Les calculs ont été effectués au Centre de calculs du Centre National de la Recherche Scientifique à Orsay (CIRCE) sur les ordinateurs CDC 3600 et IBM 360/75, à l'aide des principaux programmes suivants:

– Calculs préliminaires: *PHOTO* (Riche, 1969).
– Affinement: une modification de *ORFLS* de Busing, Martin & Levy (1962).
– Distances, angles et plans moyens: des programmes de la série NRC de Ahmed, Hall, Pippy & Huber (1966).

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The Crystal and Molecular Structure of Dichloro-(S-methyl-L-cysteine)palladium(II) Monohydrate

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Crystals of dichloro-(S-methyl-L-cysteine)palladium(II) monohydrate $[Pd(SmCH)Cl_2]H_2O$ $[SmCH = CH_3SCH_2CH(NH_2)COOH]$ are orthorhombic, space group $P2_12_12_1$, with $a=22.41$ (1), $b=7.95$ (1), $c=11.93$ (1) Å and $Z=8$. The X-ray analysis was carried out using three-dimensional Patterson, Fourier and least-squares methods (final $R=4.9\%$). There are two crystallographically independent molecules with the same square-planar coordination involving sulphur and nitrogen from the amino-acid ligand and two chlorine atoms. The coordination five-membered ring has a λ conformation. The packing is determined by $Pd\cdots S = 3.33$ and $Pd\cdots Pd = 3.74$ Å contacts along [010] and by hydrogen bonds formed by the carboxylic oxygen atoms, water molecules, chlorine atoms and amino-groups.

Introduction

The crystal structure of dichloro-(S-methyl-L-cysteine)-palladium(II) monohydrate has been investigated in order to contribute to existing information about the interactions between the metal atoms and sulphur-containing amino-acids. This problem is quite interesting from the biological point of view, since chelation plays an important role in the biological activity of the ligands. There are several preparative and spectro-

scopic studies concerning metal complexes of sulphur-containing amino-acids (e.g. Li & Manning, 1955; Lenz & Martell, 1964; Shindo & Brown, 1965; McAuliffe, Quagliano & Vallarino, 1966; Livingstone & Nolan, 1968) which show that these ligands can play different roles in the different cases as they have three points for coordination to metal. In the present report the results of the structure analysis of dichloro-(S-methyl-L-cysteine)palladium(II)monohydrate are given, which show that S-methyl-L-cysteine behaves as a bidentate ligand coordinating through sulphur and nitrogen to palladium. The carboxyl group is not involved in coordination, as observed in Mo complexes (Drew & Kay, 1971).

Crystal determination and refinement

The compound, prepared following Livingstone & Nolan (1968), occurs as prismatic yellow-orange crystals having no pleochroic effects.

Crystal data, determined from rotation and Weissenberg photographs and from diffractometer measurements (Zr-filtered Mo $K\alpha$ radiation, $\bar{\lambda} = 0.71069$ Å), are as follows:

$Pd(SCH_3CH_2CHNH_2COOH)Cl_2 . H_2O$, $M = 330.5$, $a = 22.41$ (1), $b = 7.95(1)$, $c = 11.93(1)$ Å; $V = 2124$ Å^3; $Z = 8$; $D_m = 2.10$, $D_c = 2.07$ g cm^{-3}, $F(000) = 648$, $\mu = 23.7$cm^{-1}. Space group: $P2_12_12_1$ (from systematic absences).

The intensity data were collected on a Siemens 'on line' single-crystal diffractometer, using the $\omega/2\theta$-scan technique and Mo $K\alpha$ radiation. The sample was aligned with its [100] axis coincident with the φ axis of

the diffractometer and all reflexions having $2\theta \leq 58°$ were collected. In this way the intensities of 2682 independent reflexions were measured; of these, only 1763, having $I \geq 2\sigma(I)$, were used in the analysis. The sample was a small prism with a mean radius of 0.09 mm, and the μr value (0.21) was small enough to allow absorption corrections to be neglected. After the usual data reduction, the intensities were put on absolute scale by Wilson's (1942) method.

The structure was solved using the heavy-atom technique, starting from the coordinates of the two crystallographically independent palladium atoms obtained from a three-dimensional Patterson calculation. Two successive Fourier syntheses gave the coordinates of all non-hydrogen atoms, and resulted in a conventional R index of 24.4%. At this point least-squares refinement was started, minimizing the function $\sum w|\Delta F|^2$. Unit weights were initially used ($R = 6.7$%) and the weighting scheme $w = 1/(A + B|F_o|)^2$ was then assumed, in which $A = 3.0$, $B = 0.42$, these coefficients being determined by plotting ΔF against $\bar{F}_o$. The R index dropped to 5.3% and a ΔF calculation showed all the hydrogen atoms to be well resolved with the exception of those of the water molecules. Further refinement brought the R index down to the final value of 4.9%.

Final atomic coordinates and thermal parameters are given in Tables 1 and 2. These coordinates correspond to the absolute configuration of the structure as deduced by applying the Bijvoet, Peerdeman & van Bommel (1951) method to a number of hkl and $h\bar{k}l$ pairs collected with the Cu $K\alpha$ radiation. The atomic scattering factors used throughout all the calculations

Table 1. *Final atomic fractional coordinates* ($\times 10^4$), *thermal parameters* ($\times 10$ Å^2) *and e.s.d.'s for non-hydrogen atoms*

The anisotropic temperature factors are expressed in the form:
$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* \cos \gamma^* + 2B_{13}hla^*c^* \cos \beta^* + 2B_{23}klb^*c^* \cos \alpha^*)\right].$$

	x/a (σ)	y/b (σ)	z/c (σ)	B_{11} (σ)	B_{22} (σ)	B_{33} (σ)	B_{12} (σ)	B_{13} (σ)	B_{23} (σ)
Pd(1)	1574 (1)	1100 (1)	−325 (1)	27 (0)	31 (0)	22 (0)	0 (0)	0 (0)	−1 (0)
Pd(2)	3929 (1)	4455 (1)	5078 (1)	30 (0)	31 (0)	23 (0)	0 (0)	1 (0)	0 (0)
Cl(1)	2291 (1)	2515 (5)	−1370 (3)	31 (1)	42 (2)	26 (1)	−3 (1)	3 (1)	3 (1)
Cl(2)	1044 (2)	341 (5)	−1904 (3)	34 (1)	45 (1)	29 (1)	−3 (1)	−6 (1)	0 (1)
Cl(3)	4456 (2)	4796 (6)	6722 (3)	43 (2)	53 (2)	27 (1)	−1 (1)	−4 (1)	0 (1)
Cl(4)	3035 (2)	4123 (5)	6020 (3)	36 (1)	42 (2)	33 (1)	−3 (1)	9 (1)	4 (1)
S(1)	919 (2)	−382 (5)	677 (3)	36 (1)	32 (1)	25 (1)	−7 (1)	0 (1)	1 (1)
S(2)	4773 (2)	4967 (5)	4097 (3)	29 (1)	42 (2)	27 (1)	−5 (1)	−2 (1)	1 (1)
O(1)	2448 (5)	1876 (16)	3290 (9)	33 (4)	69 (6)	42 (5)	−10 (5)	−1 (4)	5 (5)
O(2)	1584 (5)	1238 (17)	4094 (8)	42 (5)	85 (7)	25 (3)	−4 (6)	3 (4)	10 (5)
O(3)	3889 (5)	5036 (17)	676 (9)	66 (6)	76 (7)	31 (4)	−27 (6)	0 (4)	12 (4)
O(4)	3278 (5)	3113 (17)	1371 (9)	52 (5)	69 (7)	41 (5)	−28 (5)	−4 (4)	10 (5)
O(5)	2926 (5)	−1028 (16)	1090 (8)	44 (5)	63 (6)	31 (4)	0 (5)	−1 (4)	8 (5)
O(6)	3565 (6)	4003 (29)	−1213 (9)	72 (7)	187 (16)	30 (5)	−63 (10)	6 (5)	−11 (8)
N(1)	1985 (5)	1680 (12)	1161 (7)	33 (4)	21 (4)	15 (3)	−6 (3)	0 (3)	4 (3)
N(2)	3519 (5)	4091 (15)	3567 (8)	35 (5)	38 (5)	21 (3)	−1 (4)	3 (3)	−4 (4)
C(1)	1937 (6)	1555 (19)	3211 (11)	28 (5)	45 (7)	27 (5)	8 (5)	1 (4)	−5 (5)
C(2)	1593 (5)	1501 (17)	2130 (9)	22 (4)	41 (6)	18 (4)	3 (5)	−1 (4)	5 (4)
C(3)	1265 (6)	−259 (19)	2064 (12)	35 (6)	37 (7)	37 (6)	−10 (5)	−7 (5)	3 (5)
C(4)	250 (6)	877 (22)	804 (11)	25 (5)	57 (8)	35 (5)	−4 (6)	−1 (4)	0 (6)
C(5)	3632 (6)	4160 (21)	1510 (11)	29 (5)	51 (8)	27 (5)	−2 (5)	2 (4)	6 (6)
C(6)	3872 (6)	4774 (19)	2638 (10)	30 (5)	44 (6)	24 (5)	3 (5)	9 (4)	−3 (4)
C(7)	4525 (6)	4153 (20)	2724 (11)	32 (5)	43 (7)	29 (5)	−1 (5)	−3 (4)	−2 (5)
C(8)	5312 (6)	3330 (24)	4475 (14)	33 (6)	66 (9)	42 (7)	23 (6)	−1 (5)	7 (7)

were those of Cromer & Mann (1968) for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the hydrogen atoms.

Table 2. *Fractional coordinates* ($\times 10^3$) *and isotropic thermal parameters* ($\times 10$ Å^2) *with e.s.d.'s for hydrogen atoms*

	x/a (σ)	y/b (σ)	z/c (σ)	B (σ)
H(1)	232 (5)	100 (15)	121 (9)	25 (23)
H(2)	212 (5)	286 (15)	113 (9)	31 (26)
H(3)	128 (5)	241 (15)	216 (10)	28 (26)
H(4)	175 (6)	125 (20)	473 (13)	69 (40)
H(5)	156 (5)	−123 (16)	215 (9)	35 (27)
H(6)	93 (5)	−35 (15)	264 (11)	25 (25)
H(7)	6 (5)	95 (18)	10 (10)	52 (31)
H(8)	33 (5)	209 (16)	119 (11)	29 (26)
H(9)	−2 (6)	40 (18)	131 (10)	54 (33)
H(10)	347 (5)	290 (14)	344 (9)	28 (25)
H(11)	316 (5)	431 (15)	348 (9)	28 (25)
H(12)	387 (5)	−612 (17)	262 (10)	41 (28)
H(13)	458 (5)	277 (16)	278 (10)	33 (28)
H(14)	477 (5)	453 (16)	199 (10)	33 (23)
H(15)	373 (7)	484 (22)	−9 (14)	90 (46)
H(16)	568 (5)	350 (17)	412 (10)	39 (30)
H(17)	518 (5)	190 (17)	436 (11)	40 (30)
H(18)	541 (5)	345 (17)	529 (11)	45 (31)

All the calculations were performed on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, using programs written by Immirzi (1967). Structure factor tables are available from the authors on request.

Description of the structure and discussion

Fig. 1 shows a clinographic projection of the structure. Coordination around palladium is slightly distorted square-planar and involves the sulphur and the nitrogen
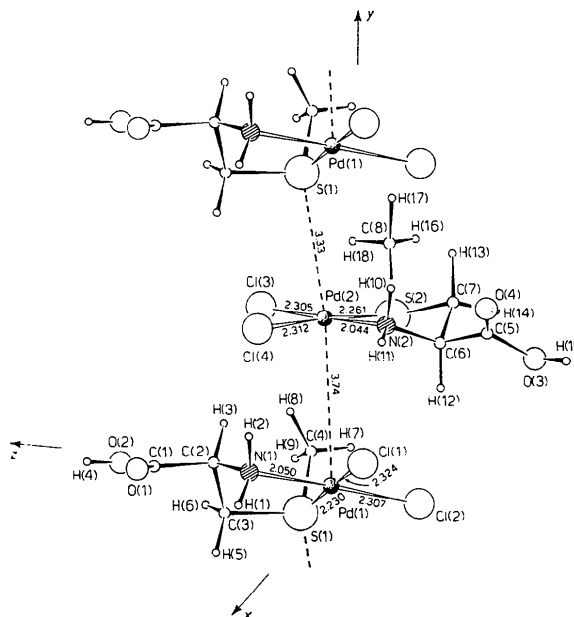

Fig. 1. Clinographic projection of the structure.

Table 3. *Bond distances and angles*

(a) In the coordination polyhedra

Pd(1)–Cl(1)	2·324 (3) Å		Pd(2)–Cl(3)	2·305 (4) Å
Pd(1)–Cl(2)	2·307 (4)		Pd(2)–Cl(4)	2·312 (7)
Pd(1)–S(1)	2·230 (4)		Pd(2)–S(2)	2·261 (4)
Pd(1)–N(1)	2·050 (9)		Pd(2)–N(2)	2·044 (10)
Cl(1)–Pd(1)–S(1)	176·8 (·4)°		Cl(4)–Pd(2)–S(2)	175·5 (·5)°
Cl(2)–Pd(1)–S(1)	87·7 (·5)		Cl(3)–Pd(2)–S(2)	89·4 (·3)
Cl(2)–Pd(1)–Cl(1)	92·5 (·2)		Cl(3)–Pd(2)–Cl(4)	92·5 (·3)
N(1) –Pd(1)–S(1)	87·2 (·3)		N(2) –Pd(2)–S(2)	86·8 (·5)
N(1) –Pd(1)–Cl(2)	174·9 (·5)		N(2) –Pd(2)–Cl(3)	175·8 (·6)
N(1) –Pd(1)–Cl(1)	92·5 (·5)		N(2) –Pd(2)–Cl(4)	91·3 (·6)
Pd(1)–S(1)—C(4)	107·3 (·9)		Pd(2)–S(2)—C(8)	107·2 (·9)
Pd(1)–S(1)—C(3)	100·2 (·8)		Pd(2)–S(2)—C(7)	98·3 (·7)
Pd(1)–N(1) –C(2)	113·1 (1·1)		Pd(2)–N(2) –C(6)	111·8 (1·2)

(b) In the amino-acid molecules

C(1)–O(1)	1·18 (2) Å		C(5)–O(4)	1·16 (2) Å
C(1)–O(2)	1·34 (2)		C(5)–O(3)	1·34 (2)
C(2)–N(1)	1·46 (2)		C(6)–N(2)	1·47 (2)
C(1)–C(2)	1·50 (2)		C(5)–C(6)	1·53 (2)
C(2)–C(3)	1·58 (2)		C(6)–C(7)	1·55 (2)
C(3)–S(1)	1·83 (2)		C(7)–S(2)	1·85 (1)
C(4)–S(1)	1·81 (2)		C(8)–S(2)	1·83 (2)
S(1)–C(3)–C(2)	106·8 (1·3)°		S(2)–C(7)–C(6)	103·4 (1·3)°
C(1)–C(2)–N(1)	111·6 (1·7)		C(5)–C(6)–N(2)	110·9 (1·8)
C(2)–C(1)–O(1)	125·0 (2·2)		C(6)–C(5)–O(4)	126·5 (2·9)
C(2)–C(1)–O(2)	111·5 (1·8)		C(6)–C(5)–O(3)	109·6 (1·9)
O(1)–C(1)–O(2)	123·5 (2·2)		O(3)–C(5)–O(4)	123·9 (2·9)
C(3)–C(2)–N(1)	109·1 (1·7)		C(7)–C(6)–N(2)	110·0 (1·8)
C(3)–C(2)–C(1)	107·8 (1·8)		C(7)–C(6)–C(5)	106·8 (1·8)
C(3)–S(1)–C(4)	104·2 (1·3)		C(7)–S(2)–C(8)	99·7 (1·3)

atoms of the amino-acid molecule and two chlorine atoms; the equations of the coordination planes for two independent molecules are:

Pd(1), Cl(1), Cl(2), S(1), N(1)

$$0{\cdot}5525X - 0{\cdot}8294Y - 0{\cdot}0826Z = 1{\cdot}2764;$$

Pd(2), Cl(3), Cl(4), S(2), N(2)

$$-0{\cdot}1844X + 0{\cdot}9825Y - 0{\cdot}0257Z = 1{\cdot}7188.$$

The amino-acid molecule acts as bidentate ligand forming a five-membered chelate ring. From the values of bond distances and angles given in Table 3 it can be deduced that the two independent molecules are not significantly different. These values agree well with those found in dichloro-DL-methioninepalladium(II) (Warren, McConnell & Stephenson, 1970) in which the coordination is similar, and in uncomplexed L-cysteine (Harding & Long, 1968), as shown in Table 4.

The conformation of the chelation ring is λ (IUPAC, 1970) with an equatorial orientation of the carboxylic group; the methyl group is axial and shows opposite orientations in the two molecules, as can be seen from Fig. 2. The absolute configuration of the amino-acid molecule is R; its conformation is similar to that found in other sulphur-containing amino-acids, as can be seen from the angles ψ_1, ψ_2 and χ_1 given in Table 5.

Coordination prevents the amino-acid molecule from adopting the zwitterion form; the carboxylic group is

Table 4. *Interatomic distances and bond angles in some amino-acid compounds*

	Present paper	PdCl₂(MtH)	L-Cysteine
Pd–Cl	2·305, 2·307 Å 2·312, 2·324	2·308, 2·332	
Pd–S	2·230, 2·261	2·265	
Pd–N	2·044, 2·050	2·061	
S–C	1·81, 1·83 1·83, 1·85	1·80, 1·83	1·77, 1·86
C–C	1·50, 1·53 1·55, 1·58	1·49, 1·54	1·50, 1·51 1·51, 1·53
C–N	1·46, 1·47	1·47	1·48, 1·50
C–O	1·16, 1·18 1·34, 1·34	1·20, 1·30	1·24, 1·25 1·26, 1·27
Cl–Pd–S	87·7, 89·4° 175·5, 176·8	85·2°	
Cl–Pd–Cl	92·5, 92·5	92·5	
N–Pd–S	86·8, 87·2	96·9	
N–Pd–Cl	91·3, 92·5 174·9, 175·8	85·3	
Pd–S–C	98·3, 100·2 107·2, 107·3	104·5, 110·2	
Pd–N–C	111·8, 113·1	123·9	
S–C–C	103·4, 106·8	117·0	114·4, 115·5°
C–C–N	109·1, 110·0 110·9, 111·6	108·0, 111·9	108·6, 109·1 109·9, 111·0
C–C–O	109·6, 111·5 125·0, 126·5	113·2, 123·0	115·8, 116·9 118·6, 120·7
C–C–C	106·8, 107·8	107·9, 113·7	111·2, 113·2
C–S–C	99·7, 104·2	100·1	
O–C–O	123·5, 123·9	123·7	123·7, 124·5

Fig. 2. Conformation of the chelation rings in the two independent molecules.

Table 5. *Values of the angles ψ_1 ψ_2, χ for sulphur-containing amino-acid derivatives*

ψ_1, ψ_2, and χ are defined according to the notation proposed by Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga (1966). For the present compound $\psi_1 = O(2)C(1)C(2){\frown}C(1)C(2)N(1)$, $O(3)C(5)C(6){\frown}C(5)C(6)N(2)$; $\psi_2 = O(1)C(1)C(2){\frown}C(1)C(2)N(1)$, $O(4)C(5)C(6){\frown}C(5)C(6)N(2)$; $\chi = N(1)C(2)C(3){\frown}C(2)C(3)S(1)$, $N(2)C(6)C(7){\frown}C(6)C(7)S(2)$.

	ψ_1	ψ_2	χ
Dichloro(S-methyl-L-cysteine)Pd(II).H₂O[a]	168·7, 174·4°	7·5, 10·5°	52·5, 60·0°
L-Cysteine[b]		−3·0, −36·1	72·6, −170·1
L(+)-Cysteine hydrochloride monohydrate[c]	169	−5	66
L-Cysteic acid monohydrate[d]	190·0	12·6	55·4
D-μ-Oxo-bis[oxo(L-cysteinato ethylester-N,S)-molybdenum(V)][e]	169·7	−3·3	56·1, 57·2

(a) This work.
(b) Harding & Long (1968).
(c) Ramachandra Ayyar (1968).
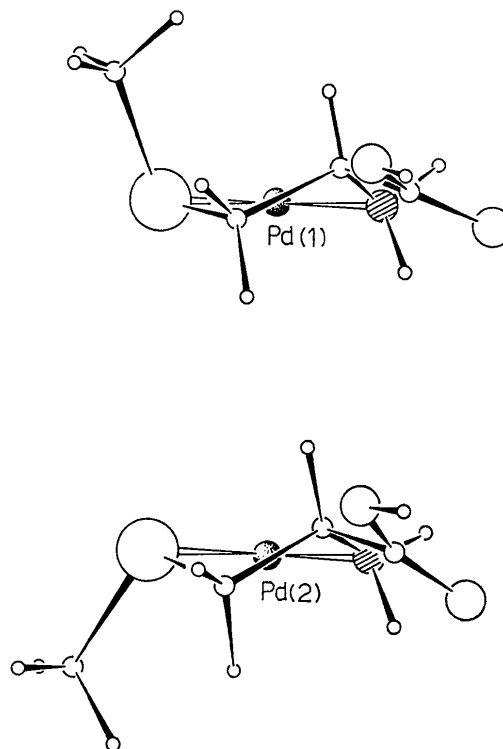(d) Hendrickson & Karle (1971).
(e) Drew & Kay (1971).

therefore protonated. In both independent molecules this group is planar with a localized double bond.

The two crystallographically independent palladium atoms, although exhibiting a similarity as far as the first coordination sphere is concerned, are not in the same situation when the other neighbours are considered. In fact Pd(1) shows only a long contact (3·74 Å) with Pd(2)($\frac{1}{2}-x, 1-y, z-\frac{1}{2}$), which makes the coordination tetragonal pyramidal, while Pd(2) shows in addition a Pd(2)–S(1) ($\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$) = 3·33 Å contact, which makes the coordination around it distorted octahedral. These long contacts given rise to $\cdots$–S–Pd–Pd–$\cdots$ chains running along [010], as shown in Fig. 1.

Packing contacts which can be considered as hydrogen bonds are:

N(1)–O(5) 3·01(2) Å   N(1)–H(1)$\cdots$O(5) 164·1(2·8)°
O(2)–O(5$^\text{v}$) 2·63(1)   O(2)–H(4)$\cdots$O(5$^\text{v}$)173·4(1·7)
O(3)–O(6) 2·51(2)   O(3)–H(15)$\cdots$O(6)162·9(3·8)

The other contacts less than 3·5 Å are shown in Table 6 and in Fig. 3 which gives the projection of the structure on (010).

Table 6. *Contacts less than 3·5 Å*

Cl(1)–O(6)	3·10 (1) Å	Cl(4)–N(1$^\text{iv}$)	3·34 (1) Å
Cl(1)–O(5$^\text{i}$)	3·29 (1)	Cl(4)–O(5$^\text{v}$)	3·27 (1)
Cl(1)–N(2$^\text{ii}$)	3·25 (1)	O(1)–O(4)	3·11 (1)
Cl(2)–O(5$^\text{i}$)	3·37 (1)	N(1)–O(4)	3·12 (2)
Cl(3)–O(6$^\text{iii}$)	3·23 (1)	N(2)–O(1)	2·99 (1)

Symmetry code

i	$\frac{1}{2}-x,$	$\bar{y}, z-\frac{1}{2}$
ii	$\frac{1}{2}-x,$	$1-y, z-\frac{1}{2}$
iii	$x,$	$y, z+1$
iv	$\frac{1}{2}-x,$	$1-y, z+\frac{1}{2}$
v	$\frac{1}{2}-x,$	$\bar{y}, z+\frac{1}{2}$

Bond distances and angles involving hydrogen atoms are in the range usually found in crystal structure analyses.
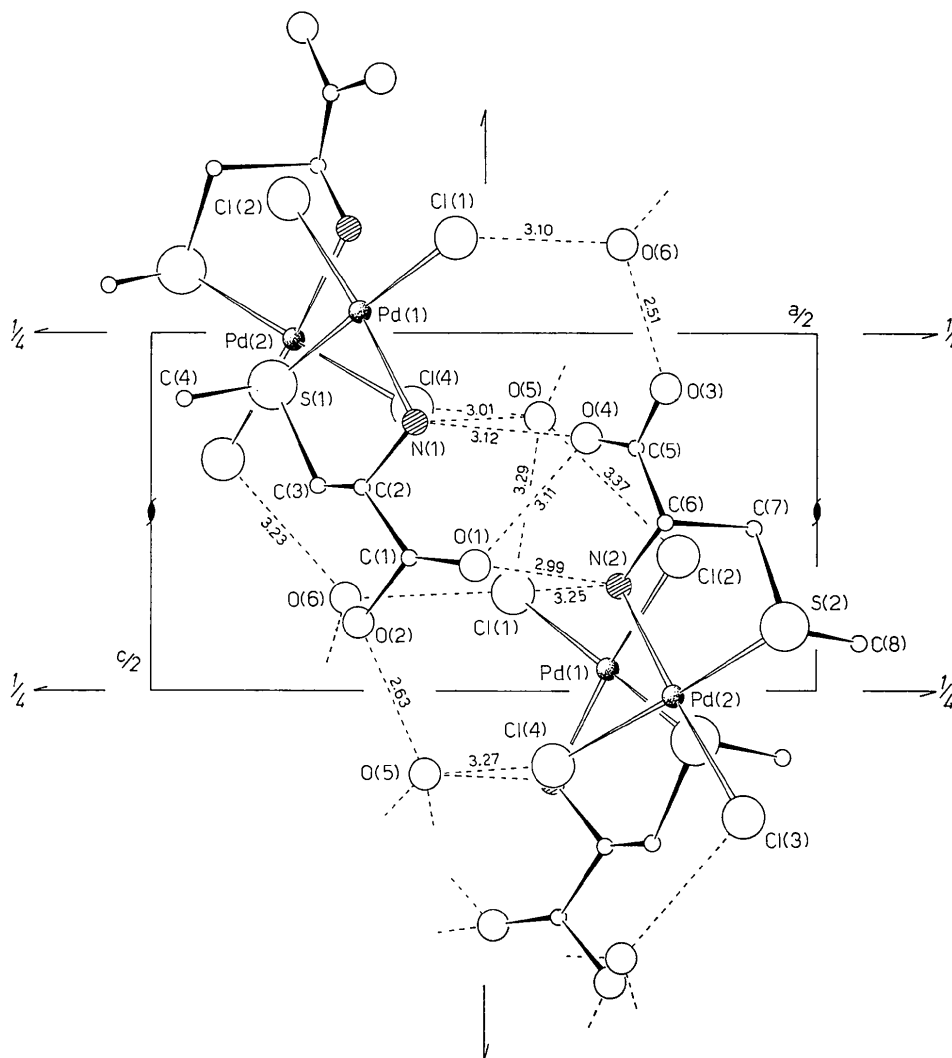

Fig. 3. Projection of the structure on (010).

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The Crystal and Molecular Structure of (3,7-Dimethyl-2,6-octadienyl)triphenylphosphonium bromide

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The title compound crystallizes in space group $P2_1/c$ with unit-cell constants $a = 12\cdot614$ (4), $b = 13\cdot845$ (5), $c = 15\cdot838$ (6) Å and $\beta = 113\cdot35$ (5)°. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares methods to an R value of 0·055 based on 2969 observed reflexions. The significantly planar phenyl groups are in a propeller configuration around the P atom. Rigid-body thermal analysis of the phenyl groups shows a libration of 8–9° around the P–C bond. The C–C bond lengths in the phenyl groups are 0·019 Å shorter for the bonds furthest away from the phosphorus atom compared with the bonds closest to this atom. The 3,7-dimethyl-2,6-octadienyl chain consists of two planar isoprene units joined head-to-tail at a dihedral angle of 75·8°. The bromine atom has eight hydrogen neighbours at distances of 2·70–3·26 Å.

Introduction

(3,7-Dimethyl-2,6-octadienyl)triphenylphosphonium bromide, $C_{28}H_{32}PBr$, is a Wittig salt (Wittig, 1956) commonly used as a reactant in the synthesis of alkenes. Examples of use are given by Kjøsen & Liaaen-Jensen (1970) and by Surmatis & Ofner (1963) who also describe the preparation of the compound. The cation is shown schematically in Fig. 1 which gives the numbering used for the carbon atoms. The 3,7-dimethyl-2,6-octadienyl chain is made up of two isoprene units as in geraniol. Later in this paper the compound will be called GTPPBR, short for geranyltriphenylphosphonium bromide.

It was of interest to study the configuration around the phosphorus atom since this is the primary reaction site. Furthermore the conformation around the C(20)–C(21)

bond might be either *cis* or *trans* and the orientation of the two isoprene units relative to each other was also unknown.

Experimental

Crystal data

The crystals were produced by crystallization from a 40–65 °C chloroform–petroleum spirit solution by Siv. ing. H. Kjøsen at the Organic Chemistry Laboratories of NTH. They are colourless prismatic needles of good crystal quality and elongated in the [100] direction. The forms {011} and {100} are well developed.

Crystallographic data:
(3,7-Dimethyl-2,6-octadienyl)triphenylphosphonium bromide, $C_{28}H_{32}PBr$.
F.W. 479·46; monoclinic, $Z = 4$; $\lambda(Cu\ K\alpha) = 1\cdot5418$ Å