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$K_2Li(NH_2)_3$ and $K_2Na(NH_2)_3$—synthesis and crystal structure of two crystal-chemically isotypic mixed-cationic amides

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Abstract

$K_2Li(NH_2)_3$ (**1**) was the only crystalline product obtained from the reaction of potassium with dilithium decahydro-*closo*-decaborate $Li_2B_{10}H_{10}$ in liquid ammonia at $-38\,^{\circ}C$. The compound crystallizes in the space group $P4_2/m$ with $Z=4$, $a=6.8720(5)$ Å, $c=11.706(1)$ Å and $V=552.81(7)$ Å^3. The investigated crystal-chemically isotypic sodium compound $K_2Na(NH_2)_3$ (**2**) was merohedrally twinned and crystallized from a reaction mixture containing potassium and disodium decahydro-*closo*-decaborate $Na_2B_{10}H_{10}$ in liquid ammonia with $a=7.0044(5)$ Å, $c=12.362(1)$ Å and $V=606.48(9)$ Å^3. The compounds contain pairs of edge sharing tetraamidolithium or tetraamidosodium tetrahedra which are interconnected by potassium ions forming three-dimensional infinite networks.

Keywords: Amide; Lithium; Sodium; Potassium; Crystal structure; Liquid ammonia

1. Introduction

Due to their widespread use, alkali metal amides are of general interest in all fields of chemistry and have been investigated for about 50 years by diffraction methods [1–12]. Mixed cationic systems of alkali metal amides have first been investigated by Franklin, who also encountered the formation of (**1**) and (**2**) in liquid ammonia and reported their very low solubility [13]. In recent times, Jacobs and coworkers did thorough research on mixed cationic alkali metal amides [14–19] where (**1**) and (**2**) were also prepared by high-pressure synthesis in steel cells [20,21]. However, the structural analysis of (**1**) was of low quality due to incomplete data. Here we present the structural characterization of the mixed cationic alkali metal amides $K_2Li(NH_2)_3$ (**1**) and $K_2Na(NH_2)_3$ (**2**).

2. Results and discussion

The asymmetric unit of structure (**1**) contains three potassium ions on the special Wyckoff positions 2*a*, 2*f*, 4*i* and a lithium ion on the 4*j* position. As anions, two amide ions NH_2^- are present, one resides on the mirror plane (4*j*), whereas the other one is located on the 8*k* position. All hydrogen atoms also reside on the latter position. The same holds true for the structure of (**2**) which is crystal-chemically isotypic.

N(1) on the 4*j* position has only one not symmetry equivalent hydrogen atom H(1A) with a bond length of 0.84(2) Å in (**1**) or 0.88(2) Å in (**2**), attached. N(2) on the general 8*k* position carries two hydrogen atoms H(2A) and H(2B) in a distance of 0.95(2) and 0.81(2) Å in (**1**) and 0.95(2) and 0.82(2) Å in (**2**).

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The lithium ion, or the sodium ion, respectively, is coordinated by the two not symmetry equivalent amide anions. By application of the 4_2 screw axis, the lithium (sodium) ion is surrounded by amide anions in a shape similar to a tetrahedron, but also another symmetry equivalent tetraamidolithium (sodium) tetrahedron is generated which shares a common edge to the former, formally resulting in a μ-diamido-bis(lithiumdiamide) ion $[Li_2(NH_2)_6]^{4-}$ in (**1**) or a μ-diamido-bis(sodiumdiamide) ion $[Na_2(NH_2)_6]^{4-}$ in (**2**), respectively (Fig. 1).

These pairs of edge sharing tetrahedra of $[M_2(NH_2)_6]^{4-}$ (M = Li, Na) are interconnected via the three not symmetry equivalent potassium ions.

Fig. 2a depicts the coordination of the edge sharing tetrahedra by the potassium ion K(1). The latter shows an octahedron-shaped coordination by the amide anions (Fig. 2b). Such an octahedron is connected to another symmetry equivalent one, forming a pair of edge sharing octahedra. These octahedron pairs share edges and corners with the edge sharing tetrahedra of μ-diamido-bis(lithiumdiamide) or μ-diamido-bis(sodiumdiamide) and generate a three-dimensional infinite network shown in Fig. 2c.

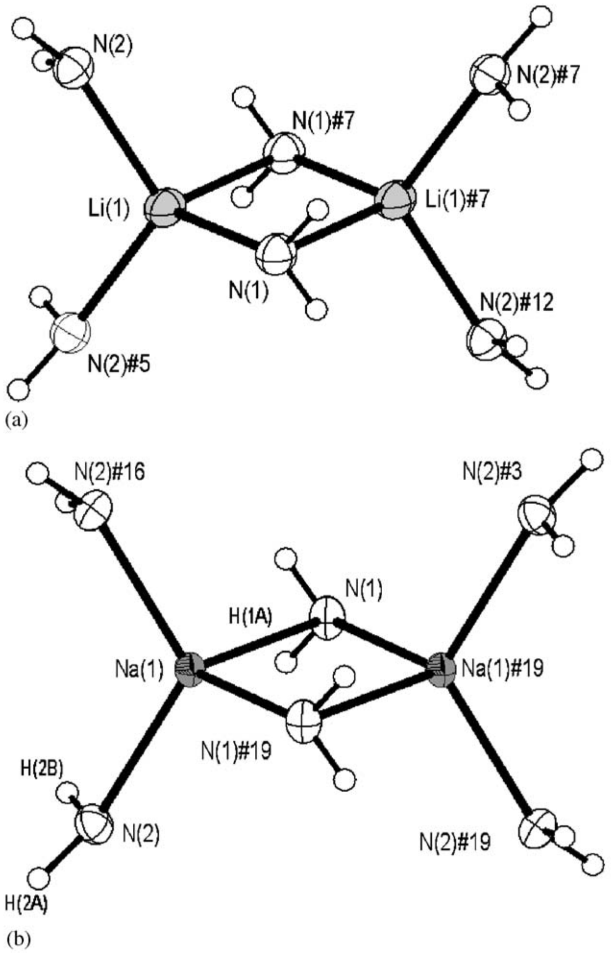

Fig. 1. shows the μ-diamido-bis(lithiumdiamide) ion (a) and the μ-diamido-bis(sodiumdiamide) ion (b). Thermal ellipsoids at 70% probability level. Selected bond lengths [Å] and angles [°]: Li(1)–N(1) 2.056(5), Li(1)–N(2) 2.086(3), Li(1)–N(1)#7 2.375(5), N(1)–Li(1)–N(2) 115.8(1); Na(1)–N(1) 2.537(3), Na(1)–N(2) 2.339(2), Na(1)–N(1)#19 2.393(3), N(1)–Na(1)–N(2) 107.69(6). Symmetry transformations to generate equivalent atoms: #3 $-x+1$, $-y-1$, $-z$; #5 x, y, $-z$; #7 $1-x$, $1-y$, z; #12 $1-x$, $1-y$, $-z$; #16 x, y, $-z$; #19 $-x+1$, $-y-1$, z.

The coordination sphere of K(2) is also octahedron-like. These octahedra are connected to the edge sharing tetrahedra via common edges and corners. Potassium ion K(2) and its symmetry equivalents form, together with the edge sharing tetrahedral, a two-dimensional infinite net in the *ab*-plane (Fig. 3).

Additionally, the $[M(NH_2)_6]^{4-}$ (M = Li in (**1**) or Na in (**2**)) anions are connected via K(3) forming a $^{1}_{\infty}[KM_2(NH_2)_6]$-strand (Fig. 4), which runs along the *c*-axis.

Taking all the previously mentioned structural elements together, the structure of $K_2Li(NH_2)_3$ and $K_2Na(NH_2)_3$ is obtained (Fig. 5).

3. Experimental part

All work was done excluding moisture and air in an atmosphere of purified argon. $Na_2B_{10}H_{10}$ was obtained by ion exchange of $[HNEt_3]_2[B_{10}H_{10}]$ with NaOH followed by thorough drying in vacuo [22]. For the preparation of (**1**), a Schlenk tube was charged with a five-fold excess of distilled lithium to one equivalent of $Na_2B_{10}H_{10}$ (2.8 mmol). Approximately 15 mL of dried ammonia were condensed into the tube at −78 °C, yielding a blue solution of the alkali metal. After storage at −38 °C for two weeks the solution decolorized and white octahedral crystals formed which were subjected to low temperature X-ray analysis.

Crystallographic data of (**1**): $H_6K_2LiN_3$, $M = 133.22$ g/mol, tetragonal, space group $P4_2/m$ (No. 84), $a = 6.8720(5)$ Å, $c = 11.706(1)$ Å, $V = 552.81(7)$ Å^3, $Z = 4$, $\rho_{calc} = 1.601$ Mg m^{-3}, $\mu(MoK_\alpha) = 1.566$ mm^{-1}. Bruker Smart Apex CCD-diffractometer with graphite monochromator [23], MoK_α-radiation $\lambda = 0.71073$ Å, $T = 123(1)$ K, ω-scan, 6677 measured reflections ($2.96° \leqslant \theta \leqslant 28.05°$, $-9 \leqslant h \leqslant 9$, $-9 \leqslant k \leqslant 8$, $-15 \leqslant l \leqslant 15$), 697 independent reflections, 620 independent reflections with $I > 2\sigma(I)$ ($R_{int} = 0.0317$), numerical absorption correction [24]. Solution using direct methods (SHELXS97) [25], refinement on F^2 (SHELXL97) [26]. All atoms were localized by Fourier cycling methods and refined isotropically, non-hydrogen atoms anisotropically using 45 refined parameters. The refinement converged ($\Delta/\sigma_{max} = 0.000$) at $wR_2 = 0.0607$ (all reflections), conventional $R = 0.0234$ for $I > 2\sigma(I)$, $S = 1.139$. Residual electron density was $0.324/-0.323$ e Å^{-3}. To certify the