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Synthesis and structural characterisation of the lead-platinum sulfido aggregates $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbX_2]$ (X = Br, I); promotion of rare tetrahedral geometry for lead(II)

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Received:

Abstract

The reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with excess $PbBr_2$ or PbI_2 in methanolic suspension result in the formation of the neutral lead(II) halide adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbX_2]$ (X = Br, I). The X-ray structure determination of the lead iodide adduct reveals an essentially tetrahedral lead(II) centre, which is a rare coordination geometry for lead(II), which almost invariably is hemidirected, with a stereochemically active lone pair. In contrast, the structure of the $PbBr_2$ adduct, although suffering from some disorder, shows a more typical, distorted arrangement of ligands; these results are discussed in terms of the tendency for soft, bulky ligands to promote symmetric, holodirected geometries. The ESI mass spectra of the adducts are reported, and yield $[M – halide]^+$ ions.

Keywords: Platinum complexes; Sulfido ligands; Lead complexes; Coordination geometry; Electrospray mass spectrometry

Introduction

The metalloligands $[Pt_2(\mu\text{-}E)_2(PPh_3)_4]$ (E = S and Se) display a diverse coordination chemistry towards a wide range of metal centres.[1,2] We are currently investigating the coordination chemistry of such complexes towards main group metal centres,[3,4] encouraged by the prospect that the bulky metalloligands promote low coordination numbers, as previously observed in a number of systems, such as the thallium(I) adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Tl]^+$ [5] and also in the transition metal derivatives $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ML]^{2+}$ [e.g. M = Rh or Ir, L = η^5-C_5Me_5 and M = Ru or Os, L = η^6-$MeC_6H_4Pr^i$].[6]

We are interested in lead(II) derivatives because of the highly variable coordination numbers and geometries that lead(II) can adopt, depending on whether the lone pair of electrons is stereochemically active.[7] Some inorganic and organometallic lead derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ have previously been explored: the organolead(IV) adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbR_3]^+$ (R = Me, Ph) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbPh_2X]^+$ (X = I, Br, SCN) have been reported [8] and the coordination chemistry towards lead(II) nitrate has also been studied, giving the complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbNO_3]^+X^-$ (X = NO_3 **1** or PF_6 **2**) [9] and $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4PbNO_3]^+$.[10] The related 1,1'-bis(diphenylphosphino)ferrocene (dppf) analogue $[Pt_2(\mu\text{-}S)_2(dppf)_2PbNO_3]NO_3$ **3** is also known.[11] A previous theoretical study [12] of the interactions between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and main group element species, including Pb(II), concluded that there is competition for interactions involving the heterometal centre, which accounted for the reluctance of the heterometal to accept additional ligands and hence the tendency for somewhat lower coordination numbers than is typical. In this contribution we report the products formed between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and lead(II) halides $PbBr_2$ and PbI_2, which generate interesting low coordination number lead(II) derivatives.

Results and discussion

Synthesis and characterisation of lead(II) halide adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

The reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with an excess of either $PbBr_2$ or PbI_2 in methanol suspension proceed rapidly, with the formation of lemon yellow or bright yellow suspensions, respectively. Following isolation by filtration, extraction of the products with dichloromethane to remove excess lead salts, and crystallisation by precipitation with petroleum spirits, lemon-yellow ($PbBr_2$) and deep yellow (PbI_2) adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbX_2]$ (**4**, X = Br; **5**, X = I) were isolated as microcrystalline solids in moderate yields. To determine the coordination geometries of these adducts, X-ray structure determinations were carried out on crystals grown from dichloromethane-diethyl ether. The molecular structure of the PbI_2 adduct **4** is shown in Figure 1 together with the atom numbering scheme, while selected bond lengths and angles are given in Table 1. The molecular structure of the $PbBr_2$ adduct **5** is shown in Figure 2, with selected bond lengths and angles in Table 2.

The structure of **4** consists of the typical butterfly $\{Pt_2S_2\}$ core acting as a bidentate metalloligand to the PbI_2 moiety, which has approximately tetrahedral coordination, as also shown in Figure 3a. The lead centre is symmetrically bonded to both sulfur atoms, with Pb-S(1) and Pb-S(2) bond lengths of 2.7809(9) and 2.7725(7) Å respectively, and a S(1)-Pb-S(2) bite angle of 67.21(2)˚. These bond distances are somewhat longer than values of 2.744(4) and 2.692(4) Å in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbNO_3]NO_3$ **2**, and 2.766(3) and 2.641(3) Å in the corresponding salt $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbNO_3]PF_6$ **3**. The S-Pb-S bite angles in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbNO_3]X$ (X = NO_3 or PF_6) are both 68.9(1)˚. Taken together, these parameters indicate that the PbI_2 moiety binds slightly more weakly (but rather more symmetrically) to the $\{Pt_2S_2\}$ core, resulting in longer Pb-S bond lengths and a more acute S-Pb-S bond angle. This is not unreasonable given that PbI_2 would be expected to be a significantly weaker Lewis acid than a lead nitrate moiety. Consistent with this, we have recently found that increasing the Lewis acidity in the series of thallium(III) adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4TlR_2]^+$ from R = Ph to R = Br increases the interaction of the Tl centre with the $\{Pt_2S_2\}$ metalloligand, giving shorter Tl-S bond distances and a wider S-Tl-S angle.[13] The Pb-S bond lengths in **4** are longer than found in lead(II) thiolate complexes such as $(Ph_4As)[Pb(SPh)_3]$ [2.647(1) Å] [14] and $[Pb(SCH_2CH_2S)]_n$ [2.655(3) and 2.660(3) Å],[15] but shorter than complexes with other neutral sulfur donors such as the phosphine sulfide-lead bond distances in

$[Pb(Ph_2P(S)CH_2C_6H_4S)_2]$ [2.950(12) and 3.151(9) Å].[16] In some mixed-metal cubanes containing $S_4M_3PbI_3$ cores (M = Mo or W), the Pb-μ_3-S bonds lie in the range 3.1-3.2 Å, while the Pb-I bonds are around 2.94 Å.[17,18] Few examples of low-coordinate lead(II) halide complexes have been structurally characterised, but the average lead(II)-iodide bond distance reported in the CSD database of 3.22(16) Å [7] compares favourably with Pb-I(1) and Pb-I(2) bond distances in **4** of 3.2113(4) and 3.1623(3) Å respectively. The I-Pb-I bond angle of 116.209(9)° is, not surprisingly, larger than the regular tetrahedral angle due to the large iodide ligands. The S-Pb-I bond angles range from 111.689(17)° [for S(2)-Pb(1)-I(2)] to 122.680° [for S(1)-Pb(1)-I(1)]. A comparison of the S-Pb and Pb-I bond distances with those of the lead(IV) iodide adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbIPh_2]^+$ reveals, as expected,[7] shorter Pb(IV)-I [2.9208(16) Å] and Pb(IV)-S [average 2.723(2) Å] bonds.

The $PbBr_2$ adduct **5** has a somewhat different structure to the iodide. One of the bromines, Br(1), is in an analogous position to the iodides of complex **4**, as can be seen in Figure 2, but Br(2) is disordered over two positions. Figure 3 shows a comparison of the geometry of the lead halide moieties for **4** and **5**, with respect to the $\{Pt_2S_2\}$ metalloligand. In one Br(2) position the coordination geometry around lead is distorted tertrahedral, whereas in the other disordered position the lead has a geometry reminiscent of a saw-horse geometry, based on a trigonal bipyramid with a vacancy in an equatorial position and atoms Br(1) and S(2) occupying the two other equatorial sites. The Pb-S bond distances [Pb-S(1) 2.841(2) and 2.6967(17) Å] indicate more asymmetric binding to the $\{Pt_2S_2\}$ metalloligand, with the bond length difference of 0.1444 Å comparable to the difference in Pb-S bond lengths of 0.125 Å in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbNO_3]PF_6$. The S-Pb-S bite angle of 66.99(5)° is comparable with the lead iodide adduct **4**.

The coordination chemistry of lead(II) is notoriously variable, resulting in structural diversity, depending on whether or not the $6s^2$ lone pair is stereochemically active. In many cases, a non-regular distribution of ligands (the *hemidirected geometry*) results in the presence of an empty face in the coordination polyhedron which is often used to infer the presence of the lone pair.[19] The hemidirected geometry was exclusively observed in the Cambridge Structural Database survey reported by Glusker *et al* for lead(II) complexes with low coordination numbers (2-5).[7] In other cases, especially involving the heavier halogens, bulky ligands, and higher coordination numbers, the *holodirected geometry* is observed, with regular coordination geometries, and a stereochemically inactive lone pair. The hardness of the ligands has a significant effect, with harder ligands being more likely to promote distortion of the coordination geometry through lone pair activity, especially in low coordination number complexes.[20] In holodirected geometries, the bonds are more covalent, and the lone pair has little *p*-character. These effects also appear to be extended to solid-state materials; a theoretical study has compared PbO (which adopts the distorted litharge structure, with a stereochemically active lone pair) with PbS (which adopts the symmetric rock salt structure, with six-coordinate, regular octahedral Pb(II) centres),[21] confirming the importance of the nature of the anion on the lone pair activity and hence on the structural chemistry.

It is therefore not unreasonable to suggest that the primary point of difference between the PbI_2 adduct (with a fairly regular tetrahedral coordination geometry) and the

$PbBr_2$ adduct (with a distorted geometry) is due to the differences in hardness of iodide compared to bromide, assisted by the steric bulk of the iodide and $\{Pt_2S_2\}$ ligands. This is consistent with the conclusions of Glusker *et al*,[7] who predicted on the basis of theoretical investigations that Pb(II) complexes with soft halide ligands should be holodirected.

We are unaware of any appropriate X-ray structures of four-coordinate lead(II) complexes containing halide- and sulfur-donor ligands, for comparative purposes. Indeed complexes such as $[PbBr_2\{SC(NH_2)_2\}_2]$ are polymeric, containing bridging thiourea ligands and have six- and seven-coordinate lead centres.[22,23] Indeed the low lead coordination numbers in **4** and **5** contrasts with the PbX_2 halides themselves; $PbBr_2$ has nine-coordinate lead, while PbI_2 has regular octahedral coordination.[24] The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbI_2]$ therefore represents a novel example of a low coordination number lead(II) complex with a holodirected geometry, and suggests that the metalloligands $[Pt_2(\mu\text{-}E)_2(PPh_3)_4]$ will continue to show utility in generating species with interesting coordination chemistry.

Mass spectrometric characterisation

The positive-ion ESI mass spectra of the adducts **4** and **5** in CH_2Cl_2-MeOH show ions formed by halide loss, *viz.* $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbX]^+$ (X = Br, *m/z* 1790; X = I, *m/z* 1837). Examination of the $PbBr_2$ adduct at higher cone voltages indicates that the ion is stable up to cone voltages of around 70 V, whereupon it begins to fragment. At 90 V $[M - Br - PPh_3]^+$ (*m/z* 1528) is observed as a low intensity ion but the base peak (*m/z* 1147) is formed by loss of PPh_3 and HBr from the $[M - Br]^+$ ion, and the resulting ion presumably contains a cyclometallated PPh_3 ligand, together with a bare Pb^{2+} centre coordinated to the $\{Pt_2S_2\}$ core. A possible structure is given by **6**; the lead heterometal in this species has analogies with the (isoelectronic) bare Tl^+ cation present in the species $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Tl]^+$. This fragmentation pattern has similarities with that observed for the lead(IV) species $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbMe_3]^+$ which initially gives $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbMe]^+$ which then fragments by loss of CH_4.[8]

When pyridine is added to a solution of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbBr_2]$ in CH_2Cl_2-MeOH, the resulting ESI mass spectrum at 20 V shows the formation of $[Pt_2S_2(PPh_3)_4 + H]^+$ (*m/z* 1504), indicating that the lead is bonded relatively weakly, and the $Pt_2S_2(PPh_3)_4$ metalloligand is displaced by a relatively weak donor ligand.

Reinvestigation of the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $Pb(NO_3)_2$

Previously, it was found that the lead bis-adducts $[\{Pt_2(\mu\text{-}E)_2(PPh_3)_4\}_2Pb]^{2+}$ could not be formed from either $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ [9] or $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ [10]. However, a number of divalent metal ions are known to form four-coordinate adducts of the type $[\{Pt_2S_2(PPh_3)_4\}_2M]^{2+}$, for M = Zn and Cd [25,26], Hg [27,28,29], Pd [27], Pt [30] and Cu.[31] Because ESI MS is a powerful technique for identifying traces of solution species, we have reinvestigated the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $Pb(NO_3)_2$ in a 2:1 molar ratio in methanol using ESI MS, but find no evidence for the formation of $[\{Pt_2S_2(PPh_3)_4\}_2Pb]^{2+}$ (calculated *m/z* 1606). The observed ions were $[Pt_2S_2(PPh_3)_4Pb]^{2+}$ (*m/z* 855, 100%), $[Pt_2S_2(PPh_3)_4PbNO_3]^+$ (*m/z* 1772, 50%) and $[Pt_2S_2(PPh_3)_4PbCl]^+$ (*m/z* 1745, 45%), the latter presumably formed from traces of adventitious chloride ions. High steric demand of $[Pt_2S_2(PPh_3)_4]$ is clearly not a significant factor here, because of the significant number of $[\{Pt_2S_2(PPh_3)_4\}_2M]^{2+}$ species now known (containing both square-planar and tetrahedral metal centres).

Experimental

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was synthesised by the literature procedure, from *cis*-$[PtCl_2(PPh_3)_2]$ and $Na_2S.9H_2O$ in benzene suspension.[32] Lead(II) bromide and lead(II) iodide were prepared by addition of NaBr or NaI (BDH) to an aqueous solution of lead(II) nitrate (BDH); the resulting $PbBr_2$ (white) or PbI_2 (yellow) was isolated by filtration, washed with distilled water, and dried *in vacuo*. Methanol was AR grade, and used as supplied. ESI mass spectra were recorded in positive-ion mode on a VG Platform II mass spectrometer using solutions prepared by dissolving the solid complex in a small quantity of CH_2Cl_2, followed by dilution with methanol. Cone voltages were varied from 5 to 90 V, with 20 V used for routine characterisation.

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbI_2]$ 4

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (331 mg, 0.220 mmol) and PbI_2 (220 mg, 0.477 mmol) in methanol (30 mL) was stirred, rapidly giving a bright yellow suspension. After stirring for 16 h the yellow solid was isolated by filtration, washed with methanol (5 mL) and air dried. The solid was extracted with dichloromethane (30 mL) and excess PbI_2 removed by filtration to give a bright yellow solution. Petroleum spirits (60 mL) was added, giving a bright yellow microcrystalline solid which was filtered, washed with petroleum spirits (5 mL) and dried *in vacuo* to give **4** (250 mg). Found: C, 44.5; H, 3.5.

$C_{72}H_{60}I_2P_4PbPt_2S_2$ requires C, 44.0; H, 3.1%. ESI MS (cone voltage 20 V) *m/z* 1837, $[M - I]^+$.

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbBr_2]$ 5

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (274 mg, 0.182 mmol) and $PbBr_2$ (230 mg, 0.627 mmol) in methanol (25 mL) was stirred, rapidly giving a lemon yellow suspension. After stirring for 7 h, the solid was filtered off, washed with methanol (5 mL) and dried. The solid was extracted with dichloromethane (30 mL) and excess $PbBr_2$ filtered off to give a yellow solution. Petroleum spirits (40 mL) was added, giving a lemon yellow microcrystalline solid which was filtered, washed with petroleum spirits (5 mL) and dried *in vacuo* to give **5**·1.5CH_2Cl_2 (147 mg). Found: C, 44.2; H, 3.2. $C_{72}H_{60}Br_2P_4PbPt_2S_2.1.5CH_2Cl_2$ requires C, 44.2; H, 3.2%. ESI MS (cone voltage 20 V) *m/z* 1790, $[M - Br]^+$; cone voltage 90 V *m/z* 1147 (100%) $[M - PPh_3 - HBr_2]^+$, 1528 (10%) $[M - PPh_3 - Br]^+$, 1790 (20%) $[M - Br]^+$.

X-ray crystal structure determinations

Crystals of the complexes suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into dichloromethane solutions at room temperature, giving lemon yellow ($PbBr_2$) and deep yellow (PbI_2) crystals, both as dichloromethane solvates. The PbI_2 adduct lost solvent upon drying *in vacuo*. Data were corrected for absorption using SADABS [33]; refinement was full-matrix least-squares based on F^2. Crystal, collection and refinement details are given in Table 3.

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbI_2]$ **4**

The asymmetric unit contains one molecule of the complex, together with two sets of disordered dichloromethane solvent molecules. One set contains two molecules of CH_2Cl_2 at partial occupancy, while the second set contains one molecule.

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbBr_2]$ **5**

The asymmetric unit contains one molecule of the complex and two CH_2Cl_2 solvent molecules, one of which is disordered. One of the bromines is disordered over two positions.

Crystallographic data (excluding structure factors) for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 755485 (**4**) and 755486 (**5**). Copies of the data can be obtained free of charge on application to 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).

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Table 1 Selected bond lengths (Å) and angles (˚) for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbI_2]$ **4**

Pt(1)-P(1)	2.2829(6)	Pt(1)-P(2)	2.2951(8)
Pt(1)-S(2)	2.3431(8)	Pt(1)-S(1)	2.3711(7)
Pt(2)-P(4)	2.2879(6)	Pt(2)-P(3)	2.2943(6)
Pt(2)-S(1)	2.3348(7)	Pt(2)-S(2)	2.3662(6)
Pb(1)-S(2)	2.7725(7)	Pb(1)-S(1)	2.7809(8)
Pb(1)-I(2)	3.1623(3)	Pb(1)-I(1)	3.2113(4)

P(1)-Pt(1)-P(2)	98.73(3)	S(2)-Pt(1)-S(1)	81.38(2)
P(4)-Pt(2)-P(3)	98.37(2)	S(1)-Pt(2)-S(2)	81.66(2)
S(2)-Pb(1)-S(1)	67.21(2)	S(2)-Pb(1)-I(2)	111.689(17)
S(1)-Pb(1)-I(2)	115.122(16)	S(2)-Pb(1)-I(1)	113.459(15)
S(1)-Pb(1)-I(1)	122.680(17)	I(2)-Pb(1)-I(1)	116.209(9)

Table 2 Selected bond lengths (Å) and angles (˚) for [$Pt_2(\mu\text{-}S)_2(PPh_3)_4PbBr_2$] **5**

Pt(1)-P(3)	2.3016(17)	Pt(1)-P(4)	2.3130(16)
Pt(1)-S(2)	2.3649(17)	Pt(1)-S(1)	2.3467(16)
Pt(2)-P(1)	2.2901(18)	Pt(2)-P(2)	2.2923(18)
Pt(2)-S(1)	2.3598(17)	Pt(2)-S(2)	2.3496(17)
Pb(1)-S(2)	2.6967(17)	Pb(1)-S(1)	2.841(2)
Pb(1)-Br(1)	2.9400(11)	Pb(1)-Br(2)	2.880(2)
Pb(1)-Br(2a)	2.975(2)		

P(3)-Pt(1)-P(4)	102.95(6)	S(2)-Pt(1)-S(1)	80.96(6)
P(1)-Pt(2)-P(2)	101.19(7)	S(1)-Pt(2)-S(2)	81.00(6)
S(2)-Pb(1)-S(1)	66.99(5)	S(2)-Pb(1)-Br(1)	101.38(4)
S(1)-Pb(1)-Br(1)	98.18(4)		

Table 3 Crystal, collection and refinement data for the X-ray structure determinations of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbI_2]$ **4** and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbBr_2]$ **5**

	4	**5**
Empirical formula	$C_{73.5}H_{63}Cl_3I_2P_4PbPt_2S_2$	$C_{73.5}H_{63}Br_2Cl_3P_4PbPt_2S_2$
Formula weight	2091.76	1997.78
Temperature (K)	223(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/c
Unit cell dimensions		
a	12.4505(5)	22.5216(8)
b	16.6834(6)	13.7994(5)
c	18.5077(7)	24.3756(9)
α	75.8380(10)	90
β	79.4060(10)	111.4790(10)
γ	80.1070(10)	90
Volume ($Å^3$)	3631.4(2)	7049.4(4)
Z	2	4
Density (calc.) ($Mg\ m^{-3}$)	1.913	1.882
Absorption coeff. (mm^{-1})	7.302	7.781
F(000)	1982	3820
Crystal size (mm^3)	0.20 x 0.16 x 0.02	0.30 x 0.20 x 0.16
Reflections collected	21339	49254
Independent reflections	12765 [$R_{(int)}$ = 0.0325]	16199 [$R_{(int)}$ = 0.0585]
Max. and min transmission	0.8677 and 0.3229	0.3691 and 0.2037
Data / restraints / parameters	12765 / 18 / 803	16199 / 14 / 819
Goodness-of-fit on F^2	1.063	1.003
Final R indices [$I > 2\sigma(I)$]		
R_1	0.0516	0.0444
wR_2	0.1242	0.1005
R indices (all data)		
R_1	0.0581	0.0719
wR_2	0.1284	0.1102
Largest peak (e $Å^{-3}$)	2.307	2.912
Largest hole (e $Å^{-3}$)	-3.100	-1.376

Captions for Figures

Figure 1 Molecular structure of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbI_2]$ **4** showing the atom numbering scheme. Triphenylphosphine carbon atoms, other than *ipso* carbons, have been omitted for clarity.

Figure 2 Molecular structure of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbBr_2]$ **5** showing the atom numbering scheme. Triphenylphosphine carbon atoms, other than *ipso* carbons, have been omitted for clarity. Bromine Br(2) is disordered over two positions indicated by Br(2) and Br(2a).

Figure 3 Alternative view showing a comparison of the cores of (a) complex **4** and (b) complex **5**, illustrating the tetrahedral geometry of the lead atom in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PbI_2]$ **4**. All triphenylphosphine carbon atoms are omitted.

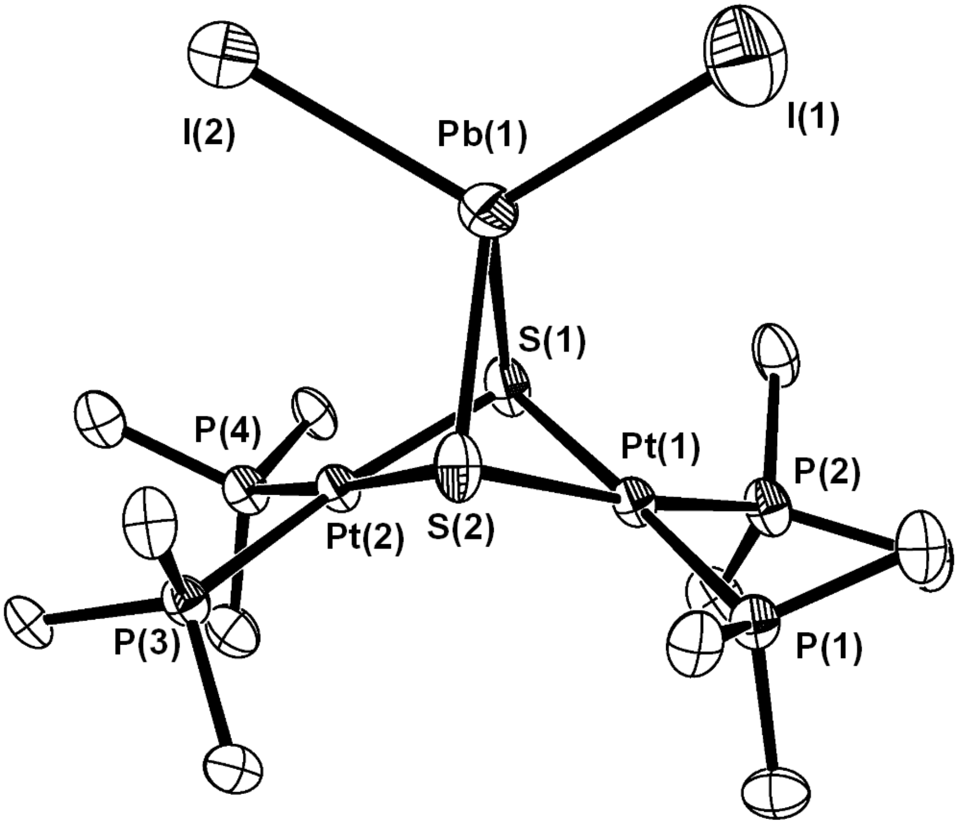

Figure 1

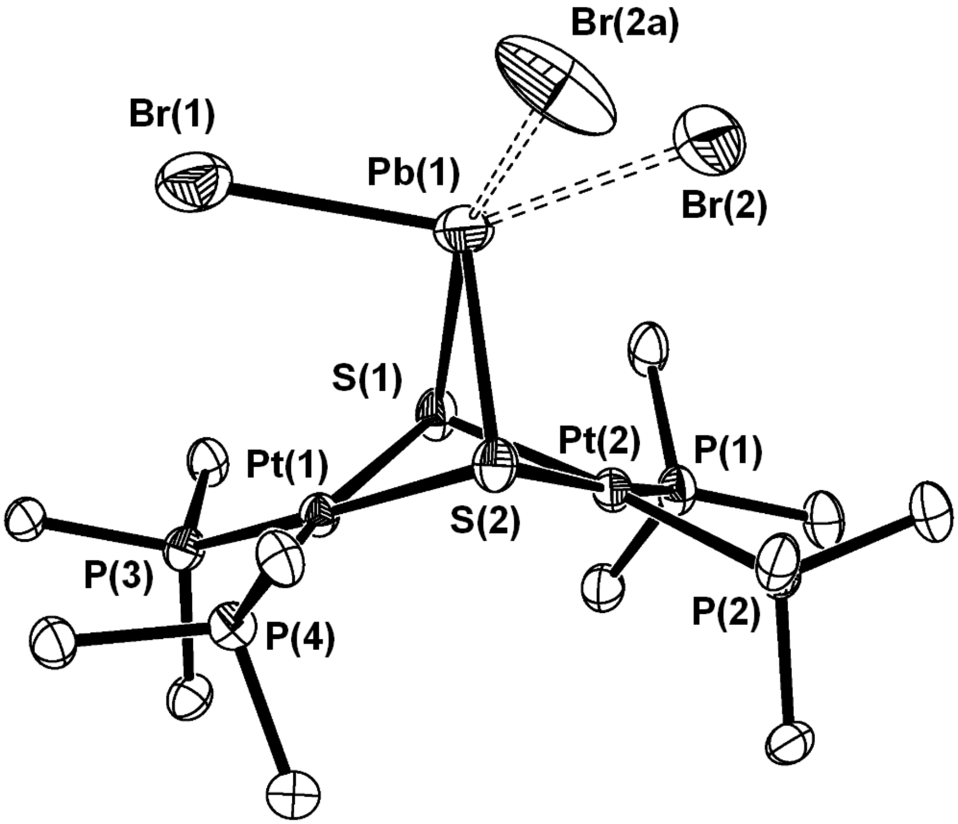

Figure 2

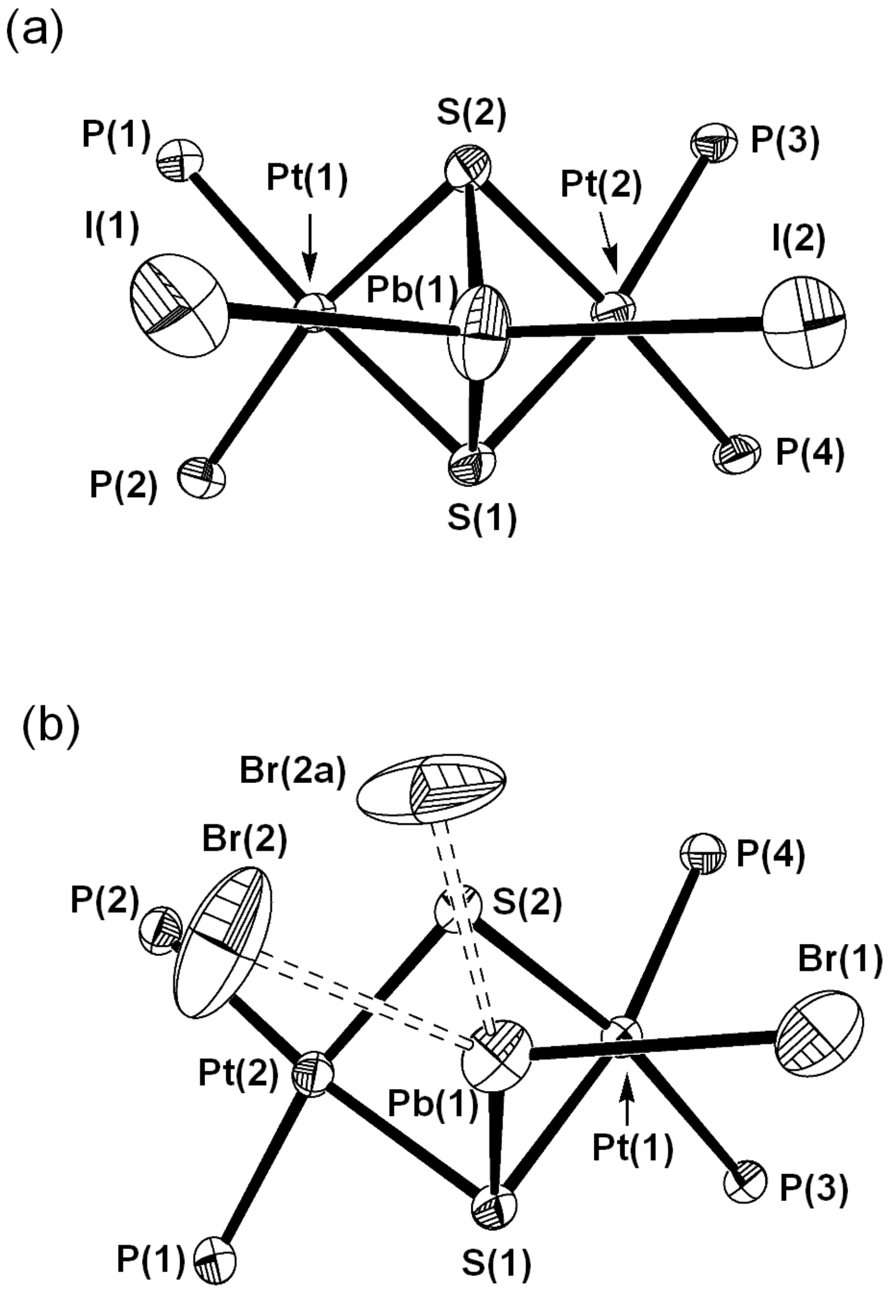
(a)
P(1)
S(2)
P(3)
Pt(1)
Pt(2)
I(1)
I(2)
Pb(1)
P(2)
S(1)
P(4)
(b)
Br(2a)
Br(2)
P(4)
P(2)
S(2)
Br(1)
Pt(2)
Pb(1)
Pt(1)
P(3)
P(1)
S(1)

Figure 3

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