Note

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The first pseudo-ternary thiocyanate containing two alkali metals – synthesis and single-crystal structure of $LiK_2[SCN]_3$

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Abstract: A procedure was empirically developed to prepare the compound $LiK_2[SCN]_3$, which forms colorless, transparent, very fragile, and extremely hygroscopic thin rectangular plates. Its unique crystal structure was determined by single-crystal X-ray diffraction. $LiK_2[SCN]_3$ adopts the orthorhombic space group $Pna2_1$ (no. 33, Z = 4) with the cell parameters a = 1209.32(9), b = 950.85(9), and c = 849.95(6) pm.

Keywords: lithium; potassium; structure elucidation; thiocyanate.

1 Introduction

The crystal structures and the vibrational spectra of Li[SCN], and Li[SCN] · 2 H_2O as well as a DSC/TG measurement of the thermal decomposition of Li[SCN] · 2 H_2O have been reported recently by us [1], but no lithium-containing, pseudo-ternary thiocyanate is known to the best of our knowledge. Studies of compounds such as $LiK[SO_4]_2$ [2], $LiK[CO_3]_2$ [3], or $LiK[C(CN)_3]_2$ [4] have shown that due to their different coordination requirements, lithium and potassium are a good combination to stabilize pseudo-ternary compounds containing small anionic moieties. Therefore, starting from plausible stoichiometries, we attempted to synthesize a pseudo-ternary compound containing lithium and potassium cations and the thiocyanate anion. Here, we present the synthesis and single-crystal structure determination of $LiK_2[SCN]_3$.

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2 Experimental section

2.1 Synthesis

All manipulations were performed under normal atmospheric conditions unless otherwise stated. Li[SCN] was obtained by exposing Li[SCN] · x H_2O (>98 %; Sigma-Aldrich, St. Louis, MO, USA) to 200 °C for 2 h under dynamic vacuum until the pressure was constant and below 200 Pa. Then the temperature was raised over 30 min to 300 °C. The sample was held at this temperature for 30 min, still under the dynamic vacuum. The water-free material obtained this way is extremely hygroscopic, colorless with a slight yellowish tint (a more intense yellow substance also appeared above the heated zone of the ampoule). K[SCN] (>99 %; Sigma-Aldrich, St. Louis, MO, USA) was kept for 2 h at 120 °C under dynamic vacuum. Both compounds were then transferred into an argon-filled glove box. For further experiments, the compounds were mixed in a 1:1, 2:1, and 1:2 molar ratio (overall mass in all cases, 350 mg).

Initially, the samples were heated under vacuum up to 350 K for 30 min, yielding some X-ray-amorphous, highly viscous material that dissolved easily in water and had then the odor of rotten eggs.

In follow-up attempts, the starting materials were filled in the aforementioned ratios into screw-top vials. Absolute ethanol (2 mL; Pharmco, Brookfield, CT, USA) was added to each vial. After dissolving the educts completely, the vials were placed in a drying furnace at 80 °C, which caused most of the solvent to evaporate. Even by applying reduced pressure, the solvent could not be removed completely, and an amorphous, colorless lump with adhering solvent drops remained. Cooling the products inside the sealed vials to 4 °C in a refrigerator produced for all starting compositions,

transparent, very fragile, and extremely hygroscopic thin rectangular plates inside the solvent drops. These plates were inspected with single-crystal methods and turned out to be the title compound in all cases.

2.2 Crystallographic studies

A few single crystals of the title compounds were secured by unscrewing the vials containing the product samples and quickly immersing them in dried polybutene oil (M_n ~ 320, isobutylene >90 %; Sigma-Aldrich). The evaluation of the crystalline material took place under a polarization microscope. The selected specimens were mounted with a drop of polybutene sustained in a plastic loop and placed onto the goniometer. A cold stream of nitrogen [T = 223(2) K] froze the polybutene oil, thus keeping the crystals stationary and protected from moisture. Intensity data sets were collected with a Bruker X8 Apex II diffractometer equipped with a 4-K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The intensity data were manipulated with the program package Apex2 [5] that came with the diffractometer. An empirical absorption correction was applied using Sadabs [6]. The intensity data were evaluated, and the input files for solving and refining the crystal structure were prepared with Xprep [7]. Reflection conditions led to the possible space groups $Pna2_1$ (no. 33) and *Pnma* (no. 62). Attempts to solve and refine the structure in the centric space group *Pnma* (no. 62) turned out to be unsuccessful. The E statistics ($|E^2 - 1|$ = 0.745, with 0.976 expected for centric and 0.736 for non-centric space groups) hinted strongly toward $Pna2_1$ (no. 33). The program Shelxs-97 [8, 9] delivered for this space group with the help of Direct Methods the positions of K and S. The N, C, and Li positions were apparent from the positions of highest electron density on the difference Fourier maps resulting from the first refinement cycles by full-matrix least-squares calculations on F^2 in Shelxl-97 [10, 11]. Doing further refinement cycles, the refinement converged and resulted in a stable structural model. Additional crystallographic details are described in Table 1. Atomic coordinates, anisotropic, and equivalent isotropic displacement coefficients are shown in Table 2. Table 3 displays selected interatomic distances and angles of the title compound and of Li[SCN] [3] and K[SCN] [14].

Further details of the crystal structure investigation may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-430274 for $LiK_2[SCN]_3$.

Table 1: Summary of the single-crystal X-ray structure determination data of $LiK_2[SCN]_3$.

Compound	$LiK_2[SCN]_3$
M_r	259.38
Crystal color	Transparent colorless
Crystal shape	Thin, rectangular plate
Crystal size, mm³	0.16 × 0.05 × 0.02
Crystal system	Orthorhombic
Space group (no.)	$Pna2_1$ (no. 33)
Z	4
Lattice parameters	
a, pm	1209.32(9)
b, pm	950.85(9)
c, pm	849.95(6)
V, Å³	977.34(14)
D_{calcd}, g/cm³	1.76
F(000), e	512
μ, mm⁻¹	1.6
Diffractometer	Bruker X8 Apex II equipped with a 4-K CCD
Radiation/λ, pm/ monochromator	MoK_α/71.073/graphite
T, K	223(2)
Scan mode	ϕ and ω scans
2 θ_{max}, deg	64.5
h, k, l range	±17, −10 →14, ±12
Data correction	Lp, Sadabs [6]
Transmission: min/max	0.636/0.746
x Flack [12, 13]	0.25(11)
Reflections: measured/ unique	7428/2946
Unique reflections with $F_o > 4\,\sigma(F_o)$	2240
R_{int}/R_σ	0.0535/0.0774
Refined parameters	110
$R1$[a]/$wR2$[b]/GoF[c] (all refl.)	0.0726/0.1158/0.992
Factors x/y (weighting scheme)[b]	0.0437/0
Max shift/esd in last refinement cycle	<0.00005
$\Delta\rho_{fin}$ (max, min), e/Å³	0.69 (7 pm to S2) −0.39 (188 pm to C2)
CSD number	430274

[a] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = [(F_o^2) + 2F_c^2]/3$ and x and y are constants adjusted by the program. [c] $GoF(S) = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, with n being the number of reflections and p being the number of refined parameters.

3 Results and discussion

3.1 Crystal structure

The basic building block of this crystal structure is the Li^+ cation coordinated tetrahedrally by three N atoms and

Table 2: Atomic coordinates and anisotropic[a] and equivalent isotropic[b] displacement parameters (pm^2) of $LiK_2[SCN]_3$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Li	0.9177(7)	0.0356(10)	0.1116(8)	342(44)	355(51)	285(37)	25(33)	−45(29)	−19(39)	327(19)
K1	0.82440(8)	0.37146(12)	0.96776(11)	309(5)	299(6)	278(4)	11(5)	−12(4)	34(5)	296(2)
K2	0.83108(8)	0.38289(12)	0.46877(11)	270(5)	295(6)	287(4)	37(5)	28(4)	32(4)	284(2)
S1	0.82729(8)	0.66837(13)	0.73824(17)	220(5)	291(6)	441(6)	19(6)	24(5)	−40(4)	317(3)
C1	0.0468(3)	0.2687(4)	0.2224(5)	224(18)	176(18)	235(16)	−27(21)	−8(18)	41(14)	211(7)
N1	0.9576(3)	0.2242(4)	0.2107(4)	200(16)	284(19)	316(18)	−21(19)	−11(15)	20(14)	267(7)
S2	0.61613(9)	0.56363(14)	0.06870(13)	282(5)	297(7)	220(4)	5(5)	17(4)	−5(5)	266(3)
C2	0.8674(3)	0.0664(5)	0.7611(5)	170(18)	157(20)	330(22)	37(16)	−15(15)	3(15)	219(9)
N2	0.8588(3)	0.0683(5)	0.8958(4)	292(22)	248(24)	260(17)	−3(17)	−12(14)	−13(17)	266(9)
S3	0.95318(8)	0.59845(11)	0.22361(17)	263(5)	221(5)	356(5)	44(6)	7(5)	33(4)	280(2)
C3	0.6126(3)	0.2500(4)	0.7147(5)	171(17)	213(20)	243(17)	18(20)	−14(17)	36(14)	209(7)
N3	0.6582(3)	0.3574(4)	0.7082(5)	237(17)	259(20)	331(20)	36(19)	−22(16)	−3(14)	276(8)

[a]The anisotropic displacement factor takes the form $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.
[b]U_{eq} is defined as a third of the orthogonalized U_{ij} tensors.

Table 3: Selected bond lengths (*d* in pm) and angles (∡ in deg) for $LiK_2[SCN]_3$.

$LiK_2[SCN]_3$		***Li[SCN]*** **[4] and K[SCN] [14]**	
Li–		*Li–*	
N2	199.3(7)	*N*	*205.9(5)*
N1	203.9(9)	*N* (2×)	*241.3(3)*
N3	209.5(9)	*S* (2×)	*266.4(3)*
S	260.4(8)	*S*	*277.6(4)*
K1–		**K–**	
N1	296.9(4)	**N (2×)**	**301.5**
N2	297.6(5)	**N (2×)**	**301.9**
N3	298.7(4)	**S (2×)**	**330.7**
S2	322.8(2)	**S (2×)**	**339.2**
S3	340.9(2)		
S1	343.2(2)		
S3	343.7(2)		
S1	351.8(2)		
K2–			
N3	292.7(4)		
N2	296.1(4)		
N1	307.1(4)		
S2	321.6(2)		
S3	327.5(2)		
S3	339.6(2)		
S1	341.6(2)		
S1	355.2(2)		
N1–C1	116.4(5)	*N–C*	*116.2(3)*
N2–C2	114.9(6)	**N–C**	**114.9(14)**
N3–C3	116.2(5)		
C1–S1	164.1(4)	*C–S*	*164.3(2)*
C2–S2	164.8(4)	**C–S**	**168.9(13)**
C3–S3	164.8(4)		
∡(N1–C1–S1)	179.8(5)	∡(*N–C–S*)	*179.1(2)*
∡(N2–C2–S2)	178.2(4)	**∡(N–C–S)**	**178.3(14)**
∡(N3–C3–S3)	179.5(4)		

Data for Li[SCN] [4] (italics) and K[SCN] [14] (bold) are given for comparison.

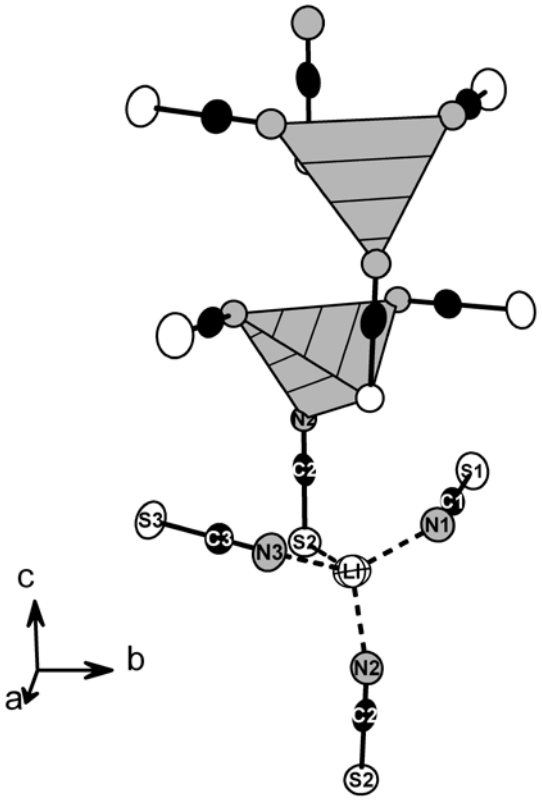

Fig. 1: Tetrahedral coordination of Li^+ in $LiK_2[SCN]_3$ forming columns parallel to the crystallographic *c* axis. Nitrogen atoms are displayed as gray, carbon atoms as black, sulfur as white spheres, and lithium atoms with white octands. Displacement ellipsoids are drawn at the 90 % probability level.

one S atom (Fig. 1). These tetrahedra are linked by $[SCN]^-$ anions (S2, C2, and N2 in Table 2 and Fig. 1) parallel to the *c* axis (also the 2_1 screw axis) forming columns (Fig. 1).

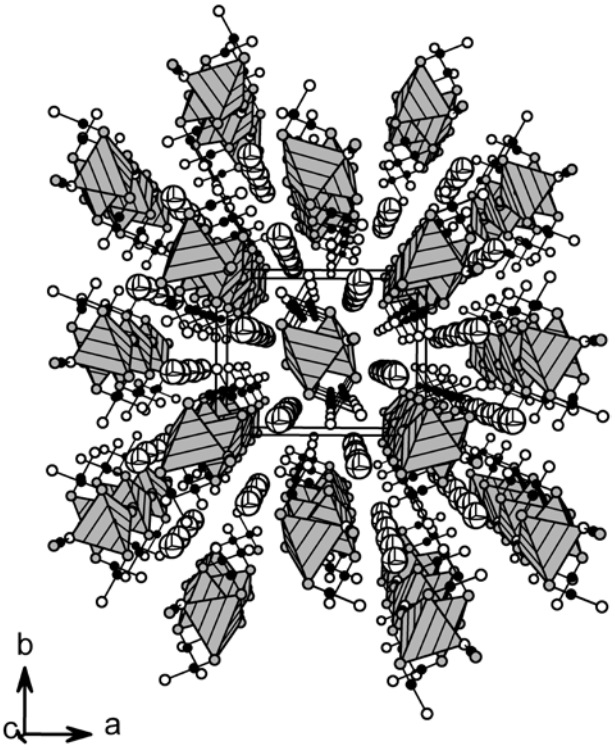

Fig.2: View along the crystallographic *c* axis of $LiK_2[SCN]_3$. The same color code as in Fig. 1 is applied with the exception of K^+, which is displayed with white octands.

These columns are packed nearly hexagonally with 8-fold coordinated K^+ cations between these columns holding them together (Fig. 2).

All bond lengths are in the expected ranges when compared to the distances observed for Li[SCN] [3] and K[SCN] [14] (Table 3).

4 Conclusion

The synthesis and crystal structure of the pseudo-ternary lithium potassium thiocyanate $LiK_2[SCN]_3$ are reported here for the first time, probably because of the hygroscopic nature and fragility of the crystals. This suggests that there are more pseudo-ternary alkali thiocyanates to be harvested with relatively simple techniques.

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