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The Crystal and Molecular Structure of Bis(dimethyl-*o*-thiophenylarsine)platinum(II)

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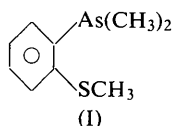
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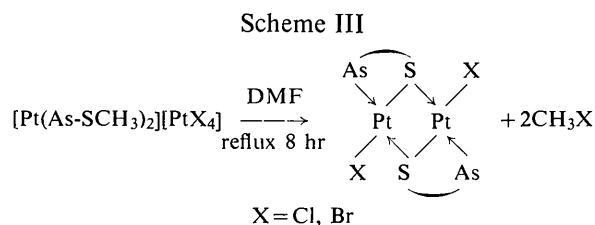
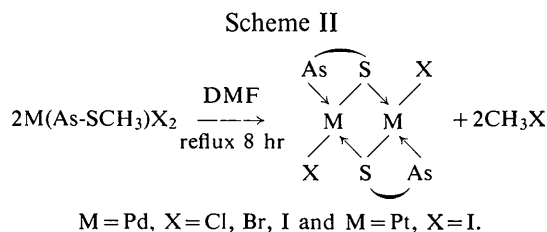
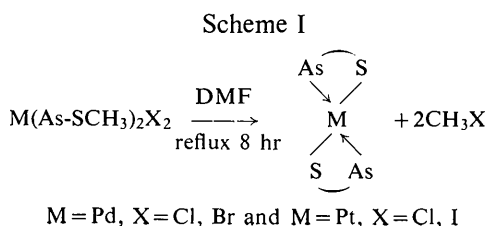
The crystal structure of the platinum thiol resulting from *S*-demethylation of the ligand dimethyl-*o*-methylthiophenylarsine has been examined using three-dimensional X-ray data collected initially by photographic techniques and finally on a Siemens automatic single-crystal diffractometer. The complex crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions $a = 7.818$ (2), $b = 9.662$ (2), $c = 13.052$ (3) Å, $\beta = 102.84$ (6)°. The molecule is a *trans* isomer in which the thiol functions as a bidentate ligand. The molecule is planar and the Pt-As bond distance is short, indicating $d\pi-d\pi$ bonding between the platinum atom and the thio-arsenic chelate.

Introduction

Mono and bis chelated complexes of dimethyl-*o*-methylthiophenylarsine (I) (As-SCH₃) of the types



$\text{Pd}(\text{As-SCH}_3)_2\text{X}_2$, $\text{M}(\text{As-SCH}_3)_2\text{X}_2$ (M = Pd, Pt; X = Cl, Br, I), $\text{Pt}(\text{As-SCH}_3)_2$ and $[\text{Pt}(\text{As-SCH}_3)_2][\text{PtX}_4]$ (X = Cl, Br) have been reported (Livingstone, 1958; Chiswell & Livingstone, 1960). *S*-Demethylation of the ligand occurs when these compounds are heated under reflux in dimethylformamide (DMF), as shown in schemes I-III (Lindoy, Livingstone & Lockyer, 1967).



There are interesting structural implications involved with these schemes. Thus, in scheme I, the compounds $\text{M}(\text{As-SCH}_3)_2\text{X}_2$ might well be examples of six-coordinate, diamagnetic d^8 complexes. Verification of octahedral coordination in these compounds has been limited (Stephenson, 1962; Stephenson & Jeffrey, 1963; Duckworth & Stephenson, 1969). In fact $\text{Pd}(\text{As-SCH}_3)_2\text{I}_2$

has been shown to be a *trans* 4-covalent square-planar complex with no metal-sulphur bonding (Beale & Stephenson, 1970). Also the compounds $M(\text{As-S})_2$ can exist as *cis* or *trans* isomers and, in addition, these complexes strongly clathrate with solvents to form compounds such as $\text{Pd}(\text{As-S})_2\text{pyridine}$.

We are investigating the crystal structures of a number of compounds which are represented in schemes I-III, and report below the structure of bis(dimethyl-*o*-thiophenylarsine)platinum(II), $\text{Pt}(\text{As-S})_2$.

Experimental

Yellow crystals of bis(dimethyl-*o*-thiophenylarsine)platinum(II) were prepared by the method of Lindoy,

Livingstone & Lockyer (1967) and recrystallized from ethanol.

Small crystals are shaped as parallelepipeds with (100), (011) and (01 $\bar{1}$) faces most prominently developed. The unit-cell dimensions and final intensity data were measured on a four-circle Siemens automatic single-crystal diffractometer using a crystal of dimensions $0.005 \times 0.012 \times 0.012$ cm. $\text{Cu K}\alpha$ radiation [$\lambda(K\alpha_1) = 1.54051$, $\lambda(K\alpha_2) = 1.54433$ Å] and Ni attenuators.

The unit-cell constants were calculated from the angular settings of five high-order axial reflexions. The integrated intensities were recorded by a θ - 2θ scan using the five-value method (Hoppe, 1965). The scan range varied from 1.0° at low 2θ to 2.8° at high 2θ while the scan speed, although automatically con-

Table 1. Observed and calculated structure factors for bis(dimethyl-*o*-thiophenylarsine)platinum(II)

The columns, from left to right, read h , k , l , F_{obs} and F_{calc} , where the values of F_{obs} and F_{calc} are recorded on ten times the absolute scale. The symbol 'U' denotes an unobserved reflexion and occurs whenever the total peak count recorded for a particular reflexion is less than one standard deviation above the background count. An asterisk denotes a reflexion affected by extinction and these data were excluded from the least-squares refinement.

H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
1	0	0	100	100	1	0	0	100	100	1	0	0	100	100	1	0	0	100	100
2	0	0	400	400	2	0	0	400	400	2	0	0	400	400	2	0	0	400	400
3	0	0	900	900	3	0	0	900	900	3	0	0	900	900	3	0	0	900	900
4	0	0	1600	1600	4	0	0	1600	1600	4	0	0	1600	1600	4	0	0	1600	1600
5	0	0	2500	2500	5	0	0	2500	2500	5	0	0	2500	2500	5	0	0	2500	2500
6	0	0	3600	3600	6	0	0	3600	3600	6	0	0	3600	3600	6	0	0	3600	3600
7	0	0	4900	4900	7	0	0	4900	4900	7	0	0	4900	4900	7	0	0	4900	4900
8	0	0	6400	6400	8	0	0	6400	6400	8	0	0	6400	6400	8	0	0	6400	6400
9	0	0	8100	8100	9	0	0	8100	8100	9	0	0	8100	8100	9	0	0	8100	8100
10	0	0	10000	10000	10	0	0	10000	10000	10	0	0	10000	10000	10	0	0	10000	10000
11	0	0	12100	12100	11	0	0	12100	12100	11	0	0	12100	12100	11	0	0	12100	12100
12	0	0	14400	14400	12	0	0	14400	14400	12	0	0	14400	14400	12	0	0	14400	14400
13	0	0	16900	16900	13	0	0	16900	16900	13	0	0	16900	16900	13	0	0	16900	16900
14	0	0	19600	19600	14	0	0	19600	19600	14	0	0	19600	19600	14	0	0	19600	19600
15	0	0	22500	22500	15	0	0	22500	22500	15	0	0	22500	22500	15	0	0	22500	22500
16	0	0	25600	25600	16	0	0	25600	25600	16	0	0	25600	25600	16	0	0	25600	25600
17	0	0	28900	28900	17	0	0	28900	28900	17	0	0	28900	28900	17	0	0	28900	28900
18	0	0	32400	32400	18	0	0	32400	32400	18	0	0	32400	32400	18	0	0	32400	32400
19	0	0	36100	36100	19	0	0	36100	36100	19	0	0	36100	36100	19	0	0	36100	36100
20	0	0	40000	40000	20	0	0	40000	40000	20	0	0	40000	40000	20	0	0	40000	40000
21	0	0	44100	44100	21	0	0	44100	44100	21	0	0	44100	44100	21	0	0	44100	44100
22	0	0	48400	48400	22	0	0	48400	48400	22	0	0	48400	48400	22	0	0	48400	48400
23	0	0	52900	52900	23	0	0	52900	52900	23	0	0	52900	52900	23	0	0	52900	52900
24	0	0	57600	57600	24	0	0	57600	57600	24	0	0	57600	57600	24	0	0	57600	57600
25	0	0	62500	62500	25	0	0	62500	62500	25	0	0	62500	62500	25	0	0	62500	62500
26	0	0	67600	67600	26	0	0	67600	67600	26	0	0	67600	67600	26	0	0	67600	67600
27	0	0	72900	72900	27	0	0	72900	72900	27	0	0	72900	72900	27	0	0	72900	72900
28	0	0	78400	78400	28	0	0	78400	78400	28	0	0	78400	78400	28	0	0	78400	78400
29	0	0	84100	84100	29	0	0	84100	84100	29	0	0	84100	84100	29	0	0	84100	84100
30	0	0	90000	90000	30	0	0	90000	90000	30	0	0	90000	90000	30	0	0	90000	90000
31	0	0	96100	96100	31	0	0	96100	96100	31	0	0	96100	96100	31	0	0	96100	96100
32	0	0	102400	102400	32	0	0	102400	102400	32	0	0	102400	102400	32	0	0	102400	102400
33	0	0	108900	108900	33	0	0	108900	108900	33	0	0	108900	108900	33	0	0	108900	108900
34	0	0	115600	115600	34	0	0	115600	115600	34	0	0	115600	115600	34	0	0	115600	115600
35	0	0	122500	122500	35	0	0	122500	122500	35	0	0	122500	122500	35	0	0	122500	122500
36	0	0	129600	129600	36	0	0	129600	129600	36	0	0	129600	129600	36	0	0	129600	129600
37	0	0	136900	136900	37	0	0	136900	136900	37	0	0	136900	136900	37	0	0	136900	136900
38	0	0	144400	144400	38	0	0	144400	144400	38	0	0	144400	144400	38	0	0	144400	144400
39	0	0	152100	152100	39	0	0	152100	152100	39	0	0	152100	152100	39	0	0	152100	152100
40	0	0	160000	160000	40	0	0	160000	160000	40	0	0	160000	160000	40	0	0	160000	160000
41	0	0	168100	168100	41	0	0	168100	168100	41	0	0	168100	168100	41	0	0	168100	168100
42	0	0	176400	176400	42	0	0	176400	176400	42	0	0	176400	176400	42	0	0	176400	176400
43	0	0	184900	184900	43	0	0	184900	184900	43	0	0	184900	184900	43	0	0	184900	184900
44	0	0	193600	193600	44	0	0	193600	193600	44	0	0	193600	193600	44	0	0	193600	193600
45	0	0	202500	202500	45	0	0	202500	202500	45	0	0	202500	202500	45	0	0	202500	202500
46	0	0	211600	211600	46	0	0	211600	211600	46	0	0	211600	211600	46	0	0	211600	211600
47	0	0	220900	220900	47	0	0	220900	220900	47	0	0	220900	220900	47	0	0	220900	220900
48	0	0	230400	230400	48	0	0	230400	230400	48	0	0	230400	230400	48	0	0	230400	230400
49	0	0	240100	240100	49	0	0	240100	240100	49	0	0	240100	240100	49	0	0	240100	240100
50	0	0	250000	250000	50	0	0	250000	250000	50	0	0	250000	250000	50	0	0	250000	250000
51	0	0	260100	260100	51	0	0	260100	260100	51	0	0	260100	260100	51	0	0	260100	260100
52	0	0	270400	270400	52	0	0	270400	270400	52	0	0	270400	270400	52	0	0	270400	270400
53	0	0	280900	280900	53	0	0	280900	280900	53	0	0	280900	280900	53	0	0	280900	280900
54	0	0	291600	291600	54	0	0	291600	291600	54	0	0	291600	291600	54	0	0	291600	291600
55	0	0	302500	302500	55	0	0	302500	302500	55	0	0	302500	302500	55	0	0	302500	302500
56	0	0	313600	313600	56	0	0	313600	313600	56	0	0	313600	313600	56	0	0	313600	313600
57	0	0	324900	324900	57	0	0	324900	324900	57	0	0	324900	324900	57	0	0	324900	324900
58	0	0	336400	336400	58	0	0	336400	336400	58	0	0	336400	336400	58	0	0	336400	336400
59	0	0	348100	348100	59	0	0	348100	348100	59	0	0	348100	348100	59	0	0	348100	348100
60	0	0	360000	360000	60	0	0	360000	360000	60	0	0	360000	360000	60	0	0	360000	360000
61	0	0	372100	372100	61	0	0	372100	372100	61	0	0	372100	372100	61	0	0	372100	372100
62	0	0	384400	384400	62	0	0	384400	384400	62	0	0	384400	384400	62	0	0	384400	384400
63	0	0	396900	396900	63	0	0	396900	396900	63	0	0	396900	396900	63	0	0	396900	396900
64	0	0	409600	409600	64	0	0	409600	409600	64	0	0	409600	409600	64	0	0	409600	409600
65	0	0	422500	422500	65	0	0	422500	422500	65	0	0	422500	422500	65	0	0	422500	422500
66	0	0	435600	435600	66	0	0	435600	435600	66	0	0	435600	435600	66	0	0	435600	435600
67	0	0	448900	448900	67	0	0	448900	448900	67	0	0	448900	448900	67	0	0	448900	448900
68	0	0	462400	462400	68	0	0	462400	462400	68	0	0	462400	462400	68				

Table 1 (cont.)

Table 1 (cont.) contains several columns of data, likely representing atomic coordinates or tensor components. The columns are labeled with letters H, K, L, F(L), F(C), and F(L). Each column contains a series of numerical values, some of which are enclosed in brackets. The data is organized into several distinct sections, possibly corresponding to different atoms or sites in the crystal structure.

standard deviations, are listed in Table 2. The components of anisotropic vibration are given in Table 3.

Table 2. Final fractional atomic coordinates for bis(dimethyl-*o*-thiophenylarsine)platinum(II)

Standard deviations are given in brackets and refer to the last two decimal places in the preceding coordinate.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Pt	0.0	0.0	0.0
As	-0.05382 (14)	-0.16862 (11)	0.11917 (8)
S	0.26108 (35)	0.04682 (27)	0.11728 (21)
C(1)	-0.2620 (14)	-0.1525 (12)	0.1752 (9)
C(2)	-0.0563 (16)	-0.3605 (11)	0.0744 (9)
C(3)	0.1412 (13)	-0.1552 (10)	0.2364 (6)
C(4)	0.2691 (13)	-0.0601 (10)	0.2283 (9)
C(5)	0.4150 (14)	-0.0487 (12)	0.3135 (9)
C(6)	0.4320 (16)	-0.1312 (14)	0.4000 (9)
C(7)	0.3037 (18)	-0.2287 (14)	0.4077 (9)
C(8)	0.1578 (16)	-0.2387 (12)	0.3267 (9)
H(1)	0.0450	-0.2801	0.3150
H(2)	0.3010	-0.3001	0.4700
H(3)	0.5240	-0.1560	0.4680
H(4)	0.5200	0.0170	0.3210
H(5)	0.0710	-0.4061	0.0867
H(6)	-0.1476	-0.3929	0.0028
H(7)	-0.0674	-0.4479	0.1332
H(8)	-0.3700	-0.1620	0.1190
H(9)	-0.2700	-0.0500	0.1780
H(10)	-0.2280	-0.2400	0.2300

Table 3. The tensor components ($\times 10^3$) describing the anisotropic vibration of the atoms in bis(dimethyl-*o*-thiophenylarsine)platinum(II)

The tensor components U_{ij} are those occurring in the temperature factor $\exp[-2\pi^2(h^2a^2U_{11} + 2hka^*b^*U_{12} + \dots)]$ so that, for instance, U_{11} is the mean-square amplitude of vibration parallel to \mathbf{a}^* .

All hydrogen atoms during the refinement were assigned, arbitrarily, an isotropic temperature factor, B , equal to 8.0 \AA^2 .

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	62.5	38.9	51.3	3.30	13.1	1.9
As	64.6	42.8	57.8	3.00	13.5	0.10
S	69.9	57.9	63.6	8.17	12.0	0.72
C(1)	67.8	82.7	98.8	5.81	21.5	5.7
C(2)	103.0	43.6	97.2	3.93	17.4	8.1
C(3)	66.8	50.6	57.6	0.15	11.9	2.3
C(4)	60.2	51.8	62.3	1.12	13.4	5.3
C(5)	64.7	73.1	71.6	3.01	9.0	5.5
C(6)	79.2	88.4	68.9	10.82	7.7	1.7
C(7)	89.6	80.5	75.5	7.28	9.8	5.7
C(8)	81.7	70.3	66.7	0.83	13.0	7.1

Description of the structure

The structure of bis(dimethyl-*o*-thiophenylarsine)platinum(II) is one in which individual molecules of $\text{PtAs}_2\text{S}_2\text{C}_{16}\text{H}_{20}$ of the *trans* isomer, depicted in Fig. 1, pack together in the manner shown in projection by Figs. 2 and 3. The packing is rather spacious with

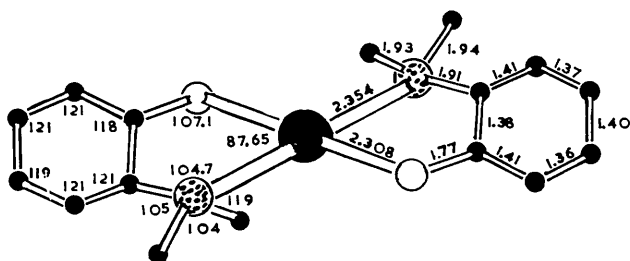


Fig. 1. A diagram illustrating the configuration of the bis(dimethyl-*o*-thiophenylarsine)platinum(II) molecule and showing some bond distances (Å) and angles (°).

intermolecular contacts generally greater than 3.6 Å. Non-bonding approach distances of less than 4.0 Å are listed in Table 4.

Table 4. Some interatomic approach distances of less than 4 Å in the crystal of bis(dimethyl-*o*-thiophenylarsine)platinum(II)

The superscripts denote the following symmetry transformations of the parameters in Table 2.

	No superscript	x	y	z
	1	\bar{x}	$\frac{1}{2} + y$	$\frac{1}{2} - z$
Pt-C(7 ¹)	3.903 (15) Å		C(4)-C(2 ¹)	3.876 (5) Å
Pt-C(8 ¹)	3.775 (12)		C(5)-C(2 ¹)	3.891 (5)
S-C(1 ¹)	3.971 (12)		C(3)-C(2 ¹)	3.922 (5)

Each individual molecule consists of a square-planar arrangement of atoms about a central, four-coordinated platinum atom. There is no evidence of interactions in the octahedral sites of the platinum atom. The closest intermolecular approach to the platinum atom is C(8) at a distance of 3.78 Å. The bond distances and angles within a molecule are listed in Tables 5 and 6.

Table 5. Bond distances in a molecule of bis(dimethyl-*o*-thiophenylarsine)platinum(II)

Standard deviations are given in brackets.

Pt-As	2.354 (1) Å	C(3)-C(4)	1.380 (12) Å
Pt-S	2.308 (3)	C(4)-C(5)	1.410 (14)
As-C(1)	1.933 (10)	C(5)-C(6)	1.364 (15)
As-C(2)	1.942 (10)	C(6)-C(7)	1.400 (16)
As-C(3)	1.909 (10)	C(7)-C(8)	1.375 (15)
S-C(4)	1.769 (10)	C(8)-C(3)	1.411 (13)

The Pt-As bond distance of 2.364(1) Å is appreciably shorter than the sum of the square covalent radius for platinum(II) and the tetrahedral radius for arsenic ($1.31 + 1.18 = 2.49$ Å) (Pauling, 1948). It is also shorter than the Pt-As bond distance of 2.380(15) Å found in Pt(diarsine)₂X₂, (Stephenson, 1962, 1964; Stephenson & Jeffrey, 1963)], where diarsine represents the ligand *o*-phenylenebisdimethylarsine and X is

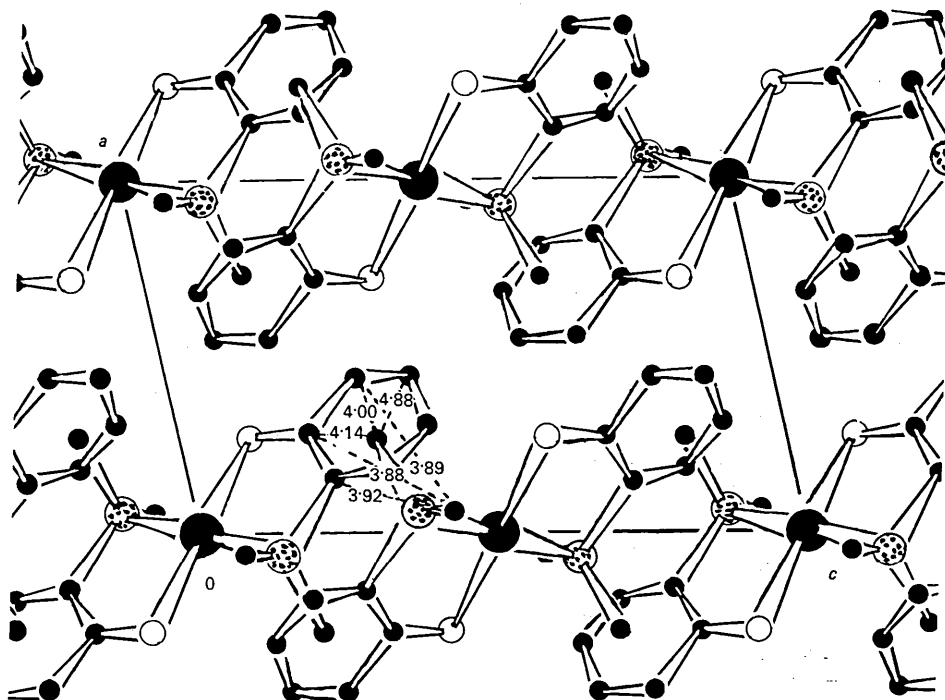


Fig. 2. An (010) projection of the unit-cell contents of bis(dimethyl-*o*-thiophenylarsine)platinum(II). Some non-bonded approach distances (Å) are shown.

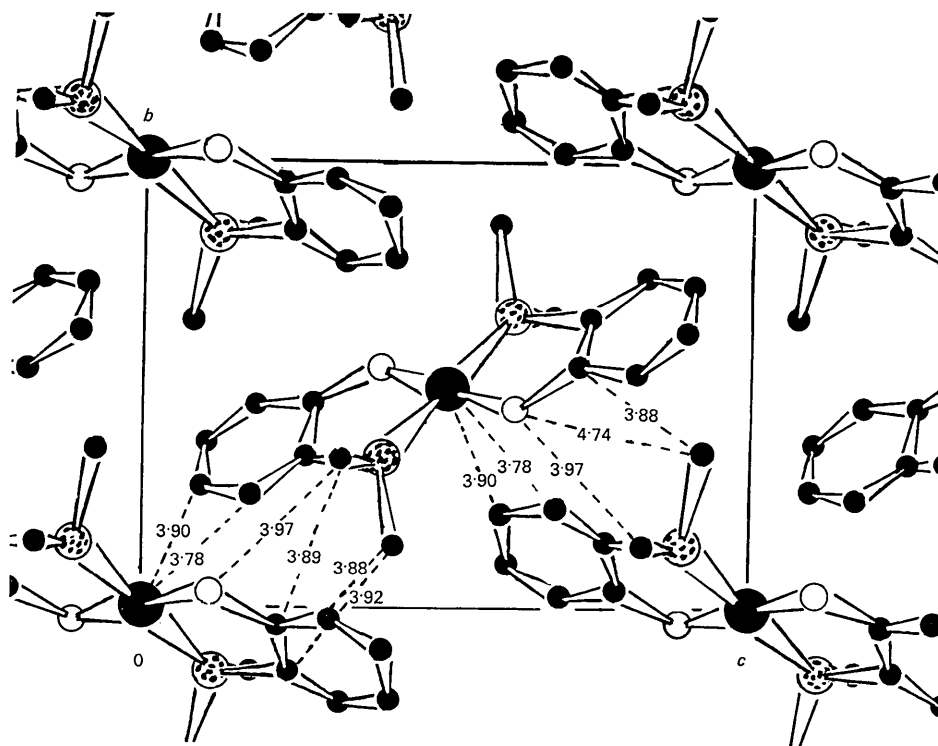


Fig. 3. A (100) projection of the unit-cell contents of bis(dimethyl-*o*-thiophenylarsine)platinum(II). Some non-bonded approach distances (Å) are shown.

either iodide or chloride. The Pt-As distances obtained for the diarsine complexes were explained as being due to the overlap between the unfilled ligand *d* orbitals and the filled metal *d* orbitals. In a similar way, the short Pt-As distance in the thio-arsenic complex may be considered to be due to *dn-dn* overlap. In both the diarsine and thio-arsenic ligand complexes the formation of the dative, σ -bond will confer a positive charge on the ligand and negative on the metal. The back donation of this negative charge from the metal atom depends upon the availability of the *d*-orbitals to accept the excess negative charge. In the case of the diarsine ligand both arsenic atoms accept the same degree of charge. However, in the thio-arsenic ligand a distinction between the amount of charge accepted by the platinum-coordinated atoms is likely. Because of the strong donor properties asso-

ciated with sulphur it is unlikely that these atoms would readily accept any large degree of negative charge. The bulk of the excess negative charge would be expected to be distributed to the arsenic atom by *dn-dn* overlap, this double bonding becoming evident in a shortening of the Pt-As bond distance from the normal covalent value. The Pt-S bond distance of 2.308(3) Å is significantly shorter than the sum of the square covalent radius for platinum(II) and the normal covalent radius for sulphur (1.31 + 1.04 = 2.35 Å).

Finally, examination of all metal-carbon distances reveals some interesting facts. The As-CH₃ distances of 1.933(10) and 1.942(19) Å are in good agreement with similar distances observed in the diarsine complexes (Stephenson, 1962, 1964; Stephenson & Jeffrey, 1963; Duckworth & Stephenson, 1969). There is a significant difference (0.03 Å) between the As-C (benzene)

Table 6. Bond angles, defined by three atoms with the central atom at the vertex

S—Pt—As	87.7 (1)°	C(1)—As—C(2)	103.8 (5)°
Pt—As—C(1)	118.9 (4)	C(1)—As—C(3)	106.3 (5)
Pt—As—C(2)	116.9 (3)	C(2)—As—C(3)	105.0 (5)
Pt—As—C(3)	104.7 (3)	C(3)—C(4)—C(5)	118 (1)
Pt—S—C(4)	107.1 (3)	C(4)—C(5)—C(6)	121 (1)
As—C(3)—C(4)	116.6 (9)	C(5)—C(6)—C(7)	129 (1)
As—C(3)—C(8)	122.7 (8)	C(6)—C(7)—C(8)	111 (1)
S—C(4)—C(3)	123.9 (8)	C(7)—C(8)—C(3)	121 (1)
S—C(4)—C(5)	118.4 (8)	C(8)—C(3)—C(4)	121 (1)

and As-CH₃ bond distances and this compares favourably with the difference between *sp*² and *sp*³ covalent bond radii for the carbon atom (Coulson, 1963). Moreover, considerable deviation from a tetrahedral arrangement about the arsenic atom with respect to the two methyl carbon atoms is obvious when it is noted that both Pt-As-CH₃ bond angles are 116.9 (0.3) and 118.9 (0.4)°, which are significantly different from the normal tetrahedral angle (109°). The sulphur-carbon distance of 1.769(10) Å is in good agreement with previously observed distances (Craig, Pallister & Stephenson, 1970).

The best least-squares planes through various atoms in the molecule have been calculated following Schomaker, Waser, Marsh & Bergman (1959), using a diagonal weight matrix. The platinum, arsenic and sulphur atoms are precisely coplanar, whereas the equation of the molecular plane is:

$$-0.584X + 0.693Y + 0.542Z - 0.022 = 0$$

where the coordinates *X*, *Y* and *Z* are in Å units refer to the crystallographic axes. There are no significant deviations of any of the atoms from this plane. The molecular plane is inclined at an angle of 48.7° to the (010) plane.

The compound bis(dimethyl-*o*-thiophenylarsine)-palladium(II) is isomorphous with the corresponding platinum(II) compound. Unit-cell dimensions and structure amplitudes were obtained from zero-level precession photographs.

*Bis(dimethyl-*o*-thiophenylarsine)palladium(II)*

PdAs₂S₂C₁₆H₂₀ F.W. 532.68

Monoclinic: $a = 7.81 \pm 0.04$, $b = 9.68 \pm 0.05$,
 $c = 12.97 \pm 0.06$ Å, $\beta = 104.0^\circ$. $U = 951$ Å³, $Z = 2$.

Space group *P*2₁/*c* from systematic absences.

S-Demethylation of a compound of the type Pd(As-SCH₃)₂X₂ thus leads to the formation of a *trans* isomer of the type Pd(As-S)₂ in which the ligand behaves as a bidentate and is strongly bound to the transition metal atom.

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