The coordination polyhedron, illustrated in Fig. 2, has imposed C_2 symmetry, the U and the water $O[O(W1)]$ atoms lying on a crystallographic twofold axis. Its geometry (Table 2) may be described as intermediate between the tricapped trigonal prism (TCTP) of symmetry D_{3h} and the capped square antiprism (CSAP) of symmetry C_{4v}. The distortion from TCTP towards CSAP is shown by the δ angles (Drew, 1977) reported in Table 2, and especially by the three δ angles over the v edges. Two possible CSAP's can be derived from the TCTP depending on which of the capping atoms [$O(W1)$ or $O(2)$] in the TCTP polyhedron is chosen as capping atom in the CSAP. One would expect the CSAP with $O(W1)$ as capping atom to be the most appropriate choice, but geometrical features (Table 3) indicate that the distortion is towards the CSAP, capped with the oxalate $O(2)$ atom [$c111$ isomer among the seven isomers proposed for the form M(unidentate)(bidentate)$_4$ by Drew (1977)]. This observation is in agreement with the results of calculations in the hard-sphere model (Burgi, 1973), which predict that s_1 edges are unsuitable for a bidentate ligand.

The crystal packing is illustrated in Fig. 3. Ba—O and O—O (probable hydrogen bonds) contacts are reported in Table 3. There are two symmetrically non-equivalent Ba atoms per asymmetric unit. They interact with the oxalate O atoms which are not coordinated to the U atom. The oxalate groups thus behave as quadridentate
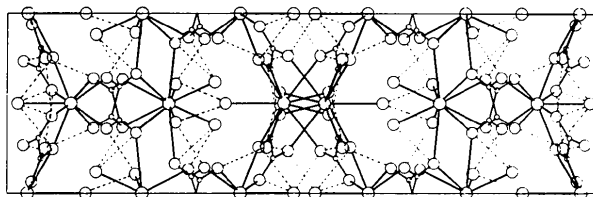

Fig. 3. View of the unit cell along the c axis.

ligands, acting as bridges between the U and Ba atoms. The two Ba atoms are also coordinated to the nearest-neighbour water O atoms and reach coordination number ten [Ba(1)] or eleven [Ba(2)]. The high temperature factors of the water O atoms $O(W4)$ and $O(W5)$ indicate some disorder in the relatively large holes of the packing.

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Structure of *trans*-Diiodobis(triphenylstibine)palladium(II) and Observations on the Pd—I Bond Length

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Abstract. [PdI$_2$\{(C$_6$H$_5$)$_3$Sb\}$_2$], $M_r = 1066\cdot34$, triclinic, $P\bar{1}$, $a = 10\cdot005$ (1), $b = 10\cdot121$ (1), $c = 10\cdot208$ (1) Å, $\alpha = 105\cdot70$ (1), $\beta = 93\cdot53$ (1), $\gamma = 116\cdot96$ (1)°, $V = 866\cdot3$ (2) Å^3, $Z = 1$, $F(000) = 500$, $D_x = 2\cdot044$, $D_m = 2\cdot0$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 38\cdot5$ cm^{-1}. Final $R = 0\cdot054$, $wR = 0\cdot050$ for 2134 reflections with $I \geq 2\sigma(I)$. Room temperature. The title compound is a centrosymmetric four-coordinate complex with no unusually short intermolecular contacts. The Pd—I distance of $2\cdot590$ (1) Å is in agreement with the average of $2\cdot596$ (12) Å from 19 reported Pd—I distances when I, N or S is the *trans* atom. The Pd—I distance increases to $2\cdot653$ (11) Å when P, As or C is the *trans* atom. A *trans* effect causes the Pd—Sb distance of $2\cdot578$ (1) Å to be significantly longer than in the only other known Pd—Sb complex [$2\cdot506$ (1) and $2\cdot527$ (1) Å].

Introduction. Mössbauer studies of palladium and platinum complexes using [121]Sb were reported by McAuliffe, Niven & Parish (1977) and using [129]I by Dickinson, Parish & Dale (1980). The [PdI₂{Sb-(C₆H₅)₃}₂] complex was assigned a *trans* configuration on the basis of the Mössbauer spectra and far infrared data. There was some question as to possible association in the solid state to give a five-coordination species. We undertook an X-ray structural study of the title compound to aid in the interpretation of the Mössbauer studies since at that time there were no reported structural studies of palladium–antimony complexes.

Experimental. Crystals of the title compound were grown from dichloromethane. The density was determined by flotation in a dibromoethane–carbon tetrachloride solution. A crystal $0 \cdot 10 \times 0 \cdot 22 \times 0 \cdot 38$ mm mounted on the end of a glass fiber and a $P\bar{1}$ diffractometer with graphite-monochromatized Mo radiation were used for the measurements. Cell dimensions were determined from 15 centered reflections in the 2θ range of 5–20°. A variable speed (1–24° min⁻¹) θ–2θ scan technique was used for the 3108 measurements at room temperature with $2\theta \leq 45 \cdot 0°$, $h = 0 \rightarrow 10$, $k = -10 \rightarrow 9$, $l = -11 \rightarrow 10$. Four standard reflections were measured after every 96 reflections. The variation in the intensity of the standards was $\pm 1 \cdot 5\%$. After averaging equivalent reflections ($R_{int} = 0 \cdot 011$), the 2134 reflections with $I \geq 2\sigma(I)$ were used in the analysis. No absorption correction was made since the value of μr was small ($0 \cdot 20$–$0 \cdot 42$). Furthermore, any absorption errors will have negligible effects on the positional parameters. There were 137 reflections with $I < 2\sigma(I)$. The structure was solved by the heavy-atom method and the 187 variables were refined by full-matrix least squares. The function minimized was $(\Delta F)^2$. Scattering factors were from *International Tables for X-ray Crystallography* (1962) and the real and imaginary components were included in the calculations. The final R and wR values were $0 \cdot 054$ and $0 \cdot 050$ respectively, with a goodness-of-fit of $1 \cdot 9$. The weights were $1 \cdot 0/[\sigma(F)]^2$ where $\sigma(F) = [\sigma(I)^2 + (0 \cdot 04I)^2]^{1/2}(Lp)^{1/2}$. In the final least-squares cycle the maximum ratio of shift to e.s.d. was less than $0 \cdot 1$. The final positional parameters are given in Table 1 with the bond distances and angles involving Pd or Sb given in Table 2.* A difference Fourier synthesis was used to locate the 15 H atoms on the phenyl rings. A block-matrix least-squares refinement of the H-atom

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* Tables of anisotropic thermal parameters, bond angles, hydrogen-atom coordinates and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43282 (14 pages). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters* ($\times 10^4$) *for the non-hydrogen atoms and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j a_i \cdot a_j \beta_{ij}.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Pd	0*	0*	0*	3·24 (4)
I	2674 (1)	1927 (1)	−279 (1)	4·94 (4)
Sb	175 (1)	2322 (1)	1979 (1)	3·04 (3)
C(1A)	948 (13)	4627 (13)	1875 (10)	3·4 (4)
C(2A)	−55 (14)	5250 (14)	2033 (12)	4·1 (5)
C(3A)	388 (15)	6732 (14)	1947 (14)	4·6 (5)
C(4A)	1825 (16)	7606 (15)	1705 (13)	4·7 (5)
C(5A)	2806 (16)	6975 (15)	1546 (13)	4·8 (5)
C(6A)	2397 (14)	5504 (14)	1632 (12)	4·1 (5)
C(1B)	1607 (13)	2729 (13)	3839 (11)	3·4 (4)
C(2B)	1488 (15)	1481 (15)	4173 (14)	4·8 (5)
C(3B)	2353 (17)	1698 (18)	5434 (15)	5·5 (7)
C(4B)	3309 (17)	3184 (21)	6310 (16)	6·2 (7)
C(5B)	3463 (21)	4460 (19)	5994 (16)	6·7 (7)
C(6B)	2579 (19)	4224 (17)	4745 (14)	5·8 (6)
C(1C)	−1873 (12)	1944 (12)	2703 (10)	3·0 (4)
C(2C)	−1914 (15)	2048 (14)	4088 (12)	4·0 (5)
C(3C)	−3271 (17)	1743 (16)	4550 (13)	5·0 (6)
C(4C)	−4585 (16)	1355 (17)	3627 (17)	5·6 (6)
C(5C)	−4531 (15)	1284 (15)	2222 (14)	4·9 (5)
C(6C)	−3177 (14)	1561 (14)	1782 (13)	4·3 (5)

* Required by symmetry.

Table 2. *Bond distances* (Å) *and angles* (°) *involving Pd or Sb and their estimated standard deviations*

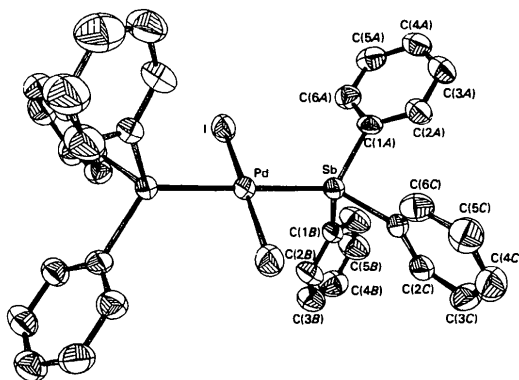|			
Pd–I	2·590 (1)	Pd–Sb	2·578 (1)
Sb–C(1A)	2·135 (13)	Sb–C(1B)	2·130 (12)
Sb–C(1C)	2·125 (12)	C(1A)–C(2A)	1·404 (22)
C(1A)–C(6A)	1·396 (16)	C(2A)–C(3A)	1·389 (20)
C(3A)–C(4A)	1·388 (19)	C(4A)–C(5A)	1·388 (26)
C(5A)–C(6A)	1·384 (21)	C(1B)–C(2B)	1·351 (22)
C(1B)–C(6B)	1·374 (14)	C(2B)–C(3B)	1·411 (22)
C(3B)–C(4B)	1·356 (18)	C(4B)–C(5B)	1·358 (30)
C(5B)–C(6B)	1·403 (24)	C(1C)–C(2C)	1·394 (16)
C(1C)–C(6C)	1·389 (18)	C(2C)–C(3C)	1·391 (21)
C(3C)–C(4C)	1·396 (22)	C(4C)–C(5C)	1·425 (22)
C(5C)–C(6C)	1·381 (20)		
Pd–Sb–C(1A)	124·2 (3)	C(1A)–Sb–C(1B)	103·5 (4)
Pd–Sb–C(1B)	109·9 (4)	C(1A)–Sb–C(1C)	99·9 (5)
Pd–Sb–C(1C)	116·4 (3)	C(1B)–Sb–C(1C)	99·8 (4)
I–Pd–Sb	87·80 (3)		

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the title compound illustrating the thermal ellipsoids and atomic numbering. The Pd atom is on a center of symmetry.

positions and an isotropic thermal parameter improved the distances but did not give a statistically significant reduction in the R values. A final difference Fourier synthesis indicated some residual electron density, four small peaks of $1 \cdot 5 - 3$ e Å^{-3} in the vicinity of the Pd, I and Sb atoms. Computer programs written or modified by one of us (GJP) were used in the analysis.

Discussion. An *ORTEP* (Johnson, 1965) drawing of the molecule is given in Fig. 1 together with the atomic numbering. The Pd—Sb distance of $2 \cdot 578$ (1) Å is significantly longer than the Pd—Sb distances of $2 \cdot 506$ (1) and $2 \cdot 527$ (1) Å reported by Roberts, Skelton, White & Wild (1982*b*) in *cis*-bis(triphenylstibine)-

Table 3. *Summary of nonbridging* Pd—I *distances*

The REFCODE is the code in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). R is the minimum of R and wR as found in the CSD. The column *trans* gives the atom *trans* to the given Pd—I bond.

REFCODE	R	Pd—I(Å)	trans
BARTUJ	0·078	2·578	I(bridge)
		2·550	I(bridge)
BUNNON	0·049	2·606	S
CALPUA	0·047	2·659	P
		2·652	P
CASDOP	0·027	2·653	P
		2·627	P
CAXJOA	0·038	2·583	N
		2·658	As
CMEPDB	0·075	2·601	N
		2·624	S
CODJAG	0·033	2·665	C
COGXEB	0·039	2·698	Pd
		2·699	Pd
COLVOO	0·059	2·587	I
		2·595	I
DIDPPD	0·081	2·587	I
DIMTPD	0·100	2·576	I
IBINPD	0·093	2·587	I
		2·611	I
IBZDP	0·056	2·593	S(bridge)
		2·600	S(bridge)
		2·593	S(bridge)
		2·601	S(bridge)
IMPPPD	0·075	2·638	I
		2·618	I
IMPPPD01	0·109	2·593	I
IMTOPD	0·028	2·602	S
		2·657	P
This work	0·050	2·590	I

References. BAJTUJ: Olmstead, Farr & Balch (1981). BUNNON: Gray, Gulliver, Levason & Webster (1983*a*). CALPUA: Gray, Gulliver, Levason & Webster (1983*b*). CASDOP: Fenske & Christidis (1983). CAXJOA: Roberts, Skelton, White & Wild (1982*a*). CMEPDB: Hirschon, Musker, Olmstead & Dallas (1981). CODJAG: Rheingold & Fultz (1984). COGXEB: Rutherford, Olmstead & Balch (1984). COLVOO: Che, Herbstein, Schaefer, Marsh & Gray (1984). DIDPPD: Debaerdemaeker, Kutoglu, Schmid & Weber (1973). DIMTPD: Beale & Stephenson (1970). IBINPD: Bailey, Walker & Williams (1972). IBZDPD: Roundhill, Roundhill, Beaulieu & Bagchi (1980). IMPPPD and IMPPPD01: Bailey & Mason (1968). IMTOPD: Clark & Orbell (1981).

(η^5-cyclopentadienide)palladium(II) hexafluorophosphate. However, in our case the Pd—Sb is *trans* to Sb rather than *cis* and the lengthening is a *trans* effect. A similar *trans* effect has been noted in phosphine complexes; see Clark & Orbell (1981) for examples and references.

The Pd—I distance of $2 \cdot 590$ (1) Å is very close to the average of $2 \cdot 595$ (18) Å calculated for the 21 values listed in Table 3 where I is *trans* to I, S or N. If the two extreme Pd—I distances of $2 \cdot 638$ and $2 \cdot 550$ Å are excluded, the average is $2 \cdot 596$ (12) Å. However, when I is *trans* to P, As or C, the Pd—I bond lengthens to $2 \cdot 653$ (11) Å. These two different Pd—I bond distances provide a dramatic illustration of the *trans* effect. The fact that P, As and C have virtually the same effect was somewhat unexpected. It appears that donor atoms *trans* to the Pd—I bond fall into two categories as shown by the Pd—I distance.

The C—C distances in the phenyl rings average $1 \cdot 389$ (17) Å, as expected. The Sb—C distances average $2 \cdot 130$ (4) Å and are slightly longer than the value of $2 \cdot 119$ (14) Å reported by Roberts, Skelton, White & Wild (1982*a*). There are no unusually short intermolecular distances between the molecules. Therefore the title compound can be viewed as a square-planar palladium complex separated by van der Waals contacts only.

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Structure of μ-Diethyldithiophosphinato-tris(diethyldithiophosphinato)-tri-μ-thio-μ₃-thio-*triangulo*-trimolybdenum(IV)

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Abstract. $[Mo_3S_4\{(C_2H_5)_2PS_2\}_4]$, $M_r = 1028 \cdot 9$, monoclinic, $P2_1/n$, $a = 11 \cdot 791$ (2), $b = 20 \cdot 721$ (3), $c = 16 \cdot 100$ (3) Å, $\beta = 107 \cdot 50$ (1)°, $V = 3752$ (1) Å³, $Z = 4$, $D_m = 1 \cdot 79$, $D_x = 1 \cdot 82$ Mg m⁻³, Mo $K\bar{\alpha}$, $\lambda = 0 \cdot 71069$ Å, $\mu = 1 \cdot 79$ mm⁻¹, $F(000) = 2056$, 6483 observed unique reflections (room temperature), $R = 0 \cdot 037$ (316 parameters). The three Mo atoms together with four bridging S atoms form a trinuclear cluster with local symmetry close to C_{3v}. Each of the Mo atoms is chelated by a bidentate diethyldithiophosphinato ligand; two Mo atoms are bridged in addition by the remaining diethyldithiophosphinato residue. Preliminary results have been reported [Keck, Kuchen, Mathow & Wunderlich (1982). *Angew. Chem.* **94**, 927–928; *Angew. Chem. Int. Ed. Engl.* **21**, 929].

Introduction. Trinuclear complexes of transition metals containing sulfur ligands are of well known importance in bioinorganic chemistry (Müller, Diemann, Jostes & Bögge, 1981). A classification of different trinuclear clusters containing no (type *A*), one (type *B*) or two (type *C*) capping μ_3-ligands has been reported by Müller, Jostes & Cotton (1980). Mo clusters of type *B* are documented in two forms: in type *B*1 three single μ-S atoms are bridging each side of the Mo triangle as in the cation $[Mo_3(\eta^5\text{-}C_5H_5)_3S_4]^+$ (Vergamini, Vahrenkamp & Dahl, 1971), while in type *B*2 these three S atoms are replaced by S_2 groups as in $Mo_3S_7Cl_4$ (Marcoll, Rabenau, Mootz & Wunderlich, 1974). In these two as well as in all structures of type *B* reported thereafter the three Mo atoms have equal coordination numbers. In the compound under study the bridging of the three Mo—Mo bonds was under debate: There was either a cluster of type *B*1 containing one dithio-

phosphinato ligand as an additional bridge (thus unequal coordination numbers of the Mo atoms) or one of type *C* with two Mo—Mo bonds bridged by a single S atom while the third side of the triangle is bridged by the dithiophosphinato group.

Experimental. The preparation of the title compound is reported by Keck, Kuchen & Mathow (1986) and yielded black opaque well shaped crystals of monoclinic habit. A crystal of approximately $0 \cdot 3 \times 0 \cdot 3 \times 0 \cdot 4$ mm was used for the refinement of the lattice parameters (15 reflections, $33 < 2\theta < 40°$, Mo $K\alpha$ radiation, crystal monochromator, Syntex $P2_1$) as well as for the data collection. From systematic absences the space group $P2_1/n$ (cell choice 1 with fully reduced mesh, *International Tables for Crystallography*, 1983) has been determined. Density, determined by flotation, yielded $Z = 4$ formula units per cell. The intensities of 7955 reflections [Mo $K\alpha$, $(\sin\theta)/\lambda < 0 \cdot 6168$ Å⁻¹] were measured using an ω scan with variable speeds and a scan width of $0 \cdot 6°$. Because of the large amount of data measurement was performed at an average rate of 115 reflections per hour. Compared with usual data collection (*ca* 40 refl. h⁻¹) this should not increase the positional e.s.d.'s by more than about 20% (Hope & Nichols, 1981). The indices ranged from 0 to $h = 14$, $k = 25$ and from $l = -19$ to $l = 18$, the intensities of three standard reflections $(7,9,\overline{11}, 783, \overline{4},13,\overline{4})$ did not show significant variations. Seven low-order reflections with too high intensities, systematically absent reflections, and symmetry-equivalent ones have been eliminated. 456 reflections showed background imbalances of more than 2:1 of which in general the higher value was in error (probably multiple reflec-