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

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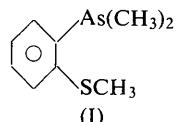
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The crystal structure of the platinum thiol resulting from *S*-demethylation of the ligand dimethyl-*o*-methylthiophenylarsine has been examined using three-dimensional X-ray data collected initially by photographic techniques and finally on a Siemens 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.

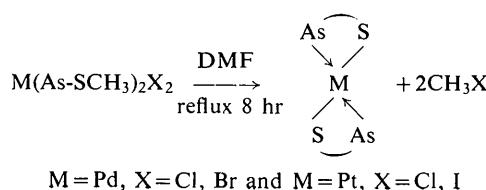
Introduction

Mono and bis chelated complexes of dimethyl-*o*-methylthiophenylarsine (I) ($\text{As}-\text{SCH}_3$) of the types

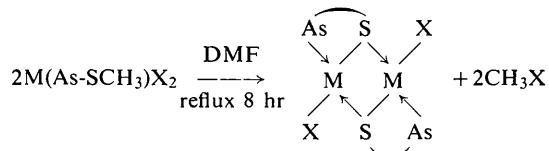


$\text{Pd}(\text{As}-\text{SCH}_3)\text{X}_2$, $\text{M}(\text{As}-\text{SCH}_3)_2\text{X}_2$ ($\text{M}=\text{Pd}, \text{Pt}; \text{X}=\text{Cl}, \text{Br}, \text{I}$), $\text{Pt}(\text{As}-\text{SCH}_3)\text{I}_2$ and $[\text{Pt}(\text{As}-\text{SCH}_3)]_2[\text{PtX}_4]$ ($\text{X}=\text{Cl}, \text{Br}$) 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).

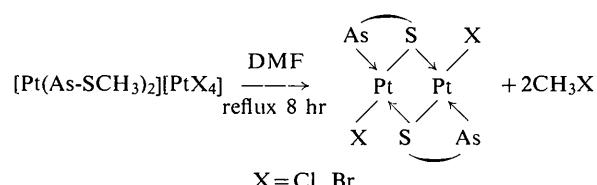
Scheme I



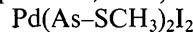
Scheme II



Scheme III



There are interesting structural implications involved with these schemes. Thus, in scheme I, the compounds $\text{M}(\text{As}-\text{SCH}_3)_2\text{X}_2$ 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



has been shown to be a *trans* 4-covalent square-planar complex with no metal-sulphur bonding (Beale & Stephenson, 1970). Also the compounds M(As-S)₂ can exist as *cis* or *trans* isomers and, in addition, these complexes strongly clathrate with solvents to form compounds such as Pd(As-S)₂pyridine.

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*-thiolophenylarsine)platinum(II), Pt(As-S)₂.

Experimental

Yellow crystals of bis(dimethyl-*o*-thiolophenylarsine)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 011 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 × 0.012 × 0.012 cm. Cu K α radiation [$\lambda(K\alpha_1) = 1.54051$, $\lambda(K\alpha_2) = 1.54433 \text{ \AA}$] 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° 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*-thiolophenylarsine)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_{calc}	H	K	L	F_{obs}	F_{calc}	H	K	L	F_{obs}	F_{calc}	H	K	L	F_{obs}	F_{calc}
1	1	1	1.2	1.2	1	1	1	1.2	1.2	1	1	1	1.2	1.2	1	1	1	1.2	1.2
1	1	2	1.2	1.2	1	1	2	1.2	1.2	1	1	2	1.2	1.2	1	1	2	1.2	1.2
1	2	1	1.2	1.2	1	2	1	1.2	1.2	1	2	1	1.2	1.2	1	2	1	1.2	1.2
1	2	2	1.2	1.2	1	2	2	1.2	1.2	1	2	2	1.2	1.2	1	2	2	1.2	1.2
2	1	1	1.2	1.2	2	1	1	1.2	1.2	2	1	1	1.2	1.2	2	1	1	1.2	1.2
2	1	2	1.2	1.2	2	1	2	1.2	1.2	2	1	2	1.2	1.2	2	1	2	1.2	1.2
2	2	1	1.2	1.2	2	2	1	1.2	1.2	2	2	1	1.2	1.2	2	2	1	1.2	1.2
2	2	2	1.2	1.2	2	2	2	1.2	1.2	2	2	2	1.2	1.2	2	2	2	1.2	1.2
3	1	1	1.2	1.2	3	1	1	1.2	1.2	3	1	1	1.2	1.2	3	1	1	1.2	1.2
3	1	2	1.2	1.2	3	1	2	1.2	1.2	3	1	2	1.2	1.2	3	1	2	1.2	1.2
3	2	1	1.2	1.2	3	2	1	1.2	1.2	3	2	1	1.2	1.2	3	2	1	1.2	1.2
3	2	2	1.2	1.2	3	2	2	1.2	1.2	3	2	2	1.2	1.2	3	2	2	1.2	1.2
4	1	1	1.2	1.2	4	1	1	1.2	1.2	4	1	1	1.2	1.2	4	1	1	1.2	1.2
4	1	2	1.2	1.2	4	1	2	1.2	1.2	4	1	2	1.2	1.2	4	1	2	1.2	1.2
4	2	1	1.2	1.2	4	2	1	1.2	1.2	4	2	1	1.2	1.2	4	2	1	1.2	1.2
4	2	2	1.2	1.2	4	2	2	1.2	1.2	4	2	2	1.2	1.2	4	2	2	1.2	1.2
5	1	1	1.2	1.2	5	1	1	1.2	1.2	5	1	1	1.2	1.2	5	1	1	1.2	1.2
5	1	2	1.2	1.2	5	1	2	1.2	1.2	5	1	2	1.2	1.2	5	1	2	1.2	1.2
5	2	1	1.2	1.2	5	2	1	1.2	1.2	5	2	1	1.2	1.2	5	2	1	1.2	1.2
5	2	2	1.2	1.2	5	2	2	1.2	1.2	5	2	2	1.2	1.2	5	2	2	1.2	1.2
6	1	1	1.2	1.2	6	1	1	1.2	1.2	6	1	1	1.2	1.2	6	1	1	1.2	1.2
6	1	2	1.2	1.2	6	1	2	1.2	1.2	6	1	2	1.2	1.2	6	1	2	1.2	1.2
6	2	1	1.2	1.2	6	2	1	1.2	1.2	6	2	1	1.2	1.2	6	2	1	1.2	1.2
6	2	2	1.2	1.2	6	2	2	1.2	1.2	6	2	2	1.2	1.2	6	2	2	1.2	1.2
7	1	1	1.2	1.2	7	1	1	1.2	1.2	7	1	1	1.2	1.2	7	1	1	1.2	1.2
7	1	2	1.2	1.2	7	1	2	1.2	1.2	7	1	2	1.2	1.2	7	1	2	1.2	1.2
7	2	1	1.2	1.2	7	2	1	1.2	1.2	7	2	1	1.2	1.2	7	2	1	1.2	1.2
7	2	2	1.2	1.2	7	2	2	1.2	1.2	7	2	2	1.2	1.2	7	2	2	1.2	1.2
8	1	1	1.2	1.2	8	1	1	1.2	1.2	8	1	1	1.2	1.2	8	1	1	1.2	1.2
8	1	2	1.2	1.2	8	1	2	1.2	1.2	8	1	2	1.2	1.2	8	1	2	1.2	1.2
8	2	1	1.2	1.2	8	2	1	1.2	1.2	8	2	1	1.2	1.2	8	2	1	1.2	1.2
8	2	2	1.2	1.2	8	2	2	1.2	1.2	8	2	2	1.2	1.2	8	2	2	1.2	1.2
9	1	1	1.2	1.2	9	1	1	1.2	1.2	9	1	1	1.2	1.2	9	1	1	1.2	1.2
9	1	2	1.2	1.2	9	1	2	1.2	1.2	9	1	2	1.2	1.2	9	1	2	1.2	1.2
9	2	1	1.2	1.2	9	2	1	1.2	1.2	9	2	1	1.2	1.2	9	2	1	1.2	1.2
9	2	2	1.2	1.2	9	2	2	1.2	1.2	9	2	2	1.2	1.2	9	2	2	1.2	1.2
10	1	1	1.2	1.2	10	1	1	1.2	1.2	10	1	1	1.2	1.2	10	1	1	1.2	1.2
10	1	2	1.2	1.2	10	1	2	1.2	1.2	10	1	2	1.2	1.2	10	1	2	1.2	1.2
10	2	1	1.2	1.2	10	2	1	1.2	1.2	10	2	1	1.2	1.2	10	2	1	1.2	1.2
10	2	2	1.2	1.2	10	2	2	1.2	1.2	10	2	2	1.2	1.2	10	2	2	1.2	1.2
11	1	1	1.2	1.2	11	1	1	1.2	1.2	11	1	1	1.2	1.2	11	1	1	1.2	1.2
11	1	2	1.2	1.2	11	1	2	1.2	1.2	11	1	2	1.2	1.2	11	1	2	1.2	1.2
11	2	1	1.2	1.2	11	2	1	1.2	1.2	11	2	1	1.2	1.2	11	2	1	1.2	1.2
11	2	2	1.2	1.2	11	2	2	1.2	1.2	11	2	2	1.2	1.2	11	2	2	1.2	1.2
12	1	1	1.2	1.2	12	1	1	1.2	1.2	12	1	1	1.2	1.2	12	1	1	1.2	1.2
12	1	2	1.2	1.2	12	1	2	1.2	1.2	12	1	2	1.2	1.2	12	1	2	1.2	1.2
12	2	1	1.2	1.2	12	2	1	1.2	1.2	12	2	1	1.2	1.2	12	2	1	1.2	1.2
12	2	2	1.2	1.2	12	2	2	1.2	1.2	12	2	2	1.2	1.2	12	2	2	1.2	1.2
13	1	1	1.2	1.2	13	1	1	1.2	1.2	13	1	1	1.2	1.2	13	1	1	1.2	1.2
13	1	2	1.2	1.2	13	1	2	1.2	1.2	13	1	2	1.2	1.2	13	1	2	1.2	1.2
13	2	1	1.2	1.2	13	2	1	1.2	1.2	13	2	1	1.2	1.2	13	2	1	1.2	1.2
13	2	2	1.2	1.2	13	2	2	1.2	1.2	13	2	2	1.2	1.2	13	2	2	1.2	1.2
14	1	1	1.2	1.2	14	1	1	1.2	1.2	14	1	1	1.2	1.2	14	1	1	1.2	1.2
14	1	2	1.2	1.2	14	1	2	1.2	1.2	14	1	2	1.2	1.2	14	1	2	1.2	1.2
14	2	1	1.2	1.2	14	2	1	1.2	1.2	14	2	1	1.2	1.2	14	2	1	1.2	1.2
14	2	2	1.2	1.2	14	2	2	1.2	1.2	14	2	2	1.2	1.2	14	2	2	1.2	1.2
15	1	1	1.2	1.2	15	1	1	1.2	1.2	15	1	1	1.2	1.2	15	1	1	1.2	1.2
15	1	2	1.2	1.2	15	1	2	1.2	1.2	15	1	2	1.2	1.2	15	1	2	1.2	1.2
15	2	1	1.2	1.2	15	2	1	1.2	1.2	15	2	1	1.2	1.2	15	2	1	1.2	1.2
15	2	2	1.2	1.2	15	2	2	1.2	1.2	15	2	2	1.2	1.2	15	2	2	1.2	1.2
16	1	1	1.2	1.2	16	1	1	1.2	1.2	16	1	1	1.2	1.2	16	1	1	1.2	1.2
16	1	2	1.2	1.2	16	1	2	1.2	1.2	16	1	2	1.2	1.2	16	1	2	1.2	1.2
16	2	1	1.2	1.2	16	2	1	1.2	1.2	16	2	1	1.2	1.2	16	2	1	1.2	1.2
16	2	2	1.2	1.2	16	2	2	1.2	1.2	16	2	2	1.2	1.2	16	2	2	1.2	1.2
17	1	1	1.2	1.2	17	1	1	1.2	1.2	17	1	1	1.2	1.2	17	1	1	1.2	1.2
17	1	2	1.2	1.2	17	1	2	1.2	1.2	17	1	2	1.2	1.2	17	1	2	1.2	1.2
17	2	1	1.2	1.2	17	2	1	1.2	1.2	17	2	1	1.2	1.2	17	2	1	1.2	1.2
17	2	2	1.2	1.2	17	2	2	1.2	1.2	17	2	2	1.2	1.2	17	2	2	1.2	1.2
18	1	1	1.2	1.2	18	1	1	1.2	1.2	18	1	1	1.2	1.2	18	1	1	1.2	1.2
18	1	2	1.2	1.2	18	1	2	1.2	1.2	18	1	2	1.2	1.2	18	1	2	1.2	1.2
18	2	1	1.2	1.2	18	2	1	1.2	1.2	18	2	1	1.2	1.2					

trolled by the instrument, was set with an upper time limit of 0·6 sec per step of 0·01°. The standard reflexion 008 was recorded after every 15 observations and used as a check on crystal and instrumental drift. The occurrence of significant drifts in crystal orientation or instrumental settings then required the calculation of new setting matrices following the method of Busing & Levy (1967).

Bis(dimethyl-o-thiolophenylarsine)platinum(II)

PtAs₂S₂C₁₆H₂ F.W. = 621.37.

Monoclinic: $a = 7.818(2)$, $b = 9.662(2)$, $c = 13.052(3)$ Å;
 $\beta = 102.814(6)^\circ$; $U = 961$ Å³; $Z = 2$.

$D_m = 2.18 \text{ g.cm}^{-3}$ (by flotation in methylene iodide and toluene solutions); $D_c = 2.15 \text{ g.cm}^{-3}$.

Linear absorption coefficient μ , for Cu $K\alpha$ radiation
is 215.57 cm^{-1} .

The intensity data were initially collected on multiple-film equi-inclination Weissenberg photographs ($\text{Cu } K\alpha$) taken around $[010]$, ($k = 0, 1, \dots, 7$). A total of 1555 intensities were estimated by visual comparison with a calibrated strip. Correlation data were obtained from zero level precession photographs and were adequate during the initial stages of the structure analysis. This visual data after corrections for Lorentz and polarization effects was used to determine the approximate structure. The diffractometer data collected at a later date and corrected for Lorentz, polarization and absorption effects were then used in the final refinement of the structure.

Determination and refinement of the structure

A three-dimensional Patterson function was computed from which the arsenic and sulphur atom posi-

Table 1 (*cont.*)

tions were determined. The platinum atoms, numbering only two in the unit cell, were placed in position 2(a) of the space group $P2_1/c$. The remaining carbon atoms were located using successive cycles of structure factors and difference Fourier syntheses.

The atomic parameters were refined by full-matrix least-squares methods in which the values of $\sum W(|F_{\text{obs}} - |F_{\text{calcl}}|)^2$ were minimized. A weighting scheme based upon the counting statistics for each observation was used in the least-squares refinement (Craig, 1969). The isotropic refinement converged to a reliability index (R) of 0.111. One further cycle using anisotropic temperature parameters reduced the value of R to 0.035. At this stage a difference Fourier synthesis was calculated from which it was possible to ascertain the approximate positions of all twenty hydrogen atoms. Further least-squares refinements were now carried out in which positional and thermal parameters of all non-hydrogen atoms were varied. Hydrogen positional par-

ameters were not varied and temperature parameters for these atoms were fixed at 8\AA^2 (Kastalsky & McConnell, 1969). The final value of R was 0.029.

For the calculation of structure factors the atomic scattering factors for Pt, As, S and C were computed from numerical Hartree-Fock wave functions using the method of Cromer & Mann (1968). The scattering factors for hydrogen were taken from *International Tables for X-ray Crystallography* (1968).

The observed and calculated structure factors are listed in Table 1.

A correction for the real and imaginary components of the anomalous dispersion of all atoms for Cu $K\alpha$ radiation was applied (Dauben & Templeton, 1955). An IBM 360/50 computer was used for all calculations together with local versions of well established programs (Craig, 1969).

The final atomic parameters for the crystallographically independent atoms, together with estimated

Table 1 (cont.)

	H	K	L	F(OBS)	F(CAL)		H	K	L	F(OBS)	F(CAL) ^a		H	K	L	F(OBS)	F(CAL)		H	K	L	F(OBS)	F(CAL)	
C						C						C						C						
	440	441					4	1	1	1	1		167	177				4	1	1	1	1		
	342	343						1	1	1	1	1		323	323				1	1	1	1	1	
	345	346							1	1	1	1		512	512				1	1	1	1	1	
	347	348							1	1	1	1		513	513				1	1	1	1	1	
	349	350							1	1	1	1		514	514				1	1	1	1	1	
	351	352							1	1	1	1		515	515				1	1	1	1	1	
	353	354							1	1	1	1		516	516				1	1	1	1	1	
	355	356							1	1	1	1		517	517				1	1	1	1	1	
	357	358							1	1	1	1		518	518				1	1	1	1	1	
	359	360							1	1	1	1		519	519				1	1	1	1	1	
	361	362							1	1	1	1		520	520				1	1	1	1	1	
	363	364							1	1	1	1		521	521				1	1	1	1	1	
	365	366							1	1	1	1		522	522				1	1	1	1	1	
	367	368							1	1	1	1		523	523				1	1	1	1	1	
	369	370							1	1	1	1		524	524				1	1	1	1	1	
	371	372							1	1	1	1		525	525				1	1	1	1	1	
	373	374							1	1	1	1		526	526				1	1	1	1	1	
	375	376							1	1	1	1		527	527				1	1	1	1	1	
	377	378							1	1	1	1		528	528				1	1	1	1	1	
	379	380							1	1	1	1		529	529				1	1	1	1	1	
	381	382							1	1	1	1		530	530				1	1	1	1	1	
	383	384							1	1	1	1		531	531				1	1	1	1	1	
	385	386							1	1	1	1		532	532				1	1	1	1	1	
	387	388							1	1	1	1		533	533				1	1	1	1	1	
	389	390							1	1	1	1		534	534				1	1	1	1	1	
	391	392							1	1	1	1		535	535				1	1	1	1	1	
	393	394							1	1	1	1		536	536				1	1	1	1	1	
	395	396							1	1	1	1		537	537				1	1	1	1	1	
	397	398							1	1	1	1		538	538				1	1	1	1	1	
	399	400							1	1	1	1		539	539				1	1	1	1	1	
	401	402							1	1	1	1		540	540				1	1	1	1	1	
	403	404							1	1	1	1		541	541				1	1	1	1	1	
	405	406							1	1	1	1		542	542				1	1	1	1	1	
	407	408							1	1	1	1		543	543				1	1	1	1	1	
	409	410							1	1	1	1		544	544				1	1	1	1	1	
	411	412							1	1	1	1		545	545				1	1	1	1	1	
	413	414							1	1	1	1		546	546				1	1	1	1	1	
	415	416							1	1	1	1		547	547				1	1	1	1	1	
	417	418							1	1	1	1		548	548				1	1	1	1	1	
	419	420							1	1	1	1		549	549				1	1	1	1	1	
	421	422							1	1	1	1		550	550				1	1	1	1	1	
	423	424							1	1	1	1		551	551				1	1	1	1	1	
	425	426							1	1	1	1		552	552				1	1	1	1	1	
	427	428							1	1	1	1		553	553				1	1	1	1	1	
	429	430							1	1	1	1		554	554				1	1	1	1	1	
	431	432							1	1	1	1		555	555				1	1	1	1	1	
	433	434							1	1	1	1		556	556				1	1	1	1	1	
	435	436							1	1	1	1		557	557				1	1	1	1	1	
	437	438							1	1	1	1		558	558				1	1	1	1	1	
	439	440							1	1	1	1		559	559				1	1	1	1	1	
	441	442							1	1	1	1		560	560				1	1	1	1	1	
	443	444							1	1	1	1		561	561				1	1	1	1	1	
	445	446							1	1	1	1		562	562				1	1	1	1	1	
	447	448							1	1	1	1		563	563				1	1	1	1	1	
	449	450							1	1	1	1		564	564				1	1	1	1	1	
	451	452							1	1	1	1		565	565				1	1	1	1	1	
	453	454							1	1	1	1		566	566				1	1	1	1	1	
	455	456							1	1	1	1		567	567				1	1	1	1	1	
	457	458							1	1	1	1		568	568				1	1	1	1	1	
	459	460							1	1	1	1		569	569				1	1	1	1	1	
	461	462							1	1	1	1		570	570				1	1	1	1	1	
	463	464							1	1	1	1		571	571				1	1	1	1	1	
	465	466							1	1	1	1		572	572				1	1	1	1	1	
	467	468							1	1	1	1		573	573				1	1	1	1	1	
	469	470							1	1	1	1		574	574				1	1	1	1	1	
	471	472							1	1	1	1		575	575				1	1	1	1	1	
	473	474							1	1	1	1		576	576				1	1	1	1	1	
	475	476							1	1	1	1		577	577				1	1	1	1	1	
	477	478							1	1	1	1		578	578				1	1	1	1	1	
	479	480							1	1	1	1		579	579				1	1	1	1	1	
	481	482							1	1	1	1		580	580				1	1	1	1	1	
	483	484							1	1	1	1		581	581				1	1	1	1	1	
	485	486							1	1	1	1		582	582				1	1	1	1	1	
	487	488							1	1	1	1		583	583				1	1	1	1	1	
	489	490							1	1	1	1		584	584				1</					

Table 1 (*cont.*)

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*-thiolophenylarsine)platinum(II)

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

	x/a	y/b	z/c
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*-thiolophenylarsine)platinum(II)

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

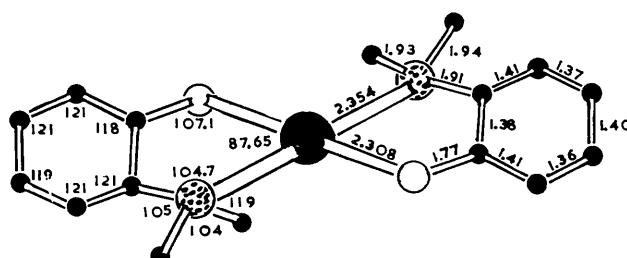
BIS(DIMETHYL-*o*-THIOLOPHENYLARSINE)PLATINUM(II)

Fig. 1. A diagram illustrating the configuration of the bis(dimethyl-*o*-thiolophenylarsine)platinum(II) molecule and showing some bond distances (\AA) and angles ($^\circ$).

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

Table 4. Some interatomic approach distances of less than 4 \AA in the crystal of bis(dimethyl-*o*-thiolophenylarsine)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) \AA	C(4)-C(21)	3.876 (5) \AA
Pt-C(8 ¹)	3.775 (12)	C(5)-C(21)	3.891 (5)
S-C(11)	3.971 (12)	C(3)-C(21)	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 \AA . 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*-thiolophenylarsine)platinum(II)

Standard deviations are given in brackets.

Pt-As	2.354 (1) \AA	C(3)-C(4)	1.380 (12) \AA
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) \AA is appreciably shorter than the sum of the square covalent radius for platinum(II) and the tetrahedral radius for arsenic ($1.31 + 1.18 = 2.49 \text{\AA}$) (Pauling, 1948). It is also shorter than the Pt-As bond distance of 2.380(15) \AA found in $\text{Pt}(\text{diarsine})_2\text{X}_2$, (Stephenson, 1962, 1964; Stephenson & Jeffrey, 1963)], where diarsine represents the ligand *o*-phenylenebisdimethylarsine and X is

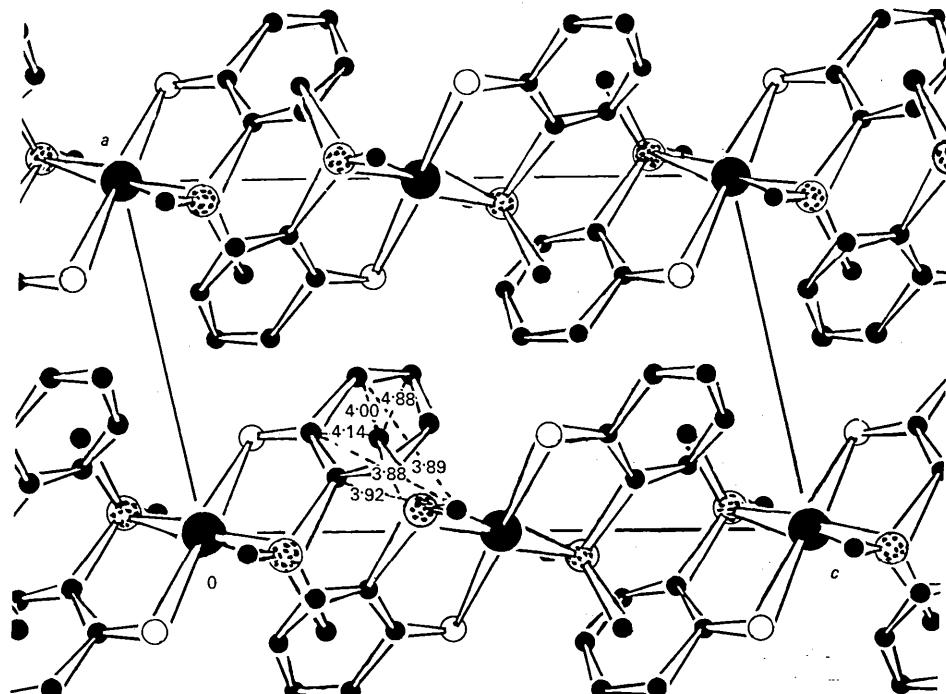


Fig. 2. An (010) projection of the unit-cell contents of bis(dimethyl-*o*-thiolophenylarsine)platinum(II). Some non-bonded approach distances (\AA) are shown.

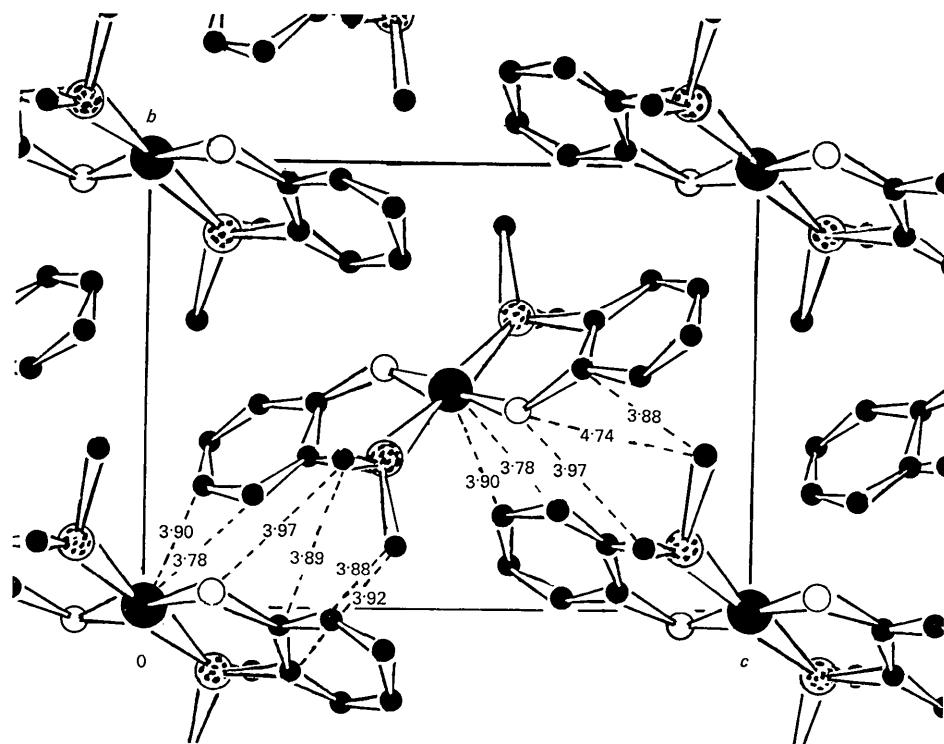


Fig. 3. A (100) projection of the unit-cell contents of bis(dimethyl-*o*-thiolophenylarsine)platinum(II). Some non-bonded approach distances (\AA) are shown.

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 $d\pi-d\pi$ 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 $d\pi-d\pi$ 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) \AA is significantly shorter than the sum of the square covalent radius for platinum(II) and the normal covalent radius for sulphur ($1.31 + 1.04 = 2.35 \text{ \AA}$).

Finally, examination of all metal-carbon distances reveals some interesting facts. The As-CH₃ distances of 1.933(10) and 1.942(19) \AA 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 \AA) 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) $^\circ$	C(1)—As—C(2)	103.8 (5) $^\circ$
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) $^{\circ}$, which are significantly different from the normal tetrahedral angle (109 $^{\circ}$). 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 $^{\circ}$ to the (010) plane.

The compound bis(dimethyl-*o*-thiolophenylarsine)-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*-thiolophenylarsine)palladium(II)*

PdAs₂S₂C₁₆H₂₀ F.W. 532.68

Monoclinic: *a*=7.81±0.04, *b*=9.68±0.05,
c=12.97±0.06 Å, β =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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