Ionic Hydrides

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Well-Defined, Nanometer-Sized LiH Cluster Compounds Stabilized by Pyrazolate Ligands**

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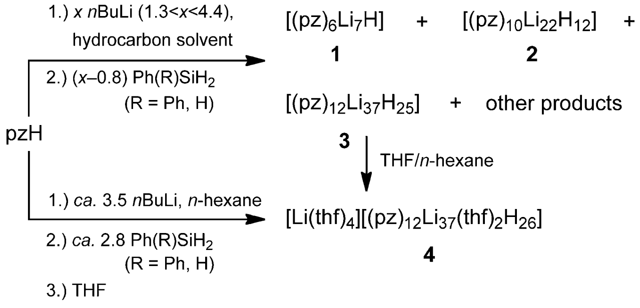
Abstract: *The assembly of well-defined large cluster compounds of ionic light metal hydrides is a synthetic challenge and of importance for synthesis, catalysis, and hydrogen storage. The synthesis and characterization of a series of neutral and anionic pyrazolate-stabilized lithium hydride clusters with inorganic cores in the nanometer region is now reported. These complexes were prepared in a bottom-up approach using alkyl lithium and lithium pyrazolate mixtures with silanes in hydrocarbon solutions. Structural characterization using synchrotron radiation revealed isolated cubic clusters that contain up to 37 Li^+ cations and 26 H^- ions. Substituted pyrazolate ligands were found to occupy all corners and some edges for the anionic positions.*

The ionic or "saline" s-block metal hydrides and their complexes are of importance as reagents in synthetic transformations, such as hydride transfers and reductions, in catalysis, or for hydrogen storage applications.[1] However, a single metal hydride that fulfils all of the properties that are required for an efficient hydrogen storage material has not been reported to date.[2] The light s-block metal hydrides show several of the properties that are required for such materials, including high hydrogen content (e.g., 12.7 % for LiH), but their bulk phases are too thermally stable for facile dihydrogen release.[2] One approach to improve those properties entails the use of nanosized materials. Nanoscale metal hydride particles are of high relevance because of an appreciable difference in properties compared with their bulk phases.[3] Many studies on the structures and properties of nanosized metal hydride clusters rely on quantum chemical calculations[3,4] under idealized conditions, and it remains unclear how these results will translate to the condensed phase, and how bulk quantities of those materials can be accessed. Furthermore, it has been proposed that soluble, ligand-stabilized, hydride-rich clusters could play a role as the active catalyst in s-block metal ion catalysis.[1,5]

The chemistry of well-defined s-block metal complexes has rapidly developed in recent years, because a convenient method for the metathesis of metal amide or alkyl groups into metal hydride fragments using commercially available silanes has been developed (silane method),[1,6] and suitable classes of stabilizing ligands have been identified that can prevent complex decomposition, which would release insoluble bulk metal hydride.[1] This has very recently led to a number of MgH cluster compounds that are stabilized by sterically demanding ligands,[7] and that were also investigated for thermal dihydrogen release;[7a,b] the largest MgH cluster compounds described to date have a central $Mg_8H_{10}^{6+}$ core.[7a] For Group 1 metals, the majority of hydride complexes are mixed element hydrides that are better described as "-ate" complexes, and the unique mixed Al/Li example $[(\{(Me_3Si)_2N\}AlH_2Li)_3(LiH)]$ contains one hydride that is only bound to Li centers.[8] Furthermore, cationic $[L_6Li_8H]^+$ (L = chelating anionic ligand) and neutral $[L_6Li_7H]$ complexes with an interstitial hydride ion have been prepared,[9,10] and the structure of the large mixed lithium alcoholate/hydride cluster $[(t\mathrm{BuOLi})_{16}(LiH)_{17}]$ was reported.[11] We have recently used the silane method to synthesize hydrocarbon-soluble $[(LLi)_4(LiH)_4]$ (L = $DipNPPh_2$, Dip = 2,6-$i\mathrm{Pr}_2C_6H_3$), which contains a central $(LiH)_4$ cube.[12] The complex was found to undergo hydrolithiation reactions with activated unsaturated organic substrates,[12,13] although the stabilizing phosphinoamide ligand L can perform competing addition reactions with the substrates.[13] Herein, we report the generation and structural characterization of a family of up to nanometer-sized, well-defined pyrazolato lithium hydride clusters from hydrocarbon solutions in a bottom-up approach.

Reacting the ligand precursor 3,5-di-*tert*-butyl-1*H*-pyrazole (pzH) with more than one equivalent of *n*-butyllithium in a hydrocarbon solvent, such as benzene, toluene, or *n*-hexane, followed by further conversion of the remaining *n*BuLi equivalents with phenyl- or diphenylsilane (Scheme 1) initially leads to clear solutions that can turn milky upon standing, and from which mixtures of pyrazolato lithium hydride clusters could be isolated after concentrating or cooling. The complexes $[(pz)_6Li_7H]$ (**1**), $[(pz)_{10}Li_{22}H_{12}]$ (**2**),



Scheme 1. Synthesis of complexes **1**–**4**. pzH = 3,5-di-*tert*-butyl-1*H*-pyrazole.

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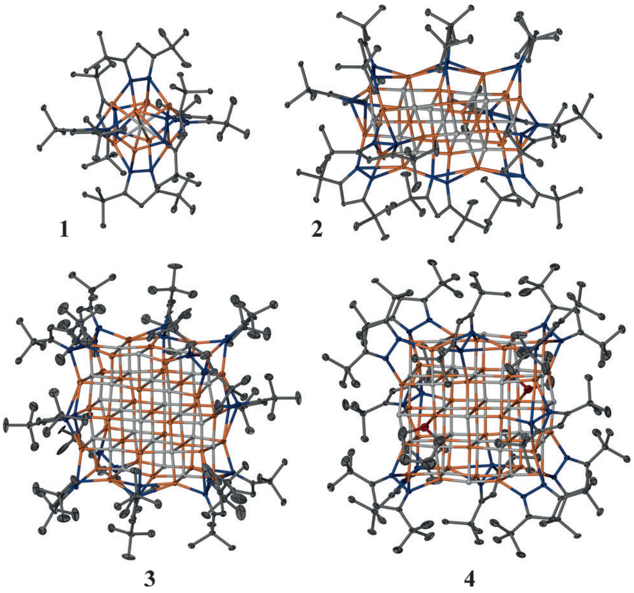

Figure 1. Molecular structures of complexes 1–4 (Thermal ellipsoids set at 25 % probability). Carbon gray, hydrogen light gray, lithium orange, nitrogen blue, oxygen red. Only hydride hydrogen atoms are shown. Minor disordered parts, solvent molecules, and the cation of **4** were omitted for clarity.

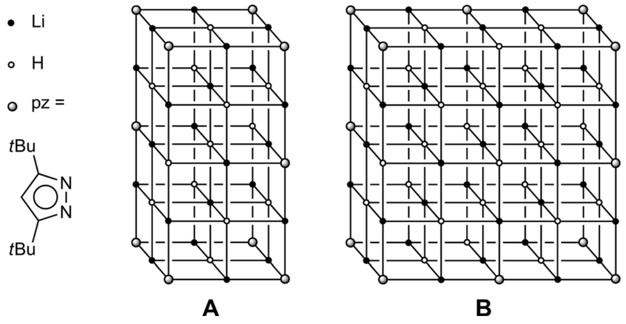

Figure 2. Lattice cutouts **A** and **B**.

and $[(pz)_{12}Li_{37}H_{25}]$ (**3**) were structurally characterized using synchrotron radiation (Figure 1).[14] The complex $[(pz)_6Li_7H]$ (**1**) could be prepared and isolated when only a small amount of LiH was generated in solution. However, product mixtures were formed across the investigated pz/hydride ratio range. The addition of THF to hydride-rich solutions reproducibly led to low to moderate yields of isolated $[Li(thf)_4][(pz)_{12}Li_{37}(thf)_2H_{26}]$ (**4**; Scheme 1 and Figure 1).[14] The same complex **4** was obtained by recrystallizing a crude product rich in $[(pz)_{12}Li_{37}H_{25}]$ (**3**) from THF/*n*-hexane.

The structure of complex $[(pz)_6Li_7H]$ (**1**; obtained as $[(pz)_6Li_7H]\cdot C_6H_{14}$ and $[(pz)_6Li_7H]_{0.6}[(pz)_6Li_8O]_{0.4}\cdot C_6H_6$)[14] derives from a rhombic dodecahedron with a central Li_8 cube, a μ^4-pz ligand on each face of the cube, and an interstitial hydride ion (Figure 1), which is an arrangement similar to that of the previously characterized complex $[(pz)_6Li_8O]$.[15] As with the latter example, the structure of **1** is poorly ordered. Furthermore, only seven lithium atoms are expected to reside on eight cube corner positions for charge-balance reasons, which is supported by the refinement model for **1**.[14] Several related examples of cationic $[L_6Li_8H]^+$ (L = chelating anionic ligand) and neutral $[L_6Li_7H]$ complexes have previously been studied by Wheatley and coworkers.[9,10]

The structure of $[(pz)_{10}Li_{22}H_{12}]$ (**2**) is based on lattice cutout **A**, the structures of neutral $[(pz)_{12}Li_{37}H_{25}]$ (**3**; structurally characterized as $[(pz)_{12}Li_{37}H_{24.62}(OH)_{0.38}]\cdot 2.5\,C_6H_{14}$ (**3′**))[14] and the salt $[Li(thf)_4][(pz)_{12}Li_{37}(thf)_2H_{26}]$ (**4**; structurally characterized as $[Li(thf)_4][(pz)_{12}Li_{37}(thf)_2H_{26}]\cdot 2\,C_6H_{14}\cdot 2\,THF$ (**4′**) and $[Li(thf)_4][(pz)_{12}Li_{37}(thf)_2H_{26}]\cdot 0.5\,C_6H_{14}\cdot THF$ (**4″**))[14] are based on lattice cutout **B** (Figure 2). For the two crystal structures of complex **4**, only the anion $[(pz)_{12}Li_{37}(thf)_2H_{26}]^-$ could be refined to a satisfactory degree.[14] Structures **A** and **B** represent three-dimensional cubic lattice cutouts of 5 × 3 × 3 (= 45) and 5 × 5 × 3 (= 75) ions, respectively, with alternating cations (Li^+) and anions (H^- or pz$^-$; Figure 2). These uneven numbers are inevitably associated with either a charge (monoanionic as found for **4**) or an expected point defect (12 H^- on 13 positions in **2**; 25 H^- on 26 positions in **3**) for the lattice cutout. The central ion is a H^- in structure **A**, and a Li^+ in structure **B**. The cores of **A** and **B** have a region of 3 × 1 × 1 (2 Li^+, 1 H^-) or 3 × 3 × 1 (5 Li^+, 4 H^-) ions, respectively, with a surrounding environment that is comparable to that in cubic bulk LiH with six identical nearest neighbors. The structural types **A** and **B** have in common that a μ^3-pz$^-$ ligand is placed at every corner of the square cuboids, and alternating μ^4-pz$^-$ or H^- ligands are found at the center of the longer cuboid edges (with a length of 5 lattice positions or ions). For structure **B**, the two outer 5 × 5 faces have two μ^4-pz$^-$ ligands at the center of two neighboring edges, and not on two opposing edges. The same is true for the respective remaining central μ^4-H^- positions on those edges. Dividing the two outer 5 × 5 square faces in **B** into four 3 × 3 squares results in one quadrant that is connected to two μ^4-pz$^-$ edge ligands, two quadrants with one μ^4-pz$^-$ edge ligand, and one quadrant without any μ^4-pz$^-$ edge ligands (see also the Supporting Information, Figure S12). For the $[(pz)_{12}Li_{37}(thf)_2H_{26}]^-$ anions in **4**, a THF molecule is coordinated to one Li^+ per outer 5 × 5 square; and this Li cation resides on the border of two quadrants with one and no μ^4-pz$^-$ edge ligands, respectively, and the THF molecule resides above the least hindered quadrant that does not have any μ^4-pz$^-$ edge ligand. In the neutral, THF-free compound $[(pz)_{12}Li_{37}H_{25}]$ (**3**), the central outer H^- ions on the least protected quadrant (i.e., no μ^4-pz$^-$ edge ligands) were subjected to partial hydrolysis (modeled as 19 % OH content),[14] which suggests that this is the most reactive site of the complex.

The edges of the inorganic cores of the LiH cluster compounds that are based on **A** and **B** are approximately 0.8–0.9 nm (5 ions) or 0.45 nm (3 ions) long, as determined from their corner pz N–N midpoints; space diagonals of approximately 1.3 nm (**B**) or just under 1.1 nm (**A**), and face diagonals of approximately 1.2 nm (**B**, 5 × 5) or just under 1.0 nm (**A**, 5 × 3) were determined. The Li–N(pz) bond lengths in the characterized examples are in a similar range to previously reported examples of (pz)Li compounds.[15,16] The Li⋯H contacts measure around 2 Å and are close to those of previously characterized examples,[8–12] and to that in cubic

LiH (ca. 2.04 Å).[1,17] Solvent-free [$(pz)_{12}Li_{37}H_{25}$] (**3**) contains 1 wt% of hydride moieties. In **4**, only twelve pz ligands stabilize an entity with 26 hydrides. Complexes **3** and **4**, which are derived from structure type **B**, contain 37 Li ions and are the largest crystallographically characterized molecular lithium aggregates that have been described to date. Very large previously reported examples include the less geometrically ordered LiH superaggregate [$(t\text{BuOLi})_{16}(\text{LiH})_{17}$] ($Li_{33}$)[11] and some polyhedral main group element lithium cluster compounds that contain 26 Li^+ ions.[18]

Complex [$(pz)_6Li_7H$] (**1**) only shows resonances for one pz environment in its ^1H and $^{13}C\{^1H\}$ NMR spectra, and one lithium environment in its $^7Li\{^1H\}$ NMR spectrum, suggesting a structure that is on average symmetric in solution. The resonances are distinct from those of the previously reported hydride-free complexes [$(pz)_4Li_4$][17b] and [$(pz)_6Li_8O$].[15] Once crystallized, the larger pyrazolato lithium hydride clusters only show a low solubility in deuterated benzene, which somewhat improves upon addition of THF. Complex [$Li(thf)_4$][$(pz)_{12}Li_{37}(thf)_2H_{26}$] (**4**) shows multiple overlapping resonances for the protons of the pyrazolate ligands in deuterated benzene. Very broad resonances (δ 3.4–4.0 ppm) are found for the LiH fragments, and only one set of resonances for the coordinated THF molecules can be found in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4**, suggesting THF exchange processes. Overlap of the two THF multiplet resonances with both the pyrazolate *t*Bu resonances and the LiH resonances in the ^1H NMR spectrum preclude the gathering of accurate information from resonance integration. The $^7Li\{^1H\}$ NMR spectrum of complex **4** shows a broad resonance region at δ 0.8–4.3 ppm that correspond to numerous lithium centers. Complex **4** slowly decomposed in deuterated benzene at elevated temperatures (80 °C), with the formation of [$(pz)_6Li_7H$] (**1**) and insoluble LiH by implication or possibly higher clusters. A similar decomposition was observed when deuterated THF was added to the solution. Partial decomposition of neutral [$(pz)_{12}Li_{37}H_{25}$] (**3**) and liberation of LiH fragments is required when forming [$Li(thf)_4$][$(pz)_{12}Li_{37}(thf)_2H_{26}$] (**4**) from recrystallization of **3** from THF/*n*-hexane (Scheme 1). A sample rich in [$(pz)_{10}Li_{22}H_{12}$] (**2**) showed overall ^1H (and $^7Li\{^1H\}$) NMR spectroscopic features that were similar to those of cluster **4**, including two broad resonances at approximately δ 3.6 ppm and δ 3.8 ppm for the LiH fragments. The fingerprint region of the IR spectrum of [$Li(thf)_4$][$(pz)_{12}Li_{37}(thf)_2H_{26}$] (**4**) showed some very broad stretches at approximately 1050–950 and 900–650 cm^{-1} (Figure S1), which, in comparison with literature values,[19] were tentatively assigned to LiH lattice fragments. No apparent gas formation was observed when complex **4** was heated to approximately 300 °C under nitrogen atmosphere. The large soluble LiH clusters, such as **4**, reacted rapidly and highly exothermic with protic reagents under hydrogen evolution.

In summary, we have presented several well-defined pyrazolato-stabilized lithium hydride clusters with inorganic cores in the nanometer region, which were prepared in a bottom-up approach using the silane method. We have identified a simple pyrazolate as a suitable stabilizing ligand that can occupy both corner and edge positions in these square cuboid ionic cluster compounds. We hope that this strategy can be further extended to other light metal hydrides and mixed metal systems with improved characteristics that are of relevance for use in synthesis, catalysis, and hydrogen storage applications.

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[1] S. Harder, *Chem. Commun.* **2012**, *48*, 11165–11177, and references therein.

[2] a) M. T. Kelly, *Struct. Bonding (Berlin)* **2011**, *141*, 169–201; b) S.-i. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, *Chem. Rev.* **2007**, *107*, 4111–4132; c) B. Sakintuna, F. Lamari-Darkrim, M. Hirscher, *Int. J. Hydrogen Energy* **2007**, *32*, 1121–1140; d) W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, *104*, 1283–1315.

[3] a) F. Cheng, Z. Tao, J. Liang, J. Chen, *Chem. Commun.* **2012**, *48*, 7334–7343; b) P. E. de Jongh, P. Adelhelm, *ChemSusChem* **2010**, *3*, 1332–1348; c) V. Bérubé, G. Radtke, M. Dresselhaus, G. Chen, *Int. J. Energy Res.* **2007**, *31*, 637–663, and references therein.

[4] For examples, see: a) E. N. Koukaras, A. D. Zdetsis, M. M. Sigalas, *J. Am. Chem. Soc.* **2012**, *134*, 15914–15922; b) L. K. Wagner, E. H. Majzoub, M. D. Allendorf, J. C. Grossman, *Phys. Chem. Chem. Phys.* **2012**, *14*, 6611–6616; c) Z. Wu, M. D. Allendorf, J. C. Grossman, *J. Am. Chem. Soc.* **2009**, *131*, 13918–13919; d) S. J. Nolan, M. J. Gillian, D. Alfe, N. L. Allan, F. R. Manby, *Phys. Rev. B* **2009**, *80*, 165109; e) K. C. Kim, B. Dai, J. K. Johnson, D. S. Scholl, *Nanotechnology* **2009**, *20*, 204001; f) R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, K. P. de Jongh, *J. Am. Chem. Soc.* **2005**, *127*, 16675–16680.

[5] S. Harder, *Chem. Rev.* **2010**, *110*, 3852–3876.

[6] M. J. Michalczyk, *Organometallics* **1992**, *11*, 2307–2309.

[7] a) J. Intemann, J. Spielmann, P. Sirsch, S. Harder, *Chem. Eur. J.* **2013**, *19*, 8478–8489; b) S. Harder, J. Spielmann, J. Intemann, H. Bandmann, *Angew. Chem.* **2011**, *123*, 4242–4246; *Angew. Chem. Int. Ed.* **2011**, *50*, 4156–4160; c) M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, *Angew. Chem.* **2009**, *121*, 4073–4076; *Angew. Chem. Int. Ed.* **2009**, *48*, 4013–4016.

[8] M. Veith, P. König, A. Rammo, V. Huch, *Angew. Chem.* **2005**, *117*, 6122–6126; *Angew. Chem. Int. Ed.* **2005**, *44*, 5968–5971.

[9] J. Haywood, A. E. H. Wheatley, *Dalton Trans.* **2008**, 3378–3397.

[10] a) S. R. Boss, M. P. Coles, V. Eyre-Brook, F. Garcia, R. Haigh, P. B. Hitchcock, M. McPartlin, J. V. Morey, H. Naka, P. R. Raithby, H. A. Sparkes, C. W. Tate, A. E. H. Wheatley, *Dalton Trans.* **2006**, 5574–5582; b) S. R. Boss, M. P. Coles, R. Haigh, P. B. Hitchcock, R. Snaith, A. E. H. Wheatley, *Angew. Chem.* **2003**, *115*, 5751–5754; *Angew. Chem. Int. Ed.* **2003**, *42*, 5593–5596; c) D. R. Armstrong, R. P. Davies, W. Clegg, S. T. Liddle, D. J. Linton, P. Schooler, R. Snaith, A. E. H. Wheatley, *Phosphorus Sulfur Silicon Relat. Elem.* **2001**, *168*, 93–98; d) D. R. Armstrong, W. Clegg, R. P. Davies, S. T. Liddle, D. J. Linton, P. R. Raithby, R. Snaith, A. E. H. Wheatley, *Angew. Chem.* **1999**, *111*, 3568–3570; *Angew. Chem. Int. Ed.* **1999**, *38*, 3367–3370.

[11] D. Hoffmann, T. Kottke, R. J. Lagow, R. D. Thomas, *Angew. Chem.* **1998**, *110*, 1630–1633; *Angew. Chem. Int. Ed.* **1998**, *37*, 1537–1539.

[12] A. Stasch, *Angew. Chem.* **2012**, *124*, 1966–1969; *Angew. Chem. Int. Ed.* **2012**, *51*, 1930–1933.

[13] A. Stasch, unpublished results.

[14] See the Supporting Information for full experimental and crystallographic details.

[15] S. Beaini, G. B. Deacon, A. P. Erven, P. C. Junk, D. R. Turner, *Chem. Asian J.* **2007**, *2*, 539 – 550.

[16] a) M.-A. Velázquez-Carmona, A.-J. Metta-Magaña, S.-A. Cortés-Llamas, V. Montiel-Palma, M.-A. Muñoz-Hernández, *Polyhedron* **2009**, *28*, 205 – 208; b) S.-A. Cortés-Llamas, R. Hernández-Lamoneda, M.-A. Velázquez-Carmona, M.-A. Muñoz-Hernández, R. A. Toscano, *Inorg. Chem.* **2006**, *45*, 286 – 294.

[17] a) A. K. M. A. Islam, *Phys. Status Solidi B* **1993**, *180*, 9 – 57; b) F. E. Pretzel, G. N. Rupert, C. L. Mader, E. K. Storms, G. V. Gritton, C. C. Rushing, *J. Phys. Chem. Solids* **1960**, *16*, 10 – 20.

[18] a) M. Driess, U. Hoffmanns, S. Martin, K. Merz, H. Pritzkow, *Angew. Chem.* **1999**, *111*, 2906 – 2909; *Angew. Chem. Int. Ed.* **1999**, *38*, 2733 – 2736; b) M. Driess, H. Pritzkow, S. Martin, S. Rell, D. Fenske, G. Baum, *Angew. Chem.* **1996**, *108*, 1064 – 1066; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 986 – 988.

[19] a) X. Wang, L. Andrews, *J. Phys. Chem. A* **2007**, *111*, 6008 – 6019; b) D. Aurbach, I. Weissman, *Electrochem. Commun.* **1999**, *1*, 324 – 331; c) W. B. Zimmerman, D. J. Montgomery, *Phys. Rev.* **1960**, *120*, 405.