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Heterobimetallic platinum–bismuth aggregates derived from [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$]

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Abstract

The metalloligand [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] reacts with Bi(S$_2$CNEt$_2$)$_3$ or Bi(S$_2$COEt)$_3$ in methanol to produce the orange cationic adducts [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Bi(S$_2$CNEt$_2$)$_2$]$^+$ and [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Bi(S$_2$COEt)$_2$]$^+$, respectively, isolated as their hexafluorophosphate salts. An X-ray structure determination on [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Bi(S$_2$CNEt$_2$)$_2$]PF$_6$ reveals the presence of a six-coordinated bismuth centre with an approximately *nido*-pentagonal bipyramidal coordination geometry. Fragmentation pathways for both complexes have been probed using electrospray ionisation mass spectrometry; ions [Pt$_2$(μ-S)$_2$(PPh$_3$)$_2$Bi(S$_2$CXEt$_n$)$_2$]$^+$ (X = O, n = 1, X = N, n = 2) are formed by selective loss of two PPh$_3$ ligands, and at higher cone voltages the species [(Ph$_3$P)PtS$_2$Bi]$^+$ is observed. Ions formed by loss of CS$_2$ are also observed for the xanthate but not the dithiocarbamate ions.
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1. Introduction

The sulfido complex [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] has been known for many years to contain highly nucleophilic sulfide centres that interact with organic and metal-based electrophiles [1]. By reaction with metal electrophiles – typically metal salts or coordination complexes containing labile anionic ligands such as halides – sulfide-bridged homo- and heterobimetallic aggregates result. The ability to attach a wide range of metal fragments to the {Pt$_2$S$_2$} core has the potential to tailor the properties of the resulting aggregate, for example to produce species with unusual structures, or with redox activity. We have been developing a mass spectrometry-based approach, whereby the reactivity of [Pt$_2$(μ-S)$_2$-(PPh$_3$)$_4$] and the selenium analogue [Pt$_2$(μ-Se)$_2$(PPh$_3$)$_4$] towards various metal complexes is carried out rapidly,

on a micro-scale, using electrospray ionisation mass spectrometry (ESI MS). This has been successfully used in a range of systems [2–8].

Relatively little work has been carried out on the chemistry of main group derivatives of the {Pt$_2$S$_2$} core, though some heterobimetallic aggregates of lead(II) [9], indium(III) and gallium(III) [10], and thallium(I) [11] have been prepared. Some of these derivatives have novel structures and have been the subject of a theoretical study [12]. The related derivative [Pt$_2$(μ-S)$_2$-(dppf)$_2$] [dppf = 1,1′-bis(diphenylphosphino)ferrocene] also forms thallium(I), indium(III) and lead(II) derivatives [13].

In the area of bismuth chemistry, earlier studies indicated that adducts with this metal can be synthesised. Reaction of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with BiCl$_3$ gave [Pt$_2$-(μ-S)$_2$(PPh$_3$)$_4$BiCl$_3$] which on metathesis with NH$_4$PF$_6$ produced [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$BiCl$_2$]PF$_6$ [14]. [Pt$_2$(μ-S)$_2$-(PPh$_3$)$_4$- BiCl$_3$] undergoes chloride dissociation followed by addition of a second equivalent of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$]

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to give the bis-adduct $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2BiCl_2]Cl$ and other Bi species such as $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2BiCl]Cl_2$ are detected in solution [15]. Given the strong affinity of the heavy main group metals (particularly bismuth) for sulfur ligands, we reasoned that $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ should form derivatives with sulfur-ligand bismuth precursors. Such sulfur-rich derivatives of the $\{Pt_2S_2\}$ core are hitherto unknown, and the utility of bismuth-dithiocarbamate and -xanthate complexes as precursors to solid-state bismuth sulfide materials [16] suggests that the heterobimetallic systems might likewise provide a potential route to novel mixed-metal-sulfide phases. In this paper we describe the synthesis and characterisation of such sulfur-rich heterobimetallic Pt–Bi aggregates, using our methodology of mass spectrometry-directed synthesis to screen for promising systems, and to characterise reaction products.

2. Results and discussion

2.1. Scoping study using ESI mass spectrometry

ESI mass spectrometry has been used to screen the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards the bismuth complexes $Bi(S_2CNEt_2)_3$ and $Bi(S_2COEt)_3$, containing bidentate dithiocarbamate and xanthate donor ligands. Intensely yellow solutions were rapidly produced, which showed primarily the adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)_2]^+$ (m/z 2008) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2COEt)_2]^+$ (m/z 1954), respectively. In each case a significant byproduct was formed, identified by characteristic m/z values and isotope patterns as the mononuclear complexes $[Pt(S_2CNEt_2)(PPh_3)_2]^+$ and $[Pt(S_2COEt)(PPh_3)_2]^+$ at m/z 867 and 840, respectively. For the dithiocarbamate reaction, an additional low intensity species was identified as the chloro complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)Cl]^+$ (m/z 1895), most likely from the presence of chloride-containing impurities in the bismuth complex(es), whose synthesis involved dissolution of bismuth(III) nitrate in hydrochloric acid, followed by addition of the dithiocarbamate or xanthate salt [16].

The formation of the mononuclear species $[Pt(S–S)(PPh_3)_2]^+$ (S–S = bidentate dithiocarbamate or xanthate) presumably arises from the product cations $[Pt_2(\mu\text{-}S)_2(PPh_3)_4M(S–S)_2]^+$; these trinuclear cations may be susceptible to attack by the liberated dithio ligand, causing breakup of the trinuclear aggregate. In an attempt to minimise the formation of these mononuclear byproducts, the reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with 1 and 2 mol. equiv. of $Bi(S_2CNEt_2)_3$ were monitored by ESI MS. After 10 min and 16 h reaction times, the observed ions for the different stoichiometries were remarkably similar, with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)_2]^+$ being the base peak in both cases, and similar amounts of

byproduct $[Pt(S_2CNEt_2)(PPh_3)_2]^+$ observed. For the reaction with excess $Bi(S_2CNEt_2)_3$, ions derived from the starting bismuth dithiocarbamate complexes were also seen, namely $[Bi(S_2CNEt_2)_2]^+$ (m/z 505) and $[Bi_2(S_2CNEt_2)_5]^+$ (m/z 1158), together with a trace of the chloro complex described above. Fig. 1 shows positive-ion ESI mass spectra for 1:1 and 1:2 mole ratios of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $Bi(S_2CNEt_2)_3$, after a reaction time of 10 min. With a 2:1 mole ratio of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to $Bi(S_2CNEt_2)_3$, the adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)_2]^+$ again dominated the spectrum, demonstrating the tendency to form this product species irrespective of the reaction stoichiometry; no species with two $\{Pt_2S_2\}$ moieties coordinated to a single bismuth were observed in this experiment. As expected, unreacted $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was observed (as its $[M + H]^+$ ion), together with the usual byproduct ion $[Pt(S_2CNEt_2)(PPh_3)_2]^+$ and some minor unidentified species.

Because it was believed that the liberated dithiocarbamate or xanthate ligands might be responsible for the formation of the mono-platinum byproducts, an experiment was carried out to try and minimise liberation of the sulfur ligand, by generation of a Bi starting complex with only 2 mol. equiv. of dithiocarbamate per Bi. Reaction of $BiBr_3$ with 2 equiv. of $Bi(S_2CNEt_2)_3$ was firstly carried out, followed by addition of the stoichiometric quantity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to give a $\{Pt_2S_2\}$:Bi ratio of 1:1. However, the ESI mass spectrum of the resulting reaction mixture again showed a mixture of the desired $\{Pt_2S_2Bi\}$ adduct, and $[Pt(S_2CNEt_2)(PPh_3)_2]^+$. Slow addition of a solution/suspension of $Bi(S_2CNEt_2)_3$ to a stirred suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in methanol did also not eliminate the formation of $[Pt(S_2CNEt_2)(PPh_3)_2]^+$.

2.2. Macroscopic syntheses and spectroscopic characterisation

The bismuth adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)_2]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2COEt)_2]^+$ were subsequently synthesised on the macroscopic scale. Products were isolated by addition of excess NH_4PF_6 to the filtered reaction solutions, giving the salts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)_2]PF_6$ (1) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2COEt)_2]PF_6$ (2) as bright orange solids. The isolated products contained small traces of the mononuclear platinum-dithiolate species $[Pt(S_2CNEt_2)(PPh_3)_2]^+$.

The complexes show a single resonance in the $^{31}P–\{^1H\}$ NMR spectrum showing coupling to ^{195}Pt ($J = 3023$ Hz for 1 and 3087 Hz for 2), and the ^1H NMR spectra shows the expected resonances due to PPh_3 ligands and ethyl groups of the dithiocarbamate or xanthate ligands. Complex 2 was unstable in chloroform solution, undergoing partial decomposition to a species at δ 4.2 showing ^1J(PtP) 3361 Hz, assigned to
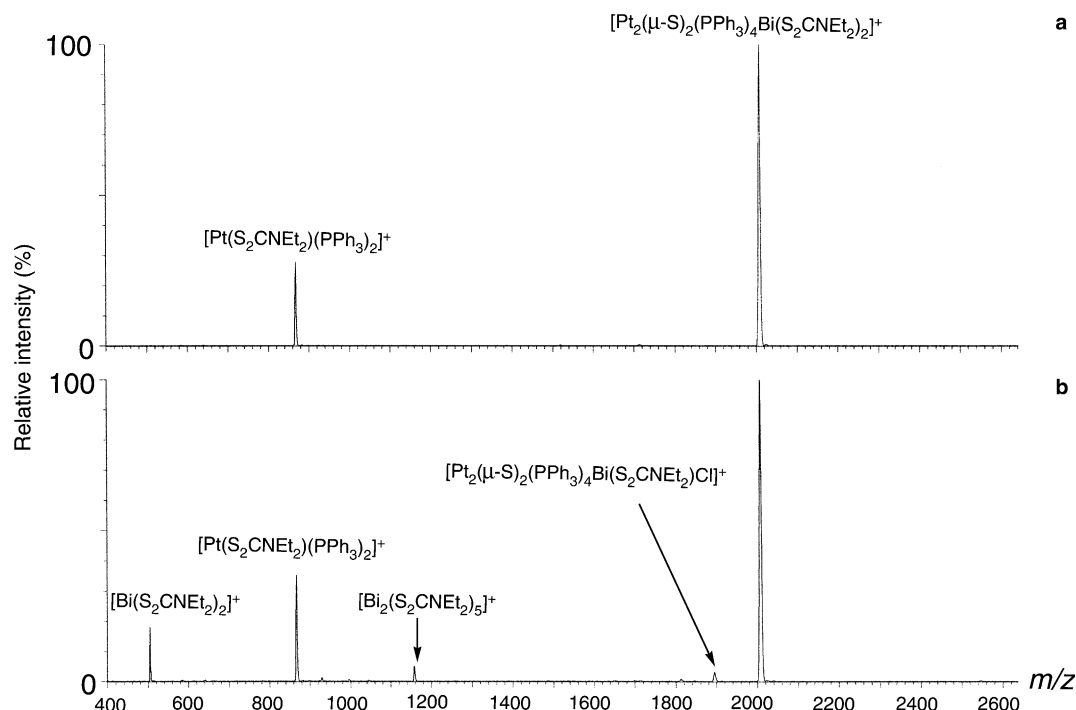
Fig. 1. Positive-ion ESI mass spectra for the reaction between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and $Bi(S_2CNEt_2)_3$ in methanol at a cone voltage of 20 V, after a reaction time of 10 min: (a) $\{Pt_2S_2\}$:Bi mole ratio = 1:1; and (b) $\{Pt_2S_2\}$:Bi mole ratio = 1:2.

$[Pt(S_2COEt)(PPh_3)_2]^+$, as well as a small peak at δ −5 tentatively assigned as free PPh_3. The ESI mass spectrum of the chloroform solution, after dilution with methanol, also showed an enhanced peak due to $[Pt(S_2COEt)(PPh_3)_2]^+$.
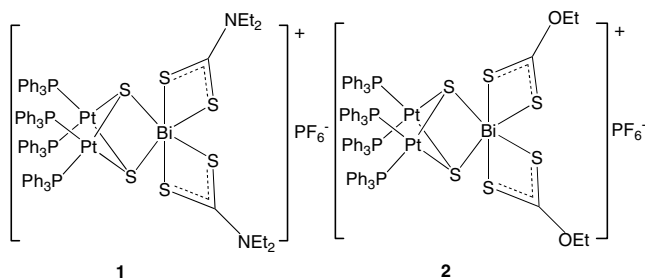
The ESI MS behaviour of complexes **1** and **2** was investigated using a range of cone voltages to effect fragmentation; there are similarities and differences between the two complexes. A freshly prepared solution of **2** in dichloromethane-methanol at a low cone voltage (20 V; Fig. 2(a)) shows predominantly the parent cation together with a trace of the mononuclear byproduct $[Pt(S_2COEt)(PPh_3)_2]^+$ as discussed earlier. The parent cation remains the dominant base peak up to a cone voltage of at least 60 V. At higher cone voltages fragment ions dominate the spectra, as illustrated by the spectrum at 90 V shown in Fig. 2(b). A wide range of fragment ions are observed, and all can be identified. Loss of one and two CS_2 from the parent ion gives low intensity ions at m/z 1878 and 1802, presumably forming ions with Bi-OEt groups. An ion at m/z 1429 is formed by loss of two PPh_3 ligands from the parent cation, but interestingly the ion formed by loss of one PPh_3, expected at m/z 1692, was not observed. The corresponding CS_2-loss ion $[Pt_2S_2(PPh_3)_2Bi(S_2COEt)\text{-}(OEt)]^+$ is also observed as a low intensity ion at m/z 1353. At a cone voltage of 90 V, the base peak in the spectrum occurs at m/z 992, and analysis of its isotope distribution pattern reveals the characteristic pattern of a *mono*-platinum species. This species is tentatively identified as $[(Ph_3P)PtS_2Bi]^+$, which gives a good match of calculated and experimental isotope patterns. The observation of this species suggests that the $\{Pt_2S_2Bi\}$ core has fragmented by loss of a platinum centre, and that the Bi–S bonds are strong. Other ions observed in the spectrum at 90 V are $[Pt(S_2COEt)(PPh_3)_2]^+$ (m/z 840), the (frequently observed) [17] cyclometallated species $[Pt(Ph_2PC_6H_4)(PPh_3)]^+$ (m/z 718), and $[Pt(S_2COEt)(PPh_3)]^+$ (m/z 578). Upon allowing the (pale yellow) analyte solution to stand overnight, it turned brown and the species observed in the ESI mass spectrum changed dramatically (Fig. 2(c)) with the base peak being the mono-platinum species $[Pt(S_2CO\text{-}Me)(PPh_3)_2]^+$ at m/z 826. This is formed by decomposition of the parent cation and exchange of the OEt

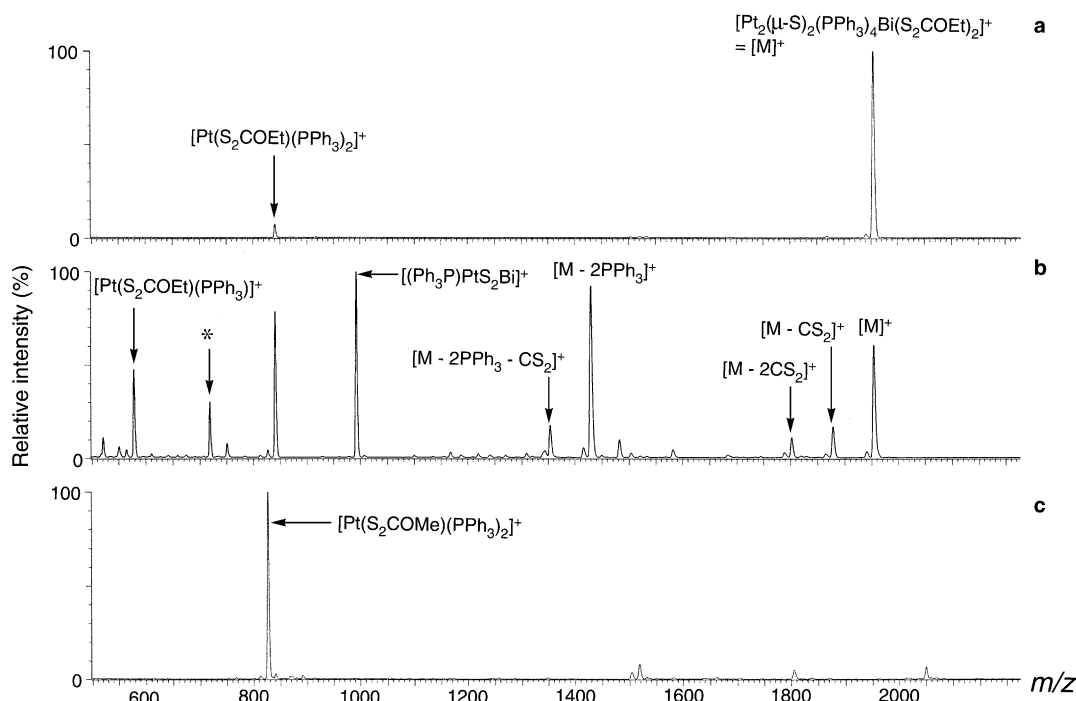Fig. 2. Positive-ion ESI mass spectra of the complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2COEt)_2]PF_6$ (**2**) in dichloromethane-methanol solution: (a) at a cone voltage of 20 V; (b) at a cone voltage of 90 V; (c) at 20 V after standing the analyte solution overnight. The peak marked * is the cyclometallated phosphine ion $[Pt(Ph_2PC_6H_4)(PPh_3)]^+$.

group of the xanthate ligand with the methanol solvent. Close examination of the spectrum in Fig. 2(b) reveals that corresponding methoxy analogues are observed as low intensity companions for the majority of species, but importantly not for $[(Ph_3P)PtS_2Bi]^+$ (m/z 992) nor $[Pt(Ph_2PC_6H_4)(PPh_3)]^+$ (m/z 718), consistent with their formulations.

Overall the major features observed for the dithiocarbamate complex **1** at a range of cone voltages are similar to those of the xanthate complex **2**. The base peak at low to moderate cone voltages (up to 70 V) is the parent cation, and a trace of the byproduct $[Pt(S_2CNEt_2)(PPh_3)_2]^+$ was observed at m/z 867. The major fragment ion, observed as the base peak at 90 V is also the ion formed by loss of two PPh_3 ligands, i.e., $[Pt_2S_2(PPh_3)_2Bi(S_2CNEt_2)_2]^+$ observed at m/z 1483. At even higher cone voltages, the species $[(Ph_3P)PtS_2Bi]^+$ at m/z 992 became prominent, and was the base peak at 110 V. However, the major difference between the xanthate and dithiocarbamate systems is that no ions formed by loss of CS_2 were observed from the dithiocarbamate system.

Given that the major initial fragment ion for both complexes **1** and **2** involves selective loss of two PPh_3 ligands, it is appropriate to speculate on the nature of this fragment ion. One possibility is that the chelating dithio ligands on bismuth have become monodentate, with the free sulfur donor coordinating to platinum, maintaining its preferred four-coordination.

When the spectrum of **2** was recorded at a very low cone voltage (3 V), no additional higher m/z ions formed by addition of methanol were observed. Similarly, addition of neither pyridine nor 2,2′-bipyridine to the sample resulted in additional ions. These observations suggest that the bismuth centre is effectively coordinatively saturated and shows no tendency to expand its coordination number. In contrast, addition of sodium diethyldithiocarbamate to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2COEt)_2]PF_6$ **2** resulted in immediate conversion to the bis(dithiocarbamate) $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)_2]^+$ as the base peak at m/z 2008.

2.3. X-ray crystal structure of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)_2]PF_6$ (**1**)

An X-ray structure determination was carried out in order to determine the coordination geometry around the bismuth centre in **1**. The complex consists of a $Bi(S_2CNEt_2)_2^+$ fragment coordinated to the $\{Pt_2S_2\}$ core, generating a BiS_6 coordination environment, as illustrated in Fig. 3. The complex has the typical trigonal arrangement of three metals (Pt_2Bi) triply-bridged by two μ_3-sulfide ligands. All three S–S bidentate ligands bind to the bismuth centre asymmetrically, with one Bi–S bond notably shorter than the other. Thus, for the two dithiocarbamate ligands, short Bi–S distances of 2.688(2) and 2.718(2) Å compare with longer distances of 2.910(2) and 2.876(2) Å for the same ligand. Additionally, each dithiocarbamate ligand has a shorter and a
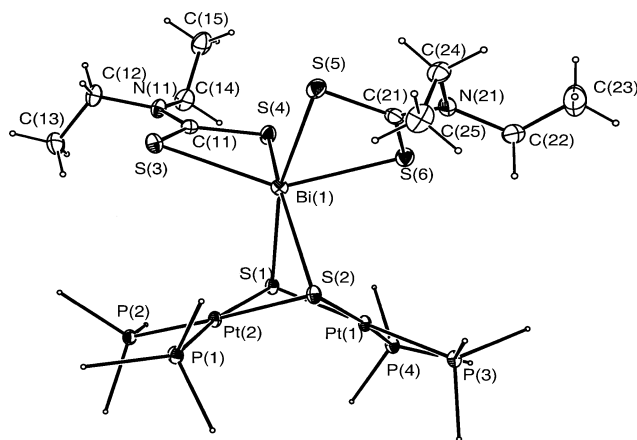
Fig. 3. Molecular structure of the cation $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2C\text{-}NEt_2)_2]^+$ of (**1**) showing the atom numbering scheme. Only the *ipso* carbon atoms of the triphenylphosphine ligands are shown for clarity.
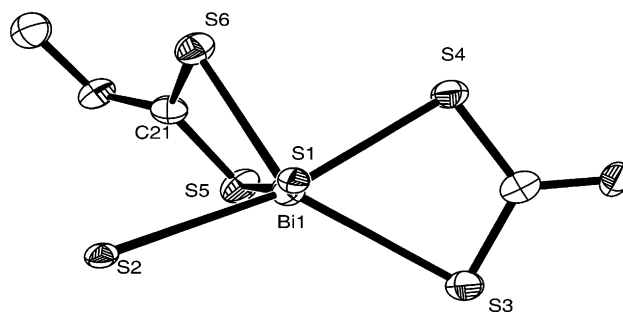

Fig. 4. The coordination geometry around the bismuth centre of **1**, showing the *nido*-pentagonal bipyramidal geometry with the lone pair located in an equatorial position located between S(2) and S(3).

longer C–S bond, for example 1.720(8) and 1.753(8) Å; the sulfur with the shorter C–S bond is the one coordinating with the longer Bi–S bond in each case. Taken together, these indicate primary coordination of the bismuth to two dithiocarbamate sulfur donors, and weaker interactions to the other two dithiocarbamate sulfurs. By comparison, in $Bi(S_2CNEt_2)_3$, are three short primary Bi–S bonds in the range 2.595(5)–2.775(5) Å, and three secondary Bi–S bonds that are longer at 2.956(5)–2.964(4) Å [18,19]. This appears to be a general feature in bismuth dithiocarbamate compounds [20]. Likewise for the coordination of the $\{Pt_2S_2\}$ metalloligand, unequal and relatively long Bi–S bond distances of 2.7341(18) and 2.9587(19) Å are also observed. The same asymmetry is seen in the previously characterised $[Pt_2(\mu\text{-}S)_2(PPh_3)_4BiCl_3]$ which has Bi–S bond distances of 2.639(3) and 2.884(3) Å, and in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4BiCl_2]^+$ [2.626(7) and 2.758(7) Å]. Bite angles for all three S–S ligands are around 65°, for example, the metalloligand bite angle S(1)–Bi(1)–S(2) is 65.16(5)°, which compares with 66.6(1)° in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4BiCl_3]$ and 70.1(2)° in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4BiCl_2]PF_6$ [14].

The geometry about the bismuth centre is approximately *nido*-pentagonal bipyramidal, with the stereochemically-active lone pair located between S(2) and S(3) as illustrated in Fig. 4. The S(2)–Bi(1)–S(3) bond angle is 127.47(5)°. In $Bi(S_2CNEt_2)_3$ the bismuth geometry is a pentagonal bipyramid with the lone pair in an axial position. The dihedral angle between the two platinum coordination planes is 152.1°, considerably larger than angles of 130.7(2)° and 128.8(3)° in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4BiCl_2]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4BiCl_3]$, respectively (see Table 1).

2.4. Conclusions

Two new sulfur-rich adducts of the $\{Pt_2S_2\}$ metalloligand system with bismuth dithiolate complexes have been reported for the first time, extending the (relatively small) list of main group adducts of this system. As was also the case with some of our other recent studies, electrospray ionisation mass spectrometry is a powerful technique for reaction screening and product characterisation.

3. Experimental

3.1. Methods and instrumentation

General instrumental details were as described in recent papers from these laboratories [2–8]. NMR spectra were recorded on freshly-prepared solutions, on a Bruker AC300P spectrometer [^{1}H 300.13 MHz, ^{31}P 121.51 MHz] in $CDCl_3$ solution. Microanalytical data were obtained from the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

Electrospray mass spectra were recorded using positive-ion mode on a VG Platform II instrument, using

Table 1
Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2C\text{-}NEt_2)_2]PF_6$ (**1**)

Pt(1)–P(3)	2.2794(18)	Pt(1)–P(4)	2.3116(18)
Pt(1)–S(1)	2.3588(17)	Pt(1)–S(2)	2.3465(17)
Pt(2)–P(1)	2.2990(18)	Pt(2)–P(2)	2.2831(19)
Pt(2)–S(1)	2.3633(17)	Pt(2)–S(2)	2.3606(17)
Bi(1)–S(1)	2.7341(18)	Bi(1)–S(2)	2.9587(19)
Bi(1)–S(3)	2.910(2)	Bi(1)–S(4)	2.688(2)
Bi(1)–S(5)	2.876(2)	Bi(1)–S(6)	2.718(2)
C(11)–S(3)	1.722(8)	C(11)–S(4)	1.743(8)
C(21)–S(5)	1.720(8)	C(21)–S(6)	1.753(8)
C(11)–N(11)	1.317(10)	C(21)–N(21)	1.335(10)
P(1)–Pt(2)–P(2)	99.87(7)	P(3)–Pt(1)–P(4)	99.29(7)
S(1)–Pt(2)–S(2)	81.10(6)	S(1)–Pt(1)–S(2)	81.49(6)
Pt(1)–S(1)–Pt(2)	97.79(6)	Pt(1)–S(2)–Pt(2)	88.13(6)
Pt(1)–S(1)–Bi(1)	91.69(6)	Pt(1)–S(2)–Bi(1)	86.53(5)
Pt(2)–S(1)–Bi(1)	82.23(5)	Pt(2)–S(2)–Bi(1)	77.54(5)
S(1)–Bi(1)–S(2)	65.16(5)	S(3)–Bi(1)–S(4)	64.24(6)
S(5)–Bi(1)–S(6)	64.28(6)	S(3)–C(11)–S(4)	118.8(5)
S(5)–C(21)–S(6)	118.1(5)		

methanol as the mobile phase and solvent. Survey reactions were carried out by dissolving $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and the bismuth compound (ca. 0.5 mg of each) in methanol (2 mL), shaking to effect reaction, centrifuging if necessary, followed by recording the positive-ion ESI mass spectrum using a cone voltage of 20 V. Stoichiometric ESI MS-monitored reactions were carried out by dissolving $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (25 mg) and the appropriate quantity of $Bi(S_2CNEt_2)_3$ in methanol with stirring, to give a dissolved solids concentration of about 1 mg mL^{-1}. Assignment of all ions was assisted by use of the ISOTOPE simulation program [21].

3.2. Materials

Reactions were carried out in LR grade methanol, without exclusion of air. Products were recrystallised from dichloromethane and diethyl ether that were dried and distilled (from CaH_2 and sodium-benzophenone ketyl, respectively) under a nitrogen atmosphere prior to use. Petroleum spirits refers to the fraction having boiling range 60–80 °C.

The following materials were used as supplied from commercial sources: bismuth(III) nitrate pentahydrate (Ajax Laboratory Chemicals, NSW, Australia), bismuth-(III) bromide (Aldrich), sodium diethyldithiocarbamate (Aldrich), ammonium hexafluorophosphate (Aldrich). The complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ [22] $Bi(S_2CNEt_2)_3$ [16] and $Bi(S_2COEt)_3$ [16] were prepared by the literature procedures.

3.3. Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2CNEt_2)_2]PF_6$ (1)

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (300 mg, 0.200 mmol) and $Bi(S_2CNEt_2)_3$ (130 mg, 0.200 mmol) were stirred in methanol (40 mL) for 15 min giving a slightly cloudy orange solution. The solution was filtered, and to the filtrate was added NH_4PF_6 (300 mg, 1.84 mmol), with stirring. After stirring for 30 min, the resulting orange solid was filtered, washed successively with water (10 mL), cold methanol (5 mL) and petroleum spirits (5 mL) and dried under vacuum to give 1 (220 mg, 51%). *Anal.* Calc. for $C_{82}H_{80}N_2BiF_6P_5Pt_2S_6$ requires C, 45.7; H, 3.7; N, 1.3. Found: C, 45.5; H, 3.75; N, 1.4%. ESI MS: m/z 2008 [M]$^+$, 100%, together with a trace of $[Pt(S_2CNEt_2)(PPh_3)_2]^+$ at m/z 867. ^{31}P–{^{1}H} NMR, δ 20.3 [s, ^1J(PtP) 3023].

3.4. Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Bi(S_2COEt)_2]PF_6$ (2)

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (300 mg, 0.200 mmol) and $Bi(S_2COEt)_3$ (114 mg, 0.200 mmol) were stirred in a mixture of methanol (30 mL) and ethanol (30 mL) for 1 h. giving a slightly cloudy orange solution. The solu-

tion was filtered, and to the filtrate was added NH_4PF_6 (300 mg, 1.84 mmol), resulting in formation of an orange precipitate. After stirring for 10 min, water (10 mL) was added, and the product filtered, washed successively with water (10 mL), ethanol (5 mL) and petroleum spirits (5 mL), and dried under vacuum to give 2 (230 mg, 55%) as a bright orange solid. *Anal.* Calc. for $C_{78}H_{70}Bi\text{-}F_6O_2P_5Pt_2S_6$ requires C, 44.6; H, 3.4. Found: C, 44.6; H, 3.4%. ESI MS: m/z 1954 [M]$^+$, 100%, together with a trace of $[Pt(S_2COEt)(PPh_3)_2]^+$ at m/z 840. ^{31}P–{^{1}H} NMR, δ 17.3 [s, ^1J(PtP) 3087]; a freshly prepared solution showed solely 2, but on standing for ca. 2 h, additional peaks due to $[Pt(S_2COEt)\text{-}(PPh_3)_2]^+$ and PPh_3 were observed (refer text). ^{1}H NMR, δ 7.30–7.08 (m, Ph), 4.61 (m, CH$_2$), 1.42 (m, CH$_3$).

3.5. X-ray crystal structure of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4\text{-}Bi(S_2CNEt_2)_2]PF_6$ (1)

Crystals of the complex were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex at 20 °C. The complex crystallises with one molecule of dichloromethane per mole of compound.

3.5.1. Crystal data

$C_{83}H_{82}BiCl_2F_6N_2P_5Pt_2S_6$, M_r 2238.78, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 17.9813(3)$, $b = 18.9953(2)$, $c = 25.2965(4)$ Å, $\beta = 103.602(1)°$, $V = 8397.9(2)$ Å^3, $D_{calc} = 1.771$ g cm^{-3}, μ(Mo Kα) = 5.780 mm^{-1}, size $0.38 \times 0.28 \times 0.22$ mm^3, $T_{max,min} = 0.3628$, 0.2174, $F(000) = 4368$, $T = 82(2)$ K. Total data 49 576, unique data 17 097 ($R_{int} = 0.0393$), $1.17° < \theta < 26.39°$, $R_1(I > 2\sigma(I)) = 0.0436$, wR_2 (all data) = 0.1143, GoF = 1.075, residual $\Delta e + 3.801/-1.745$ e Å^{-3}.

Appendix A. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 271354. 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; deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article

can be found, in the online version at doi:10.1016/j.ica.2005.07.022.

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