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Hydride Encapsulation by a Molecular Main-Group-Metal Cluster: Single-Crystal Neutron Diffraction Structure of $[\{Ph(2\text{-}C_5H_4N)N\}_6HLi_8]^+$

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Summary: The new very-intense vertical-axis Laue diffractometer (VIVALDI) at the Institut Laue-Langevin has been used to probe the single-crystal structure of $[(t\text{-}Bu_2AlMe_2)_2Li]^-[\{Ph(2\text{-}C_5H_4N)N\}_6HLi_8]^+$*, with data proving that the molecular main-group-metal cluster cation component incorporates interstitial hydride. Variations in nitrogen coordination mode and distortion of the metal core are in accord with octahedral hydride coordination* ($H-Li = 1.92(2), 2.04(2), 2.07(2)$ Å)*, two metal centers being nonbonding with respect to hydride* ($H\cdots Li = 2.86(2)$ Å)*.*

Interest in hydrogen-based fuel cells has been significant of late and has led, for example, to the development of metal-organic frameworks capable of storing hydrogen.[1] Moreover, while the ability of main-group-metal hydrides to store and deliver hydride ions has historically rendered them important reducing agents,[2] they too have more recently attracted attention as convenient hydrogen sources, with applications in the hydrogen economy having been explored.[3] However, the literature contains little structural data on molecular main-group hydrides[4−8] in a field dominated by transi-

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tion-metal species.[9] Since no previous examples of a single-crystal neutron diffraction analysis of a molecular main-group interstitial hydride have been reported, this technique has now been employed to establish the identity, position, and coordination properties of the encapsulated hydride ion in $[(t\text{-Bu}_2\text{AlMe}_2)_2\text{Li}]^-[\{\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_8]^+$ (**1**).[6]

Few examples of molecular main-group species known to incorporate hydride have been reported and, in common with **1**, the structures of the lithium hydrides $(t\text{-BuO})_{16}\text{H}_{17}\text{Li}_{33}$,[5] $\{\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_7$,[6] $[t\text{-Bu}_3\text{Zn}]^-$-$[(\text{hpp})_6\text{HLi}_8]^+$ (hpp = 1,3,4,6,7,8-hexahydro-*2H*-pyrimido-[1,2-*a*]pyrimidide),[8] and $\{(t\text{-BuCH}_2\text{O})_5\text{Al}_3\text{H}_5\}\text{Li}\cdot\text{OEt}_2$[4] and the higher group 1 complexes $[\{(i\text{-Pr})_2\text{N}\}\text{MgM}(\mu\text{-H})\cdot\text{PhMe}]_2$ (M = Na, K)[7] have been subject to X-ray diffraction studies only. It was as part of an investigation into the formation of synthetically versatile main-group heterometallic compounds that the treatment of dimethyl(2-pyridylanilido)aluminum with excess *t*-BuLi was reported to give not the expected lithium aluminate $[\{\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}\}\text{Al}(t\text{-Bu})\text{Me}_2]\text{Li}$ but rather the ion-separated complex **1** (Scheme 1).[6] X-ray crystallography suggests that in the solid state its cationic component takes the form of a $(\text{Li}^+)_8$ pseudo-cubic cluster which encapsulates a single hydride ion and that the species as a whole adopts the formulation $[(t\text{-Bu}_2\text{AlMe}_2)_2\text{Li}]^-$-$[\{\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_8]^+$. More recently, we have prepared a variety of complexes related to **1** and characterized them by single-crystal X-ray diffraction.[10] However, **1**, $[(t\text{-Bu}_2\text{AlMe}_2)_2\text{Li}]^-[\{(\text{Me-4-C}_6\text{H}_4)(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_8]^+$ (**2**), $[\text{Me}(\text{Al-}t\text{-Bu}_3)_2]^-[\{(\text{Me-2-C}_6\text{H}_4)(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_8]^+$ (**3**), $[(t\text{-Bu}_2\text{AlEt}_2)_2\text{Li}]^-[\{\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_8]^+$ (**4**), and $[(t\text{-Bu}_2\text{AlMe}_2)_2\text{Li}]^-[\{(c\text{-C}_6\text{H}_{11})(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_8]^+$ (**5**) all present the same analytical difficulty. That is, despite observation of interstitial electron density in the X-ray diffraction electron density difference map, neither solution nor solid-state ^{1}H NMR spectra afford a signal confidently attributable to a hydride ion. This notwithstanding, IR spectroscopic studies have revealed a band at 583 cm^{-1} tentatively assignable to metal−hydride stretching (lit.[11] for $(\text{HLi})_\infty$ 588 cm^{-1}). While ab initio calculations have implied the viability of H^- residence in the Li_8 cavity of the pseudo-cubic host $[(\text{H}_2\text{NCH}_2\text{NH})_6\text{Li}_8]^{2+}$, they have also predicted the *vacant* cage dication to be unstable.[6] However, this result clearly contradicts the recent characterization of $\{[(t\text{-Bu}_2\text{AlMe}_2)_2\text{Li}]^-\}_2[(\text{hpp})_6\text{Li}_8]^{2+}$.[8]

Scheme 1

$$\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{NH} + \text{Me}_3\text{Al} \xrightarrow{1.5\text{ equiv }t\text{-BuLi}} [(t\text{-Bu}_2\text{AlMe}_2)_2\text{Li}]^-[\{\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{HLi}_8]^+ \;\; \mathbf{1}$$

Results and Discussion. The neutron diffraction study described in detail here, carried out at $T = 1.5$ K, resolves the ambiguity presented by species such as **1**−**5** (see Experimental Section). The unequivocal location of hydride at the center of an octahedral cavity in the Li_8 cation of **1** has been made possible by development of the very-intense vertical-axis Laue diffractometer (VIVALDI) at the Institut Laue-Langevin (ILL), Grenoble, France. It employs Laue diffraction using a polychromatic thermal-neutron beam with a large solid-angle (8 sterad) cylindrical image-plate detector[12] to raise the detected diffracted intensity by 1−2 orders of magnitude, compared with a conventional monochromatic experiment. The very low temperature at which the data were collected ensured maximum diffraction intensity and no extraneous nuclear density in the area of primary interest owing to possible molecular disorder. The cationic component of **1** (Figure 1) is found to incorporate a $(\text{Li}^+)_8$ cubic cage whose six faces are straddled by the backbones of the six pyridylamide ligands. The $(\text{Li}^+)_8$ cluster may be described as a distorted bicapped octahedron, with Li3 and its symmetry equivalent acting as the two trans caps. The Li3 ion caps the Li1/Li2/Li4 triangular face essentially symmetrically with a mean Li3···Li nonbonding distance of 2.74(3) Å. The Li···Li nonbonded distances within the central octahedron show considerable variations (range 2.44(3)−3.24(3) Å). Overall, these perturbations are consistent with differing types of metal−nitrogen interactions; six of the cations bond to a single formally deprotonated amide and two pyridyl N centers, while Li3 and Li3A bond to three formally deprotonated N centers (N1, N3, and N5 for Li3). However, despite these coordinative variations, nitrogen−lithium distances are essentially uniform; mean N−Li3 = 2.05(2) Å (range 2.03(2)−2.07(2) Å), and mean N−Li1/Li2/Li4 = 2.03(2) Å (range 2.00(2)−2.05(2) Å).

Fourier difference synthesis allows the unambiguous identification and location of the hydride ion and, thence, anisotropic refinement on all hydrogen atoms (isotropic on all non-hydrogen atoms) and rationalization of the observed $[(t\text{-Bu}_2\text{AlMe}_2)_2\text{Li}]^-$:$[\{\text{Ph}(2\text{-C}_5\text{H}_4\text{N})\text{N}\}_6\text{Li}_8]^{2+}$ ratio. Moreover, distortion in the cluster dication superstructure correlates with coordinative variations in the bonding sphere of the encapsulated hydride. The unique nitrogen coordination modes for Li3 and Li3A, and the resultant extension of Li···Li distances involving them, are in accord with octahedral hydride coordination (H0−Li1 = 2.07(2) Å, H0−Li2 = 1.92(2) Å, H0−Li4 = 2.04(2) Å), with Li3 and Li3A clearly nonbonding with respect to the interstitial ion (H0···Li3 = 2.86(2) Å). This significant distortion of the metal cluster core results in HLi distances similar to that proposed in the X-ray crystal structure of tetrahedral $[(t\text{-BuCH}_2\text{O})_5\text{Al}_3\text{H}_5]\text{Li}\cdot\text{OEt}_2$ (H−Li = 2.00(3) Å)[4] and a coordination geometry related to that noted in

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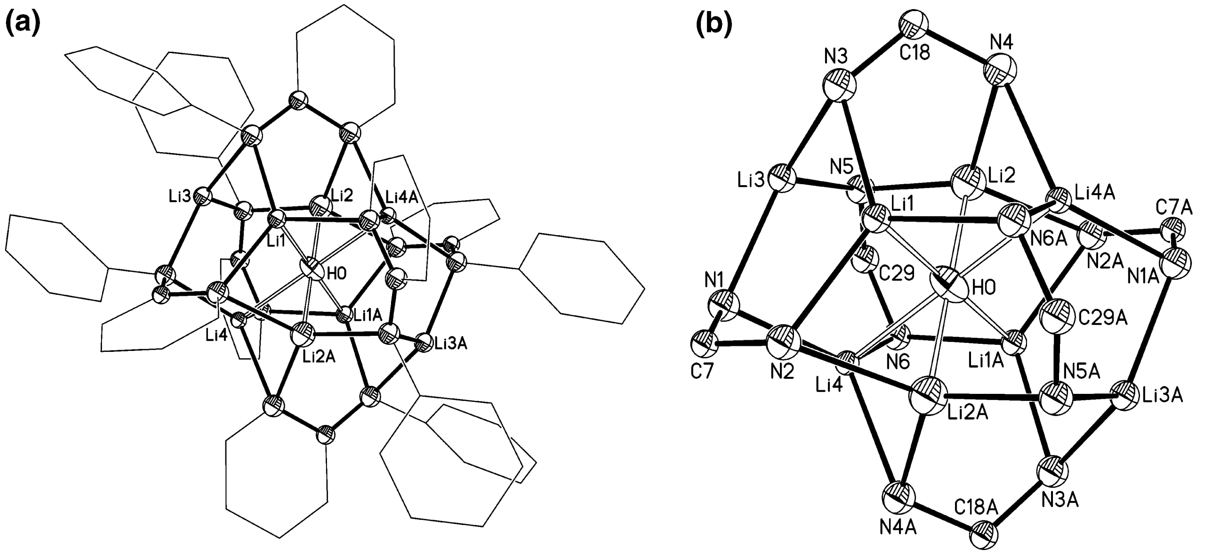

Figure 1. Structure (a) and core (b) of $[\{Ph(2\text{-}C_5H_4N)N\}_6HLi_8]^+$ in **1** drawn with 50% probability ellipsoids and with the aromatic periphery represented by thin lines. H0 resides at a crystallographic center of symmetry.

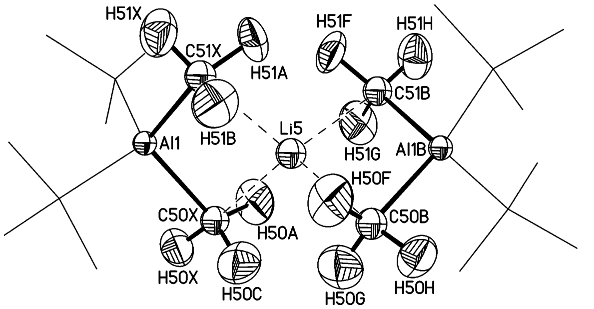

Figure 2. Structure of $[(t\text{-}Bu_2AlMe_2)_2Li]^-$ in **1** drawn with 50% probability ellipsoids and with hydrogen atoms omitted from the *t*-Bu groups, which are represented as thin lines.

the neutron diffraction structure of $(HLi)_\infty$ (H−Li = 2.043(1) Å).[13] The noted extrusion of Li3 and its symmetry equivalent in **1** is without precedent in a molecular context. Hence, an essentially regular octahedral metal polyhedron has been reported for the presumed interstitial hydride complex $[(CO)_{18}HOs_6]^-$.[9a] Moreover, in the context of neutron diffraction studies, hydride-centered niobium octahedra have been noted in a powdered sample of polymeric $(I_{11}HNb_6)_\infty$,[14] while single-crystal data indicate the regular octahedral coordination of interstitial hydride in both $[(CO)_{18}HRu_6]^-$ (mean H−Ru 2.038 Å, range 2.028(11)−2.055(12) Å)[9f] and $[(CO)_{15}HCo_6]^-$ (mean H−Co 1.823 Å, range 1.799(17)−1.872(16) Å).[9g]

In the neutron diffraction structure of **1** the $[(t\text{-}Bu_2AlMe_2)_2Li]^-$ ion is based on an $Al(\mu\text{-}Me)_2Li(\mu\text{-}Me)_2Al$ motif that induces tetrahedral coordination at Li5 (Figure 2). Although this type of bonding has been noted in $(Et_4AlLi)_\infty$[15] it is unusual in a molecular context. While $[\{Et_2Al(OPh)_2\}_2Li]^-[Li{\cdot}(DME)_3]^+$ (DME = dimethoxyethane)[16] incorporates bridging phenoxide ligands, the X-ray diffraction structures of $[\{t\text{-}Bu(Me)Al(Me)_2\}_2Li]^-[Am_3Li_4]^+$ (Am = $[(c\text{-}C_6H_{11})NC(H)N(c\text{-}C_6H_{11})]^-$, $[PhNC(Ph)NPh]^-$),[10,17] like that of $(Et_4AlLi)_\infty$,[15] fail to clearly reveal the behavior of bridging methyl groups. The present study indicates a lack of significant C−H bond activation in the Al-bonded methyl groups in **1** (range 1.03(2)−1.13(2) Å), supporting the view that the so-called agostic stabilization of lithium involves substantial C⋯Li (C50X−Li5 = 2.22(2) Å and C51X−Li5 = 2.28(2) Å) and not H⋯Li interaction.[18]

Data collection was also undertaken at 180 K, with results bearing testament to the existence of interstitial hydride as established by the 1.5 K experiment. Once again, the hydride can be located in the Fourier difference map. However, significant thermal motion now dampens the data intensity such that, while the structure can be solved, data are only sufficient to allow anisotropic refinement of the hydride ion. Additionally, the methyl groups in the counteranion are heavily disordered. Details for both the 1.5 and 180 K data collections are provided as Supporting Information.

Having definitively assigned the identity, location, and coordination of the encapsulated ion, future work on **1** and related complexes will concentrate on understanding first the structure-determining effects borne of competing N−Li and H−Li coordination and second the detailed mechanism by which hydride-encapsulating alkali-metal cages form. The most important facet of this will be to establish whether, as is implied by the isolation and characterization of $Me_3Al\{N(2\text{-}C_5H_4N)Ph\}\text{-}Li{\cdot}THF$[10] and $[Me_2Al\{N(2\text{-}C_5H_4N)Ph\}\{N(SiMe_3)_2\}Li]_\infty$,[19] β-elimination of HLi from the organolithium substrate is responsible for the presence of hydride. Thereafter, investigation of applications will be based on the recent suggestion of the viability of vacant dicationic clusters

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analogous to the hydridic component of **1**.[8] Work will center on the ability of hydride-containing cages to evolve hydride or hydrogen.

Experimental Section. Synthesis and Single-Crystal Neutron Diffraction Data for 1. The lithium aluminate complex **1** was prepared according to a literature procedure.[6] Crystal data for T = 1.5 K: $C_{86}H_{103}Al_2Li_9N_{12}$, $M_r = 1420.00$, orthorhombic, space group *Pbcn*, $a = 19.546(4)$ Å, $b = 16.0980(10)$ Å, $c = 26.168(6)$ Å, $V = 8234(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.146$ g cm^{-3}. A 2.5 × 2.0 × 0.5 mm^3 single crystal was suspended between quartz wool plugs in an argon-filled capillary that was mounted in a helium-flow cryostat and cooled to 1.5 K on VIVALDI. A polychromatic thermal-neutron beam was employed, and VIVALDI is equipped with a large solid-angle (8 sterad) cylindrical image-plate detector. A total of 15 Laue diffraction patterns, each separated by 10−20° intervals in rotation of the crystal perpendicular to the incident neutron beam, were collected over a 220° range, each diffraction image requiring a 2 h acquisition time. Images were indexed using the program LAUEGEN of the Daresbury Laboratory Laue Suite,[20] and reflections were integrated using the local program INTEGRATE+, which employs a two-dimensional version of the $\sigma(I)/I$ algorithm.[21] Individual reflections were corrected for absorption using the calculated wavelength (λ)-dependent absorption coefficient: $0.115\lambda + 0.101$ mm^{-1} (transmission range 0.412−0.730). Reflections were normalized for the incident wavelength, using a curve derived by comparing equivalent reflections and multiple observations, via the program LAUENORM.[22] Reflections in the 1.1−2.5 Å wavelength range were scaled, giving 33 746 single reflections and 3024 unique reflections. Hydrogen atoms on the Al-bonded methyl groups were located by Fourier difference analysis after structure refinement in their absence. The interstitial hydride was then unambiguously and entirely located as a *negative* peak in the Fourier difference map, after refinement of the structure with hydrogen atoms included on the methyl groups. The final model, with anisotropic displacement parameters on all hydrogen atoms, was derived by full-matrix least-squares refinement using SHELXL-97[23] to give R1 = 0.097 for 2547$F_o > 4\sigma(F_o)$ data, wR2 = 0.134, and $S = 1.940$ for all data. Slight improvement in the agreement indices was possible by refining anisotropic thermal displacement parameters for other atoms but was mostly artificial in view of their small thermal displacements and did not result in significant change in the bond lengths of interest.

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Supporting Information Available: Crystallographic data for **1** at 1.5 and 180 K as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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