Structure and Dynamic Behaviour of Palladium(II) Complexes formed from *trans*-N_2S_2 Macrocyclic Ligands and the Crystal Structure of $[PdL^1][PF_6]_2$ (L^1 = 7,8,17,18-Tetrahydro-6*H*,16*H*-dibenzo[*g,o*][1,9,5,13]dithiadiazacyclohexadecine) †

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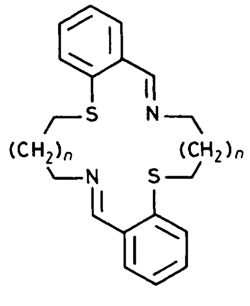
The sixteen-membered *trans*-N_2S_2 macrocycle 7,8,17,18-tetrahydro-6*H*,16*H*-dibenzo[*g,o*]-[1,9,5,13]dithiadiazacyclohexadecine, L^1, gives a complex with palladium(II) which exists in solution as an equilibrium mixture of two diastereomers, observable at low temperature by ^{13}C n.m.r. The two diastereomers are *meso* and racemic forms of the complex related by inversion at one of the two sulphur stereocentres. They interconvert on the n.m.r. time-scale at elevated temperatures, with $\Delta G^{\ddagger} = 63.3$ kJ mol^{-1} at 288 K. Measurement of the relative intensities of the two sets of resonances gives $K = 0.36$ (racemic $\longrightarrow$ *meso*) which is substantially temperature invariant in the range 230—280 K. Crystallisation from an acetonitrile–methanol (4:1) mixture, as the PF_6^- salt, yields a single compound which has been shown by *X*-ray crystallography to be the *meso* diastereomer, in which the Pd atom lies at an inversion centre and has distorted square-planar geometry with Pd–S 2.307(1) Å, Pd–N 2.047(4) Å, S–Pd–N (benzenoid chelate ring) 84.7(1)°. The PF_6^- anions lie above and below the co-ordination plane with one Pd–F 3.152 Å and other structural features which suggest some Pd–F interaction. The fourteen-membered analogue of L^1, 6,7,15,16-tetrahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine, L^2, also forms a complex with palladium(II), but, in contrast, only one of the two diastereomers exists in solution at concentrations detectable by n.m.r. spectroscopy.

Extensive investigations have been made into the complexing capabilities of dibenzenoid macrocyclic ligands, which have demonstrated correlations between the structural properties of the ligand, such as ring size, donor atom type and arrangement, and level of unsaturation, on the one hand and the structural and physicochemical properties of the complex on the other.[1] For the majority of these complexes more than a single diastereomer is potentially accessible, as a consequence of the chirality usually associated with co-ordinated sp^3-hybridised donor atoms present in the cyclic ligand, yet when isolated in the solid state generally only a single diastereomer is observed. It is frequently unclear, although there are some notable exceptions to this,[2] whether the observation of a single diastereomer in the solid state results from a crystallisation induced disequilibration of a mixture of diastereomers present in solution, or, whether there is a kinetic barrier that prevents equilibration in the first place, or, whether there are thermodynamic differences which cause that equilibrium to favour predominantly the isolated diastereomer. Often this is the case because the use of paramagnetic metal ion has frustrated attempts to make interpretable n.m.r. observations of the complex in solution. In order to shed some light on this situation, for the case of dibenzenoid macrocycles having an N_2S_2 donor atom array, we have turned to palladium(II), which forms, almost exclusively, diamagnetic square-planar complexes, and have undertaken a combined solid-state and solution structural analysis of its complexes with L^1 and L^2.



L^1; $n = 1$
L^2; $n = 0$

Complexes of L^1 and L^2 each have a pair of chiral sulphur stereocentres and consequently can exist in the *meso* (R^*,S^*) form or racemic (R^*,R^*) form as shown for $[PdL^1]^{2+}$ in Figure 1. The two diastereomers are related by inversion of one of the two stereocentres, for which the free energy of activation ($\Delta G^{\ddagger}$) is usually in the vicinity of 60 kJ mol^{-1}, or possibly higher if barriers towards conformational change within the macrocyclic framework exist.[3,4] In either case the value is sufficiently high to permit the detection of both diastereomers by n.m.r. at reasonably accessible temperatures, providing their relative thermodynamic stabilities are conducive to the presence of each as a significant proportion of the total mixture.

Experimental

Proton-decoupled ^{13}C n.m.r. spectra were recorded using $(CD_3)_2SO$–CD_3OD (4:1) as solvent on a JEOL FX90Q spectrometer. Chemical shifts are quoted on the δ scale relative to $(CD_3)_2SO$ (δ 39.6 p.p.m.).[5] Sample temperatures are ± 1 K and were verified by reference to the ^1H spectrum of methanol

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† {R^*,S^*-(7,8,17,18-Tetrahydro-6*H*,16*H*-dibenzo[*g,o*][1,9,5,13]-dithiadiazacyclohexadecine-S^5,S^{15},N^9,N^{19})}palladium(II) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

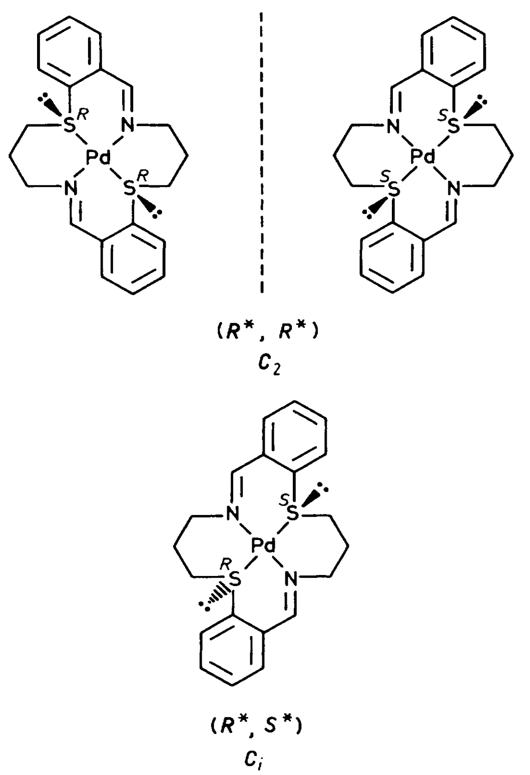

Figure 1. Diastereomeric forms of $[PdL^1]^{2+}$

according to the procedure of Van Geet.[6] Molar conductivities were measured with a Phillips PW9504 conductivity bridge on 10^{-3} mol dm^{-3} solutions at 15 °C. Elemental analyses were performed by the Australian Microanalytical Service. Synthesis of ligands L^1 and L^2 was carried out as described previously.[7]

Preparation of Complexes.—{[SP-4,1-(R*,S*)](7,8,17,18-*Tetrahydro*-6H,16H-*dibenzo*[g,o][1,9,5,13]*dithiadiazacyclohexadecine*-S^5,S^{15},N^9,N^{19})}*palladium*(II) *hexafluorophosphate*, $[Pd\{(R^*,S^*)L^1\}][PF_6]_2$. Ligand L^1 (0.4 g, 1.13 mmol) was added to a freshly prepared solution of $[PdCl_2(MeCN)_2]$ [from 0.2 g of $PdCl_2$ (1.13 mmol) dissolved in 50 cm^3 of MeCN]. After refluxing the solution for *ca.* 15 min the precipitated dichloro complex was dissolved by the addition of water (100 cm^3). An aqueous solution of ammonium hexafluorophosphate (0.7 g, 4.6 mmol in 5 cm^3 of H_2O) was then added and the mixture refluxed for a further 15 min. Concentration of the solution to *ca.* 10 cm^3 precipitated the crude product. This was collected by filtration, dissolved in acetonitrile (8 cm^3), and treated a second time with aqueous ammonium hexafluorophosphate in the manner described above. Concentration of the solution followed by recrystallization of the precipitate from acetonitrile–methanol (4:1) gave yellow crystals of the pure product (0.47 g, 55%), m.p. 277—282 °C (decomp.) (Found: C, 31.8; H, 3.1; N, 4.1. $C_{20}H_{22}F_{12}N_2P_2PdS_2$ requires C, 32.0; H, 3.0; N, 3.7%). ^{13}C N.m.r. $[(CD_3)_2SO–CD_3OD$ (4:1), 260 K], racemic complex: δ 172.5 (C=N), 137.2, 136.0, 135.2, 131.1, 127.5, 126.0 (aromatic), 58.5 (CH_2–N), 29.4 (CH_2–S), and 25.7 p.p.m. (CH_2–CH_2–CH_2); *meso* complex: δ 171.0 (C=N), 137.2, 136.0, 134.1, 131.1, 128.7, 126.0 (aromatic), 58.5 (CH_2–N), 31.5 (CH_2–S), and 23.8 p.p.m. (CH_2–CH_2–CH_2). I.r. (Nujol): 1 625 cm^{-1} [ν(C=N)]. Λ_M = 57 Ω^{-1} cm^2 mol^{-1} (Me_2SO) (1:2).

6,7,15,16-*Tetrahydrodibenzo*[f,m][1,8,4,11]*dithiadiazacyclotetradecine*-S^5,S^{14},N^8,N^{17})*palladium*(II) *hexafluorophosphate*, $[PdL^2][PF_6]_2$. This complex was prepared from $[PdCl_2(MeCN)_2]$ and ligand L^2 in an analogous manner to that described for $[PdL^1][PF_6]_2$. Recrystallization from acetone gave irregular yellow crystals, 74%, m.p. 244–245 °C (Found: C, 30.2; H, 2.6; N, 3.7. $C_{18}H_{18}F_{12}N_2P_2PdS_2$ requires C, 29.9; H, 2.5; N, 3.9%). ^{13}C N.m.r. $[(CD_3)_2SO–CD_3OD$ (4:1), 260 K]: δ 170.7 (C=N), 139.7, 136.8, 135.2, 132.1, 130.6, 128.7 (aromatic), 67.2 (CH_2–N), and 40.7 p.p.m. (CH_2–S). I.r. (Nujol): 1 630 cm^{-1} [ν(C=N)]. Λ_M = 56 Ω^{-1} cm^2 mol^{-1} (Me_2SO) (1:2).

Crystal-structure Determination of $[PdL^1][PF_6]_2$.—*Crystal data.* $C_{20}H_{22}F_{12}N_2P_2PdS_2$, M = 750.86, monoclinic, a = 9.263(1), b = 9.785(1), c = 14.193(2) Å, β = 99.00(1)°, U = 1 270.6 Å^3 (from a least-squares fit to the diffractometer setting angles of 25 reflections chosen widely in reciprocal space in the range θ = 5—20°, λ = 0.710 69 Å), space group $P2_1/c$ (precession photographs with $2/m$ Laue symmetry and characteristic systematic extinctions), D_m = 1.96(1) g cm^{-3} (flotation in toluene–1,2-dibromoethane), Z = 2, D_c = 1.963 g cm^{-3}, $F(000)$ = 744, Pd implied at a centre of symmetry. Yellow approximately hexagonal prismatic crystals. Dimensions (distance to faces from centre): 0.113 $(01\bar{1}, 0\bar{1}1)$, 0.125 $(011, 0\bar{1}\bar{1})$, 0.106 $(001, 00\bar{1})$, 0.069 $(100, \bar{1}00)$ mm, μ(Mo-K_α) = 11.14 cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω/θ mode with ω scan width = 0.80 + 0.35 tan θ, ω scan speed 0.7—6.7° min^{-1}, graphite-monochromated Mo-K_α radiation, 2 382 reflection intensities measured ($1.0 \leqslant \theta \leqslant 25°$, $+h$ $+k$ $\pm l$). Those with $I < 2.5\ \sigma(I)$ at fast speed not remeasured leaving 1 776 data. 1 666 Unique [merging R = 0.025 after absorption correction (Gaussian quadrature, 10 × 10 × 10 points, max. and min. transmission factors = 0.84, 0.79)]. Two reflections monitored every 100 min showed no significant variation in intensity.

Structure analysis and refinement. Fourier methods for non-hydrogen atoms. Hydrogen atoms in calculated positions.

The PF_6^- ion showed a ring of electron density with four broad maxima corresponding to one PF_4 plane, indicating a large oscillation about the F(1)–P–F(2) axis. This was modelled by one set of 4 partial fluorine atoms [anisotropic, equal population parameters, F(3), F(4), F(5), F(6)], and a second set of 4 [isotropic, equal population parameters, F(7), F(8), F(9), F(10)] in calculated (ideal) positions rotated 45° with respect to the first set. A single population parameter was refined so that population of the first set plus the population of the second set = 1. The first set was refined as independent atoms, the second set was held at calculated positions, with refined isotropic thermal parameters.

Full-matrix least-squares refinement [minimising $\Sigma w \Delta F^2$ where $w = 1/\sigma^2(F)$ with $\sigma(F)$ from counting statistics]. Final cycle: 183 variables, non-hydrogen atoms anisotropic [except for F(7)—F(10) as above], hydrogen atoms isotropic fixed and fixed co-ordinates recalculated before final cycle. Final R = 0.036, R' = 0.045, population [F(3), F(4), F(5), F(6)] = 0.79(1), maximum shift-error (cation) = 0.006, difference map maxima: 0.7 e Å^{-3} in the region of PF_6^-, elsewhere 0.2 e Å^{-3}.

Atomic scattering factors for neutral non-hydrogen atoms were taken from ref. 8 and for hydrogen atoms from ref. 9.

The computer programs of the XTAL system were used in this structure determination.[10] Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The proton-decoupled ^{13}C n.m.r. spectrum of the palladium(II) complex of the sixteen-membered macrocycle, $[PdL^1][PF_6]_2$, at 298 K and above in $(CD_3)_2SO–CD_3OD$ (4:1) shows the ten resonances which could be expected for a single diastereomeric

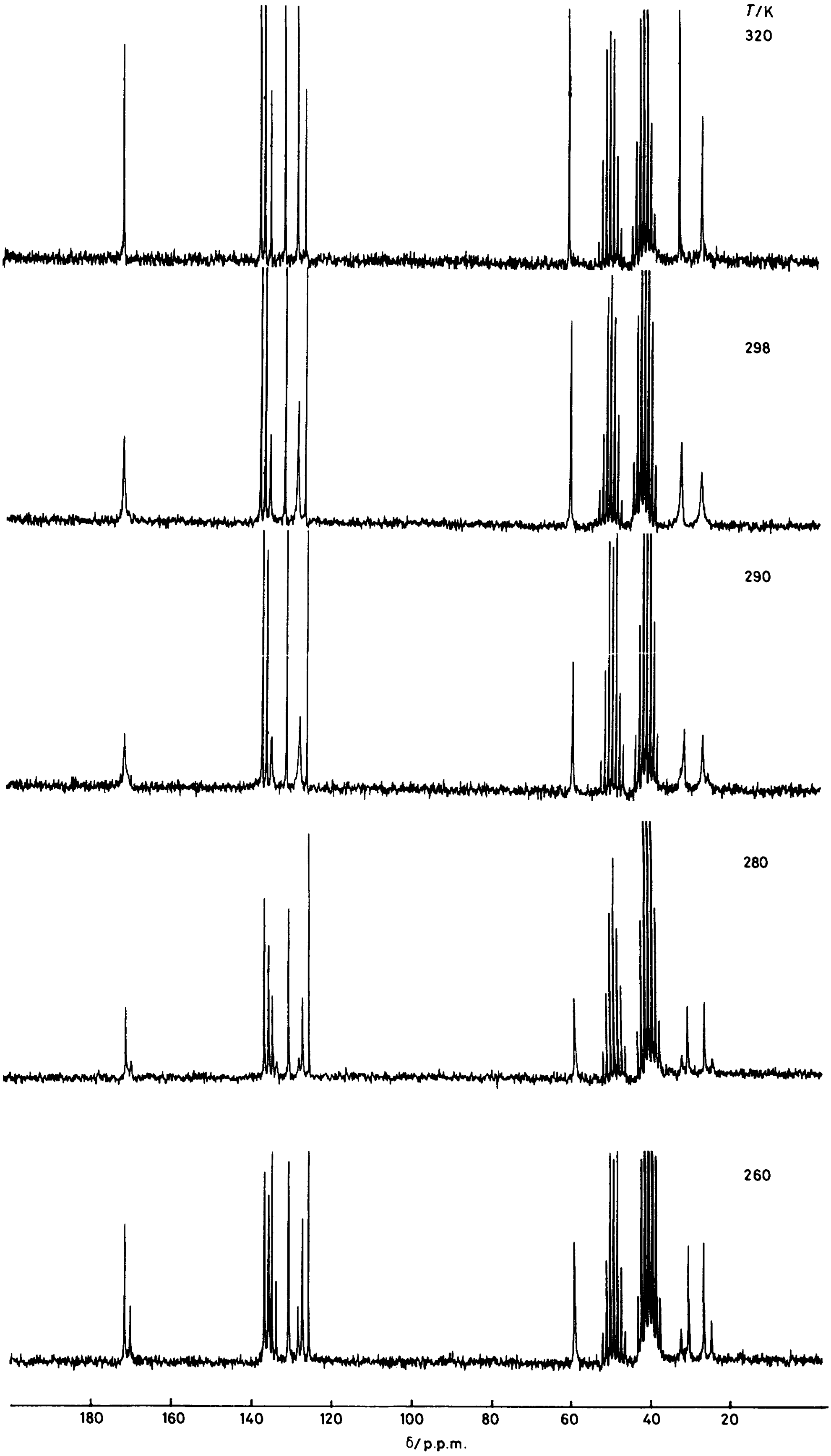

Figure 2. Variable-temperature $^{13}C-\{^1H\}$ n.m.r. spectra of $[PdL^1][PF_6]_2$ in $(CD_3)_2SO-CD_3OD$ (4:1)

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses for $[PdL^1][PF_6]_2$

Atom	x	y	z
Pd	0	0	0
S	0.0954(1)	0.1980(1)	−0.0535(1)
N	0.0697(5)	0.0379(4)	0.1416(3)
C(1)	−0.2153(6)	−0.1270(5)	0.1282(3)
C(2)	−0.3559(7)	−0.1781(6)	0.1254(4)
C(3)	−0.4390(7)	−0.1314(7)	0.1924(5)
C(4)	−0.3871(7)	−0.0367(7)	0.2594(4)
C(5)	−0.2474(7)	0.0128(7)	0.2617(4)
C(6)	−0.1603(6)	−0.0293(5)	0.1956(4)
C(7)	−0.0132(6)	0.0266(5)	0.2053(4)
C(8)	0.2214(7)	0.2587(6)	0.0489(4)
C(9)	0.3032(6)	0.1423(7)	0.1027(4)
C(10)	0.2219(7)	0.0806(8)	0.1770(4)
P	−0.2616(2)	0.3452(2)	0.0681(1)
F(1)	−0.2622(6)	0.4976(4)	0.1039(3)
F(2)	−0.2593(7)	0.1929(5)	0.0345(4)
F(3)	−0.148(1)	0.393(1)	0.0051(7)
F(4)	−0.1331(8)	0.3075(7)	0.1478(6)
F(5)	−0.372(1)	0.3041(8)	0.1290(8)
F(6)	−0.3751(9)	0.3853(7)	−0.0211(5)
F(7)	−0.2675	0.3996	−0.0407
F(8)	−0.0874	0.3483	0.0786
F(9)	−0.2523	0.2923	0.1713
F(10)	−0.4324	0.3406	0.0520

Occupancy factors of F(3)—F(6) = 0.79(1) and F(7)—F(10) = 0.21(1).

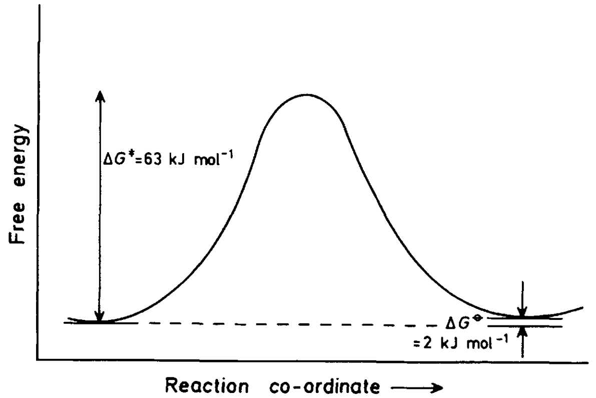

Figure 3. Energy profile at 288 K for the interconversion of racemic- and *meso*-$[PdL^1][PF_6]_2$

Table 2. Selected torsion angles (°) for $[PdL^1][PF_6]_2$

N-Pd-S-C(1*)	+121.0
N-Pd-S-C(8)	+15.1
Pd-S-C(1*)-C(2*)	−136.0
Pd-S-C(1*)-C(6*)	+50.3
S-Pd-N-C(7)	+132.0
S-Pd-N-C(10)	−48.1
S*-C(1)-C(6)-C(5)	−171.7
S*-C(1)-C(6)-C(7)	+4.5
C(5)-C(6)-C(7)-N	−157.2
C(1)-C(6)-C(7)-N	+26.5
Pd-N-C(7)-C(6)	+8.6
C(10)-N-C(7)-C(6)	−171.3
C(9)-C(10)-N-Pd	+21.1
C(9)-C(10)-N-C(7)	−159.0
C(8)-C(9)-C(10)-N	+53.0
S-C(8)-C(9)-C(10)	−87.2
C(9)-C(8)-S-Pd	+39.0
C(9)-C(8)-S-C(1*)	−65.0

* Atom at $-x$, $-y$, $-z$.

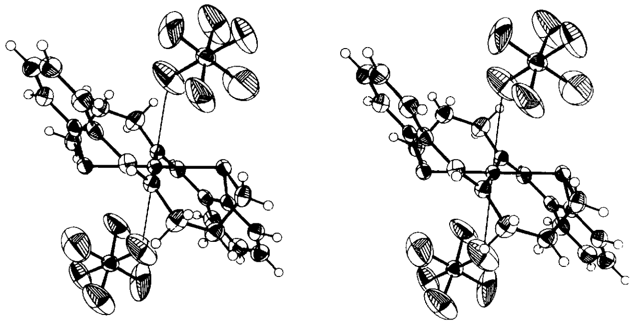

Figure 4. Stereoscopic diagram of *meso*-$[PdL^1][PF_6]_2$. Thermal ellipsoids enclose 50% probability. Hydrogen atoms are shown as arbitrary spheres. The fluorine atoms F(7)—F(10) (those with an occupancy of *ca.* 21%) are not shown

form of the complex. This may be seen in Figure 2. Cooling the sample, however, causes splitting of five of the resonances into asymmetric doublets and broadening of a sixth, indicating that at higher temperatures the two possible diastereomers are in fast exchange with each other. The resonances showing exchange phenomena appear to be those associated with the atoms composing the inner ring, whilst the four temperature independent resonances are most likely those associated with the four tertiary aromatic carbons of each benzo group. These are remote from the sulphur atom undergoing inversion and as they are not contained within the same ring structure appear to be little affected by the conformational changes taking place in the main ring. The two aromatic resonances which split have the same coalescence temperature of 288 ± 2 K and from these $\Delta G^{\ddagger}$ for the inversion process has been calculated, using the Eyring equation, as 63.3 ± 0.5 kJ mol^{-1} at this temperature. This value is consistent with values obtained for Pd^{II} complexes containing a single symmetrical bidentate bis(thioether) ligand[4,11] and indicates that the involvement of the sulphur atom in a larger macrocyclic complex need not result in a significant enhancement of the activation energy required for its inversion.

Besides kinetic data it was also possible to elicit thermodynamic data from the set of spectra shown in Figure 2, along with additional spectra recorded down to 230 K, by measuring the relative intensities of the resonances within each of the five doublets and calculating an equilibrium constant at each temperature for the transformaton of the major to minor species. The equilibrium constants obtained in this way turn out to be temperature independent, within experimental error, having a mean value of 0.36 ± 0.01. Plotting ln *K versus* reciprocal temperature gives $\Delta H^{\circ} = 0 \pm 1$ kJ mol^{-1} and $\Delta S^{\circ} = -9 \pm 4$ J K^{-1} mol^{-1}. The fact that entropy is lost as the major species converts to the minor suggests that the major species may be the racemic form of the complex which, having both aromatic rings deflected to the same side of the donor atom plane (the saddle conformation) could well be weakly solvated by $(CD_3)_2SO$ only at the less obstructed axial site and hence can gain solvent in forming the *meso* complex, which, having one aromatic ring deflected to each side of the donor atom plane (the step conformation) has more open axial sites leaving it

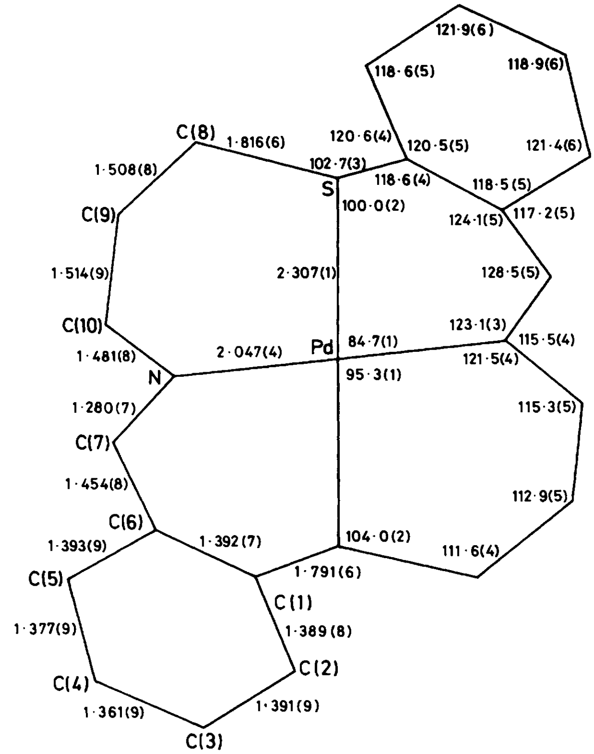

Figure 5. Bond lengths (Å), bond angles (°), and atomic numbering scheme for the *meso*-$[PdL^1]^{2+}$ cation. Standard deviations are in parentheses. P–F bond lengths range from 1.49 to 1.58 Å and F–P–F angles from 86.4 to 94.0°. C–H bond lengths range from 0.87(6) to 1.03(6) Å

amenable to disolvation. These findings are summarized by the energy profile for the transformation shown in Figure 3.

To compare the situation in solution with that in the solid state an *X*-ray diffraction structural determination of a single crystal grown from an acetonitrile–methanol (4:1) solution was undertaken. The structure of the cation is shown in Figure 4 and from this it is evident that it is the *meso* form of the complex which crystallises from this solvent mixture. As far as could be seen all crystals were of the same form indicating that a crystallisation induced disequilibration, in favour of the minor component present in solution, had occurred. Atomic co-ordinates are given in Table 1 and selected torsion angles in Table 2. Figure 5 shows the bond lengths, bond angles, and atomic numbering scheme.

The structure of *meso*-$[PdL^1][PF_6]_2$ is centrosymmetric and thus the Pd atom is coplanar with the four donor atoms giving it a distorted square-planar geometry. Each aromatic ring is inclined at an angle of 56.6(2)° to the donor atom plane. The Pd–S distance of 2.307(1) Å is remarkably consistent with data available from studies of other Pd–N_2S_2 macrocyclic complexes[12–14] and the Pd–N(imino) bond length of 2.047(4) Å is within the normally observed range of values for bonds of this type.[15,16] The PF_6^- anions lie above and below the co-ordination plane with each F(2) atom in an apical position [Pd–F(2) = 3.152(6) Å, F(2)–Pd–N = 82.5(2), F(2)–Pd–S = 83.6(1), Pd–F(2)–P = 131.6(3)°]. An interaction between Pd and F(2), which could, arguably, be a reason for viewing the complex as one having a tetragonally-distorted octahedral structure in the solid state, is suggested by the fact that whilst the four fluorine atoms in the plane at 90° to the F(1)–P–F(2) axis are not localised in fixed positions, atoms F(1), P, and F(2) are ordered, fixing this axis in relationship to the Pd atom. This may be seen in Figure 6. In the case of F(1) the order can be attributed to five non-bonded contacts with hydrogen atoms, in the range 2.63—2.75 Å; however, for F(2) there is only one such contact, at the greater distance of 2.91 Å, implying that its order may arise from interaction with the metal. This is supported by the disorder noted in the F(3)—F(6) plane which exists even though these atoms have as many as three F···H contacts (1, 2, 3, and 2 interactions respectively of less than 3 Å). A similar phenomenon has been observed previously with another bis(hexafluorophosphate) salt of a palladium(II) macrocyclic complex,[12] although in that case the positioning of F atoms 3.259 Å above and below Pd could be explained in terms of an adjacent interaction between an F atom and an N–H group (F–N 3.064 Å) without it being necessary to suspect direct Pd–F interaction as appears to be the case here.

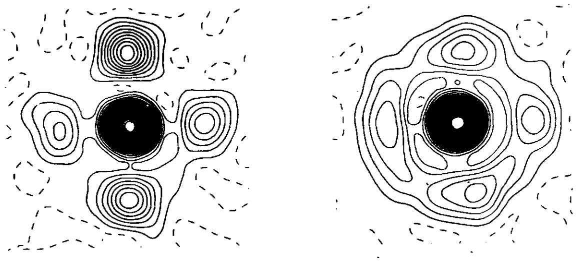

Figure 6. Sections through the electron density of the PF_6^- ion. The section on the left contains the F(1), F(2), and P axis (vertical) and the one on the right contains P and F(3)—F(6). Contours are at intervals of 0.5 e Å^{-3}

The palladium(II) complex of the fourteen-membered macrocycle, $[PdL^2][PF_6]_2$, can be synthesised in the same manner as $[PdL^1][PF_6]_2$, but is manifestly less stable and crystals suitable for *X*-ray diffraction could not be grown due to partial decomposition during the growth period which led to deposition of the free ligand. This was not entirely unexpected since earlier studies of both L^2 (ref. 17) and its reduced, diamino, derivative,[18] with Ni^{II}, which is of similar ionic radius (high-spin Ni^{2+} 0.69 Å, Pd^{2+} 0.64 Å)[19] have revealed the tendency that this macrocycle has to fold about the S–metal–S axis to form *cis*-octahedral species. Since this is a stereochemistry which is not usually observed for stable palladium(II) species an obvious mechanism for ligand dissociation exists. Folding occurs more readily for the complex of L^2 than L^1 because of the relatively small binding cavity, for Pd^{II}, presented by fourteen-membered macrocycles, which prevents the metal ion from lying within the donor atom plane.[2,20] Work by Lindoy and co-workers[1] suggests that square-planar Pd^{II} would best be accommodated by fifteen- or sixteen-membered macrocycles.

The ^{13}C n.m.r. spectra of $[PdL^2][PF_6]_2$ recorded under the same conditions as $[PdL^1][PF_6]_2$ in the temperature range 230—373 K each show a set of nine sharp resonances consistent with the presence of a single, though unidentifiable, diastereomer. Available data[4] have shown that the reduction of chelate ring size from six to five members, with other factors that affect the rate of inversion of sulphur, such as the nature of the *trans* ligand, held constant, as is the case here, causes an increase in the free energy of activation for inversion of between 5 and 15 kJ mol^{-1}. Thus it is highly improbable that the two diastereomers are still in fast exchange at 230 K, and that the spectra observed are averaged, since this could only be the case if $\Delta G^{\ddagger}$ has fallen below *ca.* 50 kJ mol^{-1} which would represent a significant reversal of the normally observed trend. There appear to be three potential reasons for the observation of only one diastereomer which should be considered.

(*i*) The energy barrier for inversion is so high that the single diastereomer, which might be formed as a result of a stereospecific complexation process, is kinetically trapped in its initial configuration. This seems unlikely in view of the small magnitude of the increase in $\Delta G^{\ddagger}$ expected, compared to $[PdL^1][PF_6]_2$, noted above, and also the observation of Moore and co-workers[3] in which the square-planar Ni^{II} complex of the fourteen-membered S_4 macrocycle 1,4,8,11-tetrathiacyclotetradecane was seen to undergo inversion at sulphur with an activation free energy of *ca.* 66.8 kJ mol^{-1} at 301 K. Furthermore heating the sample at 423 K for 30 min produced no indication of the second diastereomer, only incipient decomposition.

(*ii*) The structure of the complex could be such that one sulphur atom is not co-ordinated, in which case there would only be a single chiral centre and no pair of diastereomers. This has been observed with ligand L^2 in a tetrahedral Cu^I complex in which triphenylphosphine has displaced one of the sulphur donors,[21] but seems unlikely with palladium(II) in the absence of a competing ligand.

(*iii*) The relative thermodynamic stability of the two diastereomers is such that whilst they may be in slow exchange at the lower temperatures the population of the minor species is so low as to escape detection by n.m.r. This is quite plausible and represents an extension of what has been seen with $[PdL^1][PF_6]_2$ where the equilibrium is biased towards the racemic diastereomer to the extent of 74% of the mixture being racemic and 26% *meso*. It can be rationalised in terms of the fact that, unlike the case with the sixteen-membered macrocycle, the metal must sit out of the donor atom plane of the fourteen-membered macrocycle. This could well be a situation which can be accommodated with considerably greater stability by one of the two diastereomeric forms of the ligand rather than the other.

We conclude therefore that where diastereoisomerism of metal complexes is determined by inversion at sulphur alone kinetic stability in solution is unlikely, and that it is thermodynamic control, brought about by the mutual interaction of metal ion and ligand that dictates the ratio of diastereomers present. The structure of the isolated solid gives incomplete information about the situation pertaining in solution owing to the disequilibration that accompanies precipitation.

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