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Preliminary communication

SYNTHESIS AND CHARACTERISATION OF $[Ag_2Pt_4(\mu\text{-}S)_4(PPh_3)_8](BF_4)_2 \cdot 0.25CHCl_3$

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Summary

$[Pt_2(\mu_2\text{-}S)_2(PPh_3)_4]$ functions effectively as a bridging bidentate ligand towards Ag^+ to form $[Ag_2Pt_4(\mu_3\text{-}S)_4(PPh_3)_8]^{2+}$. A single crystal X-ray crystallographic analysis of the BF_4^- salt has demonstrated that both Ag^+ ions are linearly coordinated to the sulphur atoms, but the small bite angle of the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ ligand leads to an Ag···Ag contact distance of only 2.815(4) Å.

Considerable interest has been shown recently in the synthesis of heterometallic cluster compounds of the transition metals, because it is thought that such compounds may lead to an enhancement of catalytic activity [1]. Although a large number of compounds of this type have been synthesized their enhanced catalytic potential remains to be demonstrated [2]. This could arise because of the coordinative saturation of the metals in such compounds, and therefore we have initiated a programme aimed at synthesising heterometallic aggregates of coordinatively unsaturated square-planar metal species. Recently, we have reported that $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ is a most effective starting material for the synthesis of such compounds, because the lone pairs on the sulphur atoms linking the square-planar platinum moieties are capable of being donated to other metal centres. Some examples, of aggregates which can be synthesised in this fashion are illustrated below [3]. X-ray crystallographic studies on I, II and III have demonstrated the absence of any direct metal—metal bonding in these compounds [3].

In this paper we report the ability of I to function additionally as a bridging bidentate ligand connecting two metal toms. The complexes $[Ag_2\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2]Y_2$ ($Y = BF_4^-$, or NO_3^-) were obtained as yellow crystalline solids by adding a stoichiometric quantity of either $AgBF_4$ or $AgNO_3$ to a suspension

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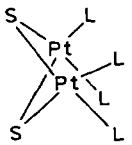
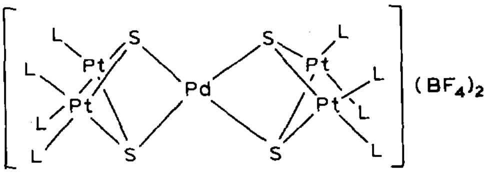
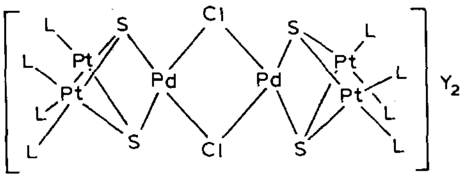


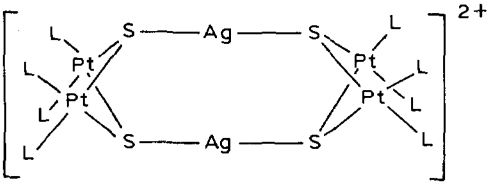
(I)





(II) (III)

of I in THF. Their molar conductivities in nitromethane ($\Lambda_m \simeq 180$ ohm^{-1} cm^2 mol^{-1}) suggested that they were 2:1 electrolytes and their ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectra demonstrated that the phosphorus and platinum nuclei were in chemically equivalent environments suggesting the formulation IV (^{31}P{^{1}H} to high frequency of TMP in CH_2Cl_2 δ 18.49 ppm, $^1J(^{31}P—^{195}Pt)$ 2967, $^3J(^{31}P—^{195}Pt)$ 22 Hz; ^{195}Pt{^{1}H} to high frequency of Na_2PtCl_6 in D_2O, in CD_2Cl_2 δ −4227 ppm (t, $^1J(^{195}Pt—^{31}P)$ 2953 Hz)).



(IV)

In view of the unusual structure proposed for IV and in order to establish whether the S····S contact of ca. 3.1 Å in I resulted in some Ag—Ag bonding a single crystal X-ray crystallographic analysis of IV was undertaken.

Crystal data

$C_{144}H_{120}B_2F_8P_8S_4Ag_2Pt_4 \cdot 0.25CHCl_3$ (IV), $M = 3425.74$, monoclinic a 24.638(7), b 19.722(7), c 32.619(9) Å, β 94.40(4)°, U 15850 Å^3, space group $P2/a$, $Z = 4$, D_c 1.44 g cm^{-3}, $F(000)$ 6682 electrons, μ(Mo-K_α) 41.27 cm^{-1}. Intensity data were collected at ca. 291 K on an Enraf Nonius CAD4F diffractometer using graphite monochromated Mo-K_α (λ 0.71069 Å) radiation. Of 12104 unique reflections measured in the θ range 1.5—20°, 7917 with $I \geqslant 3\sigma(I)$ were used to solve (Patterson and Fourier methods) and refine (blocked matrix least-squares) the structure to a current R of 0.069 (R_w = 0.099)*.

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

The structure illustrated in the Fig. 1 for the cation $[Ag_2\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2]^{2+}$ (IV) confirms the proposed structure with the two binuclear hinged $Pt_2S_2(PPh_3)_4$ moieties bridging the silver atoms via the sulphido ligands.

The coordination geometries about the silver atoms are close to linear (S(1)—Ag(1)—S(3) 176.2(3) and S(2)—Ag(2)—S(4) 174.1(3)°) consistent with their formulation as Ag^I ions. The Ag—S distances are not statistically different and have a mean of 2.389(9) Å, which is significantly shorter than the Ag—S distances in $[W_2Ag_4S_8(PPh_3)_4]$ [4] and $[Ag_2WS_4(PPh_3)_2]$ [5].

A striking feature of the structure is the Ag(1)—Ag(2) distance of 2.815(4) Å, which is significantly shorter than the metal—metal distance in elemental silver, 2.889(6) Å [6] and suggests the occurrence of significant metal—metal bonding in IV. Similar Ag· · ·Ag bonding interactions have been observed in other Ag^I and Au^I complexes [7—10]. The presence of metal—metal bonding in these formally d^{10} complexes has been rationalised from a molecular orbital point of view in terms of electron donation from the filled orbitals of one metal atom to the empty *p* orbitals on the second metal atom [11]. The Ag· · ·Pt distances in IV lie in the range 3.450(3)—3.905(3) Å and are outside the range normally associated with significant metal—metal bonding. From Fig. 1 it is also apparent that although the S—Ag—S moieties are approximately linear they do not adopt an eclipsed conformation. The dihedral angle between S(4)—Ag(2)—S(2) and

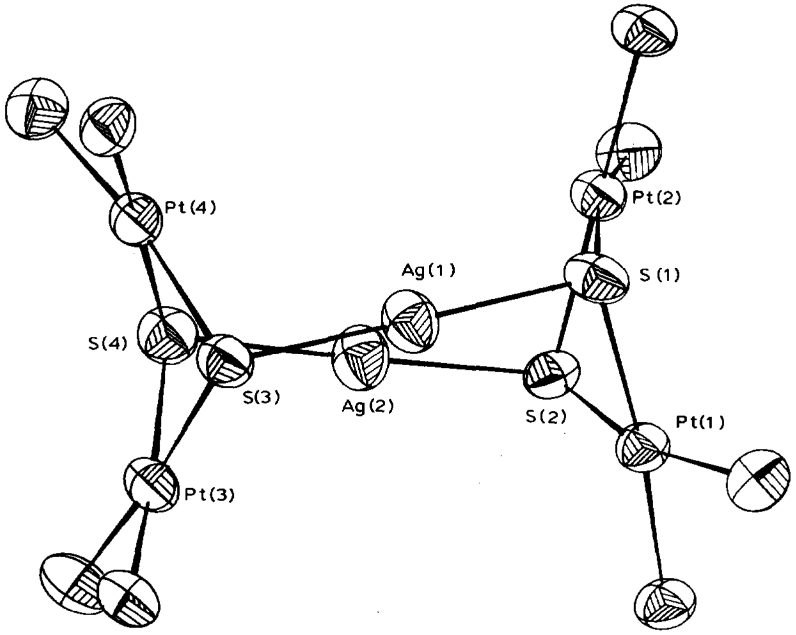

Fig. 1. A view of the $[Ag_2\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2]^{2+}$ cation. For reasons of clarity the phenyl rings have been omitted. Important interatomic distances include: Ag(1)—Ag(2) 2.815(4), Ag(1)—S(1) 2.381(9), Ag(1)—S(3) 2.385(8), Ag(2)—S(2) 2.399(8), Ag(2)—S(4) 2.391(9), Pt(1)—S(1) 2.353(8), Pt(1)—S(2) 2.326(9), Pt(2)—S(1) 2.353(8), Pt(2)—S(2) 2.350(8), Pt(3)—S(3) 2.374(8), Pt(3)—S(4) 2.361(9), Pt(4)—S(3) 2.364(9), Pt(4)—S(4) 2.353(8), Ag(1)—Pt(1) 3.517(3), Ag(1)—Pt(2) 3.743(3), Ag(1)—Pt(3) 3.905(3), Ag(1)—Pt(4) 3.634(3), Ag(2)—Pt(1) 3.893(3), Ag(2)—Pt(2) 3.531(3), Ag(2)—Pt(3) 3.450(3), Ag(2)—Pt(4) 3.823(3), Pt(1)—Pt(2) 3.350(2), Pt(3)—Pt(4) 3.278(2) Å; and bond angles S(1)—Ag(1)—S(3) 176.2(3), S(2)—Ag(2)—S(4) 174.1(3), S(1)—Pt(1)—S(2) 81.8(3), S(1)—Pt(2)—S(2) 81.3(3), S(3)—Pt(3)—S(4) 83.0(3), S(3)—Pt(4)—S(4) 83.4(3)°.

S(3)—Ag(1)—S(1) is 143°. This twist distortion reduces the non-bonded repulsions between the sulphur atoms by increasing their contact distances to 3.06(1) and 3.14(1) Å.

The results described above suggest that the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ molecule has suitable geometric characteristics to function not only as a bidentate ligand, but also as a bidentate bridging ligand which places two metal atoms in bonding proximity. In this respect it resembles dppm and related ligands [12], and suggests the development of heterometallic complexes analogous to the A-frame complexes.

Acknowledgements

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