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Structure of Bis- μ -[(trimethylsilyl)methanolato-*O*]-bis(trimethylsilylmethyl)gallium] and Bis- μ -[(trimethylsilyl)methanolato-*O*]-bis(trimethylsilylmethyl)indium]

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Abstract

Two new compounds, (I) bis- μ -[(trimethylsilyl)methanolato-*O*]-bis[bis(trimethylsilylmethyl)gallium] and (II) bis- μ -[(trimethylsilyl)methanolato-*O*]-bis[bis(trimethylsilylmethyl)indium], have been obtained with dimeric structures, with planar four-membered Ga_2O_2 and In_2O_2 rings, respectively.

Comment

The asymmetric unit of (I) consists of two independent molecules each with an inversion centre in the middle of the four-membered ring. As these two molecules are almost identical, only one is shown in Fig. 1 (weighted r.m.s deviation 0.17 Å). Owing to the inversion centre the four-membered ring is exactly planar. On average, the endocyclic angles are O—Ga—O 81.6 (1) and Ga—O—Ga 98.4 (1)°. The exocyclic angles are increased by the steric

demand of the bulky $\text{CH}_2\text{Si}(\text{CH}_3)_3$ groups [C—Ga—C 126.8 (2)°]. The observed average bond lengths Ga—O 1.967 (4) and Ga—C 1.966 (4) Å agree well with values found in the analogous compound $[(\text{C}_5\text{H}_5)_2\text{GaOEt}]_2$ (Cowley, Mehrota, Atwood & Hunter, 1985).

In contrast to (I), compound (II) does not possess any crystallographic symmetry. The four-membered In_2O_2 ring is almost planar (mean deviation from least-squares plane 0.06 Å). The mean endocyclic angles are O—In—O 79.3 (1) and In—O—In 100.3 (1)°. As in (I), the exocyclic angles on the In atoms are increased by the steric demand of the $\text{CH}_2\text{Si}(\text{CH}_3)_3$ groups. The different values for each In atom are caused by the different arrangement of the $\text{CH}_2\text{Si}(\text{CH}_3)_3$ groups [C5—In1—C6 130.9 (1) and C3—In2—C4 144.2 (1)°]. As in (I), no unusual bond lengths were found. The mean bond lengths In—O 2.173 (2) and In—C 2.152 (4) Å are in good agreement with values found in $[(\text{t-Bu})\text{InOEt}]_2$ (Bradley, Frigo, Hursthouse & Hussain, 1988).

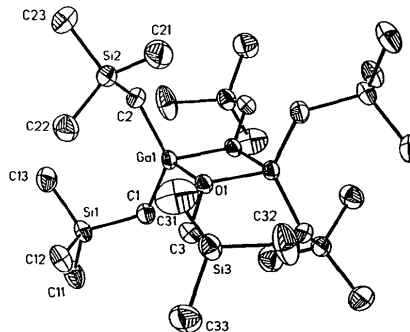


Fig. 1. Structure of one molecule of (I) showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.

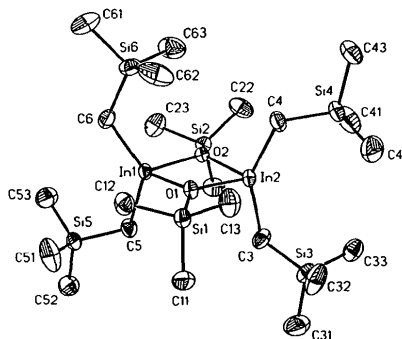


Fig. 2. Structure of (II) showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.

Experimental

Compound (I)

Crystal data

$[\text{Ga}_2(\text{C}_4\text{H}_{11}\text{OSi})_2(\text{C}_4\text{H}_{11}\text{Si})_4]$
 $M_r = 694.75$

$D_x = 1.131 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation

Triclinic	$\lambda = 0.71073 \text{ \AA}$
$P\bar{1}$	Cell parameters from 57 reflections
$a = 12.240 (2) \text{ \AA}$	$\theta = 10\text{--}12.5^\circ$
$b = 12.642 (2) \text{ \AA}$	$\mu = 1.514 \text{ mm}^{-1}$
$c = 14.039 (2) \text{ \AA}$	$T = 153.0 (10) \text{ K}$
$\alpha = 103.860 (10)^\circ$	$0.3 \times 0.3 \times 0.1 \text{ mm}$
$\beta = 104.160 (10)^\circ$	Colourless
$\gamma = 90.620 (10)^\circ$	Crystal source: Dembowski (1991)
$V = 2039.5 (5) \text{ \AA}^3$	
$Z = 2$	

C41	0.6441 (5)	0.6380 (4)	0.4999 (4)	0.059 (4)
C42	0.6716 (4)	0.4157 (4)	0.3678 (4)	0.048 (3)
C43	0.5798 (4)	0.5952 (4)	0.2695 (4)	0.060 (3)
C5	1.0498 (4)	0.7346 (3)	0.5925 (3)	0.034 (2)
Si5	0.98585 (10)	0.86112 (10)	0.64570 (9)	0.0339 (7)
C51	0.9066 (4)	0.8380 (4)	0.7379 (4)	0.051 (3)
C52	1.1003 (5)	0.9717 (4)	0.7160 (4)	0.057 (3)
C53	0.8883 (4)	0.9111 (4)	0.5429 (4)	0.051 (3)
C6	0.9451 (4)	0.5267 (4)	0.6700 (3)	0.039 (3)
Si6	0.87380 (12)	0.42726 (11)	0.71961 (9)	0.0391 (8)
C61	0.7190 (4)	0.4252 (5)	0.6710 (4)	0.056 (3)
C62	0.9169 (5)	0.4827 (4)	0.8608 (3)	0.051 (4)
C63	0.9197 (5)	0.2868 (4)	0.6855 (4)	0.050 (4)

Data collection

Stoe-Siemens AED four-circle diffractometer	5248 observed reflections
Profile data from $2\theta/\omega$ scans	$[I > 2\sigma(I)]$
Absorption correction: Empirical	$R_{\text{int}} = 0.1159$
$T_{\text{min}} = 0.800$, $T_{\text{max}} = 0.926$	$\theta_{\text{max}} = 24.99^\circ$
7716 measured reflections	$h = -14 \rightarrow 14$
7139 independent reflections	$k = -15 \rightarrow 14$
	$l = -15 \rightarrow 16$
	3 standard reflections
	frequency: 90 min
	intensity variation: none

Refinement

Refinement on F^2	Calculated weights
Final $R = 0.0441$ ($R = 0.0744$ for all data)	$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 3.2018P]$
$wR = 0.0822$ ($wR = 0.1015$ for all data)	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.054$	$(\Delta/\sigma)_{\text{max}} = -0.001$
7139 reflections	$\Delta\rho_{\text{max}} = 0.789 \text{ e \AA}^{-3}$
327 parameters	$\Delta\rho_{\text{min}} = -0.526 \text{ e \AA}^{-3}$
Riding-model refinement of H-atom parameters	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)

$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$				
	x	y	z	U_{eq}
Ga1	0.55260 (4)	-0.01132 (4)	-0.08650 (3)	0.0268 (3)
O1	0.4662 (2)	0.0924 (2)	-0.0132 (2)	0.028 (2)
C1	0.4528 (4)	-0.0866 (4)	-0.2190 (3)	0.033 (3)
Si1	0.46176 (11)	-0.04948 (10)	-0.33735 (8)	0.0327 (7)
C11	0.3714 (5)	-0.1491 (4)	-0.4512 (3)	0.054 (4)
C12	0.4135 (4)	0.0900 (4)	-0.3386 (3)	0.045 (3)
C13	0.6116 (4)	-0.0509 (5)	-0.3475 (4)	0.051 (3)
C2	0.7131 (4)	0.0386 (4)	-0.0574 (3)	0.036 (2)
Si2	0.76133 (11)	0.18503 (11)	-0.02706 (10)	0.0389 (7)
C21	0.7534 (5)	0.2542 (5)	0.1038 (4)	0.059 (4)
C22	0.6731 (5)	0.2560 (4)	-0.1185 (4)	0.054 (3)
C23	0.9113 (4)	0.1972 (5)	-0.0348 (5)	0.065 (3)
C3	0.3730 (4)	0.1403 (4)	-0.0705 (3)	0.034 (3)
Si3	0.32912 (12)	0.27141 (11)	0.00053 (10)	0.0382 (8)
C31	0.4470 (5)	0.3776 (5)	0.0384 (5)	0.076 (4)
C32	0.2842 (6)	0.2564 (5)	0.1146 (4)	0.071 (6)
C33	0.2085 (5)	0.3096 (5)	-0.0910 (4)	0.062 (4)
Ga2	0.95791 (4)	0.60893 (4)	0.49298 (3)	0.0300 (3)
O2	0.9399 (2)	0.4946 (2)	0.5623 (2)	0.032 (2)
C4	0.8262 (4)	0.6148 (4)	0.3827 (3)	0.038 (3)
Si4	0.68226 (10)	0.56556 (10)	0.38148 (9)	0.0348 (7)

Table 2. Geometric parameters (\AA , $^\circ$) for (I)

Ga1—O1	1.953 (3)	Ga2—C4	1.959 (4)
Ga1—C1	1.968 (4)	Ga2—O2	1.964 (3)
Ga1—C2	1.970 (4)	Ga2—C5	1.967 (4)
Ga1—O1 ⁱ	1.975 (3)	Ga2—O2 ⁱⁱ	1.976 (3)
O1—Ga1—C1	108.5 (2)	C4—Ga2—O2	113.5 (2)
O1—Ga1—C2	113.3 (2)	C4—Ga2—C5	126.5 (2)
C1—Ga1—C2	127.2 (2)	O2—Ga2—C5	108.8 (2)
O1—Ga1—O1 ⁱ	81.60 (12)	C4—Ga2—O2 ⁱⁱ	108.7 (2)
C1—Ga1—O1 ⁱ	107.76 (15)	O2—Ga2—O2 ⁱⁱ	81.53 (12)
C2—Ga1—O1 ⁱ	108.94 (15)	C5—Ga2—O2 ⁱⁱ	108.66 (15)
C3—O1—Ga1	119.0 (2)	C6—O2—Ga2	118.6 (2)
C3—O1—Ga1 ⁱ	122.7 (2)	C6—O2—Ga2 ⁱⁱ	122.2 (3)
Ga1—O1—Ga1 ⁱ	98.40 (12)	Ga2—O2—Ga2 ⁱⁱ	98.47 (12)

Symmetry code: (i) $1 - x, -y, -z$; (ii) $2 - x, 1 - y, 1 - z$.

Compound (II)

Crystal data

$[\text{In}_2(\text{C}_4\text{H}_{11}\text{OSi})_2(\text{C}_4\text{H}_{11}\text{Si})_4]$	$D_x = 1.265 \text{ Mg m}^{-3}$
$M_r = 756.90$	Mo $K\alpha$ radiation
Triclinic	$\lambda = 0.71073 \text{ \AA}$
$P\bar{1}$	Cell parameters from 51 reflections
$a = 9.887 (4) \text{ \AA}$	$\theta = 10\text{--}12.5^\circ$
$b = 11.879 (4) \text{ \AA}$	$\mu = 1.356 \text{ mm}^{-1}$
$c = 17.586 (6) \text{ \AA}$	$T = 153.0 (10) \text{ K}$
$\alpha = 104.40 (2)^\circ$	$0.4 \times 0.3 \times 0.3 \text{ mm}$
$\beta = 93.43 (3)^\circ$	Colourless
$\gamma = 94.66 (2)^\circ$	Crystal source: Pape (1990)
$V = 1987.1 (12) \text{ \AA}^3$	
$Z = 2$	

Data collection

Stoe-Siemens AED four-circle diffractometer	5071 observed reflections
Profile data from $2\theta/\omega$ scans	$[I > 2\sigma(I)]$
Absorption correction: Empirical	$R_{\text{int}} = 0.0209$
$T_{\text{min}} = 0.761$, $T_{\text{max}} = 0.938$	$\theta_{\text{max}} = 24.01^\circ$
6013 measured reflections	$h = -11 \rightarrow 11$
5968 independent reflections	$k = -13 \rightarrow 13$
	$l = -5 \rightarrow 20$
	3 standard reflections
	frequency: 90 min
	intensity variation: none

Refinement

Refinement on F^2	Calculated weights
Final $R = 0.0260$ ($R = 0.0356$ for all data)	$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 1.4675P]$
$wR = 0.0543$ ($wR = 0.0627$ for all data)	where $P = (F_o^2 + 2F_c^2)/3$
	$(\Delta/\sigma)_{\text{max}} = 0.001$

$S = 1.049$
5964 reflections
310 parameters
Riding-model refinement of
H-atom parameters

$\Delta\rho_{\max} = 0.426 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.358 \text{ e } \text{\AA}^{-3}$
Atomic scattering factors
from *International Tables*
for *Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

For both compounds: Data collection: Stoe *DIF4*, version 7.08. Cell refinement: Stoe *DIF4*, version 7.08. Data reduction: Stoe *REDU4*. Program(s) used to solve structure: *SHELXS92* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL92*.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
In1	0.27762 (2)	0.59884 (2)	0.316886 (12)	0.02375 (14)
In2	0.22009 (2)	0.76616 (2)	0.193749 (13)	0.02486 (14)
O1	0.3550 (2)	0.7631 (2)	0.29591 (12)	0.0251 (12)
O2	0.1282 (2)	0.6125 (2)	0.22508 (12)	0.0247 (12)
Si1	0.49915 (9)	0.84184 (8)	0.33258 (5)	0.0280 (5)
Si2	0.01570 (9)	0.50427 (8)	0.17776 (5)	0.0277 (5)
Si3	0.41147 (11)	0.77613 (10)	0.03269 (6)	0.0376 (6)
Si4	0.01058 (11)	0.98014 (8)	0.17185 (6)	0.0343 (6)
Si5	0.48484 (10)	0.38086 (8)	0.31469 (6)	0.0333 (6)
Si6	0.08412 (11)	0.73994 (10)	0.46630 (6)	0.0385 (6)
C11	0.6383 (4)	0.7862 (4)	0.2709 (2)	0.049 (2)
C12	0.5421 (4)	0.8283 (3)	0.4343 (2)	0.040 (2)
C13	0.4805 (4)	0.9974 (3)	0.3342 (2)	0.048 (3)
C21	0.0808 (4)	0.4179 (3)	0.0865 (2)	0.047 (2)
C22	-0.1428 (4)	0.5631 (4)	0.1502 (3)	0.053 (2)
C23	-0.0204 (5)	0.4072 (4)	0.2446 (2)	0.053 (3)
C3	0.3310 (4)	0.6897 (3)	0.0952 (2)	0.040 (2)
C31	0.5375 (5)	0.6909 (5)	-0.0264 (3)	0.075 (3)
C32	0.5015 (5)	0.9180 (4)	0.0928 (3)	0.061 (3)
C33	0.2777 (4)	0.8084 (4)	-0.0360 (2)	0.049 (3)
C4	0.0925 (4)	0.9017 (3)	0.2383 (2)	0.039 (2)
C41	-0.0773 (5)	0.8743 (4)	0.0828 (2)	0.065 (3)
C42	0.1410 (5)	1.0794 (4)	0.1422 (3)	0.067 (4)
C43	-0.1194 (4)	1.0692 (3)	0.2233 (2)	0.052 (3)
C5	0.3986 (4)	0.4670 (3)	0.2558 (2)	0.035 (2)
C51	0.6119 (5)	0.4798 (4)	0.3885 (3)	0.075 (4)
C52	0.5745 (5)	0.2656 (4)	0.2496 (3)	0.059 (3)
C53	0.3590 (5)	0.3096 (4)	0.3674 (3)	0.062 (3)
C6	0.2016 (4)	0.6270 (3)	0.4313 (2)	0.038 (2)
C61	0.0257 (6)	0.7249 (5)	0.5625 (3)	0.085 (4)
C62	0.1707 (5)	0.8892 (4)	0.4792 (3)	0.072 (3)
C63	-0.0680 (4)	0.7225 (4)	0.3958 (3)	0.064 (3)

Table 4. Geometric parameters (\AA , $^\circ$) for (II)

In1—C6	2.147 (4)	In2—C4	2.149 (4)
In1—C5	2.158 (4)	In2—C3	2.154 (4)
In1—O1	2.163 (2)	In2—O2	2.180 (3)
In1—O2	2.168 (2)	In2—O1	2.182 (2)
C6—In1—C5	130.87 (13)	C4—In2—O1	104.21 (11)
C6—In1—O1	110.42 (12)	C3—In2—O1	103.61 (13)
C5—In1—O1	107.23 (12)	O2—In2—O1	78.93 (8)
C6—In1—O2	113.73 (12)	Si1—O1—In1	127.65 (12)
C5—In1—O2	103.02 (11)	Si1—O1—In2	130.18 (12)
O1—In1—O2	79.62 (8)	In1—O1—In2	100.37 (9)
C4—In2—C3	144.17 (14)	Si2—O2—In1	123.63 (12)
C4—In2—O2	104.96 (12)	Si2—O2—In2	132.62 (12)
C3—In2—O2	102.17 (12)	In1—O2—In2	100.29 (9)

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55973 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1019]

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Cu^{II} and Pd^{II} Complexes of 3-Hydroxy-1,3-bis(2-thienyl)prop-2-en-1-one

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Abstract

The 1:2 complexes formed between Cu^{II} or Pd^{II} and the anion of 3-hydroxy-1,3-bis(2-thienyl)prop-2-en-1-one [LH: Baxter, Blake, Heath & Stephenson (1990). *Acta Cryst.* **C46**, 508–510], bis[(3-hydroxy- $\kappa O'$)-1,3-bis(2-thienyl)prop-2-en-1-onato(1-)- κO]copper(II) and bis[(3-hydroxy- $\kappa O'$)-1,3-bis(2-thienyl)prop-2-en-1-onato(1-)- κO]palladium(II), crystallize with the metal ions occupying crystallographic inversion centres and coordinated by approximately square planes of four O atoms. The similarities within the pairs of M—O, C—C and C—O bonds in the chelate rings indicate the latter are behaving as delocalized systems. The mean Cu—O and Pd—O distances are