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Structure of Diiodo[1,2-bis(phenylthio)benzene]palladium(II) Diiodine (1/1), $[Pd(C_{18}H_{14}S_2)I_2]I_2$

BY L. R. GRAY, D. J. GULLIVER, W. LEVASON AND M. WEBSTER*

Department of Chemistry, The University, Southampton SO9 5NH, England

(*Received* 13 *January* 1983; *accepted* 14 *April* 1983)

Abstract. $M_r = 908\cdot43$, monoclinic, $C2/c$, $a = 16\cdot551\,(9)$, $b = 11\cdot588\,(2)$, $c = 12\cdot521\,(5)$ Å, $\beta = 99\cdot12\,(4)°$, $V = 2371\cdot1$ Å^3, $Z = 4$, $D_m = 2\cdot56\,(2)$, $D_x = 2\cdot544$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu(\text{Mo } K\alpha) = 6\cdot08$ mm^{-1}, $F(000) = 1648$, room temperature, $R = 0\cdot0668$ for 2218 observed reflections. The palladium atom, which lies on the twofold axis, is planar four-coordinate (S_2I_2 donor set) Pd—S = 2·293 (2), Pd—I = 2·606 (1) Å, with adjacent molecules linked by diiodine (I···I—I···I) producing essentially linear I_4 groups I···I = 3·563 (2), I—I = 2·733 (2) Å. The chelating dithioether has an *anti* conformation of the phenyl groups.

Introduction. Palladium(IV) complexes of types $[R_4N][PdLX_5]$ and $[Pd(L\text{—}L)X_4]$ (L, $L\text{—}L$ respectively mono- and bidentate amine, phosphine or arsine, X = Cl, Br) have recently been obtained by halogen oxidation of the palladium(II) analogues (Gulliver & Levason, 1982*a*; Gray, Gulliver, Levason & Webster, 1983*a*). The corresponding reactions of $[Pd(L'\text{—}L')I_2]$ [$L'\text{—}L'$ = *cis*-$Ph_2PCH{=}CHPPh_2$, $Me_2As(CH_2)_3AsMe_2$] with molecular iodine gave black materials of empirical formula $Pd(L'\text{—}L')I_4$, and the X-ray structure determination of Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_4 revealed a planar (P_2I_2) arrangement about the palladium(II) with iodine molecules linking the Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_2 units (Gray, Gulliver, Levason & Webster, 1983*b*). The reaction of $[Pd\{o\text{-}C_6H_4(SPh)_2\}I_2]$ with iodine gave a black material of composition $Pd\{o\text{-}C_6H_4(SPh)_2\}I_3$, and a crystal structure analysis of this was undertaken to establish the nature of the (presumed) palladium(II) polyiodide. It should be noted that one genuine palladium(IV) iodocomplex is known, Cs_2PdI_6 (Sinram, Brendel & Krebs, 1982).

Experimental. Air-stable black crystals prepared (Gray *et al.*, 1983*b*) by recrystallization from $C_2H_4Cl_2$, D_m by flotation, preliminary data obtained from Weissenberg photographs, data collection on Enraf–Nonius CAD-4 diffractometer, cell dimensions from 25 accurately centred reflections, systematic absences hkl, $h + k \neq 2n$; $h0l$, ($h \neq 2n$), $l \neq 2n$; $0k0$, ($k \neq 2n$) indicated Cc (No. 9) or $C2/c$ (No. 15), the latter established by structure determination; 3881 reflections (3540 not including systematic absences), crystal 0·20 × 0·10 × 0·05 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation ($1\cdot5 \leq \theta \leq 30\cdot0°$); three check reflections showed no deterioration; $R_{\text{int}} = 0\cdot0041$, 2221 reflections [$F > 2\sigma(F)$] used in refinement, index range h −23–22, k 0–16, l 0–17, empirical absorption correction based on a φ scan applied [transmission: 99·9 (max.), 75·5 (min)] plus usual Lorentz and polarization factors; distribution of E's (normalized structure factors) favoured a centrosymmetric space group.

Structure solved by Patterson methods; initial attempts in $C2/c$ by both direct methods and inspection of the Patterson function failed to yield a solution. An electron density synthesis phased on Pd and two I atoms in Cc gave a recognizable ligand fragment and the remaining I atoms and the model was developed by conventional structure factor and electron density

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* To whom correspondence should be addressed.

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syntheses to locate all the non-hydrogen atoms. It became apparent from the atomic positions that the model could be described in *C*2/*c* and comparison of the *R* factor for similar stages of refinement led to the final model in the centrosymmetric space group *C*2/*c*. Difference electron density synthesis showed peaks corresponding to some of the H atoms; H atoms introduced with a common refined temperature factor [H(2) in an observed position, H(5) to H(9) in geometrically calculated positions, $d(C-H) = 1{\cdot}08$ Å], three reflections apparently suffering from extinction omitted from final refinement; least-squares refinement on F converged to $R = 0{\cdot}0668$ ($R_w = 0{\cdot}0493$), 115 parameters, anisotropic (I, Pd, S, C) and isotropic (H), $w = 1/[\sigma^2(F) + 0{\cdot}0001\,F^2]$, max. shift/error 0·2; final difference electron density synthesis showed all features in the range + 1·60 to −1·23 e Å^{-3} with the largest peak near the Pd atom; scattering factors and anomalous-dispersion terms for neutral atoms taken from *SHELX* (Sheldrick, 1976) (S, C, H) and *International Tables for X-ray Crystallography* (1974). All calculations with *SHELX* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1979), *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1978) on an ICL 2970 computer.

Discussion. Tables 1 and 2 show the final atomic coordinates* and selected bond lengths and angles, respectively. Fig. 1 shows the atom numbering scheme.

Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2 × 10^3)

	x	*y*	*z*	U_{eq}*
Pd	0·0000	0·2288 (1)	0·2500	32·0
I(1)	0·0330 (1)	0·3846 (1)	0·1131 (1)	49·4
I(2)	0·1720 (1)	0·2860 (1)	0·4630 (1)	75·7
S	0·0323 (1)	0·0881 (2)	0·1352 (1)	35·0
C(1)	0·0183 (4)	−0·0444 (7)	0·2025 (6)	34·3
C(2)	0·0382 (6)	−0·1474 (7)	0·1596 (6)	46·6
C(3)	0·0187 (6)	−0·2513 (7)	0·2044 (7)	51·6
C(4)	0·1398 (5)	0·0875 (7)	0·1327 (7)	42·5
C(5)	0·1950 (6)	0·0705 (11)	0·2240 (9)	69·6
C(6)	0·2789 (6)	0·0703 (12)	0·2194 (11)	88·7
C(7)	0·3037 (6)	0·0899 (10)	0·1199 (11)	77·4
C(8)	0·2488 (7)	0·1082 (11)	0·0289 (11)	76·8
C(9)	0·1647 (6)	0·1070 (9)	0·0347 (9)	60·0

* $U_{eq} = \frac{1}{3}$ trace U.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* $[Pd\{o\text{-}C_6H_4(SPh)_2\}I_4]$

Pd–I(1)	2·606 (1)	I(1)···I(1^i)	3·76 (1)
Pd–S	2·293 (2)	S···S^i	3·22 (1)
I(2)–I(2^{ii})	2·733 (2)	S···I(1)	3·45 (1)
I(1^i)–I(2)	3·563 (2)	C–C minimum	1·36 (2)
S–C(1)	1·783 (8)	C–C maximum	1·42 (2)
S–C(4)	1·785 (8)	C–C mean	1·38
I(1)–Pd–I(1^i)	92·3 (1)	S–C(1)–C(2)	120·5 (6)
I(1)–Pd–S	89·2 (1)	S–C(1)–C(1^i)	120·1 (5)
S–Pd–S^i	89·3 (1)	S–C(4)–C(5)	121·6 (7)
Pd–S–C(1)	104·8 (3)	S–C(4)–C(9)	117·1 (7)
Pd–S–C(4)	110·2 (3)	Pd–I(1^i)–I(2)	70·4 (1)
C(1)–S–C(4)	102·1 (4)	I(1^i)–I(2)–I(2^{ii})	175·7 (1)

C–C–C in the range 118 (1) to 122 (1)°

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

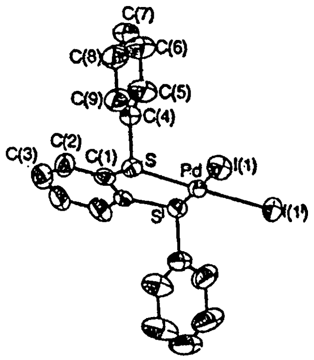

Fig. 1. $Pd\{o\text{-}C_6H_4(SPh)_2\}I_4$ showing the coordination around the palladium atom, and the atom numbering scheme. H atoms excluded for clarity and atoms drawn with 60% probability ellipsoids. Symmetry code: (i) $-x, y, \frac{1}{2}-z$.

The structure determination revealed that the complex present in the crystal examined was $[Pd\{o\text{-}C_6H_4(SPh)_2\}I_4]$. The Pd atom is located on a twofold axis and the dithio ligand has twofold symmetry. The structure (Fig. 1) consists of a Pd atom bonded to two I atoms and two S atoms of the chelating dithioether. The individual molecules are linked *via* the I atoms by molecular iodine giving the polymeric arrangement shown in Fig. 2. An alternative description is of palladium–dithioether units linked by bridging tetraiodide(2−) ligands. The essentially planar environment of the palladium is indicative of d^8 Pd^{II} rather than d^6 Pd^{IV} which is invariably octahedrally coordinated (Gulliver & Levason, 1982*b*). Few dithioether or diselenoether complexes have been structurally characterized (Murray & Hartley, 1981); the known examples containing four-coordinate metal centres are $[Pt\{CF_3SCH(CH_3)CH_2SCF_3\}Cl_2]$ (Manojlović-Muir, Muir & Solomun, 1977), $[Pd(MeSCH_2CH_2SMe)(^tBuC\text{-}CHCHCCl^tBu)Cl]$ (Mann, Bailey & Maitlis, 1975), and $[Pd(^iPrSeCH_2CH_2Se^iPr)Cl_2]$ (Whitfield, 1970), all of

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates, benzene-ring bonds and angles and equations of planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38498 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

which contain the substituents on the Group VI atom in the *syn* configuration. The present structure differs in that the phenyl groups are arranged *anti*. Proton NMR spectra of Pt^{II} and Pd^{II} dithioether complexes have shown that in solution both *meso* (*syn* terminal groups) and (±) (*anti*) forms of the dithioether are present, and that these interconvert by pyramidal inversion at sulphur (Murray & Hartley, 1981). The presence of only one form in the solids may reflect small differences in solubility or crystal packing forces. In $[Pd\{o\text{-}C_6H_4(SPh)_2\}I_4]$ there are no obvious intramolecular contacts which would preclude the complex having *syn* phenyl groups. The Pd—S bond length in the title complex [2·293 (2) Å] is comparable with that in $[Pd\{o\text{-}C_6H_4(PPh_2)(SMe)\}I_2]$ [2·288 (2) Å] (Clark & Orbell, 1981) and with the Pt—S bond length in *cis*-$[Pt\{(4\text{-}ClC_6H_4)_2S\}_2Cl_2]$ [2·292 (6), 2·278 (2) Å] (Spofford, Amma & Senoff, 1971). The C—S and C—C bond lengths and the angles within the dithioether are unexceptional.

The Pd—I distance 2·606 (1) Å is not significantly different from the $Pd—I_{transS}$ in $[Pd\{o\text{-}C_6H_4(PPh_2)(SMe)\}I_2]$ [2·602 (1) Å] (Clark & Orbell, 1981), but is much shorter than the $Pd—I_{transP}$ in $[Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)I_4]$ [2·660 (1), 2·652 (1) Å] (Gray *et al.*, 1983*b*), demonstrating the much weaker *trans* influence of sulphur. The geometry and dimensions of the polyiodide unit are similar to those in $[Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)I_4]$ and comparison with the structural data for other examples (Tebbe, 1982) suggests that in the present complex the $I\cdots I_2$ interaction is very weak. The $I\cdots I_2$ distance 3·563 (2) Å is the longest reported for a metal–I_4 unit, and indeed is only *ca* 0·2 Å shorter than the I···I separation between the *cis* iodines in the Pd(dithioether)I_2 unit, which are regarded as non-bonded. There are no close approaches between the sulphur and the iodine molecules, ruling out any significant 'secondary bonding' (Alcock, 1972) between them.

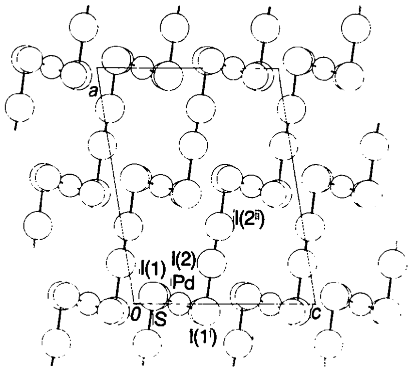

Fig. 2. Unit cell of $Pd\{o\text{-}C_6H_4(SPh)_2\}I_4$ showing the Pd, I and S atoms only, viewed from the positive *y* direction. Symmetry code: (i) $-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

The analytical data (C, H, I) on the batch from which the crystal was selected corresponded well with a $Pd\{o\text{-}C_6H_4(SPh)_2\}I_3$ composition. Under the microscope the sample appeared homogeneous, although since crystals of $[Pd\{o\text{-}C_6H_4(SPh)_2\}I_2]$ are purple-black, and in view of the very small size of many of the crystals, optical distinction of the two is uncertain. In the light of the X-ray data which showed the iodine to be only weakly associated with the palladium(II) complex, the formation of iodine-deficient 'Pd(*L*—*L*)I_4' materials is likely. However, there was no evidence that the single crystal examined had significantly less than four I atoms per Pd atom. A calculation in which the iodine molecule was given a partial population (0·5) corresponding to a composition Pd(*L*—*L*)I_3 failed to refine and had a large *R* factor supporting the I_4 formulation for this crystal.

We thank Dr M. B. Hursthouse for the data collection on the QMC/SERC Enraf–Nonius CAD-4 diffractometer and Southampton University for financial support (LRG and DJG).

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