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## COMMUNICATION

A pyrazolate-stabilized sodium hydride complex<sup>†</sup>

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**The reaction of a sterically demanding sodium pyrazolate complex with n-butylsodium and diphenylsilane afforded the first well-defined molecular sodium hydride complex [(pz)<sub>6</sub>Na<sub>7</sub>H] **1** (pz = 3,5-di-tert-butylpyrazolate) that could be structurally characterised.**

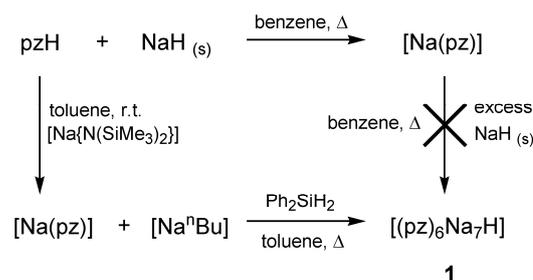
The alkali metal hydrides are long known ionic solids of rock salt structure and the lighter congeners LiH, NaH and KH are common laboratory reagents.<sup>1,2</sup> Especially in recent years have novel, well-defined s-block metal hydride complexes been investigated because facile synthetic routes and stabilizing ligand systems have been developed, and because of their potential for novel synthetic transformations, hydrogen storage applications, and as catalysts, especially in various hydroelementation reactions.<sup>3</sup> In addition, many s-block metals are cheap, abundant and non-toxic and as such well-suited for wider and large scale applications.

For the alkali metals, only well-defined molecular complexes of LiH are known.<sup>3</sup> These include monohydride complexes with a central hydride ion in a cage compound,<sup>4-6</sup> and larger aggregates with central (LiH)<sub>4</sub> core,<sup>7</sup> or up to nanometer-sized LiH clusters<sup>4,8,9</sup> such as [(pz)<sub>12</sub>Li<sub>37</sub>H<sub>25</sub>] and [(pz)<sub>12</sub>Li<sub>37</sub>(thf)<sub>2</sub>H<sub>26</sub>]<sup>-</sup> (pz = 3,5-di-tert-butylpyrazolate).<sup>4</sup> These soluble and molecular complexes generally show a different and higher reactivity compared with their parent ionic solids.<sup>3</sup> In addition, other concepts have been realised to obtain more reactive 'MH' (M = Li, Na, K) materials, such as the fresh preparation of highly reactive MH solids,<sup>10</sup> the use of hydropryridyllithium species,<sup>11</sup> or metal-containing frustrated Lewis pairs to solubilise and activate MH solids for reactions.<sup>12</sup> The majority of alkali metal and hydride-containing species are mixed metal '-ate' complexes, such as LiAlH<sub>4</sub>, NaBH<sub>4</sub> and derivatives,<sup>2,3,12,13</sup> that have the hydride ligand most strongly bound to the non-alkali metal or metalloid. Of relevance are few molecular examples of mixed metal hydride species containing another s-block metal that form ligand-stabilized MHMg (M = Na, K) aggregates,<sup>14,15</sup> including the large cluster [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>8</sub>Mg<sub>6</sub>Na<sub>6</sub>H<sub>10</sub>.<sup>14</sup> Here we report on our attempts of the extension of the successful [(pz)<sub>n</sub>Li<sub>m</sub>H<sub>m-n</sub>]-system,<sup>4</sup> which was

obtained as soluble and structurally characterized complexes from pzH, <sup>n</sup>BuLi and silane mixtures, to two heavier alkali metals.

As a suitable starting material, we synthesized the pyrazolate complex [Na(pz)] from the corresponding pyrazole pzH and [Na{N(SiMe<sub>3</sub>)<sub>2</sub>}] or NaH, respectively, in aromatic solvents; the latter reaction was carried out at elevated temperatures (Scheme 1). [Na(pz)] and some derivatives, have previously been prepared from pzH and sodium metal,<sup>16,17</sup> and [Na(pz)] forms one-dimensional chains in the solid state. During the course of this study, we characterised a new solvate of this complex, see the crystallographic section (ESI<sup>†</sup>).

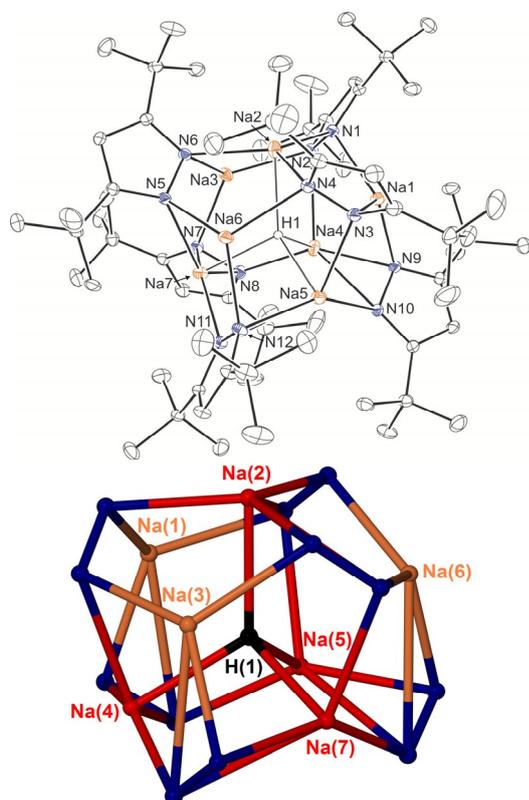
Reacting mixtures of [Na(pz)], [Na<sup>n</sup>Bu] and Ph<sub>2</sub>SiH<sub>2</sub> in hydrocarbon solvents at room temperature afforded crystals of the new hydride complex [(pz)<sub>6</sub>Na<sub>7</sub>H] **1**, but the reaction mixtures were very difficult to work-up (see ESI<sup>†</sup>). Changing the reactions conditions to toluene and elevated temperatures (e.g. 90°C) afforded the colourless complex [(pz)<sub>6</sub>Na<sub>7</sub>H] **1** in 65% isolated yield (Scheme 1).



**Scheme 1** Synthesis of [Na(pz)] and [(pz)<sub>6</sub>Na<sub>7</sub>H] **1**

Complex **1**·0.5 C<sub>6</sub>H<sub>6</sub> crystallises in the tetragonal crystal system with a full molecule in the asymmetric unit (Fig. 1). In **1**, a central hydride is coordinated by four Na ions (red in Fig. 1, bottom) in a slightly distorted tetrahedral fashion, and three of the four tetrahedron faces are capped by further Na ions (orange in Fig. 1, bottom). Six bridging 3,5-di-tert-butylpyrazolate ligands complete the cluster by each bridging between three or four Na ions. Alternatively, this arrangement can be regarded as a cube of Na

ions with six face-capping pyrazolates (yielding a rhombic dodecahedron-based structure) having one Na-corner missing, which leads to a significant distortion of the ionic cluster around the central hydride. In contrast, the crystal structure of  $[(pz)_6Li_7H]$  shows a central hydride ion coordinated by seven Li ions disordered over eight cube corners.<sup>4</sup> This leads to a higher hydride coordination (7) compared to that in **1** (4), and the related crystallographically characterized complexes  $[(pz)_6Na_7OH]$ <sup>16</sup> and  $[(pz)_6Na_8O]$ <sup>17</sup> are derived from a  $Na_8$ -cube structure with a central 7- or 8-coordinated oxygen atom, respectively.



**Fig. 1** Molecular structure of  $[(pz)_6Na_7H]$  **1**·0.5  $C_6H_6$ . Top: ORTEP drawing (30% thermal ellipsoids); solvent molecule, minor disordered parts and hydrogen atoms except H1 omitted for clarity. Bottom: Stick-and-ball diagram of the inorganic core of **1** (Na: orange and red, N: blue, H1: black). Selected interatomic distances (Å): Na1 Na2 3.0021(15), Na1 Na4 3.0669(15), Na1 Na5 3.1234(14), Na2 Na3 3.0219(14), Na2 Na6 3.0094(14), Na2 Na7 3.9522(15), Na2 Na5 3.9610(15), Na2 Na4 4.0166(16), Na3 Na4 3.1005(15), Na3 Na7 3.0516(14), Na4 Na5 3.4822(15), Na4 Na7 3.4665(15), Na5 Na6 3.0441(15), Na5 Na7 3.4964(15), Na6 Na7 3.1221(14), Na1 N1 2.396(2), Na1 N3 2.408(2), Na1 N9 2.329(2) (shortest), Na1 N10 3.017(2), Na2 N1 2.350(2), Na2 N3 3.055(2), Na2 N4 2.365(2), Na2 N5 3.057(2), Na2 N6 2.353(2), Na4 N2 2.671(2), Na4 N8 2.368(2), Na4 N9 2.357(2), Na4 N10 2.780(2), Na2 H1 2.38(3), Na4 H1 2.25(2), Na5 H1 2.27(3), Na7 H1 2.29(3).

The three Na ions in **1** (red in Fig. 1, bottom) on the inner tetrahedron face that is not capped with another Na ion (Na4, Na5, Na7) show shorter Na...H contacts (2.25(2)–2.29(3) Å) than the remaining Na...H one (2.38(3) Å to Na2) of the inner tetrahedron (also see Fig. S1, ESI<sup>†</sup>). The Na...H distances to the outer three Na ions (orange in Fig. 1, bottom) are significantly longer and range

from *ca.* 2.74 to 2.82 Å. The former short distances are approximately comparable to the Na...H contacts in Hill's mixed *s*-block metal hydride cluster  $[(Me_3Si)_2N]_8Mg_6Na_6H_{10}$ , though some of these hydrides are only three-coordinated and all have their closest contacts to the more Lewis-acidic  $Mg^{2+}$  ions.<sup>14</sup> Shorter Na...H contacts (*ca.* 2.1 Å) than those in **1** were found in a sodium hydridoziroconate complex having lower hydride coordination and the closest hydride contacts to Zr.<sup>18</sup> As expected, the shortest Na...H contacts in **1** lie between the bond length in the NaH molecule (*ca.* 1.89 Å),<sup>19</sup> and the shortest contacts in the cubic NaH lattice (*ca.* 2.45 Å)<sup>3,20</sup> with octahedrally coordinated ions.

The slight asymmetry in the overall structure of **1** is also reflected in their interatomic Na...Na distances. Those between neighbouring orange and red Na ions (Fig. 1, bottom) are approximately 3 Å, they are approximately 3.5 Å within the red tetrahedron on the uncapped face (Na4, Na5 and Na7), and are approximately 4 Å between Na2 and Na4, Na5 or Na7, respectively, in the inner tetrahedron. Due to a "missing" Na ion to reach a full cube, three of the six pyrazolate ligands coordinate to four Na ions each (all involving Na2), and three to three Na ions each (around the Na4, Na5 and Na7 tetrahedron face); the shortest Na...N contact measures *ca.* 2.33 Å. The Na ions furthermore show several contacts (Na...H  $\geq 2.5$  Å) to methyl groups from the pyrazolate tert-butyl groups. Complex  $[(pz)_6Na_7H]$  **1** can be regarded as the first well-defined and structurally characterized NaH complex, though an "inverse NaH complex" has previously been prepared and structurally characterized, that remarkably combines an encapsulated  $H^+$  and the highly reactive sodide anion,  $Na^-$ .<sup>21</sup>

In solution, complex **1** shows one set of singlet resonances for the pyrazolate ligand, and a broadened NaH resonance at  $\delta$ 5.17 ppm of correct integration. For comparison, only a very broad LiH resonance was observed for  $[(pz)_6Li_7H]$  at around  $\delta$ 3.5–3.6 ppm.<sup>4</sup> The <sup>1</sup>H NMR pyrazolate resonances of **1** appear only slightly upfield from those of [Na(pz)] and the chemical shift of the NaH resonance is almost identical to those of strong silane resonances, and thus, *in-situ* NMR studies on the formation of  $[(pz)_6Na_7H]$  **1** in solution from [Na(pz)],  $[Na^nBu]$  and  $Ph_2SiH_2$  were not very meaningful, although a main symmetric pyrazolate-containing species was formed. A mixture of  $[(pz)_6Na_7H]$  **1** and [Na(pz)] shows two close, but separated sets of singlets for the pyrazole resonances of the two compounds, and still one broadened resonance for the NaH unit both at room temperature and at 60°C.

We found no evidence that an excess of solid NaH, which reacts with *pzH* at 60°C in benzene to form [Na(pz)], further reacts under these conditions to form hydride complex  $[(pz)_6Na_7H]$  **1** or a similar species after longer reaction times (Scheme 1). As such, it is unlikely that well-defined and soluble NaH complexes (bearing no other metal or metalloid element) can be easily obtained from commercially available solid NaH. This is not unexpected considering the ionic bonding in these types of complexes and the relatively large lattice energy of solid NaH (–808 kJ/mol),<sup>1</sup> and many well-defined *s*-block metal hydride systems require kinetic stabilization by the ligand sphere.<sup>3</sup>

We carried out related experiments for the potassium system. To this end, we synthesised the known [K(pz)] complex<sup>16</sup> from the corresponding pyrazole and  $[K\{N(SiMe_3)_2\}]$  or KH, respectively (ESI<sup>†</sup>). Reactions of [K(pz)],  $[K^nBu]$  and  $Ph_2SiH_2$  in an analogue manner to the synthesis of  $[(pz)_6Na_7H]$  **1** so far only led to the isolation of [K(pz)]. The latter compound and potentially newly obtained products are virtually insoluble in aromatic solvents and

thus THF was used to dissolve, separate and crystallize products from the reaction mixture. Only large quantities of solvent-free polymeric [K(pz)] were obtained from neat THF, that crystallized in one-dimensional chains as was reported previously.<sup>16</sup> It is likely that a more sterically demanding ligand system, or one with differently orientated donor atoms, is required to encapsulate a  $K_n^+H^-$  fragment due to the larger size of the ionic radii (crystal, six-coordinate) of  $K^+$  (1.52 Å) vs.  $Na^+$  (1.16 Å).<sup>22</sup>

In conclusion, we have reported the first synthesis and structural characterization of a well-defined molecular sodium hydride complex using a sterically demanding pyrazolate ligand.

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## Notes and references

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† Electronic supplementary information (ESI) available: Experimental procedures and crystal data. CCDC 1043423 (1-0.5 C<sub>6</sub>H<sub>6</sub>) and 1043424 ([Na(pz)]·0.167 C<sub>7</sub>H<sub>8</sub>). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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### Table of contents entry:

The synthesis and structural characterisation of the first sodium hydride complex stabilised by sterically demanding pyrazolate ligands is presented.

