Single-Crystal Structures and Vibrational Spectra of Li[SCN] and Li[SCN] · 2 H_2O

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The crystal structure of Li[SCN] · 2 H_2O has been determined by single-crystal X-ray diffraction on commercially available material. Crystals of this compound are colorless, transparent and hygroscopic. Li[SCN] · 2 H_2O adopts the orthorhombic space group *Pnma* with the cell parameters $a = 572.1(3)$, $b = 809.3(4)$ and $c = 966.9(4)$ pm and $Z = 4$. Li[SCN] was obtained by dehydration of the afore-mentioned dihydrate and also crystallizes orthorhombically in *Pnma* with the lattice parameters $a = 1215.1(3)$, $b = 373.6(1)$ and $c = 529.9(2)$ pm ($Z = 4$). Both compounds contain Li^+ cations in sixfold coordination. Four water molecules and two nitrogen-attached thiocyanate anions $[SCN]^-$ arrange as *trans*-octahedra $[Li(\mathbf{O}H_2)_4(\mathbf{N}CS)_2]^-$ in the case of Li[SCN] · 2 H_2O. Anhydrous Li[SCN] displays *fac*-octahedra $[Li(\mathbf{N}CS)_3(\mathbf{S}CN)_3]^{5-}$ with six thiocyanate anions grafting *via* both nitrogen and sulfur atoms, three each. Infrared and Raman spectra of both compounds were recorded and a DSC/TG measurement was performed on Li[SCN] · 2 H_2O.

Key words: Lithium, $[SCN]^-$ Anion, Thiocyanates, DSC/TG Measurements, Vibrational Spectra

Introduction

Pseudobinary compounds containing lithium cations next to complex polyatomic anionic moieties have been synthesized and characterized early on, in the case of Li[CN] as early as 1942 [1]. Due to the recently increased interest in materials for lithium batteries, lithium-related research was fueled again and led to reports such as the structure and properties of Li[OCN] [2]. It still came as a surprise to us that physical properties of Li[SCN] and Li[SCN] · 2 H_2O can be found in the literature [3 – 5] and that "Li[SCN] · x H_2O" is commercially available, but no crystal structures have been reported for these two compounds as yet. So here we present the single-crystal structure determinations and the vibrational spectra of Li[SCN] and Li[SCN] · 2 H_2O as well as the DSC/TG measurement for the thermal decomposition of Li[SCN] · 2 H_2O.

Experimental Section

Synthesis

All manipulations were performed under normal atmospheric conditions unless otherwise stated. Li[SCN] · x H_2O was bought from Sigma-Aldrich (St. Louis, MO, U. S. A.) as minimally 98 % pure material ($M_n \sim 65$). Li[SCN] could be obtained by transferring some of the hygroscopic Li[SCN] · x H_2O into a glass ampoule and exposing it at 200 °C for two hours to a dynamic vacuum till the pressure was constant and below 200 Pa. Then the temperature was raised within 30 min. up to 300 °C. The sample was kept for 30 more min at this temperature, while still being under dynamic vacuum. The anhydrous material obtained in this way is extremely hygroscopic, colorless with a slight yellowish tint (a more intense yellow substance also showed up above the heated zone of the ampoule). The ampoule with the anhydrous Li[SCN] was flame-sealed and then transferred into an argon-filled glove box, where it was handled further on.

Table 1. Vibrational spectra of Li[SCN] and Li[SCN] · $2\,H_2O$ compared to literature data. All numbers are given in cm^{-1}, bold print indicates data obtained by IR techniques. All compounds were used as solids, if not indicated otherwise.

Compound	δ([SCN])	ν(SC)	2δ([SCN])	ν(CN)	$\nu(H_2O)$
Free anion (calcd.) [6, 7]	470	743	–	2066	–
Li[SCN]$_{(l)}$ [3]	499	764	–	2083	–
Li[SCN]$_{(aq)}$ [3]	496	745	–	2072	–
Li[SCN]	479	771	–	2070	–
This work	**491**	**731/774**	**967**	**2078**	**1653/3238/3294**
Li[SCN] · $2\,H_2O$	457/470	752	927	2050/2089	1660/3393
This work	**480**	**730/778**	**958/982**	**2064**	**1623/1635/3400**
Ca$[SCN]_2$ [8]	477/490/500	777	951/974/995	2010/2029/2048	–
	469/477/481	**764/770**	**942/958/967**	**2013/2077**	–
Ca$[SCN]_2$ · $2\,H_2O$ [8]	440/451/473/488	768	933	2100/2116/2124/2185	1628/3252/3360
	469/478	**769**	**951/957**	**2077/2096/2123**	**1628/3242/3398**

Raman and IR spectroscopy

The crystals of Li[SCN] and Li[SCN] · $2\,H_2O$ were sealed under a protective argon atmosphere in thin-walled glass capillaries. Raman spectroscopic investigations were performed on a microscope laser Raman spectrometer (Jobin Yvon, 4 mW, equipped with a HeNe laser using an excitation line at $\lambda = 632.817$ nm, 50 × magnification, 8 × 240 s accumulation time). The infrared spectra (IR) were obtained with a Bruker AFS 66 FT-IR instrument with the KBr pellet technique (2 mg of product being ground together with 400 mg of dried KBr). The IR spectrum showed some absorptions typical for CO_2 in the region between 1300 and 1600 cm^{-1} (asymmetric stretching mode), since the measurements were performed in normal atmosphere. The combined IR and Raman spectra for each compound are displayed in Fig. 1b for Li[SCN] · $2\,H_2O$ and in Fig. 1a for Li[SCN], the exact frequencies and their assigned modes are shown in Table 1.

DSC/TG measurements

19.026 mg of commercial "Li[SCN] · $x\,H_2O$" were taken from the batch and placed on a DSC/TG alumina pan. This set-up was introduced into a Netzsch STA 449C instrument under a constant stream of pure argon. Even during this short transfer time the already hydrated material absorbed some

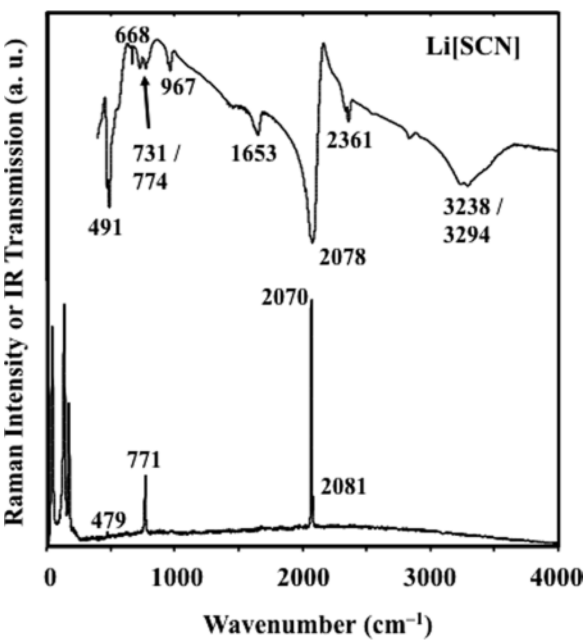

Fig. 1a. Vibrational spectra of Li[SCN].

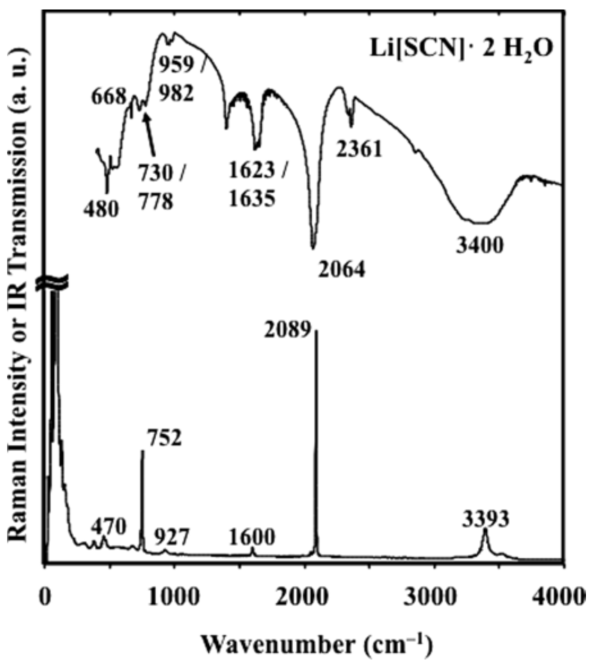

Fig. 1b. Vibrational spectra of Li[SCN] · $2\,H_2O$.

Table 2. Summary of the single-crystal X-ray diffraction structure determination data of Li[SCN] and Li[SCN] · $2\,H_2O$.

Compound	Li[SCN]	Li[SCN] · $2\,H_2O$
M_r	65.02	101.05
Crystal color	transparent, colorless	transparent, colorless
Crystal shape	irregular plate	elongated plate
Crystal size, mm^3	$0.05 \times 0.03 \times 0.01$	$0.12 \times 0.03 \times 0.02$
Crystal system	orthorhombic	orthorhombic
Space group (no.); Z	*Pnma* (62); 4	*Pnma* (62); 4
Lattice parameters: $a; b; c$, pm	1215.1(3); 373.6(1); 529.9(2)	572.1(3); 809.3(4); 966.9(4)
V, Å^3	240.6(1)	447.7(2)
$D_{calcd.}$, g cm^{-3}	1.80	1.50
$F(000)$, e^-	128	208
$\mu(MoK_\alpha)$, mm^{-1}	0.9	0.6
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD	Bruker X8 Apex II equipped with a 4 K CCD
Radiation; λ, pm; monochromator	MoK_α; 71.073; graphite	MoK_α; 71.073; graphite
Scan mode; T, K	ϕ- and ω-scans; 173(2)	ϕ- and ω-scans; 173(2)
Ranges $2\theta_{max}$, deg; h, k, l	58.65; $-16 \rightarrow 15$, $-4 \rightarrow 5$, $-5 \rightarrow 7$	58.01; $-6 \rightarrow 7$, $-8 \rightarrow 11$, $-13 \rightarrow 7$
Data correction	LP, SADABS [10]	LP, SADABS [10]
Transmission: min./max.	0.625/0.746	0.690/0.746
Reflections: measured/unique	1555/354	2661/649
Unique reflections with $F_o > 4\,\sigma(F_o)$	297	556
R_{int}/R_σ	0.0309/0.0319	0.0297/0.0301
Refined parameters	25	42
R_1[a]/wR_2[b]/GoF[c] (all refls.)	0.0365/0.0559/1.080	0.0338/0.0594/1.076
Factors x/y (weighting scheme)[b]	0.0192/0.15	0.0264/0.02
Max. shift/esd, last refinement cycle	< 0.00005	< 0.00005
$\Delta\rho_{fin}$ (max/min), e^- Å^{-3}	0.29 (75 pm to C)/−0.42 (78 pm to S)	0.21 (143 pm to C)/−0.28 (70 pm to S)
CSD number	425 060	425 061

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = [(F_o^2) + 2F_c^2]/3$ and x and y are constants adjusted by the program; [c] GooF(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.

moisture. After flushing the sample at room temperature for ten minutes, the mass balanced back to 19.026 mg, however. The substance was then heated with 1 K min^{-1} up to 550 °C for thermoanalytic studies (Fig. 2). DSC/TG measurements for anhydrous Li[SCN] turned out to be even more difficult.

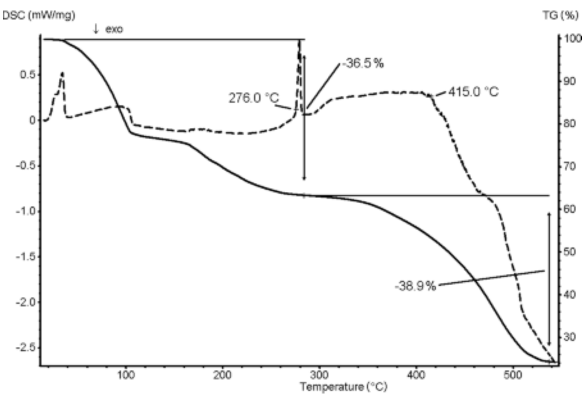

Fig. 2. Graph of the DSC/TG measurement on Li[SCN] · $2\,H_2O$.

A sample loaded under normal atmospheric conditions absorbed readily up to 5 weight-% of water, but showed comparable results as obtained for "Li[SCN] · $x\,H_2O$".

Crystallographic studies

Samples of Li[SCN] · $2\,H_2O$ were taken from the container and quickly immersed in dried polybutene oil (Sigma-Aldrich: $M_n \sim 320$, isobutylene $> 90\,\%$), while Li[SCN] was removed from the glove box already protected by the same dried polybutene oil. In both cases, the evaluation of the crystalline material took place under a polarization microscope. The selected specimens were mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen ($T = 173(2)$ K) froze the polybutene oil, thus keeping the crystals stationary and protected from oxygen and moisture in the air. 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 ($\lambda = 71.073$ pm). The intensity data were manipulated with the program package APEX2 [9] that came with the diffractometer. An empirical absorption correction was applied using SADABS [10].

The intensity data were evaluated, and the input files for solving and refining the crystal structure were prepared by XPREP [11]. The program SHELXS-97 [12, 13] delivered with the help of Direct Methods the positions of S, C, N and O (if present). The Li and H 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 [14, 15]. Doing further refinement cycles with all atoms being refined unrestained, the refinement converged and resulted in stable models for both crystal structures. Additional crystallographic details are described in Table 2. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 3. Table 4 displays selected interatomic distances and angles of the title compounds and their alkali-metal thiocyanate analogs.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-425060 for Li[SCN] · 2 H_2O and CSD-425061 for Li[SCN].

Results and Discussion

Optical spectra

The frequencies obtained from the infrared (IR) and Raman spectra of the title compounds compare well to the calculated frequencies for the free $[SCN]^-$ anion [6, 7] and to the vibrational frequencies reported in the literature [3, 8] (Table 4). The bands known for H_2O (about 1640 and 3400 cm^{-1}) appeared in the IR spectra of both compounds as well as the frequencies known for CO_2 (668 and 2360 cm^{-1}), since the measurements could not be performed under strictly inert conditions and the materials being very hygroscopic, but the Raman spectroscopic measurements done on single crystals in capillaries showed clearly the absence or the presence of water in Li[SCN] and Li[SCN] · 2 H_2O, respectively.

DSC/TG measurements

The DSC/TG measurement on Li[SCN] · 2 H_2O showed an endothermic effect below 40 °C connected

Table 3a. Fractional atomic coordinates and equivalent isotropic displacement parameters[a] of Li[SCN] (top) and Li[SCN] · 2 H_2O (bottom).

Atom	Wyckoff site	x/a	y/b	z/c	U_{eq} (pm^2)
Li	4*c*	0.3985(3)	1/4	0.0590(8)	247(9)
S	4*c*	0.18762(5)	1/4	0.85799(11)	142(2)
C	4*c*	0.10922(17)	1/4	0.1105(4)	125(5)
N	4*c*	0.05491(16)	1/4	0.2911(4)	188(5)
Li	4*c*	0.1073(5)	1/4	0.2833(3)	246(6)
S	4*c*	0.70072(7)	1/4	0.62914(5)	213(2)
C	4*c*	0.4603(3)	1/4	0.53326(18)	191(3)
N	4*c*	0.2983(2)	1/4	0.46250(18)	302(4)
O	8*d*	0.66201(14)	0.58204(11)	0.81819(10)	211(2)
H1	8*d*	0.681(3)	0.567(2)	0.9030(18)	497(54)
H2	8*d*	0.656(3)	0.493(2)	0.7777(19)	584(57)

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensors, here: $U_{eq} = 1/3(U_{11}+U_{22}+U_{33})$.

Table 3b. Anisotropic displacement parameters[a] U_{ij} (pm^2) of Li[SCN] (top) and Li[SCN] · 2 H_2O (bottom).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li	181(21)	319(27)	239(23)	0	−56(18)	0
S	123(3)	201(3)	103(3)	0	15(2)	0
C	96(10)	139(11)	140(12)	0	−49(9)	0
N	129(9)	299(12)	138(10)	0	0(8)	0
Li	165(12)	305(16)	267(17)	0	4(13)	0
S	195(2)	242(2)	202(3)	0	−25(2)	0
C	218(7)	197(7)	157(8)	0	40(7)	0
N	236(7)	436(9)	232(9)	0	−24(7)	0
O	203(4)	229(5)	200(5)	−16(4)	−16(4)	−6(3)

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

Table 4. Selected bond lengths (pm) and angles (deg) for Li[SCN] (right) and Li[SCN] · 2 H_2O (left).

Li[SCN] ·2 H_2O				Li[SCN]			
Li –	N	(1×)	204.8(4)	Li –	N	(1×)	205.9(5)
	O	(2×)	208.2(2)		N	(2×)	241.3(3)
	O	(2×)	213.4(2)		S	(2×)	266.4(3)
	N	(1×)	296.2(4)		S	(1×)	277.6(4)
	Li	(2×)	293.2(2)		Li	(2×)	315.5(7)
N –	C	(1×)	115.2(2)	N –	C	(1×)	116.2(3)
C –	S	(1×)	165.9(2)	C –	S	(1×)	164.3(2)
O –	H1	(1×)	84(16)	∢(Li – N – C)		(1×)	147.3(2)
	H2	(1×)	82(17)	∢(Li – N – C)		(2×)	110.6(1)
∢(H1 – O – H2)		(1×)	110(1)	∢(Li – S – C)		(2×)	104.9(1)
∢(Li – N – C)		(1×)	158.7(2)	∢(Li – S – C)		(1×)	102.9(1)
∢(N – C – S)		(1×)	177.6(2)	∢(N – C – S)		(1×)	179.1(2)

with virtually no decrease of mass. This may be attributed to either a phase transition or melting as found for $Ca[SCN]_2 \cdot 2\,H_2O$ [8]. The subsequently following loss of mass can be roughly separated into three steps. The first step ranges from room temperature to about 150 °C with a mass loss of 23.3 %, the second step ranges from 150 to 280 °C with about 13.2 % mass decrease, and the last one is finished at 538 °C. The first two steps (added up: 36.5 % mass loss) can be attributed to the loss of water, which would cause a decrease in mass by 17.8 % for each water molecule, thus meaning in addition 35.6 %. Because these two dehydration steps did not show the equivalent weight loss of 2 × 17.8 %, this behavior leaves no evidence for the formation of the monohydrate Li[SCN] · H_2O, which was postulated already, but never could be observed or isolated [5]. If one assumes a two-step dehydration to be correct, the composition of the intermediate would be close to Li[SCN] · 0.75 H_2O. Our measurements show furthermore that the dehydration is complete just before the melting point of Li[SCN] at 276 °C, which is indicated by an endothermic peak. Increasing the temperature further results in a slow decrease of mass resulting from the beginning decomposition shown by DSC at 415 °C. The yellow substance forming at this stage is found to be sulfur. But sulfur would account only for 33.0 % of the mass loss, the observed decrease in mass is more like 39.0 %, however. Elemental lithium and compounds such as $Li_2[C_2]$, Li_3N or $Li_2[CN_2]$ are not subliming, evaporating or decomposing [17] under ambient pressure and temperatures below 600 °C as used for the DTA/DSC/TG studies. Due to the set-up of the instrument we had no opportunity to check the composition of the residue or the vapor. Therefore, we compared our results to experiments with a similar compound under comparable conditions, *e. g.* the thermal analysis of $Li[N(CN)_2]$ [18]. In this case, the residual material was chemically analyzed to have the composition "$Li_{0.2}CN_{0.7}$". For our experiment, this would hypothetically mean a residual mass of 23.2 %, which is very close to our experimental value of 24.5 %.

Crystal structures

Both compounds crystallize in the orthorhombic space group *Pnma* (no. 62) with all atoms (Li, S, C and N) being located on special positions 4*c* ($y/b = {}^1\!/_4$ and ${}^3\!/_4$). In anhydrous Li[SCN], the Li^+ cations are surrounded octahedrally by three nitrogen atoms (d(Li–N) = 206 pm and 2 × 241 pm) and three sulfur atoms (d(Li–S) = 2 × 266 pm and 278 pm) from six different thiocyanate anions $[SCN]^-$ in a way that *fac*-$[LiN_3S_3]$ octahedra ($[Li(\mathbf{N}CS)_3(\mathbf{S}CN)_3]^{5-}$, Fig. 3a) result. In turn, each $[SCN]^-$ anion is surrounded by a trigonal antiprism of Li^+ cations (Fig. 3b). Along [010], the $[LiN_3S_3]$ octahedra are first condensed by sharing *trans*-oriented edges *via* one sulfur and one nitrogen atom to form chains $^1_\infty\{[Li(N,S)^e_{4/2}NS]\}$ and further through common *cis*-oriented edges *via* two nitrogen atoms to generate double chains $^1_\infty\{[LiN_{3/3}S_{2/2}S_{1/1})]\}$. A three-dimensional structure from the hexagonal rod-packing motif of these double chains (Fig. 4) is erected in such a way that on one hand corners of the double chains share their terminal sulfur atoms $^1_\infty\{[LiN_{3/3}S_{2/3}S_{1/3})]\}$ and on the other hand additional bonding contacts between them are formed via the covalent bonds of the thiocyanate units ($^-$S–C≡N: d(N≡C) = 116 pm, d(S–C) = 164 pm; ∢(N–C–S) = 179°). Thereby each $[SCN]^-$ anion is connecting three of the above-mentioned double chains of fused *fac*-$[LiN_3S_3]$ octahedra (Fig. 4).

In the dihydrate Li[SCN] · 2 H_2O, the lithium atom is surrounded in an almost octahedral fashion

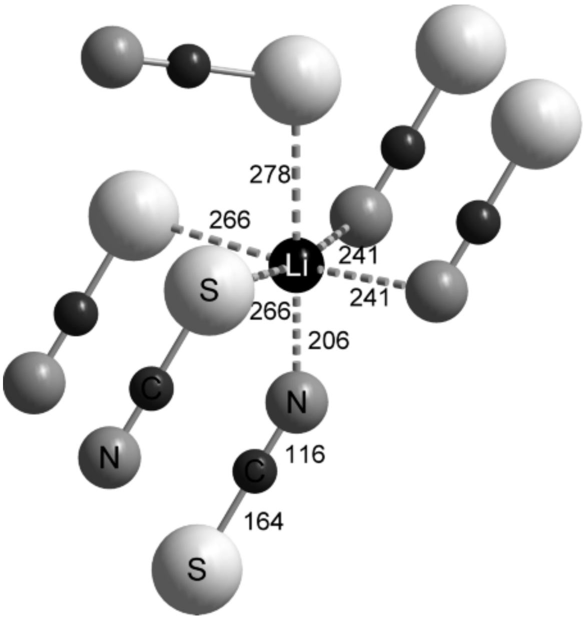

Fig. 3a. Coordination of Li^+ in Li[SCN].

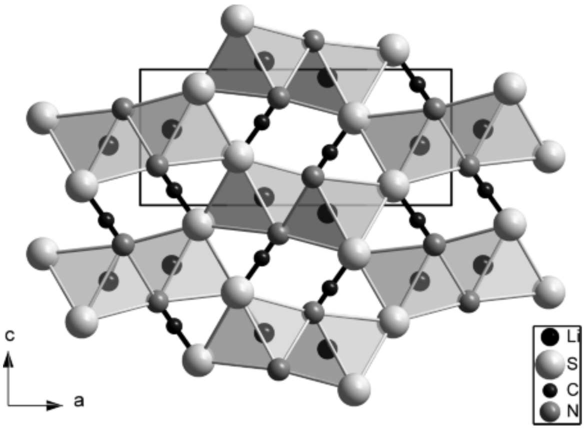

Fig. 4. View at the unit cell of Li[SCN] along [010].

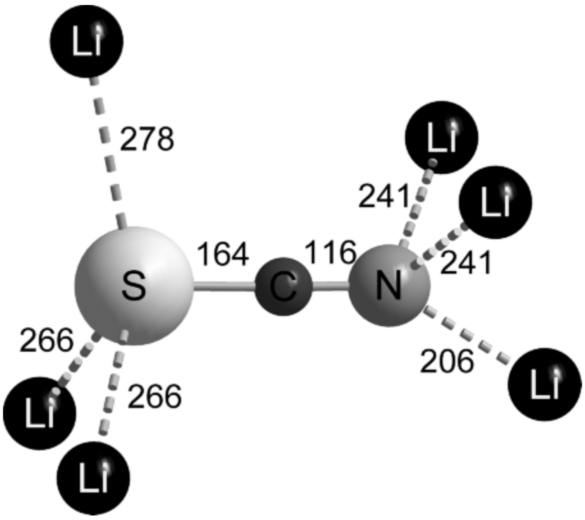

Fig. 3b. Coordination of $[SCN]^-$ in Li[SCN].

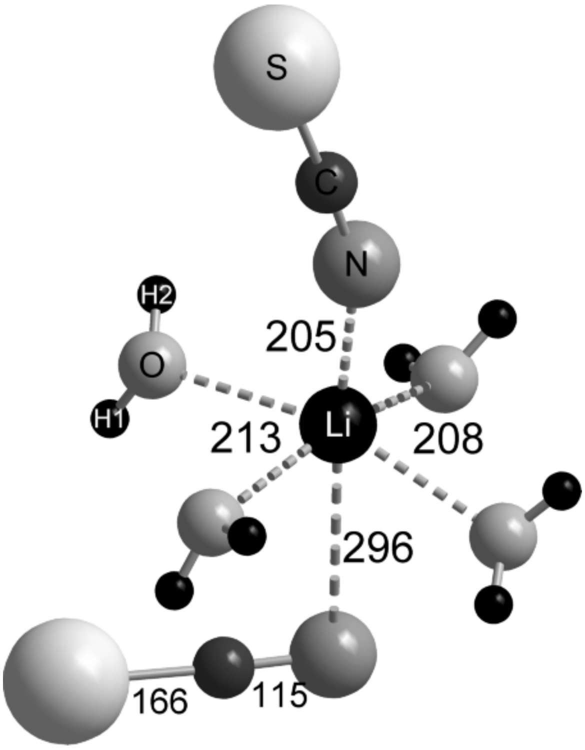

Fig. 5. Coordination of Li^+ in Li[SCN] · 2 H_2O.

by four water molecules (d(Li–O) = 2×208 pm and 2×213 pm) and two nitrogen atoms of two different $[SCN]^-$ anions as *trans*-octahedra $[Li(\mathbf{O}H_2)_4(\mathbf{N}CS)_2]^-$. One nitrogen atom with a Li–N distance of 205 pm happens to be very close to the sum of the ionic radii (205 pm) with its Li^+ partner according to Shannon [16], while the other Li–N contact of 296 pm might be best called a weak coordinative bond (Fig. 5). This Li–N contact with the rather large interatomic distance does not only complete the distorted octahedral environment of lithium, but also connects the *trans*-octahedra to each other forming $^{1}_{\infty}\{[Li(OH_2)_{4/2}(NCS)_{2/2}]\}$ chains (Fig. 6). These chains are packed next to each other to form a kind of

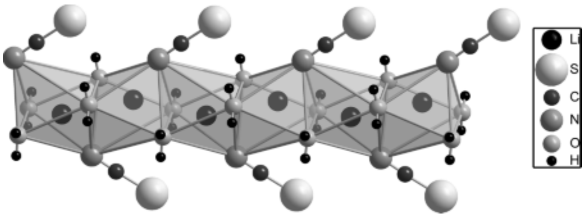

Fig. 6. $^1_\infty\{[Li(OH_2)_{4/2}(NCS)_{2/2}]\}$ chains in Li[SCN]·2H_2O.

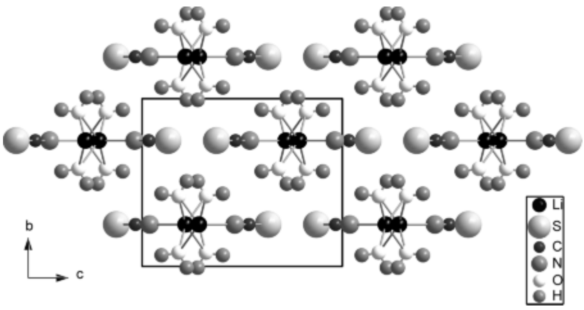

Fig. 7. View at the unit cell of Li[SCN] · 2 H_2O along [100].

layered structure, while the next layers are arranged in such a way that the chains are located in the grooves (Fig. 7). The thiocyanate anions ($^-$S–C≡N: d(N≡C) = 115 pm, d(S–C) = 166 pm; ∢(N–C–S) = 178°) have only two Li^+ cations as closest neighbors, but the connectivity between the layers is exclusively maintained by the hydrogen bonds of the water molecules (H_2O: d(O–H1) = 84 pm, d(O–H2) = 82 pm; ∢(H1–O–H2) = 110°). These relatively weak hydrogen bonds occur between the water molecules and the negatively charged sulfur atoms of the thiocyanate anions (S···H1–O: d(H1–O) = 84 pm, d(H1···S) = 273 pm, ∢(S···H1–O) = 138°; S···H2–O: d(H2–O) = 82 pm, d(H2···S) = 245 pm; ∢(S···H2–O) = 169°) within the hexagonal rod-packing motif (Fig. 7) of the $^1_\infty\{[Li(OH_2)_{4/2}(NCS)_{2/2}]\}$ chains.

Conclusion

The crystal structures of the lithium thiocyanates Li[SCN] and Li[SCN] · 2 H_2O have been successfully determined from single-crystal X-ray diffraction data. The vibrational spectra of both compounds show the results expected for ionic thiocyanates similar to that for the calcium thiocyanate analogs. DSC/TG measurements show a two-step dehydration of Li[SCN] · 2 H_2O with inequivalent weight losses indicating that a monohydrate reported as “Li[SCN] · H_2O” does not exist. The dehydration is finished completely just before the melting point of Li[SCN] at 276 °C. At higher temperatures Li[SCN] decomposes into elemental sulfur and a conglomerate of different compounds with the approximate general composition “$Li_{0.2}CN_{0.7}$” such as observed before for the thermal decomposition of Li[N(CN)$_2$].

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