], the $Li–O_{hmp}$ bond lengths span the range 1.898(15)–2.063(15) Å. This compares with a range of 1.856–2.063 Å in the heterometallic cluster $[(Bu^tOLi)_6(Bu^tOK)_2(Li_2O)(TMEDA)_2]$,[11] and a range of 1.830–2.101 Å in the heterometallic cluster $[\{(Bu^tOLi)_5(Bu^tORb)_4(Li_2O_2)(TMEDA)_2\}_\infty]$,[12] and agrees well with a recently reported series of lithium phenoxides.[13] The overall larger range observed in **1** reflects the various coordination modes adopted by the hmp ligands. The $Li–O_{THF}$ bond lengths span the range 1.933(16)–2.010(15) Å, which is in good agreement with previously reported values for neutral oxygen donor co-ordinated organolithium complexes.[14] The Li–N bond lengths span the range 1.996(15)–2.678(16) Å, reflecting the distorted nature of the cage and, discounting the longest Li(9)–N(4) contact of 2.678(16) Å, compare well with values previously reported for tertiary amine coordinated organolithium complexes.[15] The Li–C bond lengths are distinctly longer than the Li–O and Li–N average bond lengths in accord with periodic considerations, spanning the range 2.198(16)–2.300(20) Å; this is in good agreement with Li–C bond lengths reported previously.[3c,14] The bond angles around the benzylic carbons span the range 99.9(7)–108.3(8)°, indicating geometries more in keeping with sp^3 hybridised centres. This relatively wide range of bonding angles implies a complicated situation in terms of the electronic environment of the hmp dianion ligand, and is in keeping with the highly polar nature of bonding exhibited by Group I metals. This is also indicated by inspection of the $O–C_{ipso}$ bond lengths, which span the range 1.284(9)–1.343(9) Å; this range is in between values generally quoted for C–O (1.43 Å) and C=O (1.20 Å) bond lengths, and indicates a bond order greater than one.

Recorded in $[^2H]_8THF$ solution at 298 K, the ^1H NMR (200 MHz) spectrum consists of multiplets at 1.40 and 3.61 ppm characteristic of THF, a broad multiplet at 2.35–2.85 ppm attributed to the methyl and benzylic protons, and three broad multiplets centred at 5.47, 6.43 and 7.46 ppm attributed to the three pyridyl protons. Integration indicated an average loss of approximately three THF. The broad appearance of these signals implies that a dynamic process is operating in solution. Dynamic exchange in solution is a process for which alkoxides are notorious, and alkali metal complexes are also well known for their partial to full deaggregation in solution. However, no coalescence was observed in a variable temperature study over the range 200–323 K, indicating that this dynamic process continues to operate over that temperature range. The ^7Li NMR (116.6 MHz) spectrum in $[^2H]_8THF$ at 298 K exhibits six identifiable signals at 1.92, 1.67, 0.66, −0.04, −1.02 and −1.17 ppm. No further signals were apparent from a variable temperature study over the range 200–323 K.

In conclusion, we have demonstrated that 2-hydroxy-6-methylpyridine can be deprotonated not only at the hydroxy site, but also subsequently at the methyl site. This allows the possibility of preparing structurally diverse alkoxo clusters with varying degrees of alkyl character, and thus the possibility of tuning the properties such clusters may display. Further work will explore such avenues and will also investigate hetero-bimetallic complexes of hmp with higher alkali metals. These should prove to be interesting as it is likely that the lithiate centres will be the first to be substituted by higher alkali metals.

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Notes and references

† *Crystal data* for **1**: $C_{80}H_{120}Li_{10}N_6O_{17}$, $M = 1507.2$, triclinic, space group *P*1, $a = 12.1861(12)$, $b = 13.4120(12)$, $c = 14.5875(14)$ Å, $\alpha = 106.156(2)$, $\beta = 99.760(2)$, $\gamma = 104.451(2)$°, $U = 2143.1(4)$ Å^3, $Z = 1$, $D_c = 1.168$ g cm^{-3}, $\mu = 0.08$ mm^{-1}, (Mo-Kα, $\lambda = 0.71073$ Å), $T = 160$ K, $R(F^2 > 2\sigma) = 0.093$, $R_w(F^2$, all data) = 0.210, for all 12522 unique data (13722 measured, $R_{int} = 0.028$, $2\theta < 50°$, CCD diffractometer) and 932 refined parameters. Programs: standard Bruker AXS control and integration software and SHELXTL.[16] Structure solution was accomplished by SIR 97.[17] Uncoordinated THF solvent was too highly disordered for individual atoms to be resolved; this was treated by the SQUEEZE procedure of PLATON,[18] which indicated the correct total electron density and void volume for two molecules of THF per cluster molecule.

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