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Research paper

The water-solubilisation of the metalloligand $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ using 1,3, 5-triaza-7-phospha-adamantane (PTA)



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ARTICLEINFO	A B S T R A C T	
A R T I C L E I N F O Keywords: Platinum Sulfide PTA Water solubility ESI mass spectrometry	The synthesis of the platinum(II) μ_2 -sulfide complex [Pt ₂ (μ_2 -S) ₂ (PTA) ₄] (PTA = phosphatriazaadamantane), as a water-soluble analogue of the well-known triphenylphosphine complex [Pt ₂ (μ_2 -S) ₂ (PPh ₃) ₄], has been explored through a range of synthetic routes. A direct synthesis, from <i>cis</i> -[PtCl ₂ (PTA) ₂] and Na ₂ S-9H ₂ O in benzene was found to be the most effective, while attempted ligand substitution of the PPh ₃ ligands of [Pt ₂ (μ_2 -S) ₂ (PPh ₃) ₄] with PTA resulted in rearrangement of the {Pt ₂ S ₂ } core, and formation of a series of PTA-substituted trinuclear species of the general composition [Pt ₃ (μ_3 -S) ₂ (PPh ₃) ₄ (PTA) _{6-x}] ²⁺ . The fully-substituted complex [Pt ₃ (μ_3 -S) ₂ (PTA) ₆] ²⁺ was also obtained when <i>cis</i> -[PtCl ₂ (PTA) ₂] was reacted with a sulfide ion-exchange resin. Reaction of [PtCl ₂ (cod)] (cod = 1,5-cyclooctadiene) with Na ₂ S-9H ₂ O in benzene gave a red solid identified as crude [Pt ₂ (μ_2 -S) ₂ (cod) ₂]. Reaction of this labile {Pt ₂ S ₂ } precursor with PTA resulted in the formation of [Pt ₂ (μ_2 -S) ₂ (PTA) ₄] along with PTA -oxide and -sulfide. ESI mass spectrometry was widely employed as a convenient tool for exploring this chemistry, in conjunction with ³¹ P{ ¹ H} MRR spectroscopy. These PTA-Pt-sulfide species, especially those containing {Pt ₂ S ₂ cores, have a tendency to decompose in solution. Additional confirmation of the formation of [Pt ₂ (μ_2 -S) ₂ (PTA) ₄] was provided by its reaction with [Rh ₂ (μ_2 -Cl) ₂ (cod) ₂], resulting in the formation of the adduct [Pt ₂ (μ_3 -S) ₂ (PTA) ₄] was provided by its reaction with [Rh ₂ (μ_2 -Cl) ₂ (cod) ₂], resulting in the formation of the adduct [Pt ₂ (μ_3 -S) ₂ (PTA) ₄ Rh(cod)] ⁺ , identified using ESI MS.	

1. Introduction

Dinuclear platinum(II) sulfido complexes, containing the { $Pt_2(\mu_2-S)_2$ } core, are an interesting class of coordination complexes, because of their very high reactivity towards alkylating and arylating agents, and in their extensive role as metalloligands. The chemistry of these systems has been reviewed on several occasions [1–3]. The archetypal compound is [$Pt_2(\mu_2-S)_2(PPh_3)_4$] [1], due to the favourable solubility properties, air-stability, and low cost of PPh₃. Complexes containing PPh₃ ligands also show good propensity to form stable, crystalline derivatives, promoted in part by the well-documented sextuple phenyl embrace [4,5].

A modest number of complexes containing $\{Pt_2(\mu_2-S)_2\}$ cores have also been prepared using other phosphine ligands. For example, complexes containing PMe₂Ph [6], the bis(phosphines) Ph₂P(CH₂)_nPPh₂ (n = 2 or 3), the ferrocene-derived phosphine Fe(η^5 -C₅H₄PPh₂)₂ (dppf) [7,8], the pyridyl phosphine Ph₂Ppy [9], the chiral diop phosphine ligand [10], and the triphenylphosphine analogue P(C₆H₄Me-p)₃ [11] have been reported. Complexes containing closely-related tertiary arsine ligands, namely AsPh₃ [12] and Ph₂As(CH₂)₂AsPh₂ [13] are also known. In all of these examples, the ancillary phosphine or arsine ligand is considerably lipophilic.

Accordingly, it was desirable to address the water solubility of the $\{Pt_2(\mu_2-S)_2\}$ core by the use of a suitable water-soluble ancillary (phosphine) ligand. A water-soluble $\{Pt_2S_2\}$ derivative would open up new, previously unexplored avenues for investigation of such systems, including the biological activity of these complexes, which requires a degree of water-solubility. As far as we are aware, the biological activity of complexes with $\{Pt_2S_2\}$ sulfide cores has not been investigated to date, despite many different derivatives being synthesised. Although the biological properties of the PTA ligand itself do not appear to have been explored, metal complexes (especially of the arene-ruthenium moiety) containing PTA ligands have been displaying considerable promise in this area [14,15].

We have previously investigated improving the water solubility of derivatives containing the $\{Pt_2(\mu_2-S)_2\}$ core. This initial approach utilised alkylation of a sulfide ligand with a polyether-functionalised alkylating agent [16]. However, this approach results in the formation of a monoalkylated $\{Pt_2(\mu_2-S)(\mu_2-SR)\}^+$ core, which has substantially reduced nucleophilicity [17]. We therefore wished to address the problem through phosphine substitution, thereby retaining the reactivity of the $\{Pt_2S_2\}$ core. 1,3,5-Triaza-7-phospha-adamantane (PTA, Scheme 1) was

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Scheme 1. The structure of PTA.

chosen for initial investigations due to its ready accessibility [18,19] and proven use in the development of water soluble metal-phosphine complexes [20]. In this contribution, we describe investigations into the chemistry of the { $Pt_2(\mu_2-S)_2$ } core containing PTA ligands.

2. Results and discussion

2.1. Direct synthesis from cis-[PtCl₂(PTA)₂]

The standard method for the synthesis of $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ utilises the ligand substitution reaction of *cis*- $[PtCl_2(PPh_3)_2]$ with Na₂S-9H₂O in benzene suspension [21]. Accordingly, we reasoned that the corresponding reaction of *cis*- $[PtCl_2(PTA)_2]$ could form a direct, analogous route. PTA has been shown to act as a ligand towards group 10 transition metals forming complexes of the type $[MCl_2(PTA)_2]$ (M = Ni, Pd, Pt) [22,23]. *cis*- $[PtCl_2(PTA)_2]$ was synthesised from $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) by ligand substitution with PTA. While $[PtCl_2(PTA)_2]$ is water-soluble, it is unfortunately not inert, and undergoes a decomposition reaction in water producing PTA oxide. The decomposition is suspected to occur by oxidative addition of water producing a hydridohydroxido platinum(IV) species [23]. Some water stability can be achieved with an excess of PTA in solution [23].

 ${}^{31}P{}^{1}H$ NMR spectroscopy was used to corroborate the instability of *cis*-[PtCl₂(PTA)₂] in aqueous (D₂O) solution. The initially colourless solution quickly became more yellow over about 1 h, and was brown after a week. After 2 weeks, the ${}^{31}P$ NMR resonance for the initial Pt complex [PtCl₂(PTA)₂] [-51.3 ppm, ${}^{1}J$ (PtP) 3410 Hz] was very small, and a large peak due to PTA oxide (-2.9 ppm) was observed. These values are consistent with the literature [19,24]. When the ${}^{31}P{}^{1}H$ } NMR spectrum of *cis*-[PtCl₂(PTA)₂] was recorded in d⁶-DMSO, a clean spectrum was obtained, with no indications of decomposition, and the spectroscopic parameters are in agreement with literature values for the complex in this NMR solvent [25].

Reaction of *cis*-[PtCl₂(PTA)₂] with solid Na₂S·9H₂O in a benzene suspension was investigated as an initial route to the desired [Pt₂(μ_2 -S)₂(PTA)₄], the proposed structure of which is shown in Scheme 2. The nonahydrate is the commercially available, pure form of sodium sulfide, and its use will result in the introduction of some water into the reaction mixture, resulting in some decomposition and formation of PTA oxide. Isolation of the product by filtration gave a solid with a yellow-green colouration. Positive-ion ESI MS was used (methanol-water solution) to confirm the presence of [Pt₂(μ_2 -S)₂(PTA)₄], from the observation of [M + Na]⁺ (observed m/z 1105.24, calculated m/z



Scheme 2. The proposed structure of $[Pt_2(\mu_2-S)_2(PTA)_4]$



Fig. 1. Initial positive-ion ESI mass spectrum of the isolated solid $[Pt_2(\mu_2-S)_2(PTA)_4]$. The inset shows the observed isotope patterns for $[Pt_2(\mu_2-S)_2(PTA)_4 + Na]^+$ and $[Pt_2(\mu_2-S)_2(PTA)_4 + K]^+$ along with the calculated pattern (dashed line) for $[Pt_2(\mu_2-S)_2(PTA)_4 + Na]^+$. Capillary exit voltage 150 V, water/MeOH (2:5) solution.

1105.17) and $[2 \text{ M} + \text{Na}]^+$ (observed *m/z* 2188.39, calculated *m/z* 2188.35) ions, as shown in Fig. 1. The dominance of sodium adduct ions is not unexpected, given the large amount of sodium salts (Na₂S and by-product NaCl) in the reaction mixture. The water-solubility of $[\text{Pt}_2(\mu_2\text{-S})_2(\text{PTA})_4]$ became apparent in the preparation of the mass spectrometry samples, as it required the addition of water to the methanolic sample to assist dissolution. In the synthesis of $[\text{Pt}_2(\mu_2\text{-S})_2(\text{PTA})_4]$ the filtered product would normally be washed with water to remove the sodium salts, however this method was inapplicable for $[\text{Pt}_2(\mu_2\text{-S})_2(\text{PTA})_4]$ due to its water solubility. It is worth noting that in ESI MS studies of the triphenylphosphine analogue $[\text{Pt}_2(\mu_2\text{-S})_2(\text{PPh}_3)_4]$ the protonated $[\text{M} + \text{H}]^+$ and oxidised $[\text{M}]^+$ ions are typically observed [26], and not the sodiated adduct $[\text{M} + \text{Na}]^+$. This suggests that the site of sodium ion attachment may be the nitrogen atoms of the PTA ligand, in line with HSAB characteristics [27].

Attempted purification of the complex by extraction into methanol and filtration to remove sodium salts was only partly successful. The initial green solid produced an initial green solution, but on evaporation of the solvent at room temperature, an orange solid was produced. ESI MS of this solid showed the product cation $[Pt_2(\mu_2 - \mu_2)]$ $S_{2}(PTA)_{4} + Na]^{+}$, together with a range of non-platinum containing species (easily identified as such from their isotope pattern), together with a variety of oxidised species. The intensities of these non-platinum species increase with time, with a concomitant decrease in the intensity of $[Pt_2(\mu_2-S)_2(PTA)_4 + Na]^+$. Fig. 2 shows an ESI mass spectrum, together with the variety of oxidised species observed. Two dications, assigned as $[{Pt_2(\mu_2-S)_2(PTA)_4O}_2 + Na + H]^{2+}$ and $[{Pt_2(\mu_2-S)_2(PTA)_4O}_2 + Na + H]^{2+}$ $S_2(PTA)_4O_2$ + Na + H]²⁺ represent mono- and di-oxidised product respectively, and are assigned on the basis of their m/z values, and 0.5 m/z separation of peaks in the isotope pattern, the signature of a dication. While the site of oxidation is not discernible from ESI MS alone, the most likely site is the bridging sulfido ligand(s). Oxidation of the triphenylphosphine analogue $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ has been reported in the literature, and the X-ray crystal structure of the oxidised and protonated species $[Pt_2(\mu_2-SO)_2H(PPh_3)_4](CF_3SO_3)$ has been reported [28].

Characterisation of the isolated orange solid by ${}^{31}P{}^{1}H$ NMR spectroscopy (Fig. 3) showed a platinum-containing species at -55.0 ppm, showing ${}^{1}J(PtP)$ coupling of 2640 Hz. Singlet peaks at -2.9 and -17.9 ppm are assigned to PTA oxide and PTA sulfide respectively. These chemical shifts are in good agreement with literature values [29], and with authentic samples of these compounds that were



Fig. 2. Positive-ion ESI mass spectrum of orange decomposition solution of $[Pt_2(\mu_2 \cdot S)_2(PTA)_4]$. The inset spectrum shows the entire recorded spectrum. Capillary exit voltage 150 V, water/MeOH (2:5) solution.

synthesised and their ³¹P NMR spectra obtained. Small amounts of PTA oxide were present in the platinum starting material, however the PTA sulfide must have been produced in the reaction with Na₂S, or as a result of the partial decomposition. The ¹J(PtP) coupling constant of 2617 Hz for the Pt-containing species is consistent with [Pt₂(μ_2 -S)₂(PTA)₄], containing a high *trans*-influence [30] sulfide ligand, and is comparable to the values of 2740 Hz (n = 2) and 2615 Hz (n = 3) for the complexes [Pt₂(μ_2 -S)₂((PtA)₄], erg (PtA)₂)] [31]. By comparison, *cis*-[PtCl₂(PTA)₂] has a ¹J(PtP) value of around 3300 Hz. When a sample of [Pt₂(μ_2 -S)₂(PTA)₄], in D₂O was allowed to stand for 17 days at room temperature, the ³¹P{¹H} NMR spectrum showed, in addition to the starting [Pt₂(μ_2 -S)₂(PTA)₄], significant peaks due to PTA = O (-2.2 ppm) and PTA = S (-17.2 ppm), together with other substantial peaks at -58.6 and -62.2 ppm, which have not been identified.

Further studies into the stability of the crude $[Pt_2(\mu_2-S)_2(PTA)_4]$ were carried out by storing a freshly-prepared sample at 4 °C in a sealed container for 2 weeks. Samples were periodically removed and analysed by positive-ion ESI MS. No visible decomposition was observed, and there was little alteration to the mass spectra. The experiment was repeated, using a (sealed) sample stored at room temperature, this time resulting in a colour change from greenish to increasingly yellow. ³¹P {¹H} NMR analysis of the resulting yellow solid showed a single platinum species, $[Pt_2(\mu_2-S)_2(PTA)_4]$, at -54.2 ppm, and also ³J(PtP) coupling of 46 Hz (this latter coupling was not resolved in previouslyrecorded spectra). The value of ³J(PtP) is similar in magnitude to other dinuclear platinum complexes, for example $[Pt_2(\mu_2\text{-SPh})_2(dppm)_2]$ (BPh₄)₂ which shows ³J(PtP) 27 Hz [32]. In addition, small peaks due to PTA = O (-2.1 ppm) and PTA = S (-17.2 ppm) were observed. These observations suggest that $[Pt_2(\mu_2\text{-S})_2(PTA)_4]$ is fairly stable when stored as a solid, and that any visible changes to the solid are not reflected in any significant changes to the composition. The observation of oxidised species as intense ions in the ESI mass spectra probably reflects a stronger ionisation potential of the more basic, oxidised dinuclear platinum species.

Attempts at growing crystals of $[Pt_2(\mu_2-S)_2(PTA)_4]$ suitable for X-ray crystallography were unsuccessful.

2.2. Confirmation of $[Pt_2(\mu_2-S)_2(PTA)_4]$ by complex formation

The complex $[Pt_2(\mu_2-S)_2(PTA)_4]$ is a close analogue of $[Pt_2(\mu_2-S)_2(PTA)_4]$ $S_{2}(PPh_{3})_{4}$]. Therefore, a brief ESI mass spectrometric investigation was performed to determine if the $\{Pt_2(u_2-S)_2\}$ core shares the same reactivity, acting as a metalloligand towards heterometal centres through the electron-rich sulfide bridges [1]. Small quantities of crude [Pt₂(μ_2 - $S_{2}(PTA)_{4}$ and $[RhCl(cod)]_{2}$ (cod = 1,5-cyclooctadiene) were reacted in methanol solution, and the reaction mixture analysed by positive-ion ESI MS. This resulted in the observation of the complex $[Pt_2(\mu_3 S_2(PTA)_4Rh(cod)$ ⁺ at m/z 1293.08; the proposed structure of the complex is shown in Scheme 3. Macroscopic reaction resulted in the formation of some dark precipitate (which was removed by filtration); the resulting solution was evaporated to dryness to give a dark maroon solid. The positive ion ESI mass spectrum of this solid (Fig. 4) confirmed the presence of the complex $[Pt_2(\mu_3-S)_2(PTA)_4Rh(cod)]^+$. The ³¹P{¹H} NMR spectrum of the maroon solid showed a singlet at -56.8 ppm showing ¹J(PtP) 2965 Hz, together with two small peaks at -2.2 and -17.2 ppm, due to PTA-oxide and -sulfide, respectively. The increase in the ¹J(PtP) coupling constant on coordination to rhodium is consistent with reduced electron density and lower trans-influence of the μ_3 -sulfide ligands, when compared to μ_2 -sulfide ligands. The triphenylphosphine analogue $[Pt_2(\mu_3-S)_2(PPh_3)_4Rh(cod)]^+$ shows a similar, but slightly larger ¹J(PtP) coupling constant of 3151 Hz [33].

Attempts at growing crystals of the complex, which is presumably its chloride salt, were unsuccessful. Likewise, metathesis, by addition of either NaBF₄ or NaBPh₄ to solutions of $[Pt_2(\mu_3-S)_2(PTA)_4Rh(cod)]Cl$ also did not yield crystals suitable for X-ray crystallography.

2.3. Investigation of alternative sulfide ion sources in the synthesis of $[Pt_2(\mu_2-S)_2(PTA)_4]$

The complex $[Pt_2(\mu_2-S)_2(PTA)_4]$ has, as desired, significant water solubility. However, this makes purification of the complex from



Fig. 3. ${}^{31}P{}^{1}H{}$ NMR (162 MHz, D₂O) of the orange solid product of [Pt₂(μ_2 -S)₂(PTA)₄], synthesised from *cis*-[PtCl₂(PTA)₂] and Na₂S-9H₂O.



Scheme 3. The proposed structure of $[Pt_2(\mu_3-S)_2(PTA)_4Rh(cod)]^+$.



Fig. 4. Positive-ion ESI mass spectrum of $[Pt_2(\mu_3-S_2)(PTA)_4Rh(cod)]Cl.$ Inset spectrum shows observed (solid line) and calculated (dashed line) isotope patterns. Capillary exit voltage 150 V, MeOH solution.



Fig. 5. Positive-ion ESI mass spectrum of the reaction product of *cis*-[PtCl₂(PTA)₂] and a sulfide ion exchange resin, showing the triplatinum complex [Pt₃(μ_3 -S)₂(PTA)₆]²⁺ and its chloride adduct [Pt₃(μ_3 -S)₂(PTA)₆ + Cl]⁺. The inset spectrum shows both the experimental (solid line) and calculated (dashed line) isotope pattern for [Pt₃(μ_3 -S)₂(PTA)₆]²⁺. Capillary exit voltage 150 V, water/MeOH (2:5) solution.

soluble salts - viz. excess sodium sulfide and sodium chloride byproduct - more difficult. A sodium-free source of sulfide was therefore used, in the form of a sulfide-containing anion exchange resin. A sulfide ion exchange resin column was constructed using Dowex® 1X8 resin and a solution of sodium sulfide. Sulfide exchange columns of this type have been established previously [34]. Subsequent elution of a methanolic solution of *cis*-[PtCl₂(PTA)₂] was carried out, and the resulting eluent collected, and evaporated to dryness to give a white solid. Positive-ion ESI MS analysis showed a dominant triplatinum dication at m/z 795.78, readily assigned as $[Pt_3(\mu_3-S)_2(PTA)_6]^{2+}$, together with the chloride (ion pair) adduct $[Pt_3(\mu_3-S)_2(PTA)_6 + Cl]^+$, as shown in Fig. 5. When the capillary exit voltage was increased to 210 V, a considerable number of fragment ions appeared or increased in intensity, two of which were identified as $[Pt_3(\mu_3-S)_2(PTA)_5 + Cl]^+ (m/z \ 1470.44)$ and $[Pt_3(\mu_3-S)_2(PTA)_6 + Cl]^+$ (m/z 1627.54). The desired product $[Pt_2(\mu_2-\mu_3)_2(PTA)_6 + Cl]^+$ S)₂(PTA)₄] was not observed in the spectrum at any of these voltages.

The {Pt₂(μ_2 -S)₂} core is a well-known metalloligand which coordinates to a third metal centre through the μ_2 -sulfur bridges [1,2]. There are many complexes that contain the triplatinum core {Pt₃(μ_3 -S)₂}²⁺, and can be readily formed with (for example) Ph₂PCH₂PPh₂ (dppm) and PMe₂Ph ligands [6,35,36]. The analogous triplatinum PTA complex observed here has not been documented in the literature previously. However, the mixed PPh₃-PTA derivative [Pt₃(μ_3 -S)₂(PPh₃)₄(PTA)₂]²⁺ has been synthesised by the reaction of [Pt₂(μ_2 -S)₂(PPh₃)₄] with *cis*-[PtCl₂(PTA)₂] [37].

The ³¹P{¹H} NMR of the $[Pt_3(\mu_3-S)_2(PTA)_6]^{2+}$ species shows a single phosphorus resonance at -60.3 ppm with a number of satellites due to coupling to ¹⁹⁵Pt. The ubiquitous PTA-oxide and -sulfide were also observed, so the complex was only characterised by spectroscopic methods. The spectral features of $[Pt_3(\mu_3-S)_2(PTA)_6]^{2+}$ are very similar to those observed in a detailed analysis of the ³¹P NMR spectrum of $[Pt_3(\mu-S)_2(PMe_2Ph)_6](BEt_4)_2$, which included spectral simulation [36]. The symmetry of the $\{Pt_3(\mu_3-S)_2\}^{2+}$ core and the abundance of both ${}^{31}P$ and ^{195}Pt nuclei results in four differing isotopomers of the $\{\text{Pt}_3(\mu_3$ S_{2}^{+} core, each giving slightly different NMR resonances. That is, the ${Pt_3(\mu_3-S)_2}^{2+}$ core will occur with one, two, or all three of the platinum atoms being NMR active. This complexity gives rise to several smaller satellites from the differing ¹J(PtP) and ³J(PtP) couplings occurring, which are seen as small resonances either side of the larger ¹J (PtP) satellites. The $\{Pt_3(\mu_3-S)_2\}^{2+}$ core has very similar ¹J(PtP) values in both complexes with PTA [¹J(PtP) 3041 Hz], and PMe₂Ph [¹J(PtP) 3202 Hz] [36]. Attempts at growing crystals suitable for X-ray crystallography were unsuccessful.

2.4. Attempted synthesis of $[Pt_2(\mu_2-S)_2(PTA)_4]$ by ligand substitution of $[Pt_2(\mu_2-S)_2(PPh_3)_4]$

The direct synthesis of $[Pt_2(\mu_2-S)_2(PTA)_4]$ from the triphenylphosphine analogue $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ by a phosphine exchange reaction was also explored. This would allow the elimination of sodium salts from the synthesis of $[Pt_2(\mu_2-S)_2(PTA)_4]$, which is problematic due to the water solubility of the complex (*vide supra*). Phosphine exchange of $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ has been demonstrated previously, albeit with close analogues of PPh₃ [38] and not PTA.

Reactions of $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ and PTA in molar ratios 1:1, 1:2, 1:3, and 1:4 were carried out in a biphasic toluene-water mixture, at ambient temperature, stirred rapidly for seven days and then the aqueous phase (after settling) was analysed by ESI MS. It was expected that during the reaction, substituted species of the type $[Pt_2(\mu_2-S)_2(PPh_3)_x$ (PTA)_{4-x}] would be observed. However, while PTA does substitute for PPh₃, the dinuclear {Pt₂S₂} core does not stay intact during the process. The mass spectrum of the aqueous phase showed platinum species with isotope patterns that indicate triplatinum sulfur {Pt₃(μ_3 -S)₂}²⁺ cores in various degrees of phosphine substitution. Small amounts of the starting material [Pt₂(μ_2 -S)₂(PPh₃)₄] were also observed. The intensity of the completely substituted [Pt₃(μ_3 -S)₂(PTA)₆]²⁺ complex increased



Fig. 6. Positive-ion ESI mass spectrum (water/MeOH 2:5 solution, capillary exit voltage 150 V) of a mixture of $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ and 4 equivalents of PTA, showing partially and completely substituted trinuclear complexes of the general form $[Pt_3(\mu_3-S)_2(PTA)_x(PPh_3)_{6-x}]^{2+}$.

Table 1

The various $[Pt_3(\mu_3-S)_2(L)_6]^{2+}$ species present in differing stages of ligand substitution between PTA and PPh₃.

Observed m/z	Calculated m/z	Formula
796.21 813.70 848.71 901.23 953.74 1470.29 1627.38 1732.40	795.65 814.56 848.16 900.66 953.17 1470.19 1627.27 1732.28	$\begin{array}{l} [Pt_3(\mu_3 \cdot S)_2(PTA)_6]^{2+} \\ [Pt_3(\mu_3 \cdot S)_2(PTA)_6 + Cl + H]^{2+} \\ [Pt_3(\mu_3 \cdot S)_2(PTA)_5(PPh_3)_1]^{2+} \\ [Pt_3(\mu_3 \cdot S)_2(PTA)_4(PPh_3)_2]^{2+} \\ [Pt_3(\mu_3 \cdot S)(PTA)_3(PPh_3)_3]^{2+} \\ [Pt_3(\mu_3 \cdot S)_2(PTA)_5 + Cl]^+ \\ [Pt_3(\mu_3 \cdot S)_2(PTA)_6 + Cl]^+ \\ [Pt_3(\mu_3 \cdot S)_2(PTA)_5(PPh_3) + Cl]^+ \end{array}$

with the ratio of PTA. The positive-ion ESI mass spectrum of the aqueous phase for the 1:4 reaction is shown in Fig. 6, and ion assignments are shown in Table 1. The successfully identified substituted complexes and their adducts observed in the mass spectrum all possess a trinuclear $\{Pt_3(\mu_3-S)_2\}^{2+}$ core. No ligand-substituted complex ions were present with a dinuclear $\{Pt_2(\mu_2-S)_2\}$ core in either the positive- or negative-ion ESI mass spectra.

When $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ is stirred in a biphasic water-toluene mixture no $[Pt_3(\mu_3-S)_2(PPh_3)_6]^{2+}$ was observed in the mass spectrum, indicating that it is the presence of PTA, and not the reaction conditions *per se* which are responsible for the dinuclear \rightarrow trinuclear conversion.

2.5. Synthesis of $[Pt_2(\mu_2-S)_2(PTA)_4]$ via the 1,5-cyclooctadiene (cod) complex $[Pt_2(\mu_2-S)_2(cod)_2]$

The reaction between [PtCl₂(cod)] and Na₂S·9H₂O in a stirred benzene suspension was explored, as a potential route to the complex [Pt₂(μ_2 -S)₂(cod)₂] which would contain a very labile cod ligand, that could be easily displaced by PTA. The reaction of platinum(II) cod complexes with phosphine ligands, as a route to platinum(II) phosphine complexes, is well-established [39]. Both starting materials are individually colourless, but upon mixing in benzene a yellow colouration was observed. During the 48 h stirring period, the reaction mixture changed from the starting yellow to a red. The red solid product was collected by filtration of the reaction suspension. The positive-ion ESI mass spectrum of this solid revealed a single platinum complex ion [Pt₂(μ_2 -S)₂(cod)₂ + Na]⁺ at *m*/*z* 692.84. During attempted purification of the complex to remove insoluble salts, the complex decomposed. The high nucleophilicity of complexes containing {Pt₂(μ_2 -S)₂} cores is well-documented [1–3]. The presence of a labile cod ligand might be

expected to exacerbate this reactivity. Therefore the stability of the compound was assessed.

A dried sample of $[Pt_2(\mu_2-S)_2(cod)_2]$ was stored in a sealed vial for 14 days at 4 °C. The positive-ion ESI mass spectrum of this sample was recorded periodically throughout this period. The mass spectra recorded all showed the same ion for $[Pt_2(\mu_2-S)_2(cod)_2]$, suggesting that the complex did not decompose at low temperature. An ambient temperature thermal decomposition assessment was also undertaken, where a sample of $[Pt_2(\mu_2-S)_2(cod)_2]$ was stored at ambient temperature in a sealed vial for 16 days. This resulted in the decomposition of the complex, easily ascertainable due to the distinctive smell of cod coming from the solid, with a concomitant colour change, as the orange became lighter over time. Positive-ion ESI mass spectra were recorded periodically over the two weeks, and the intensity of the $[Pt_2(\mu_2-S)_2(cod)_2 + Na]^+$ peak decreased over time, and was negligible after 16 days.

A freshly prepared sample of $[Pt_2(\mu_2-S)_2(cod)_2]$ was characterised by NMR spectroscopy. The ¹H NMR spectrum in d⁶-benzene shows features consistent with the complex, in particular a singlet resonance at 4.8 ppm, showing platinum satellites with ²J(PtH) 55 Hz. This resonance is readily assigned as the cod alkene protons. Two multiplets centred around 1.9 and 1.4–1.5 ppm are assigned to the cod CH₂ protons in two different environments as a result of coordination to platinum. By comparison, the ¹H NMR of $[PtCl_2(cod)]$ shows a resonance at 5.6 ppm $[^2J(PtH) 68$ Hz] for the = CH hydrogen atoms, and two peaks at 2.73 and 2.28 ppm for the CH₂ hydrogens [40]. The lower value of ²J(PtH) for $[Pt_2(\mu_2-S)_2(cod)_2]$ compared to $[PtCl_2(cod)]$ is consistent with the lower *trans*-influence of chloride compared to sulfide. For example, the cod alkene ligand *trans* to thiolate in [Pt (SC₆H₄CO₂)(cod)] shows a ²J(PtH) value of around 50 Hz [41].

In order to demonstrate the feasibility of ligand exchange of $[Pt_2(\mu_2-S)_2(cod)_2]$ the reaction with PPh₃ was initially carried out, in an attempt to prepare the well-known $[Pt_2(\mu_2-S)_2(PPh_3)_4]$. $[Pt_2(\mu_2-S)_2(cod)_2]$ was synthesised as above (without isolation), after which PPh₃ was added to the benzene reaction suspension to give a molar ratio of 1:4 complex:ligand. The solution was stirred for 24 h, during which time a colour change from red to orange occurred. The mixture was filtered to produce an orange solid, having the same appearance as authentic $[Pt_2(\mu_2-S)_2(PPh_3)_4]$. The positive-ion ESI mass spectrum of this solid showed a base peak for the ion $[Pt_2(\mu_2-S)_2(PPh_3)_4 + H]^+$ (m/z 1503.86) together with a lower intensity ion due to $[Pt_2(\mu_2-S)_2(PPh_3)_4O + H]^+$ (m/z 1518.84), respectively. Several smaller, unidentified ions with discernible platinum isotope patterns at m/z 1602.71 and 1702.63, together with a triplatinum complex at m/z 2280.53, were also observed.

Ligand exchange reaction between PTA and $[Pt_2(\mu_2-S)_2(cod)_2]$ was partially successful, with the ion $[Pt_2(\mu_2-S)_2(PTA)_4 + Na]^+$ strongly visible in the positive-ion ESI mass spectrum. The ion $[Pt_2(\mu_2-S)_2(PTA)_4 + H]^+$, as well as some potassium-containing ions, were also observed (Fig. 7).

The ³¹P{¹H} NMR spectrum of the sample of $[Pt_2(\mu_2-S)_2(PTA)_4]$ prepared from $[Pt_2(\mu_2-S)_2(cod)_2]$ showed $[Pt_2(\mu_2-S)_2(PTA)_4]$ at relatively low intensity, with significant amounts of PTA-oxide and -sulfide (-2.3 and -17.2 ppm, respectively), and a number of unidentified species. This suggests that the cod route to $[Pt_2(\mu_2-S)_2(PTA)_4]$ produces a very impure product. Despite this, the ESI mass spectrum of this $[Pt_2(\mu_2-S)_2(PTA)_4]$ + H]⁺ sample showed and $[Pt_2(\mu_2 S_{2}(PTA)_{4} + Na]^{+}$ as the only ions in the spectrum. This suggests that $[Pt_2(\mu_2-S)_2(PTA)_4]$ has a high ESI ionisation efficiency, and that other techniques, such as ³¹P NMR, should be used in conjunction with ESI MS, wherever there may be cases of species with considerably different ESI behaviours.

3. Conclusions

A number of routes to the water-soluble platinum sulfide complex



Fig. 7. Part of the positive-ion ESI mass spectrum of $[Pt_2(\mu_2-S)_2(PTA)_4]$ formed *via* ligand exchange between $[Pt_2(\mu_2-S)_2(cod)_2]$ and PTA. Capillary exit voltage 150 V, MeOH/water (2:5) solution.

 $[Pt_2(\mu_2-S)_2(PTA)_4]$ have been explored, with varying degrees of success. While $[Pt_2(\mu_2-S)_2(PTA)_4]$ can be synthesised, it was not possible to obtain it in a pure state, with PTA-oxide and -sulfide observed ubiquitously in these systems. Accordingly, the current study employed spectroscopic tools, since it was considered that elemental analyses were not appropriate. However, the combination of ESI mass spectrometry, coupled with ³¹P{¹H} NMR spectroscopy, is a powerful set of tools for investigating this chemistry. This study suggests that while PTA offers some attractive features, it is not the best choice of watersolubilising ligand in $\{Pt_2S_2\}$ chemistry. Instead, studies might be profitably directed towards water-soluble analogues of PPh₃ itself, and in this context, sulfonated triphenylphosphine ligands have been shown to find considerable utility [42].

4. Experimental

4.1. Materials

Sodium sulfide nonahydrate (Aldrich) and Dowex[®] 1X8 ion exchange resin beads (BDH) were used as supplied from commercial sources. The following compounds were prepared by the literature procedures: PTA [18], [RhCl(cod)]₂ [43], [PtCl₂(cod)] [44] and [Pt₂(μ_2 -S)₂(PPh₃)₄] [21]. Reactions were carried out in LR grade solvents, without regard for exclusion of air or moisture unless otherwise stated.

4.2. Instrumentation

Unless otherwise stated, ³¹P{¹H} NMR spectra were recorded at 121.5 MHz on a Bruker Avance DRX 300 spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DRX 400 MHz spectrometer. ESI mass spectra were recorded on Bruker MicrOTOF instrument with the Skimmer 1 Voltage a third that of the Capillary Exit Voltage (CEV). Spectra routinely used a CEV of 150 V. Samples were diluted with methanol prior to analysis, and injected with a flow rate of 180 μ L h⁻¹ by means of a syringe pump. Mass spectra data processing software used to generate figures and calculated isotope patterns was *mMass* version 5.5.0 [45,46].

4.3. Synthesis of cis-[PtCl₂(PTA)₂]

The complex was prepared using the literature method [22], from $[PtCl_2(cod)]$ (0.967 g, 2.5 mmol) and PTA (0.813 g, 5.1 mmol); the reaction was performed under a nitrogen atmosphere. Yield 1.38 g

(92%). ${}^{31}P{}^{1}H$ NMR (DMSO- d_6 , 162 MHz) s, -53.2 ppm, ${}^{1}J(PtP)$ 3307 Hz.

4.4. Synthesis of crude $[Pt_2(\mu_2-S)_2(PTA)_4]$

A modified literature method for the synthesis of $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ was used [19]. A mixture of *cis*- $[PtCl_2(PTA)_2]$ (0.418 g, 0.72 mmol) and Na₂S·9H₂O (0.86 g, 3.5 mmol) in a benzene suspension (10 mL) was continually stirred for 48 h. The suspended solids collected in the bottom of the flask, as a light brown paste. After collection of the solid by filtration and washing with benzene (5 mL), no further purification attempts were made. The solid was dried under vacuum. ³¹P {¹H} NMR (D₂O): s, -54.3 ppm, ¹J(PtP) 2616 Hz.

In a repeated synthesis, the solid was collected by filtration, and attempted purification was investigated, to preferentially dissolve the present sodium salts in MeOH. This led to the partial decomposition of $[Pt_2(\mu_2-S)_2(PTA)_4]$ while in solution.

4.5. Attempted synthesis of $[Pt_2(\mu_2-S)_2(PTA)_4]$ using a sulfide exchange column

A small column was prepared from a glass pasteur pipette containing a small plug of glass wool and Dowex[®] 1X8 beads (4 cm deep). The column was washed with distilled water (15 mL) followed by methanol (15 mL). The eluent was discarded. A solution of Na₂S·9H₂O (200 mg) in methanol (10 mL) was passed down the column (producing a colour change from orange to brown). The column was further washed with methanol until a fresh sample of the eluate was clear when tested with a drop of aqueous lead nitrate solution. If the eluent formed a black precipitate of PbS, further washing was needed (washing with 10 mL of methanol was needed).

A solution of *cis*-[PtCl₂(PTA)₂] (0.01 g, 0.02 mmol) in methanol (15 mL) was passed down the column, followed by methanol (15 mL). The eluate was collected and evaporated to dryness using a rotary evaporator, producing a white solid that was shown by ESI MS to contain $[Pt_3(\mu_3-S)_2(PTA)_6]^{2+}$. ³¹P{¹H} NMR (D₂O): s, -60.3 ppm, ¹J (PtP) 3041 Hz. ESI MS: *m/z* 795.78, [M]²⁺.

4.6. Synthesis of [Pt₂(µ₃-S)₂(PTA)₄Rh(cod)]Cl

A modified literature method [33] for the synthesis of $[Pt_2(\mu_3-S)_2(PPh_3)_4Rh(cod)]Cl$ was used: crude $[Pt_2(\mu_2-S)_2(PTA)_4]$ (0.054 g, 0.05 mmol) was reacted with $[RhCl(cod)]_2$ (0.0123 g, 0.02 mmol) using methanol (60 mL) in place of THF. After stirring for 1 h, the resulting mixture was filtered to remove some precipitate. The maroon filtrate was evaporated to dryness using a rotary evaporator, resulting in the deposition of $[Pt_2(\mu_3-S)_2(PTA)_4Rh(cod)]Cl$ as a maroon solid. ³¹P{¹H} NMR (D₂O): s, -56.8 ppm,¹J(PtP) 2965 Hz. ESI MS: *m/z* 1293.08, [M]⁺.

4.7. Attempted synthesis of $[Pt_2(\mu_2-S)_2(PTA)_4]$ via ligand exchange

A mixture of $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ (0.04 g, 0.026 mmol) and PTA (0.016, 0.106 mmol) in distilled water (20 mL) and toluene (20 mL) were stirred continuously for 7 days in a capped glass vial. The sparingly soluble, orange $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ floated in the aqueous phase and around the phase boundary. The reaction was simultaneously repeated with $[Pt_2(\mu_2-S)_2(PPh_3)_4]$ to PTA molar ratios of 1:1, 1:2 and 1:3. The phases were allowed to separate, before samples of the aqueous phase were taken for positive-ion ESI MS analysis

4.8. Synthesis of PTA sulfide

PTA sulfide was first synthesised by Daigle and Pepperman in 1975 [47], through reaction of PTA with elemental sulfur, though the product was only characterised by IR. A modification of this method is used

here. A small sample of PTA in distilled water with an excess of powdered elemental sulfur was stirred continually in distilled water at 60 °C for 3 h. After insoluble solids were filtered off, the phosphine sulfide was obtained by evaporation of the solvent. ³¹P{¹H} NMR: s, -17.2 ppm (D₂O).

4.9. Synthesis of PTA oxide

PTA oxide was prepared through the reaction of a small sample of cis-[PtCl₂(PTA)₂] in an aqueous solution [23]. ³¹P{¹H} NMR: s, -2.9 ppm (D₂O).

4.10. Synthesis of $[Pt_2(\mu_2-S)_2(cod)_2]$

A suspension of [PtCl₂(cod)] (0.05 g, 0.13 mmol) and Na₂S·9H₂O (0.16 g, 0.66 mmol) in benzene (10 mL) was continually stirred for 48 h. The suspension began with a yellow colouration and after 24 h the solution was red, and after the 48 h, a red solid had deposited on the bottom of the flask. The solid was filtered, washed with benzene (5 mL), and dried under vacuum. No further purification attempts were made. The positive-ion ESI MS spectrum showed [Pt₂(μ_2 -S)₂(cod)₂ + Na]⁺ (*m*/*z* 693.10) as the major ion.

4.11. Synthesis of $[Pt_2(\mu_2-S)_2(PTA)_4]$ from $[Pt_2(\mu_2-S)_2(cod)_2]$

A sample of crude $[Pt_2(\mu_2-S)_2(cod)_2]$ (0.053 g, 0.086 mmol) was added to benzene (10 mL) followed by 4 mol equivalents of PTA (0.0577 g, 0.37 mmol), and the suspension stirred for 24 h. The initial red $[Pt_2(\mu_2-S)_2(cod)_2]$ clumped at the bottom of the flask, and over 24 h changed to the yellow-green colouration of $[Pt_2(\mu_2-S)_2(PTA)_4]$. The suspension was filtered, washed with benzene (10 mL), and dried under vacuum. The positive-ion ESI mass spectrum of the solid showed a strong ion due to $[Pt_2(\mu_2-S)_2(PTA)_4 + H]^+$ (m/z 1083.88) and the related sodium adduct. The ³¹P{¹H}</sup> NMR (D₂O) showed a resonance for $[Pt_2(\mu_2-S)_2(PTA)_4]$ at -54.3 ppm, ¹J(PtP) 2616 Hz, at far lower intensity than expected for a pure product. Significant resonances for PTA-sulfide (-17.2) ppm and -oxide (-2.2) ppm were observed.

CRediT authorship contribution statement

Ryan B. Sutton: Investigation, Writing - original draft. **William Henderson:** Conceptualization, Methodology, Project administration, Resources, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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