A Case of Twinning: Structure of Dichloro[1,2-dicyclohexyl-1,2-bis(diethylamino)-1,2-dithioxodi-λ^5-phosphane]palladium(II)*

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Abstract

$[PdCl_2\{[(C_2H_5)_2N](C_6H_{11})P(S)-P(S)(C_6H_{11})[N(C_2H_5)_2]\}]$, $M_r = 614\cdot0$, monoclinic, $P2_1/c$, $a = 15\cdot627$ (3), $b = 19\cdot207$ (6), $c = 18\cdot422$ (5) Å, $\beta = 90\cdot05$ (4)°, $V = 5529$ (4) Å^3, $Z = 8$, $D_m = 1\cdot46$ (2), $D_x = 1\cdot47$ Mg m^{-3}, μ(Mo $K\bar{\alpha}$) = $1\cdot08$ mm^{-1}, $F(000) = 2544$, $T = 293$ K. Pseudo-orthorhombic: the asymmetric unit is constituted of two crystallographically independent molecules related by a pseudo glide plane. The sample used proved to be a twin. Separate contributions by the two crystals in the twin to the measured intensities have been estimated. Full-matrix least-squares refinements using 4370 observed reflections gave $R = 0\cdot058$ for one crystal and $R = 0\cdot067$ for the other. The final agreement factor between observed and calculated composite intensities was $R_1 = 0\cdot100$. The structure is built up of monomeric molecules. The ligands, in the *gauche* conformation [torsion angles $47\cdot2$ (1) and $46\cdot3$ (1)°], chelate the Pd atoms through the S atoms. The Pd atoms are in a square-planar environment. The P—P bond length, $2\cdot252$ (4) Å, is not modified on coordination.
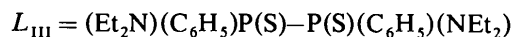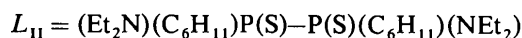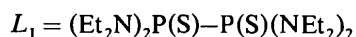
Introduction

Because of the donor properties of the S atoms, the tetrasubstituted dithioxodi-λ^5-phosphanes $RR'P(S)-P(S)R''R'''$ (more usually designated as diphosphine disulphides) are expected to form complexes with transition metals. Until recently only the tetraallyl and tetraalkyl derivatives had been investigated from this point of view. A large number of complexes of the ligands $R_2P(S)-P(S)R_2$ (R = Me, Et, Pr, Bu, C_3H_5) with various metals have been obtained and spectroscopically studied,† but there is a lack of molecular structure determinations using diffraction methods. Only the Cu^I and Cu^{II} complexes of the tetra-

methyldithioxodi-λ^5-phosphane $[\{CuCl[(CH_3)_2P(S)-P(S)(CH_3)_2]\}_2]$ and $[\{CuCl_2[(CH_3)_2P(S)-P(S)(CH_3)_2]\}_n]$ have been investigated by X-ray diffraction (Cotton, Frenz, Hunter & Mester, 1974). However, because of the possibility of rotation about the P—P bond, knowledge of the molecular geometry of the complexes is of importance. The free ligands have always been observed in the *trans* conformation in the solid state. In the complex $[\{CuCl_2[(CH_3)_2P(S)-P(S)(CH_3)_2]\}_n]$ the ligand retains the *trans* conformation whereas it has a *gauche* conformation in $[\{CuCl[(CH_3)_2P(S)-P(S)(CH_3)_2]\}_2]$. On the basis of spectroscopic data the ligand is considered to have the *cis* conformation in some chelates in solution (Meek & Nicpon, 1965; Beg & Khawaja, 1968). Obviously more molecular structure determinations are needed.

As an extension of our work on tetrasubstituted diphosphanes (Troy, 1981), we have started to investigate a new sub-class of ligands: the alkylaminodithioxo-di-λ^5-phosphanes of general formulae $(R_2N)_2P(S)-P(S)(NR_2)_2$ and $(R_2N)R'P(S)-P(S)R'(NR_2)$.

The ligands

$$L_I = (Et_2N)_2P(S)-P(S)(NEt_2)_2$$

$$L_{II} = (Et_2N)(C_6H_{11})P(S)-P(S)(C_6H_{11})(NEt_2)$$

$$L_{III} = (Et_2N)(C_6H_5)P(S)-P(S)(C_6H_5)(NEt_2)$$

have been synthesized and previously studied (Troy, Galy & Legros, 1980; Troy, Legros & McQuillan, 1982a). Solid complexes have been obtained with Cu^I, Pd^{II} and Pt^{II} and studied spectroscopically (Troy, Legros & McQuillan, 1982b). The X-ray structure determination of one of them, of abbreviated formula $L_{II}PdCl_2$, is reported here.

Experimental

The complex $L_{II}PdCl_2$ was obtained from the *meso* form of the ligand L_{II} as described elsewhere (Troy *et al.*, 1982b). Thin, elongated, plate-like, dark-orange crystals were obtained by recrystallizations from a mixture of methylene chloride and diethyl ether. The

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crystal (1·0 × 0·18 × 0·025 mm) selected for space-group determination and intensity-data collection was stuck to the end of a glass fibre. Precession photographs were taken using a Stoe camera and the intensity data were collected on a CAD-4 Enraf–Nonius diffractometer using graphite-mono-chromatized Mo $K\bar{\alpha}$ radiation. Crystal data are listed in the *Abstract*.

From the precession photographs the crystal lattice appears orthorhombic. Systematic absences $h0l$, $l = 2n + 1$ and $0kl$, $k = 2n + 1$ are consistent with the space groups *Pbcm* (No. 57) or *Pbc*2_1 (standard symbol *Pca*2_1, No. 29). The cell parameters were determined by a least-squares fit to the observed θ angles of 25 reflections measured on the diffractom-eter. The density measured by flotation in an aceto-nitrile–carbon tetrachloride mixture is in good agree-ment with the value calculated for eight $L_{II}PdCl_2$ molecules per unit cell.

Intensity data were collected at room temperature up to a Bragg angle $\theta = 20°$. The reflections were scanned at constant speed ($1°$ min^{-1} in ω) in the ω–2θ mode, scan width ω: $(1·0 + 0·35$ tg $\theta)°$. The intensities of three standard reflections were monitored throughout the data collection. Careful examination of the recorded intensities showed the extinction $h0l$, $l = 2n + 1$ to be not perfectly systematic: 14 'forbidden' reflections were observed with $5 < I/\sigma(I) < 18$. The systematic absences to be considered are thus $00l$, $l = 2n + 1$ and $0kl$, $k = 2n + 1$. They do not correspond to any orthorhombic space group; the crystal lattice is, in fact, monoclinic with $\beta \simeq 90°$. Let $h_o k_o l_o$ be the ortho-rhombic indices and $h_m k_m l_m$ the monoclinic indices; the permutation

$$\begin{pmatrix} h_o \\ k_o \\ l_o \end{pmatrix} \begin{pmatrix} 0 & 0 & \bar{1} \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} h_m \\ k_m \\ l_m \end{pmatrix}$$

leads to the systematic absences $h_m 0 l_m$, $l_m = 2n + 1$ and $0k_m 0$, $k_m = 2n + 1$: the space group is $P2_1/c$. The pseudo absence $h_o 0 l_o$, $l_o = 2n + 1$ must be written $h_m k_m 0$, $h_m = 2n + 1$.

A total of 5143 independent $hk \pm l$ reflections were recorded. The net intensities were corrected for a slight decay (5% at the end of the data collection) and assigned standard deviations according to the formula $\sigma^2(I) = \sigma_c^2(I) + (0·03I)^2$ where $\sigma_c(I)$ is based on counting statistics. The usual Lorentz–polarization correction was applied and absorption corrections were calculated by the Gaussian-integration method using a 192-point grid. The transmission factor was in the range 0·745–0·973. An internal consistency test was run to verify the monoclinic symmetry. The ratio $R = \sum |\langle I \rangle - I_o| / \sum 2\langle I \rangle$ where $\langle I \rangle$ is the mean intensity of the pair $(hkl, hk\bar{l})$ and I_o the intensity of one member of the pair, was computed, summation being carried out

over the whole set of measured reflections. The value obtained ($R = 0·22$) clearly means that the hkl and $hk\bar{l}$ reflections are not equivalent.

Structure determination and refinement

Determination of the structural model

Application of direct methods led to the location of the heavy atoms (Pd, Cl, S and P), in agreement with the interpretation of the Patterson map. The N and C atoms were located from a series of least-squares refinements and a difference Fourier synthesis. The asymmetric unit is constituted of two crystallo-graphically independent molecules (I and II) related by a pseudo a glide plane situated at $z \simeq \frac{1}{8}$:

$$x_{II} \simeq \tfrac{1}{2} + x_I$$
$$y_{II} \simeq y_I \qquad\qquad (1)$$
$$z_{II} \simeq \tfrac{1}{4} - z_I.$$

It is responsible for the pseudo absence $h_m k_m 0$, $h_m = 2n + 1$.

The full-matrix least-squares refinement of the 58 non-hydrogen atoms was performed with anisotropic thermal parameters for the non-C atoms; the C atoms were assigned isotropic thermal parameters. At this stage of refinement the individual N–C and C–C bond lengths displayed a number of unrealistic values. Constraints were thus applied: the N–C bonds were forced to be equal and their common length refined; the C–C bonds in the ethyl and cyclohexyl groups were treated in the same way. The contribution of the H atoms was calculated on the basis of geometrical criteria (sp^3 hybridization of the C atom, C–H = 0·97 Å, arbitrary isotropic thermal factor $U = 0·063$ Å^2). After convergence the conventional reli-ability factors (defined in Table 2) were $R = 0·139$ and $R_w = 0·158$.

Trivial measurement errors only could not explain the high values of the reliability factors. An analysis of

Table 1. *Analysis of the variance of* $(|F_o| - |F_c|)^2$ *as a function of the parity group of the hkl indices (O: odd; E: even)*

First row: conventional refinement; second and third rows: refinements using data corrected for twinning, crystals A and B respectively. The variance is defined as

$$V = 100[m \textstyle\sum_n w(k|F_o| - |F_c|)^2/n \textstyle\sum_m w]^{1/2};$$

w = weight of the reflection, n = number of reflections in the group, m = total number of reflections.

Parity	EEE	OEE	EOE	OOE	EEO	OEO	EOO	OOO
	985	1019	906	942	1756	1501	1615	1604
Variance	487	425	442	429	417	385	434	389
	472	404	431	425	449	409	440	415

the variance of the quantity $(|F_o| - |F_c|)^2$ as a function of the parity group of the hkl indices revealed that the agreement between the observed and calculated structure factors is worse when l is odd than when l is even (Table 1). As a check, the data set was split into two files according to the parity of the l index and a refinement was carried out with each. The reliability factors were:

$$l = 2n \qquad R = 0.074 \quad R_w = 0.076$$
$$l = 2n + 1 \quad R = 0.17 \quad R_w = 0.20.$$

Obviously, the odd-l reflections were preferentially affected by a systematic error.

Hypothesis of twinning

Let us consider Fig. 1 where, for the sake of clarity, the heavy atoms only have been drawn in projection onto the (010) plane. The lattice is represented in bold lines in the orientation (x,y,z). By rotation about the x axis, the lattice is brought into the orientation $(x,\bar{y},\bar{z})$. A subsequent translation $(-\frac{1}{2},\frac{1}{2},\frac{1}{4})$ of the origin brings a molecule II of the $(x,\bar{y},\bar{z})$ lattice into coincidence with a molecule I of the (x,y,z) lattice. It is thus possible to imagine a twinning process [twinning plane (100)] in which the same molecule plays the role of molecule I or molecule II towards one or the other orientation of the lattice. Of course this implies a certain tolerance since molecules I and II are only related by a pseudosymmetry operation.

How does this hypothesis account for the systematic error which only affects the odd-l reflections? If the twin is considered as made of two crystals, one (A) in the orientation (x,y,z) and the other (B) in the orientation $(x,\bar{y},\bar{z})$, every observed intensity $I(hkl)$ results from two overlapping reflections: hkl from crystal A and $h\bar{k}\bar{l}$ from crystal B; it may be written

$I(hkl) = I_A + I_B$, I_A and I_B being the contributions by crystals A and B to the total intensity. Taking into account the equivalence of the hkl and $h\bar{k}\bar{l}$ reflections in the monoclinic system and noting that the hkl and $h\bar{k}\bar{l}$ reflections have the same Lorentz–polarization factor (since $\beta \simeq 90°$ they have the same Bragg angle), one may write

$$I(hkl) = s \operatorname{Lp} A[V_A|F(hkl)|^2 + V_B|F(h\bar{k}\bar{l})|^2] \qquad (2)$$

where s is a scale factor, Lp the Lorentz–polarization factor, A the absorption factor and V_A and V_B are the volumes of crystals A and B respectively. It can be shown (Appendix I) that, because of the pseudo glide plane, $|F(hkl)| = |F(h\bar{k}\bar{l})|$ when l is even whereas $|F(hkl)| \neq |F(h\bar{k}\bar{l})|$ when l is odd. Thus, for a reflection indexed as hkl with l even, the composite intensity observed for the twin is the same as the intensity diffracted by a single crystal of the same volume $V_A + V_B$ (anomalous dispersion being ignored); in contrast, when l is odd the intensities diffracted by the twin and by a single crystal of the same volume are different. So, the model of the twin explains why it is possible to solve the structure using the l-even reflections only.

Structure refinement with twin data

The iterative method developed by Sudarsanan, Young & Donnay (1973) for estimating the individual contributions by the two crystals in the twin to the observed intensities has been adapted to the present problem. Calculations are summarized in Appendix II. They enable us to estimate the twinning ratio $K = V_B/V_A$ and to perform separate refinements using corrected data sets for crystals A and B. The iterative process was carried out using corrected data for crystal A. Convergence was reached after four cycles and led to a twinning ratio $K = 0.322$. As a check, a refinement was also performed using the final corrected data set for crystal B. The reliability factors are given in Table 2.
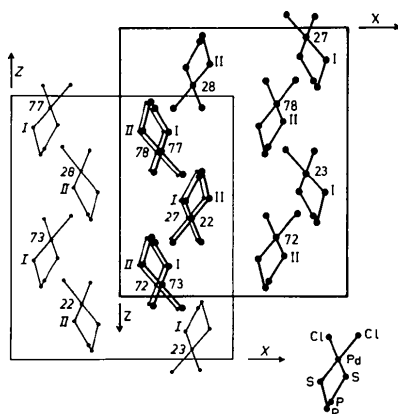

Fig. 1. Sketch of the process proposed to explain the twinning. Heavy atoms only have been drawn. The y coordinates ($\times 100$) of the Pd atoms are indicated. Bold lines and roman characters: (x,y,z) orientation; thin lines and italic characters: $(x,\bar{y},\bar{z})$ orientation with origin translation $(-\frac{1}{2},\frac{1}{2},\frac{1}{4})$.

Table 2. *Results of the refinements*

Number of independent reflections: 5143
Number of reflections utilized [$I > 2\sigma(I)$]: 4370

Determination of the twinning ratio

Twinning ratio $K = 0.322$
Reliability factor $R_I = 0.100$
$R_I = \sum |SI_o(hkl) - I_c(hkl)|/\sum SI_o(hkl)$ (see Appendix II)

Final refinements

Number of refined parameters: 350
Constraints: all N—C bond lengths equal, common length refined;
  in C_2H_5: C—C bond lengths equal, common length refined;
  in C_6H_{11}: C—C bond lengths equal, common length refined.

Reliability factors	Crystal A	Crystal B
$R = \sum \|k\|F_o\| - \|F_c\|\|/\sum k\|F_o\|$	0.058	0.067
$R_w = [\sum w(k\|F_o\| - \|F_c\|)^2/\sum wk^2\|F_o\|^2]^{1/2}$	0.068	0.075
with $w = 1/\sigma^2(F_o)$		

Table 3. *Final atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$), with e.s.d.'s in parentheses, for the non-hydrogen atoms (crystal A of the twin)*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Molecule I

	x	y	z	U or U_{eq}
Pd(1)	-1839 (1)	2713 (1)	385 (1)	41·3 (5)
Cl(11)	-1463 (2)	3608 (2)	-389 (1)	74 (2)
Cl(12)	-2723 (2)	2183 (2)	-462 (1)	59 (2)
S(11)	-984 (2)	3311 (2)	1187 (1)	60 (2)
S(12)	-2124 (2)	1750 (1)	1083 (1)	55 (2)
P(11)	-1371 (2)	3012 (1)	2179 (1)	39 (2)
P(12)	-1478 (2)	1853 (1)	2017 (1)	37 (2)
N(11)	-604 (4)	3194 (4)	2755 (3)	41 (5)
N(12)	-512 (5)	1569 (4)	1990 (4)	55 (6)
C(111)	-2336 (5)	3453 (4)	2478 (5)	44 (3)
C(112)	-3118 (5)	3285 (5)	2027 (5)	56 (3)
C(113)	-3902 (7)	3634 (5)	2339 (7)	86 (4)
C(114)	-3768 (8)	4412 (5)	2387 (8)	110 (5)
C(115)	-2969 (6)	4593 (7)	2809 (7)	90 (4)
C(116)	-2192 (6)	4231 (4)	2498 (6)	66 (3)
C(117)	306 (5)	3285 (4)	2531 (6)	56 (3)
C(118)	530 (8)	4012 (5)	2413 (7)	75 (4)
C(119)	-746 (8)	3108 (5)	3552 (4)	71 (4)
C(110)	-819 (11)	3752 (6)	3963 (8)	121 (5)
C(121)	-2046 (5)	1357 (3)	2712 (5)	38 (3)
C(122)	-2935 (5)	1626 (4)	2870 (5)	45 (3)
C(123)	-3372 (7)	1158 (4)	3415 (5)	57 (3)
C(124)	-3376 (5)	394 (4)	3223 (5)	49 (3)
C(125)	-2475 (5)	149 (5)	3072 (5)	51 (3)
C(126)	-2051 (6)	597 (3)	2502 (4)	45 (3)
C(127)	16 (7)	1525 (5)	2664 (5)	62 (3)
C(128)	293 (12)	826 (6)	2857 (10)	140 (6)
C(129)	11 (8)	1577 (6)	1313 (5)	86 (4)
C(120)	224 (13)	886 (7)	1042 (10)	154 (7)

Molecule II

	x	y	z	U or U_{eq}
Pd(2)	3150 (1)	2773 (1)	2190 (1)	41·7 (5)
Cl(21)	3577 (2)	3653 (2)	2972 (1)	79 (2)
Cl(22)	2305 (2)	2224 (2)	3055 (1)	60 (2)
S(21)	3934 (2)	3399 (1)	1367 (1)	50 (2)
S(22)	2842 (2)	1822 (1)	1490 (1)	55 (2)
P(21)	3602 (2)	3063 (1)	372 (1)	35 (2)
P(22)	3516 (2)	1908 (1)	567 (1)	36 (2)
N(21)	4386 (4)	3257 (4)	-183 (3)	34 (5)
N(22)	4496 (5)	1646 (4)	628 (3)	53 (6)
C(211)	2626 (5)	3466 (4)	13 (5)	41 (3)
C(212)	1831 (5)	3298 (5)	446 (5)	60 (3)
C(213)	1063 (6)	3608 (5)	65 (6)	76 (4)
C(214)	1164 (7)	4384 (5)	-29 (7)	82 (4)
C(215)	1986 (6)	4565 (6)	-415 (6)	75 (4)
C(216)	2747 (6)	4245 (4)	-33 (6)	55 (3)
C(217)	5280 (5)	3380 (4)	74 (5)	43 (3)
C(218)	5494 (7)	4113 (4)	161 (6)	62 (3)
C(219)	4286 (7)	3141 (5)	-980 (4)	62 (3)
C(210)	4147 (11)	3759 (6)	-1420 (8)	115 (5)
C(221)	2994 (5)	1355 (4)	-105 (5)	39 (3)
C(222)	2102 (5)	1584 (5)	-312 (5)	51 (3)
C(223)	1702 (8)	1071 (4)	-834 (5)	72 (4)
C(224)	1739 (6)	319 (5)	-600 (6)	67 (3)
C(225)	2644 (6)	118 (5)	-404 (6)	72 (4)
C(226)	3019 (7)	609 (3)	153 (5)	52 (3)
C(227)	5033 (7)	1617 (5)	-40 (5)	57 (3)
C(228)	5318 (9)	929 (5)	-268 (8)	100 (5)
C(229)	4988 (8)	1604 (6)	1322 (5)	78 (4)
C(220)	5057 (11)	891 (6)	1581 (9)	127 (6)

After such a treatment the variance of the quantity $(|F_o| - |F_c|)^2$ is no longer dependent upon the parity of the l index (Table 1). This together with the success of the refinements make up an *a posteriori* proof of the twinning hypothesis. It must be noted that, although in the above discussion the twin has been considered as composed of two crystals A and B, the specimen may as well be a 'polysynthetic twin' constituted of microcrystals piling up arbitrarily with the orientations A and B (Müller, 1971).

Final atomic parameters for the non-hydrogen atoms of crystal A are listed in Table 3; those obtained for crystal B do not differ by more than 2σ.* Selected bond lengths and bond angles are given in Table 4. The numbering scheme of the atoms is displayed in Fig. 2 together with a stereoscopic view of one of the two independent molecules.

All calculations were performed at the Centre Interuniversitaire de Calcul de Toulouse on a CII IRIS 80 computer. The main programs used were: *CAD4CICT* 10, a local program for data reduction by J. Aussoleil and J.-P. Legros (unpublished); *MULTAN* 78 by Main, Hull, Lessinger, Germain, Declercq &

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* Lists of structure factors (for crystals A and B), anisotropic thermal parameters and positional parameters of H atoms (for crystal A) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38302 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses (crystal A of the twin)*

Common lengths		
N–C		1·493 (4)
C–C in –N(C$_2$H$_5$)$_2$		1·455 (5)
C–C in –C$_6$H$_{11}$		1·511 (2)

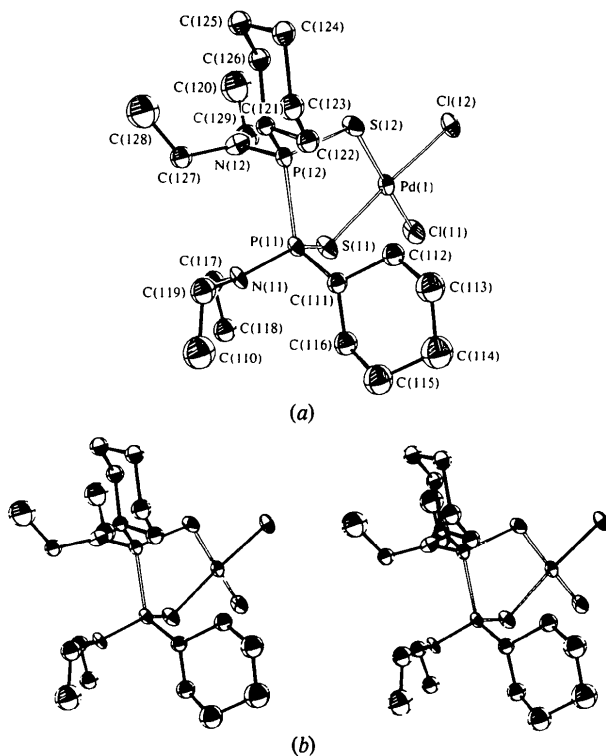| Molecule I		Molecule II	
Pd(1)–Cl(11)	2·310 (3)	Pd(2)–Cl(21)	2·318 (3)
Pd(1)–Cl(12)	2·318 (3)	Pd(2)–Cl(22)	2·324 (3)
Pd(1)–S(11)	2·298 (3)	Pd(2)–S(21)	2·291 (3)
Pd(1)–S(12)	2·295 (3)	Pd(2)–S(22)	2·286 (3)
P(11)–S(11)	2·010 (3)	P(21)–S(21)	2·011 (3)
P(12)–S(12)	2·005 (3)	P(22)–S(22)	2·008 (3)
P(11)–P(12)	2·252 (4)	P(21)–P(22)	2·251 (4)
P(11)–N(11)	1·638 (7)	P(21)–N(21)	1·640 (7)
P(12)–N(12)	1·606 (8)	P(22)–N(22)	1·616 (8)
P(11)–C(111)	1·816 (9)	P(21)–C(211)	1·833 (9)
P(12)–C(121)	1·826 (9)	P(22)–C(221)	1·823 (9)
Cl(11)–Pd(1)–Cl(12)	93·6 (1)	Cl(21)–Pd(2)–Cl(22)	93·9 (1)
Cl(11)–Pd(1)–S(11)	82·9 (1)	Cl(21)–Pd(2)–S(21)	82·8 (1)
Cl(12)–Pd(1)–S(12)	84·7 (1)	Cl(22)–Pd(2)–S(22)	84·5 (1)
Cl(12)–Pd(1)–S(11)	176·0 (1)	Cl(22)–Pd(2)–S(21)	175·3 (1)
Cl(11)–Pd(1)–S(12)	174·1 (1)	Cl(21)–Pd(2)–S(22)	173·2 (1)
S(11)–Pd(1)–S(12)	99·0 (1)	S(21)–Pd(2)–S(22)	99·1 (1)
Pd(1)–S(11)–P(11)	105·5 (1)	Pd(2)–S(21)–P(21)	107·3 (1)
Pd(1)–S(12)–P(12)	107·7 (1)	Pd(2)–S(22)–P(22)	107·5 (1)
S(11)–P(11)–P(12)	100·6 (1)	S(21)–P(21)–P(22)	100·7 (1)
S(12)–P(12)–P(11)	104·4 (1)	S(22)–P(22)–P(21)	104·4 (1)
S(11)–P(11)–N(11)	108·0 (3)	S(21)–P(21)–N(21)	107·7 (2)
S(12)–P(12)–N(12)	114·4 (3)	S(22)–P(22)–N(22)	114·4 (3)
S(11)–P(11)–C(111)	113·1 (3)	S(21)–P(21)–C(211)	114·0 (3)
S(12)–P(12)–C(121)	107·8 (3)	S(22)–P(22)–C(221)	107·0 (3)
N(11)–P(11)–P(12)	110·6 (3)	N(21)–P(21)–P(22)	111·7 (3)
N(12)–P(12)–P(11)	105·6 (3)	N(22)–P(22)–P(21)	105·1 (3)
C(111)–P(11)–P(12)	116·1 (3)	C(211)–P(21)–P(22)	115·1 (3)
C(121)–P(12)–P(11)	117·3 (2)	C(221)–P(22)–P(21)	119·5 (2)
N(11)–P(11)–C(111)	108·1 (4)	N(21)–P(21)–C(211)	107·5 (3̄)
N(12)–P(12)–C(121)	107·6 (4)	N(22)–P(22)–C(221)	106·8 (4)
P(11)–N(11)–C(117)	122·9 (6)	P(21)–N(21)–C(217)	122·5 (5)
P(11)–N(11)–C(119)	120·3 (6)	P(21)–N(21)–C(219)	120·1 (6)
P(12)–N(12)–C(127)	120·9 (6)	P(22)–N(22)–C(227)	119·2 (6)
P(12)–N(12)–C(129)	122·6 (7)	P(22)–N(22)–C(229)	124·4 (7)
C(117)–N(11)–C(119)	115·3 (7)	C(217)–N(21)–C(219)	115·6 (7)
C(127)–N(12)–C(129)	113·1 (9)	C(227)–N(22)–C(229)	114·5 (8)

Fig. 2. (a) Perspective and (b) stereoscopic drawings of molecule I. H atoms are omitted, and ellipsoids are scaled to enclose 25% probability. The numbering scheme refers to molecule I; for molecule II the first digit of each number is 2.

Fig. 3. Apparent bond-length shortening resulting from a large deformation vibration (after Willis & Pryor, 1975).

Woolfson (1978) for direct methods; *AGNOST* for absorption corrections according to the method described by Coppens, Leiserowitz & Rabinovich (1965); *SHELX* 76 by Sheldrick (1976) for least-squares refinement, Fourier synthesis and bond-length and -angle calculations; *ORTEP* by Johnson (1965) for illustrations. The least-squares-refinement program minimizes the function $\sum w(k|F_o| - |F_c|)^2$. In the first steps of refinement all reflections were given unit weight, the weighting scheme $w = 1/\sigma^2(F_o)$ being applied in the final stages. Scattering factors were calculated analytically using the coefficients listed in *International Tables for X-ray Crystallography* (1974). A correction for anomalous dispersion was applied.

Discussion

The common length of the ethyl C—C bonds resulting from the constrained refinement is 1·455 (6) Å. This rather low value reveals some peculiar phenomenon not accounted for by the model. A qualitative explanation can be proposed on the basis of the large isotropic thermal factors of the terminal C atoms. The thermal motion of these atoms undoubtedly involves a large N—C—C deformation vibration causing the electronic density to be spread over a bean-like volume (Fig. 3).
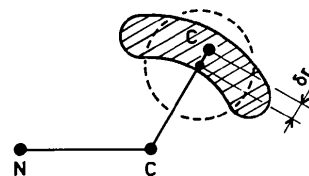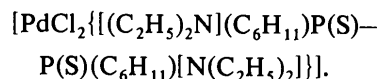
Fitting such a volume to a sphere (or an ellipsoid) results in an apparent shortening of the bond length (Willis & Pryor, 1975). No attempt was made to correct the model for this artefact since the essential features of the molecular geometry are still well defined.

The structure is built up of monomeric complex molecules

$$[PdCl_2\{[(C_2H_5)_2N](C_6H_{11})P(S)-$$
$$P(S)(C_6H_{11})[N(C_2H_5)_2]\}].$$

This should be pointed out since the Pd^{II} complexes with thioxo ligands are often di- or trimeric (McPartlin & Stephenson, 1969; King, McQuillan & Milne, 1973). In addition, the complexes of the tetramethyldithioxo-di-λ^5-phosphane $(CH_3)_2P(S)-P(S)(CH_3)_2$ with CuCl and $CuCl_2$ are respectively dimeric and polymeric (Cotton *et al.*, 1974).

The Pd atoms are chelated through the S atoms, thus forming a five-membered ring. The metal atoms are in a slightly tetrahedrally distorted square-planar environment (Table 5). The Pd—S and Pd—Cl bond lengths [mean values 2·293 (3) and 2·317 (3) Å respectively] can be compared to those recently reported by Aurivillius & Bertinsson (1981) in $[Pd_2(C_{31}H_{34}P_2S_2)-Cl_4]$: Pd—S $= 2·273$ (2) Å and Pd—Cl $= 2·310$ (3) Å when Cl is *trans* to S. The bond angles around the Pd atoms range from 82·8 (1) to 99·1 (1)°, the S—Pd—S angles being the larger. The mean value 107·0 (1)° of the Pd—S—P bond angles is consistent with an sp^3 hybridization of the S atoms.

The P atoms are largely out of and on opposite sides of the mean planes defined by the Pd, S, S, Cl, Cl atoms (Table 5). Thus the ligand is in the *gauche* conformation with SPPS torsion angles of 47·2 (1) and 46·3 (1)° for molecules I and II respectively. This geometry is quite similar to that of the tetramethyl derivative in its dimeric cuprous complex $[\{CuCl-[(CH_3)_2P(S)-P(S)(CH_3)_2]\}_2]$: SPPS torsion angle 45°. These results disagree with the hypothesis, made by some authors on the basis of IR and Raman studies, that the $R_2P(S)-P(S)R_2$ molecule would adopt the *cis* conformation when chelating a metal atom (Meek & Nicpon, 1965; Beg & Khawaja, 1968). It should be noted that the *cis* conformation of L_{II} in $L_{II}PdCl_2$ should not be hindered by any geometric strain. Indeed, the S···S distance in the complex is 3·5 Å; for the

Table 5. *Mean least-squares planes* S_2PdCl_2 *and* SPPS *torsion angles*

Molecule I	Molecule II
Atoms defining the plane	Atoms defining the plane
Pd(1), Cl(11), Cl(12), S(11), S(12)	Pd(2), Cl(21), Cl(22), S(21), S(22)
Equation of the plane	Equation of the plane
$0.7939X - 0.4908Y - 0.3590Z$	$0.8191X - 0.4865Y + 0.3041Z$
$+ 5.0656 = 0$	$-2.6859 = 0$

Distances to the plane (Å)		Distances to the plane (Å)	
Pd(1)	−0.029 (2)	Pd(2)	−0.022 (2)
Cl(11)	0.108 (3)	Cl(21)	0.140 (3)
Cl(12)	−0.065 (3)	Cl(22)	−0.107 (3)
S(11)	−0.063 (3)	S(21)	−0.063 (3)
S(12)	0.063 (3)	S(22)	0.082 (3)
P(11)	−0.918 (3)	P(21)	−0.729 (3)
P(12)	0.148 (3)	P(22)	0.348 (3)

Torsion angle	Torsion angle
S(11)P(11)P(12)S(12): 47·2 (1)°	S(21)P(21)P(22)S(22): 46·3 (1)°

ligand in the *cis* conformation this distance would remain unchanged provided the S—P—P angle was close to 109°. Yet, this angle is equal to 109·4° in the free ligand but has a mean value of 102·5° in the complex. This clearly indicates the strong tendency of the ligand to adopt the *gauche* conformation notwithstanding the resulting angular strains.

The decrease of the S—P—P bond angles is attended by an increase of the C—P—P bond angles (from 104·9° in the free ligand to 117·0° in the complex). Other angles around the P atoms are almost unchanged by the complexation. Chelation through the S atoms results in a lengthening of the P—S bond from 1·954 (1) Å in the free ligand to 2·008 (3) Å in the complex. For comparison, the P—S bond lengths range between 1·967 (7) and 2·026 (1) Å in the cuprous complexes of $(CH_3)_3P(S)$ (Eller & Corfield, 1971; Tiethof, Stalick & Meek, 1973) and between 1·973 (2) and 1·995 (2) Å in the dimeric cuprous complex of $(CH_3)_2P(S)-P(S)(CH_3)_2$ (Cotton *et al.*, 1974).

The P—P bond length is not modified by the complexation, nor is the geometry of the substituents on the P atoms: the C_6H_{11} rings remain in the chair conformation and the N atoms are still in a planar environment.

APPENDIX I

For the space group $P2_1/c$, the structure factors are calculated from the following equations (*International Tables for X-ray Crystallography*, 1969):

$$A = 4 \cos 2\pi(hx + lz) \cos 2\pi ky \quad \text{when } k + l = 2n \quad (3a)$$

$$A = -4 \sin 2\pi(hx + lz) \sin 2\pi ky$$

$$\text{when } k + l = 2n + 1 \quad (3b)$$

and

$$F(hkl) = \sum_r f_r A_r. \quad (4)$$

f_r: scattering factor, corrected for thermal vibration, of the *r*th atom; A_r: A calculated from the coordinates of the *r*th atom. The summation is taken over the $2N$ atoms in the asymmetric unit and the anomalous-dispersion terms are ignored.

Since the asymmetric unit is constituted of two molecules, I and II, related by a non-crystallographic glide plane [equations (1)], it is worthwhile to make them apparent in equation (4):

$$F(hkl) = \sum_r f_r(A_{Ir} + A_{IIr}). \quad (4')$$

A_{Ir}, A_{IIr}: A calculated from the coordinates of the *r*th atom of molecule I and of the related atom of molecule II respectively. The summation is taken over the N atoms of the individual molecule.

Let us consider first equation (3a). One may write for an *hkl* reflection:

$$A(hkl) = A_I + A_{II}$$
$$= 4 \cos 2\pi(hx_I + lz_I) \cos 2\pi ky_I$$
$$+ 4 \cos 2\pi(hx_{II} + lz_{II}) \cos 2\pi ky_{II}.$$

Replacing x_{II}, y_{II}, z_{II} by their values as functions of x_I, y_I, z_I [equations (1)], one obtains:

$$A(hkl) = 4 \cos 2\pi ky_I \{\cos 2\pi(hx_I + lz_I)$$
$$+ \cos 2\pi[hx_I - lz_I + \tfrac{1}{4}(2h + l)]\}.$$

For the sake of brevity let us set

$$C = 4 \cos 2\pi ky_I, \quad U = hx_I + lz_I$$
$$\text{and} \quad V = hx_I - lz_I.$$

(i) *If* $l = 2n$

For the *hkl* reflections, one obtains:

$$A(hkl) = C\{\cos 2\pi U + \cos 2\pi[V + \tfrac{1}{2}(h + n)]\}$$

and for the *hkl̄* reflections

$$A(hk\bar{l}) = C\{\cos 2\pi V + \cos 2\pi[U + \tfrac{1}{2}(h - n)]\}.$$

Since $h + n$ and $h - n$ are integers of the same parity

$$|A(hkl)| = |A(hk\bar{l})| \quad \text{and} \quad |F(hkl)| = |F(hk\bar{l})|.$$

(ii) *If* $l = 2n + 1$

$$A(hkl) = C(\cos 2\pi U + \cos 2\pi\{V + \tfrac{1}{4}[2(h + n) + 1]\})$$
$$= C(\cos 2\pi U \pm \sin 2\pi V)$$

$$A(hk\bar{l}) = C(\cos 2\pi V + \cos 2\pi\{U + \tfrac{1}{4}[2(h - n) - 1]\})$$
$$= C(\cos 2\pi V \pm \sin 2\pi U)$$

Thus $|A(hkl)| \neq |A(hk\bar{l})|$ and $|F(hkl)| \neq |F(hk\bar{l})|$.

Starting from equation (3b), the same calculation holds and leads to the same results.

APPENDIX II

Equation (2) may be re-written in a more convenient form by setting $K = V_B/V_A$ (the twinning ratio) and $S = 1/sV_A$; one obtains

$$\frac{S}{Lp\,A} I(hkl) = SI_o(hkl) = |F(hkl)|^2 + K|F(hk\bar{l})|^2 \quad (5)$$

where $I_o(hkl)$ is the observed intensity corrected by Lorentz–polarization and absorption factors. The calculation comprises four steps.

(1) The atomic parameters resulting from the last conventional refinement are used to compute the structure-factor moduli

$$|F_c(hkl)| \quad \text{and} \quad |F_c(hk\bar{l})|.$$

(2) A least-squares calculation of the scale factor S and of the twinning ratio K is performed by minimization of the function

$$\sum [SI_o(hkl) - I_c(hkl)]^2$$

where $I_c(hkl) = |F_c(hkl)|^2 + K|F_c(hk\bar{l})|^2$, the summation being carried out over all measured reflections. An agreement factor R_1 is computed:

$$R_1 = \sum |SI_o(hkl) - I_c(hkl)|/\sum SI_o(hkl).$$

(3) The individual contributions of the two crystals in the twin to the composite observed intensities are calculated through the following equations:

$$SI_o(hkl) = |F_{oA}(hkl)|^2 + K|F_{oB}(hk\bar{l})|^2$$

$$|F_{oA}(hkl)|^2 = SI_o(hkl)\frac{|F_c(hkl)|^2}{|F_c(hkl)|^2 + K|F_c(hk\bar{l})|^2}.$$

$F_{oA}(hkl)$ and $F_{oB}(hk\bar{l})$ are the corrected 'observed' structure factors of the hkl and $hk\bar{l}$ reflections for crystal A and crystal B respectively. They approximate $F(hkl)$ and $F(hk\bar{l})$ in equation (5). Standard deviations are estimated according to

$$\frac{\sigma_A(hkl)}{\sigma_B(hk\bar{l})} = \frac{|F_{oA}(hkl)|^2}{|F_{oB}(hk\bar{l})|^2}$$

$$\sigma_A(hkl) + K\sigma_B(hk\bar{l}) = S\sigma_o(hkl).$$

$\sigma_A(hkl)$ and $\sigma_B(hk\bar{l})$ are the standard deviations assigned to $|F_{oA}(hkl)|^2$ and $|F_{oB}(hk\bar{l})|^2$ respectively and $\sigma_o(hkl)$ is the standard deviation assigned to the observed composite intensity $I_o(hkl)$.

(4) Positional and thermal parameters of the structural model are refined in the usual way using one or the other of the corrected data sets F_{oA} and F_{oB}.

The refined model can then be used as a starting model in step (1) and the procedure is repeated until convergence.

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