Electronic Supporting Information

A 32 vertex polyhedron via supramolecular assembly of silanedithiolate silanolate units

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Experimental

All reactions are carried out under inert atmosphere using modified Schlenk techniques or a glove box. Solvents are dried over Al_2O_3 columns by the PureSolv solvent purification system. NMR spectra (^{1}H, ^{7}Li, ^{13}C, ^{29}Si) have been recorded on a Bruker AMX 360 using external references at 298 K. Mass spectra have been measured using an Agilent 5975C inert XL MSD with SIS direct insertion probe (EI) and Bruker Daltonics Biflex IV + micrOTOF (MALDI-TOF). Elemental analysis have been performed using a Hekatech Euro EA. Compound **1** was prepared according to a modified literature procedure.[1, 2]

Synthesis of **4**

In a three-necked-round-bottom flask were placed 10 ml THF and cooled to -80°C. Then a slight stream of H_2S was passed through the solution for ten minutes and 1.4 ml *n*-BuLi (2.2 mmol, Sigma Aldrich, Germany) in hexane were added. This mixture was stirred for ten minutes at -80°C and allowed to warm to room temperature. After all the excess H_2S has evaporated the vessel was recooled to -80°C and 0.31 g $DmpSiCl_3$ (0.7 mmol) dissolved in 10

ml of THF are added slowly via a dropping funnel. Stirring was continued for one hour at -80°C and the reaction mixture was allowed to warm to room temperature over a period of 3 hours. Then the solvent was removed in vacuum and the white crystalline residue was extracted with 20 ml of pentane. After some days crystals in the form of blocks could be isolated. Yield: 0.29 g (91 %). M.p.: 81° (dec.) ^{1}H-NMR (d_8THF, 360.13 MHz): 2.11 (s, 12H), 2.21 (s, 6H), 6.68 (d, 2H, J = 7.6 Hz), 6.73 (s, 4H), 7.21 (t, 1H, J = 7.6 Hz) ^{13}C-NMR (THF, d_8THF cap, 90.56 MHz) 18.60 (p-CH_3), 19.67 (o-CH_3), 125.51, 126.40, 133.03, 134.36, 134.84, 135.14, 140.21, 144.38 ^{7}Li-NMR (THF, d_8THF cap, 139.96 MHz): -1.8 (s) ^{29}Si-NMR (THF, d_8THF cap, 71.54 MHz): 2.3 (s). IR (KBr): 3041 (w), 2969 (s), 2912 (s), 2857 (s), 2731 (ms), 2541 (ms), 2359 (w), 1610 (s), 1557 (s), 1444 (vs), 1377 (s), 1178 (s), 1122 (ms), 1087 (s), 1034 (ms), 920 (ms), 849 (vs), 809 (vs), 749 (s), 731 (s), 570 (vs). Elemental analysis (%) for $C_{116}H_{148}Cl_2Li_{14}O_4S_8Si_4$ (= $C_{96}H_{100}Cl_2Li_{14}O_4S_8Si_4$ • 4 C_5H_{12}): C 65.00, H 6.96; found: C 64.83, H 6.95. MS (EI, 70eV): 884 ([DmpSi(SLi)$_2$OLi]$_2^+$, 0.1 %), 854 ([DmpSi(SLi)$_2$OLi]$_2^+$-Li_2O, 1 %), 816 ([DmpSi(SLi)$_2$OLi]$_2^+$-Li_2O-LiSH, 60 %), 503 ([DmpSi(SLi)$_2$OLi]$_2^+$-DmpSOHLi_3, 60%), 339 (DmpSi$^+$-2H, 100 %). MS (MALDI-TOF, THF solutition on DTCB matrix): 424 (DmpSi(SH)$_2$OH$^+$).

Crystal structure determination

The crystal structures were determined with a Bruker APEX-II CCD diffractometer using graphite-monochromatized MoK_α radiation (0.71073 Å). Structures were solved by direct methods and refined using the SHELXL and SHELXS suite of programs.[3] Further details are listed in Table S1. Crystallographic data for this paper can be obtained free of charge quoting CCDC 883190, 883191 and 883192 from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 – Summary of structural and refinement data of **4**, **4'** and **4''.**

	4	**4'**	**4''**
Empirical formula	$C_{96}H_{100}Cl_2Li_{14}O_4S_8Si_4$ * 2 C_5H_{12}	$C_{96}H_{100}Cl_2Li_{14}O_4S_8Si_4$ * 4 C_5H_{12}	$C_{96}H_{100}Cl_2Li_{14}O_4S_8Si_4$ * 5 C_6H_6
Formula weight	1999.04	2143.24	2245.20,
Crystal description	block, colorless	block, colorless	block, colorless
Crystal size [mm]	0.26 x 0.24 x 0.16	0.30 x 0.28 x 0.16	0.38 x 0.38 x 0.32
Temperature [K]	95	95	95
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	triclinic, P -1	tetragonal, I -4	triclinic, P -1
Unit cell dimensions			
a [Å]	13.929(3)	15.287(3)	14.445(2)
b [Å]	16.604(3	15.287(3)	16.804(3)
c [Å]	24.310(4)	25.661(5)	27.691(3)
α [deg]	98.031(14)	90	102.661(13)
β [deg]	94.466(15)	90	90.088(12)
γ [deg]	96.054(15)	90	110.203(13)
Volume [Å^3]	5511.6(18)	5997(2)	6132.7(17)
Z	2	2	2
Calculated density	1.205	1.187	1.216
F(000)	2104	2272	2356
Linear absorption coefficient μ [mm^{-1}]	0.302	0.281	0.279
Theta range for data collection [deg]	2.51 to 26.0	2.73 to 26.00	2.51 to 26.00
Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -4 ≤ l ≤ 29	0 ≤ h ≤ 18, 0 ≤ k ≤ 18, 0 ≤ l ≤ 31	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -10 ≤ l ≤ 34
Reflections collected / unique	23361 / 21637	3232 / 3226	25420 / 24099
R(int)	0.0352	0.0696	0.0335
Completeness to theta	99.9%	99.5%	99.9%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameter	21637 / 1313 / 0	3226 / 358 / 12	24099 / 1416 / 0
Goodness-of-fit on F^2	1.051	1.007	1.016
Absorption correction	Empirical	empirical	Empirical
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1054	R1 = 0.0584, wR2 = 0.1277	R1 = 0.0476, wR2 = 0.1098
R indices (all data)	R1 = 0.0791, wR2 = 0.1192	R1 = 0.0814, wR2 = 0.1409	R1 = 0.0655, wR2 = 0.1209
Largest diff. peak and hole [e/Å^3]	0.537 and -0.427	0.346 and -0.303	0.538 and -0.600

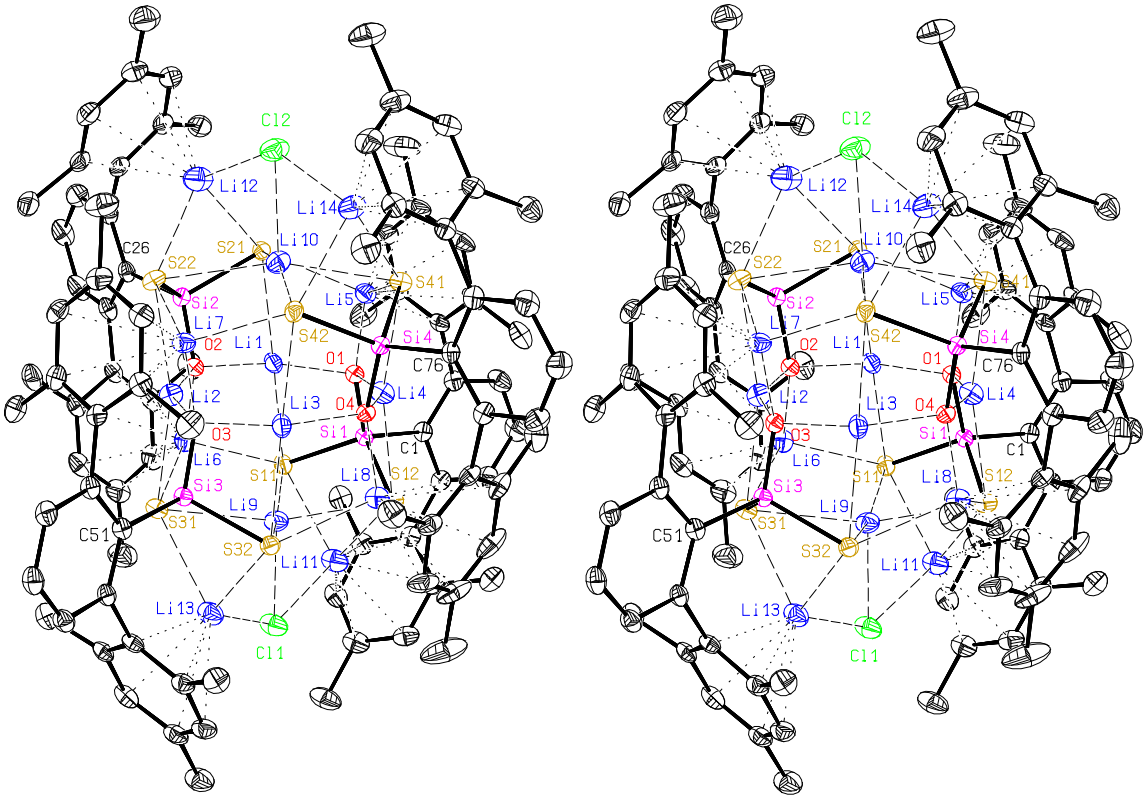

Fig. S1 - ORTEP-Stereo-plot of **4** showing the atomic numbering scheme for the inorganic core and the quaternary carbon atoms directly bonded to it. The probability ellipsoids are drawn at the 50% probability level. The *n*-pentane molecules are omitted as well as the H atoms for clarity reasons. The lithium-chalcogen contacts are plotted with dashed lines, the contacts between the Li^+ cations and the mesityl ring atoms in the cation-π complexes are drawn with dotted lines. For a more detailed view on the inorganic core see Fig. S2.

Table S2 – Comparison of averaged bond lengths in the three different polymorphs of **4**. Values are given in Å.

	4	**4'**	**4''**
Si1-O1	1.614(2)	1.617(4)	1.617(2)
Si1-C1	1.918(3)	1.924(6)	1.926(2)
Si1-S1	2.112(1)	2.112(2)	2.115(1)
Si1-S2	2.115(1)	2.112(2)	2.119(1)
O-Li	1.878(5)	1.884(11)	1.885(4)
S-Li	2.602(5)	2.602(11)	2.614(4)
Li-Cl	2.405(5)	2.378(11)	2.384(5)

Table S3 – Bond lengths of **4** in Å.

Si1 –O1	1.6122(19)	Si2 -O2	1.617(2)	Si3 -O3	1.613(2)	Si4 -O4	1.6122(19)
Si1 –C1	1.919(3)	Si2 –C26	1.919(3)	Si3 –C51	1.913(3)	Si4 –C76	1.919(3)
Si1 –S12	2.1112(11)	Si2 –S21	2.1104(11)	Si3 –S31	2.1124(11)	Si4 –S42	2.1134(11)
Si 1 –S11	2.1115(11)	Si2 –S22	2.1137(11)	Si3 –S32	2.1158(11)	Si4 –S41	2.1173(11)
S11 -Li	2.517(5)	S21 –Li5	2.535(5)	S31 –Li6	2.561(5)	S41 –Li5	2.561(5)
S11 –Li11	2.534(6)	S21 –Li1	2.606(5)	S31 –Li2	2.581(5)	S41 –Li4	2.607(5)
S11 –Li1	2.578(5)	S21 –Li10	2.644(5)	S31 –Li13	2.637(6)	S41 –Li14	2.610(5)
S11 –Li9	2.826(5)	S21 –Li12	2.716(6)	S31 –Li9	2.684(5)	S41 –Li10	2.660(5)
S12 –Li8	2.542(5)	S22 –Li7	2.481(5)	S32 –Li8	2.518(5)	S42 –Li7	2.515(5)
S12 –Li11	2.598(6)	S22 –Li12	2.500(6)	S32 –Li13	2.546(6)	S42 –Li14	2.558(6)
S12 –Li4	2.622(5)	S22 –Li2	2.578(5)	S32 –Li3	2.588(5)	S42 –Li3	2.588(5)
S12 –Li9	2.623(5)	S22 –Li10	2.736(5)	S32 –Li9	2.672(5)	S42 –Li10	2.744(5)
O1 –Li5	1.855(5)	O2 –Li6	1.845(5)	O3 –Li7	1.840(5)	O4 –Li8	1.845(5)
O1 –Li4	1.900(5)	O2 –Li1	1.887(5)	O3 –Li3	1.887(5)	O4 –Li3	1.885(5)
O1 –Li1	1.903(5)	O2 –Li2	1.904(5)	O3 –Li2	1.900(5)	O4 –Li4	1.890(5)

Table S4 – S-Li-S angles in **4**. Values are given in deg.

S11-Li1-S21	167.4(2)	S22-Li2-S31	164.7(2)
S11-Li6-S31	111.58(19)	S22-Li10-S42	97.85(17)
S11-Li11-S12	82.50(16)	S31-Li9-S11	99.29(17)
S12-Li9-S11	76.68(13)	S32-Li8-S12	107.28(18)
S12-Li9-S32	100.63(18)	S32-Li9-S31	78.71(14)
S12-Li9-S31	164.0(2)	S32-Li9-S11	163.4(2)
S21-Li5-S41	107.33(18)	S32-Li13-S31	81.85(16)
S21-Li10-S41	101.43(17)	S41-Li4-S12	166.6(2)
S21-Li10-S22	78.22(14)	S41-Li10-S22	162.4(2)
S21-Li10-S42	163.7(2)	S41-Li10-S42	77.48(14)
S22-Li12-S21	81.07(17)	S42-Li14-S41	81.77(15)
S22-Li7-S42	111.54(18)	S42-Li3-S32	166.7(2)

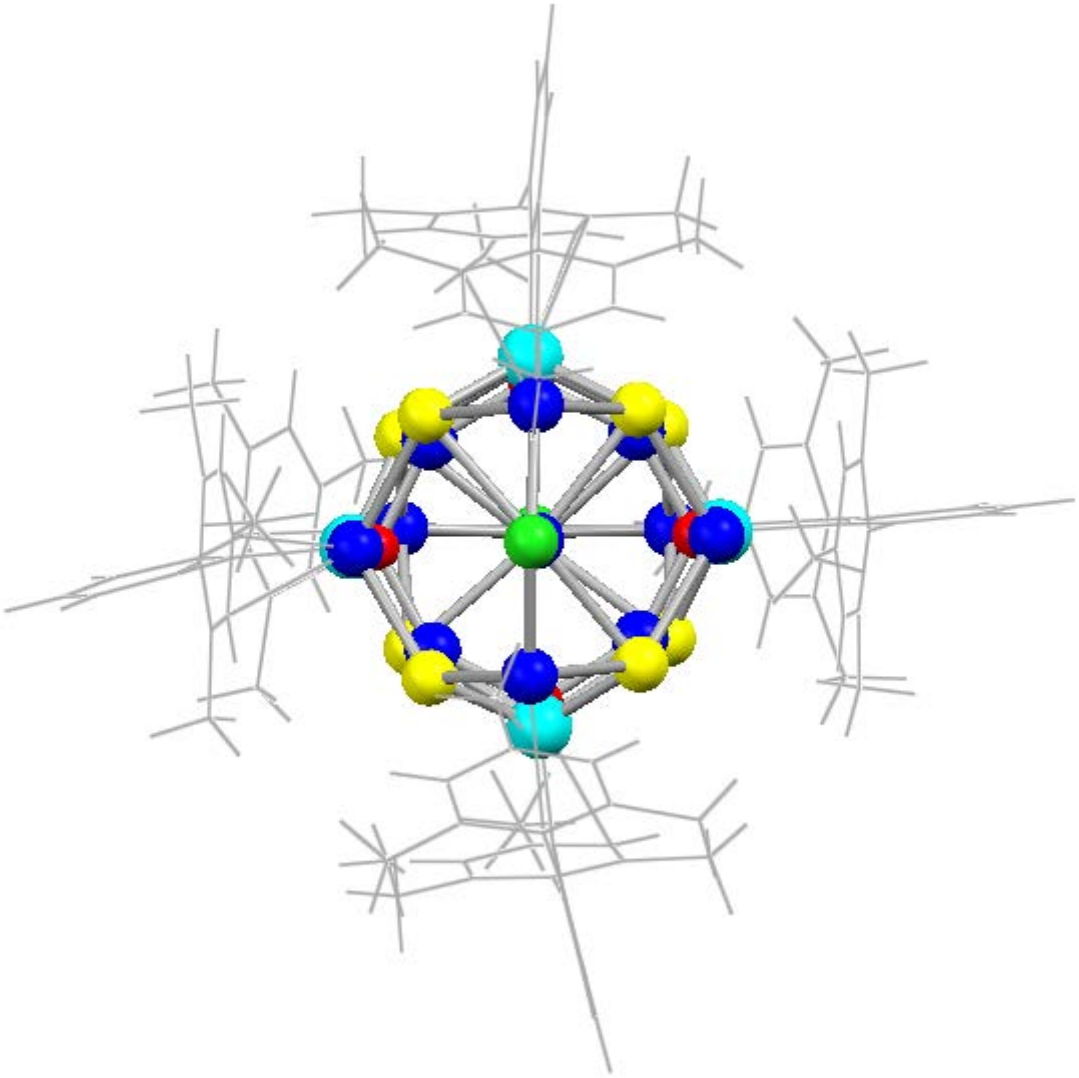

Fig. S2 – Top view on the 100 plane of **4**. Carbon and hydrogen atoms are drawn as wireframe in gray. Color code: blue = lithium, red = oxygen, cyan = silicon, yellow = sulfur, green = chlorine.

References

1. R. Pietschnig, F. Belaj and J. J. Tirrée, *Organometallics*, 2004, 23, 4897-4901.
2. R. Simons, S. T. Haubrich, B. V. Mork, M. Niemeyer and P. P. Power, *Main Group Chem.*, 1998, 2, 275-283.
3. G. Sheldrick, *Acta Cryst. C*, 2008, A64, 112.