Supplementary Information

Phase Characterization of Li[SCN] · THF

The X-ray powder diffraction (XRPD) pattern for structure determination was collected at room temperature on a laboratory powder diffractometer in *Debye-Scherrer* geometry (STADI P diffractometer from STOE, Cu-$K_{\alpha1}$ radiation from primary Ge(111)-*Johann*-type monochromator, Mythen 1 K detector from Dectris). The sample was sealed in a 0.5 mm borosilicate glass capillary (Hilgenberg glass, no. 14), which was spun during the measurement. The pattern was measured in a 2θ range from 5 to 110° applying a total scan time of 20 h.

Single-Crystal X-Ray Diffraction of Li[SCN] · 2 THF

The whole laboratory was cooled to roughly 8 °C on a Swabian winter day. Afterwards, a *Schlenk* flask with single crystals of Li[SCN] · 2 THF in a THF solution was cooled to 0 °C using an ice bath. Subsequently, a single crystal was selected and transferred to a watch glass with cooled perfluorinated oil using *Schlenk* techniques. Afterwards, it was mounted on a STADIVARI single-crystal X-ray diffractometer (STOE equipped with a Dectris Pilatus detector, a graded multilayer mirror monochromator, a Mo-K_{α} source and an Oxford cryosystem) and frozen on top of the sample holder by immediate cooling to 100 K. Finally, the experiment was started as soon as the low temperature was stable.

Elemental CHNS Combustion Analysis

Roughly 1 mg of Li[SCN] · THF were filled into a thin tin capsule (IVA Analysentechnik, Meerbusch, Germany), which was subsequently pleated in such a way that no argon remained within the capsule. Afterwards, the now airtight capsule was discharged, the actual mass of the sample was determined using a WXTS3DU ultra-microbalance (METTLER TOLEDO GmbH, Albstadt, Germany) and subsequently placed inside a vario MICRO cube (Elementar Analysentechnik, Langenselbold, Germany) together with roughly 1 mg of tungsten trioxide (WO_3: Elementar Analysentechnik, Langenselbold, Germany) placed inside another tin capsule, which is then wrapped around the original one as combustion support. The constant weight of the sample on the balance confirms the airtightness of the original capsule as a non-airtight capsule would gain weight over time, due to the sample taking up moisture from the atmosphere. The combustion analysis was conducted four times against cysteine (HEKAtech Analysentechnik, Wegberg, Germany) as standard and the samples were weighed out one after another leading to the shortest exposure time to the open argon atmosphere of about 10 minutes for the first experiment up to the longest one of roughly an hour for the last experiment.

Vibrational Spectroscopy

A powder sample of Li[SCN] · THF was carefully pestled with a mortar to avoid the release of THF as much as possible and sealed into a thin-walled glass capillary (Hilgenberg GmbH, glass no. 14) with a hot-wire in the argon atmosphere of a glove box. Afterwards, *Raman* spectra were obtained using a Typ V 010 labram single grating spectrometer (HORIBA Jobin Yvon, Bensheim, Germany; max. 1 mW) equipped with a He/Ne gas LASER with an excitation line at 632.8 nm and a resolution of 1 cm^{-1}. The ATR-FTIR spectrum was obtained by placing some the pestled powder into the beam of an ALPHA II FTIR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with an attenuated total reflection (ATR) unit.

Thermal Analysis of Li[SCN] · THF

169.6 mg of Li[SCN] · THF were filled into a silica crucible. Afterwards, the sample was exposed to atmospheric conditions for a few seconds during the transfer of the crucible into the measurement chamber of a Netzsch STA 449 instrument (Selb, Germany) located outside of the glove box. The exhaust gas of the TGA was analysed by a Balzers Prisma quadrupole mass spectrometer. The thermogravimetric analysis (TGA) of the sample was subsequently performed under protective nitrogen gas with a heating rate of 2 $K \cdot min^{-1}$ and a coupled exhaust gas analysis by a Balzers Prisma quadrupole mass spectrometer.

Differential scanning calorimetry (DSC) was conducted on a DSC 214 *Polyma* from Netzsch (Selb, Germany) 5.8 mg of Li[SCN] · THF were transferred into an aluminium pan, fitted with an aluminium lid and cold welded. To avoid the release of THF prior to the measurement, the sample was not pestled in advance. Afterwards, the aluminium pan was transferred into the DSC device and constantly flushed with 40 $mL \cdot min^{-1}$ of protective and 60 $mL \cdot min^{-1}$ of purging nitrogen gas. The measurement was conducted with a heating and cooling rate of 10 $K \cdot min^{-1}$ using a cold welded and pierced empty aluminium pan as reference.

Crystallographic Data

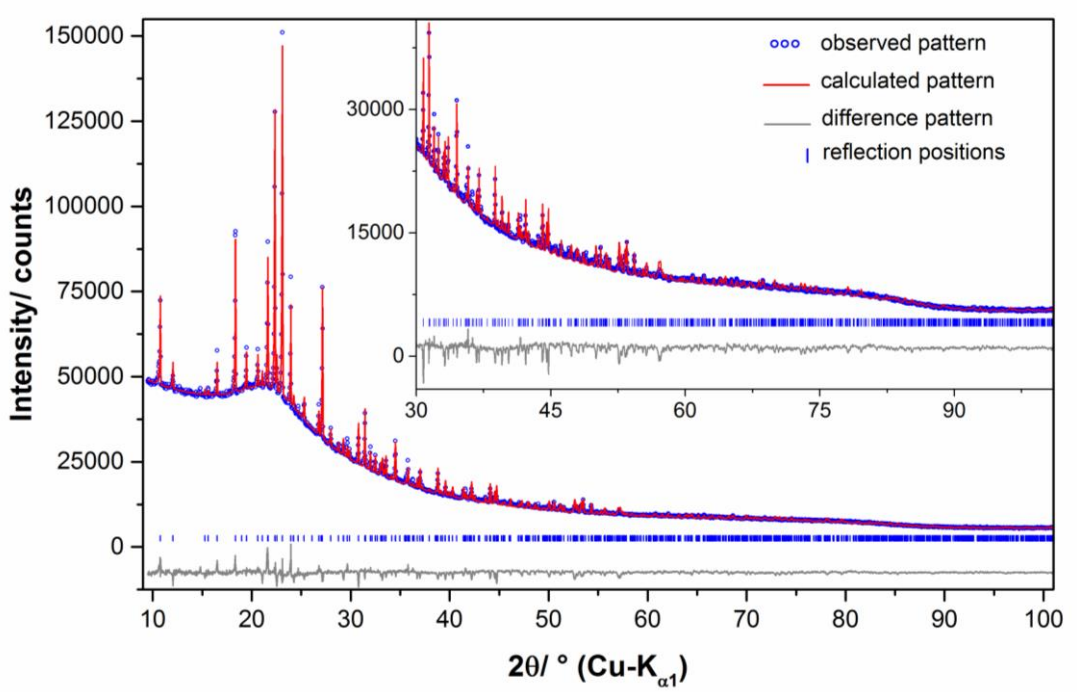

Figure S1. Final *Rietveld* refinement of the crystal structure of Li[SCN] · THF at ambient conditions, the region above $2\theta = 30°$ is enlarged for clarity (insert).

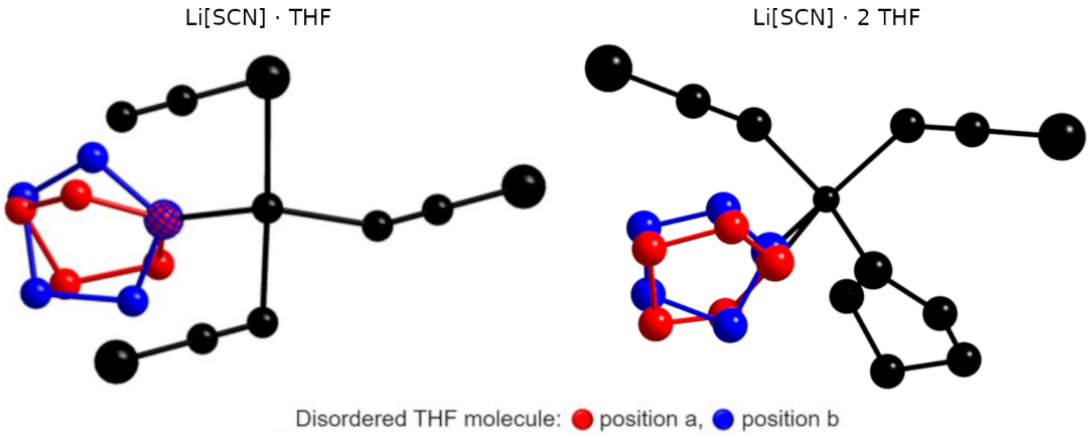

Figure S2. Positional disorder of the Li^+-bonded THF molecule (red and blue atoms and bonds) in the crystal structures of Li[SCN] · THF at room temperature (*left*) and Li[SCN] · 2 THF at 100 K (*right*).

Table S1. Crystallographic and *Rietveld*-refinement data of Li[SCN] · THF.

Compound name	Li[SCN] · THF
Molecular formula	Li[SCN] · C_4H_8O
Empirical formula	C_5H_8NLiOS
Molar mass, M / g · mol^{-1}	137.13
Temperature, T / K	295
Space group	$P2_1/c$ (no. 14)
a / pm	574.41(2)
b / pm	1643.11(6)
c / pm	830.15(3)
β / °	99.009(2)
Number of formula units, Z	4
Molar volume, V_m / cm^3 · mol^{-1}	116.52(1)
Calculated density, ρ_{cal} / g · cm^{-3}	1.177
Wavelength, λ / pm	154.06
R-exp / % [a)]	0.06
R-p / % [a)]	1.77
R-wp / % [a)]	2.55
R-F^2 / % [a)]	2.87
Number of variables	42

[a)] R-exp, R-p, R-wp and R-F^2 as defined in TOPAS (Bruker AXS) [1].

Table S2. *Wyckoff* sites, site symmetry, site-occupation probability (s.o.p), fractional atomic coordinates and isotropic displacement parameters of Li[SCN] · THF at ambient conditions.

Atom	**Site**	**Symmetry**	**s.o.p.**	***x* / *a***	***y* / *b***	***z* / *c***	***B* / Å^2**
Li	4e	1	1	0.109(7)	0.989(3)	0.360(7)	2.50(15)
C	4e	1	1	0.605(4)	0.920(1)	0.371(2)	2.50(15)
N	4e	1	1	0.782(3)	0.954(1)	0.400(2)	2.50(15)
S	4e	1	1	0.352(5)	0.871(1)	0.335(2)	2.50(15)
Oa	4e	1	0.53(4)	0.890(2)	0.908(1)	0.795(2)	2.50(15)
C1a	4e	1	0.53(4)	1.078(7)	0.867(3)	0.856(5)	2.50(15)
C2a	4e	1	0.53(4)	0.677(6)	0.899(3)	0.857(6)	2.50(15)
C3a	4e	1	0.53(4)	0.752(17)	0.836(4)	0.984(9)	2.50(15)
C4a	4e	1	0.53(4)	0.926(15)	0.796(3)	0.924(11)	2.50(15)
Ob	4e	1	0.47(4)	0.890(2)	0.908(1)	0.795(2)	2.50(15)
C1b	4e	1	0.47(4)	0.957(15)	0.8400(2)	0.773(7)	2.50(15)
C2b	4e	1	0.47(4)	0.740(7)	0.927(3)	0.922(4)	2.50(15)
C3b	4e	1	0.47(4)	0.760(17)	0.844(4)	1.001(9)	2.50(15)
C4b	4e	1	0.47(4)	0.80(2)	0.789(2)	0.862(13)	2.50(15)

Table S3. Selected bond lengths (d / pm) and angles ($\sphericalangle$ / °) in Li[SCN] · THF at ambient conditions.

Atoms	***d* / pm**	**Atoms**	**$\sphericalangle$ / °**
Li–N	190(3)	N–Li–N	100(2)
	225(5)	N–Li–Oa/b	104(2)
Li–Oa/b	194(5)	N–Li–S	114(2)
Li–S	250(5)	Oa/b–Li–S	111(2)

Table S4. Crystallographic and single-crystal refinement data of Li[SCN] · 2 THF.

Compound name	Li[SCN] · 2 THF
Molecular formula	Li[SCN] · 2 C_4H_8O
Empirical formula	$C_9H_{16}NLiO_2S$
Crystal colour	colourless, transparent
Crystal shape	lath-shaped
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
a / pm	1132.73(6)
b / pm	1637.98(9)
c / pm	1264.86(7)
β / °	94.393(3)
Number of formula units, Z	8
Molar volume, V_m / $cm^3 \cdot mol^{-1}$	176.14(2)
Calculated density, ρ_{cal} / $g \cdot cm^{-3}$	1.188
Diffractometer	StadiVari (STOE)
Radiation	Mo-K_α (λ = 71.07 pm)
Ranges, $2\theta_{max}$ / °; $\pm h$, $\pm k$, $\pm l$	63.76; 16, 24, 18
Temperature, T / K	100(2)
Absorption coefficient, μ / mm^{-1}	0.250
Measured / unique reflections	182393 / 7860
R_{int} / R_σ	0.045 / 0.025
R_1[a] /wR_2[b] / GooF[c] (all reflections)	0.065 / 0.116 / 1.107
Residual electron density, $10^{-6} \cdot pm^{-3}$ (max./min)	0.43 / –0.52

[a] $R_1 = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$;
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ with $P = [(F_o^2) + 2F_c^2]/3$;
[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 parameters.

Table S5. Selected interatomic distances (d / pm) and angles ($\sphericalangle$ / °) in Li[SCN] · 2 THF.

Atoms	***d* / pm**	**Atoms**	**$\sphericalangle$ / °**	**Atoms**	**$\sphericalangle$ / °**
Li1–O1	190.9(2)	O1–Li1–O2	114.46(10)	O2–Li1–N1	105.45(9)
Li1–O2	191.3(2)	O1–Li1–N1	113.21(9)	O2–Li1–N2	115.77(9)
Li1–N1	205.4(2)	O1–Li1–N2	109.31(10)	N1–Li1–N2	97.41(9)
Li1–N2	207.9(2)				
Li2–O4b	182.3(4)	O3–Li2–O4a	105.69(11)	O4a–Li2–N1	115.52(11)
Li2–O3	190.5(2)	O3–Li2–O4b	109.47(15)	O4b–Li2–N2	106.66(15)
Li2–O4a	198.4(3)	O3–Li2–N2	114.14(10)	O4b–Li2–N1	117.64(15)
Li2–N2	201.9(2)	O3–Li2–N1	108.67(10)	N2–Li2–N1	100.18(9)
Li2–N1	203.0(2)	O4a–Li2–N2	112.83(11)		

Table S6. Site-occupation probability (s.o.p.), fractional atomic coordinates and equivalent or isotropic displacement parameters (U_{eq}/pm^2 [a)], U_{iso}/pm^2) for Li[SCN] · 2 THF at 100 K with all atoms on the general *Wyckoff* site 4*e*. Hydrogen-atom data are omitted for clarity.

Atom	**s.o.p.**	***x* / *a***	***y* / *b***	***z* / *c***	U_{eq}	U_{iso}
Li1	1	0.42174(17)	0.56407(12)	0.24965(14)	261(4)	–
Li2	1	0.90798(17)	0.95266(11)	0.23504(15)	260(4)	–
S1	1	0.75845(3)	0.17928(2)	0.07862(3)	371(1)	–
C1	1	0.85265(9)	0.11128(6)	0.12662(8)	221(2)	–
N1	1	0.91947(9)	0.06172(6)	0.16038(7)	259(2)	–
S2	1	0.22074(3)	0.36372(2)	0.11979(3)	415(1)	–
C2	1	0.34175(10)	0.41150(6)	0.16085(8)	237(2)	–
N2	1	0.42845(10)	0.44603(6)	0.18994(7)	279(2)	–
O1	1	0.21159(7)	0.07399(5)	0.16768(6)	275(2)	–
C11	1	0.32383(10)	0.11500(8)	0.18965(9)	313(3)	–
C12	1	0.41188(10)	0.06980(8)	0.12638(10)	333(3)	–
C13	1	0.33335(11)	0.03711(8)	0.03300(9)	307(2)	–
C14	1	0.22349(11)	0.01301(7)	0.08596(9)	296(2)	–
O2	1	0.43625(7)	0.64998(5)	0.14896(6)	257(2)	–
C21	1	0.54114(11)	0.65561(7)	0.09056(9)	306(3)	–
C22	1	0.53931(12)	0.74156(8)	0.04710(11)	388(3)	–
C23	1	0.48859(13)	0.78938(8)	0.13569(12)	421(3)	–
C24	1	0.39750(13)	0.73086(8)	0.17445(11)	382(3)	–
O3	1	0.71652(7)	0.45839(5)	0.17214(6)	286(2)	–
C31	1	0.83384(10)	0.48458(8)	0.21017(9)	294(2)	–
C32	1	0.90606(12)	0.48662(9)	0.11471(10)	376(3)	–
C33	1	0.84567(14)	0.42057(9)	0.04510(11)	459(4)	–
C34	1	0.71681(12)	0.43101(8)	0.06385(9)	345(3)	–
O4a	0.653(4)	0.87000(17)	0.85763(11)	0.14122(15)	–	227(5)
C41a	0.653(4)	0.85493(19)	0.78900(12)	0.21446(2)	–	288(5)
C42a	0.653(4)	0.90424(19)	0.71697(12)	0.15952(17)	–	341(5)
C43a	0.653(4)	0.9987(3)	0.75232(16)	0.0992(2)	–	442(6)
C44a	0.653(4)	0.9483(3)	0.83394(14)	0.06472(19)	–	305(6)
O4b	0.347(4)	0.8893(4)	0.8615(2)	0.1527(3)	–	254(9)
C41b	0.347(4)	0.8357(4)	0.7829(2)	0.1807(4)	–	312(9)
C42b	0.347(4)	0.9507(4)	0.7343(2)	0.2054(3)	–	365(10)
C43b	0.347(4)	0.0314(3)	0.7640(2)	0.1258(3)	–	237(7)
C44b	0.347(4)	0.9781(4)	0.8394(2)	0.0767(3)	–	226(9)

[a)] $U_{eq} = {}^1/_3(U_{22}+1/\sin^2\beta(U_{11}+U_{22}+2U_{12}\cos\beta))$.

Table S7. Anisotropic displacement parameters (U_{ij}/pm^2) [a] of Li[SCN] · 2 THF at 100 K.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li1	260(9)	285(9)	245(9)	22(7)	64(7)	7(7)
Li2	239(9)	276(9)	268(9)	15(7)	52(7)	4(7)
S1	424(2)	332(2)	364(2)	48(1)	84(1)	160(1)
C1	259(5)	237(5)	175(4)	–13(4)	67(4)	–25(4)
N1	287(5)	282(4)	211(4)	20(3)	35(4)	3(4)
S2	315(2)	500(2)	422(2)	73(1)	–28(1)	–173(1)
C2	260(5)	246(5)	210(5)	30(4)	53(4)	13(4)
N2	270(5)	310(5)	259(4)	–34(4)	44(4)	–26(4)
O1	241(4)	326(4)	268(4)	–90(3)	93(3)	–51(3)
C11	245(5)	418(6)	279(5)	–73(5)	43(4)	–82(5)
C12	224(5)	455(7)	323(6)	23(5)	47(5)	14(5)
C13	316(6)	359(6)	261(5)	–11(4)	114(5)	20(5)
C14	315(6)	319(6)	264(5)	–91(4)	90(4)	–33(5)
O2	278(4)	269(4)	235(4)	26(3)	87(3)	18(3)
C21	302(6)	349(6)	284(5)	70(5)	131(5)	35(5)
C22	350(7)	405(7)	420(7)	157(6)	112(6)	–2(5)
C23	423(7)	287(6)	553(8)	15(6)	41(6)	–29(5)
C24	438(7)	292(6)	438(7)	20(5)	182(6)	71(5)
O3	246(4)	405(4)	216(4)	–67(3)	70(3)	–65(3)
C31	225(5)	379(6)	281(5)	–14(5)	45(4)	–42(4)
C32	318(6)	453(7)	379(7)	–22(5)	159(5)	–36(5)
C33	583(9)	430(7)	400(7)	–124(6)	284(7)	–45(7)
C34	462(7)	383(6)	194(5)	–40(4)	54(5)	–82(5)

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

Vibrational Data

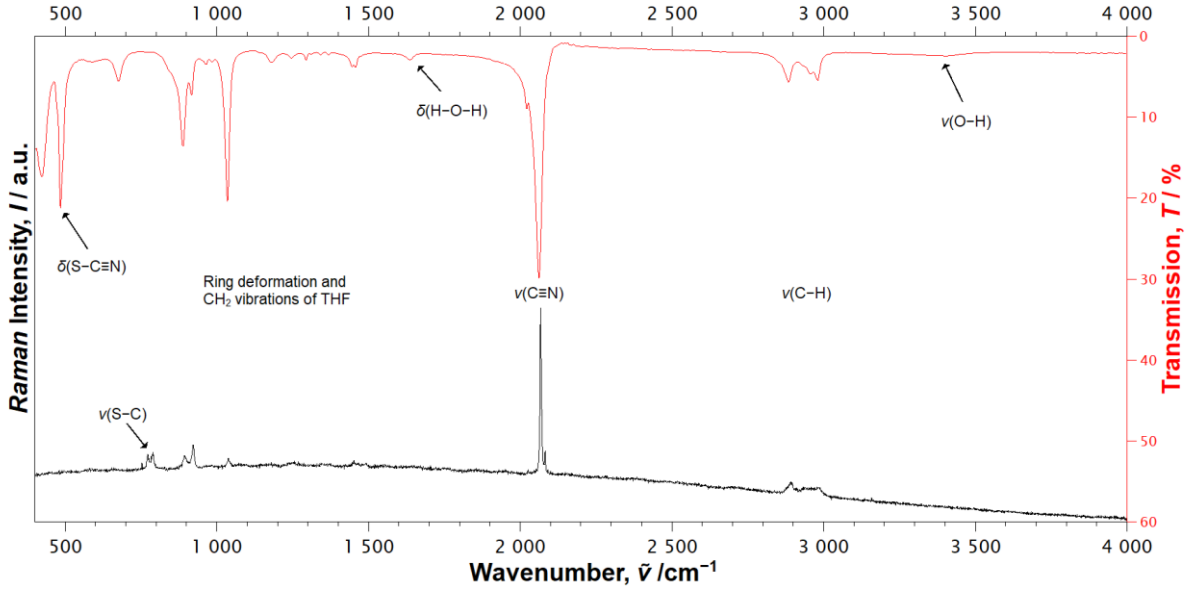

Figure S3. Combined and full vibrational spectra (ATR-FTIR, red line, *top*; *Raman*, black line, *bottom*) of Li[SCN] · THF.

References

[1] Bruxer-AXS, *TOPAS 6.0: Software for Bragg and PDF Refinements Including Profile Fitting Techniques and Related Applications*, Karlsruhe, **2017**.