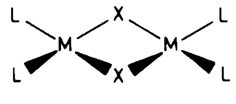
Chemistry of Platinum Sulphido-complexes. Part 4.[1] Dimeric μ-Alkylsulphido-complexes: Crystal and Molecular Structures of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]PF_6\cdot MeOH$ and *cis*-$[Pt_2(\mu\text{-}SMe)_2(NO_2)_2(PPh_3)_2]$ †

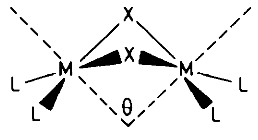
Clive E. Briant, Christopher J. Gardner, T. S. Andy Hor, Nigel D. Howells, and D. Michael P. Mingos *
Inorganic and Chemical Crystallography Laboratories, University of Oxford, South Parks Road, Oxford OX1 3QR

A study of the reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with halogenoalkanes has led to the isolation and and characterisation (^1H, ^{13}C, ^{31}P, and ^{195}Pt n.m.r.) of the complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]Y$ (R = Me or CH_2Cl; Y = Cl, I, PF_6, or BPh_4). The molecular structure of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]$-$PF_6\cdot MeOH$ has been determined by single-crystal *X*-ray techniques using diffractometer data. The compound crystallises in the monoclinic space group $P2_1/c$ with four formula units in a cell of dimensions $a = 22.835(7)$, $b = 13.094(4)$, $c = 24.357(9)$ Å, and $\beta = 110.99(3)°$. Least-squares refinement of the structure has led to the final *R* value of 0.056 using 3 551 observed intensities $[I \geqslant 3\sigma(I)]$. The related methylsulphido-complex *cis*-$[Pt_2(\mu\text{-}SMe)_2(NO_2)_2(PPh_3)_2]$ has been isolated from the reaction of $[Pt(SMe)_2(PPh_3)_2]$ and NO gas and characterised by single-crystal *X*-ray analysis. The compound crystallises in the triclinic space group $P\bar{1}$ with cell dimensions $a = 10.476(3)$, $b = 12.781(2)$, $c = 16.814(4)$ Å, $\alpha = 111.27(2)$, $\beta = 93.79(2)$, $\gamma = 76.06(2)°$, and $Z = 2$. Least-squares refinement led to a final *R* factor of 0.062 using 3 138 reflections having $I \geqslant 3\sigma(I)$.

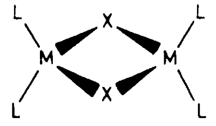
Three distinct co-ordination geometries have been established in the solid state for binuclear d^8 metal complexes by means of *X*-ray crystallographic studies. These alternative structures which are illustrated below can be derived either from square-planar [(A) and (B)] or tetrahedral [(C)] fragments and commonly have bridging groups such as S^{2-}, SR^-, PPh_2^-, and halide anions.[2] Examples include $[Pt_2Br_6]^{2-}$ [3] for (A) $[Rh_2Cl_2(CO)_4]$ [4] for (B), and $[Ir_2(PPh_2)_2(CO)_2(PPh_3)_2]$ [5] for (C). The structures (A) and (B) are closely related and very subtle electronic and crystal-packing effects appear to influence the extent of the hinge distortion since seemingly closely related complexes adopt alternative structures. In square-planar rhodium, palladium, and platinum complexes the dihedral angle (θ) which defines the extent of the hinge distortion in (B) varies from 120 to 140°. Structures of type (A) and (B) are commonly observed with bridging halide and alkylsulphido-ligands, whereas structure (C) is observed exclusively with diarylphosphido-ligands. The metal–metal bond lengths in compounds of type (C) are substantially shorter than those in comparable compounds of types (A) and (B). This observation can be rationalised in valence-bond terms by formulating the compounds with a formal double metal–metal bond. A molecular orbital analysis of this type of complex by Summerville and Hoffmann [2] has rationalised the occurrence of enhanced metal–metal bonding in (C) and suggested that the adoption of the alternative square-planar and tetrahedral geometries is related to the π-donor capabilities of the bridging ligands, with π-donor ligands such as S^{2-} and SR^- stabilising structures of the types (A) and (B).[2]



Flat square-planar
(A)



Hinged square-planar
(B)



Edge-shared tetrahedra
(C)

In 1970 Chatt and Mingos [6] reported the synthesis of the platinum(II) complex $[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$ and a subsequent *X*-ray crystallographic analysis established that the complex had the hinged square-planar geometry (B) with θ = 121°.[7] A similar complex was reported by Ugo *et al.*[8] in 1971, *i.e.* $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ from a reaction of elemental sulphur with $[Pt(PPh_3)_3]$. We have reinvestigated the reactions of this complex with alkyl halides and metal complexes. The current paper describes the characterisation of the products of the former class of reaction by spectroscopic and crystallographic techniques. Such a study also provided an opportunity for examining the way in which structures of types (A)—(C) could be influenced by the introduction of alkyl groups on the sulphido-ligands.

---

† μ-Methylsulphido-μ-sulphido-tetrakis(triphenylphosphine)-diplatinum(II) hexafluorophosphate-methanol (1/1) and *cis*-di-μ-methylsulphido-dinitrobis(triphenylphosphine)diplatinum(II) respectively.

Supplementary data available (No. SUP 23943, 35 pp.): full co-ordinates, thermal parameters, least-squares planes, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

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. Infrared spectra were obtained as Nujol mulls using a Pye Unicam SP2000 spectrometer. Melting points were measured using an Electrothermal apparatus and conductivities were recorded on a Philips 9505 bridge using a standard conductivity cell with a cell constant of 0.7 cm^{-1}.

^1H N.m.r. data were recorded using a Bruker WH-300 spectrometer and ^{13}C-$\{^1H\}$ spectra were recorded on the same spectrometer using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. The spectrum of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]PF_6$ (3a) was recorded on an enriched sample prepared from ^{13}C (90.5%) CH_3I as supplied by B.O.C. Ltd. ^{31}P-$\{^1H\}$ N.m.r. spectra were recorded on a Bruker WH90 spectrometer operating at 36.43 MHz, with trimethyl phosphate as the external standard. ^{195}Pt-$\{^1H\}$ N.m.r. spectra were recorded on a Bruker WH-400 spectrometer operating at 86.02 MHz at the University of Warwick. The samples were run in deuteriated solvents and the chemical shifts are reported with respect to $Na_2[PtCl_6]$ in D_2O as an external reference.

The complex $[Pt_2S_2(PPh_3)_4]$ was synthesised by standard literature methods, either from $[Pt(PPh_3)_3]$ and elemental sulphur or from $[PtCl_2(PPh_3)_2]$ and $Na_2S\cdot 9H_2O$.[8]

Preparations.—*μ-Methylsulphido-μ-sulphido-tetrakis(triphenylphosphine)diplatinum*(II) *iodide* (2a). An excess of MeI (1.5 cm^3, 24 mmol) was injected using a syringe into a suspension of $[Pt_2S_2(PPh_3)_4]$ (0.30 g, 0.20 mmol) in diethyl ether and then stirred for 3 h. The yellow precipitate was filtered off and recrystallised from CH_2Cl_2–light petroleum (b.p. 40—60 °C) to yield lemon yellow crystals of $[Pt_2(S)(SMe)(PPh_3)_4]I$ (2a), m.p. 255—258 °C, yield 0.22 g (67%) (Found: C, 52.4; H, 3.9; I, 9.1. $C_{73}H_{63}IP_4Pt_2S_2$ requires C, 53.2; H, 3.8; I, 7.7%). Molar conductivity: $\Lambda_m = 64.8$ ohm^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in nitromethane solution. I.r. (hexachlorobutadiene mull): $\nu_{asym}(CH_3)$, 3 070m; $\nu_{sym}(CH_3)$, 2 910w cm^{-1}. N.m.r. data: ^1H ($CDCl_3$ solution), δ 7.05—7.45 (m, 60 H, Ph), 1.48 p.p.m. [t, 3 H, SCH_3, $^3J(Pt-H)$ 34.3, $^4J(P_{trans}-H)$ 4.7 Hz]; ^{13}C-$\{^1H\}$ ($CDCl_3$ solution), δ 127—134 (m, 72 C, Ph), 21.93 p.p.m. [quin, 1 C, SCH_3, $^2J(CPt)$ 23.2 Hz]; ^{195}Pt-$\{^1H\}$ (CD_2Cl_2 solution), δ −4 368 p.p.m. [$^1J(PtP_A)$ 2 591, $^1J(PtP_B)$ 3 220, $^2J(Pt-Pt)$ 969.0 Hz]; ^{31}P-$\{^1H\}$ ($CHCl_3$ solution), δ 21.77 (P_A), 21.28 p.p.m. (P_B) [$^1J(P_A-Pt)$ 2 588, $^1J(P_B-Pt)$ 3 220, $^2J(P_A-P_B)$ 24, $^3J(P_A-Pt)$ 25, $^4J(P_A-P_{A'})$ 20, $^4J(P_A-P_{B'})$ 2, $^3J(P_B-Pt)$ 20, $^4J(P_B-P_{A'})$ 2, $^4J(P_B-P_{B'})$ 20 Hz].

μ-Methylsulphido-μ-sulphido-tetrakis(triphenylphosphine)diplatinum(II) *hexafluorophosphate* (3a). Addition of a saturated solution of NH_4PF_6 in methanol to a solution of (2a) in methanol led to a precipitation of $[Pt_2(S)(SMe)(PPh_3)_4]PF_6$ as microcrystals which were recrystallised from $CHCl_3$–MeOH to give orange-yellow prismatic crystals suitable for a single crystal *X*-ray analysis, m.p. 325—326 °C (Found: C, 52.5; H, 3.8. $C_{73}H_{63}F_6P_5Pt_2S_2$ requires C, 52.6; H, 3.8%).

μ-Methylsulphido-μ-sulphido-tetrakis(triphenylphosphine)diplatinum(II) *tetraphenylborate* (3b). Addition of a solution of $NaBPh_4$ in methanol to a solution of (2a) in methanol resulted in the precipitation of a yellow microcrystalline sample of $[Pt_2(S)(SMe)(PPh_3)_4]BPh_4$ (3b), m.p. 240—241 °C (Found: C, 62.7; H, 5.4. $C_{97}H_{83}BP_4Pt_2S_2$ requires C, 63.3; H, 5.4%).

μ-Chloromethylsulphido-μ-sulphido-tetrakis(triphenylphosphine)diplatinum(II) *chloride* (2b). Recrystallisation of $[Pt_2S_2(PPh_3)_4]$ from CH_2Cl_2–MeOH yielded $[Pt_2(S)(SCH_2Cl)(PPh_3)_4]Cl$ (2b) in high yield (90%) as a yellow crystalline solid, m.p. 220—224 °C (Found: C, 53.5; H, 4.0; Cl, 4.5. $C_{76}H_{74}Cl_2O_3P_4Pt_2S_2$ requires C, 54.2; H, 4.4; Cl, 4.2%). N.m.r. data: ^1H ($CDCl_3$ solution), δ 7.05—7.45 (m, 60 H, Ph), 4.14 p.p.m. [t, 2 H, SCH_2, $^3J(Pt-H)$ 29.8, $^4J(P_{trans}-H)$ 3.0 Hz]; ^{31}P-$\{^1H\}$ (CH_2Cl_2 solution) δ, 20.00 [P_A(*trans* to μ-S)], 20.00 p.p.m. (P_B) [$^1J(P_A-Pt)$ 2 622, $^1J(P_B-Pt)$ 3 419 Hz]; ^{195}Pt-$\{^1H\}$ (CD_2Cl_2 solution), δ −4 401 p.p.m. [$^1J(Pt-P_A)$ 2 612, $^1J(Pt-P_B)$ 3 402 Hz].

The analogous PF_6^- (3c) and BPh_4^- (3d) salts were prepared by adding saturated methanolic solutions of NH_4PF_6 and $NaBPh_4$ to a methanolic solution of (2b), and were recrystallised from CH_2Cl_2–MeOH. $[Pt_2(S)(SCH_2Cl)(PPh_3)_4]PF_6$ (3c), m.p. 245—246 °C (Found: C, 51.5; H, 3.6; Cl, 2.0. $C_{73}H_{62}ClF_6P_5Pt_2S_2$ requires C, 51.6; H, 3.7; Cl, 2.1%). Molar conductivity: $\Lambda_m = 72.5$ ohm^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in nitromethane solution. $[Pt_2(S)(SCH_2Cl)(PPh_3)_4]BPh_4$ (3d), m.p. 185—187 °C (decomp.) (Found: C, 60.6; H, 4.5. $C_{98}H_{84}BCl_3P_4Pt_2S_2$ requires C, 60.1; H, 4.3%).

μ-Dichloromethylsulphido-μ-sulphido-tetrakis(triphenylphosphine)diplatinum(II) *chloride*. Recrystallisation of $[Pt_2S_2(PPh_3)_4]$ from $CHCl_3$–MeOH gave a yellow crystalline sample of $[Pt_2(S)(SCHCl_2)(PPh_3)_4]Cl$ in high yield (90%) (Found: C, 54.0; H, 3.7; Cl, 6.1. $C_{73}H_{61}Cl_3P_4Pt_2S_2$ requires C, 54.0; H, 3.8; Cl, 6.6%).

Di-iodobis(iodomethyl)bis(triphenylphosphine)platinum(IV)–*ethanol* (1/1), $[Pt(CH_2I)_2I_2(PPh_3)_2]\cdot EtOH$. To a suspension of $[Pt_2S_2(PPh_3)_4]$ (0.20 g, 0.13 mmol) in ethanol (20 cm^3) was added excess CH_2I_2 (0.10 cm^3) in ethanol (20 cm^3). The colour of the suspension slowly turned from orange to yellow and prolonged stirring (3 d) yielded a pale yellow precipitate. The precipitate was filtered off, washed well with ethanol and diethyl ether, and dried *in vacuo* for 6 h, m.p. 230—234 °C (decomp.), yield 0.19 g (57%) (Found: C, 37.6; H, 2.9; I, 39.0. $C_{40}H_{40}I_4OP_2Pt$ requires C, 36.9; H, 3.1; I, 39.0%). The complex was only sparingly soluble in $CHCl_3$ and CH_2Cl_2 and insoluble in all other common organic solvents.

Di-μ-sulphido-tetrakis(triphenylphosphine)diplatinum(II)–*tetracyanoethylene* (1/1). A solution of tetracyanoethylene (tcne) (0.05 g) in diethyl ether (10 cm^3) was slowly added to a suspension of $[Pt_2S_2(PPh_3)_4]$ (0.15 g) in diethyl ether (50 cm^3). The solution turned dark green on mixing and on standing for 1.5 h a dark green solid separated from the mixture. The precipitate was filtered off and washed well with diethyl ether, yield 0.13 g (81%) (Found: C, 57.5; H, 4.2; N, 3.3. $C_{78}H_{60}N_4P_4Pt_2S_2$ requires C, 57.4; H, 3.7; N, 3.4%). Molar conductivity: $\Lambda_m = 46$ ohm^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in nitromethane. I.r. (Nujol mull): $\nu(C\equiv N)$, 2 195; $\nu(C=C)$, 1 372 cm^{-1}. Electronic spectra (CH_2Cl_2 solution): $\lambda_{max.}$ 262 (log $\varepsilon_{max.}$ 4.13), 274 (4.03), 305 (3.80), 400 nm (3.70).

Di-μ-methylsulphido-dinitro-bis(triphenylphosphine)diplatinum(II) (4). *cis*-$[Pt(SMe)_2(PPh_3)_4]$ (0.40 g, 0.49 mmol) was dissolved in $CHCl_3$ (30 cm^3) and NO gas was bubbled through the solution for 5 min. The solution was concentrated under reduced pressure and slow addition of hexane resulted in the precipitation of a pale yellow solid, which was recrystallised from benzene–hexane, m.p. 224 °C, yield 0.30 g (Found: C, 41.7; H, 3.7; N, 2.1. $C_{38}H_{36}N_2O_4P_2Pt_2S_2$ requires C, 41.5; H, 3.3; N, 2.5%). N.m.r. data: ^1H (CD_2Cl_2 solution), δ 7.2—7.8 (m, 30 H, Ph), 1.94 p.p.m. [d, 3 H, SCH_3, $^3J(Pt-H)$ 45.8, $^4J(P-H)$ 6.3 Hz]; ^{31}P-$\{^1H\}$ (CH_2Cl_2 solution), δ 12.52 p.p.m. [s, 2 P, $^1J(Pt-P)$ 3 050 Hz].

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

Table 1. Fractional co-ordinates for $[Pt_2(S)(SMe)(PPh_3)_4]PF_6\cdot MeOH$ (3a)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt(1)	0.337 04(4)	0.302 54(8)	0.530 02(3)	C(311)	0.098(1)	0.091(2)	0.419(1)
Pt(2)	0.188 98(4)	0.302 44(8)	0.439 89(3)	C(312)	0.127(1)	0.087(2)	0.477(1)
P(1)	0.373 0(3)	0.367 0(5)	0.622 6(3)	C(313)	0.109(2)	0.017(3)	0.517(1)
P(2)	0.405 5(3)	0.170 4(5)	0.536 9(3)	C(314)	0.060(1)	−0.046(2)	0.484(1)
P(3)	0.131 0(3)	0.176 9(5)	0.379 4(3)	C(315)	0.031(2)	−0.047(3)	0.427(2)
P(4)	0.111 6(3)	0.380 2(5)	0.462 3(3)	C(316)	0.051(2)	0.026(3)	0.394(2)
S(1)	0.283 5(3)	0.246 2(5)	0.432 2(3)	C(321)	0.173(1)	0.089(2)	0.348(1)
S(2)	0.256 3(3)	0.420 2(5)	0.503 3(3)	C(322)	0.185(1)	0.126(2)	0.300(1)
C(1)	0.297(1)	0.347(2)	0.387(1)	C(323)	0.220(2)	0.058(3)	0.277(2)
C(111)	0.351(1)	0.286(2)	0.672 8(9)	C(324)	0.235(2)	−0.033(3)	0.295(2)
C(112)	0.354(1)	0.323(2)	0.727(1)	C(325)	0.221(2)	−0.072(3)	0.342(2)
C(113)	0.337(1)	0.257(2)	0.765(1)	C(326)	0.190(1)	−0.003(2)	0.370(1)
C(114)	0.315(1)	0.162(2)	0.747(1)	C(331)	0.070(1)	0.225(2)	0.314(1)
C(115)	0.311(1)	0.126(2)	0.692(1)	C(332)	0.076(1)	0.318(2)	0.297(1)
C(116)	0.328(1)	0.189(2)	0.655 1(9)	C(333)	0.034(2)	0.360(3)	0.243(2)
C(121)	0.344(1)	0.490(2)	0.632(1)	C(334)	−0.015(2)	0.307(3)	0.213(1)
C(122)	0.284(1)	0.502(2)	0.636(1)	C(335)	−0.022(2)	0.211(3)	0.226(2)
C(123)	0.264(1)	0.597(2)	0.645(1)	C(336)	0.022(2)	0.164(3)	0.278(2)
C(124)	0.296(1)	0.681(2)	0.644(1)	C(411)	0.030(1)	0.366(2)	0.414(1)
C(125)	0.351(1)	0.672(2)	0.639(1)	C(412)	−0.001(1)	0.443(2)	0.374(1)
C(126)	0.375(1)	0.579(2)	0.631(1)	C(413)	−0.062(1)	0.430(2)	0.332(1)
C(131)	0.456(1)	0.382(2)	0.654(2)	C(414)	−0.088(1)	0.339(2)	0.338(1)
C(132)	0.490(1)	0.360(2)	0.713(1)	C(415)	−0.063(1)	0.265(2)	0.374(1)
C(133)	0.554(2)	0.379(3)	0.735(2)	C(416)	−0.000(1)	0.279(2)	0.414(1)
C(134)	0.582(2)	0.423(3)	0.701(2)	C(421)	0.110(1)	0.337(2)	0.533(1)
C(135)	0.551(2)	0.445(3)	0.644(2)	C(422)	0.158(1)	0.299(2)	0.573(1)
C(136)	0.487(1)	0.425(2)	0.621(1)	C(423)	0.157(1)	0.260(2)	0.627(1)
C(211)	0.432(1)	0.186(2)	0.474 0(9)	C(424)	0.102(1)	0.270(2)	0.638(1)
C(212)	0.423(1)	0.106(2)	0.434(1)	C(425)	0.051(1)	0.315(2)	0.598(1)
C(213)	0.445(1)	0.127(2)	0.387(1)	C(426)	0.055(1)	0.350(2)	0.545(1)
C(214)	0.473(1)	0.215(2)	0.382(1)	C(431)	0.123(1)	0.519(2)	0.465(1)
C(215)	0.481(1)	0.290(2)	0.422(1)	C(432)	0.117(1)	0.579(2)	0.508(1)
C(216)	0.459(1)	0.270(2)	0.469(1)	C(433)	0.130(1)	0.680(2)	0.509(1)
C(221)	0.366(1)	0.048(2)	0.528 5(9)	C(434)	0.143(1)	0.726(2)	0.462(1)
C(222)	0.304(1)	0.041(2)	0.523(1)	C(435)	0.147(1)	0.667(2)	0.420(1)
C(223)	0.279(1)	−0.054(2)	0.520(1)	C(436)	0.138(1)	0.565(2)	0.421(1)
C(224)	0.309(1)	−0.142(2)	0.523(1)	P(5)	0.189 3(5)	0.563 6(9)	0.247 0(5)
C(225)	0.373(1)	−0.136(2)	0.530(1)	F(1)	0.260 3(9)	0.557(2)	0.279(1)
C(226)	0.400(1)	−0.043(2)	0.532(1)	F(2)	0.118 6(9)	0.571(2)	0.216(1)
C(231)	0.474(1)	0.147(2)	0.601(1)	F(3)	0.179(2)	0.539(3)	0.304(1)
C(232)	0.471(1)	0.108(2)	0.651(1)	F(4)	0.198(2)	0.586(3)	0.189(1)
C(233)	0.524(2)	0.095(3)	0.700(1)	F(5)	0.185(2)	0.449(2)	0.234(1)
C(234)	0.580(1)	0.118(2)	0.699(1)	F(6)	0.193(2)	0.676(2)	0.261(2)
C(235)	0.589(2)	0.157(3)	0.653(1)	C(99)	0.684(2)	0.368(4)	0.570(2)
C(236)	0.536(1)	0.174(2)	0.602(1)	O(99)	0.616(2)	0.426(3)	0.528(2)

Crystal data for $[Pt_2(S)(SMe)(PPh_3)_4]PF_6$ (3a). $C_{74}H_{67}F_6OP_5Pt_2S_2$, M = 1 694, monoclinic, space group $P2_1/c$ (no. 14), a = 22.835(7), b = 13.094(4), c = 24.357(9) Å, β = 110.99(3)°, U = 6 799.5 Å^3, Z = 4, D_c = 1.66 g cm^{-3}, $F(000)$ = 3 344 electrons, μ(Mo-K_α) = 45.65 cm^{-1}.

Orange-yellow prismatic crystals of compound (3a) were grown by the slow diffusion of methanol into a dichloromethane solution and a suitable crystal of dimensions 0.5 × 0.3 × 0.2 mm was sealed in a 0.7 mm Lindemann capillary tube and mounted on an Enraf-Nonius CAD4F diffractometer. The intensities of 6 347 reflections ($\theta_{max.}$ = 20°) were measured using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). 3 551 Independent reflections [$I \geqslant 3\sigma(I)$], corrected for absorption empirically,[12] 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. The Pt, S, and P atoms were refined anisotropically. Ring hydrogens were located in difference maps and then placed geometrically (C–H = 0.90 Å, U_{iso} = 0.075 Å^2), their positions being adjusted after each cycle. The final R value was 0.056 [R' = 0.070 (400 parameters)]. The SMe hydrogen atoms could not be located and therefore were omitted from the final cycles of least-squares refinement.

A Chebyshev weighting scheme was used with the coefficients 17.039, 21.937, and 7.737.[13] Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1 and selected intramolecular bond lengths and angles in Table 2.

Crystal data for $[Pt_2(SMe)_2(NO_2)_2(PPh_3)_2]$ (4). $C_{38}H_{36}N_2O_4P_2Pt_2S_2$, M = 1 100.8, triclinic, space group $P\bar{1}$ (no. 2), a = 10.476(3), b = 12.781(2), c = 16.814(4) Å, α = 111.27(2), β = 93.79(2), γ = 76.06(2)°, U = 2 035.5 Å^3, Z = 2, D_c = 1.79 g cm^{-3}, $F(000)$ = 1 056 electrons, μ(Mo-K_α) = 74.4 cm^{-1}.

The data were collected as described above (crystal dimensions 0.3 × 0.1 × 0.1 mm) for compound (3a) and the solution of the structure and the refinement followed the patterns described above. For 6 525 independent reflections ($\theta_{max.}$ = 22.5°) 3 138 had $I \geqslant 3\sigma(I)$, which were used in the refinement. The final R value was 0.062 [R' = 0.080 (231 parameters)]. A Chebyshev weighting scheme [13] was used with the coefficients 59.460, 80.795, and 28.364. Final atomic co-

Table 2. Selected geometric parameters for the $[Pt_2(S)(SMe)(PPh_3)_4]^+$ cation in (3a)

(*a*) Distances (Å)			
Pt(1)–S(1)	2.374(6)	Pt(2)–S(1)	2.351(6)
Pt(1)–S(2)	2.311(6)	Pt(2)–S(2)	2.329(6)
Pt(1)–P(1)	2.269(5)	Pt(2)–P(3)	2.286(5)
Pt(1)–P(2)	2.298(5)	Pt(2)–P(4)	2.268(5)
Pt(1)–Pt(2)	3.306(1)	S(1)–S(2)	3.058(8)
S(1)–C(1)	1.81(2)		
Mean			
P(1)–C(phenyl)	1.79(1)	P(2)–C(phenyl)	1.82(1)
P(3)–C(phenyl)	1.81(1)	P(4)–C(phenyl)	1.83(1)
(*b*) Angles (°)			
S(1)–Pt(1)–S(2)	81.5(2)	S(1)–Pt(2)–S(2)	81.6(2)
S(1)–Pt(1)–S(2)	86.0(2)	S(1)–Pt(2)–P(3)	93.4(2)
S(2)–Pt(1)–P(1)	90.0(2)	S(2)–Pt(2)–P(4)	85.9(2)
P(1)–Pt(1)–P(2)	102.3(2)	P(3)–Pt(2)–P(4)	99.0(2)
Pt(1)–S(1)–Pt(2)	88.9(2)	Pt(1)–S(2)–Pt(2)	90.9(2)
C(1)–S(1)–Pt(1)	104.0(8)	C(1)–S(1)–Pt(2)	100.2(8)
Mean			
Pt(1)–P(1)–C(phenyl)	114(1)	Pt(2)–P(3)–C(phenyl)	114(1)
Pt(1)–P(2)–C(phenyl)	113(3)	Pt(2)–P(4)–C(phenyl)	114(3)
(*c*) Torsion angles (°)			
C(1)–S(1)–Pt(1)–P(1)	94(1)	C(1)–S(1)–Pt(1)–P(2)	−111(1)
C(1)–S(1)–Pt(2)–P(3)	108(1)	C(1)–S(1)–Pt(2)–P(4)	−78(1)

Table 3. Fractional co-ordinates for *cis*-$[Pt_2(SMe)_2(NO_2)_2(PPh_3)_2]$ (4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt(1)	−0.010 7(1)	0.679 3(1)	−0.105 2(1)
Pt(2)	0.014 4(1)	0.442 5(1)	−0.280 5(1)
P(1)	−0.195 2(6)	0.817 9(5)	−0.049 5(4)
P(2)	−0.143 6(7)	0.378 5(6)	−0.371 0(4)
S(1)	−0.101 8(6)	0.631 0(5)	−0.238 0(4)
S(2)	0.163 1(6)	0.525 3(6)	−0.180 2(4)
N(1)	0.078 4(19)	0.705 0(17)	0.009 8(12)
O(11)	0.148 3(22)	0.769 4(20)	0.030 2(15)
O(12)	0.063 8(23)	0.653 8(21)	0.054 0(16)
N(2)	0.130 4(22)	0.280 9(19)	−0.306 9(14)
O(21)	0.091 5(25)	0.207 4(23)	−0.293 2(17)
O(22)	0.235 2(27)	0.255 3(24)	−0.342 5(17)
C(1)	−0.023 6(34)	0.686 9(31)	−0.299 9(23)
C(2)	0.210 4(33)	0.440 5(30)	−0.112 3(22)
C(111)	−0.197 2(24)	0.932 9(22)	0.056 7(16)
C(112)	−0.203 9(25)	1.051 6(23)	0.065 5(17)
C(113)	−0.211 9(32)	1.124 6(29)	0.142 1(22)
C(114)	−0.205 1(31)	1.099 6(29)	0.215 2(21)
C(115)	−0.183 9(34)	0.985 3(31)	0.204 3(22)
C(116)	−0.176 3(30)	0.901 3(26)	0.125 4(20)
C(121)	−0.255 6(25)	0.894 7(22)	−0.121 5(16)
C(122)	−0.168 3(28)	0.952 4(25)	−0.141 3(19)
C(123)	−0.211 1(33)	1.005 5(29)	−0.201 7(21)
C(124)	−0.328 8(33)	1.001 4(30)	−0.238 7(22)
C(125)	−0.412 1(37)	0.941 4(33)	−0.221 0(24)
C(126)	−0.371 9(28)	0.889 1(25)	−0.162 5(18)
C(131)	−0.325 9(25)	0.754 1(22)	−0.034 9(16)
C(132)	−0.324 5(29)	0.638 9(26)	−0.083 9(18)
C(133)	−0.423 7(33)	0.590 6(29)	−0.066 6(21)
C(134)	−0.531 2(34)	0.660 0(31)	−0.018 3(22)
C(135)	−0.542 5(29)	0.773 5(26)	0.018 4(19)
C(136)	−0.436 6(29)	0.822 8(26)	0.015 1(19)
C(211)	−0.266 8(28)	0.349 0(25)	−0.315 1(18)
C(212)	−0.228 3(28)	0.317 4(25)	−0.246 5(18)
C(213)	−0.321 4(27)	0.288 9(23)	−0.205 6(17)
C(214)	−0.441 1(34)	0.293 1(30)	−0.229 1(21)
C(215)	−0.484 4(33)	0.328 4(30)	−0.295 1(22)
C(216)	−0.395 5(33)	0.351 6(29)	−0.346 0(21)
C(221)	−0.088 5(28)	0.245 8(25)	−0.459 5(18)
C(222)	−0.166 9(28)	0.169 4(25)	−0.488 3(18)
C(223)	−0.117 1(35)	0.066 6(31)	−0.561 9(23)
C(224)	−0.002 7(37)	0.051 6(33)	−0.594 2(24)
C(225)	0.084 0(33)	0.127 4(30)	−0.569 6(22)
C(226)	0.032 0(24)	0.238 7(21)	−0.497 9(15)
C(231)	−0.232 8(26)	0.480 3(23)	−0.420 7(17)
C(232)	−0.194 3(31)	0.471 9(28)	−0.499 2(20)
C(233)	−0.249 4(38)	0.555 0(34)	−0.532 0(25)
C(234)	−0.342 6(39)	0.643 1(35)	−0.489 0(26)
C(235)	−0.387 7(38)	0.652 9(35)	−0.414 9(26)
C(236)	−0.331 1(31)	0.577 5(28)	−0.373 1(21)

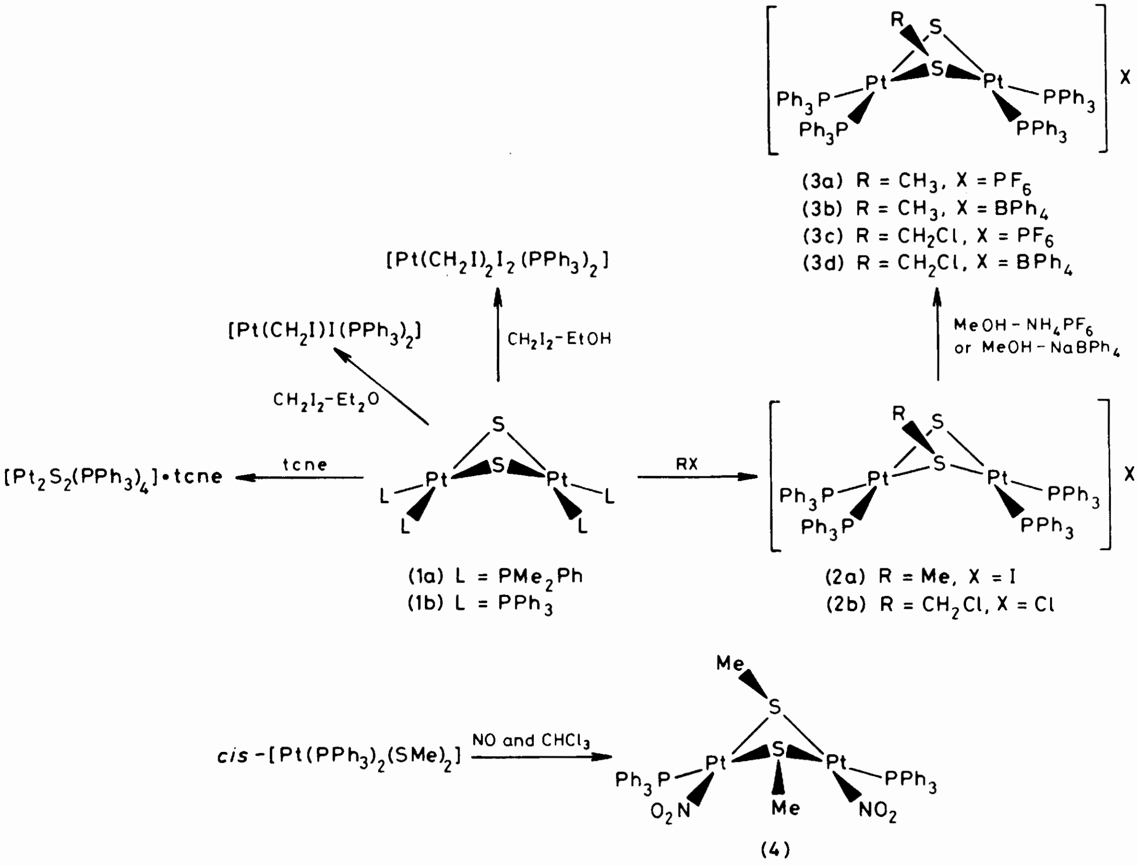
ordinates for the non-hydrogen atoms are given in Table 3 and selected intramolecular bond lengths and bond angles are presented in Table 4.

Results and Discussion

In 1971 Ugo *et al.*[8] reported the synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (1b), which is presumably isostructural with the complex $[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$ (1a), synthesised by Chatt and Mingos [6] and characterised using *X*-ray crystallography by Mason *et al.*[7] Attempts structurally to characterise (1b) by crystallographic techniques were hampered by its insolubility in the majority of organic solvents and its reactivity towards halogenated solvents. These reactions are summarised in the Scheme.

When a suspension of (1b) in Et_2O was treated with an excess of MeI, $[Pt_2(S)(SMe)(PPh_3)_4]I$ (2a) was obtained as a yellow microcrystalline solid. Its formulation as a 1 : 1 electrolyte was confirmed by its molar conductance in nitromethane (Λ_m = 64.8 ohm^{-1} cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} solution) and the isolation of the corresponding PF_6^- and BPh_4^- salts (3a) and (3b) by the metathetical reactions indicated in the Scheme. The related compound $[Pt_2(S)(SCH_2Cl)(PPh_3)_4]Cl$ (2b) was isolated when $[Pt_2S_2(PPh_3)_4]$ was recrystallised from CH_2Cl_2 and converted into the corresponding PF_6^- and BPh_4^- salts (3c) and (3d) also by metathetical reactions. With the more reactive CH_2I_2 the yields of the binuclear monomethylated compound were found to be lower and the compound $[Pt(CH_2I)I(PPh_3)_2]$ previously reported by Lappert and co-workers [14] was also isolated when the reaction was undertaken in Et_2O. When the reaction was repeated in ethanol then the platinum(IV) compound $[Pt(CH_2I)_2I_2(PPh_3)_2]$ was isolated as the major product.

A single-crystal *X*-ray analysis of $[Pt_2(S)(SMe)(PPh_3)_4]PF_6$ (3a) has confirmed that it had been formulated correctly as the monomethylated derivative. We have no evidence in our studies of the dimethylated derivatives proposed by Ugo *et al.*[8] on the basis of analytical and conductivity measurements. The molecular geometry of (3a) illustrated in Figure 1 clearly established that the complex belongs to the hinged square-planar class of compound (B). The hinge angle in (3a) is approximately 138° (see Table 5). A similar hinged square-planar geometry has been observed for $[Pt_2S_2(PMe_2Ph)_4]$ (1a) (hinge angle = 121°) [7] and in both complexes there is no evidence for substantial metal–metal bonding since the platinum atoms are separated by at least 3.10 Å. In (3a) the methyl group of the methylsulphido-ligand is directed away from the direction of the hinge distortion in a manner which might have been anticipated from simple steric considerations. A more detailed comparison of the structural parameters associated with $[Pt_2S_2(PMe_2Ph)_4]$ (1a) and $[Pt_2(S)(SMe)(PPh_3)_4]PF_6$ (3a) is given in Table 5 and will be discussed further in relation to the structure of $[Pt_2(SMe)_2(NO_2)_2(PPh_3)_2]$ (4).



Scheme.

Table 4. Selected geometric parameters for *cis*-$[Pt_2(SMe)_2(NO_2)_2(PPh_3)_2]$ (4)

(*a*) Distances (Å)			
Pt(1)–S(1)	2.298(6)	Pt(2)–S(1)	2.291(6)
Pt(1)–S(2)	2.356(6)	Pt(2)–S(2)	2.351(6)
Pt(1)–P(1)	2.265(6)	Pt(2)–P(2)	2.267(6)
Pt(1)–Pt(2)	3.342(1)	S(1)–S(2)	3.040(9)
S(1)–C(1)	1.79(3)	S(2)–C(2)	1.82(3)
Pt(1)–N(1)	2.04(2)	Pt(2)–N(2)	2.03(2)
N(1)–O(11)	1.18(3)	N(2)–O(21)	1.21(3)
N(1)–O(12)	1.19(3)	N(2)–O(22)	1.21(3)
Mean P(1)–C(phenyl)	1.83(1)	P(2)–C(phenyl)	1.82(1)
(*b*) Angles (°)			
S(1)–Pt(1)–S(2)	81.6(2)	S(1)–Pt(2)–S(2)	81.8(2)
S(1)–Pt(1)–P(1)	90.4(2)	S(1)–Pt(2)–P(2)	92.9(2)
S(2)–Pt(1)–N(1)	93.7(5)	S(2)–Pt(2)–N(2)	91.9(6)
N(1)–Pt(1)–P(1)	94.2(5)	N(2)–Pt(2)–P(2)	93.4(6)
Pt(1)–S(1)–Pt(2)	93.5(2)	Pt(1)–S(2)–Pt(2)	90.5(2)
Pt(1)–N(1)–O(11)	118(2)	Pt(2)–N(2)–O(21)	121(2)
Pt(1)–N(1)–O(12)	122(2)	Pt(2)–N(2)–O(22)	121(2)
O(11)–N(1)–O(12)	120(2)	O(21)–N(2)–O(22)	118(3)
Mean Pt(1)–P(1)–C(phenyl)	115(4)	Pt(2)–P(2)–C(phenyl)	114(2)
(*c*) Torsion angles (°)			
P(1)–Pt(1)–S(1)–C(1)	106(1)	P(1)–Pt(1)–S(2)–C(2)	−121(1)
P(2)–Pt(2)–S(1)–C(1)	−100(1)	P(2)–Pt(2)–S(2)–C(2)	115(1)
N(1)–Pt(1)–S(1)–C(1)	−112(1)	N(1)–Pt(1)–S(2)–C(2)	42(1)
N(2)–Pt(2)–S(1)–C(1)	93(1)	N(2)–Pt(2)–S(2)–C(2)	−46(1)

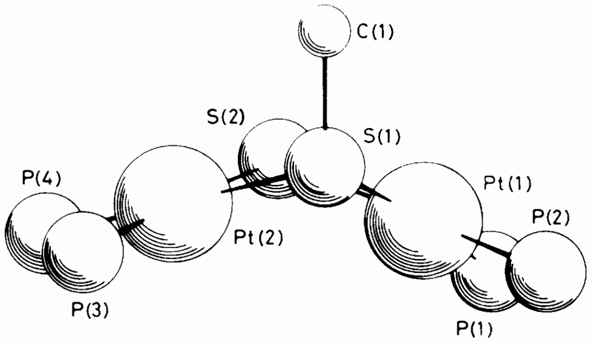


Figure 1. Molecular structure of the cation in $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]PF_6{\cdot}MeOH$ (3a). For reasons of clarity the phenyl rings have not been shown

Chatt and Hart [15] isolated di-μ-alkylsulphido-complexes of platinum(II) of the type $[Pt_2(\mu\text{-}SR)_2X_2(PR_3)_2]$ (X = Cl or SR) from the corresponding binuclear halide-bridged complexes. The complexes were isolated as *cis*- and *trans*-isomers and an example of the former type, *viz.* $[Pt_2(\mu\text{-}SEt)_2Cl_2(PR_3)_2]$,[16] has been characterised by a single-crystal *X*-ray analysis. As part of a general study of the reactions of mononuclear complexes of the type *cis*-$[Pt(SR)_2(PPh_3)_2]$ [17] we have isolated $[Pt_2(\mu\text{-}SMe)_2(NO_2)_2(PPh_3)_2]$ (4) and characterised it by a single-crystal *X*-ray analysis. The results for (4) are also presented here because of their obvious relevance to a discussion of the structure of (3a).

Table 5. Comparison of the geometric parameters [distances (Å) and angles (°)] for $[Pt_2S_2(PMe_2Ph)_4]$ (1a), $[Pt(S)(SMe)(PPh_3)_4]PF_6$ (3a), $[Pt(SMe)_2(NO_2)_2(PPh_3)_2]$ (4), and $[Pt(SEt)_2Cl_2(PPr^i{}_3)_2]$ (5)

	(1) [a]	(3a) [b]	(4) [b]	(5) [c]
Mean Pt-S	2.340(8)	2.320(8)		
Mean Pt-SR		2.363(11)	2.294(3), [d] 2.354(2) [e]	2.274(7), [d] 2.371(7) [e]
Mean Pt-P	2.265(7)	2.276(7)	2.266(1)	2.262(5)
Pt-Pt	3.175(2)	3.306(1)	3.342(1)	3.206(1)
S-S	3.06(2)	3.06(1)	3.04(1)	2.99(1)
Mean Pt-S-Pt	85.5(4)	90.0(10)	92.0(15)	87.0(20)
Mean S-Pt-P	89.5(3)	88.8(18)	91.7(1)	96.1(2)
Mean S-Pt-S	81.6(4)	81.6(1)	81.7(1)	80.2(3)
Dihedral angle between square planar units [f]	121	138	141	130

[a] From ref. 7. [b] Present work. [c] From ref. 16. [d] *cis* to PR_3. [e] *trans* to PR_3. [f] Equations of least-squares planes are given in SUP No. 23943.

The molecular structure of (4) which is illustrated in Figure 2 has demonstrated that the compound also has a hinged square-planar geometry with a hinge angle of 141°. The methyl groups of the methylsulphido-ligands adopt an *anti* conformation [18] with the methyl group adjacent to the *cis* PPh_3 ligands pointing away from the direction of the hinge distortion and the methyl group adjacent to the NO_2 ligands pointing in the hinge direction. This conformation can readily be rationalised in terms of the different steric requirements of the PPh_3, SMe, and NO_2 ligands.

A comparison of the geometric parameters for $[Pt_2S_2(PMe_2Ph)_4]$ (1a),[7] $[Pt_2(S)(SMe)(PPh_3)_4]PF_6$ (3a), $[Pt_2(SMe)_2(NO_2)_2(PPh_3)_2]$ (4), and $[Pt_2(\mu\text{-}SEt)_2Cl_2(PPr^i{}_3)_2]$ (5) [16] is given in Table 5 and demonstrates the close relationship between the four structures. All the complexes have the hinged geometry (B). The hinge angle in the disulphido-complex is the smallest (121°), the others lying in the range 130—141°. The Pt-Pt and S-S distances similarly lie within narrow ranges, 3.18—3.34 (Pt-Pt) and 2.99—3.06 Å (S-S).

The platinum-phosphorus bond lengths in the compounds are almost identical (2.26—2.30 Å) although the substituents and the number of phosphine ligands on each platinum differ. In contrast the Pt-S bond lengths are very sensitive to the *trans* influence of the *trans* ligands.[19] When the sulphido-ligands are *trans* to PR_3 the Pt-S bond length lies in the range 2.32—2.37 Å, whereas it is 2.294(3) Å when *trans* to NO_2 and 2.274(7) Å when *trans* to Cl. It is interesting that although the alkyl- or aryl-phosphine or sulphido-ligands have comparable electronegativities and polarisabilities it is the sulphur ligands which show the largest variation in metal-ligand bond lengths.

A comparison of the Pt-S bond lengths in $[Pt_2(S)(SMe)(PPh_3)_4]PF_6$ (3a) suggests a lengthening of the mean Pt-S bond length from 2.320(8) to 2.363(11) Å on methylation. The former is somewhat shorter than the mean Pt-S bond length in $[Pt_2S_2(PMe_2Ph)_4]$ (1a) [2.340(8) Å]. The S-Pt-S bond angles in the compounds are remarkably constant.

In summary the structural analyses on (1a), (3a), (4), and (5) have demonstrated that methylation of the sulphido-ligands does not reduce the π-donor characteristics of the bridging ligands sufficiently to cause a change in geometry from hinged square-planar to edge-shared tetrahedral. Nevertheless, the consistency of the hinged geometry combined with the nucleophilicity of the bridging sulphido-ligands suggested that the complexes (1) might function as ligands towards other metal ions, and as donor functions in charge-transfer complexes. The ability of (1a) and (1b) to function as ligands has been described elsewhere.[6,20] Their ability to function as donors in charge-transfer complexes was tested with tcne.

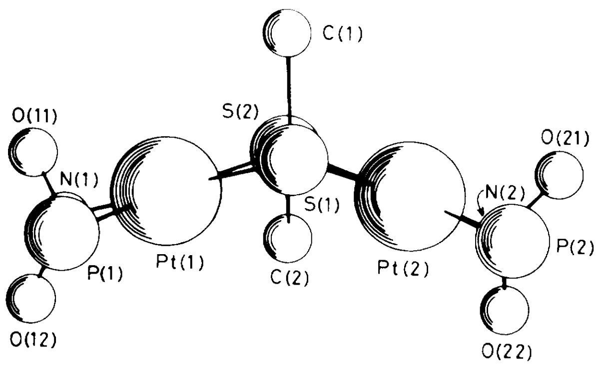


Figure 2. Molecular structure of *cis*-$[Pt_2(\mu\text{-}SMe)_2(NO_2)_2(PPh_3)_2]$ (4). For reasons of clarity the phenyl rings have not been shown

When tcne was added to a suspension of (1b) in diethyl ether (1 : 1 mol ratio) an intense dark green colouration developed, and the green solid which was isolated from the reaction analysed correctly for $[Pt_2S_2(PPh_3)_4]\cdot tcne$. An electronic spectrum of the adduct in CH_2Cl_2 showed a complex series of bands at *ca.* 400 nm characteristic of the $tcne^-$ radical anion,[21] and the conductivity of the compound in nitromethane gave a value approximately half that anticipated for a 1 : 1 electrolyte. These data are consistent with the occurrence of the following dissociation of the charge-transfer complex [equation (i)]. Similar adducts could not be prepared

$$[Pt_2S_2(PPh_3)_4]\cdot tcne \rightleftharpoons [Pt_2S_2(PPh_3)_4]^+ + tcne^- \qquad (i)$$

from olefins and acetylenes with inferior π-acid qualities, *e.g.* ethylene, acetylene, diphenylacetylene, acrylonitrile, and dimethyl acetylenedicarboxylate.

N.M.R. Spectral Properties.—Proton, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$, and $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectra have been recorded for the binuclear platinum alkylsulphido-complexes (2)—(4) and the detailed spectroscopic parameters are given in the Experimental section. The n.m.r. parameters are consistent with the retention in solution of the structures of (3a) and (4) observed in the solid state, and therefore only the more interesting features of the spectral analyses will be presented in this discussion.

The central methyl resonance in the ^1H n.m.r. spectrum of (2a) is observed at δ 1.48 p.p.m. and is flanked by satellites which can be attributed to the isotopomers $[Pt^{195}PtS(SMe)(PPh_3)_4]^+$ (44.7% abundance) and $[^{195}Pt_2S(SMe)(PPh_3)_4]$ (11.3% abundance). The resultant multiplet approximates to a 1 : 8 : 18 : 8 : 1 pattern with $^3J(Pt\text{-}H) = 34.3$ Hz. These resonances are further split into triplets resulting from couplings to the *trans*-phosphorus atoms, $^4J(P\text{-}H) = 4.7$ Hz. Similar $^4J(P\text{-}H)$ coupling constants have been reported for *trans*-$[Pt_2Cl_2(SMe)_2(PMe_3)_2]$ (5.4 Hz),[22] and $[Pt_2(SMe)_2(PMe_3)_4][BF_4]_2$ (5 Hz).[23]

The ^{13}C resonance of the SMe ligand could not be observed on samples at natural abundance and therefore a ^{13}C-enriched sample was synthesised from 90.5 atmos.% abundant $[^{13}C]$-methyl iodide. The SMe resonance was observed as a 1 : 8 : 18 : 8 : 1 multiplet at 21.93 p.p.m. with $^2J(^{13}C\text{-}^{195}Pt) = 23.2$ Hz. A comparable coupling constant has been reported for $[PtCl_2\{S(CH_2)_5\}_2]$.[24]

The $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum of $[Pt_2(S)(SMe)(PPh_3)_4]I$ (2a) consists of four sharp singlet peaks of equal intensity, each of which is flanked by a pair of much less intense satellites, and centred about δ −4 368 p.p.m. with respect to $Na_2[PtCl_6]$. The more intense lines in the spectrum result from the isotopomer with only a single ^{195}Pt nucleus (44.7% abundance). The resultant AA′BB′X spin system approximates to an ABX first-order pattern because the long range $^3J(\text{Pt-P}_A)$, $^3J(\text{Pt-P}_B)$, and ^4J(P–P) coupling constants are smaller than the linewidths of the main resonances ($\Delta\nu_{\frac{1}{2}} \sim 60$ Hz), and can be interpreted in terms of the following coupling constants: $^1J(\text{Pt-P}_A) = 2\,591$ and $^1J(\text{Pt-P}_B) = 3\,220$ Hz.

The satellites of lower intensity observed in the spectrum originate from the isotopomer with two ^{195}Pt nuclei (abundance 11.3%), The spectrum has been interpreted in terms of a combination if aa′xx′ and bb′xx′ sub-spectra, although not all the lines associated with these spin systems have been observed because of the relatively large linewidths of the platinum resonances. The ^2J(Pt–Pt) coupling constant was estimated to be 969 Hz from the separations of the satellites located either side of the main resonance. In dimeric platinum complexes where the Pt–Pt distance exceeds 3.0 Å, *i.e.* where no direct Pt–Pt bonding is invoked, the ^2J(Pt–Pt) coupling constant generally lies between 100 and 900 Hz.[25] The large value observed for (2a) and the related complexes must reflect the high efficiency with which the sulphido- and methylsulphido-bridging ligands transmit spin density, since the *X*-ray crystallographic studies have demonstrated that the platinum atoms are separated by more than 3.0 Å.

The ^{31}P-{^{1}H} spectrum of (2a) was initially puzzling because of an accidental near-equivalence of the chemical shifts for the P_A and P_B nuclei which led to the presence of only a single sharp resonance for the isotopomer with no ^{195}Pt nuclei. However, two sets of satellites resulting from $^1J(\text{Pt-P}_A)$ and $^1J(\text{Pt-P}_B)$ couplings of 2 591 and 3 220 Hz were discernible. The spectrum was analysed in terms of the spin systems AA′BB′X and AA′BB′XX′ for the ^{195}Pt isotopomers containing one or two ^{195}Pt nuclei. The assignment of the spectrum was confirmed by computer simulation techniques and the resultant parameters are summarised in the Experimental section. The detailed analysis demonstrated a chemical shift difference of only 0.5 p.p.m. separating P_A and P_B.

Acknowledgements

The S.E.R.C. is thanked for financial support and Johnson-Matthey Ltd. for a generous loan of platinum metal.

References

1 Part 3, C. E. Briant, M. J. Calhorda, T. S. A. Hor, N. D. Howells, and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1983, 1325.
2 R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 7240.
3 D. R. Russell, P. A. Tucker, and C. Whittaker, *Acta Crystallogr., Sect. B*, 1975, **31**, 2530; N. C. Stephenson, *Acta Crystallogr.*, 1964, **17**, 587.
4 L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, 1961, **83**, 1761.
5 R. Mason, I. Sotofte, S. D. Robinson, and M. F. Uttley, *J. Organomet. Chem.*, 1972, **46**, C61.
6 J. Chatt and D. M. P. Mingos, *J. Chem. Soc. A*, 1970, 1243.
7 R. Mason, B. Law, and D. M. P. Mingos, unpublished work.
8 R. Ugo, G. LaMonica, S. Cenini, A. Segre, and F. Conti, *J. Chem. Soc. A*, 1971, 522.
9 J. R. Carruthers, 'CRYSTALS user manual,' Oxford University Computer Centre, 1975; E. K. Davies, CHEMGRAF User manual, Chemical Crystallography Laboratory, University of Oxford, 1981.
10 'International Tables of *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 99.
11 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
12 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
13 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698.
14 N. J. Kermode, M. F. Lappert, B. W. Skelton, A. H. White, and J. Holton, *J. Chem. Soc., Chem. Commun.*, 1981, 698.
15 J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 2807.
16 M. C. Hall, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc., Dalton Trans.*, 1972, 1544.
17 C. E. Briant, G. R. Hughes, P. C. Minshall, and D. M. P. Mingos, *J. Organomet. Chem.*, 1980, **202**, C18.
18 E. W. Abel and K. G. Orrell, *Prog. Inorg. Chem.*, in the press.
19 F. R. Hartley, 'Chemistry of Palladium and Platinum,' Applied Science, London, 1973.
20 C. E. Briant, T. S. A. Hor, N. D. Howells, and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 1118.
21 O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, 1962, **84**, 3678.
22 P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J. Chem. Soc. A*, 1971, 2031.
23 M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.*, 1976, 2490.
24 E. W. Abel, M. Booth, and K. G. Orrell, *J. Chem. Soc., Dalton Trans.*, 1980, 1582.
25 P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247.

Received 3rd *November* 1983; *Paper* 3/1957