

# $K_2Li(NH_2)_3$ 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  $Z=4$ ,  $a=6.8720(5)\text{ \AA}$ ,  $c=11.706(1)\text{ \AA}$  and  $V=552.81(7)\text{ \AA}^3$ . 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  $a=7.0044(5)\text{ \AA}$ ,  $c=12.362(1)\text{ \AA}$  and  $V=606.48(9)\text{ \AA}^3$ . The compounds contain pairs of edge sharing tetraamidolithium or tetraamidosodium tetrahedra which are interconnected by potassium ions forming three-dimensional infinite networks.

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**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  $2a$ ,  $2f$ ,  $4i$  and a lithium ion on the  $4j$  position. As anions, two amide ions  $NH_2^-$  are present, one resides on the mirror plane ( $4j$ ), whereas the other one is located on the  $8k$  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  $4j$  position has only one not symmetry equivalent hydrogen atom H(1A) with a bond length of  $0.84(2)\text{ \AA}$  in (**1**) or  $0.88(2)\text{ \AA}$  in (**2**), attached. N(2) on the general  $8k$  position carries two hydrogen atoms H(2A) and H(2B) in a distance of  $0.95(2)$  and  $0.81(2)\text{ \AA}$  in (**1**) and  $0.95(2)$  and  $0.82(2)\text{ \AA}$  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  $\mu$ -diamido-bis(lithiumdiamide) ion  $[\text{Li}_2(\text{NH}_2)_6]^{4-}$  in (1) or a  $\mu$ -diamido-bis(sodiumdiamide) ion  $[\text{Na}_2(\text{NH}_2)_6]^{4-}$  in (2), respectively (Fig. 1).

These pairs of edge sharing tetrahedra of  $[\text{M}_2(\text{NH}_2)_6]^{4-}$  ( $M = \text{Li}, \text{Na}$ ) 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

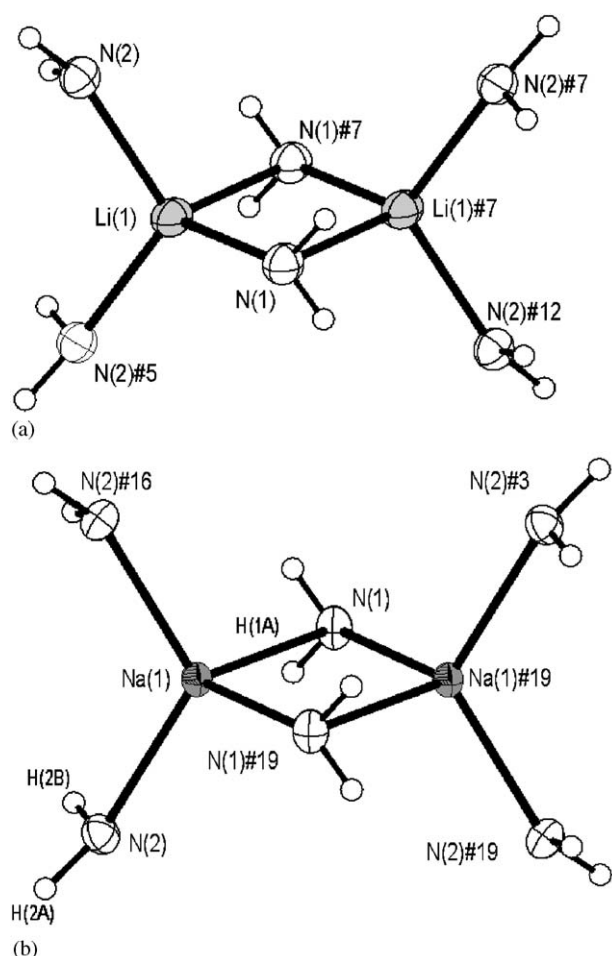


Fig. 1. shows the  $\mu$ -diamido-bis(lithiumdiamide) ion (a) and the  $\mu$ -diamido-bis(sodiumdiamide) ion (b). Thermal ellipsoids at 70% probability level. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: Li(1)–N(1) 2.056(5), Li(1)–N(2) 2.086(3), Li(1)–N(1)#7 2.375(5), N(1)–Li(1)–N(2) 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  $-x+1, -y-1, z$ .

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  $\mu$ -diamido-bis(lithiumdiamide) or  $\mu$ -diamido-bis(sodiumdiamide) and generate a three-dimensional infinite network shown in Fig. 2c.

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  $[\text{M}(\text{NH}_2)_6]^{4-}$  ( $M = \text{Li}$  in (1) or  $\text{Na}$  in (2)) anions are connected via K(3) forming a  $^1_\infty[\text{KM}_2(\text{NH}_2)_6]$ -strand (Fig. 4), which runs along the  $c$ -axis.

Taking all the previously mentioned structural elements together, the structure of  $\text{K}_2\text{Li}(\text{NH}_2)_3$  and  $\text{K}_2\text{Na}(\text{NH}_2)_3$  is obtained (Fig. 5).

### 3. Experimental part

All work was done excluding moisture and air in an atmosphere of purified argon.  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  was obtained by ion exchange of  $[\text{HNEt}_3]_2[\text{B}_{10}\text{H}_{10}]$  with  $\text{NaOH}$  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  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  (2.8 mmol). Approximately 15 mL of dried ammonia were condensed into the tube at  $-78^\circ\text{C}$ , yielding a blue solution of the alkali metal. After storage at  $-38^\circ\text{C}$  for two weeks the solution decolorized and white octahedral crystals formed which were subjected to low temperature X-ray analysis.

Crystallographic data of (1):  $\text{H}_6\text{K}_2\text{LiN}_3$ ,  $M = 133.22$  g/mol, tetragonal, space group  $P4_2/m$  (No. 84),  $a = 6.8720(5)$   $\text{\AA}$ ,  $c = 11.706(1)$   $\text{\AA}$ ,  $V = 552.81(7)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.601$   $\text{Mg m}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 1.566$   $\text{mm}^{-1}$ . Bruker Smart Apex CCD-diffractometer with graphite monochromator [23],  $\text{MoK}\alpha$ -radiation  $\lambda = 0.71073$   $\text{\AA}$ ,  $T = 123(1)$  K,  $\omega$ -scan, 6677 measured reflections ( $2.96^\circ \leq \theta \leq 28.05^\circ$ ,  $-9 \leq h \leq 9$ ,  $-9 \leq k \leq 8$ ,  $-15 \leq l \leq 15$ ), 697 independent reflections, 620 independent reflections with  $I > 2\sigma(I)$  ( $R_{\text{int}} = 0.0317$ ), 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 ( $\Delta/\sigma_{\text{max}} = 0.000$ ) at  $wR_2 = 0.0607$  (all reflections), conventional  $R = 0.0234$  for  $I > 2\sigma(I)$ ,  $S = 1.139$ . Residual electron density was  $0.324/-0.323$   $\text{e \AA}^{-3}$ . To certify the

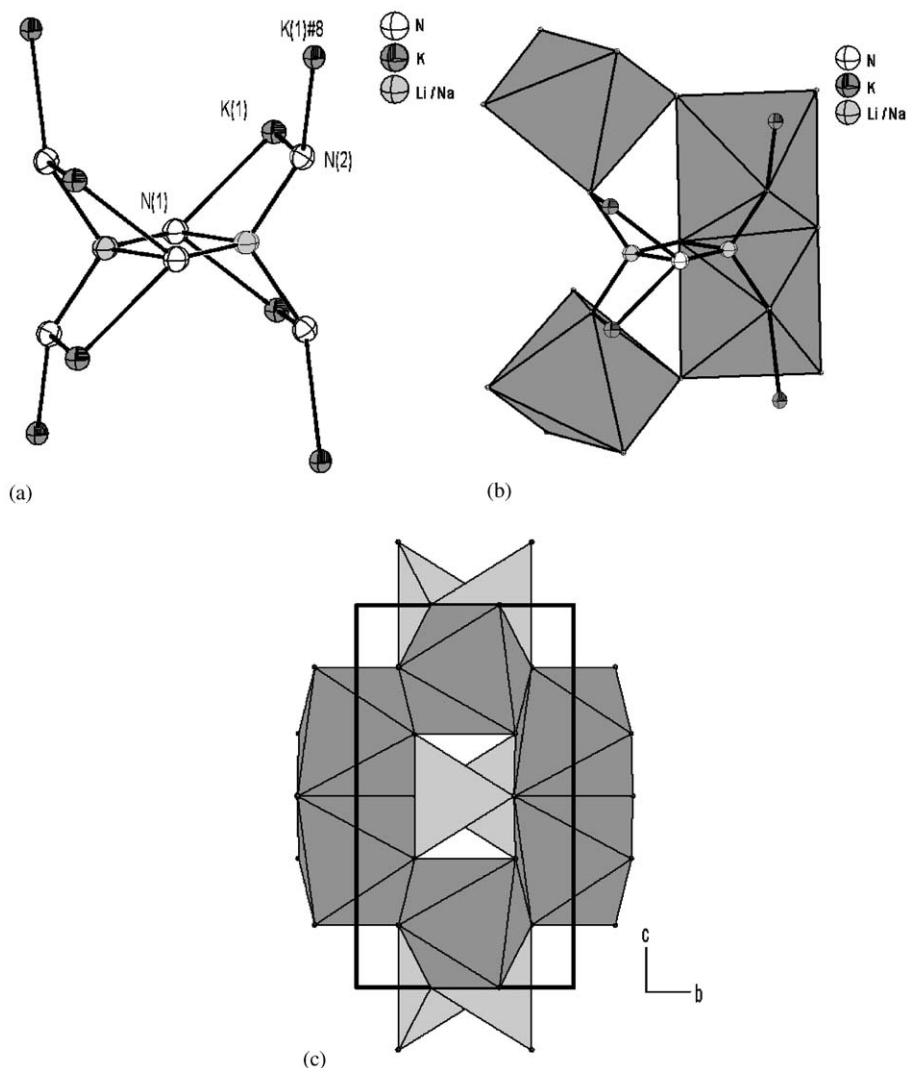


Fig. 2. (a) Shows the coordination of the edge sharing tetrahedra by symmetry equivalent potassium ions K(1). (b) Shows some coordination polyhedra of the symmetry equivalent K(1) cations and their attachment to the edge sharing tetrahedra of  $[M_2(NH_2)_6]^{4-}$  ( $M = \text{Li}$  in (1) or  $\text{Na}$  in (2)). (c) Projection on the bc-plane showing the coordination polyhedra involved and the three-dimensional infinite network generated by the interconnection of the edge sharing tetrahedra by K(1). Selected bond lengths [ $\text{\AA}$ ] for (1): K(1)–N(1) 2.889(2), K(1)–N(2) 2.832(2), K(1)#8–N(2) 3.086(2). Selected bond lengths [ $\text{\AA}$ ] for (2): K(1)–N(1) 2.856(2), K(1)–N(2) 2.906(2), K(1)#8–N(2) 3.111(2). Thermal ellipsoids at 70% probability level. Symmetry transformation to generate equivalent atoms: #8  $y, 1-x, 0.5-z$ .

selection of the space group  $P4_2/m$  searches for additional symmetry were performed using PLATON [27] and Kplot [28], which stated the correctness of the assignment.

For the preparation of (2) a Schlenk tube was charged with 553 mg of distilled potassium (14.1 mmol) and 464 mg of  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  (2.8 mmol). Approximately 15 mL of dried ammonia were condensed into the tube at  $-78^\circ\text{C}$ , yielding a blue solution of the alkali metal. After storage at  $-38^\circ\text{C}$  for eight weeks the solution decolorized and colorless needle-shaped crystals formed which were subjected to low temperature X-ray analysis.

Crystallographic data of (2):  $\text{H}_6\text{K}_2\text{N}_3\text{Na}$ ,  $M = 149.27$  g/mol, tetragonal, space-group  $P4_2/m$  (No. 84),  $a = 7.0044(5)$   $\text{\AA}$ ,  $c = 12.362(1)$   $\text{\AA}$ ,  $V = 606.49(9)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.635$   $\text{Mg m}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 1.503$   $\text{mm}^{-1}$ . Bruker Smart Apex CCD-diffractometer with graphite monochromator [23],  $\text{MoK}\alpha$ -radiation  $\lambda = 0.71073$   $\text{\AA}$ ,  $T = 123(1)$  K,  $\omega$ -scan, 16636 measured reflections ( $1.65^\circ \leq \theta \leq 32.63^\circ$ ,  $-10 \leq h \leq 10$ ,  $-10 \leq k \leq 10$ ,  $-18 \leq l \leq 18$ ), 1148 independent reflections, 909 independent reflections with  $I > 2\sigma(I)$  ( $R_{\text{int}} = 0.0825$ ), numerical absorption correction [24]. Solution using direct methods (SHELXS97) [25], refinement on  $F^2$  (SHELXL97) [26] using a two-fold rotation as a twin-matrix to

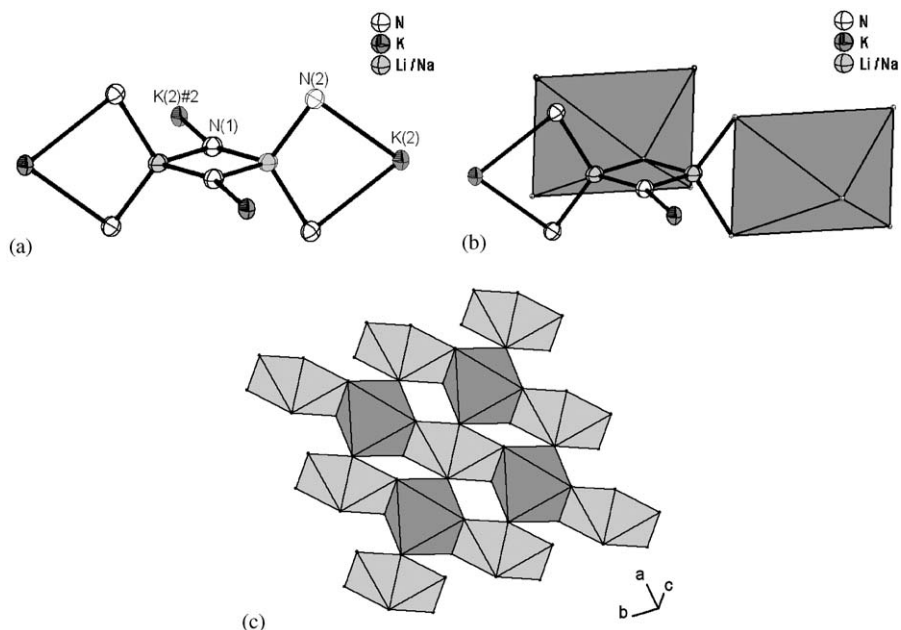
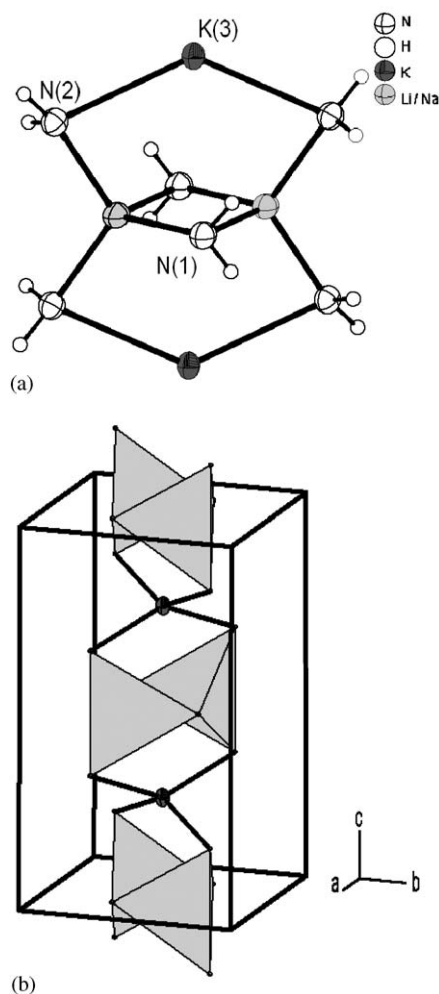


Fig. 3. (a) Shows the coordination of the  $[M_2(\text{NH}_2)_6]^{4-}$  edge sharing tetrahedra ( $M = \text{Li}$  in (1) or  $\text{Na}$  in (2)) by potassium ion  $\text{K}(2)$ . (b) Depicts the octahedral coordination sphere of the potassium ions. (c) A cutout of the two dimensional infinite net in the *ab*-plane and the connectivity of the polyhedra is shown. Thermal ellipsoids at 70% probability level. Selected bond lengths [ $\text{\AA}$ ] for (1):  $\text{K}(2)\text{--N}(2)$  2.951(2),  $\text{K}(2)\#2\text{--N}(1)$  3.183(2). Selected bond lengths [ $\text{\AA}$ ] for (2):  $\text{K}(2)\text{--N}(2)$  3.068(2),  $\text{K}(2)\#2\text{--N}(1)$  3.063(2). Symmetry transformations to generate equivalent atoms:  $\#2\ x + 1, y, z$ .



describe the merohedral twinning since the pretended space-group was  $P4_222$  (Laue group  $4/mmm$ ). The twin matrix improved the  $R_1$ -value (all data) from over 0.18 to 0.05. All atoms were localized by Fourier cycling methods and refined isotropically, non-hydrogen atoms anisotropically using 45 refined parameters. The refinement converged ( $\Delta/\sigma_{\text{max}} = 0.000$ ) at  $wR_2 = 0.0564$  (all reflections), conventional  $R = 0.0295$  for  $I > 2\sigma(I)$ ,  $S = 0.916$ . Residual electron density was  $0.404/-0.304\ \text{e}\ \text{\AA}^{-3}$ . To certify the selection of the space group  $P4_2/m$  searches for additional symmetry were performed using PLATON [27] and Kplot [28], which stated the correctness of the assignment.

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-414252 for (1) and CSD-414253 for (2), the name of the authors, and citation of the paper.

Fig. 4. (a) Shows the coordination of  $\text{K}(3)$  to the edge sharing tetrahedra. (b) Projection of the interconnection of the edge sharing tetrahedra to a  $\frac{1}{\infty}[\text{KM}_2(\text{NH}_2)_6]$ -strand ( $M = \text{Li}$  in (1) or  $\text{Na}$  in (2)), running along the *c*-axis by  $\text{K}(3)$ . Thermal ellipsoids at 70% probability level. Selected bond lengths [ $\text{\AA}$ ] for (1):  $\text{K}(3)\text{--N}(2)$  2.805(2),  $\text{K}(3)\text{--N}(1)$  3.391(1). Selected bond lengths [ $\text{\AA}$ ] for (2):  $\text{K}(3)\text{--N}(2)$  2.903(2),  $\text{K}(3)\text{--N}(1)$  3.6478(1)  $\text{\AA}$ .

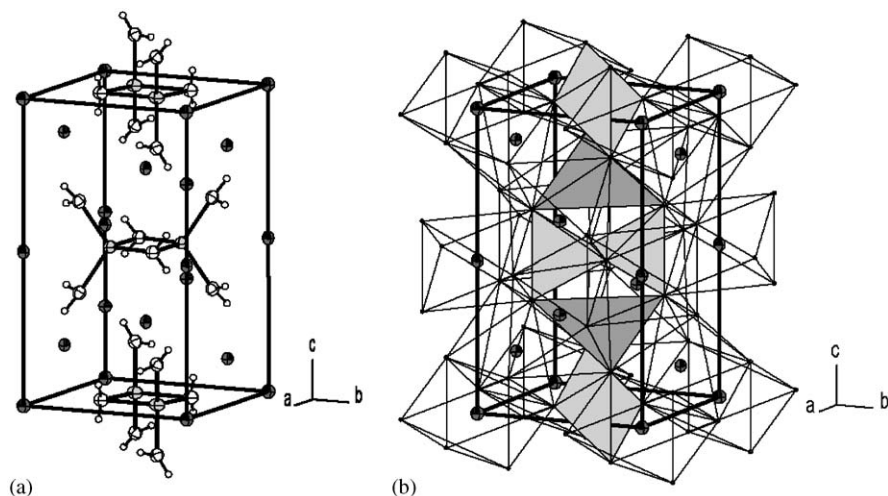


Fig. 5. (a) Projection of the unit cell, and (b) projection of the unit cell with polyhedra shown. Thermal ellipsoids at 70% probability level.

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### Appendix A

#### 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) of $\text{K}_2\text{Li}(\text{NH}_2)_3$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
K(1)	5000	0	1530(1)	14(1)	N(1)	6442(3)	2967(3)	0	18(1)
K(2)	0	0	0	15(1)	H(1A)	7180(40)	3190(40)	560(19)	43(7)
K(3)	5000	5000	2500	14(1)	N(2)	2007(2)	2832(2)	1484(1)	16(1)
Li(1)	3513(6)	3577(7)	0	18(1)	H(2A)	1570(30)	1910(30)	2026(19)	30(6)
					H(2B)	970(40)	3330(30)	1320(20)	32(7)

#### 2. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) of $\text{K}_2\text{Li}(\text{NH}_2)_3$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
K(1)	15(1)	13(1)	14(1)	0	0	1(1)	Li(1)	14(2)	25(2)	14(2)	0	0	0(2)
K(2)	14(1)	14(1)	18(1)	0	0	-3(1)	N(1)	15(1)	21(1)	17(1)	0	0	0(1)
K(3)	12(1)	12(1)	17(1)	0	0	0	N(2)	14(1)	18(1)	18(1)	1(1)	0(1)	1(1)

#### 3. Atomic coordinates ( $10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) of $\text{K}_2\text{Na}(\text{NH}_2)_3$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
K(1)	0	-5000	1521(1)	13(1)	N(1)	-2735(3)	-6589(4)	0	14(1)
K(2)	0	0	0	14(1)	N(2)	2673(3)	-8072(3)	1635(1)	15(1)
K(3)	-5000	-5000	2500	16(1)	H(1A)	-2890(40)	-7390(30)	539(16)	45(8)
Na(1)	3644(2)	-6705(2)	0	11(1)	H(2A)	1700(30)	-8510(40)	2110(18)	39(7)
					H(2B)	3200(30)	-9100(30)	1520(20)	42(9)

4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) of  $\text{K}_2\text{Na}(\text{NH}_2)_3$ 

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
K(1)	12(1)	15(1)	13(1)	0	0	2(1)	Na(1)	10(1)	11(1)	12(1)	0	0	-1(1)
K(2)	12(1)	12(1)	19(1)	0	0	-1(1)	N(1)	10(1)	12(1)	20(1)	0	0	2(1)
K(3)	13(1)	13(1)	22(1)	0	0	0	N(2)	16(1)	13(1)	16(1)	2(1)	1(1)	0(1)

## References

- [1] R. Juza, K. Opp, *Z. Anorg. Allg. Chem.* 266 (1951) 313–324.  
 [2] R. Juza, K. Opp, *Z. Anorg. Allg. Chem.* 266 (1951) 325–330.  
 [3] R. Juza, H.H. Weber, K. Opp, *Z. Anorg. Allg. Chem.* 284 (1956) 73–82.  
 [4] R. Juza, H. Liedtke, *Z. Anorg. Allg. Chem.* 290 (1957) 205–208.  
 [5] R. Juza, A. Mehne, *Z. Anorg. Allg. Chem.* 299 (1959) 33–40.  
 [6] R. Juza, A. Mehne, *Z. Anorg. Allg. Chem.* 299 (1959) 41–50.  
 [7] R. Juza, H. Jacobs, W. Klose, *Z. Anorg. Allg. Chem.* 338 (1965) 171–178.  
 [8] H. Jacobs, R. Juza, *Z. Anorg. Allg. Chem.* 391 (1972) 271–279.  
 [9] H. Jacobs, E. Von Osten, *Z. Naturforsch. B: Chem. Sci.* 31B (1976) 385–386.  
 [10] M. Müller, J. Senker, B. Asmussen, W. Press, H. Jacobs, W. Kockelmann, H.M. Mayer, R.M. Ibberson, *J. Chem. Phys.* 107 (1997) 2363–2373.  
 [11] M. Müller, B. Asmussen, W. Press, J. Senker, H. Jacobs, H. Schober, H. Büttner, *J. Chem. Phys.* 109 (1998) 3559–3567.  
 [12] D. Peters, A. Tenten, H. Jacobs, *Z. Anorg. Allg. Chem.* 628 (2002) 1521–1524.  
 [13] E.C. Franklin, *J. Phys. Chem.* 23 (1919) 36–53.  
 [14] H. Jacobs, J. Kockelkorn, *Z. Anorg. Allg. Chem.* 456 (1979) 147–154.  
 [15] H. Jacobs, B. Harbrecht, *J. Less Comm. Met.* 85 (1982) 87–95.  
 [16] H. Jacobs, B. Harbrecht, *Z. Anorg. Allg. Chem.* 518 (1984) 87–100.  
 [17] B. Harbrecht, H. Jacobs, *Z. Anorg. Allg. Chem.* 546 (1987) 48–54.  
 [18] H. Jacobs, A. Schardey, B. Harbrecht, *Z. Anorg. Allg. Chem.* 555 (1987) 43–56.  
 [19] H. Jacobs, P. Bohger, W. Kockelmann, *Z. Anorg. Allg. Chem.* 628 (2002) 1794–1798.  
 [20] B. Harbrecht, Rheinisch-Westfälische Technische Hochschule Aachen, 1981.  
 [21] T. Tacke, Rheinisch-Westfälische Technische Hochschule Aachen, 1982.  
 [22] M.F. Hawthorne, A.R. Pitochelli, *J. Am. Chem. Soc.* 81 (1959) 5519.  
 [23] Bruker, SMART, Bruker AXS: Madison, Wisconsin, USA, 2000.  
 [24] Bruker SADABS, Bruker AXS: Madison, Wisconsin, USA, 2000.  
 [25] G.M. Sheldrick, SHELXS-97, University of Göttingen, 1997.  
 [26] Sheldrick, G. M. SHELXL-97, University of Göttingen, 1997  
 [27] A.L. Spek, PLATON—A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2003.  
 [28] R. Hundt, KPLOT, University of Bonn, 2004.