Crystal chemistry of layered structures formed by linear rigid silyl-capped molecules

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Crystal chemistry of layered structures formed by linear rigid silyl-capped molecules - Experimental details

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1. Single crystal diffraction

Crystals of the title compounds were embedded in perfluorinated oil and attached to a thin glass fiber. Intensity data were collected using MoKα radiation (λ = 0.71073 Å) on a Bruker Kappa APEX II diffractometer with κ-geometry and a 0.7 mm collimator. Due to weak diffraction, notably of platy crystals, in some cases crystals of a size slightly exceeding the beam diameter were used to maximize intensities. It has been shown that this generally does not affect the refinement quality (Tan & Ng, 2014). Full spheres were collected in fine-sliced ω- and φ-scans up to a 2θ angle where reflections were still visible in preliminary scans, with the exception of polymorph III of oxB-SEM, which was only measured up to 2θ = 27.6°, albeit scattering to higher angles. In general frame data were reduced to intensity values with SAINT-Plus and corrected for absorption effects using the multi-scan approach implemented in SADABS or TWINABS (Bruker, 2008). The structures were solved by charge-flipping implemented in SUPERFLIP (Palatinus & Chapuis, 2007) and refined against F values...
with JANA2006 (Petříček et al., 2014). Non-H atoms were refined with anisotropic ADPs. H atoms were placed at computed positions and refined as riding on the parent C-atoms. Details of data collections and structure refinements are compiled in Tables 1–4. Deviations from the standard procedure and specific remarks will be given in the following sections.

Table 1. Details on the crystal structure determinations of the methylthio compounds BSEM (1), TSEM (2), and both of DSEM (4).

|                      | BSEM            | TSEM            | DSEM, polytype I | DSEM, polytype II |
|----------------------|-----------------|-----------------|------------------|-------------------|
| formula              | C$_{22}$H$_{30}$S$_2$Si$_2$ | C$_{20}$H$_{28}$S$_3$Si$_2$ | C$_{22}$H$_{32}$O$_2$S$_3$Si$_2$ | C$_{22}$H$_{32}$O$_2$S$_3$Si$_2$ |
| molecular weight     | 414.8           | 420.8           | 480.8            | 480.8             |
| crystal color        | clear yellow    | clear yellow    | clear yellow     | clear yellow      |
| crystal habit        | plate           | fragment        | rhombic prism    | plate             |
| crystal size [mm$^3$]| 0.77×0.25×0.03  | 0.09×0.07×0.01  | 0.87×0.66×0.03   | 0.60×0.51×0.01    |
| temperature [K]      | 100             | 100             | 100              | 100               |
| space group          | C2/c            | I2/c            | C2/c             | Pccn              |
| a [Å]                | 34.148(6)       | 34.434(3)       | 34.344(2)        | 33.630(10)        |
| b [Å]                | 6.8690(12)      | 6.7415(4)       | 8.1665(5)        | 8.271(2)          |
| c [Å]                | 10.3442(18)     | 10.1978(8)      | 20.0791(12)      | 19.717(6)         |
| α [°]                | 90              | 90              | 90               | 90                |
| β [°]                | 98.343(8)       | 96.889(5)       | 100.532(2)       | 90                |
| γ [°]                | 90              | 90              | 90               | 90                |
| V [Å$^3$]            | 2400.7(7)       | 2350.8(3)       | 5536.7(6)        | 5484(3)           |
| Z                    | 4               | 4               | 8                | 8                 |
| Z’                   | $\frac{1}{2}$  | $\frac{1}{2}$  | 1                | 1                 |
| density [g cm$^{-3}$]| 1.147           | 1.189           | 1.153            | 1.164             |
| θ range [°]          | 1.2–35.0        | 1.2–30.2        | 1.2–27.6         | 1.2–25.1          |
| μ [mm$^{-1}$]        | 0.326           | 0.419           | 0.369            | 0.373             |
| Trans. coeff.        | 0.91, 0.99      | 0.97, 1.00      | 0.74, 0.99       | 0.90, 1.00        |
| reflections total    | 38270           | 29932           | 77428            | 48785             |
| reflections unique   | 5255            | 3045            | 6397             | 4671              |
| reflections obs. [I > 3σI] | 4193 | 2366 | 4903 | 3185 |
| parameters           | 118             | 115             | 262              | 262               |
| $R_{int}$            | 0.0347          | 0.0643          | 0.0380           | 0.0792            |
| h                    | -54–54          | -45–48          | -44–44           | -9–9              |
| k                    | -11–11          | -9–9            | -10–10           | -13–13            |
| l                    | -16–16          | -14–14          | -26–26           | -17–17            |
| $Δρ_{max}$ [e Å$^{-3}$] | 0.43        | 1.53            | 0.87             | 0.75              |
| $Δρ_{min}$ [e Å$^{-3}$] | -0.22        | -1.41           | -0.75            | -0.74             |
| GooF                 | 2.19            | 2.56            | 3.02             | 3.22              |
| $R_{obs}$            | 0.0307          | 0.0780          | 0.0489           | 0.0869            |
| wR$_{all}$           | 0.0442          | 0.0625          | 0.0588           | 0.0848            |
| twin operation       | -               | two-fold rotation about [001] | - | - |
| twin volume fraction | -               | 50.39:49.61(17) | -               | -                 |
Table 2. Details on the crystal structure determinations of the methylsulfonyl compounds oxBSEM (1) (polymorphs I, II and III) and oxESEM (3b).

|                        | oxBSEM, I | oxBSEM, II | oxBSEM, III | oxESEM |
|------------------------|-----------|------------|-------------|--------|
| **formula**            | C_{22}H_{30}O_{4}S_{2}Si_{2} | C_{22}H_{30}O_{4}S_{2}Si_{2} | C_{22}H_{30}O_{4}S_{2}Si_{2} | C_{22}H_{30}O_{8}S_{2}Si_{2} |
| **molecular weight**   | 478.8     | 478.8      | 478.8       | 574.8  |
| **crystal color**      | clear colorless | clear colorless | clear colorless | clear yellow |
| **crystal habit**      | plate     | plate      | plate       | block  |
| **crystal size [mm^3]**| 0.70×0.65×0.10 | 0.70×0.65×0.10 | 0.45×0.15×0.03 | 0.63×0.45×0.28 |
| **temperature [K]**    | 150       | 100        | 100         | 100    |
| **space group**        | P         | P          | P           | P      |
| **a [Å]**              | 6.8197(3) | 7.3096(2)  | 5.7300(3)   | 10.5399(4) |
| **b [Å]**              | 12.1073(5)| 11.3935(3) | 10.9801(6)  | 19.9987(8)  |
| **c [Å]**              | 16.1213(7)| 18.7425(6) | 10.2961(5)  | 19.9987(8)  |
| **α [°]**              | 92.3607(19)| 73.167(2)  | 85.9433(17) | 79.940(2)   |
| **β [°]**              | 93.9781(19)| 105.319(2) | 79.7181(16) | 84.589(2)   |
| **γ [°]**              | 98.3425(19)| 118.926(2) | 80.1150(15) | 89.771(2)   |
| **V [Å^3]**            | 1311.34(10)| 1293.21(7) | 627.39(6)   | 2856.81(19) |
| **Z**                  | 2         | 2          | 1           | 4      |
| **Z’**                 | 2         | 2/4        | 1/2         | 2      |
| **density [g cm^{-3}]**| 1.212     | 1.229      | 1.267       | 1.336  |
| **θ range [°]**        | 1.3–35.1  | 1.15–30.15 | 1.89–27.6   | 1.0–30.1 |
| **μ [mm^{-1}]**        | 0.318     | 0.323      | 0.332       | 0.385  |
| **Trans. coeff. T_{min}, T_{max}** | 0.81,0.97 | 0.81,0.97  | 0.89,0.98   | 0.81,0.90 |
| **reflections total**  | 57779     | 40880      | 16087       | 57022  |
| **reflections unique** | 11485     | 7541       | 2909        | 13689  |
| **reflections obs. [I > 3σI]** | 8331     | 5106       | 2371        | 11291  |
| **parameters**         | 271       | 271        | 136         | 632    |
| **R_{int}**            | 0.0297    | 0.0625     | 0.0237      | 0.0348 |
| **h**                  | -9→11     | -10→10     | -9→7        | -14→14 |
| **k**                  | -19→19    | -15→16     | -13→13      | -19→19 |
| **l**                  | -26→25    | -26→26     | -14→14      | -28→28 |
| **Δρ_{max} [e Å^{-3}]**| 0.44      | 1.17       | 0.31        | 0.45   |
| **Δρ_{min} [e Å^{-3}]**| -0.39     | -0.70      | -0.26       | -0.60  |
| **GooF**               | 2.15      | 3.05       | 2.19        | 1.96   |
| **R_{obs}**            | 0.0350    | 0.0740     | 0.0300      | 0.0372 |
| **wR_{all}**           | 0.0443    | 0.0925     | 0.0393      | 0.0422 |
| **twin operation**     | -         | -          | -           | twofold rotation about [100] |
| **twin volume fraction**| -         | -          | -           | 60.92:39.08(7) |

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Table 3. Details on the crystal structure determinations of the non-spacer extended compounds NSEM-TBDM (5) and ASYM (6)

|                  | NSEM-TBDM             | ASYM               |
|------------------|-----------------------|--------------------|
| **formula**      | C$_{22}$H$_{38}$S$_2$Si$_2$ | C$_{13}$H$_{22}$S$_1$Si$_2$ |
| **molecular weight** | 422.8 | 266.6 |
| **crystal color** | clear | colorless |
| **crystal habit** | block | block |
| **crystal size [mm$^3$]** | 0.70×0.56×0.50 | 0.82×0.61×0.20 |
| **temperature [K]** | 100 | 100 |
| **space group**  | $P2_12_12_1$ | $P1$ |
| **$a$ [Å]**      | 7.7849(4) | 7.2016(4) |
| **$b$ [Å]**      | 10.5146(5) | 9.7603(4) |
| **$c$ [Å]**      | 31.2712(14) | 12.2829(4) |
| **$\alpha$ [°]** | 90 | 95.4952(16) |
| **$\beta$ [°]** | 90 | 92.510(2) |
| **$\gamma$ [°]** | 90 | 101.346(2) |
| **$V$ [Å$^3$]**  | 2559.7(2) | 840.86(6) |
| **$Z$**          | 4 | 2 |
| **$Z'$**         | 1 | 1 |
| **density [g cm$^{-3}$]** | 1.097 | 1.052 |
| **$\theta$ range [°]** | 2.04–35.05 | 1.7–30.2 |
| **$\mu$ [mm$^{-1}$]** | 0.306 | 0.313 |
| **Trans. coeff. $T_{min}$, $T_{max}$** | 0.78, 0.81 | 0.80, 0.94 |
| **reflections total** | 101389 | 21588 |
| **reflections unique** | 11125 | 4622 |
| **reflections obs. [$I > 3\sigma I$]** | 10833 | 3651 |
| **parameters**   | 236 | 146 |
| **$R_{int}$**    | 0.0238 | 0.0345 |
| **$h$**          | -12→11 | -9→9 |
| **$k$**          | -16→16 | -13→13 |
| **$l$**          | -48→50 | -17→17 |
| **$\Delta \rho_{max}$ [e Å$^{-3}$]** | 0.33 | 0.61 |
| **$\Delta \rho_{min}$ [e Å$^{-3}$]** | -0.28 | -0.39 |
| **GooF**         | 2.72 | 2.27 |
| **$R_{obs}$**    | 0.0267 | 0.0524 |
| **$wR_{all}$**   | 0.0400 | 0.0549 |
| **Flack parameter** | 0.03(3) | - |
| **twin operation** | - | twofold rotation about [100] |
| **twin volume fraction** | - | 83.78:16.22(11) |
Table 4. Details on the crystal structure determinations of the incommensurately modulated structure ESEM (3).

|                                | ESEM             |
|--------------------------------|-----------------|
| formula                        | C_{22}H_{30}O_{2}S_{3}Si_{2} |
| molecular weight               | 478.8           |
| crystal color                  | clear yellow    |
| crystal habit                  | plate           |
| crystal size [mm³]             | 0.62×0.23×0.02  |
| temperature [K]                | 100             |
| superspace group               | I2/c(0σ20)00    |
| a [Å]                          | 32.4653(8)      |
| b [Å]                          | 8.4003(5)       |
| c [Å]                          | 10.0737(3)      |
| β [°]                          | 102.301(2)      |
| V [Å³]                         | 2684.20(19)     |
| q                              | 0.6223(1)b      |
| Z                              | 4               |
| θ range [°]                    | 1.8–27.5        |
| μ [mm⁻¹]                       | 0.38            |
| unique reflections (all, obs)  | 15382, 9184     |
| unique main reflections (all, obs) | 3080, 2307   |
| unique first order sat (all, obs) | 6156, 4248   |
| unique second order sat (all, obs) | 6146, 2629 |
| observation criterion          | I > 3σI        |
| parameters                     | 510             |
| R_{int}                        | 0.0672          |
| h                              | -41→41          |
| k                              | -11→11          |
| l                              | -13→12          |
| m                              | -2→2            |
| GooF                           | 2.36            |
| R_{obs}/wR_{all}               |                 |
| all reflections                | 6.28/6.69       |
| main reflections               | 5.87/6.47       |
| first order satellites         | 4.78/4.91       |
| second order satellites        | 11.35/12.71     |

1.1. Twinning of TSEM (2), oxESEM (3b) and ASYM (6).

For TSEM (2), oxESEM (3b) and ASYM (6), automatic unit cell determination failed at determining reasonable lattice parameters. Therefore the locations of the diffraction spots in reciprocal space were analyzed manually using RLATT (Bruker, 2008). In all three cases the spots could be assigned to two domains, related by rotation
of 180° about [001] (TSEM (2)) and [100] (oxESEM (3b), ASYM (6)). Intensity data of the twin domains were integrated concurrently and written to “HKLF5” files with overlap information.

1.2. TSEM (2).

TSEM (2) was refined in the non-standard space group setting \(I2/c\) (standard setting \(C2/c\)) to highlight the close crystallographic relationship with BSEM (1). The standard setting is related to the chosen one by

\[
(a_{\text{std}}, b_{\text{std}}, c_{\text{std}}) = (a, b, c) \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{T} & 0 \\ 1 & 0 & \bar{T} \end{pmatrix}.
\]

Due to the small size, the crystal was only weakly diffracting, leading to mediocre residuals and large peaks in the difference Fourier density.

1.3. DSEM (4).

The two polytypes of DSEM (4) were isolated from the same crystallization vessel. Polytype I grew on the walls and featured satisfactory diffraction quality. Polytype II was isolated from the bottom of the vessel among oil and featured weak diffraction intensities and diffuse scattering. Accordingly, the residuals were comparatively large.

1.4. oxBSEM (1b).

When mounting samples of oxBSEM (1b) on the diffractometer cooled in a stream of \(N_2\) to our routine measurement temperature of 100 K, the crystals burst suggesting a phase transition. Therefore we slowly (2 K/min) cooled a crystal from room temperature to 150 K, while monitoring the lattice parameters. Since no phase transition was observed down to 150 K, a data set was collected at this temperature. On further cooling, a phase transition was apparent by fragmentation of the crystal accompanied by a dramatic worsening of reflection quality. Despite mediocre data quality we were
able to solve and refine the structure, though with high residuals and large peaks in the difference Fourier density.

To highlight the structural relationship between polymorphs I and II of oxBSEM (1b), the latter was refined using a non-reduced setting. The reduced setting is related to the chosen one by

\[
(a_{\text{red}}, b_{\text{red}}, c_{\text{red}}) = (a, b, c) \begin{pmatrix} 1 & 1 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\]

1.5. ESEM (3).

Since automatic indexing of the reflections failed, the locations of the diffraction spots in reciprocal space were analyzed manually using RLATT (Bruker, 2008). The strongest spots could be indexed using a $C$-centered monoclinic lattice. The remaining diffraction spots were interpreted as satellites located at $\pm \sigma_2 b^*$ and $\pm 2 \sigma_2 b^*$ from main reflections, with irrational $\sigma_2$ close to $\frac{5}{8}$.

Data reduction turned out to be difficult, since first and second order satellites were close and reflections featured distinct enlargement in $a^*$ direction. The best overall result was obtained using EVAL14 (Duisenberg et al., 2003), by tuning anisotropic mosaicity. Nevertheless, intensities of the strongest reflections were systematically overestimated, leading to slightly worse partial reliability factors of main reflections compared to first order satellites.

Systematic absences of the main reflections indicated a superspace group derived from $Ic$ or $I2/c$. Since satellites $0k0m$ with $|m| = 1$ were absent, a structure solution in superspace group $I2/c(0\sigma_20)s0$ was attempted. The correctness of the choice was confirmed by the symmetry of the four-dimensional electron density obtained by charge-flipping as implemented in SUPERFLIP (Palatinus & Chapuis, 2007). The positions of all non-H atoms and first order displacive modulation functions were
directly located in SUPERFLIP output. To achieve decent reliability factors, notably concerning satellites, the positions of the non-H atoms were refined with second order harmonics. The ADPs of the heavy atoms S and Si were modulated with second order harmonics, for C and O atoms with first order harmonics. H atoms were placed at computed positions and refined as riding on the parent C-atoms. The methyl groups were fixed into \textit{anti}-positions to obtain converging refinements.

The C9 atom of the TMS group features large ADPs in parts of internal space hinting towards disorder. Introducing discontinuous modulation functions for C9 (Legendre polynomials) led to distinctly more reasonable ADPs. Unfortunately attachment of H atoms to this C9 atom resulted in non-converging refinements and thus the continuous harmonics were used in the final refinements.

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