Acta Cryst. (1972). B**28**, 557

A Structural Study of a Pyridine Inclusion Compound of Bis(dimethyl-*o*-thiolophenylarsine)palladium(II)

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(*Received* 30 *March* 1971)

The crystal structure of bis(dimethyl-*o*-thiolophenylarsine)palladium(II) has been examined. The complex crystallizes from pyridine as a solvate, with composition $PdAs_2S_2C_{16}H_{20}.C_5H_5N$ in space group *Cc* or *C*2/*c* with four molecules in a unit cell of dimensions $a=18{\cdot}81$, $b=9{\cdot}38$, $c=14{\cdot}11$ Å, $\beta=112{\cdot}0°$ (all to $\pm0{\cdot}5\%$). The structure contains *trans* square-planar palladium(II) molecules in which the thiol functions as a bidentate ligand. The clathrated pyridine molecules, although influencing the packing geometry of the metal complex within the crystal, do not induce any unusual stereochemical features.

Introduction

S-Demethylation of the ligand dimethyl-*o*-methylthiophenylarsine, $(As\text{–}SCH_3)$, has been observed when complexes of the type $M(As\text{–}SCH_3)_2X_2$ ($M=Pd$, Pt; $X=Cl$, Br, I) are refluxed in dimethylformamide solution (Livingstone, 1958; Chiswell & Livingstone, 1960). The crystal structure of one of these *S*-demethylated products, bis(dimethyl-*o*-thiolophenylarsine)platinum(II), $Pt(As\text{–}S)_2$, has been reported (Beale & Stephenson, 1971).

The complexes $M(As\text{–}S)_2$, ($M=Pt$, Pd), recrystallize from pyridine or benzene, with one or more molecules of solvent per molecule of complex. Interest in this species lies in whether the solvent molecules are coordinated to the metal complex or merely pack into vacant regions of the crystal.

Experimental

Orange crystals of $Pd(As\text{–}S)_2$ were obtained by the method of Lindoy, Livingstone & Lockyer (1967) and recrystallized from pyridine. Small crystals are shaped as parallelepipeds with (100), (011) and $(0\bar{1}1)$ faces most prominently developed. A crystal of dimensions $0{\cdot}02\times0{\cdot}025\times0{\cdot}0075$ cm was used to collect photographic data by the equi-inclination Weissenberg method (Cu $K\alpha$ radiation; $k=0,1,\ \ldots,\ 7$ levels). A total of 1722 independent intensities were estimated by visual comparison with a calibration strip.

Correlation data were obtained from zero-level Weissenberg photographs taken around [001] but interlayer scale factors were introduced as variates during the final stages of refinement. Unit-cell dimensions were obtained from zero-level precession photographs with Mo $K\alpha$ radiation. Corrections were made for shrinkage and the cell dimensions are considered accurate to 0·5% (Evans, 1950).

Bis(dimethyl-*o*-thiolophenylarsine)palladium(II)–pyridine
$PdAs_2S_2C_{16}H_{20}.C_5H_5N$, F.W. 611·69
$a=18{\cdot}81\pm0{\cdot}09$, $b=9{\cdot}38\pm0{\cdot}05$, $c=14{\cdot}11\pm0{\cdot}07$ Å
$\beta=112{\cdot}0\pm0{\cdot}3°$, $U=2309$ Å^3, $Z=4$, $D_c=1{\cdot}87$ g.cm^{-3}
$D_m=1{\cdot}85$ g.cm^{-3} (flotation in methylene iodide-toluene)
Space group *Cc* or *C*2/*c*.

Absorption corrections ($\mu=128{\cdot}40$ cm^{-1}) were applied (Coppens, Leiserowitz & Rabinovich, 1965) using a grid of 192 points ($4\times6\times8$). Extinction corrections were not applied. For the calculation of structure factors (listed in Table 1), the scattering factors for Pd,

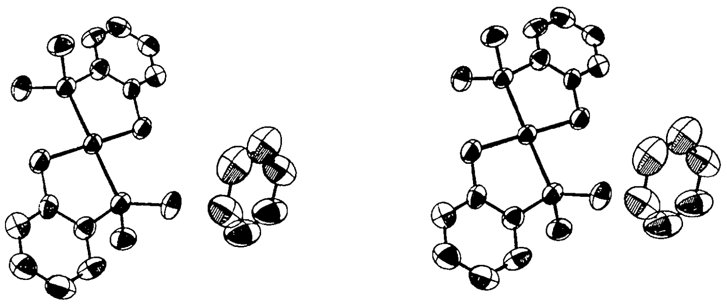
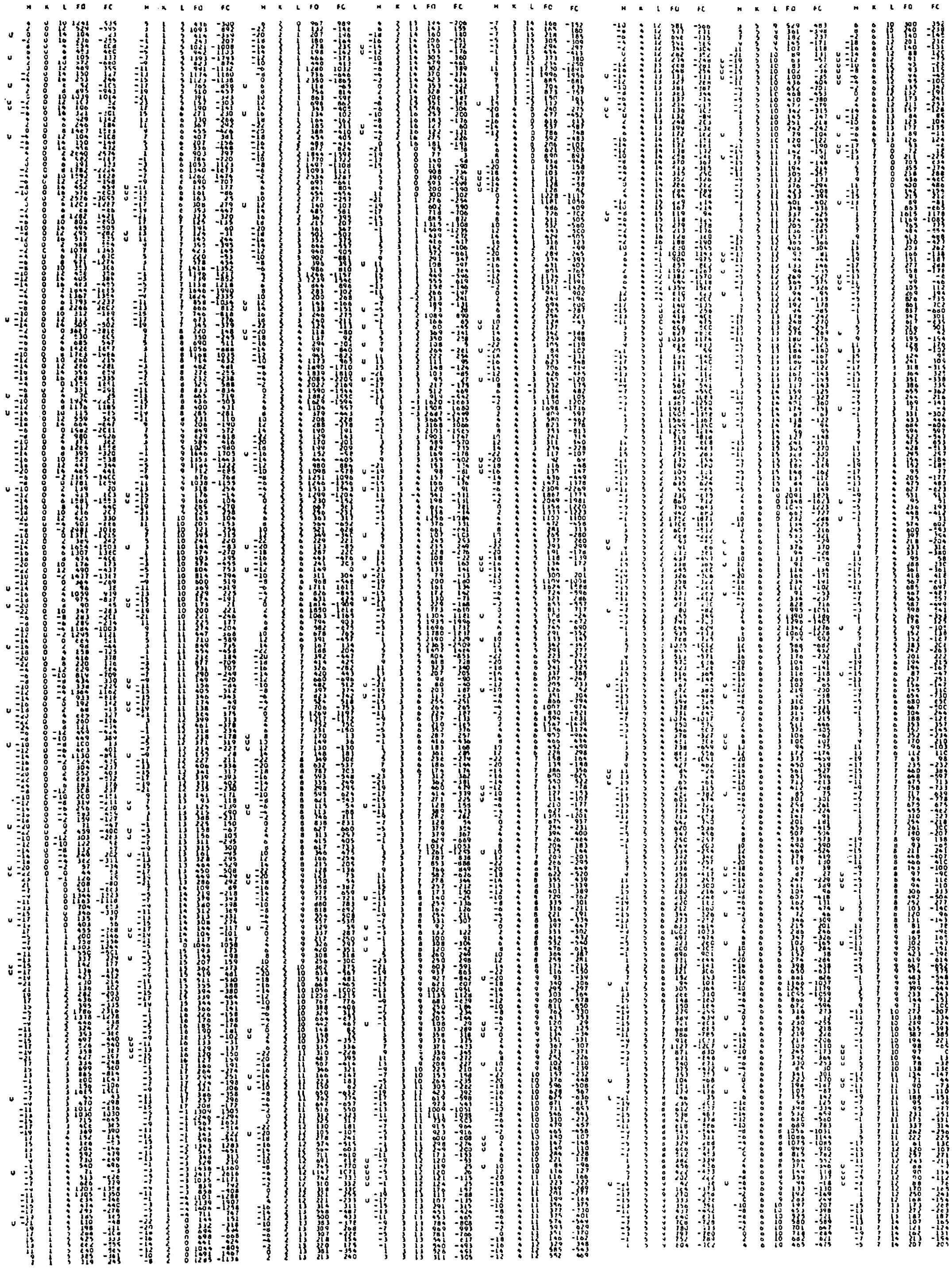


Fig. 1. A stereoscopic view of a molecule of bis(dimethyl-*o*-thiolophenylarsine)palladium(II) with a neighbouring pyridine molecule.

As, S and carbon were computed from numerical Hartree–Fock wave functions (Cromer & Mann, 1968). $\Delta f'$ corrections were applied to all scattering curves (Dauben & Templeton, 1955) and all calculations were done on an IBM 360/50 computer using local versions of well established programs (Craig, 1970).

Table 1. *Observed and calculated structure factors for bis(dimethyl-o-thiolophenylarsine)palladium*(II)*–pyridine*

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 which has been assigned an I_{obs} value corresponding to half the minimum observed intensity.



H K L FO FC H K L FO FC H K L FO FC H K L FO FC H K L FO FC H K L FO FC H K L FO FC H K L FO FC

Determination of the structure

The structure was solved from the three-dimensional Patterson function followed by successive cycles of structure factors and difference Fourier syntheses. The Patterson symmetry was consistent with space group *C*2/*c* with the palladium atoms in special position 2(*c*) (or 2*d*). The positional (Table 2) and isotropic thermal parameters for all non-hydrogen atoms were refined in this centric space group by full-matrix least-squares procedures using the Cruickshank (1965) weighting scheme and minimizing $\sum w(|F_{\text{obs}}|-|F_{\text{calc}}|)^2$ values. Isotropic refinement converged to an *R* value of 0·131 and one cycle of anisotropic refinement (with fixed interlayer scale factors), reduced this index to 0·105.

Table 2. *Final fractional atomic coordinates for bis(dimethyl-o-thiolophenylarsine)palladium*(II)*pyridine*

Standard deviations are given in brackets and refer to the least significant places in the preceding coordinate. All values are × 10^4.

	x/*a*	*y*/*b*	*z*/*c*
Pd	2500·0	2500·0	0·0
As	2221·2 (9)	850·1 (1·9)	1059·3 (1·2)
S	3617·4 (2·2)	2950 (5)	1365 (3)
C(1)	3626 (8)	1967 (18)	2401 (11)
C(2)	4252 (10)	2103 (22)	3349 (13)
C(3)	4282 (11)	1301 (35)	4202 (15)
C(4)	3706 (13)	329 (26)	4129 (17)
C(5)	3055 (10)	208 (21)	3215 (13)
C(6)	3031 (9)	1013 (17)	2339 (11)
C(7)	1292 (12)	977 (22)	1306 (15)
C(8)	2280 (11)	−1090 (22)	690 (15)
C(9)	5336 (16)	6458 (37)	2940 (20)
C(10)	5626 (14)	7685 (29)	3379 (19)
C(11)	5329 (14)	8987 (28)	2946 (18)

Description of the structure

A crystal of $Pd(As–S)_2$.pyridine contains discrete molecules of the *trans* square-planar palladium complex, bis(dimethyl-*o*-thiolophenylarsine)palladium(II) packed together with uncoordinated pyridine molecules in a 1:1 ratio. The packing mode of the molecules is shown in Fig. 1 and this is generally more compact than in the previously reported structure of Pt $(As–S)_2$ (Beale & Stephenson, 1971), *viz.* there are more intermolecular contacts less than 4 Å. Fig. 2 shows the contents of the unit cell of bis(dimethyl-*o*-thiolophenylarsine)palladium(II)-pyridine.

There is no evidence of increased coordination about the palladium atom. The closest intermolecular approach to the palladium atom is from symmetry-related thiol ligand atoms C(4) and C(5) at distances of 3·973 (25) and 3·983 (2) Å respectively. The bond distances and angles within the molecules are listed in Tables 3 and 4 and reveal the negligible influence of the solvent molecules upon the intramolecular bond distances within the $Pd(As–S)_2$ molecule.

Table 3. *Intramolecular bond distances* (Å) *in the structure of bis(dimethyl-o-thiolophenylarsine)palladium*(II)–*pyridine*

Standard deviations are given in brackets.
C(*n*′) refers to an atom related to C(*n*) by the twofold symmetry axis of space group *C*2/*c*.

Pd —As	2·344 (8)	C(4) —C(5)	1·411 (30)
Pd —S	2·296 (19)	C(5) —C(6)	1·435 (22)
As —C(6)	1·883 (22)	C(6) —C(1)	1·409 (21)
As —C(7)	1·911 (17)	C(9) —C(10)	1·324 (38)
As —C(s)	1·907 (20)	C(10) –C(11)	1·387 (34)
S——C(1)	1·724 (18)	C(11) –C(11′)	1·395 (48)
C(1)–C(2)	1·419 (24)	C(11′)–C(10′)	1·387 (34)
C(3)–C(3)	1·403 (27)	C(10′)–C(9′)	1·324 (38)
C(3)–C(4)	1·390 (30)	C(9′)—C(9)	1·401 (58)

The Pd–As distance of 2·344 (8) Å is significantly shorter than the sum of the square-covalent radius for palladium(II) and the tetrahedral radius for arsenic (1·31 + 1·18 = 2·49 Å; Pauling, 1960). It is also significantly shorter than the Pd–As distances reported for diiodobis(*o*-phenylenebisdimethylarsine)palladium(II), (Stephenson, 1962), and diiodobis(dimethyl-*o*-thiolophenylarsine)palladium(II) (Beale & Stephenson, 1970) of 2·39 (1) Å. This substantial shortening of the bond length has been noted in most complexes of this type and is attributed to d_π–d_π bonding between the arsenic and palladium atoms.

Similarly, the Pd–S distance of 2·296 (19) Å is significantly shorter than the normal covalent sum (1·31 + 1·04 = 2·33 Å; Pauling, 1960) but comparable to previously reported Pd–S distances in 2,2′-dimercaptodiethylsulphidepalladium(II), (McPartlin & Stephenson, 1969).

Twofold axes of the space group *C*2/*c* pass through pairs of opposite sides of the pyridine molecules. It was not possible to detect any ordering of the atoms of the pyridine molecules by refining in the non-centric

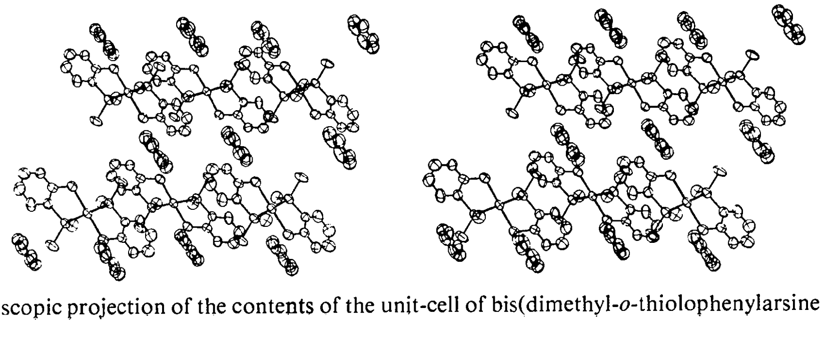


Fig. 2. An [010] stereoscopic projection of the contents of the unit-cell of bis(dimethyl-*o*-thiolophenylarsine)palladium(II)–pyridine.

Table 4. *Bond angles (°) defined by three atoms with the central atom at the vertex*

C(*n*′) refers to an atom related to C(*n*) by the twofold symmetry axis of space group *C*2/*c*.

S——Pt——As	86·50 (38)	C(1) —C(2) —C(3)	120·9 (1·8)
Pt——As —C(6)	105·33 (55)	C(2) —C(3) —C(4)	120·6 (1·8)
Pd —As —C(7)	120·91 (68)	C(3) —C(4) —C(5)	120·4 (1·6)
Pd —As —C(8)	113·97 (70)	C(4) —C(5) —C(6)	118·8 (1·7)
Pd —S——C(2)	109·22 (62)	C(5) —C(6) —C(1)	120·8 (1·5)
As —C(6)–C(1)	116·7 (1·1)	C(6) —C(1) —C(2)	118·4 (1·5)
As —C(6)–C(5)	122·5 (1·3)	C(9) —C(10) –C(11)	122·1 (2·2)
S——C(2)–C(6)	122·1 (1·2)	C(10) –C(11) –C(11′)	118·2 (1·3)
S——C(2)–C(2)	119·5 (1·3)	C(11) –C(11′)–C(10′)	118·2 (1·3)
C(6)–As —C(8)	103·37 (76)	C(10′)–C(9′)—C(9)	119·4 (1·4)
C(7)–As —C(8)	105·07 (83)	C(9′)—C(9) —C(10)	119·4 (1·4)
C(6)–As —C(7)	106·65 (90)		

space group *Cc*. However there is a significant shortening of the bond distances C(9)–C(10) ($\Delta = 0{\cdot}06$ Å) which may indicate that the nitrogen atom of the pyridine ring is to be found in either the C(9) or C(10) position.

Best least-squares planes were calculated (Schomaker, Waser, Marsh & Bergman, 1959) for the following atomic assemblages:

Palladium, arsenic and sulphur atoms:

$$-0{\cdot}626\,X + 0{\cdot}730\,Y + 0{\cdot}488\,Z - 1{\cdot}273 = 0$$

Pyridine molecule:

$$-0{\cdot}841\,X + 0{\cdot}817\,Z - 5{\cdot}025 = 0$$

where *X*, *Y* and *Z* are in Å and refer to the crystallographic axes. Both groups are planar.

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Acta Cryst. (1972). B**28**, 560

Structure Cristalline et Moléculaire de l'Oestradiol Hemihydrate

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(*Reçu le* 26 *fevrier, revu le* 1 *avril* 1971)

Crystals of hemihydrated estradiol ($C_{18}H_{24}O_2,\frac{1}{2}H_2O$) are orthorhombic. Unit cell is: $a = 12{\cdot}055$, $b = 19{\cdot}280$, $c = 6{\cdot}632$ Å. Space group is $P2_12_12$ with $Z = 4$. The structure was solved by direct minimization of the residual index *R*, to a final value of 0·065. The conformation of estradiol corresponds approximately to that found for estriol. The water molecule which is involved in the hydrogen bonding system is located on the binary axis.

Pour essayer d'apporter des éléments nouveaux à l'étude des relations existant entre structures et activités biologiques nous avons entrepris un travail cristallographique sur les hormones sexuelles. Le premier problème abordé est celui des hormones oestrogènes. La molécule d'oestradiol qui est l'hormone naturelle, sert de référence à tous les tests concernant l'activités des composés supposés actifs.