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analysis of the main-group metal tris(chelate) complex bis(tetraphenylarsonium) tris(2,2-diselenido-1,1-ethylenedicarbonitrile-*Se,Se'*)stannate(IV).

The geometry of the anion (Fig. 1) is comparable with $[Ni\{Se_2C{=}C(CN)_2\}_3]^{2-}$; the six Se atoms define an irregular octahedron and the average distance to the central metal is 2.661 (3) Å. The coordination around the Sn^{IV} is distorted octahedral. The average projected twist angle of the two Se_3 triangles (Fig. 2) of the $SnSe_6$ polyhedron is 43.2°, intermediate between the 60 and 0° expected for octahedral and trigonal prismatic geometry, respectively.

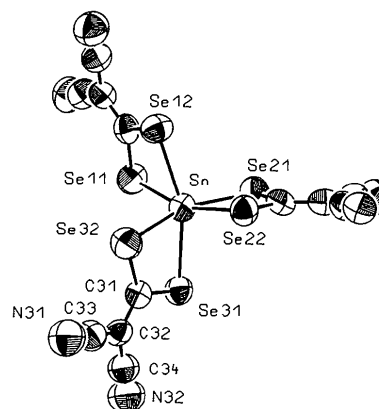*Acta Cryst.* (1993). C49, 1307–1309

Structure of [As(C₆H₅)₄]₂-[Sn{Se₂C=C(CN)₂}₃]

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Fig. 1. Structure of the $[Sn\{Se_2C{=}C(CN)_2\}_3]^{2-}$ complex anion.

Abstract

In the complex anion $[Sn\{Se_2C{=}C(CN)_2\}_3]$ in bis-(tetraphenylarsonium) tris(2,2-diselenido-1,1-ethylenedicarbonitrile-*Se,Se'*)stannate(IV), the Sn atom is at the center of a distorted octahedron formed of six Se atoms of the chelate ligands with an average Sn—Se bond length of 2.661 (3) Å. The bis(selenium) chelates show only small deviations from planarity and the average Se—C distance is 1.88 (1) Å.

Comment

Up to now only a few tris(chelate) complexes with unsaturated 1,1-diselenolato ligands have been structurally characterized. For these transition-metal complexes two different coordination geometries have been found. Whereas the central ion, Ni^{IV} in $[Ni\{Se_2CN(C_4H_9)_2\}_3]Br$ (Beurskens & Cras, 1971) and $[As(C_6H_5)_4][Ni\{Se_2C{=}C(CN)_2\}_3]$ (Kaiser, Dietzsch, Richter, Golič & Šiftar, 1980) has a distorted octahedral arrangement, the complex $[Fe\{Se_2CN(CH_2Ph)_2\}_3]BF_4$ has D_3 macrosymmetry with a coordination polyhedron intermediate between the idealized trigonal prismatic and trigonal antiprismatic geometries (Deplano, Trogu, Bigoli, Leporati, Pellinghelli, Perry, Saxton & Wilson, 1983). Here we describe the X-ray crystal structure

Fig. 2. SnSe₆ core with the two Se₃ triangles.

The average Se—Sn—Se' angle involving two different chelate ligands is 160.4 (1)° (180° in the perfect octahedron) while the intra-chelate angles Se—Sn—Se are in the narrow range 73.7 (1)–74.0 (1)° and reflect the rigid chelate geometry with Se—C—Se of about 116°.

The three selenolate ligands are nearly planar ($\Delta_{max} = 0.3$ Å) and the system of bond lengths and angles compares well with values expected for covalent coordinated diselenolates (Dietzsch, Franke, Hoyer, Gruß & Hummel, 1991).

Experimental

Crystal data

[As(C₆H₅)₄][Sn(C₄N₂Se₂)₃]
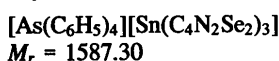
$[As(C_6H_5)_4][Sn(C_4N_2Se_2)_3]$
$M_r = 1587.30$
Triclinic
$P\bar{1}$
$a = 14.581 (9)$ Å
$b = 14.62 (1)$ Å
$c = 16.88 (1)$ Å
$\alpha = 102.40 (2)°$
$\beta = 105.45 (2)°$
$\gamma = 113.53 (2)°$
$V = 2963 (3)$ Å^3
$Z = 2$
$D_x = 1.779$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7099$ Å

Cell parameters from 87
reflections
$\theta = 8-13°$
$\mu = 5.230$ mm^{-1}
$T = 293$ K
Prism
$0.08 \times 0.06 \times 0.03$ mm
Red
Crystal source: SnCl₂
added to Ph₄AsCl.H₂O
+ K₂(C₄N₂Se₂) (Jensen
& Henricksen, 1970) in
MeOH at room tempera-
ture; recrystallized from
acetone-ether

Data collection

Huber diffractometer
Lehmann-Larsen profile
analysis; θ scan width
$(1.0 + 0.20\tan\theta)°$; θ scan
rate 0.8° min^{-1}
Absorption correction:
empirical
$T_{min} = 0.836$, $T_{max} = 1.150$
5505 measured reflections

4572 observed reflections
$[F > 4.0\sigma(F)]$
$\theta_{max} = 20°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 0$
4 standard reflections
frequency: 100 min
intensity variation: 2%

Refinement

Refinement on F
Final $R = 0.062$
$wR = 0.055$
$S = 1.712$
4572 reflections
455 parameters
H-atom parameters not re-
fined
$w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{max} = 0.231$
$\Delta\rho_{max} = 0.352$ e Å^{-3}
$\Delta\rho_{min} = -0.257$ e Å^{-3}
Atomic scattering factors
from International Tables
for X-ray Crystallogra-
phy (1974, Vol. IV, Table
2.2B)

Data collection: PWCOM (Gomm, 1992). Cell refinement: PWCOM. Data reduction: Xtal3.0 ADDREF, SORTRF (Hall & Stewart, 1990). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1986). Program(s) used to refine structure: SHELX76 (Sheldrick, 1976). Molecular graphics: ORTEP (Johnson, 1965); SCHAKAL (Keller, 1988). Software used to prepare material for publication: Xtal3.0 BONDLA, CIFIO.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for the complex anion*

Atomic coordinates for the cation have been deposited (see footnote).
$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn1	0.2107 (1)	0.5765 (1)	0.2105 (1)	0.0574 (5)
Se11	0.2807 (1)	0.7200 (1)	0.1378 (1)	0.0670 (7)
Se12	0.4082 (1)	0.7284 (1)	0.3273 (1)	0.0670 (7)
C11	0.4063 (9)	0.7932 (8)	0.2424 (7)	0.057 (2)
C12	0.4912 (9)	0.8873 (9)	0.2555 (8)	0.060 (2)
C13	0.585 (1)	0.9453 (9)	0.3350 (9)	0.063 (2)
C14	0.4933 (9)	0.9305 (9)	0.1890 (9)	0.067 (2)
N11	0.6582 (9)	0.9921 (9)	0.4008 (8)	0.098 (2)
N12	0.4908 (8)	0.9619 (8)	0.1325 (8)	0.085 (2)

Se21	0.2504 (1)	0.4373 (1)	0.1159 (1)	0.0694 (8)
Se22	0.2057 (1)	0.4383 (1)	0.2919 (1)	0.0634 (7)
C21	0.2278 (8)	0.3687 (9)	0.1970 (8)	0.056 (2)
C22	0.2294 (9)	0.275 (1)	0.1879 (8)	0.064 (2)
C23	0.237 (1)	0.217 (1)	0.1130 (9)	0.075 (2)
C24	0.2206 (9)	0.227 (1)	0.2514 (9)	0.074 (2)
N21	0.2418 (9)	0.1732 (9)	0.0508 (8)	0.097 (2)
N22	0.2152 (8)	0.1901 (8)	0.3053 (8)	0.085 (2)
Se31	0.0009 (1)	0.4826 (1)	0.1063 (1)	0.0626 (7)
Se32	0.1185 (1)	0.6544 (1)	0.3031 (1)	0.0766 (8)
C31	−0.0111 (8)	0.5649 (8)	0.2015 (7)	0.049 (2)
C32	−0.1080 (9)	0.5611 (8)	0.1956 (8)	0.054 (2)
C33	−0.1169 (9)	0.618 (1)	0.2678 (9)	0.074 (2)
C34	−0.199 (1)	0.506 (1)	0.1148 (9)	0.080 (2)
N31	−0.1236 (9)	0.6669 (9)	0.3284 (8)	0.106 (2)
N32	−0.2698 (9)	0.4648 (9)	0.0482 (8)	0.097 (2)

Table 2. *Geometric parameters* (Å, °)

Sn1—Se11	2.648 (3)	Se22—C21	1.88 (1)
Sn1—Se21	2.658 (3)	C21—C22	1.36 (2)
Sn1—Se31	2.661 (2)	C22—C24	1.41 (2)
Sn1—Se12	2.665 (2)	C22—C23	1.42 (2)
Sn1—Se22	2.666 (3)	C23—N21	1.14 (2)
Sn1—Se32	2.669 (3)	C24—N22	1.16 (2)
Se11—C11	1.875 (9)	Se31—C31	1.88 (1)
Se12—C11	1.88 (1)	Se32—C31	1.887 (8)
C11—C12	1.36 (1)	C31—C32	1.37 (2)
C12—C14	1.40 (2)	C32—C33	1.39 (2)
C12—C13	1.41 (1)	C32—C34	1.41 (2)
C13—N11	1.14 (1)	C33—N31	1.17 (2)
C14—N12	1.14 (2)	C34—N32	1.13 (2)
Se21—C21	1.89 (1)		
Se11—Sn1—Se21	94.64 (9)	C14—C12—C13	116 (1)
Se11—Sn1—Se31	96.63 (8)	N11—C13—C12	178 (2)
Se11—Sn1—Se12	73.83 (8)	N12—C14—C12	177.1 (9)
Se11—Sn1—Se22	160.77 (8)	Se22—C21—Se21	116.6 (7)
Se11—Sn1—Se32	102.30 (9)	C22—C21—Se22	122 (1)
Se21—Sn1—Se31	94.91 (7)	C22—C21—Se21	121 (1)
Se21—Sn1—Se12	103.32 (9)	C21—C22—C24	122 (1)
Se21—Sn1—Se22	74.03 (8)	C21—C22—C23	123 (1)
Se21—Sn1—Se32	160.48 (7)	C24—C22—C23	115 (1)
Se31—Sn1—Se12	159.93 (9)	N21—C23—C22	176 (2)
Se31—Sn1—Se22	99.74 (7)	N22—c24—C22	178 (1)
Se31—Sn1—Se32	73.74 (8)	Se31—C31—Se32	116.0 (7)
Se12—Sn1—Se22	93.37 (8)	C32—C31—Se31	121.4 (7)
Se12—Sn1—Se32	90.79 (8)	C32—C31—Se32	122.6 (9)
Se22—Sn1—Se32	91.96 (9)	C31—C32—C33	120.7 (9)
Se11—C11—Se12	116.4 (5)	C31—C32—C34	121 (1)
C12—C11—Se11	122 (1)	C33—C32—C34	118 (1)
C12—C11—Se12	122.0 (8)	N31—C33—C32	179 (1)
C11—C12—C14	121.7 (9)	N32—C34—C32	177 (2)
C11—C12—C13	122 (1)		

Lists of structure factors, anisotropic thermal parameters, coordinates of the cation, bond distances, bond angles, torsion angles and mean-planes data, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55905 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1016]

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Structure of Bis-μ-[(trimethylsilylmethanolato-O)-bis(trimethylsilylmethyl)gallium] and Bis-μ-[(trimethylsilylmethanolato-O)-bis(trimethylsilylmethyl)-indium]

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Abstract

Two new compounds, (I) bis-μ-(trimethylsilylmethanolato-O)-bis[bis(trimethylsilylmethyl)gallium] and (II) bis-μ-(trimethylsilylmethanolato-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 $CH_2Si(CH_3)_3$ 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 $[(C_5H_5)_2GaOEt]_2$ (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 $CH_2Si(CH_3)_3$ groups. The different values for each In atom are caused by the different arrangement of the $CH_2Si(CH_3)_3$ 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 [('Bu)InOEt]_2 (Bradley, Frigo, Hursthouse & Hussain, 1988).
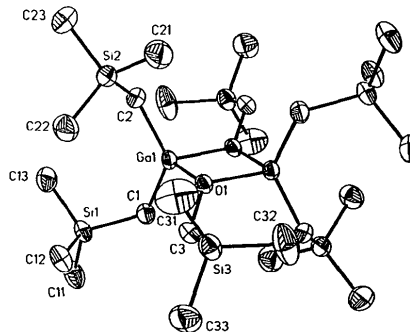

Fig. 1. Structure of one molecule of (I) showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.
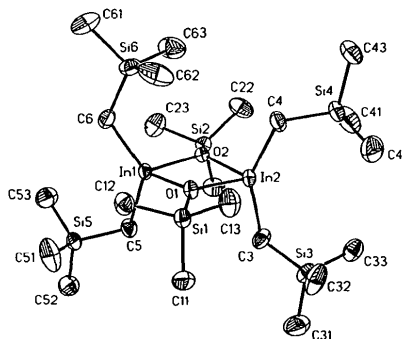

Fig. 2. Structure of (II) showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.

Experimental

Compound (I)

Crystal data

$[Ga_2(C_4H_{11}OSi)_2(C_4H_{11}Si)_4]$	D_x = 1.131 Mg m^{-3}
M_r = 694.75	Mo $K\alpha$ radiation