

Spontaneous assembly of a nine-vertex lithium framework encapsulating the peroxide dianion†

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Investigation of the structure of the lithiated bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) has led to the reproducible isolation of compounds containing the 'Li₉(hpp)₇(O₂)' core, in which a peroxide dianion has been encapsulated within a mono-capped, cubic array of lithium ions.

A high degree of oxophilicity is recognized as a primary characteristic of many useful lithium reagents, such as organo-lithium compounds and lithium amides, and is manifest in the necessary exclusion of oxygen and moisture when successfully manipulating these species.¹ As such, the isolation of products in which the incorporation of 'adventitious' oxygen has taken place is not uncommon, and several varied and elaborate structural motifs have been observed.² The principal types of compound afforded from such accidental oxidation/hydrolysis are those in which an oxygen atom has inserted in a lithium-carbon or lithium-heteroatom bond, to form organo- or inorgano-oxides, or those in which the oxide dianion, O₂²⁻, has become encapsulated within an inorganic skeleton. A much more unusual reaction is that in which the reduction of molecular oxygen is arrested at the peroxide stage, with the resultant O₂²⁻ dianion becoming immobilized within the molecular framework of the product. A few isolated examples have been previously reported (Fig. 1), including the "hydrolyzed product" of dilithium *N,N'*-bis(trimethylsilyl)hydrazide (a),³ a complex structure isolated from the reaction of 1,3-dimethyl-2-iminoimidazoline and MeLi consisting of a 'Li₉Cl₂N₈O₂' core (b)⁴ and oxygen-containing, intermetallic lithium-magnesium⁵ and lithium-rubidium⁶ clusters (c and d). Peroxo species such as these have been implicated as intermediates in the formation of many of the aforementioned oxide end-products, but genuine examples remain rare.

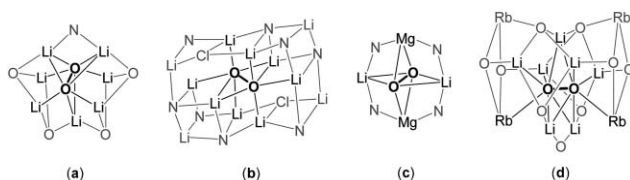


Fig. 1 The core structures of selected lithium-peroxo and related compounds. O–O distances: (a) 1.557(3),³ (b) 1.544(4),⁴ (c) 1.551(4)⁵ and (d) 1.541(9) Å.⁶

† Electronic Supplementary Information (ESI) available: Experimental details for compounds **1**, **1a**, **2** and **2a**. See <http://www.rsc.org/suppdata/cc/b5/b504022a/>

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The encapsulation of small ions within polyhedral clusters of lithium atoms is, perhaps, best illustrated by the detailed studies of Wheatley and co-workers of complexes containing interstitial hydride.⁷ Both cationic 'Li₈' and neutral 'Li₇' polyhedral arrays of lithium atoms containing the hydride anion have been observed, based on a pseudo-cubic array of lithium atoms, and a related structure in which one vertex is missing, respectively. A survey of the types of ligand able to support these clusters identified the anion of the bicyclic guanidine, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) as a viable candidate. It was shown that the hpp⁻ anion not only afforded the hydride-containing compound [Li₈(hpp)₆(H)]⁺ [Zn⁺Bu₃]⁻, analogous to those observed previously with 2-pyridylanilido anions, but was also able to support a dicationic arrangement of lithium atoms containing an interstitial void as in [Li₈(hpp)₆]²⁺ [Li(Al⁺Bu₂Me₂)₂]⁻.⁸ Work in our group has utilized the hpp⁻ anion as an electron-rich guanidinate ligand at a number of metal centers,^{9,10} regularly introducing it to the metal center *via* a transmetalation protocol, employing the lithium reagent. This prompted us to investigate the structure of the Li salt, leading to the isolation of an unprecedented mono-capped, cubic array of nine lithium atoms incorporating an interstitial peroxide dianion.

hppH was deprotonated using ^tBuLi in THF to quantitatively form the corresponding hpp⁻ guanidinate anion. For convenience, we primarily generate this reagent *in situ*; however for the purposes of this study we wish to report a series of isolated lithium species from this reaction. Initial attempts to isolate lithium species relied

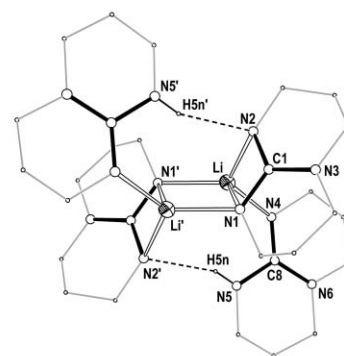


Fig. 2 The molecular structure of [Li(hpp)(hppH)]₂ [**1a**]₂ (−*x* + 1, −*y* + 1, −*z* + 1). Selected bond lengths (Å) and angles (°): Li–N1 2.140(6), Li–N2 2.060(6), Li–N1' 2.011(6), Li–N4 2.030(6), C1–N1 1.332(2), C1–N2 1.333(3), C1–N3 1.376(3), C8–N4 1.289(4), C8–N5 1.367(5), C8–N6 1.361(5), H5n–N2' 2.24; N1–Li–N1' 107.3(3), Li–N1–Li' 72.7(3), N1–Li–N2 65.0(2), N1–Li–N4 105.7(3), N1'–Li–N2 116.3(3), N1'–Li–N4 122.6(3), N2–Li–N4 119.9(3).

on the coordinating potential of the THF solvent to form stable base adducts. Whilst colourless crystals could be isolated directly by cooling the reaction mixture to 0 °C, variable degrees of solvation were suggested both from the ¹H NMR spectra and the results of elemental analyses. In an attempt to overcome this inconsistency by forming more stable, chelating base adducts, deprotonation using dimethoxyethane (dme) as solvent was investigated. In this instance however, an insoluble white powder, identified as the base-free species [Li(hpp)]_n (**1**)[‡] was deposited from the reaction.¹¹

The simplest method to reproducibly isolate a stable adduct of 'Li(hpp)' was to employ the neutral guanidine itself as the base, achieved using 0.5 equivalents of ⁿBuLi during lithiation. The ¹H NMR spectrum of the resultant product, Li(hpp)(hppH) (**1a**),[‡] does not allow distinction to be made between the neutral guanidine and anionic guanidinate groups, indicating a rapidly fluxional system on this timescale. X-ray diffraction data[§] revealed **1a** to exist as the dimer in the solid-state, containing a central 'Li₂N₂' core formed *via* one bridging nitrogen atom of the

chelating guanidinate ligand (Fig. 2). Each lithium atom is present in a distorted tetrahedral geometry (angles in the range 65.0(2)–122.6(3)°), where the smallest value corresponds to the bite angle of the hpp[−] anion. The coordination sphere is completed by a neutral hppH molecule, η¹-bound through the imine nitrogen atom, with additional stabilization from intramolecular hydrogen bonding to nitrogen (H5n⋯N2' 2.24 Å).¹²

Inclusion of oxygen into the system was initially achieved inadvertently. However, to ensure a reproducible synthesis of the isolated product, the reaction was repeated with a deliberate sparge of dry oxygen gas through a solution of the lithiated guanidinate. In each case, colourless crystals were isolated in reasonable yield (**2**: 25%, **2a**: 15%) and analysed by X-ray diffraction. This revealed a previously unobserved array of nine lithium atoms encapsulating the O₂^{2−} dianion.[‡] The compounds differ in molecular formula according to the solvent of crystallization, affording either base-free Li₉(hpp)₇(O₂) (**2**), from toluene or mono-solvated Li₉(hpp)₇(O₂)(THF) (**2a**), from THF.¹³

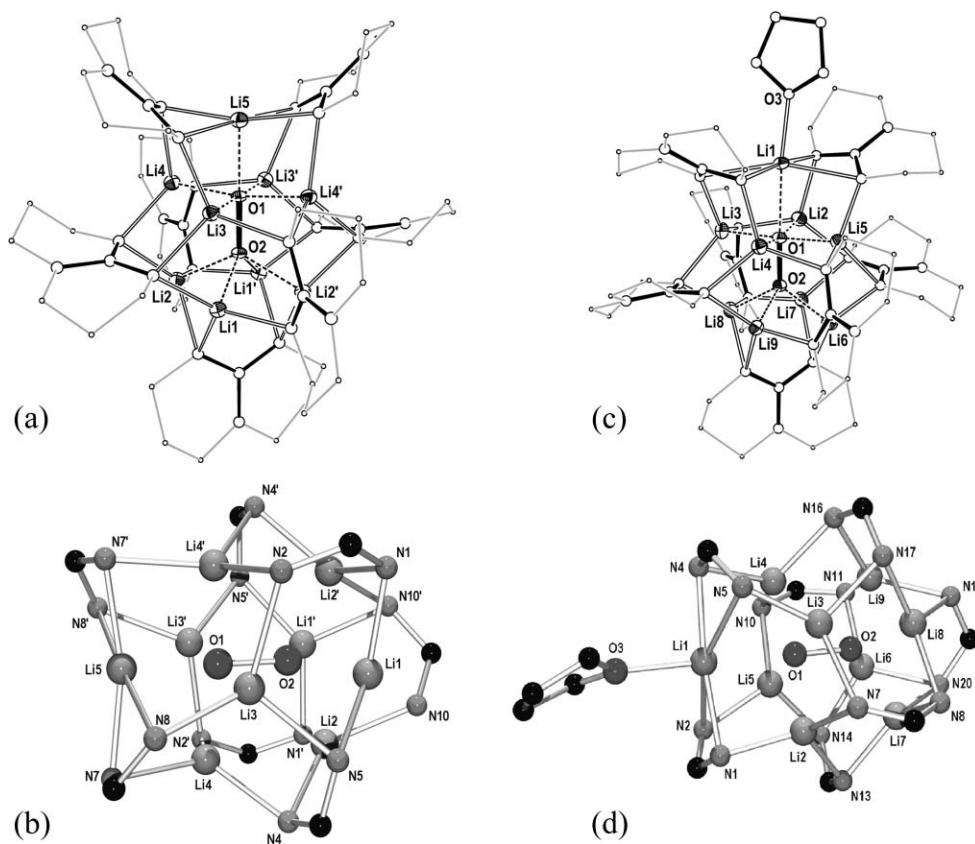


Fig. 3 (a) Molecular structure of Li₉(hpp)₇(O₂) **2** (−*x*, *y*, −*z* + 1/2). (b) Core structure of **2**, selected bond lengths (Å) and angles (°): O1–O2 1.501(3), Li1–O2 1.976(5), Li2–O2 1.921(5), Li3–O1 1.893(4), Li4–O1 1.911(5), Li5–O1 1.988(7), N1–Li1 2.022(5), N1–Li2' 2.032(5), N2–Li3 2.205(5), N2–Li4' 2.206(5), N4–Li2 2.036(5), N4–Li4 2.101(5), N5–Li1 2.023(5), N5–Li3 2.085(5), N7–Li4 2.126(5), N7–Li5 2.041(3), N8–Li3 2.073(5), N8–Li5 2.355(2), N10–Li1 2.036(5), N10–Li2 2.058(5), O2–O1–Li3 90.43(15), O2–O1–Li4 95.24(15), Li3–O1–Li4 92.3(2), Li3–O1–Li4' 87.6(2), Li3–O1–Li5 89.57(15), Li4–O1–Li5 84.76(15), O1–O2–Li1 121.09(14), O1–O2–Li2 117.09(14), Li1–O2–Li2 76.3(2), Li1–O2–Li2' 76.48(19), Li1–O2–Li1' 117.8(3), Li2–O2–Li2' 125.8(3). (c) Molecular structure of Li₉(hpp)₇(O₂)(THF) **2a**, selected bond lengths (Å) and angles (°): O1–O2 1.505(3), Li1–O1 2.337(5), Li2–O1 1.882(5), Li3–O1 1.902(5), Li4–O1 1.881(5), Li5–O1 1.892(5), Li6–O2 1.945(6), Li7–O2 1.927(6), Li8–O2 1.944(6), Li9–O2 1.943(6), N1–Li1 2.166(5), N1–Li2 2.095(6), N2–Li5 2.057(6), N4–Li1 2.178(5), N4–Li4 2.104(6), N5–Li3 2.077(6), N7–Li2 2.243(6), N7–Li3 2.177(6), N8–Li7 2.030(6), N8–Li8 2.027(6), N10–Li4 2.211(6), N10–Li5 2.164(6), N11–Li6 2.055(6), N11–Li9 2.027(6), N13–Li2 2.119(6), N13–Li7 2.033(6), N14–Li5 2.131(6), N14–Li6 2.003(6), N16–Li4 2.135(6), N16–Li9 2.030(6), N17–Li3 2.120(6), N17–Li8 1.993(6), N19–Li8 2.067(6), N19–Li9 2.083(6), N20–Li6 2.059(6), N20–Li7 2.088(6), O2–O1–Li2 97.0(2), O2–O1–Li3 92.70(19), O2–O1–Li4 93.69(19), O2–O1–Li5 89.81(19), O1–O2–Li6 121.8(2), O1–O2–Li7 116.3(2), O1–O2–Li8 119.4(2), O1–O2–Li9 118.4(2).

X-Ray data§ show that an equivalent framework of metal ions is manifest in both **2** and **2a**; both consisting of a mono-capped, cubic skeleton of lithium atoms surrounded by seven guanidinate ligands (Fig. 3). The Li···Li distances along the cube edges are in the range 2.408(7)–2.743(7) and 2.390(7)–2.727(7) Å for **2** and **2a** respectively. These distances indicate much less symmetrical structures than previously seen for cubic 'Li₈(hpp)₆', containing an interstitial hydride anion (range 2.473(14)–2.527(14) Å) or an internal void (range 2.751(7)–2.795(7) Å).⁸ Longer distances are observed to the capping lithium (range **2**: 2.627(7)–2.735(7), **2a**: 2.855(7)–3.006(7) Å), with a notable displacement of this atom in **2a** upon coordination to THF. The internal volume¶ of the cubic fraction of the two structures is not significantly different (**2**: 16.16 Å³, **2a**: 16.10 Å³). Dislocation of the capping lithium, however, results in an overall increase in the internal volume of the mono-capped cubes from 21.18 Å³ (**2**) to 21.96 Å³ (**2a**). This represents an expansion of 3.7% upon solvation, demonstrating a simple method by which the internal capacity of such structures may be modified. The peripheral guanidinate ligands adopt two different bonding modes around the central lithium scaffold. Five of the ligands span the faces of the cubic component of the structure, bonding to four lithium atoms, as noted in related Li₈-cubes.⁸ The distortion from an ideal cubic array is apparent from the range of Li–N bond lengths within these facially-bound ligands (**2**: 2.022(5)–2.206(5), **2a**: 1.993(6)–2.243(6) Å), with distances encompassing those found for the coordination of anionic and neutral ligands to lithium in (**1a**)₂. The remaining ligands bridge one cube edge and chelate to the capping lithium in a previously unobserved κ^{1,2}-N,κ^{1,3}-N'-mode,¹⁰ where two of these distances in **2a** (Li1–N2 2.473(6) and Li1–N4 2.493(6) Å) are significantly longer than the others.

Located within the mono-capped cubic array of lithium atoms in **2** and **2a** is an 'O₂' moiety which must be present as the peroxide dianion, O₂²⁻, in order to maintain the charge balance. The O–O distances in **2** and **2a** (1.501(3) and 1.505(3) Å, respectively) are considerably shorter than those observed in related encapsulated peroxide dianions (Fig. 1), approaching the accepted value of 1.49 Å for purely ionic group 1 peroxides.¹⁴ The dianion is positioned such that O(1) is located within the Li₄-plane of the capped cubic face, causing the other oxygen to be more centrally-positioned within the cube. Two types of Li–O bonds result from this arrangement, with those to the facially included oxygen (**2**: av. 1.902(5), **2a**: av. 1.905(6) Å) on average shorter than those to the central oxygen (**2**: av. 1.949(5), **2a**: av. 1.940(6) Å). As expected, the distance to the capping lithium is significantly greater in the THF-containing compound (**2**: 1.988(7), **2a**: 2.337(5) Å), suggesting a much weaker interaction. We are currently investigating the ability of ligands known to support hydride encapsulation products,⁷ to also form related polyhedral cluster species, and aim to explore the feasibility and scope of incorporating additional species within structures of this type.

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Notes and references

‡ Selected analytical data. **1**: Yield 73%. Found: C, 57.77; H, 8.60; N, 28.52. C₇H₁₂N₃Li requires C, 57.93; H, 8.33; N, 28.95%. **1a**: Yield 86%.

Found: C, 59.18; H, 9.03; N, 29.66. C₁₄H₂₅N₆Li requires C, 59.14; H, 8.86; N, 29.56%. δ_H (300 MHz, [²H₅]-toluene) 7.51 (1 H, s, NH), 3.27 (8 H, m, CH₂), 2.76 (8 H, m, CH₂), 1.64 (8 H, m, CH₂). δ_C (75 MHz, [²H₅]-toluene) 156.7 (CN₃), 48.9 (CH₂), 43.2 (CH₂), 24.8 (CH₂). δ_{Li} (194 MHz, [²H₅]-toluene) –1.23. **2**: Yield 25%. Found: C, 56.27; H, 8.11; N, 25.79. C₅₃H₉₂N₂₁Li₉O₃ requires C, 56.14; H, 8.18; N 25.94%. **2a**: Yield 15%. Found: C, 55.39; H, 7.87; N, 27.88. C₄₉H₈₄N₂₁Li₉O₂ requires C, 55.43; H, 7.97; N, 27.70%.

§ Crystal data for C₂₈H₅₀Li₂N₁₂ (**1a**)₂: *M* = 568.68, monoclinic, *P*₂/c (No.14), *a* = 8.7372(3), *b* = 17.5586(7), *c* = 10.1750(5) Å, β = 108.875(2)°, *V* = 1561.52(11) Å³, *T* = 253(2) K, *Z* = 2, μ(Mo–Kα) = 0.08 mm⁻¹, independent reflections = 2137 (*R*_{int} = 0.069), *R*₁ (for 1594 reflections with *I* > 2σ(*I*)) = 0.082, *wR*₂ (all data) = 0.239. Crystal data for C₄₉H₈₄Li₉N₂₁O₂·(C₇H₈) (**2**): *M* = 1153.97, monoclinic, *C*2/c (No.15), *a* = 12.6157(2), *b* = 21.5537(3), *c* = 24.0890(4) Å, β = 105.080(1)°, *V* = 6324.60(17) Å³, *T* = 173(2) K, *Z* = 4, μ(Mo–Kα) = 0.08 mm⁻¹, independent reflections = 6602 (*R*_{int} = 0.063), *R*₁ (for 5590 reflections with *I* > 2σ(*I*)) = 0.082, *wR*₂ (all data) = 0.228. Crystal data for C₅₃H₉₂Li₉N₂₁O₃ (**2a**): *M* = 1133.94, monoclinic, *P*₂/c (No.14), *a* = 21.0281(5), *b* = 17.3718(3), *c* = 17.3118(3) Å, β = 100.257(1)°, *V* = 6222.9(2) Å³, *T* = 173(2) K, *Z* = 4, μ(Mo–Kα) = 0.08 mm⁻¹, independent reflections = 10745 (*R*_{int} = 0.067), *R*₁ (for 6922 reflections with *I* > 2σ(*I*)) = 0.079, *wR*₂ (all data) = 0.226. CCDC 260940 (**1a**), 260941 (**2**) and 260942 (**2a**). See <http://www.rsc.org/suppdata/cc/b5/b504022a/> for crystallographic data in CIF or other electronic format.

¶ The internal volume of the mono-capped cubes were calculated as the sum of the cube and square-based pyramid components using the NIntegrate routine within Mathematica 4.1. This gives a numerical approximation to the multidimensional integral. NIntegrate uses an adaptive algorithm which recursively subdivides the integration region as required and continues doing so until the error estimate it calculates implies that the final result achieves the PrecisionGoal specified (in our case 2 decimal places). NIntegrate uses quasi Monte Carlo methods to obtain an estimate of the result, sampling at the number of points specified. In our case we needed 1 million sample points to reach a convergent of 2 decimal places.

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