

**Crystal data**

[Hf <sub>2</sub> Cl <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) <sub>2</sub> ]	Mo K $\alpha$ radiation
$M_r = 759.17$	$\lambda = 0.71069 \text{ \AA}$
Monoclinic	Cell parameters from 56 reflections
$P2_1/n$	$\theta = 9.59\text{--}10.30^\circ$
$a = 7.7771 (12) \text{ \AA}$	$\mu = 10.55 \text{ mm}^{-1}$
$b = 13.148 (2) \text{ \AA}$	$T = 100 \text{ K}$
$c = 10.0967 (15) \text{ \AA}$	Needle
$\beta = 90.944 (9)^\circ$	$0.13 \times 0.13 \times 0.11 \text{ mm}$
$V = 1032.3 (3) \text{ \AA}^3$	Orange
$Z = 2$	
$D_x = 2.442 \text{ Mg m}^{-3}$	
$D_m$ not measured	

**Data collection**

Refurbished Picker diffractometer	2015 reflections with $F^2 > 2.33\sigma(F^2)$
$\theta/2\theta$ scans	$R_{\text{int}} = 0.025$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.567, T_{\text{max}} = 0.743$	$h = -10 \rightarrow 3$
3330 measured reflections	$k = 0 \rightarrow 17$
2366 independent reflections	$l = -13 \rightarrow 13$
	4 standard reflections every 400 reflections
	intensity decay: $-1.3\%$

**Refinement**

Refinement on $F$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
$R = 0.028$	$\Delta\rho_{\text{min}} = 0.20 \text{ e \AA}^{-3}$
$wR = 0.028$	Extinction correction: Larson (1967)
$S = 1.259$	Extinction coefficient: $0.5 (3) \times 10^{-7}$
2015 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
161 parameters	
All H atoms refined	
$w = 1/[\sigma^2(F) + (0.04F)^2]$	
$(\Delta/\sigma)_{\text{max}} = 0.05$	

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

Hf1—Cl2	2.5649 (16)	Hf1—C6	2.519 (6)
Hf1—Cl2 <sup>1</sup>	2.5668 (15)	Hf1—C7	2.453 (6)
Hf1—Cl3	2.3977 (18)	Hf1—C9	2.450 (6)
Hf1—C4	2.358 (3)	Hf1—C10	2.519 (6)
Hf1—C5	2.459 (6)		
Cl2—Hf1—Cl2 <sup>1</sup>	75.54 (5)	Cl2 <sup>1</sup> —Hf1—C4	135.90 (9)
Cl2—Hf1—Cl3	138.76 (6)	Cl3—Hf1—C4	88.88 (9)
Cl2 <sup>1</sup> —Hf1—Cl3	83.33 (6)	Hf1 <sup>1</sup> —Cl2—Hf1	104.46 (5)
Cl2—Hf1—C4	82.64 (9)		

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

The structure was readily solved by direct methods (*MULTAN78*; Main *et al.*, 1978) and standard Fourier techniques. During refinement it was observed that some disorder is present between the terminal methyl and terminal chloride groups. The refinement results are: Cl3 = 15.0(11)%C and 85.0(11)%Cl, while C4 = 60.2(16)%C and 39.8(16)%Cl. Given that occupancy refinement is highly correlated with displacement parameters, the above may or may not indicate the presence of a small amount of [HfCl<sub>2</sub>( $\mu$ -Cl)( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>], in spite of the reported s.u.'s. H atoms were refined [ $U_{\text{iso}} = 0.01 (2)\text{--}0.06 (2) \text{ \AA}^2$ ] to yield C—H bond distances in the range 0.82 (15)–1.07 (12)  $\text{\AA}$ .

Data collection: *PCPS* (local software). Cell refinement: *XTEL* (local software). Data reduction: *XTEL*. Program(s) used

to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *XTEL*. Molecular graphics: *XTEL*. Software used to prepare material for publication: *XTEL*.

This research was partially supported by an award from the Research Corporation. Acknowledgement of support is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank the Indiana Academy of Sciences and the Ball State University Office of Academic Research and Sponsored Programs, for funds supporting this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1091). Services for accessing these data are described at the back of the journal.

**References**

- Arnold, J., Roddick, D. M., Tilley, T. D., Rheingold, A. L. & Geib, S. J. (1988). *Inorg. Chem.* **27**, 3510–3514.
- Atwood, J. L., Hunter, W. E., Hrcir, D. C., Samuel, E., Alt, H. & Rausch, M. D. (1975). *Inorg. Chem.* **14**, 1757–1762.
- Ewen, J. A., Jones, R. L., Razavi, A. & Ferrara, J. D. (1988). *J. Am. Chem. Soc.* **110**, 6255–6258.
- Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
- Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- Shaw, S. L. & Morris, R. J. (1995). *J. Organomet. Chem.* **489**, C4–6.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

*Acta Cryst.* (1998). **C54**, 1618–1622

## 2:1 Adducts of Halotris(*p*-tolyl)tin(IV) with 1,9-Bis(4-oxopent-2-en-2-ylamino)-3,7-dithianonane

STANLEY A. BAJUE,<sup>a</sup> FITZGERALD B. BRAMWELL,<sup>b</sup>  
CAROLYN PRATT BROCK<sup>b</sup> AND JEUNEVETTE BONTEMPS<sup>c</sup>

<sup>a</sup>Department of Physical Sciences and Computer Science, Medgar Evers College, City University of New York, Brooklyn, NY 11225-2298, USA, <sup>b</sup>Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA, and <sup>c</sup>Department of Chemistry, Brooklyn College, Brooklyn, NY 11210-2889, USA. E-mail: cpbrock@ukcc.uky.edu

(Received 23 January 1998; accepted 29 April 1998)

**Abstract**

The structures of ( $\mu$ -5,15-diaza-8,12-dithianodeca-3,16-diene-2,18-dione-*O,O'*bis[halotris(*p*-tolyl)tin] {halo is bromo, [Sn<sub>2</sub>Br<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>)<sub>6</sub>(C<sub>17</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>)], iodo, [Sn<sub>2</sub>-

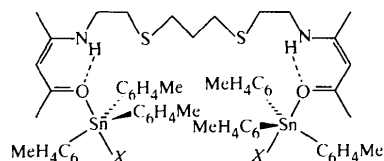
$\text{I}_2(\text{C}_7\text{H}_7)_6(\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_2)$ , and chloro} have been determined. The three compounds are isostructural, but the chlorine-containing structure is imprecise and its structure data are not reported. Of the six potential coordination sites on the bridging dithianone ligand, only the two carbonyl O atoms are bonded to Sn atoms [Sn—O = 2.30 (1)–2.35 (1) Å for the bromine and iodine compounds]. The carbonyl O atoms also interact with amine N atoms through N—H···O hydrogen bonds [N—O = 2.62 (2)–2.66 (1) Å]. The direction of greatest expansion [ $\Delta c$  (space group  $Pna2_1$ ) = 0.598 (3) Å at 296 K when Br is changed to I] is nearly perpendicular [ $76(1)$ – $88(1)^\circ$ ] to the tin–halogen bonds.

### Comment

Several adducts of organotin(IV) halides with tetradentate (Smith & Dodd, 1971; Ruddick & Sams, 1973) and tridentate (Teoh *et al.*, 1997) Schiff base ligands are known (coordination of Sn by O and N atoms). The structure of a five-coordinate tin(IV) compound containing a tridentate Schiff base ligand analogous to one end of the ligand used here is also known (Okechukwu *et al.*, 1993; coordination of Sn by O, N, and S atoms). Organotin(IV) halide adducts of potentially hexadentate Schiff base ligands containing two potentially tridentate Schiff base moieties appear, however, to be unknown.

Crystals of the three title compounds [bromo, (I), iodo, (II), and chloro analogs] are isostructural (see *Experimental*). The ligand is coordinated to two Sn atoms through the carbonyl O atoms at the two ends of the chain. The N atoms appear to participate in N—H···O hydrogen bonds (see Table 1), but do not interact

with the Sn atoms. The S atoms are uncoordinated. There are no Br···Br or I···I contacts less than 7.6 Å.



(I) X = Br

(II) X = I

The geometry around each Sn atom is trigonal bipyramidal with only very minor distortions (see Table 1).

When I is substituted for Br, the cell constants  $a$ ,  $b$  and  $c$  change by  $-0.047(2)$ ,  $+0.043(1)$  and  $+0.598(3)$  Å, respectively. On first glance, these changes suggest that the Sn—X vectors are approximately parallel to  $c$ . In fact, however, the two Sn—X vectors are nearly perpendicular to  $c$  [angles  $76(1)$  and  $88(1)^\circ$  for the two vectors in each of the two structures]. It is the whole molecule that expands slightly in the  $c$  direction when the Sn—X bonds are lengthened (see Fig. 3). The intermolecular contacts responsible for this expansion seem to be between the halide X2 atom and the H atoms attached to C4 and C17, and between the X1 atom and the H atom attached to C6. If the Sn—Br bonds are stretched to the length of the Sn—I bonds but all else in the bromine-containing structure is left unchanged, then three very short contacts are found:  $\text{I}2 \cdots \text{H}4\text{B}(x, 1+y, z) = 2.6$ ,  $\text{I}2 \cdots \text{H}17\text{C}(\frac{1}{2}+x, \frac{3}{2}-y, z) = 2.8$  and  $\text{I}1 \cdots \text{H}6(x, 1+y, z) = 3.0$  Å (calculated H-atom positions; van der

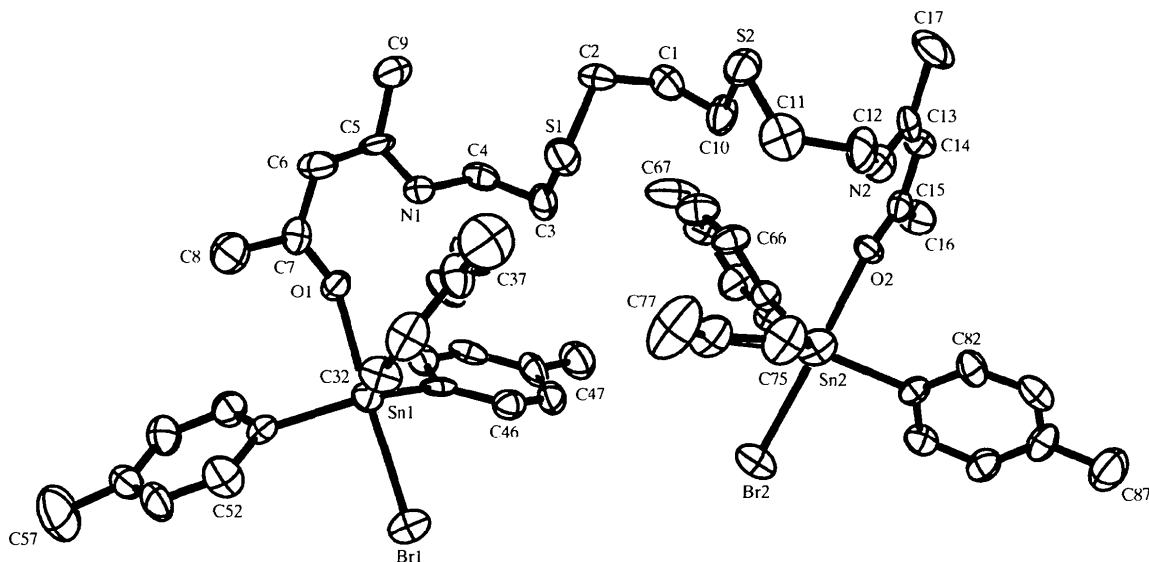


Fig. 1. Perspective drawing of the bromine-containing molecule, (I), showing the atom-numbering scheme. Numbers not shown can be inferred from those given. The shapes of the ellipsoids correspond to 30% probability contours of atomic displacement. H atoms have been omitted for clarity.

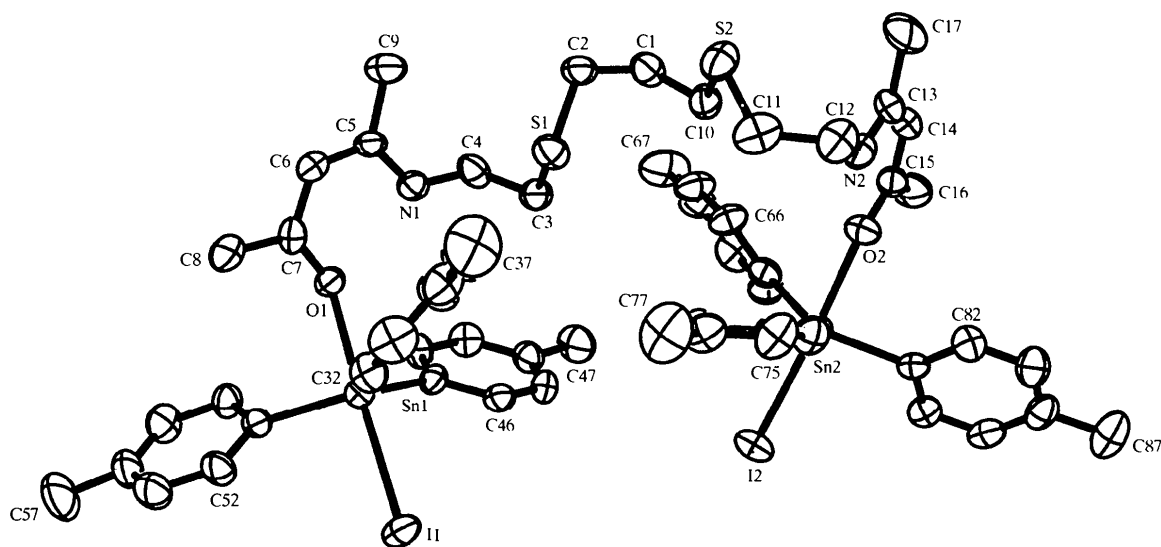


Fig. 2. Perspective drawing of the iodine-containing molecule, (II), represented as in Fig. 1.

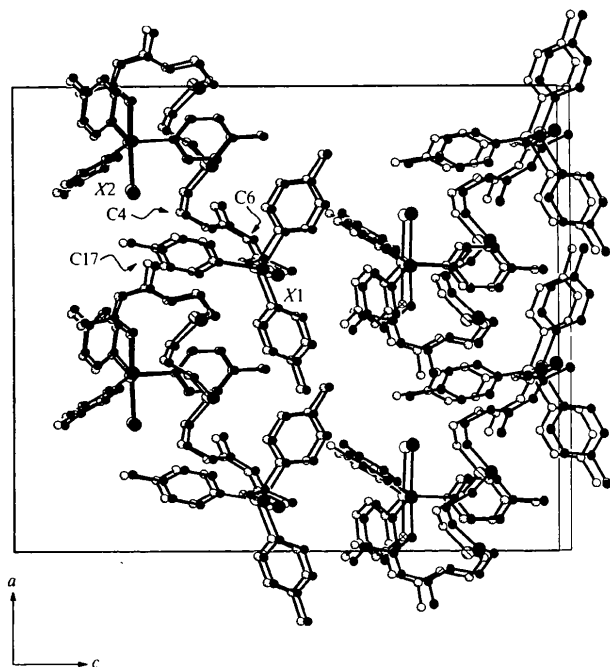


Fig. 3. Packing diagram showing superimposed projections onto the *ac* plane of the bromine- (light circles) and iodine-containing (dark circles) structures. The left edges of the unit cells have been aligned. All marked atoms are in molecules related by the translation along *b*, except for C17, which is in a molecule related by the *a* glide.

The differences between the chlorine- and bromine-containing structures are similar to the differences between the bromine- and iodine-containing structures.

### Experimental

The ligand was prepared by condensing 2,4-pentanedione with H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>S(CH<sub>2</sub>)<sub>3</sub>S(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>. The tin adducts were prepared by refluxing 2:1 molar amounts of the organotin halides with the ligand in ethanol. Crystals of (I) and (II) were grown by slow evaporation of toluene/petroleum ether solutions.

### Compound (I)

#### Crystal data

[Sn<sub>2</sub>Br<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>)<sub>6</sub>(C<sub>17</sub>H<sub>30</sub>-  
N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>)]  
*M<sub>r</sub>* = 1302.56  
 Orthorhombic  
*Pna*2<sub>1</sub>  
*a* = 22.8039 (11) Å  
*b* = 10.3340 (8) Å  
*c* = 26.1543 (15) Å  
*V* = 6163.4 (7) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.404 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

#### Data collection

Enraf-Nonius CAD-4 VAX  
 diffractometer  
 $\omega$  scans  
 Absorption correction:  
 empirical based on 7  $\psi$   
 scans (Flack, 1977)  
*T<sub>min</sub>* = 0.41, *T<sub>max</sub>* = 0.80  
 5553 measured reflections  
 5553 independent reflections

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 22  
 reflections  
 $\theta$  = 12.2–12.8°  
 $\mu$  = 2.20 mm<sup>-1</sup>  
*T* = 296 (1) K  
 Plate; major faces are {100}  
 (largest), {201}, {001}  
 and {110}  
 0.55 × 0.48 × 0.10 mm  
 Light yellow

Waals radii sum 3.35 Å). In the iodine-containing structure, the corresponding observed distances are 3.0, 2.8 and 3.3 Å, respectively. The lengthened contacts result from a slight stretching of the molecule in the *c* direction and a slight rearrangement of the ligand that affects the I2...C17 separation in the *a* direction (see Fig. 3).

2861 reflections with  
 $I > 2\sigma(I)$   
 $\theta_{\max}$  = 25°  
*h* = 0 → 27  
*k* = 0 → 12  
*l* = 0 → 31  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 1.7%

**Refinement**

Refinement on  $F^2$   
 $R[\mathcal{I}^2 > 2\sigma(\mathcal{I}^2)] = 0.044$   
 $wR(F^2) = 0.131$   
 $S = 1.01$   
 5535 reflections  
 622 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 1.30P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$   
 $\Delta\rho_{\max} = 0.91 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.63 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)  
 Absolute structure:  
 Flack (1983)  
 Flack parameter =  $-0.01$  (2)

**Compound (II)****Crystal data**

$[\text{Sn}_2\text{I}_2(\text{C}_7\text{H}_7)_6(\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_2)]$   
 $M_r = 1396.55$   
 Orthorhombic  
 $Pna2_1$   
 $a = 22.7565$  (12)  $\text{\AA}$   
 $b = 10.3774$  (11)  $\text{\AA}$   
 $c = 26.752$  (3)  $\text{\AA}$   
 $V = 6317.6$  (10)  $\text{\AA}^3$   
 $Z = 4$   
 $D_x = 1.468 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 23 reflections  
 $\theta = 12.2\text{--}14.4^\circ$   
 $\mu = 1.86 \text{ mm}^{-1}$   
 $T = 296$  (1) K  
 Block; major faces are  
 $\{001\}$  (largest),  $\{201\}$ ,  
 $\{011\}$  and  $\{110\}$   
 $0.55 \times 0.48 \times 0.30 \text{ mm}$   
 Yellow

**Data collection**

Enraf–Nonius CAD-4 VAX diffractometer  
 $\omega$  scans  
 Absorption correction: empirical based on 10  $\psi$  scans (Flack, 1977)  
 $T_{\min} = 0.46$ ,  $T_{\max} = 0.57$   
 5674 measured reflections  
 5674 independent reflections

3588 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 25^\circ$   
 $h = 0 \rightarrow 26$   
 $k = 0 \rightarrow 12$   
 $l = 0 \rightarrow 31$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 3.5%

**Refinement**

Refinement on  $F^2$   
 $R[\mathcal{I}^2 > 2\sigma(\mathcal{I}^2)] = 0.028$   
 $wR(F^2) = 0.073$   
 $S = 1.040$   
 5654 reflections  
 622 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 2.04P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.006$   
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)  
 Absolute structure:  
 Flack (1983)  
 Flack parameter = 0.00 (2)

Sn2—C81	2.143 (14)	2.142 (8)
N1...O1	2.620 (15)	2.638 (9)
N2...O2	2.657 (16)	2.663 (9)
O1—Sn1—X1	177.9 (2)	178.3 (1)
C31—Sn1—X1	93.3 (4)	93.8 (2)
C41—Sn1—X1	95.9 (4)	96.5 (2)
C51—Sn1—X1	93.7 (4)	93.2 (2)
C31—Sn1—O1	86.5 (4)	85.9 (3)
C41—Sn1—O1	82.2 (4)	82.1 (3)
C51—Sn1—O1	88.2 (4)	88.3 (3)
C31—Sn1—C41	113.5 (5)	112.2 (3)
C31—Sn1—C51	123.9 (5)	124.5 (3)
C41—Sn1—C51	120.9 (5)	121.5 (3)
O2—Sn2—X2	178.0 (2)	177.0 (2)
C61—Sn2—X2	92.1 (4)	91.4 (2)
C71—Sn2—X2	95.5 (4)	94.3 (2)
C81—Sn2—X2	93.9 (4)	94.2 (2)
C61—Sn2—O2	87.7 (5)	88.8 (3)
C71—Sn2—O2	82.8 (5)	83.0 (3)
C81—Sn2—O2	87.9 (5)	88.2 (3)
C61—Sn2—C71	115.7 (6)	114.9 (4)
C61—Sn2—C81	122.0 (5)	123.6 (3)
C71—Sn2—C81	120.9 (5)	120.5 (3)

The structures of the bromine- and iodine-containing compounds were solved and refined without difficulty. Some of the displacement ellipsoids, however, are surprisingly eccentric and/or elongated in directions incompatible with reasonable mechanical models for molecular motion. The average values for the  $U_{\text{iso}}$  values of the C, N and O atoms ( $0.081 \text{ \AA}^2$  in the bromine structure and  $0.086 \text{ \AA}^2$  in the iodine structure) are larger than usual. We believe that the unusual ellipsoids reflect conformational flexibility in these loosely packed structures. The crystals of the iodine-containing compound were approximately equidimensional, those of the bromine-containing compound were thick plates and those of the chlorine-containing compound were thin lozenges. The lozenges scattered very poorly, even after the crystals were cooled to 177 (1) K. Some crystals were obviously twinned. Even for the best crystal found, only about 60% of the reflections had  $I > 2\sigma(I)$  at a  $\theta_{\max}$  value of  $22.5^\circ$ . Many of the peaks were badly split. Full anisotropic refinement gave unacceptable displacement parameters for some of the C atoms, and some of the phenyl rings deviated significantly from planarity. The C, N and O atoms were therefore refined isotropically, and the six phenyl rings were restrained to be planar and to have similar C—C bond lengths. The final agreement factors were  $R$  [on  $F$ ; 2311 reflections having  $I > 2\sigma(I)$ ] = 0.105 and  $wR$  (on  $F^2$ ; all 3962 reflections) = 0.278 for 307 variables and 115 restraints. Some of the isotropic  $U$  values are clearly too small. The identity of the compound and the overall crystal packing are not, however, in doubt. The H atoms of both the bromine- and iodine-containing compounds were refined as riding with N—H 0.90  $\text{\AA}$ , C—H 0.96  $\text{\AA}$  and  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the attached N or C atom. Details of the chlorine-containing compound have been deposited.

For both compounds, data collection: *CAD-4 Manual* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Manual*; program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993).

This work was supported in part by grants provided by the City University of New York Professional Staff Conference Faculty Research Awards Program (#95-666 288) and by the New York State Science and Technology Entry Program (#554540).

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I) and (II)

	(I) ( $X = \text{Br}$ )	(II) ( $X = \text{I}$ )
Sn1—X1	2.660 (2)	2.8831 (8)
Sn2—X2	2.649 (2)	2.8987 (8)
Sn1—O1	2.350 (9)	2.337 (6)
Sn2—O2	2.331 (9)	2.302 (5)
Sn1—C31	2.124 (13)	2.132 (8)
Sn1—C41	2.10 (2)	2.134 (9)
Sn1—C51	2.126 (14)	2.128 (8)
Sn2—C61	2.124 (14)	2.127 (9)
Sn2—C71	2.125 (13)	2.124 (9)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1121). Services for accessing these data are described at the back of the journal. Full structural data for the chlorine analog have also been deposited and are included in the CIF.

## References

- Enraf–Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Flack, H. D. (1977). *Acta Cryst.* **A33**, 890–898.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Okechukwu, R. C., Fun, H.-K., Teoh, S.-G., Teo, S.-B. & Chinnakali, K. (1993). *Acta Cryst.* **C49**, 368–370.
- Ruddick, J. N. R. & Sams, J. R. (1973). *J. Organomet. Chem.* **60**, 233–246.
- Sheldrick, G. M. (1990). *SHELXTL/PC*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Smith, P. J. & Dodd, D. (1971). *J. Organomet. Chem.* **32**, 195–199.
- Teoh, S.-G., Yeap, G., Loh, C.-C., Foong, L.-W., Teo, S.-B. & Fun, H.-K. (1997). *Polyhedron*, **16**, 2213–2221.

*Acta Cryst.* (1998). **C54**, 1622–1624

## (1,1-Dimercaptoethene-2,2-dicarbonitrilato-*S,S'*)bis(triphenylphosphine)palladium(II) Diacetonitrile Solvate

MUTAI BAO, RONG CAO, WEIPING SU AND MAOCHUN HONG

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, People's Republic of China. E-mail: hmc@ms.fjirm.ac.cn

(Received 30 September 1997; accepted 5 May 1998)

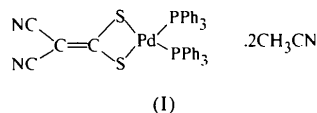
## Abstract

The title palladium(II) compound, [Pd(PPh<sub>3</sub>)<sub>2</sub>{S<sub>2</sub>C=C(CN)<sub>2</sub>}].2CH<sub>3</sub>CN or [Pd(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)(C<sub>18</sub>H<sub>15</sub>P)<sub>2</sub>].2C<sub>2</sub>H<sub>3</sub>N, was obtained from the reaction of PPh<sub>3</sub>, PdCl<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>C=C(CN)<sub>2</sub> (i-mnt) in CH<sub>3</sub>CN. The Pd atom is coordinated by two P and two S atoms in a distorted square-planar arrangement. The average Pd–P and Pd–S distances are 2.3184(11) and 2.3420(11) Å, respectively, the P–Pd–P and S–Pd–S angles are 99.11(4) and 74.68(4)°, respectively.

## Comment

Transition metal complexes with phosphine ligands have been studied extensively, not only due to the variation in their geometric and electronic structures and properties,

but also because of their application for homogeneous or heterogeneous catalytic functions (Puddephatt, 1983; Cotton *et al.*, 1987; Kiess & Eisenberg, 1989). Metal–thiolate complexes are known as ubiquitous biological electron-transfer mediators and have been studied for two decades (Blower & Dilworth, 1987). However, complexes blending both phosphine and thiolate ligands have received attention only in recent years. Many palladium complexes containing such mixed ligands (Fenn & Segrott, 1972; Dance, 1986; Wolf *et al.*, 1980) have been structurally characterized. Recently, studies of metal–thiolate–phosphine complexes began in our laboratory, resulting in a series of palladium(II) complexes, such as [Pd<sub>2</sub>(SC<sub>2</sub>H<sub>4</sub>S)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (Cao *et al.*, 1995), [Pd<sub>2</sub>(HOC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (Cao *et al.*, 1996) and [Pd(SC<sub>3</sub>H<sub>6</sub>S){Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>}] (Su *et al.*, 1996). We report herein the synthesis and crystal structure of a mononuclear palladium complex, namely, (1,1-dimercaptoethene-2,2-dicarbonitrilato-*S,S'*)bis(triphenylphosphine)palladium(II) diacetonitrile solvate, [Pd(PPh<sub>3</sub>)<sub>2</sub>{S<sub>2</sub>C=C(CN)<sub>2</sub>}].2CH<sub>3</sub>CN, (I).



Selected bond distances and angles are listed in Table 1. The molecular structure of the complex consists of a discrete monopalladium complex and two CH<sub>3</sub>CN solvent molecules. As depicted in Fig. 1, the complex molecule does not possess any crystallographic symmetry. The Pd atom is surrounded by two

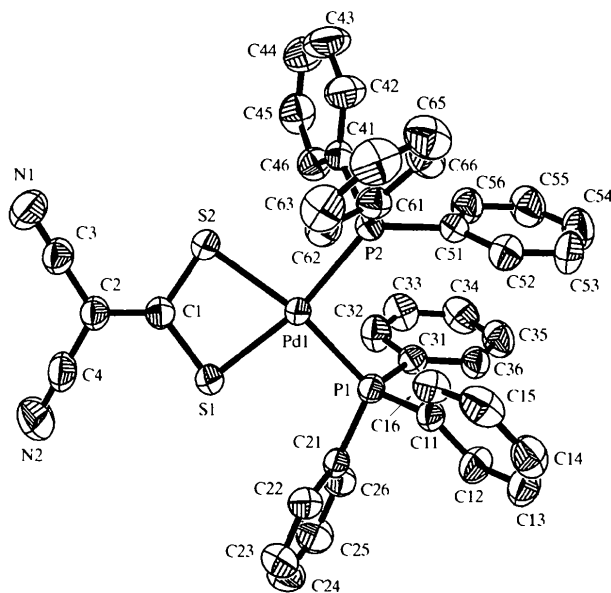


Fig. 1. The crystal structure of [Pd(PPh<sub>3</sub>)<sub>2</sub>{S<sub>2</sub>C=C(CN)<sub>2</sub>}].2CH<sub>3</sub>CN, with displacement ellipsoids plotted at the 50% probability level.