DOI: 10.1002/ejic.200800821

Hydrogen Bonding in Crystalline Alcohol Solvates of the Platinum(II) Sulfido Complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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Keywords: Platinum complexes / Sulfide complexes / Hydrogen bonding

Suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in lower alcohols results in recrystallisation, forming yellow to yellow-orange microcrystals of the solvates $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot n$ROH (R = Me, Et, *n*Bu). The di-ethanol solvate was characterised by means of a single-crystal X-ray diffraction study and ^{1}H NMR spectroscopy. The structure consists of an ethanol molecule hydrogen-bonded in an asymmetric bifurcated fashion to the $\{Pt_2S_2\}$ group, with the second, disordered ethanol molecule involved in a cooperative hydrogen-bonding interaction with the oxygen of the first ethanol. Thermogravimetric analysis shows that the alcohol is relatively easily lost, regenerating orange, unsolvated $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ readily dissolves in hexafluoro-2-propanol, yielding yellow crystals of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 6(CF_3)_2CHOH$ on evaporation. Characterisation by X-ray diffraction shows that the structure contains a $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ hydrogen-bonded to a single $(CF_3)_2CHOH$ molecule, with the additional $(CF_3)_2CHOH$ molecules forming a discrete hydrogen-bonded pentameric cluster in the crystal.

Introduction

The platinum(II) sulfido complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$[1] (**1**) possesses electron-rich sulfide centres, and is well-known to act as a metalloligand towards a diverse range of metal centres (giving sulfide-bridged multimetallic assemblies), and towards organic electrophiles (giving platinum-thiolate complexes).[2,3] The reactivity of **1**, and related analogues containing alternative terminal phosphane ligands, towards the simplest electrophile, the proton, has also been the subject of a number of studies. In our early investigations concerning the use of electrospray ionisation mass spectrometry to explore the chemistry of **1**, we demonstrated that the complex gives a strong $[M + H]^+$ ion in its positive-ion ESI mass spectrum. These studies led to the synthesis and crystallographic characterisation of the monoprotonated species $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4]^+$.[4,5] The high proton affinity of **1** was easily demonstrated by ESI MS analysis of an equimolar solution of **1** and the cationic derivative $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$, which gives equal intensity signals for the two species. Subsequently, detailed experimental and theoretical studies of the protonation chemistry of complexes with $\{Pt_2(\mu\text{-}S)_2\}$ cores have been carried out by González-Duarte and co-workers, such that this chemistry is now well understood.[6–8]

During our investigations into the chemistry of **1**, invariably carried out using methanol (occasionally ethanol) solvent, low reactivity towards any particular substrate results in the initial orange suspension converting (over the course of several minutes) to a bright yellow suspension, still showing $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$ ions in the ESI mass spectrum. In light of the strong proton affinity of **1**, we suspected that hydrogen-bonded adduct formation between **1** and the alcohol could be occurring, and our investigations in this area are reported in this paper.

Results and Discussion

When the orange powder of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was stirred in ethanol, partial dissolution rapidly occurred (giving a light yellow solution), from which a bright yellow microcrystalline solid **2a** was deposited, and isolated by filtration and air-drying. Analysis of the product by ^{1}H NMR spectroscopy in $CDCl_3$ solution showed the presence of ethanol; integration relative to the PPh_3 resonances suggested the presence of two ethanol molecules per mol of $[Pt_2(\mu\text{-}S)_2\text{-}(PPh_3)_4]$. Complexes with $\{Pt_2S_2\}$ cores are known to react with chlorinated hydrocarbon solvents such as CH_2Cl_2 and $CHCl_3$,[9–11] but this does not invalidate the determination of the presence and amount of ethanol solvent. Elemental microanalytical data for **2a** were also supportive of the assignment, thought it must be noted that the theoretical C and H percentages for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (57.5, H 4.0) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot$2EtOH (C 57.2, H 4.6) are rather similar, and within the error of the determination. Thermogravimetric analysis (Figure 1) showed a small gradual weight loss at temperatures up to ca. 130 °C, followed by the onset of a significant weight loss at 130–150 °C that corresponds to

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the loss of 2 mol-equiv. of ethanol; the weight loss was, as expected, endothermic, from DSC measurements. Heating of a bulk sample of the yellow ethanol-treated material at 100 °C for several minutes turned it orange.

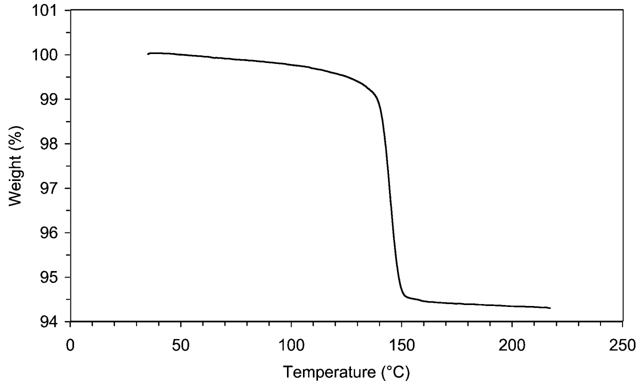

Figure 1. Thermogravimetric analysis plot of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 2EtOH$ (**2a**).

SEM analysis of the ethanol solvate **2a** indicated significant morphological changes when compared to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (Figure 2, a), which contained small, irregular prismatic-shaped microcrystals, consistent with its method of synthesis [from insoluble *cis*-$PtCl_2(PPh_3)_2$] in a benzene suspension. In contrast, the ethanol-treated material shows (Figure 2, b) the presence of significantly larger rhombs with well-formed crystal faces, indicative of a crystallisation process occurring.

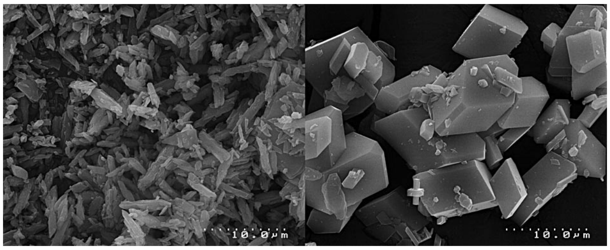

Figure 2. SEM micrograph images (scale bar 10 µm in each case) of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (a) before and (b) after allowing to stand in ethanol, resulting in the formation of crystals of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 2EtOH$ (**2a**).

Unambiguous characterisation of **2a** was provided by a single-crystal X-ray structure determination. Suitable crystals were obtained by allowing an ethanol suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to stand undisturbed at room temperature for several days, resulting in the formation of small yellow-orange blocks. The structure of the complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 2EtOH$ (**2a**) is shown in Figure 3, together with the atom numbering scheme. Selected bond lengths and angles are given in Table 1. The structure consists of the usual puckered $\{Pt_2S_2\}$ butterfly core, with the hydrogen atom of one ethanol molecule hydrogen-bonded to sulfide S(2) [S(2)···O(1) 3.42, S(2)···H 2.62 Å]. These S···O and S···H distances are similar to the mean S···O and S···H distances of 3.43(3) and 2.51(3) Å, respectively, obtained from a structural analysis of transition metal–S–C acceptors with water molecule donors.[12] The hydrogen atom also appears to interact more weakly with the other more distant sulfide S(1) [S(1)···O(1) 3.59 Å, S(1)···H 2.95], so that the interaction of the ethanol hydroxyl proton can probably be best described as a bifurcated interaction with major and minor components.[12,13] The second, disordered, ethanol molecule is hydrogen-bonded to the oxygen of the first, in a cooperative hydrogen bond[12,13] with an O···O separation of 2.92 Å, which fixes O(2) in place, but permits disorder in the ethyl group of the second ethanol molecule.

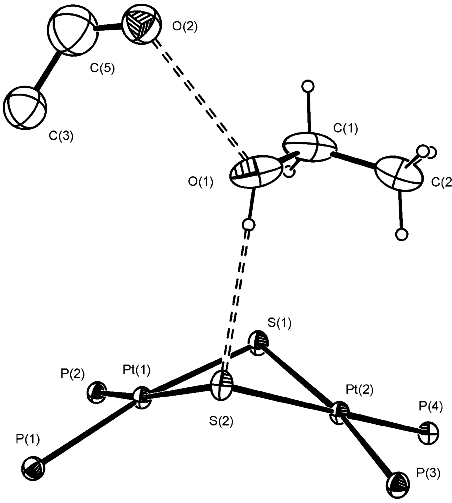

Figure 3. A view of the core of the complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 2EtOH$ (**2a**), showing the hydrogen bonding involving the two ethanol molecules. Phenyl rings on the P atoms have been omitted, and only the major component of the second, disordered ethanol molecule is shown (without H atoms).

Table 1. Selected bond lengths [Å] and angles [°] for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 2EtOH$ (**2a**).

Pt(1)–P(1)	2.2774(9)	Pt(1)–P(2)	2.2986(9)
Pt(1)–S(2)	2.3352(8)	Pt(1)–S(1)	2.3416(8)
Pt(2)–P(3)	2.2783(9)	Pt(2)–P(4)	2.2793(9)
Pt(2)–S(1)	2.3220(8)	Pt(2)–S(2)	2.3629(9)
P(1)–Pt(1)–P(2)	100.40(3)	P(1)–Pt(1)–S(2)	93.31(3)
P(2)–Pt(1)–S(1)	84.77(3)	S(2)–Pt(1)–S(1)	81.63(3)
P(3)–Pt(2)–P(4)	105.31(3)	P(4)–Pt(2)–S(1)	89.51(3)
P(3)–Pt(2)–S(2)	83.63(3)	S(1)–Pt(2)–S(2)	81.46(3)
Pt(2)–S(1)–Pt(1)	88.52(3)	Pt(1)–S(2)–Pt(2)	87.70(3)
Ethanol molecules			
O(1)–C(1)	1.439(6)	C(1)–C(2)	1.509(7)
O(2)–C(5)	1.208(15)	C(3)–C(5)	1.426(15)
O(1)–C(1)–C(2)	112.2(4)	O(2)–C(5)–C(3)	118.0(13)

It is noteworthy that the second ethanol molecule is not hydrogen-bonded to the second sulfide S(1). In this regard we note that in alkylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, alkylation of the first sulfide proceeds readily with a wide range of alkylating and arylating agents under mild conditions to form a monoalkylated product, but subsequent (di)alkylation of the second sulfide is much more difficult, requiring powerful alkylating agents or forcing conditions. It is therefore conceivable that involvement of one sulfide in a hydrogen-bonding interaction decreases the propensity of the second sulfide to participate, and the second ethanol molecule then interacts with the best-available hydrogen-bond acceptor, the inner-sphere ethanol. The average Pt–S bond length to the hydrogen-bonded S(2) [2.3491(8) Å] is 0.017(1) Å longer than the average Pt–S(1) distance [2.3318(8) Å].

The $\{Pt_2S_2\}$ butterfly core of **2a** is folded, with a fold angle (θ) between the two P_2PtS_2 planes of 133.3°. The parent complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ has been structurally characterised, but the structure determination was of very poor quality and unreliable. Indeed it has been commented[14] that the anomalous Pt–S and S···S distances, substantially shorter (by about 0.25 Å) than in related complexes, with unidentified solvent molecules in the crystal, may be due to partial oxidation. Structure determinations on the monoprotonated complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)\{Ph_2P(CH_2)_nPPh_2\}_2]^+$ ($n = 2$, $\theta = 138.3°$; $n = 3$, $\theta = 127.4°$),[7] reveal fold angles that are only slightly smaller (by 2° and 7° respectively) than the respective unprotonated complexes $[Pt_2(\mu\text{-}S)_2\{Ph_2P(CH_2)_nPPh_2\}_2]$ ($n = 2$, $\theta = 140.2°$;[15] $n = 3$, $\theta = 134.8°$[9]) suggesting that protonation has minimal effect on the puckering of the $\{Pt_2S_2\}$ ring. Given that the fold angle in the monoprotonated triphenylphosphane complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4]^+$ is 135°, the apparent fold angle of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (167.5°) seems somewhat out of line, even though fold angles in complexes $[Pt_2(\mu\text{-}S)_2L_4]$ can vary widely depending on the ligand L, from 180° for L = 2-diphenylphosphanylpyridine, to 121° for L = $PhPMe_2$. If we consider that the hydrogen-bonded structure of **2a** represents a situation part way to complete proton transfer, the similar fold angles in **2a** and $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4]^+$ are to be expected, both also being similar to the monomethylated complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ (fold angle 138°).

The methanol adduct of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**2b**) can be similarly obtained by stirring the complex in methanol, which results in rapid formation of a bright yellow solid. TGA analysis indicates that the methanol is lost much more readily than is ethanol, with the major weight loss occurring at <100 °C. Vacuum drying of a sample of the methanol solvate resulted in conversion of the yellow to an orange colour after ca. 4 hours. Similarly, briefly heating a sample to 100 °C resulted in conversion from a yellow to orange solid, with the weight loss being consistent with the formation of unsolvated $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ by loss of two mol of MeOH per mol of complex. The resulting orange solid shows exclusively $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$ in the positive-ion ESI mass spectrum, and turns yellow on re-suspension in methanol. We have been unable to obtain satisfactory microanalytical data on the methanol solvate, with two independently prepared samples {using different batches of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$} giving low carbon elemental microanalyses.

Increasing the alkyl chain length in primary alcohols ROH substantially decreases the rate of solvate formation. Standing (orange powder) suspensions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in butan-1-ol, hexan-1-ol and octan-1-ol for 4 days resulted in no visible change in appearance of the starting material, and SEM analysis of the hexanol-treated material showed no significant morphological changes. However, when a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in butan-1-ol is allowed to stand for prolonged periods (several weeks) slow recrystallisation to form orange microcrystals occurred. After air-drying for several days, the ^1H NMR spectrum showed the presence of approximately 2 equiv. of butanol, which was supported by microanalytical data. The complex is similarly assigned as the solvate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 2n\text{BuOH}$ (**2c**). TGA analysis showed a ca. 9% endothermic weight loss between ca. 140 and 160 °C (slightly higher than for the corresponding ethanol solvate), which compares well with the calculated weight loss of 8.96% for loss of two equivalents of butanol.

We reasoned that the use of a more acidic alcohol than ethanol (pK_a 16.0[16]) would enhance hydrogen bond formation with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. Indeed, one can easily envisage a continuum from weak hydrogen-bond formation, to complete proton transfer giving $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4]^+$, depending on the acidity of the proton donor. Hexafluoropropan-2-ol, $(CF_3)_2CHOH$ is such an alcohol (pK_a 9.3), being a strong hydrogen-bond donor but a much poorer hydrogen-bond acceptor; it is known to form strong hydrogen-bonded adducts with Lewis bases e.g. piperidine.[17] Further interest in the interaction of $\{Pt_2(\mu\text{-}S)_2\}$ complexes with fluoro-alcohols comes from very recent work by González-Duarte and co-workers, who found that $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ [dppp = $Ph_2P(CH_2)_3PPh_2$] is alkylated by $FCH_2CH(OH)CH_2F$ to form $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH(OH)CH_2F\}(dppp)_2]^+$, the alkylation reaction being assisted by an intramolecular O–H···F hydrogen bond.[18]

It was found that $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ dissolved rapidly in hexafluoropropan-2-ol giving a slightly cloudy, pale yellow solution. Upon filtration and slow evaporation at room temperature, large yellow blocks were obtained which lost crystallinity on removal from the solvent. ESI MS showed $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$ (*m/z* 1503), confirming that reactivity was, at least in the isolated crystals, confined to hydrogen bond formation. In order to characterise this material, an X-ray structure determination was carried out, which showed that the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ crystallises with *six* hexafluoropropan-2-ol molecules per platinum complex, viz. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 6(CF_3)_2CHOH$ (**3**). Only one of these is involved in a hydrogen-bonding interaction, to a single sulfide centre, with the oxygen atom disordered equally over two positions. The core of the structure is shown in Figure 4, and selected bond lengths and angles are given in Table 2. Thus, O–H(6) is a hydrogen-bond donor to S(1) with O(6)···S(1) distances of 3.14 and 3.27 Å from the two disordered components respectively. These distances are shorter than the equivalent O···S distance for the ethanol adduct of 3.43 Å, consistent with the fluorinated alcohol being a better hydrogen-bond donor. The hinge angle involving the Pt coordination planes is 129.5°, compared to 133.3° in the EtOH solvate.

There are a further five $(CF_3)_2CHOH$ molecules in the lattice, hydrogen-bonded with each other to give a discrete pentamer (Figure 5), which is not hydrogen-bonded to the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot(CF_3)_2CHOH$ adduct. In contrast, the X-ray structure determination of solid $(CF_3)_2CHOH$ shows

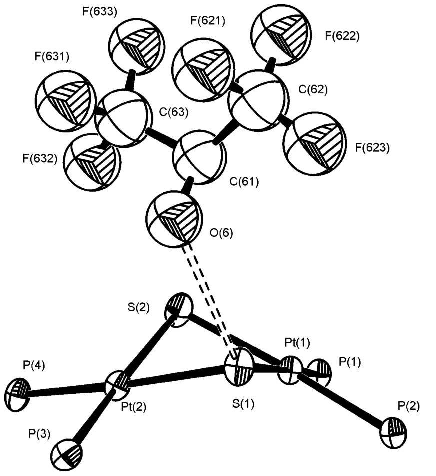

Figure 4. The core of the solvate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 6(CF_3)_2CHOH$ (**3**), showing the presence of a single hexafluoropropan-2-ol molecule hydrogen-bonded to a sulfide ligand. Phenyl rings and hydrogen atoms have been omitted, and only one component of the disordered hydroxyl group is shown. The other hexafluoropropan-2-ol molecules form a hydrogen-bonded pentameric unit (not shown) which does not interact with the platinum complex.

Table 2. Selected bond lengths [Å] and angles [°] for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 6(CF_3)_2CHOH$ (**3**).

Pt(1)–P(1)	2.294(2)	Pt(1)–P(2)	2.296(2)
Pt(1)–S(2)	2.345(2)	Pt(1)–S(1)	2.353(2)
Pt(2)–P(3)	2.276 (2)	Pt(2)–P(4)	2.306(2)
Pt(2)–S(1)	2.337(2)	Pt(2)–S(2)	2.358(2)
P(1)–Pt(1)–P(2)	110.64(7)	P(1)–Pt(1)–S(2)	95.25(7)
P(2)–Pt(1)–S(1)	85.96(7)	S(2)–Pt(1)–S(1)	78.09(7)
P(3)–Pt(2)–P(4)	99.06(7)	P(4)–Pt(2)–S(2)	91.10(7)
P(3)–Pt(2)–S(1)	91.94(7)	S(1)–Pt(2)–S(2)	78.14(7)
Pt(2)–S(1)–Pt(1)	89.77(7)	Pt(1)–S(2)–Pt(2)	89.49(7)
$(CF_3)_2CHOH$ molecule H-bonded to S(1)			
O(6)–C(61)	1.24(2)	O(6A)–C(61)	1.41(2)
C(61)–C(62)	1.60(3)	C(61)–C(63)	1.48(2)

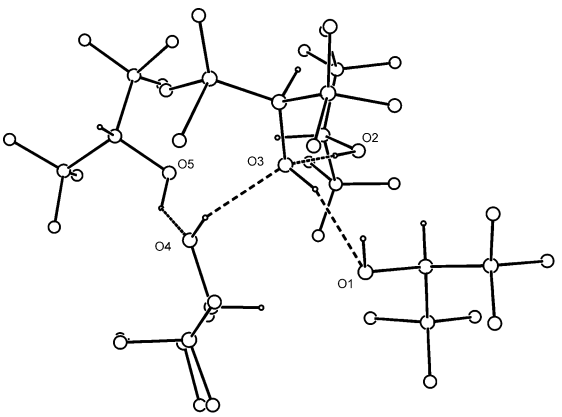

Figure 5. The pentameric unit of hydrogen-bonded hexafluoropropan-2-ol molecules of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 6(CF_3)_2CHOH$ (**3**), showing the atom labelling scheme and hydrogen bond interactions. Hydrogen atoms are numbered according to the oxygen atom they are from e.g. H(4)–O(4).

an infinite helix structure, formed from O–H···O hydrogen bonds.[19] The solvent molecules of **3** were generally not well-defined, with rotational disorder involving the CF_3 groups. Hydroxyl O–H(1) solely acts as a receptor from O–H(3), which is a donor to O(1) and a receptor from both O–H(2) and O–H(4). O–H(5) is a donor to O(4); details are given in Table 3. These hexafluoro-2-propanol molecules occupy a significant volume of the unit cell, and it is not surprising that isolation of crystals of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 6(CF_3)_2CHOH$ from solvent results in loss of crystallinity, through loss of some or all of these solvent molecules. The pentameric units present a hydrophobic surface, similar to the hexameric hydrogen-bonded cluster unit observed in the structure of $2(CH_2)_5NH\cdot 4(CF_3)_2CHOH$.[17]

Table 3. Details of the hydrogen-bonding involving the hexafluoro-2-propanol pentamer of **3**.

Hydrogen bond	O···O distance [Å]
O–H(3)···O(1)	2.69
O–H(2)···O(3)	2.57
O–H(4)···O(3)	2.54
O–H(5)···O(4)	2.71

Conclusions

In this paper we have addressed a longstanding enigma concerning $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ through demonstration that the yellow-orange colour changes result from the formation of hydrogen-bonded alcohol solvates. While protonation (and alkylation) of the $\{Pt_2S_2\}$ core has been known for many years, hydrogen bonding has not been previously observed, and our studies have now essentially trapped a type of "intermediate" on the protonation reaction coordinate. This interaction affects the $\{Pt_2S_2\}$ chromophore; the mono-protonated $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4]^+$ and mono-alkylated $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ derivatives are also yellow, as are many metal derivatives (in the absence of a coloured metal centre), e.g. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4HgPh]^+$, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4SnR_3]^+$ etc. Given the known nucleophilicity and basicity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, these results are, with hindsight, not surprising. However, our results do suggest that such metal-sulfido complexes could form hydrogen-bonded assemblies with other hydrogen-bond donors more widely, and we are currently investigating these possibilities.

Experimental Section

General: $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) was prepared by the literature procedure from *cis*-$[PtCl_2(PPh_3)_2]$ and $Na_2S\cdot 9H_2O$ in benzene suspension.[20] The orange product was isolated by filtration, washing with several portions of benzene, followed by copious amounts of distilled water. The resulting orange powder was air-dried. Alcohol solvents were of AR grade. Hexafluoropropan-2-ol (BDH, spectroscopic grade) was used as received.

Elemental microanalyses were performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of

Otago, New Zealand. TGA analysis was carried out on a TA SDT 2960 simultaneous DAT-TGA with a heating rate of 20 °C min^{-1}, from room temperature to 300 °C.

Synthesis of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$]·2EtOH (2a): A suspension of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] (444 mg, 0.295 mmol) in ethanol (30 mL) was stirred for 17 h, giving a yellow-orange suspension. The solid was filtered, washed with cold ethanol (5 mL), and air-dried to give the product **2a** (368 mg, 78 %). $C_{76}H_{72}O_2P_4Pt_2S_2$ (1595.5) calcd. C 57.2, H 4.6; found C 56.0, H 4.3.

Synthesis of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$]·2MeOH (2b): A suspension of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] (508 mg, 0.338 mmol) in methanol (30 mL) was stirred for 17 h, giving a bright yellow suspension. The solid was filtered, washed with cold methanol (5 mL), and air-dried to give the product **2b** (418 mg, 78 %). $C_{76}H_{72}O_2P_4Pt_2S_2$ (1567.5): calcd. C 56.7, H 4.4; found (2 independently prepared samples): C 54.9, 54.5; H 3.8, 4.3.

Synthesis of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$]·2*n*BuOH (2c): A suspension of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] (159 mg, 0.106 mmol) in butan-1-ol (20 mL) was allowed to stand at room temperature for 6 weeks resulting in the slow formation of an orange microcrystalline solid. The solvent was removed by decantation, the solid washed with five 5 mL portions of *n*-hexane, and air-dried to give 130 mg (74 %) of product **2c**. $C_{80}H_{80}O_2P_4Pt_2S_2$ (1651.6) calcd. C 58.2, H 4.9; found C 57.0, H 5.0.

Synthesis of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$]·6$(CF_3)_2CHOH$ (3): [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] (240 mg, 0.160 mmol) was dissolved in hexafluoropropan-2-ol (10 mL) giving a slightly cloudy pale yellow solution, which was filtered through a short celite column, and washed with an additional 2 mL of hexafluoropropan-2-ol. The solution was allowed to spontaneously evaporate to dryness at room temperature. The solution became slightly more yellow in colour, and deposited large yellow block crystals of **3**, plus some yellow oily material. Washing with *n*-hexane (5 mL) followed by rapid washing with a small quantity of hexafluoropropan-2-ol gave yellow blocks suitable for an X-ray diffraction study which were briefly air-dried (yield 220 mg) and stored in a sealed vial under a vapour of hexafluoropropan-2-ol. The crystals could be handled for short periods in air with no apparent change, but exposing crystals to air overnight resulted in loss of clarity, presumably through loss of hexafluoropropan-2-ol. Elemental microanalytical data were not obtained.

X-Ray Structure Determination of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$]·2EtOH (2a): Yellow-orange crystals suitable for an X-ray structural study were obtained by allowing an undisturbed suspension of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] in ethanol to stand at room temperature for several days. Crystal, data collection and refinement details are given in Table 2. The hydroxyl H atom of the ordered EtOH solvent (hydrogen-bonded to S) was included in the refinement using the HFIX 147

Table 4. Crystal, collection and refinement data for [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$]·2EtOH **2a** and [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$]·6$(CF_3)_2CHOH$ (**3**).

	2a	**3**
Crystal data		
Empirical formula	$C_{76}H_{72}O_2P_4Pt_2S_2$	$C_{90}H_{72}F_{36}O_6P_4Pt_2S_2$
Formula weight	1595.52	2511.66
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a [Å]	23.0476(8)	14.1196(17)
b [Å]	12.9544(5)	18.851(2)
c [Å]	23.4958(9)	19.410(2)
α [°]	90	85.925(7)
β [°]	110.923(2)	78.420(7)
γ [°]	90	88.813(7)
V [Å^3]	6552.5(4)	5048.2(11)
Z	4	2
D_c [g cm^{-3}]	1.617	1.652
Data collection		
Crystal size [mm]	0.10 × 0.10 × 0.09	0.78 × 0.62 × 0.15
Radiation, wavelength [Å]	Mo-K_α, λ = 0.71073	Mo-K_α, λ = 0.71073
Temperature [K]	93(2)	89(2)
θ range for data collection [°]	2.64 to 27.50	1.64 to 27.50
Reflections collected	64237	76885
Independent reflections	15011 (R_{int} 0.0346)	22985 (R_{int} 0.0667)
Absorption coefficient [mm^{-1}]	4.474	2.989
F(000)	3168	2464
Structure analysis and refinement		
Solution by	direct methods	Patterson methods
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data / restraints / parameters	15011 / 0 / 772	22985 / 0 / 1216
Goodness-of-fit on F^2	1.053	1.040
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0243 wR_2 = 0.0528	R_1 = 0.0616 wR_2 = 0.1587
R indices (all data)	R_1 = 0.0428 wR_2 = 0.0598	R_1 = 0.0840 wR_2 = 0.1785
Largest difference peak [e Å^{-3}]	2.223	3.653
Largest difference hole [e Å^{-3}]	–0.917	–2.507

procedure of SHELXL.[21] The second, disordered ethanol is hydrogen-bonded to the O of the first in a cooperative hydrogen bond, but the ethyl group was disordered over two sites, so the atoms were treated isotropically and hydrogen atoms were not included. Residual electron density was adjacent to the disordered ethanol molecule.

X-Ray Structure Determination of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 6(CF_3)_2CHOH$ (3): The structure was solved using Patterson methods, and developed routinely, to reveal a Pt_2S_2 core, hydrogen-bonded through S(1) to a single $(CF_3)_2CHOH$ molecule. There were a further five $(CF_3)_2CHOH$ molecules in the lattice, hydrogen-bonded with each other to give a discrete pentameric unit. The solvent molecules were generally not well-defined, with rotational disorder involving the CF_3 groups. The molecule hydrogen-bonded to the S atom was further disordered with the OH group equally split over two sites, both involving H-bonding to the same S. This molecule was treated isotropically and the H-atoms were not included in the refinement in this case. The final residual peaks were higher than usual at ca. 3 $e\,Å^{-3}$ but these were closely adjacent to phenyl rings so were clearly not assignable to anything chemically sensible (Table 4).

CCDC-687104 (for **2a**) and -687105 (for **3**). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

We thank the University of Waikato (UW) and the National University of Singapore (NUS) for financial support of this work. We also thank Dr. Jan Wikaira (University of Canterbury) for collection of the X-ray data sets, Yuanji Zhang for TGA data, and Helen Turner for SEM images.

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[1] S.-W. A. Fong, T. S. A. Hor, *J. Chem. Soc., Dalton Trans.* **1999**, 639.

[2] W. Henderson, S. H. Chong, T. S. A. Hor, *Inorg. Chim. Acta* **2006**, *359*, 3440.

[3] S. H. Chong, L. L. Koh, W. Henderson, T. S. A. Hor, *Chem. Asian J.* **2006**, *1–2*, 264.

[4] S.-W. A. Fong, J. J. Vittal, W. Henderson, T. S. A. Hor, A. G. Oliver, C. E. F. Rickard, *Chem. Commun.* **2001**, 421.

[5] S.-W. A. Fong, W. T. Yap, J. J. Vittal, T. S. A. Hor, W. Henderson, A. G. Oliver, C. E. F. Rickard, *J. Chem. Soc., Dalton Trans.* **2001**, 1986.

[6] R. Mas-Ballesté, G. Aullón, P. A. Champkin, W. Clegg, C. Mégret, P. González-Duarte, A. Lledós, *Chem. Eur. J.* **2003**, *9*, 5023.

[7] G. Aullón, M. Capdevila, W. Clegg, P. González-Duarte, A. Lledós, R. Mas-Ballesté, *Angew. Chem. Int. Ed.* **2002**, *41*, 2776.

[8] P. González-Duarte, A. Lledós, R. Mas-Ballesté, *Eur. J. Inorg. Chem.* **2004**, 3585.

[9] R. Mas-Ballesté, M. Capdevila, P. A. Champkin, W. Clegg, R. A. Coxall, A. Lledós, C. Mégret, P. González-Duarte, *Inorg. Chem.* **2002**, *41*, 3218.

[10] R. R. Gukathasan, R. H. Morris, A. Walker, *Can. J. Chem.* **1983**, *61*, 2490.

[11] M. Zhou, C. F. Lam, K. F. Mok, P.-H. Leung, T. S. A. Hor, *J. Organomet. Chem.* **1994**, *476*, C32.

[12] T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48.

[13] J. Bernstein, M. C. Etter, L. Leiserowitz, in *Structure Correlation* (Eds.: H.-B. Bürgi, J. D. Dunitz), ch. 11, VCH, Weinheim, **1994**.

[14] G. Aullón, M. Hamidi, A. Lledós, S. Alvarez, *Inorg. Chem.* **2004**, *43*, 3702.

[15] M. Capdevila, Y. Carrasco, W. Clegg, R. A. Coxall, P. González-Duarte, A. Lledós, J. Sola, G. Ujaque, *Chem. Commun.* **1998**, 597.

[16] L. M. Mukherjee, E. Grunwald, *J. Phys. Chem.* **1958**, *62*, 1311.

[17] J.-F. Berrien, M. Ourévitch, G. Morgant, N. E. Ghermani, B. Crousse, D. Bonnet-Delpon, *J. Fluorine Chem.* **2007**, *128*, 839.

[18] A. Nova, R. Mas-Ballesté, G. Ujaque, P. González-Duarte, A. Lledós, *Chem. Commun.* **2008**, 3130.

[19] A. Berkessel, J. A. Adrio, D. Hüttenhain, J. M. Neudörfl, *J. Am. Chem. Soc.* **2006**, *128*, 8421.

[20] R. Ugo, G. La Monica, S. Cenini, A. Segre, F. Conti, *J. Chem. Soc. A* **1971**, 522.

[21] G. M. Sheldrick, *SHELXL-97 Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Received: August 18, 2008