

9685 measured reflections
8908 independent reflections

4 standard reflections
frequency: 180 min
intensity decay: none

Refinement

Refinement on F^2

$R(F) = 0.033$

$wR(F^2) = 0.084$

$S = 1.049$

8854 reflections

613 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 11.2195P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.726 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.618 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Ru1—Ru3	2.7759 (6)	Ru2—C23	1.898 (5)
Ru1—Ru2	2.8787 (6)	Ru2—C22	1.902 (5)
Ru2—Ru3	2.8744 (6)	Ru2—C24	1.936 (5)
Ru1—CB	2.069 (4)	Ru2—C21	1.937 (5)
Ru3—CB	2.068 (4)	Ru3—C32	1.847 (5)
Ru1—C13	1.860 (4)	Ru3—C31	1.892 (5)
Ru1—C11	1.882 (5)	Ru3—C33	1.944 (5)
Ru1—C12	1.946 (5)	CB—OB	1.200 (5)
Ru3—Ru1—Ru2	61.075 (15)	OB—CB—Ru3	137.7 (3)
Ru3—Ru2—Ru1	57.697 (14)	OB—CB—Ru1	137.6 (3)
Ru1—Ru3—Ru2	61.228 (15)	C13—Ru1—CB	90.8 (2)
Ru3—CB—Ru1	84.29 (15)	C11—Ru1—CB	98.1 (2)
CB—Ru1—Ru2	83.91 (11)	C12—Ru1—CB	143.2 (2)
CB—Ru1—Ru3	47.83 (11)	C32—Ru3—CB	89.8 (2)
CB—Ru3—Ru1	47.88 (11)	C31—Ru3—CB	96.9 (2)
CB—Ru3—Ru2	84.05 (11)	C33—Ru3—CB	147.1 (2)

No extinction correction was applied. All non-H atoms were refined anisotropically. The H-atom positional parameters were calculated assuming ideal geometries around C atoms. The isotropic displacement parameters for H atoms were set to $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$ for CH groups in phenyl rings and the CH₂ group in CH₂Cl₂, and to $U_{\text{iso}} = 1.5U_{\text{iso}}(\text{C})$ for CH₃ groups. The positional and displacement parameters were fixed during the refinement.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *XPREP* in *SHELXTL* (Siemens, 1994). Program(s) used to solve structure: *XS* in *SHELXTL*. Program(s) used to refine structure: *XL* in *SHELXTL*. Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *XCIF* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1022). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 30–32

[PPh₄]₂[Pd{Se₂C₂(COOCH₃)₂]₂]

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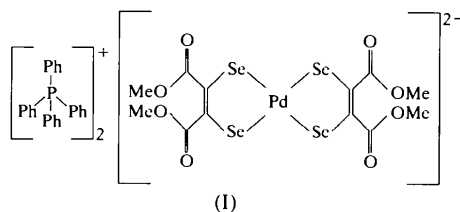
(Received 2 April 1998; accepted 4 August 1998)

Abstract

The title compound, bis(tetraphenylphosphonium) bis(*cis*-1,2-dicarbomethoxyethylene-1,2-diseleno)palladate(II) {alternative name: bis(tetraphenylphosphonium) bis[dimethyl 2,3-bis(selenido)but-2-ene-1,4-dioato-*Se,Se'*]-palladate(II)}, (C₂₄H₂₀P)₂[Pd(C₆H₆O₄Se₂)₂], shows a similar structure to the telluro, seleno, and sulfido analogues with other transition metals.

Comment

The reaction of activated acetylenes with polychalcogenide chains is well documented (Bolinger & Rauchfuss, 1982). One reaction of interest is that of dimethyl acetylenedicarboxylate with selenometalates (Ansari *et al.*, 1989). Whereas many reactions of this type have been attempted, few of the products have been structurally characterized (Ansari *et al.*, 1990). In addition, no reactions had been attempted with the use of Group X selenometalates. By reacting dimethyl acetylenedicarboxylate with a selenopalladate species, the title compound, (I), was synthesized.



This structure possesses similar bond lengths to the other known *cis*-1,2-dicarbomethoxyethylene-1,2-di-

selenometalates, with Se—C distances of 1.887 (5) and 1.901 (5) Å compared to 1.880 (14) and 1.869 (13) Å in $[\text{W}\{\text{Se}_2\text{C}_2(\text{COOMe})_2\}_3]^{2-}$, and 1.905 (6), 1.857 (6), 1.899 (6), and 1.852 (6) Å in $[\text{W}_2\text{Se}_2\{\text{Se}_2\text{C}_2(\text{COOMe})_2\}_4]^{2-}$ (Ansari *et al.*, 1989). The C=C distance is also comparable, with a distance of 1.347 (7) Å in (I) compared to 1.339 (25) Å in $[\text{W}\{\text{Se}_2\text{C}_2(\text{COOMe})_2\}_3]^{2-}$, 1.340 (8) Å in $[\text{W}_2\text{Se}_2\{\text{Se}_2\text{C}_2(\text{COOMe})_2\}_4]^{2-}$, 1.342 (6) Å in $[\text{Fe}_2\{\text{S}_2\text{C}_2(\text{COOMe})_2\}_4]^{2-}$ (Kanatzidis & Coucouvanis, 1984), 1.35 (1) Å in $[\text{Hg}\{\text{Te}_2\text{C}_2(\text{COOMe})_2\}_2]^{2-}$, 1.328 (13) Å in $[\text{Au}\{\text{Te}_2\text{C}_2(\text{COOMe})_2\}_2]^{1-}$ (Smith *et al.*, 1996), and 1.317 (10) Å in $[\text{MoO}\{\text{Te}_2\text{C}_2(\text{COOMe})_2\}_3]^{2-}$ (Flomer & Kolis, 1989). The C—COOMe bond distances are comparable in all cases, between 1.469 (7) and 1.505 (3) Å. This new species has the expected square-planar environment around the Pd^{II} center.

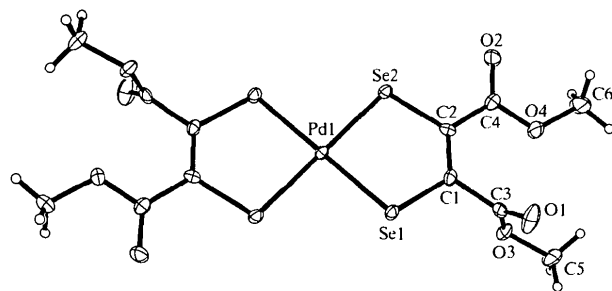


Fig. 1. The structure of the anion of (I) showing 50% probability displacement ellipsoids. H atoms are displayed as arbitrarily small circles.

Experimental

A solution of 75 mg (0.05 mmol) $[\text{PPh}_4]_2[\text{Pd}(\text{Se}_4)_2]$ (Ansari *et al.*, 1990) in 10 ml of dimethylformamide (DMF) was reacted with 0.25 ml (0.2 mmol) dimethyl acetylenedicarboxylate. The solution was then diluted with 20 ml of toluene. Yellow–orange needles were isolated in 16% yield based on $[\text{PPh}_4]_2[\text{Pd}(\text{Se}_4)_2]$. Electronic absorption (UV/VIS) spectrum [DMF; λ_{max} (nm) (ϵ_m)] 320 (3600), 464 (470). CHN analyses were satisfactory.

Crystal data

$(\text{C}_{24}\text{H}_{20}\text{P})_2[\text{Pd}(\text{C}_6\text{H}_6\text{O}_4\text{Se}_2)_2]$

$M_r = 1385.20$

Triclinic

$P\bar{1}$

$a = 10.273 (2) \text{ \AA}$

$b = 11.077 (2) \text{ \AA}$

$c = 13.803 (3) \text{ \AA}$

$\alpha = 69.43 (1)^\circ$

$\beta = 68.45 (1)^\circ$

$\gamma = 79.33 (1)^\circ$

$V = 1364.9 (5) \text{ \AA}^3$

$Z = 1$

$D_x = 1.685 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 15.0\text{--}17.5^\circ$

$\mu = 3.121 \text{ mm}^{-1}$

$T = 113 (2) \text{ K}$

Needle

$0.40 \times 0.09 \times 0.08 \text{ mm}$

Yellow–orange

Data collection

Picker diffractometer

ω scans

Absorption correction:

analytical (de Meulenaer & Tompa, 1965)

$T_{\text{min}} = 0.73$, $T_{\text{max}} = 0.80$

9590 measured reflections

4826 independent reflections

3371 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.066$

$\theta_{\text{max}} = 25.05^\circ$

$h = -12 \rightarrow 12$

$k = -13 \rightarrow 13$

$l = -16 \rightarrow 16$

6 standard reflections

every 100 reflections

intensity decay: $< 2\%$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.089$

$S = 0.90$

4826 reflections

341 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0400F_o^2)^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$

Extinction correction:

SHELXTL97 (Sheldrick, 1997)

Extinction coefficient:

0.0036 (4)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Pd1—Se1	2.4051 (7)	C3—O1	1.188 (7)
Pd1—Se2	2.3996 (7)	C3—O3	1.342 (7)
Se1—C1	1.887 (5)	C4—O2	1.208 (6)
Se2—C2	1.901 (5)	C4—O4	1.339 (6)
C1—C2	1.347 (7)	O3—C5	1.432 (6)
C1—C3	1.500 (7)	O4—C6	1.444 (7)
C2—C4	1.469 (7)		
Se2—Pd1—Se1	90.03 (2)	C1—C2—Se2	121.7 (4)
Se2'—Pd1—Se1	89.97 (2)	O1—C3—O3	124.1 (5)
Se1—Pd1—Se1'	180	O2—C4—O4	121.1 (5)
C1—Se1—Pd1	101.36 (16)	C3—O3—C5	114.5 (5)
C2—Se2—Pd1	102.03 (15)	C4—O4—C6	116.8 (5)
C2—C1—Se1	123.9 (4)		

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

Data collection: *PCPS* (local program). Cell refinement: *CELREF* (local program). Data reduction: *NUPICK* (local program). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL97*. Software used to prepare material for publication: *SHELXTL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1405). Services for accessing these data are described at the back of the journal.

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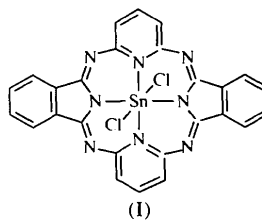
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Acta Cryst. (1999). **C55**, 32–33

trans-Dichloro(hemiporphyrinato)tin(IV)†

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Abstract

trans-Dichloro(hemiporphyrinato)tin(IV), [SnCl₂(C₂₆H₁₄N₈)], is a planar macrocyclic complex with six-coordinate tin in an N₄ coordination site bound to axial Cl ligands. The molecule has *D*_{2h} symmetry and is characterized by two short Sn—N(isoindole) bonds [2.041 (3) Å] and two long Sn—N(pyridine) bonds [2.213 (4) Å].

Comment

Transition metal, main-group and lanthanide complexes of the phthalocyanine macrocyclic ligand have been extensively studied. Complexes of the related hemiporphyrin ligand (Elvidge & Linstead, 1952), however, have received much less attention. We have started to examine the chemistry of the hemiporphyrin (hp) macrocycle, especially complexes of the main-group and lanthanide elements. In an attempt to form eight-coordinate Sn^{IV}-bis(hp) dimers similar to those reported for the phthalocyanine (pc) ligand (Bennett *et al.*, 1973), we first synthesized and structurally characterized the complex *trans*-(Cl)₂(hp)Sn^{IV}, (I) (Meyer *et al.*, 1975). This represents the second structure determination of a main-group hemiporphyrin complex (Hecht & Luger, 1974).

† Alternative name: dichloro(5,26:13,18-diimino-7,11:20,24-dinitrilo-benzoc[*c,n*][1,6,12,17]tetrazacyclodocosinato)tin(IV).

Tin(IV) forms a six-coordinate complex with the hp ligand (Fig. 1). The asymmetric unit consists of half of the macrocycle, with tin located on an inversion center. The tin cation is thus located exactly in the plane of the N₄ coordination sphere; chloride ligands bond to tin in the axial positions. Two different Sn—N distances result from the *D*_{2h} symmetry of the complex. The Sn—N(isoindole) distance is 2.041 (3) Å, while the Sn—N(pyridine) distance is considerably longer at 2.213 (4) Å. The Sn—Cl distance is 2.421 (1) Å. Unusually short intermolecular contacts are observed between the Cl⁻ ion and H3A from the molecule at ($\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$) and H4A from the molecule at ($1 - x, -y, -z$); these distances are 2.7 and 2.9 Å, respectively. All other Cl⁻···H intermolecular contacts are greater than 3 Å. The molecule packs in a herringbone motif (see figure in supplementary material).

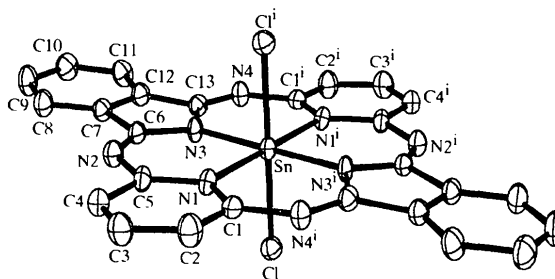


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The planarity of the hp macrocycle of (I) is in marked contrast with the related *trans*-dichloro-(phthalocyaninato)tin(IV) complex. In the pc complex, the macrocycle assumes a ruffled non-planar geometry to accommodate the large radius of the Sn^{IV} ion (Rogers & Osborn, 1971). The Sn—N distances are 2.051 Å. The larger coordination site in the hp macrocycle, resulting from the replacement of two of the four isoindole groups found in phthalocyanine with pyridines, is readily seen in the long Sn—N(pyridine) distances, although the Sn—N(isoindole) distance of 2.041 (3) Å is shorter than the Sn—N distance in the pc complex. Two different metal–nitrogen bond distances have also been observed for transition metal–hp complexes (Agostinelli *et al.*, 1984; Collamati *et al.*, 1986).