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#### Key indicators

Single-crystal X-ray study  
T = 199 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$   
Disorder in main residue  
R factor = 0.043  
wR factor = 0.111  
Data-to-parameter ratio = 19.6

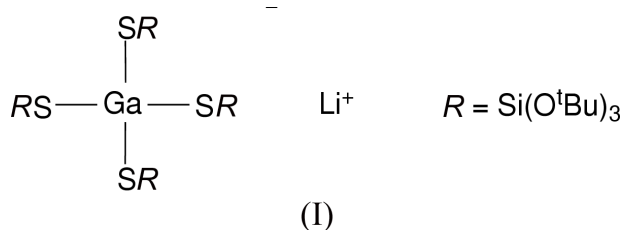
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Lithium tetrakis(tri-*tert*-butoxysilane-thiolato)gallate(III)

The title compound,  $\text{Li}[\text{Ga}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_4]$ , has been obtained as a by-product of the reaction of a metastable GaBr solution with  $(^t\text{BuO})_3\text{SiLi}$ . The asymmetric unit is composed of two separate molecules. Each lithium cation is coordinated by two O atoms from butoxy groups of the ligand.

### Comment

The structure and chemistry of silanethiolanes has not only been subject of our research for many years (*e.g.* Wojnowski *et al.*, 1985; Becker, Dolega *et al.*, 2001), but also generated some interest among other scientific groups (Kovacs *et al.*, 2000; Komuro *et al.*, 2002). The tri-*tert*-butoxysilanethiolate ligand usually produces oligomeric structures with metals, in which it behaves as an *S*-ligand or as a chelating *O,S*-ligand. So far, electrically neutral mono- or oligonuclear complexes have been most frequently obtained and characterized. The first ionic species containing the ligand obtained recently were both heteroleptic: positive  $[\text{Co}(\text{SR})_2(\text{NH}_3)_4]^+ \cdot \text{RS}^-$  and negative  $\text{Co}(\text{SR})_3(\text{H}_2\text{O})^- \cdot \text{HNET}_3^+$  (Becker, Zalewska *et al.*, 2001; Becker *et al.*, 2002).



Previous attempts to obtain silanethiolatogallium compounds has led to  $(\text{RS})_3\text{Ga}(\text{H}_2\text{O})$  (Chojnacki *et al.*, 2001). Now, under more careful experimental conditions, in the absence of water, the coordination shell of gallium was completed by a fourth thiolate anion, giving the title compound, (I). The molecular structure of (I) is shown in Fig. 1. The asymmetric unit is composed of two molecules not related by symmetry (Spek, 2002). An interesting feature of the thiolate is the internal twofold coordination of the lithium cation by two *tert*-butoxy O atoms, forming a kind of zwitterion. The  $\text{Li} \cdots \text{S}$  contacts are too long to be regarded as coordination bonds. The EI positive ion mass spectrum contains no molecular peak, but the strongest peaks can be assigned to the most stable cationic degradation products:  $\text{Ga}(\text{SR})_3\text{Li}$ ,  $m/e$  915;  $\text{Ga}(\text{SR})_2$ ,  $m/e$  629;  $\text{Li}_2\text{SR}_2$ ,  $m/e$  293;  $^t\text{Bu}$   $m/e$  57. To our best knowledge, the gallate(III) reported here is the first structurally characterized homoleptic anionic metal complex of the ligand.

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## Experimental

The work was carried out using a standard vacuum–nitrogen line and Schlenk techniques. The title compound was obtained as a by-product of the reaction of a metastable GaBr solution (0.3 mol l<sup>-1</sup>) in toluene–tetrahydrofuran (THF) (3:1) (Dohmeier *et al.*, 1996) with a (tBuO)<sub>3</sub>SiSLi solution in Et<sub>2</sub>O. Both reactants were used in 1 mmol amounts. The lithium salt was obtained by reaction of the metal with (tBuO)<sub>3</sub>SiSH (Piekos & Wojnowski, 1962) dissolved in Et<sub>2</sub>O. Recrystallization of the crude product from toluene afforded colourless cuboidal crystals of (I), suitable for X-ray diffraction analysis. The MS spectrum was recorded on a FINNIGAN MAT MS8230 spectrometer.

### Crystal data

Li[Ga(C <sub>12</sub> H <sub>27</sub> O <sub>3</sub> SSi) <sub>4</sub> ]	$D_x = 1.101 \text{ Mg m}^{-3}$
$M_r = 1194.65$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8000 reflections
$a = 25.071 (5) \text{ \AA}$	$\theta = 10\text{--}15^\circ$
$b = 23.872 (5) \text{ \AA}$	$\mu = 0.61 \text{ mm}^{-1}$
$c = 26.189 (5) \text{ \AA}$	$T = 199 (2) \text{ K}$
$\beta = 113.16 (3)^\circ$	Cube, colourless
$V = 14411 (6) \text{ \AA}^3$	$0.50 \times 0.20 \times 0.10 \text{ mm}$
$Z = 8$	

### Data collection

Stoe IPDS diffractometer	18748 reflections with $I > 2\sigma(I)$
$\varphi$ scans	$R_{\text{int}} = 0.036$
Absorption correction: numerical (IPDS; Stoe & Cie, 1997)	$\theta_{\text{max}} = 26.0^\circ$
$T_{\text{min}} = 0.750$ , $T_{\text{max}} = 0.942$	$h = -30 \rightarrow 27$
65926 measured reflections	$k = -29 \rightarrow 29$
27232 independent reflections	$l = -31 \rightarrow 28$

### Refinement

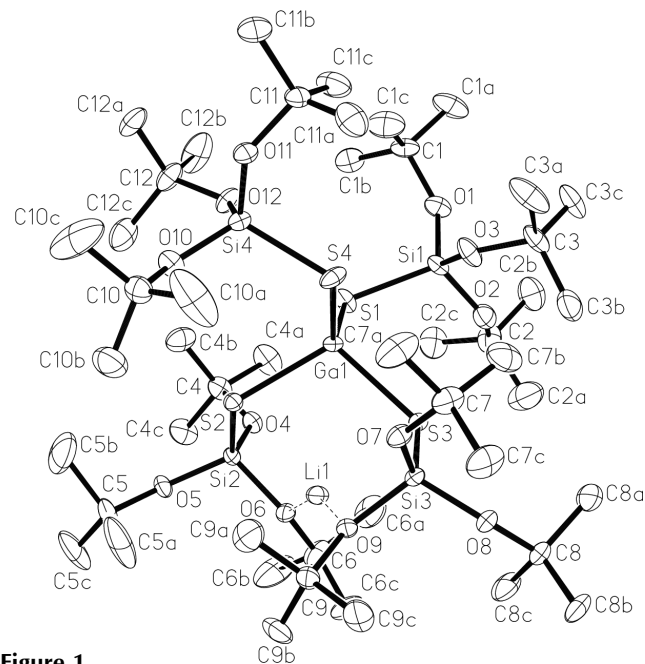
Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0758P)^2]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\text{max}} = 0.039$
27232 reflections	$\Delta\rho_{\text{max}} = 1.08 \text{ e \AA}^{-3}$
1391 parameters	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ga1–S4	2.2234 (11)	S2–Si2	2.1065 (12)
Ga1–S1	2.2261 (9)	S2–Li1	2.534 (4)
Ga1–S3	2.3353 (8)	S3–Si3	2.1086 (11)
Ga1–S2	2.3363 (7)	S3–Li1	2.502 (4)
Ga2–S5	2.2280 (9)	S4–Si4	2.1049 (10)
Ga2–S7	2.2285 (9)	O6–Li1	1.929 (5)
Ga2–S8	2.3231 (10)	O9–Li1	1.930 (5)
Ga2–S6	2.3302 (8)	O16–Li2	1.943 (4)
S1–Si1	2.0994 (10)	O22–Li2	1.924 (5)
S4–Ga1–S1	120.54 (3)	Si3–S3–Ga1	113.36 (4)
S4–Ga1–S3	105.01 (3)	Si4–S4–Ga1	107.45 (4)
S4–Ga1–S2	109.18 (3)	O22–Li2–O16	146.9 (2)
Si1–S1–Ga1	107.57 (4)	O6–Li1–O9	150.0 (2)
Si2–S2–Ga1	111.60 (3)		

All H atoms were positioned geometrically and allowed to ride on their parent atoms. The three *tert*-butyl groups were refined as disordered, using three independent occupancy ratios. Group C5A–C5C was disordered with occupation factors 0.704 (7)/0.296, group C10A–C10C with factors 0.67 (2)/0.33 and group C21A–C21C with factors 0.654 (14)/0.346. Atoms of the C5 group were refined isotropically to avoid excessively prolate displacement ellipsoids. A check with *PLATON/SQUEEZE* (Spek, 2002) showed that there are



**Figure 1**

A view of one molecule of the asymmetric unit of (I), showing 25% displacement ellipsoids and the atom-numbering scheme.

27 void regions, of which four were of volume  $73 \text{ \AA}^3$ . The only molecule we could place there is water, but it is not very likely in this hydrophobic environment. The residual density peaks are located outside the large voids, close to O1 and O2.

Data collection: *STADIA* (Stoe & Cie, 1997); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *RESVIEW* (Schwenk, 1998); software used to prepare material for publication: *SHELXL97*.

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## References

- Becker, B., Dolega, A., Konitz, A., Swinder, L. & Wojnowski, W. (2001). *Z. Anorg. Allg. Chem.* **627**, 280–286.
- Becker, B., Pladzyk, A., Konitz, A. & Wojnowski, W. (2002). *Appl. Organomet. Chem.* **16**, 517–524.
- Becker, B., Zalewska, A., Konitz, A. & Wojnowski, W. (2001). *Z. Anorg. Allg. Chem.* **627**, 271–279.
- Chojnacki, J., Schnepf, A. & Wojnowski, W. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 198–200.
- Dohmeier, C., Loos, D. & Schnöckel, H. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 129–149.
- Komuro, T., Kawaguchi, H. & Tatsumi, K. (2002). *Inorg. Chem.* **41**, 5083–5090.
- Kovacs, I., Pearson, C. & Shaver, A. (2000). *J. Organomet. Chem.* **596**, 193–203.
- Piekos, R. & Wojnowski, W. (1962). *Z. Anorg. Allg. Chem.* **318**, 212–216.
- Schwenk, H. (1998). *RESVIEW*. Version 2.21. University of München, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2002). *PLATON* (<http://www.Cryst.Chem.uu.nl/PLATON>). University of Utrecht, The Netherlands.
- Stoe & Cie (1997). *IPDS*, *STADIA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
- Wojnowski, W., Wojnowski, M., Peters, K., Peters, E.-M. & von Schnering, H. G. (1985). *Z. Anorg. Allg. Chem.* **530**, 79–88.