Chemistry of Platinum Sulphido-complexes. Part 3.[1,2] Crystal and Molecular Structure of Tetrasulphido[1,2-bis(diphenylphosphino)ethane]platinum(II) † and a Study of its Bonding and Reactions

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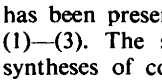
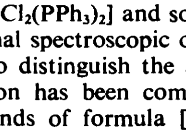
The structure of [$PtS_4(Ph_2PCH_2CH_2PPh_2)$] has been determined by single-crystal *X*-ray techniques using diffractometer data. The compound crystallises in the monoclinic space group $P2_1/a$, with four molecules in a cell of dimensions a = 9.736(3), b = 30.964(7), c = 9.806(5) Å, and β = 117.81(4)°. Least-squares refinement of the structure led to a final R value of 0.043 using 3 292 observed intensities. The complex is approximately square planar and the tetrasulphido-ligand behaves as a dianionic chelating ligand. The resultant PtS_4 ring adopts an approximately C_2 conformation. The central S–S bond is 0.046 Å shorter than the outer S–S bonds [average 2.058(15) Å]. A molecular orbital analysis of the bonding in this and related complexes has been used to interpret this geometric feature.

In 1970 Chatt and Mingos[1] reported the syntheses of palladium and platinum tetrasulphido-complexes of the general type [$M(S_4)L_2$] [where M = Pd or Pt and L = PPh_3 or L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe)] from either [$M(PPh_3)_4$] or [$M(dppe)_2$] and elemental sulphur. However, on the basis of available spectroscopic evidence, it was not possible to distinguish between the alternative structures (1)—(3). Subsequently, there have been reports of the syntheses of identical compounds either from [$Pt(S_5)_3$]$^{2-}$ and tertiary phosphines in alcohols,[3] or from [$PtCl_2(PPh_3)_2$] and sodium polysulphides.[4] However, no additional spectroscopic or structural evidence has been presented to distinguish the alternative structures (1)—(3). The situation has been complicated by reported syntheses of compounds of formula [$Pt_2S_2(PPh_3)_4$][5] under conditions similar to those described by Chatt and Mingos.[1] In the present paper a single-crystal *X*-ray crystallographic analysis of [$Pt(S_4)(dppe)$] is presented which clearly establishes that this class of compound has the tetrasulphido(2–) structure (1).[6] In addition, the recent interest shown in the structural parameters of tetrasulphido-ligands co-ordinated to tungsten[7] and molybdenum[8] has prompted us to complete some molecular orbital calculations on this type of complex. These calculations account for the observed alternation in S–S bond lengths within the PtS_4 ring. The reactions of the tetrasulphido-complexes with a variety of electrophilic and nucleophilic reagents have also been investigated.



(1)



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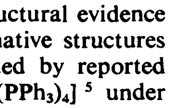

(3)

a; L_2 = dppe, b; L = PPh_3

Experimental

Reactions were generally carried out under pure dry nitrogen and in dry oxygen-free solvents. Microanalyses (C, H, Cl, and S) were performed by Mr. M. Gascoyne and his staff, of this laboratory. N.m.r. spectra were recorded on a Bruker WH90 spectrometer ($^{31}P-\{^1H\}$) operating at 36.43 MHz, with trimethyl phosphate as the external standard. Infrared spectra were obtained for Nujol mulls using a Pye Unicam SP 2000 spectrometer. Melting points were measured using an Electrothermal apparatus and conductivities were recorded on a Philips 9505 bridge using a standard conductivity cell with cell constant 0.7 cm^{-1}.

The complexes [$PtS_4(PPh_3)_2$] (1b) and [$PtS_4(dppe)$] (1a) were prepared according to the method of Chatt and Mingos,[1] and also from the dihalides [$PtCl_2L_2$] (L = PPh_3 or L_2 = dppe) and sodium polysulphides as reported by Schmidt and Hoffmann.[4] Samples prepared by the alternative methods were identical on the basis of their melting points [(1a) 282—283 °C; (1b) 142—144 °C], elemental analyses, and i.r. absorption characteristics: (1b) ν(Pt–S) 310, 312, and 315 cm^{-1}; (1a) ν(Pt–S) 315 and 326 cm^{-1}.

Reactions of [$PtS_4(PPh_3)_2$] *and* [$PtS_4(dppe)$] *with* MeI.—A solution of MeI (0.07 cm^3, 1.12 mmol) in tetrahydrofuran (thf) (5 cm^3) was added to a suspension of [$PtS_4(PPh_3)_2$] (0.47 g, 0.56 mmol) in thf (25 cm^3) and the mixture was stirred for 36 h. The volume of the resultant brown suspension was reduced to *ca.* 10 cm^3, and the brown precipitate collected by filtration and dried *in vacuo* to give [$PtS_4(PPh_3)_2(MeI)_2$] (Found: C, 39.7; H, 3.0; S, 11.3. $C_{38}H_{36}I_2P_2PtS_4$ requires C, 40.3; H, 3.2, S, 11.3%). This solid proved too insoluble in common organic solvents for n.m.r. studies, and decomposed in CH_2Cl_2.

When the above reaction was repeated with [$PtS_4(dppe)$], a mixture of products was obtained.

When the reaction was repeated with [$PtS_4(dppe)$] and MeI in 1 : 2 molar ratio, and CH_2Cl_2 as solvent, a yellow solution was obtained after 24 h and the addition of methanol to this solution gave crystals of [$PtI_2(dppe)$] (Found: C, 36.9; H, 2.5; I, 33.0. $C_{26}H_{24}I_2P_2Pt$ requires C, 36.8; H, 2.8; I, 30.0%).

Reactions of [$PtS_4(dppe)$] *and* [$PtS_4(PPh_3)_2$] *with Metal Salts and Complexes.*—$AgBF_4$ (0.11 g, 0.57 mmol) in thf (5 cm^3) was added to a suspension of [$PtS_4(dppe)$] (0.2 g, 0.28 mmol) in thf (25 cm^3). A lemon-yellow suspension formed over 1.5 h, and was filtered off; after washing with thf it was dried *in vacuo* to give [$PtS_4(dppe)Ag]BF_4$ (Found:

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† *Supplementary data available* (No. SUP 23564, 22 pp.): atomic co-ordinates, structure factors, vibrational parameters, bond lengths and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

C, 35.4; H, 3.0; S, 13.3. $C_{26}H_{24}AgBF_4P_2PtS_4$ requires C, 34.0; H, 2.6; S, 14.0%).

The following compounds were prepared in an analogous manner. [PtS_4(dppe)($HgCl_2$)] as a yellow microcrystalline precipitate, m.p. 270—273 °C (Found: C, 32.7; H, 2.3. $C_{26}H_{24}Cl_2HgP_2PtS_4$ requires C, 32.4; H, 2.4%). Attempted recrystallisation from CH_2Cl_2 led to complete conversion into [$PtCl_2$(dppe)]. [$PtS_4(PPh_3)_2$\{Hg(dppe)\}][PF_6]$_2$ as a brown precipitate, m.p. 177—179 °C, only sparingly soluble in acetone and methanol and decomposing in CH_2Cl_2 (Found: C, 41.7; H, 3.1. $C_{62}H_{54}F_{12}HgP_6PtS_4$ requires C, 42.8; H, 3.1%). [PtS_4(dppe)($PdCl_2$)] as a maroon precipitate, m.p. 247—250 °C, insoluble in all common organic solvents (Found: C, 34.6; H, 2.4. $C_{26}H_{24}Cl_2P_2PdPtS_4$ requires C, 34.7; H, 2.7%).

Table 1. Fractional co-ordinates for [PtS_4(dppe)]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt(1)	0.944 65(5)	0.125 19(1)	0.207 95(4)
S(1)	1.195 4(3)	0.139 6(1)	0.248 1(4)
S(2)	1.337 4(4)	0.107 0(1)	0.449 5(5)
S(3)	1.239 2(4)	0.125 1(2)	0.581 1(4)
S(4)	1.020 9(4)	0.099 9(1)	0.458 5(3)
P(1)	0.693 1(3)	0.120 4(1)	0.151 4(3)
P(2)	0.860 4(3)	0.139 50(9)	−0.043 5(3)
C(1)	0.579(1)	0.124 6(4)	−0.059(1)
C(2)	0.657(1)	0.154 9(4)	−0.120(1)
C(111)	0.624(1)	0.163 2(4)	0.232(1)
C(112)	0.496(1)	0.189 1(4)	0.143(1)
C(113)	0.449(2)	0.219 1(5)	0.216(2)
C(114)	0.521(2)	0.225 3(5)	0.368(2)
C(115)	0.647(2)	0.200 5(5)	0.455(2)
C(116)	0.700(2)	0.169 4(5)	0.389(2)
C(121)	0.625(1)	0.070 3(4)	0.193(1)
C(122)	0.479(1)	0.069 1(5)	0.190(2)
C(123)	0.427(2)	0.029 5(5)	0.211(2)
C(124)	0.516(2)	−0.007 4(6)	0.249(2)
C(125)	0.658(2)	−0.005 8(5)	0.251(2)
C(126)	0.712(1)	0.033 5(4)	0.225(2)
C(211)	0.951(1)	0.182 2(4)	−0.098(1)
C(212)	0.937(1)	0.224 4(4)	−0.065(1)
C(213)	1.008(2)	0.257 1(5)	−0.103(2)
C(214)	1.093(2)	0.248 0(5)	−0.180(2)
C(215)	1.112(2)	0.205 3(5)	−0.212(2)
C(216)	1.040(1)	0.172 3(4)	−0.174(1)
C(221)	0.864(1)	0.093 4(4)	−0.150(1)
C(222)	0.985(2)	0.062 1(5)	−0.079(2)
C(223)	0.992(2)	0.027 5(5)	−0.160(2)
C(224)	0.884(2)	0.021 8(5)	−0.309(2)
C(225)	0.767(2)	0.049 0(5)	−0.381(2)
C(226)	0.757(1)	0.085 7(4)	−0.302(1)

Crystal Structure Determination.—Data reduction, structure solution, and refinement were carried out with the Oxford CRYSTALS package.[9] The Oxford CHEMGRAF [10] system was used for diagrams and molecular modelling. Neutral atom scattering factors were taken from ref. 11 and those of the heavier elements were modified for anomalous dispersion, taking the $\Delta f'$ and $\Delta f''$ values given in ref. 12. Final atomic co-ordinates for the compound are given in Table 1.

Crystal data. $C_{26}H_{24}P_2PtS_4$ (1a), $M = 721.8$, Monoclinic, space group $P2_1/a$ (no. 14), $a = 9.736(3)$, $b = 30.964(7)$, $c = 9.806(5)$ Å, $\beta = 117.81(4)°$, $U = 2\,615$ Å^3, $Z = 4$, $D_c = 1.83$ g cm^{-3}.

Orange-yellow prismatic crystals of compound (1a) were grown by slow diffusion of ethanol into a chloroform solution, and a suitable crystal was sealed in a 0.5-mm Lindemann capillary tube. The crystal, of dimensions 0.2 × 0.3 × 0.7 mm was mounted on an Enraf-Nonius CAD4F diffractometer, and the intensities of 6 383 (5 409 unique) reflections were measured using graphite monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). 3 292 Independent reflections [$I \geqslant 3\sigma(I)$], corrected for absorption empirically [μ(Mo-K_α) = 60.90 cm^{-1}], were used in the refinement procedure. The structure was solved by heavy atom and Fourier methods and refined by least squares with a large block approximation to the normal matrix. Non-hydrogen atoms were refined anisotropically. Ring hydrogens were located in difference maps and then placed geometrically (C–H = 1.0 Å; $U_{iso} = 0.05$ Å^2), their positions being adjusted after each cycle. The final R value was 0.043 [$R' = 0.049$].

A Chebyshev weighting scheme was used [13] with the coefficients 62.72, 84.95, and 34.57.

Results and Discussion

A view of the molecular structure of [PtS_4(dppe)] is given in the Figure. The important bond lengths and angles, and torsion angles of the molecule, are presented in Tables 2 and 3. Least-squares planes and deviations of atoms from them are given in Table 4.

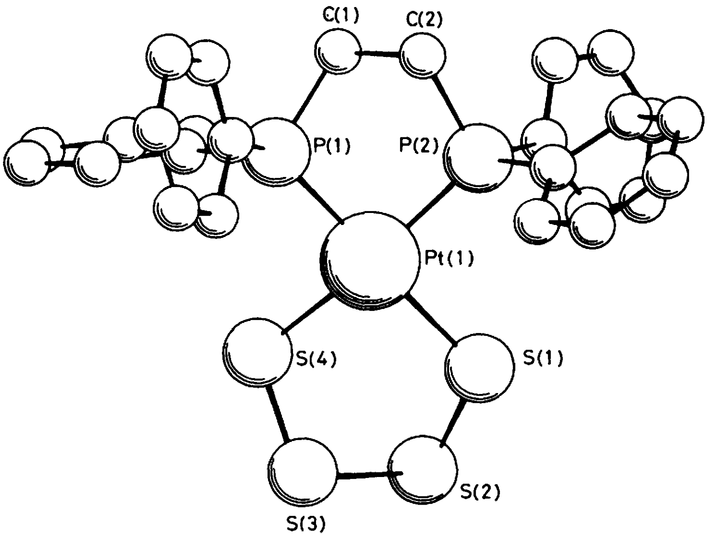


Figure. Molecular structure of [PtS_4(dppe)]; for clarity the hydrogen atoms on the phenyl rings have been omitted

Table 2. Selected intramolecular bond lengths (Å) in [PtS_4(dppe)] with estimated standard deviations in parentheses

Pt(1)–S(1)	2.327(3)	P(1)–C(1)	1.83(1)
Pt(1)–S(4)	2.344(3)	P(1)–C(111)	1.82(1)
Pt(1)–P(1)	2.250(2)	P(1)–C(121)	1.81(1)
Pt(1)–P(2)	2.250(2)	P(2)–C(2)	1.83(1)
S(1)–S(2)	2.069(5)	P(2)–C(211)	1.81(1)
S(2)–S(3)	2.012(6)	P(2)–C(212)	1.78(1)
S(3)–S(4)	2.047(5)	C(1)–C(2)	1.50(2)

Average phenyl C–C distances 1.38(2) Å

Table 3. Selected bond angles (°) with estimated standard deviations in parentheses

S(1)–Pt(1)–S(4)	95.3(1)	Pt(1)–S(1)–S(2)	104.5(2)
S(1)–Pt(1)–P(1)	171.8(1)	S(1)–S(2)–S(3)	99.8(2)
S(1)–Pt(1)–P(2)	88.0(1)	S(2)–S(3)–S(4)	101.0(2)
S(4)–Pt(1)–P(1)	90.7(1)	Pt(1)–S(4)–S(3)	102.9(2)
S(4)–Pt(1)–P(2)	171.7(1)	P(1)–Pt(1)–P(2)	86.8(1)
Pt(1)–P(1)–C(1)	107.0(3)	P(1)–C(1)–C(2)	109.5(8)
Pt(1)–P(1)–C(111)	115.0(4)	P(2)–C(2)–C(1)	108.2(8)
Pt(1)–P(1)–C(121)	118.4(4)	C(1)–P(1)–C(111)	106.5(5)
Pt(1)–P(2)–C(2)	106.1(4)	C(1)–P(1)–C(121)	102.7(5)
Pt(1)–P(2)–C(211)	119.4(4)	C(111)–P(1)–C(122)	106.0(6)
Pt(1)–P(2)–C(221)	112.7(4)	C(2)–P(2)–C(221)	106.4(5)
		C(211)–P(2)–C(221)	105.7(5)

Ring torsion angles (°)

Pt(1)–S(1)–S(2)–S(3)	−46.6	Pt(1)–P(1)–C(1)–C(2)	−34.8
S(1)–S(2)–S(3)–S(4)	61.8	P(1)–C(1)–C(2)–P(2)	−50.4
S(2)–S(3)–S(4)–Pt(1)	−50.5	C(1)–C(2)–P(2)–Pt(1)	−43.5
S(3)–S(4)–Pt(1)–S(1)	19.9	C(2)–P(2)–Pt(1)–P(1)	17.2
S(4)–Pt(1)–S(1)–S(2)	15.4	P(2)–Pt(1)–P(1)–C(1)	6.2

Average phenyl ring C–C–C bond angle 120(1.5)°

Table 4. Least-squares planes and deviations (Å) of atoms from the planes; X, Y, and Z are fractional co-ordinates in the direct cell

Plane A

Equation: $1.7127X - 29.5367Y - 2.9137Z = -2.667$

P(1) *	−0.143	Pt(1)	−0.019
P(2) *	0.147	S(2)	0.486
S(4) *	0.128	S(3)	−0.600
S(1) *	−0.131	C(1)	0.150
		C(2)	−0.434

Plane B

Equation: $-2.2230X + 28.7600Y + 3.5757Z = 2.244$

Pt(1) *		S(2)	−0.532
S(1) *		S(3)	0.678
S(4) *		P(1)	0.219
		P(2)	−0.300

Plane C

Equation: $1.0446X - 30.2630Y - 2.0725Z = -3.233$

Pt(1) *		S(1)	−0.257
P(1) *		S(4)	0.325
P(2) *		C(1)	0.189
		C(2)	−0.521

Dihedral angle between planes B and C = 170.2°

* These atoms define the plane.

The co-ordination geometry about the platinum atom in [PtS_4(dppe)] is best described as square planar, with two five-membered chelate rings associated with the dppe and S_4 ligands meeting at the metal atom. Thus the crystallographic determination confirms the tetrasulphido-structure (1) favoured by Chatt and Mingos [1], and eliminates the alternative structures (2) and (3). An examination of the best least-squares planes given in Table 4 suggests that the molecule is slightly distorted towards a tetrahedral geometry since the atoms S(1) and S(4) are displaced by −0.13 and 0.13 Å, respectively, and P(1) and P(2) by −0.14 and 0.15 Å, respectively, from the best least-squares plane passing through P(1), P(2), S(1), and S(4). The normals to the S(1)S(4)Pt(1) and P(1)P(2)Pt(1) planes consequently make an angle of 170.2°. The Pt(1)–P(1) and Pt(1)–P(2) distances are both 2.250(2) Å, and the P(1)Pt(1)P(2) bond angle is 86.8(1)°. These parameters are similar to those reported for dppe complexes of the platinum metals.[14] The slight difference in the Pt(1)–S(1) and Pt(1)–S(4) bond lengths of 0.017 Å is on the verge of statistical significance. A similar difference has been noted previously in $[Mo(S_4)_2S]^{2-}$, where the Mo–S distances are 2.387(1) and 2.331(1) Å, respectively.[15] Whether these small differences in bond lengths originate from packing or from subtle electronic effects is impossible to determine on the basis of the limited data currently available. The average Pt(1)–S distance of 2.336(3) Å is similar to that reported for the square-planar platinum(II) complex $[Pt(SH)_2(PPh_3)_2]$ [2.350(2) Å],[2] but somewhat shorter than that reported for the pentasulphidoplatinum(IV) complex $[Pt(S_5)_3]^{2-}$ [average 2.39(2) Å].[16]

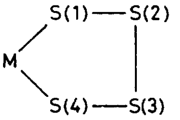
The S(1)–Pt(1)–S(4) bond angle of 95.3(1)° is somewhat larger than that reported for other MS_4 complexes, *e.g.* $[W(\eta\text{-}C_5H_5)_2S_4]$ [89.1(1)°],[17] $[Mo(\eta\text{-}C_5H_5)_2S_4]$ [88.2(2)°],[18] $[Mo(S_4)_2S]^{2-}$ [90.3(3)°],[15] and $[Mo_2S_{10}]^{2-}$ [85.1(1)°].[19] It is also larger than that reported for the corresponding angle in $[Pt(S_5)_3]^{2-}$ [average 92.3(3)°][16] and $[Pt(SH)_2(PPh_3)_2]$ [83.2(1)°].[2]

In common with other MS_4 complexes, the S_4 ring in [PtS_4(dppe)] is non-planar. The central sulphur atoms S(2) and S(3) are displaced −0.53 and 0.68 Å from the Pt(1)S(1)-S(4) plane. This leads to an approximate C_2 conformation for the PtS_4 ring. This conformation has been observed previously in $[Mo(\eta\text{-}C_5H_5)_2S_4]$[18] and $[W(\eta\text{-}C_5H_5)_2S_4]$,[17] where the displacements of atoms S(2) and S(3) are very similar (see Table 5). In $[Mo(S_4)_2S]^{2-}$ the MS_4 ring adopts a similar conformation, but the displacements of the central atoms are not equal, *i.e.* they are −0.22 and 1.20 Å. The MoS_4 ring in $[Mo_2S_{10}]^{2-}$ adopts a different conformation,[19] with both central sulphur atoms on the same side of the MoS(1)S(4) plane (see Table 5). In this molecule, however, crystallographic disorder problems have limited the accuracy of the structure.[19]

There is a small but distinct variation in the three S–S bond lengths in the PtS_4 ring of [PtS_4(dppe)]. The outer S(1)–S(2) and S(3)–S(4) bonds have an average length of 2.058(15) Å, which is 0.046 Å longer than the central S(2)–S(3) bond. These S–S bond distances lie in the range expected for sulphur rings; for example, the S–S bond length in orthorhombic sulphur is 2.037 Å.[20] Similar alternations in S–S bond lengths have been noted previously in molybdenum and tungsten MS_4 complexes (see Table 5, for example) and have been rationalised in terms of significant $M(d_\pi)$–$S(d_\pi)$ interactions which perturb the $S(d_\pi)$–$S(d_\pi)$ bonding between the central sulphur atoms. Extended Hückel molecular orbital calculations which we have completed on these molecules and which are described below suggest that d_π–d_π bonding effects are not an important contributor to the observed bond alternation effects.

Jones and Katz,[16] in their discussion of the structure of the $[Pt(S_5)_3]^{2-}$ ion, noted that the S–S–S bond angles, which are

Table 5. Comparison of the geometric parameters in related MS_4 systems [bond lengths (Å), bond angles (°)] *

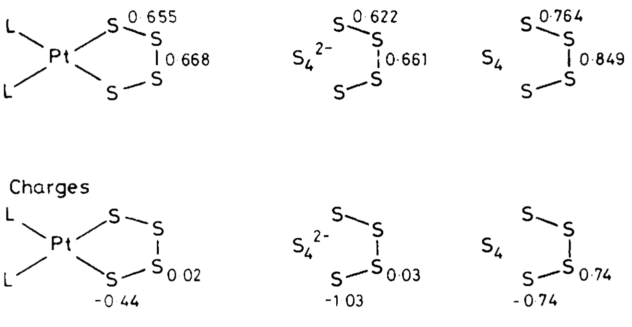


Parameter	Pt(A)	W(B)	Mo(C)	Mo(D)	Mo(E)	
					(a)	(b)
M-S(1)	2.327	2.420	2.450	2.331	2.403	
M-S(4)	2.344	2.419	2.456	2.387	2.408	
S(1)-S(2)	2.069	2.103	2.082	2.166	2.116	2.096
S(2)-S(3)	2.012	2.016	2.019	2.012	1.970	1.937
S(3)-S(4)	2.047	2.099	2.085	2.107	2.018	2.167
M-S(1)-S(2)	104.5	109.1	108.8	112.3	110.5	104.0
S(1)-S(2)-S(3)	99.8	101.0	100.8	100.2	102.1	81.5
S(1)-M-S(4)	95.3	89.1	88.2	90.3	85.1	85.1
S(2)-S(3)-S(4)	101.0	100.1	99.9	101.8	105.8	100.4
S(3)-S(4)-M	102.9	109.2	108.4	103.6	97.1	109.7
Deviations from least-squares plane (Å)						
S(2)	−0.53	−0.53	−0.53	−0.22	0.31	1.62
S(3)	0.68	0.65	0.65	1.20	1.32	0.38

* Pt(A), $[PtS_4(dppe)]$, this work; W(B), $[W(\eta\text{-}C_5H_5)_2S_4]$ from ref. 17; Mo(C), $[Mo(\eta\text{-}C_5H_5)_2S_4]$ from ref. 18; Mo(D), $[Mo(S_4)_2S]^{2-}$ from ref. 15; Mo(E), $[Mo_2S_{10}]^{2-}$ from ref. 19 [(a) and (b) refer to crystallographically distinct ions].

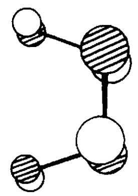
in the range 100.7—109.8°, were larger than those reported for S_8 rings (98.3—100.6°) and suggested that the PtS_5 rings in this ion might be experiencing considerable ring strain. The S-S-S bond angles in the $[PtS_4(dppe)]$ complex are 99.8(2) and 101.0(2)°, which suggests the presence of less ring strain. This difference in strain energies may be a contributing factor to the observation that $[Pt(S_5)_3]^{2-}$ reacts with PPh_3 to give $[PtS_4(PPh_3)_2]$, which has a smaller MS_4 ring.[3] Similarly, we have noted that the PtS_4 ring is resistant to further ring contraction when treated with tertiary phosphines.

Molecular Orbital Analysis of the Bonding in $[PtS_4(PH_3)_2]$.—In the previous section it was noted that the alternation of the S-S bond lengths within the MS_4 ring was a general structural feature of this class of compound. Therefore it was of interest to attempt to account for this observation using molecular orbital calculations. To this end we have completed molecular orbital calculations based on the extended Hückel [21] approximation on the model compound $[PtS_4(PH_3)_2]$. This approximate semi-empirical method has many well recognised deficiencies; nonetheless when used judiciously it can give considerable insight to bonding problems such as those posed above.[22] The relevant parameters used in the calculation are summarised in the Appendix. The computed Mulliken overlap populations and charges are summarised in the Scheme.



Scheme. Mulliken overlap populations and charges

For the $[PtS_4(PH_3)_2]$ complex, calculations on the S_4^{2-} ion and the neutral S_4 molecule are based on parameters which gave no weight to the 3*d* orbitals of sulphur. Subsequently, calculations were performed which included these orbitals in order to evaluate the importance of such interactions. The overlap populations (computed without sulphur 3*d* orbitals) summarised above reproduce the geometric feature associated with MS_4 complexes since the central S-S overlap population is larger than the other symmetry-related overlap populations. Furthermore, the related calculations on the S_4 species suggest that the bond alternation has its origins in the electronic characteristics of the free ligand. The larger difference in computed overlap populations for the free S_4 molecule can be ascribed to the nodal characteristics of the highest occupied molecular orbital in S_4^{2-}, (4). Since this molecular orbital is particularly strongly antibonding between the two central sulphur atoms, depopulation of this level leads to a corresponding strengthening of the S-S bond.



(4)

The calculated charge distributions for the S_4 species and the corresponding complex suggest a substantial donation of electron density from the S_4^{2-} ligand to the $Pt(PH_3)_2$ fragment, leading to a charge distribution for the co-ordinated S_4 ligand intermediate between those for S_4 and S_4^{2-}. Therefore, in this context it is interesting that a small degree of

Table 6. Orbital parameters

	Atomic orbital	H_{ij}/eV [a]	Slater exponent(s)	Ref.
H	1*s*	−13.60	1.300	27
P	3*s*	−18.60	1.600	27
	3*p*	−14.00	1.600	27
S	3*s*	−20.00	1.817	*b*
	3*p*	−13.30	1.817	*b*
	3*d*	−8.00	1.500	*b*
Pt	6*s*	−9.80	2.554	*c*
	6*p*	−5.35	2.554	*c*
	5*d*	−10.61	6.013 (c_1 0.633) 2.696 (c_2 0.551)	*d*

[a] 1 eV = 96.5 kJ mol^{-1}. [b] M. M.-L. Chen and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **8**, 1647. [c] F. A. Cotton and C. B. Harns, *Inorg. Chem.*, 1967, 6, 367. [d] H. Bash and H. B. Gray, *Theor. Chim. Acta*, 1966, 4, 367.

bond alternation has been noted in the *X*-ray structural determination of Na_2S_4 [terminal S–S 2.074(1), central S–S 2.061(1) Å],[23] but the difference is on the verge of statistical significance.

The introduction of 3*d* orbitals on the sulphur into the calculation with a valence state ionization of −8.00 eV (*i.e.* a value which would overemphasise any effects which resulted from *d* orbital involvement) leads to computed overlap populations which are in disagreement with the observed structures (*i.e.* a smaller overlap population for the central S–S bond), suggesting that the *d* orbital interactions do not play a major role in deciding the observed trends in bond lengths.

^{31}P-{^{1}H} *N.M.R. Spectra and Reactivity Studies.*—The ^{31}P-{^{1}H} n.m.r. spectra of $[PtS_4(dppe)]$ (1a) and $[PtS_4(PPh_3)_2]$ (1b) in halogenated solvents consist of simple 1 : 4 : 1 triplets characteristic of *cis*-$[PtL_2X_2]$ platinum(II) complexes [(1a) J_{Pt-P} = 2 814 Hz; (1b) J_{Pt-P} = 2 964 Hz].

Furthermore, a variable-temperature study of (1a) in CH_2Cl_2 in the temperature range +35 to −70 °C showed no large variations in chemical shift, coupling constant, or linewidths. This behaviour mirrors that reported previously for $[Mo(\eta\text{-}C_5H_5)_2S_4]$,[24] and contrasts with that reported for related compounds with MS_5 rings where the chair conformation leads to chemical inequivalence of the two cyclopentadienyl ligands.[25] The associated fluxional process has been studied by n.m.r. The observed n.m.r. characteristics for the tetrasulphidoplatinum complexes are therefore consistent with the solid-state structure.

Recently we have shown that the bridging sulphido ligands in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ are reasonably nucleophilic; for example they can be methylated with MeI giving $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$. This complex also reacts with a wide range of metal complexes, thereby providing a convenient route to mixed metal sulphido complexes.[26] Therefore, it was of interest to study the corresponding reactions of the tetrasulphido complexes of platinum(II).

Methyl iodide reacts readily with $[PtS_4(PPh_3)_2]$ and $[PtS_4(dppe)]$ in either thf or alcohols. However, the nature of the products is very sensitive to the molar ratios of the reactants and the reaction times. If long reaction times were used, with an excess of MeI, then the major product was $[PtI_2(PPh_3)_2]$ {or $[PtI_2(dppe)]$}. It also proved possible to isolate an intermediate of formula $[Pt(S_4Me_2)(PPh_3)_2]I_2$, when a molar ratio of 1 : 2 was used. Unfortunately, this product proved too insoluble for spectroscopic characterisation.

Both $[PtS_4(dppe)]$ and $[PtS_4(PPh_3)_2]$* react readily with the metal complexes $[PdCl_2(PhCN)_2]$ and $[Hg(dppe)Cl_2]$, in addition to $AgBF_4$ and $HgCl_2$. In each case analytical data for the resulting complexes suggested that 1 : 1 adducts were formed, but the complexes proved either too insoluble or unstable in halogenated organic solvents for them to be characterised completely.

Appendix

The molecular orbital calculations described in this paper were of the extended Hückel type;[27] and the relevant orbital parameters are summarised in Table 6. These parameters have been found to be satisfactory for molecular geometries of organometallic compounds.[22] The off-diagonal terms H_{ij} were estimated in the usual fashion[22] from $H_{ij} = kS_{ij}(H_{ii} + H_{jj})/2$ with $k = 1.75$. The geometry of the hypothetical $[PtS_4(PH_3)_2]$ molecule was derived from the structural parameters described in the paper for $[PtS_4(dppe)]$, except that the S–S bond lengths were all set equal to 2.043 Å in order not to bias the Mulliken overlap population analysis.

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* *Note added in proof*: Since submission of this paper, the structure of the related compound $[PtS_4(PPh_3)_2]\cdot CHCl_3$ has been reported (D. Dudis and J. P. Fackler, jun., *Inorg. Chem.*, 1982, **21**, 3577).

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