# Palladium(II) Complexes of the Macrocycle 3,3,7,7,11,11,15,15-Octamethyl-1,9-dithia-5,13-diazacyclohexadecane. Crystal Structure Analysis of 3,3,7,7,11,11,15,15-Octamethyl-1,9-dithia-5,13-diazacyclohexadecanepalladium(II) Bis(hexafluorophosphate)

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The preparation of 1 : 1 complexes, (1a) and (1b), of palladium(II) chloride with the macrocycle 3,3,7,7,11,11,15,-15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane (L) and with its 2,2,16,16-tetradeuterio (L') analogue is reported. These behave as 1 : 1 electrolytes in acetonitrile. Proton n.m.r. spectra of solutions of the complexes in acetonitrile or chloroform are consistent with the presence of two major stereoisomers, the proportions of which depend on the amount of water present in the solution. It is suggested that both isomers have trigonal bipyramidal structures with the nitrogen atoms occupying axial positions and differ only in the stereochemistries at nitrogen. The spectral properties of (1a) in aqueous solution are very similar to those of the derived $PdL(PF_6)_2$ (2) and are consistent with the presence of two isomeric square planar dications. In contrast, an X-ray structural investigation of crystalline (2) shows the presence of only one isomer. Crystals of (2) are Monoclinic, $a = 9.529(2)$, $b = 10.750(2)$, $c = 14.996(3)$ Å, $\beta = 93.28(2)°$, $Z = 2$, space group $P2_1/n$. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares methods to $R = 0.042$ and $R' = 0.050$ for 2 017 reflections with $I > 3\sigma(I)$. The Pd atom lies on an inversion centre and has distorted square-planar co-ordination with Pd–S 2.307(1), Pd–N 2.090(4) Å, S–Pd–N 95.6(1)° and the PdS_2N_2 moiety necessarily planar. Both six-membered chelate rings adopt chair conformations, one of them being severely flattened. The PF_6^- anions are linked to the cation via N–H $\cdots$ F hydrogen bonds (N $\cdots$ F 3.064 Å) and the orientation adopted leads to fluorine atoms lying above and below the co-ordination plane with Pd $\cdots$ F 3.259 Å.

In connection with our studies of the properties of potentially chelating ligands containing quaternary carbon atoms in their backbones, we recently reported [1] the preparation of the macrocycle 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane (L) and of a derived palladium complex, $PdLCl_2 \cdot H_2O$ (1a). The present paper deals with the structure and behaviour of compound (1a) and of its corresponding bis(hexafluorophosphate) analogue, $PdL(PF_6)_2$ (2).
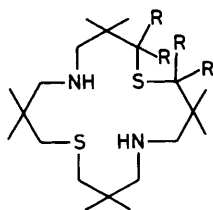
L; R = H
L'; R = D

(1a) $PdLCl_2 \cdot H_2O$
(1b) $PdL'Cl_2 \cdot H_2O$
(2) $PdL(PF_6)_2$

There have been relatively few studies [2] of complexes of metals with S_2N_2 macrocycles and the literature [3,4] on the chemistry of macrocyclic derivatives of palladium is not extensive. The complex most closely related to those dealt with here is 1-oxa-7,10-dithia-4,13-diazacyclo-pentadecanepalladium(II) nitrate, for which an X-ray crystallographic study [3] shows that the ligand adopts a square pyramidal geometry around palladium with nitrogen and sulphur atoms in the plane and the oxygen atom apical.

RESULTS

The complex $PdLCl_2 \cdot H_2O$ (1a) was prepared by reacting L with a solution of palladium(II) chloride in acetonitrile. Purification of the solid remaining on evaporation of the solvent was effected by preparative thin-layer chromatography (t.l.c.) followed by crystallisation. Upon drying *in vacuo*, the highly crystalline material obtained on using ethanol–acetone as a solvent crumbled to a pale yellow powder which analysed for $PdLCl_2 \cdot H_2O$. This product is quite soluble both in chloroform and in water. Its ^1H n.m.r. spectrum in $CDCl_3$ (Table 1) at ambient temperature suggests the presence of two major species, the relative proportions of which depend on the water content of the solvent. At -20 °C the spectrum is little changed, while at -50 °C, broadening of most of the peaks is observed. When as much water as possible is removed by azeotroping with chloroform, the ^1H n.m.r. spectrum (see Figure 1) shows the presence of one major component (X) which has two distinct NH protons and four distinct kinds of SCH, NCH, and CH_3
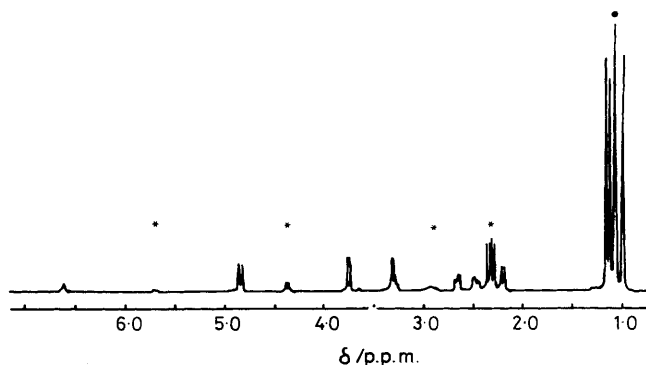

FIGURE 1 Proton n.m.r. spectrum at 400 MHz of (1a) in $CDCl_3$ after distillation of solvent to remove water. The intensities of peaks marked with an asterisk increase as the water content is raised

protons. Particularly striking are the large chemical shift differences between the NH protons (*ca.* 2.7 p.p.m.) and between the geminal SCH_2 pairs (*ca.* 2.5 and 1.5 p.p.m.). The SCH_2 pairs were distinguished from the NCH_2 pairs both by the observation that the latter are coupled to the NH protons and by comparison of this spectrum with that

spectrum of a 1 : 1 mixture of (1a) and (2) in acetonitrile is virtually superposable on that of (1a) alone, in this solvent. The ^1H n.m.r. spectrum of such a mixture in CD_3CN shows a similar peak pattern (Table 1) to that of (1a) in the same solvent although certain resonances are shifted markedly upfield in the mixture, namely, the lower field NH proton in

TABLE 1

Hydrogen-1 n.m.r. data (δ/p.p.m.) for complexes (1a) and (2) at ambient temperature

Compound	Solvent	CMe	NCH	SCH [a]	NH
(1a) $\{\begin{smallmatrix}X\\Y\end{smallmatrix}$	$CDCl_3$	$\{\begin{smallmatrix}1.13, 1.20, 1.26, 1.30\\1.20, 1.21\end{smallmatrix}$	$\{\begin{smallmatrix}2.34,^b 2.61,^c 2.83,^c 3.50^b\\ca. 2.5,^d 3.05\end{smallmatrix}$	$\{\begin{smallmatrix}2.46, 2.49, 3.91, 4.94\\2.44, 4.49\end{smallmatrix}$	$\{\begin{smallmatrix}3.50, 6.69\\6.09\end{smallmatrix}$
(1a) $\{\begin{smallmatrix}X\\Y\end{smallmatrix}$	CD_2CN	$\{\begin{smallmatrix}1.06, 1.12, 1.15, 1.23\\1.13, 1.15\end{smallmatrix}$	$\{\begin{smallmatrix}2.43, 2.46, 2.78, 3.26\\2.45, 2.98\end{smallmatrix}$	$\{\begin{smallmatrix}2.58, 2.64, 3.72, 4.75\\2.58, 4.26\end{smallmatrix}$	$\{\begin{smallmatrix}3.70, 6.38\\5.94\end{smallmatrix}$
(1a) + (2)^e $\{\begin{smallmatrix}X\\Y\end{smallmatrix}$	CD_3CN	$\{\begin{smallmatrix}1.07, 1.10, 1.16, 1.23\\1.10, 1.15\end{smallmatrix}$	$\{\begin{smallmatrix}2.41, 2.49, 2.86, 3.18\\2.45, 2.95\end{smallmatrix}$	$\{\begin{smallmatrix}2.65, 2.68, 3.70, 4.64\\2.69, 3.95\end{smallmatrix}$	$\{\begin{smallmatrix}3.50, 5.13\\4.83\end{smallmatrix}$
(1a) ^{f}	D_2O	0.98, 1.07	2.39,^{c} 2.77 ^{c}	2.80, 3.31	—
(2) ^{f}	$(CD_3)_2CO$	1.17, 1.25	2.66,^{c} 3.04	3.10, 3.43	—

^{a} J = 12 Hz.　^{b} J = 12.5 Hz.　^{c} J = 13.5 Hz.　^{d} Obscured.　^{e} 1 : 1.　^{f} Predominant isomer only.

of complex (1b) prepared from L', the 2,2,16,16-tetradeuterio analogue of L. The second major species (Y) builds up when the solution is exposed to moist air. Its ^1H n.m.r. spectrum (Table 1) contains resonances attributable to only one type of NH proton and two types of SCH, NCH, and CH_3 protons. The ^1H n.m.r. spectra suggest that the same two

FIGURE 2 Electronic spectra at concentrations of *ca.* 0.1 mg cm^{-3} for (1a) in acetonitrile (· · · ·), (1a) in water (——), and (2) in acetonitrile (– – – –)

species, X and Y, are present when the complex is dissolved in acetonitrile. Conductivity measurements in this solvent give values (see Experimental section) at the lower end of the range expected [5] for a mono-monovalent electrolyte.

A third type of ^1H n.m.r. spectrum (Table 1) is obtained for solutions of complex (1a) in D_2O. In this case the spectrum shows the same number of resonances as was found for species Y in chloroform but now the shift positions for the SCH and NCH protons are close to those expected [6] for planar palladium(II) complexes. This spectrum also contained several weaker, broadened resonances presumably ascribable to the presence of configurational isomers of (1a). A similar spectrum (Table 1) was found for a deuterioacetone solution of $PdL(PF_6)_2$ (2) [prepared by mixing aqueous solutions of (1a) and ammonium hexafluorophosphate]. The electronic spectra of (1a) in water and of (2) in acetonitrile are also very similar but differ significantly from that of (1a) in acetonitrile (see Figure 2). However, the

X (1.25 p.p.m.) and the NH (1.11) and lower field SCH (0.31) protons in Y.

Attempts to obtain crystals of (1a) suitable for X-ray analysis have, to date, not been successful. We have however been able to prepare compound (2) in crystalline form and have determined its structure by X-ray crystallography. The final fractional co-ordinates for non-hydrogen atoms (with estimated standard deviations in parentheses) are given in Table 2 and the molecular dimensions in Table 3. Views of the molecule with our numbering scheme and a crystal packing diagram are shown in Figures 3 and 4 respectively.

DISCUSSION

Structure of Compound (1) *in Non-aqueous Solution.*— The conductivity measurements for (1a) in acetonitrile suggest that it is either five-co-ordinate, or four-co-ordin-
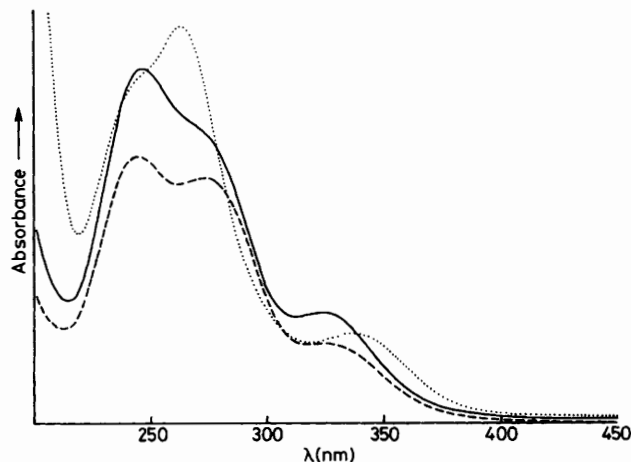
TABLE 2

Final fractional co-ordinates ($\times 10^4$) for $PdL(PF_6)_2$ (2) with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Pd	0	0	0
S	436(1)	−29(1)	1 529(1)
P	3 068(2)	3 012(1)	233(1)
F(1)	3 402(6)	1 676(4)	640(3)
F(2)	2 715(6)	4 316(4)	−184(3)
F(3)	1 920(6)	2 424(5)	−399(4)
F(4)	4 219(8)	3 568(5)	884(4)
F(5)	4 126(7)	2 798(8)	−448(5)
F(6)	2 058(8)	3 234(7)	965(5)
N	−2 020(4)	749(4)	30(2)
C(1)	−1 196(6)	34(4)	2 095(4)
C(2)	−2 224(5)	997(4)	1 748(3)
C(3)	−2 856(5)	607(5)	827(3)
C(4)	−1 624(6)	2 282(5)	1 784(4)
C(5)	−3 474(6)	921(6)	2 353(4)
C(6)	2 071(7)	−2 039(6)	345(3)
C(7)	2 218(5)	−2 086(5)	1 368(3)
C(8)	870(5)	−1 634(5)	1 780(3)
C(9)	2 411(8)	−3 463(6)	1 626(5)
C(10)	3 495(6)	−1 348(7)	1 728(4)

ate with the ligand acting in a terdentate fashion, in this medium. The electronic spectra are consistent with this conclusion. Thus the bathochromic shift in the lowest energy band on going from compound (2) to both the
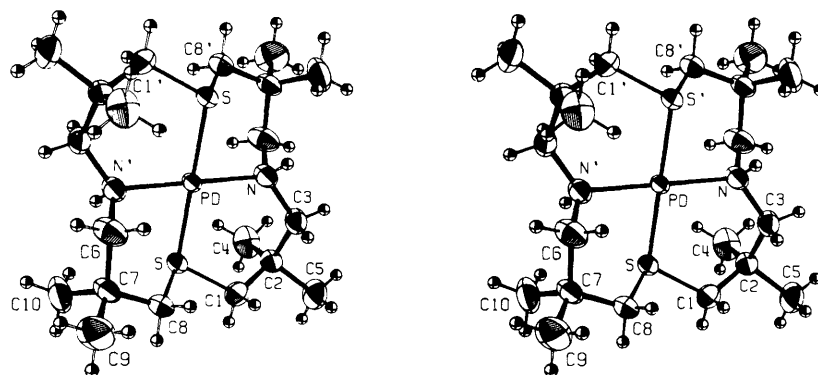
FIGURE 3 Stereoview of a molecule of (2) with the crystallographic numbering scheme

monochloro-analogue and the dichloride (1a) could result from chloride entering the co-ordination sphere to give either a five-co-ordinate species [7] or a four-co-ordinate one by displacing a ligand atom. The five-co-ordinate case, which we favour, is discussed first. Although this type of co-ordination is well established [8] for palladium, it is normally found only when good π-accepting ligands are present. However, such co-ordination may be favoured in the present instance since the bonds from Pd to the macrocycle L may be relatively weak due to steric constraints imposed by the skeleton.

In discussing the stereochemistry of complexes of L, in which the ligand acts as a tetradentate ligand, five possible configurations have to be considered. These are summarised in Figure 5, the positive and negative signs denoting the relative orientations of the NH protons and the sulphur lone pairs with respect to the ring plane. The observation that the [1]H n.m.r. spectrum of (1a) in $CDCl_3$ is not significantly broadened at -20 °C probably indicates [6] that inversion at sulphur is not occurring rapidly on the n.m.r. time-scale even at ambient temperature. The broadening observed at -50 °C probably results from a slowing of conformational averaging of the chelate rings. For the five-co-ordinate complex two idealised geometries are possible, a square pyramid or a trigonal bipyramid, in each of which the chloride could occupy either an equatorial or an axial site. In addition,

in the trigonal bipyramid where the chlorine is equatorial, the axial sites may be occupied either by two nitrogens or by two sulphurs. The [1]H n.m.r. spectral investigations permit a decision as to the stereochemistry of the species present in solutions of compound (1a) in non-aqueous solvents.

The [1]H n.m.r. patterns for X and Y (see Table 1) appear too simple to arise from either trigonal bipyramidal (halogen is axial) or square pyramidal structures (halogen in the basal plane). In any case, a study of models shows that severe non-bonded interactions, involving the chelate rings formed by the macrocycle, are present in such structures. Of the remaining gross structural possibilities, trigonal bipyramidal with an equatorial chloride offers a ready explanation for the observation that the separations of the geminal SCH_2 pairs in both X and Y are much more pronounced than those of the NCH_2 pairs. In constructing molecular models of such trigonal bipyramidal species, it becomes obvious that one must consider not only the configurations at the four macrocyclic heteroatoms and whether N or S occupies the axial sites but also, in some cases, whether the NH protons and sulphur lone pairs are cis or trans to the Pd–Cl bond. A systematic study of the many possibilities enabled us to eliminate all but two for each of X and Y, either on the grounds of unfavourable steric interactions, or symmetry requirements incon-
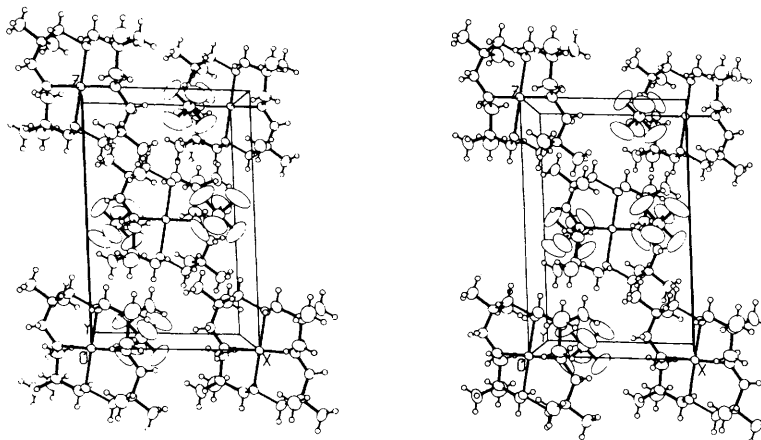

FIGURE 4 Stereoview of the crystal structure of (2)

TABLE 3

Interatomic distances (Å) and angles (°) for PdL(PF$_6$)$_2$ (2) with estimated standard deviations in parentheses

(a) Bond distances

Pd–S	2.307(1)
Pd–N	2.090(4)
S–C(1)	1.816(5)
S–C(8)	1.809(5)
N–C(3)	1.481(6)
N–C(6^I)	1.496(7)
C(1)–C(2)	1.498(7)
C(2)–C(3)	1.534(6)
C(2)–C(4)	1.496(7)
C(2)–C(5)	1.540(6)
C(6)–C(7)	1.534(7)
C(7)–C(8)	1.536(7)
C(7)–C(9)	1.538(8)
C(7)–C(10)	1.526(7)
P–F(1)	1.585(4)
P–F(2)	1.564(5)
P–F(3)	1.542(4)
P–F(4)	1.545(5)
P–F(5)	1.494(5)
P–F(6)	1.519(5)

(b) Angles

S–Pd–N	95.6(1)	F(1)–P–F(2)	178.7(3)
Pd–S–C(1)	110.8(2)	F(1)–P–F(3)	89.1(3)
Pd–S–C(8)	104.2(2)	F(2)–P–F(3)	89.6(3)
C(1)–S–C(8)	97.5(3)	F(1)–P–F(4)	89.4(3)
Pd–N–C(3)	121.1(3)	F(2)–P–F(4)	91.9(3)
Pd–N–C(6^I)	111.1(3)	F(3)–P–F(4)	178.4(3)
C(3)–N–C(6^I)	113.1(4)	F(1)–P–F(5)	89.7(4)
S–C(1)–C(2)	115.0(3)	F(2)–P–F(5)	90.1(4)
C(1)–C(2)–C(3)	109.9(4)	F(3)–P–F(5)	89.9(4)
C(1)–C(2)–C(4)	112.6(4)	F(4)–P–F(5)	90.5(5)
C(1)–C(2)–C(5)	105.7(4)	F(1)–P–F(6)	89.2(4)
C(3)–C(2)–C(4)	114.5(4)	F(2)–P–F(6)	91.0(4)
C(3)–C(2)–C(5)	103.9(4)	F(3)–P–F(6)	93.0(4)
C(4)–C(2)–C(5)	109.5(4)	F(4)–P–F(6)	86.5(5)
N–C(3)–C(2)	119.8(4)	F(5)–P–F(6)	176.9(5)
N^L–C(6)–C(7)	113.9(4)		
C(6)–C(7)–C(8)	111.2(4)		
C(6)–C(7)–C(9)	106.6(4)		
C(6)–C(7)–C(10)	111.3(5)		
C(8)–C(7)–C(9)	107.1(4)		
C(8)–C(7)–C(10)	111.2(4)		
C(9)–C(7)–C(10)	109.3(5)		
S–C(8)–C(7)	113.9(3)		

(c) Inter-ion contacts

N^I···F(1)	3.064	Pd···F(3)	3.259
H(N^I)···F(1)	2.20	N^L–H(N^I)···F(1)	150.7

(d) Torsion angles

Pd–S–C(1)–C(2)	−46.6	Pd–S–C(8)–C(7)	−64.1
S–C(1)–C(2)–C(3)	71.3	S–C(8)–C(7)–C(6)	62.6
C(1)–C(2)–C(3)–N	−76.7	C(8)–C(7)–C(6)–N^I	−69.5
C(2)–C(3)–N–Pd	53.1	C(7)–C(6)–N^L–Pd	81.7
C(3)–N–Pd–S	−24.0	C(6)–N^L–Pd–S	−67.8
N–Pd–S–C(1)	20.2	N^L–Pd–S–C(8)	56.0

Superscript I refers to equivalent position −x, −y, −z.

sistent with the observed peak patterns. For X, both likely structures have the c,c,t(N) configuration (Figure 5) of the macrocycle with the S lone pairs *trans* to the Pd–Cl bond and differ only as to whether nitrogens or sulphurs occupy the axial positions. A study of molecular models suggests that the form with axial nitrogens should be more stable. Similarly for Y, both have the c,c,c configuration with the S lone pairs and NH protons *trans* to the Pd–Cl bond and differ only in the axial *versus* equatorial disposition of the nitrogen and sulphur atoms.

A choice between the two possibilities for X and for Y

could be made if the principal cause of the unusual downfield shifts of certain SCH protons were identified. Two deshielding mechanisms have been considered. In the
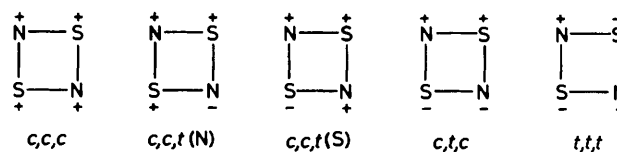

FIGURE 5 The five possible configurations of (L) when acting as a tetradentate ligand

first, the relevant protons are held in close proximity to the bonded chloride [9] which requires that the sulphurs be axial. In the second, these protons are held close to Pd [10] which requires that the sulphurs occupy equatorial positions with the deshielded hydrogens lying behind the Pd–Cl bond. A decision that this second mechanism is operating appears possible for Y on the basis of the chemical shift changes observed when the counter ion is changed from chloride to hexafluorophosphate. The large upfield shift found for the single NH resonance in Y suggests that the counter ion lies on the same side of the molecule as these NH protons, the shift reflecting a marked decrease in hydrogen bonding on going from chloride to hexafluorophosphate. The fact that the only other large upfield shift is suffered by the lower field SCH protons suggests that these also lie on the same side as the counter ion where they are deshielded by Pd and that the sulphur atoms are equatorial in Y (see Figure 6). Presumably the downfield SCH protons in X are deshielded for similar reasons. Smaller chemical shift changes are observed for these SCH protons in X when the chloride counter ion is replaced by hexafluorophosphate because the face of the complex, on the side
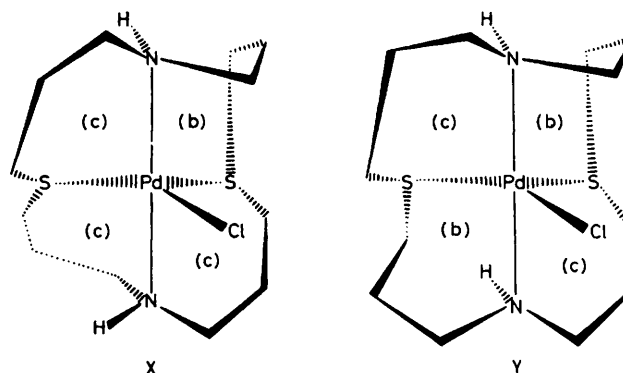

FIGURE 6 Suggested structures for the species X and Y present in non-aqueous solutions of (1a); (c) and (b) denote chair and boat conformations respectively

remote from the bonded chloride, is more crowded than in Y.

The possibility that solutions of compound (1a), in non-aqueous solvents, contain square-planar four-coordinate species with L acting as a tridentate ligand has been mentioned above. Three distinct situations can be envisaged, depending on whether or not exchange of free

and bonded ligand atoms is occurring rapidly on the n.m.r. time-scale. First, in the absence of such exchange, the ^{1}H n.m.r. peak pattern associated with Y could not be obtained. That of X would be obtained only if a nitrogen rather than a sulphur atom were free, which seems unlikely,[11] and if the sulphur lone pairs were mutually cis. Secondly, exchange could be taking place, presumably via a trigonal bipyramidal inter-mediate, but without inversion at the exchanging atoms. Here, for the reasons discussed above for the various trigonal bipyramidal possibilities, X and Y could have square planar structures with the sulphur atoms under-going exchange via intermediates having structures similar to those in Figure 6. Thirdly, if exchange and inversion are feasible then various square planar struc-tures of this type are possible for Y but none for X.

Structures of Compounds (1) *(in Aqueous Solution) and* (2).—Since compound (2) is expected to contain a square square palladium dication in $(CD_3)_2CO$ and since its ^{1}H n.m.r. spectrum in this solvent is very similar to that of compound (1a) in D_2O, then the latter presumably has this geometry also. This conclusion is reinforced by the close similarity of the electronic spectra of compounds (1a) and (2) in water and acetonitrile respectively. The observation of only two different kinds of NCH, SCH, and CMe protons for the predominant component in their ^{1}H n.m.r. spectra indicates that, in the absence of rapid (on the n.m.r. time-scale) inversion at sulphur, the ligand in this species has either the *c,c,c* or the *t,t,t* (Figure 5) configuration. Since our X-ray analysis (see below) shows that the ligand in (2) adopts the *c,t,c* configuration in the solid state, we have considered the possibility that a species of this nature is also present in solution. If it were the major component, then the ^{1}H n.m.r. peak pattern requires that both sulphurs undergo rapid inversion presumably via the *c,c,t*(N) configuration. However, if such inversion is taking place, we have not succeeded in freezing it out at −60 °C since the ^{13}C n.m.r. spectra of (2) in $(CD_3)_2CO$ (see Experimental section), at both ambient and this lower temperature, show only single resonances due to carbon adjacent to nitrogen and adjacent to sulphur, in the major species. The low-temperature ^{13}C n.m.r. spectrum shows additional resonances arising from a minor species, including a pair ascribable to carbon adjacent to nitrogen, and possibly a pair ascribable to carbon adjacent to sulphur, one of the signals being obscured by the corresponding resonance arising from the major isomer. Indeed the entire spectrum would be most readily explained if (2) were to exist in acetone solution as a mixture of *c,c,c* and *c,c,t*(N) isomers, as deduced above for (1) in chloroform or acetonitrile, with square-planar palladium in (2) rather than trigonal-bipyramidal palladium as in (1).

In the solid, the dication of (2) lies on an inversion centre (Figure 4) and the PdS_2N_2 moiety is necessarily planar with a *c,t,c* configuration (Figure 5). The PF_6^- anions lie above and below the co-ordination plane and are linked in (centrosymmetric) pairs to the cation via N-H $\cdots$ F hydrogen bonds (N $\cdots$ F 3.064 Å). The

orientation adopted [see (3)] by the PF_6^- groups leads to one F atom from each anion being above and below the Pd atom (Pd $\cdots$ F 3.259 Å). In the PF_6^- anion the P-F distances are in the range 1.494—1.585(5) Å, the longest bond being associated, as expected, with the N-H $\cdots$ F hydrogen bonding.
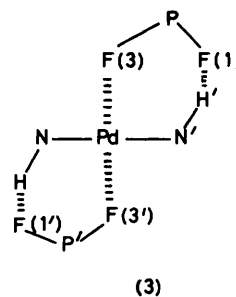
(3)

The Pd-S [2.307(1)] and Pd-N [2.090(4) Å] bond lengths are similar to values observed in a number of related complexes summarized in ref. 3 (Pd-S 2.26—2.35, Pd-N 2.03—2.09 Å). The ring torsion angles and Figure 3 clearly show that the Pd,S,C(1) $\cdots$ C(3),N ring has a very flattened chair conformation and there is a con-comitant increase in the Pd-N-C(3) [121.1(3)] and Pd-S-C(1) [110.8(2)°] angles compared with the other bond angles at sulphur (97.5, 104.2) and nitrogen (111.1, 113.1°). The other independent six-membered ring Pd,N^1,C(6)—C(8),S adopts a more nearly normal chair conformation. The remaining mean bond lengths in the cation (S-C 1.813, N-C 1.489, C-C 1.525 Å) are un-exceptional.

EXPERIMENTAL

Preparative t.l.c. plates were spread with Kieselgel G (Merck) and developed with dichloromethane-methanol (9 : 1). Hydrogen-1 and ^{13}C n.m.r. spectra were recorded on Bruker WH 400 (South Western Ontario n.m.r. Centre) and WP 60 spectrometers respectively, with $SiMe_4$ as internal standard (non-aqueous solvents). Electronic spectra were obtained on a Varian DMS 90 instrument and molar con-ductivities were calculated from the electrical resistance of solutions in freshly dried acetonitrile measured with a Beckmann model RC-18A conductance bridge. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

Preparations.—3,3,7,7,11,11,15,15-*Octamethyl*-1,9-*dithia*-5,13-*diazacyclohexadecane* (L). A preparation of this ligand has been described earlier.[1] Better yields have been ob-tained using the following procedure. A solution prepared by dissolving 2,2,6,6-tetramethyl-4-thiaheptane-1,7-diamine dihydrochloride (2.06 g, 7.82 mmol) in methanolic sodium methoxide [from sodium (0.36 g) in dry methanol (50 cm³)] was added to a solution containing 2,2,6,6-tetramethyl-4-thiaheptanedial (1.58 g, 7.82 mmol) and trimethyl borate (2 cm³) in dry methanol (300 cm³). The resulting solution was allowed to stand for 2 h, then sodium (0.72 g) and, once this had dissolved, sodium tetrahydroborate (1.50 g) were added. The reaction mixture was left at ambient temperature over-night, then most of the solvent was evaporated, and the residue was partitioned between water and dichloromethane.

Evaporation of the dried (Na_2SO_4) dichloromethane extract gave a white solid which was crystallised from diethyl ether–methanol to give L (1.32 g, m.p. 113—115 °C). Evaporation of the mother-liquors from crystallisation and Kugelrohr distillation of the residue (95—110 °C, 5 × 10⁻³ Torr *) gave more of this product (0.18 g, total yield, 53%).

2,2,16,16-*Tetradeuterio*-3,3,7,7,11,11,15,15-*octamethyl*-1,9-*dithia*-5,13-*diazacyclohexadecane* (L′). This ligand was obtained as outlined above using 3,3,5,5-tetradeuterio-2,2,6,6-tetramethyl-4-thiaheptanedial, which was in turn prepared from hexadeuteriodimethyl sulphoxide as described earlier [1] for the undeuteriated analogue.

Complexes of Palladium(II) *Chloride with* L *and* L′.—A hot solution of $PdCl_2$ (88.7 mg) in acetonitrile (20 cm³) was added to a solution of L (180.4 mg) in a mixture of acetonitrile (10 cm³) and dichloromethane (5 cm³). The mixture turned cloudy initially but subsequently clarified on stirring at ambient temperature. The resulting clear solution was evaporated to dryness, and the residue was subjected to preparative t.l.c. This gave what appeared to be a single major component, with only minor amounts of less polar and more polar material. Elution with ethanol and evaporation of the ethanol eluate gave an orange solid (242 mg, 90%) which on crystallisation from ethanol–acetone gave large prisms which crumbled to a yellow powder (1a) (decomp. 230 °C) on drying *in vacuo* (Found: C, 41.95; H, 8.05; N, 5.05. $C_{20}H_{42}Cl_2N_2PdS_2\cdot H_2O$ requires C, 42.15; H, 7.8; N, 4.9%); molar conductivity (Ω^{-1} mol⁻¹ cm²), 89 (16.2 × 10⁻⁴ mol dm⁻³), 103 (9.08 × 10⁻⁴), 118 (4.06 × 10⁻⁴). The tetradeuterio-derivative (1b) was prepared similarly.

Preparation of 3,3,7,7,11,11,15,15-*Octamethyl*-1,9-*dithia*-5,13-*diazacyclohexadecanepalladium*(II)   *Bis*(*hexafluorophosphate*) (2).—A solution of ammonium hexafluorophosphate (17.9 mg, 0.11 mmol) in water (5 cm³) was added to an aqueous ethanolic (5 + 2 cm³) solution of (1) (26.9 mg, 0.05 mmol). The pale yellow crystalline material which deposited on standing was filtered off, washed several times with water, and dried to give (2) (31.1 mg, 82%). Crystallization of this compound from acetone–toluene gave pale yellow prisms, m.p. 215 °C (decomp.), ¹³C n.m.r. (at −60 °C): major isomer, δ (p.p.m.) 29.2, 34.8 (both CH_3), 44.1 (SC), and 62.3 (NC); minor isomer, δ 41.8, 44.1 (?) (both SC) and 62.8, 66.4 (both NC) (other resonances obscured by solvent).

Crystal Data for (2).—$C_{20}H_{42}N_2PdS_2\cdot 2PF_6$, $M = 771.0$, Monoclinic, $a = 9.529(2)$, $b = 10.750(2)$, $c = 14.996(3)$ Å, $\beta = 93.28(2)°$, $U = 1\ 533.6$ Å³, $Z = 2$, $D_c = 1.67$ g cm⁻³, $F(000) = 646$; space group $P2_1/n$ (from systematic absences; $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$), $\lambda(\text{Mo-}K_\alpha) = 0.710\ 69$ Å, $\mu = 8.4$ cm⁻¹.

Data were collected to a maximum θ of 25° on an Enraf–Nonius CAD4 diffractometer by the θ–2θ scan method using monochromatised Mo-K_α radiation. Following machine location and centring of 25 reflections with θ in the range 10 < θ < 15°, accurate cell dimension and the orientation matrix were obtained by a least-squares refinement. A total of 3 012 reflections were collected of which 2 017 had in-

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* Throughout this paper 1 Torr = (101 325)/760 Pa.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

tensities greater than 3σ and were used in structure solution and refinement. Data were corrected for Lorentz and polarization factors and then for absorption.

The co-ordinates of the Pd atom were obtained from an analysis of a three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Initial refinement by full-matrix least-squares calculations with isotropic temperature factors for the non-hydrogen atoms lowered R to 0.097 which further dropped to 0.052 after four cycles of anisotropic refinement. A difference map computed at this stage revealed maxima (0.7—0.5 e Å⁻³) corresponding to the 21 hydrogen atoms which were included in the subsequent refinement in geometrically idealised positions (C–H, 0.95 Å), and in addition overall isotropic thermal parameters were refined for the various types of hydrogen atoms. In the final four refinement cycles a weighting scheme of the form $w = 1/[\sigma^2 F + pF^2]$ was employed where the final p parameter was 0.0005. Scattering factors used in the structure factor calculations were taken from ref. 12 for non-hydrogen atoms and ref. 13 for hydrogen atoms and allowance was made for anomalous dispersion.[14] Refinement converged with $R = 0.042$ and $R' = [\Sigma w \Delta^2/\Sigma w F_0^2]^{\frac{1}{2}} = 0.050$ for the 2 017 reflections with $I > 3\sigma(I)$. A final difference map was devoid of any significant features. The observed and calculated structure factors, hydrogen atom co-ordinates, and thermal parameters have been deposited as Supplementary Publication No. SUP 23271 (13 pp.).†

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