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Further studies on the coordination chemistry of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ towards indium(III) substrates

William Henderson^{a,*}, Allen G. Oliver^b

^a Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand ^b Molecular Structure Facility, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

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ABSTRACT

The reactivity of the metalloligand $[Pt_2(\mu-S)_2(PPh_3)_4]$ towards a variety of indium(III) substrates has been explored. Reaction with excess $In(NO_3)_3$ and halide (KBr or NaI) gave the four-coordinate adducts $[Pt_2(\mu-S)_2(PPh_3)_4InX_2]^+[InX_4]^-$ (X = Br, I). An X-ray structure determination on the iodo complex revealed a slightly distorted tetrahedral coordination geometry at indium. In contrast, reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with indium(III) chloride was more complex; the ion $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^+$ was initially observed in solution (using ESI mass spectrometry), and isolated as its BPh₄⁻ salt. Analysis of $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^+[BPh_4]^-$ by ESI MS showed the parent cation when analysed in MeCN solution. However in solutions containing methanol, partial solvolysis occurred to give the di-indium species $[{Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)}_2]^{2+}$ (proposed to contain an $In_2(\mu-OMe)_2$ unit with five-coordinate indium) and its fragment ion $[Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)]^+$. Reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with $InCl_3 \cdot 3H_2O$, 8-hydroxyquinoline (HQ) and trimethylamine in methanol gave the adduct $[Pt_2(\mu-S)_2(PPh_3)_4InQ_2]^+$, isolated as its PF_6^- salt. The same cationic complex is formed when $[Pt_2(\mu-S)_2(PPh_3)_4]$ is reacted with InQ₃ in methanol, but in this case the product is contaminated with the mononuclear complex $[(Ph_3P)_2PtQ]^+$ formed by disintegration of the trinuclear complex $[Pt_2(\mu-S)_2(PPh_3)_4InQ_2]^+$ with byproduct Q^{-} . [(Ph₃P)₂PtQ]⁺BPh₄⁻ was independently prepared from *cis*-[PtCl₂(PPh₃)₂] and HQ/Me₃N, and is the first example of a platinum 8-hydroxyquinolinate complex containing phosphine ligands.

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1. Introduction

The metalloligand properties of dinuclear platinum(II) sulfido complexes, typified by $[Pt_2(\mu-S)_2(PPh_3)_4]$ **1**, are well-known [1,2]. Reactions of this complex with a variety of metal-based substrates have provided a general synthetic methodology for the synthesis of tri- and polymetallic sulfide-bridged aggregates. While the majority of known adducts are with transition metals, main group metal adducts are also known for a number of metals.

In the area of group 13 metal chemistry, although aluminium adducts of $[Pt_2(\mu-S)_2(PPh_3)_4]$ have not been reported, there are a number of adducts with the heavier (and chemically softer) congeners gallium, indium and thallium, which have also been studied using theoretical methods [3]. Reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with InCl₃ gave the neutral adduct $[Pt_2(\mu-S)_2(PPh_3)_4InCl_3]$ **2** (which was structurally characterised) while reaction with 2 equivalents of GaCl₃ gave the salt $[Pt_2(\mu-S)_2(PPh_3)_4GaCl_2]^+[GaCl_4]^-$ [4]. The analogous InCl₃ adduct has also been prepared from $[Pt_2(\mu-S)_2(dppf)_2]$ [dppf = 1,1'-bis(diphenylphosphino)ferrocene] [5]. Both thallium(I) and thallium(III) adducts are known; $[Pt_2(\mu-S)_2(PPh_3)_4]$

E-mail address: w.henderson@waikato.ac.nz (W. Henderson).

reacts with TINO₃ to give $[Pt_2(\mu-S)_2(PPh_3)_4TI]^+$ (isolated as NO₃⁻ and PF₆⁻ salts) [6], and the same behaviour is again seen with the dppf analogue [5]. Thallium(III) adducts $[Pt_2(\mu-S)_2(PPh_3)_4$ TIBr_nPh_{2-n}]⁺ (n = 0-2) have been obtained from reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with TIBr₃, PhTIBr₂ or Ph₂TIBr [7]. Additional studies also indicate that adducts can also be formed by related systems, such as the selenide $[Pt_2(\mu-Se)_2(PPh_3)_4]$ (which forms the four-coordinate adduct $[Pt_2(\mu-Se)_2(PPh_3)_4]$ (which forms the four-coordinate adduct $[Pt_2(\mu-Se)_2(PPh_3)_4IBr_2]^+$ [8] (as well as $[Pt_2(\mu-Se)_2(PPh_3)_4TIPh_2]^+$ [7], $[Pt_2(\mu-Se)_2(PPh_3)_4Ga(NO_3)_2]^+$ [8], and $[Pt_2(\mu-Se)_2(PPh_3)_4TI]^+$ [8]). Likewise, the palladium analogue $[Pd_2(\mu-S)_2(dppf)_2]$ forms adducts including the five-coordinate indium adduct $[Pd_2(\mu-S)_2(dppf)_2TII]^+$ [9].

In this contribution we describe some new indium adducts of $[Pt_2(\mu-S)_2(PPh_3)_4]$ containing a range of monodentate and chelating ligands, including a reinvestigation of adducts formed by $[Pt_2(\mu-S)_2(PPh_3)_4]$ with InCl₃. Indium–chalcogenide materials are of technological importance for example in photovoltaic applications [10–13] and the possibility that such compounds might be useful in the synthesis of new indium–chalcogenide materials is suggested by the reaction of $[Pt_2(\mu-Se)_2(PPh_3)_4]$ with In(ClO₄)₃. 8H₂O which yielded a novel complex $[{Pt_2(\mu-Se)_2(PPh_3)_4}_2]$ $In_2(\mu-Se)_2]^{2+}$, containing an $\{In_2Pt_4Se_6\}$ core [14]. Our methodology





^{*} Corresponding author. Fax: +64 7 838 4219.

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is to apply electrospray ionisation mass spectrometry (ESI MS) to characterise reaction mixtures and products in the $\{Pt_2S_2\}$ -In system. ESI MS is now a fully established technique for the characterisation of coordination and organometallic compounds, and has been applied to the characterisation of a number of indium systems including organo-indium compounds [15–17], indium trihalide solutions [18], and a variety of coordination complexes [19–24].

2. Results and discussion

2.1. Chemistry of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with indium(III) and halide ions

Reactions between $[Pt_2(\mu-S)_2(PPh_3)_4]$, excess $In(NO_3)_3$ and an excess of either NaBr or KI proceeded straightforwardly, with positive-ion ESI MS showing the ions $[Pt_2(\mu-S)_2(PPh_3)_4InX_2]^+$ (X = Br, m/z 1777.988; X = I, m/z 1870.963) as the dominant ions in the reaction mixtures. In the iodide case, the complex $[Pt_2(\mu-S)(\mu-I)]$ $(PPh_3)_4$ ⁺ was seen as a weak ion at m/z 1598; this ion has been found to be rather ubiquitous in reactions of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with metal iodide complexes [25], so its presence is not unexpected. On a macroscopic scale, reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with excess In(NO₃)₃ proceeded rapidly in methanol, giving an almost colourless solution. Upon addition of a large excess of either NaBr or KI, white (Br) or pale cream (I) precipitates of the products $[Pt_2(\mu-S)_2(PPh_3)_4InX_2][InX_4]$ (**3a** X = Br; **3b** X = I) were obtained in good yields and high purities as shown by elemental microanalysis. ESI MS analysis of 3a in MeOH solution showed the expected $[Pt_2(\mu-S)_2(PPh_3)_4InBr_2]^+$ ion as the dominant ion at m/z 1777.988, together with a trace of $[Pt_2(\mu-S)_2(PPh_3)_4InBrCl]^+$ (*m/z* 1733.036), presumably formed from adventitious chloride ions.

Crystals of the indium iodide adduct **3b** were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the complex. In order to characterise the binding of the indium to the platinum–sulfide metalloligand, a single-crystal X-ray diffraction study was carried out. The structure of the cation is shown in Fig. 1 together with the atom numbering scheme, while Table 1 gives selected bond lengths and angles.

There are four molecules of the cation and associated anion, plus six molecules of dichloromethane of crystallisation in the unit cell of the primitive, centrosymmetric space group $P2_1/n$. The cation consists of a trimetallic Pt₂In core, bridged by two μ_3 -sulfur atoms. The In coordination sphere is completed by two iodine atoms and the platinum centres are each coordinated by two



Fig. 1. Molecular structure of the cation of $[Pt_2(\mu-S)_2(PPh_3)_4lnl_2][Inl_4]$ **3b** with only *ipso* carbons of the PPh₃ ligands shown for clarity, and thermal ellipsoids at the 50% probability level.

Table 1

Selected bond lengths (Å) and angles (°) for [Pt₂(µ-S)₂(PPh₃)₄InI₂][InI₄] 3b.

Pt(1) - P(2)	2.2864(12)	Pt(1) - P(1)	2.3021(12)
P((1) - S(1))	2.3849(11)	Pl(1) - S(2)	2.3870(11)
Pt(2)-P(4)	2.2758(12)	Pt(2) - P(3)	2.2936(11)
Pt(2)-S(2)	2.3748(11)	Pt(2)-S(1)	2.3883(12)
In(1)-S(1)	2.4906(12)	In(1)-S(2)	2.5081(12)
In(1)-I(1)	2.7059(5)	In(1)–I(2)	2.7068(5)
P(2)-Pt(1)-P(1)	99.79(4)	P(2)-Pt(1)-S(1)	92.06(4)
P(1)-Pt(1)-S(2)	86.62(4)	S(1)-Pt(1)-S(2)	81.57(4)
P(4) - Pt(2) - P(3)	97.74(4)	P(4)-Pt(2)-S(2)	92.94(4)
P(3)-Pt(2)-S(1)	87.57(4)	S(2)-Pt(2)-S(1)	81.76(4)
S(1)-In(1)-S(2)	77.16(4)	S(1)-In(1)-I(1)	123.64(3)
S(2)-In(1)-I(1)	112.48(3)	S(1)-In(1)-I(2)	112.82(3)
S(2)-In(1)-I(2)	120.60(3)	I(1)-In(1)-I(2)	108.152(18)
Pt(1)-S(1)-Pt(2)	85.06(4)	Pt(2)-S(2)-Pt(1)	85.31(4)
$[InI_4]^-$ anion:			
In(2) - I(3)	2.7055(6)	In(2)-I(5)	2.7059(6)
In(2) - I(4)	2.7072(6)	In(2)-I(6)	2.7205(6)
I(3) - In(2) - I(5)	107.821(18)	I(3)-In(2)-I(4)	110.465(18)
I(5)-In(2)-I(4)	109.171(17)	I(3) - In(2) - I(6)	108.543(17)
I(5) - In(2) - I(6)	112.46(2)	I(4) - In(2) - I(6)	108.38(2)

triphenylphosphine ligands. As can be seen in Figs. 1 and 2, the binding of the InI_2^+ fragment to the two sulfide centres is fairly symmetrical, but slightly distorted by a twist between the InI_2 and InS_2 planes of 81.7°, compared to the value of 90° expected for a symmetrical tetrahedral structure. The In–S bond distances of 2.4906(12) and 2.5081(12) Å are longer than those of 2.484(1) and 2.486(1) Å in the only other structurally characterised four-coordinate indium complex containing an S_2InI_2 donor set, $N(Ph_2PS)_2InI_2$ [26]. This is presumably because the $[N(Ph_2PS)_2]^-$ ligand is monoanionic and binds more strongly to In than neutral 1. The In–I bond distances of $[Pt_2(\mu-S)_2(PPh_3)_4InI_2]^+$ [2.7068(5) and 2.7059(5) Å] are also considerably longer than in $N(Ph_2PS)_2InI_2$ [2.6768(6) and 2.6872(7) Å].

The In–S bond distances of **3b** can be compared with somewhat longer values of 2.614(2) Å in the neutral adduct $[Pt_2(\mu-S)_2(PPh_3)_4InCl_3]$ [4], probably reflecting the cationic, four-coordinate nature of the Inl_2^+ fragment in **3b** which results in stronger binding. The dihedral angle between the two PtS₂ planes is 126.88°,



Fig. 2. Side view [along the S(1) \cdots S(2) vector] of the core of $[Pt_2(\mu-S)_2(PPh_3)_4|nl_2|^*$ in **3b**, showing the symmetric binding of the lnl_2^* fragment to the metalloligand in the Pt_2ln plane.

which is similar to that in $[Pt_2(\mu-S)_2(PPh_3)_4InCl_3]$ **2** [128.3(2)°]. The counterion in the structure is $[InI_4]^-$, with a fairly regular tetrahedral geometry; its presence was confirmed by negative-ion ESI MS analysis, though $[InI_3Cl]^-$ and I^- were also observed.

The species present in $[Pt_2(\mu-S)_2(PPh_3)_4]$ – indium(III) chloride reaction mixtures have also been further investigated using positive-ion ESI MS, a technique only in its infancy at the time of original investigations in this area [4]. However, it must be noted that ESI MS only allows detection of charged species, so a neutral adduct such as $[Pt_2(\mu-S)_2(PPh_3)_4InCl_3]$ **2** would not be observed unless some mechanism were operating to provide a charge. The most likely pathway is chloride loss, giving $[Pt_2(\mu-S)_2(PPh_3)_4]$ InCl₂]⁺, since other ionisation pathways such as protonation are inaccessible because of an absence of basic lone pair sites. It was previously noted [4] that addition of $InCl_3$ to $[Pt_2(u-S)_2(PPh_3)_4$ InCl₃] in CH₂Cl₂ increased the conductivity around 30-fold, consistent with the formation of an ionic chloride complex $[Pt_2(u-$ S)₂(PPh₃)₄InCl₂][InCl₄] analogous to the bromide and iodide complexes 3a and 3b reported herein. We find that the reaction between $[Pt_2(\mu-S)_2(PPh_3)_4]$ and $InCl_3$ in methanol yields a clear, pale yellow solution which forms a white precipitate on addition of a large anion (BPh₄⁻). This complex gave microanalytical data that match well for [Pt₂(µ-S)₂(PPh₃)₄InCl₂][BPh₄] **3c**. Complexes **3a**, **3b** and **3c** all give a single sharp resonance in their ³¹P{¹H} NMR spectra, with virtually identical couplings to ¹⁹⁵Pt, ranging from 3172 to 3177 Hz.

ESI MS analysis of $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2][BPh_4]$ **3c** yielded variable spectra, with the observed ions dependent on the solvent used, the fragmentation conditions, and the freshness of the sample solution. When a freshly prepared solution of **3c** in MeCN solution was analysed, the expected $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^+$ was observed as the base peak in the spectrum (Fig. 3) under a range of fragmentation conditions. However, analysis in a dichloromethane-methanol mixture showed, in addition to $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^+$ as the base peak, an additional *dication* at *m/z* 1684 whose isotope pattern partly overlaps that of $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^+$. When the analyte solution was allowed to stand overnight, the intensity of the dication increased significantly; under gentle fragmentation conditions the dication was the major peak, but fragmentation occurred to a monocation at approximately the same

m/z value (vide infra) when the fragmentation was increased (by increasing the capillary exit voltage); $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^+$ was still observed as part of the overlapping isotopic envelope. Fig. 4 shows selected mass spectra to illustrate the observed species in (a) a fresh solution of **3c**, (b) on standing overnight, and (c) on varying the fragmentation conditions.

The dication at m/z 1684 is assigned to the di-indium species $[{Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)}_2]^{2+}$, while its corresponding monomer (formed by fragmentation) is $[Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)]^+$. This is supported by MS measurements; the base peak for the dication is observed at m/z 1684.644 (calculated m/z 1684.629); this m/z value is distinctly different from the monocation, which was observed at m/z 1684.167 (calculated m/z 1684.129). We propose the dication to have a structure with an $\{In(u-OMe)_2In\}$ unit (and thus terminal chloride ligands) on the basis that (a) the parent chloro complex [Pt₂(µ-S)₂(PPh₃)₄InCl₂]⁺ shows no evidence for formation of a corresponding dicationic dimer in ESI mass spectra. and (b) there is a demonstrated tendency for alkoxide versus chloride bridging in indium complexes containing both of these ligands [27–29], for example [XMeInOR]₂ (X = Cl, Br; R = ^tBu or $o-C_6H_4$ OMe) [30]. Such a dimeric species would be expected to undergo fragmentation to the monomer, as is observed in the mass spectra. We have seen similar behaviour for the copper-methoxy analogue $[{Pt_2(\mu-S)_2(PPh_3)_4Cu(OMe)}_2]^{2+}$, which fragments to $[Pt_2(\mu-S)_2$ $(PPh_3)_4Cu(OMe)]^+$ [31].

When a small quantity of pyridine was added to a fresh solution of **3c** in CH₂Cl₂–MeOH, the dominant species were the methoxy species [{Pt₂(μ -S)₂(PPh₃)₄InCl(OMe)]₂]²⁺ and its monomer [Pt₂(μ -S)₂(PPh₃)₄InCl(OMe)]⁺, with essentially no parent [Pt₂(μ -S)₂(PPh₃)₄InCl₂]⁺ observed, consistent with greater formation of OMe⁻ ions under the basic conditions. It is noteworthy that the simple fivecoordinate adduct [Pt₂(μ -S)₂(PPh₃)₄InCl₂(NC₅H₅)]⁺ was not observed, consistent with previous observations that the [Pt₂(μ -S)₂(PPh₃)₄] metalloligand supports the formation of adducts with low coordination numbers [6,32,33]. A summary of the proposed solution speciation is given in Scheme 1.

The dimer $[{Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)}_2]^{2+}$ was synthesised on the macroscopic scale by reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with $InCl_3$ in methanol in the presence of added trimethylamine base, fol-



Fig. 3. Positive-ion ESI mass spectrum of $[Pt_2(\mu-S)_2(PPh_3)_4|nCl_2][BPh_4]$ **3c** in MeCN solution (*Capillary Exit* voltage 60 V). The inset shows the expanded isotope pattern for the dominant cation $[Pt_2(\mu-S)_2(PPh_3)_4|nCl_2]^*$, which agrees well with the theoretical pattern.



Fig. 4. Positive-ion ESI mass spectra of **3c** dissolved in CH_2Cl_2 -MeOH solution: (a) fresh solution, *Capillary Exit* 60 V; (b) solution allowed to stand overnight, *Capillary Exit* 60 V; (c) solution from (b), *Capillary Exit* 150 V.



Scheme 1. The proposed interrelationship between indium-chloride adducts of the metalloligand $[Pt_2(\mu-S)_2(PPh_3)_4]$.

lowed by precipitation of the cation by the addition of excess NaB-Ph₄, giving a white precipitate of $[\{Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)\}_2]$ (BPh₄)₂ **4a**. ESI MS analysis showed $[\{Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)\}_2]^{2+}$ to be the dominant ion product, though some $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^+$ was observed. The ³¹P{¹H} NMR spectrum of **4a** showed a single central resonance with ¹⁹⁵Pt coupling of 3124 Hz, slightly less than in the four-coordinate dichloro complex **3c** (3172 Hz); this can be rationalised by the fact that in **4a** the indium is five-coordinate and therefore probably less Lewis acidic than in **3c**, resulting in the (more electron-rich) sulfide ligands of **4a** exerting a slightly higher *trans*-influence, decreasing ¹J(PtP) to the *trans* phosphine.

Unfortunately, attempts at obtaining single crystals of **4a** suitable for an X-ray structural study have been unsuccessful; vapour diffusion of diethyl ether into a dichloromethane solution of the complex gave colourless, finely acicular crystals. The corresponding hexafluorophosphate salt [$\{Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)\}_2$](PF₆)₂ **4b** was also synthesised in high purity (as shown by ESI MS and microelemental analysis) but also yielded no crystals suitable for X-ray crystallographic study.

2.2. Chemistry of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with indium(III) complexes of bidentate chelating ligands

Reaction of a methanolic suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with InCl₃·3H₂O, 2 mole equivalents of 8-hydroxyquinoline (HQ) and excess trimethylamine base gave a bright yellow solution from which the salt $[Pt_2(\mu-S)_2(PPh_3)_4InQ_2]PF_6$ 5 was isolated in 70% yield as a yellow solid by addition of excess ammonium hexafluorophosphate. The complex is soluble in chloroform and dichloromethane. The ³¹P{¹H} NMR spectrum of the complex in CDCl₃ showed two well-resolved singlet resonances at δ 21.5 and 16.4, showing coupling to ¹⁹⁵Pt of 3175 and 3069 Hz, respectively. These arise due to two inequivalent sets of PPh₃ ligands that arise because of the N/O asymmetry of the Q ligand. The ESI mass spectrum shows a single ion at m/z 1906.323 which shows excellent agreement of its isotope pattern and m/z value with theoretical values. In contrast to the bright yellow luminescence displayed by InQ_3 [34–36] $[Pt_2(\mu-S)_2(PPh_3)_4InQ_2]PF_6$ displayed only an extremely faint yellow luminescence when irradiated at either 254 or 312 nm. Like InQ₃, complex **5** is proposed to also contain six -coordinate indium, though we were unable to obtain single crystals suitable for an X-ray study. When $[Pt_2(\mu-S)_2(PPh_3)_4]$ was reacted with 1 mole equivalent of each of InCl₃·3H₂O and 8-hydroxyquinoline in an attempt to synthesise the mono-chloro complex $[Pt_2(\mu-S)_2(PPh_3)_4InClQ]^+$, a light yellow solid was obtained, which was found by ESI MS to be a mixture of all three Cl/Q complexes $[Pt_2(\mu-S)_2(PPh_3)_4InCl_nQ_{2-n}]^+$ (*n* = 0–2).

The reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with InQ_3 itself proceeds less smoothly; reaction in methanol suspension gives a yellow suspension found to contain $[Pt_2(\mu-S)_2(PPh_3)_4InQ_2]^+$, but contaminated with a species at m/z 863, identified as the platinum(II) species $[(Ph_3P)_2PtQ]^+$. The formation of $[(Ph_3P)_2PtQ]^+$ presumably arises from attack of the librated Q^- anion on the initially-formed $[Pt_2(\mu-S)_2(PPh_3)_4InQ_2]^+$, resulting in breakup of the $\{Pt_2S_2\}$ core. Similar behaviour has been observed before in reactions of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with diketonate complexes of cobalt(II) and zinc(II), where the liberated diketonate anion leads to mononuclear complexes $[(Ph_3P)_2Pt(diketonate)]^+$ [37].

Examination of the literature indicated that while a substantial number of platinum complexes containing chelating hydroxyquinolinate ligands have been reported [38–43], complexes containing ancillary phosphine ligands are surprisingly unknown. $[(Ph_3P)_2 PtQ]^*$ was readily prepared by reaction of *cis*-[PtCl₂(PPh₃)₂] with excess HQ in hot methanol, in the presence of trimethylamine base. The resulting cation was isolated in good yield as its bright yellow tetraphenylborate salt **6**, which displays a dull red luminescence when irradiated at either 254 or 312 nm. The complex is soluble in chlorinated hydrocarbon solvents and gives the expected cation as the sole peak in the positive-ion ESI mass spectrum at m/z863.214 (calcd. 863.192). The X-ray structure of **6** was determined, and the cation together with the atom numbering scheme are shown in Fig. 5.

In 6, the Pt–O bond distance [2.0356(17)Å] is slightly longer than in the complex PtQ₂ [44], 2.014(3) Å. The Pt-N distance of **6** [2.115(2) Å] is also significantly longer than the Pt–N distance of PtQ_2 [1.993(4)Å]. These increased bond lengths in **6** reflect the relatively high *trans*-influence [45] of the phosphine ligands, which cause of lengthening of the trans Pt-ligand bonds. A similar lengthening was observed for the Pt-O bond of a platinum Q complex containing a cyclometallated phenylpyridine ligand (with the Pt-O bond *trans* to the strong *trans*-influence σ -phenyl ligand) [39]. The Pt-P(1) bond *trans* to oxygen O(1) is slightly longer [2.2626(7)Å] compared to Pt-P(2) trans to quinoline nitrogen [2.2578(7) Å], reflecting a slightly higher trans-influence for the anionic oxygen donor. The bite angle of the ligand [O(1)-Pt(1)-N(1)]is 80.53(8)°, somewhat reduced from the idealised bond angle of 90° at platinum(II), with a concomitant widening of the P(1)-Pt(1)-P(2) angle to 96.14(3)°. As a result of the geometry of the Q ligand, the bond angle $N(1)-P(1)[95.58(6)^{\circ}]$ is wider than on the other side of the complex $[O(1)-Pt(1)-P(2) 87.64(5)^{\circ}]$. As is common in platinum(II) complexes, the metal is slightly distorted from an idealised square-planar geometry, with an angle of $6.27(6)^{\circ}$ between the P(1)-Pt(1)-P(2) and O(1)-Pt(1)-N(1) planes; the platinum-oxyquinolinate system is, however, highly planar.

Attempts at the synthesis of related indium adducts of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with other ancillary chelating ligands on indium have met with partial success, with some mixed-ligand complexes also being formed by the method used to prepare **5**. Thus, reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with 1 mole equivalents of $InCl_3 \cdot 3H_2O$ and 2 mole equivalents of the dithiocarbamate $NH_4[S_2CN(CH_2)_4]$, followed by precipitation of the cationic products with NH_4PF_6



95.58(6), P(2)-Pt(1)-P(1) 96.14(3).



gave a light yellow solid found by ESI MS to contain predominantly $[Pt_2(\mu-S)_2(PPh_3)_4In\{S_2CN(CH_2)_4\}_2]^+$ (*m/z* 1910) but contaminated with around 25% $[Pt_2(\mu-S)_2(PPh_3)_4InCl\{S_2CN(CH_2)_4\}]^+$ (*m/z* 1799). When this reaction is repeated but using 2 mole equivalents of Na(S_2CNEt_2) as the dithiocarbamate ligand, and the product precipitated using NaBPh₄, analogous cationic species were formed, but with the chloro complex $[Pt_2(\mu-S)_2(PPh_3)_4InCl(S_2CNEt_2)]^+$ (*m/z* 1801) the major species, and $[Pt_2(\mu-S)_2(PPh_3)_4InCl(S_2CNEt_2)_2]^+$ (*m/z* 1914) at about 30% relative intensity. No further studies were carried out on these systems.

In summary, we have extended the range of known indium(III) adducts of the metalloligand $[Pt_2(\mu-S)_2(PPh_3)_4]$ to include four-coordinate chloro-, bromo- and iodo-complexes, with partial methanolysis being observed for solely the chloro system. ESI MS has again found to be a useful methodology for probing the chemistry of this system, and we are continuing our investigations into hydroxyquinolinate adducts with other metals.

3. Experimental

 $[Pt_2(\mu-S)_2(PPh_3)_4]$ [46,47] and InQ_3 [48] were prepared by the literature procedures. Ammonium hexafluorophosphate (Aldrich), sodium tetraphenylborate (BDH), indium trichloride trihydrate (BDH), indium nitrate hydrate (BDH), sodium bromide (BDH), potassium iodide (BDH), aqueous trimethylamine solution (25–30% w/v, BDH), ammonium pyrollidinedithiocarbamate (NH₄[S₂CN(CH₂)₄], BDH), sodium diethyldithiocarbamate (BDH) and 8-hydroxyquinoline (Riedel de Haën) were used as supplied from commercial sources.

Low resolution ESI mass spectra were recorded on a VG Platform II instrument. High resolution ESI mass spectra were recorded on a Bruker MicrOTOF instrument, which was periodically calibrated using a solution of sodium formate. Samples of isolated products were typically prepared for analysis by dissolution in a few drops of dichloromethane followed by dilution with methanol and centrifugation. Typical parameters used a *Capillary Exit* voltage of 150 V though this was varied in increments between 60 and 180 V to investigate variable fragmentation conditions on ion speciation. Assignment of ions was assisted by comparison of experimental and theoretical isotope patterns, the latter calculated using an internet-based program [49] or instrument-based software.

³¹P{¹H} NMR spectra were recorded in CDCl₃ solution on a Bruker DRX instrument at 162 MHz. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Reactions were carried out in LR grade methanol solvent without regard for the exclusion of light, air, or moisture.

3.1. Synthesis of $[Pt_2(\mu-S)_2(PPh_3)_4InBr_2][InBr_4]$ **3a**

To a suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (333 mg, 0.222 mmol) in methanol (20 mL) was added an excess (300 mg) of $In(NO_3)_3 \cdot xH_2O$, rapidly giving a clear pale yellow solution. After stirring for 5 min a large excess (2.5 g) of sodium bromide was added, giving a white flocculent precipitate that was stirred for 5 min and then water (60 mL) added. After stirring for 20 min the white product was filtered, washed with water (2 × 10 mL) and dried under vacuum to give **3a** (298 mg, 61%). $C_{72}H_{60}Br_6In_2P_4Pt_2S_2$ (M_r 2211.6) requires C, 39.07; H, 2.73; N, 0.00. Found: C, 38.83; H, 2.77; N, 0.00%. Positiveion ESI MS (MeOH solvent): $[Pt_2(\mu-S)_2(PPh_3)_4InBr_2]^+$ (*m*/*z* 1777.988, calcd. 1777.977) together with a trace of $[Pt_2(\mu-S)_2$ (PPh_3)_4InBrCl]^+ (*m*/*z* 1733.036, calcd. 1733.028). ³¹P{¹H} NMR, δ 16.9 [s, ¹J(PtP) 3177]. Recrystallisation by vapour diffusion of diethyl ether into a dichloromethane solution of the complex gave colourless crystals.

3.2. Synthesis of $[Pt_2(\mu-S)_2(PPh_3)_4InI_2][InI_4]$ **3b**

Following the procedure for the InBr₂ adduct **3a**, but replacing NaBr with KI, $[Pt_2(\mu-S)_2(PPh_3)_4]$ (273 mg, 0.182 mmol) gave a cream precipitate of $[Pt_2(\mu-S)_2(PPh_3)_4|II_2][III_4]$ **3b** (337 mg, 74%). C₇₂H₆₀I₆In₂P₄Pt₂S₂ (M_r 2493.5) requires C, 34.65; H, 2.42; N, 0.00. Found: C, 34.80; H, 2.46; N, 0.00%. Positive-ion ESI MS (MeOH solvent): $[Pt_2(\mu-S)_2(PPh_3)_4|II_2]^+$ (*m*/*z* 1870.963, calcd. 1870.950). Negative-ion ESI MS (MeOH): I⁻ (*m*/*z* 126.886), $[III_3CI]^-$ (*m*/*z* 530.533), $[III_4]^-$ (*m*/*z* 622.463). ³¹P{¹H} NMR, δ 17.0 [s, ¹J(PtP) 3175]. Recrystallisation by vapour diffusion of diethyl ether into a dichloromethane solution of the complex gave very pale cream crystals suitable for a single-crystal X-ray study.

3.3. Synthesis of $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2][BPh_4]$ 3c

A suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (300 mg, 0.200 mmol) and $InCl_3 \cdot 3H_2O$ (57 mg, 0.207 mmol) in methanol (30 mL) was stirred at room temp. for 1.5 h, giving a clear, very pale yellow solution. Solid NaBPh₄ (200 mg, 0.585 mmol) was added to the stirred solution, immediately forming a white precipitate. The product was filtered, washed with cold methanol (2 × 3 mL) and dried under vacuum to give **3c** as a white solid (310 mg, 77%). $C_{96}H_{30}BCl_2InP_4Pt_2S_2$ (M_r 2007.4) requires C, 57.39; H, 4.02; N, 0.00. Found: C, 56.73; H, 3.88; N, 0.00%. Positive-ion ESI MS (MeCN) $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^+$ (*m*/*z* 1689.093, calcd. 1689.079); refer also Section 2. ³¹P{¹H} NMR, δ 17.27 [s, ¹J(PtP) 3172].

3.4. Synthesis of $[{Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)}_2](BPh_4)_2$ 4a

To a suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (298 mg, 0.198 mmol) in methanol (30 mL) was added $InCl_3 \cdot 3H_2O$ (80 mg, 0.29 mmol) and the mixture stirred for 30 min to give a clear, very pale yellow solution. Aqueous trimethylamine solution (10 drops) was added, resulting in some precipitate formation. Dichloromethane (*ca.* 3 mL) was then added, and the mixture gravity filtered. To the resulting clear pale yellow filtrate was added NaBPh₄ (300 mg, 0.877 mmol), giving a white precipitate. The product was filtered, washed with cold methanol (5 mL) and dried under vacuum to give **4a** (214 mg, 54%). C₁₉₄H₁₆₆B₂Cl₂ln₂O₂P₈Pt₄S₄ requires C, 58.12; H, 4.18. Found: C, 56.94; H, 4.29%. Positive ion ESI MS (CH₂Cl₂–MeOH) [$Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)_2]^{2^+}$ (*m/z* 1684.167, calcd. 1684.129). ³¹P{¹H} NMR, δ 17.6 [s, ¹](PtP) 3124].

3.5. Synthesis of $[{Pt_2(\mu-S)_2(PPh_3)_4InCl(OMe)}_2](PF_6)_2$ 4b

Following the general procedure for the synthesis of **4a**, complex **4b** was prepared in 49% yield, from $[Pt_2(\mu-S)_2(PPh_3)_4]$ (242 mg, 0.161 mmol) with NH₄PF₆ (300 mg) as the precipitating agent; water (10 mL) was added to assist precipitation. Positive ion ESI MS (CH₂Cl₂–MeOH) showed the product to contain pure $[\{Pt_2(\mu-S)_2(PPh_3)_4|nCl(OMe)\}_2]^{2+}$ with no other Pt–In species. C₁₄₆ H₁₂₆Cl₂F₁₂In₂O₂P₁₀Pt₄S₄ requires C, 47.90; H, 3.47. Found: C, 47.50; H, 3.36%.

3.6. Synthesis of $[Pt_2(\mu-S)_2(PPh_3)_4InQ_2]PF_6$ 5

A suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (344 mg, 0.229 mmol) and $InCl_3 \cdot 3H_2O$ (65 mg, 0.236 mmol) in methanol (30 mL) was stirred at room temp. for 20 min giving a clear, very pale yellow solution. To this was added 8-hydroxyquinoline (HQ; 67 mg, 0.462 mmol) giving a slightly more yellow solution, followed by aqueous trimethylamine (1 mL, excess). After stirring for 40 min the yellow

solution was filtered to remove a trace of insoluble matter, and NH₄PF₆ (200 mg, 1.23 mmol) added to the filtrate, giving a yellow precipitate. Water (10 mL) was added to assist precipitation, and the product was isolated by filtration, washed with methanol-water (1:1, 10 mL) and dried under vacuum to give **5** (330 mg, 70%). C₉₀H₇₂F₆lnN₂O₂P₅Pt₂S₂ (M_r 2050.3) requires C, 52.67; H, 3.54; N, 1.37. Found: C, 51.88; H, 3.46; N, 1.33%. Positive-ion ESI MS *m/z* 1906.323 (100%); calcd. for [Pt₂(μ -S)₂(PPh₃)₄InQ₂]⁺ *m/z* 1906.233. ³¹P{¹H} NMR, δ 21.5 [s, ¹J(PtP) 3175] and 16.4 [s, ¹](PtP) 3069].

3.7. Attempted synthesis of $[Pt_2(\mu-S)_2(PPh_3)_4InClQ]PF_6$

A suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (221 mg, 0.147 mmol) and $InCl_3 \cdot 3H_2O$ (41 mg, 0.149 mmol) in methanol (30 mL) was stirred at room temp. for 5 min giving a clear, very pale yellow solution. 8-Hydroxyquinoline (22 mg, 0.152 mmol) was added, followed after 5 min by four drops of aqueous Me₃N solution, giving a light yellow solution. After stirring (with no further change) for 1.5 h, the solution was filtered to remove a trace of insoluble material, and NH₄PF₆ (200 mg, 1.23 mmol) added to the filtrate, giving a light lemon-yellow precipitate. The solid was filtered, washed with cold methanol (5 mL) and dried under vacuum to give 198 mg of a light yellow solid. Positive-ion ESI MS showed major ions due to $[Pt_2(\mu-S)_2(PPh_3)_4InQ_2]^*$ (*m*/*z* 1906), $[Pt_2(\mu-S)_2(PPh_3)_4InClQ]^*$ (*m*/*z* 1797) and $[Pt_2(\mu-S)_2(PPh_3)_4InCl_2]^*$ (*m*/*z* 1689).

3.8. Synthesis of $[Pt_2(\mu-S)_2(PPh_3)_4In\{S_2CN(CH_2)_4\}_2]PF_6$

A mixture of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (360 mg, 0.240 mmol) and $InCl_3 \cdot 3H_2O$ (68 mg, 0.248 mmol) in methanol (25 mL) was stirred at room temp. for 10 min giving a clear, very pale yellow solution. $NH_4[S_2CN(CH_2)_4]$ (81 mg, 0.493 mmol) was added and the mixture stirred for 10 min giving a light yellow solution. After filtration to remove a trace of insoluble material, NH_4PF_6 (200 mg, 1.23 mmol) was added giving a light yellow precipitate. The product was isolated by filtration, washed with water (5 mL) and dried under vacuum to give 349 mg of product as a yellow powder. Positive-ion ESI MS of the product showed predominantly $[Pt_2(\mu-S)_2(PPh_3)_4] \ln\{S_2CN(CH_2)_4\}_2]^+$ at m/z 1910.164 (relative intensity 100%, calcd m/z 1910.162) together with around 25% relative intensity of the chloro-derivative $[Pt_2(\mu-S)_2(PPh_3)_4InCl\{S_2CN(CH_2)_4\}]^+$ at m/z 1799.124 (calcd. 1799.121).

When the above reaction was repeated using $[Pt_2(\mu-S)_2(PPh_3)_4]$ (369 mg, 0.246 mmol), $InCl_3$ ·3H₂O (68 mg, 0.248 mmol), $Na(S_2C-NEt_2)$ (85 mg, 0.497 mmol) and $NaBPh_4$ (200 mg, 0.585 mmol), 374 mg of a light yellow solid was obtained that was found to be a mixture of $[Pt_2(\mu-S)_2(PPh_3)_4InCl(S_2CNEt_2)]^+$ (major product, m/z1801.131, calcd. 1801.136) and $[Pt_2(\mu-S)_2(PPh_3)_4In(S_2CNEt_2)_2]^+$ (minor product, m/z 1914.186, calcd. 1914.193).

3.9. Synthesis of [PtQ(PPh₃)₂]BPh₄ 6

A suspension of *cis*-[PtCl₂(PPh₃)₂] (225 mg, 0.285 mmol) and 8-hydroxyquinoline (200 mg, 1.38 mmol) in methanol (30 mL) with aqueous trimethylamine (1 mL, excess) was heated to reflux for 20 min to give a clear, bright yellow solution. After filtration to remove a trace of insoluble material, NaBPh₄ (250 mg, 0.73 mmol) was added to the warm filtrate, giving a bright yellow precipitate. This was isolated by filtration, washed with cold methanol (2 × 5 mL) and dried under vacuum to give **6** (296 mg, 88%). C₆₉H₅₆BNOP₂Pt (M_r 1182.5) requires C, 70.02; H, 4.77; N, 1.18. Found: C, 70.15; H, 4.83; N, 1.15%. Positive-ion ESI MS *m/z* 863.214 (100%); calcd, for [Pt(PPh₃)₂Q]⁺ *m/z* 863.192. ³¹P{¹H} NMR (CDCl₃), δ 14.1 [d, ¹J(PtP) 3680, ²J(PP) 19] and 8.7 [d, ¹J(PtP) 3396, ²J(PP) 19].

3.10. X-ray structure determination on $[Pt_2(\mu-S)_2(PPh_3)_4InI_2][InI_4]$ **3b**

Crystals were obtained from dichloromethane-diethyl ether.

Crystal data for $C_{73.50}H_{63}Cl_3I_6In_2P_4Pt_2S_2$; $M_r = 2621.81$; monoclinic; space group $P2_1/n$; a = 17.472(2) Å; b = 22.264(3) Å; c = 21.028(2) Å; $\beta = 93.744(2)^\circ$; V = 8162.5(16) Å³; Z = 4; T = 120 (2) K; λ (Mo K α) = 0.71073 Å; μ (Mo K α) = 6.511 mm⁻¹; $d_{calc} = 2.133$ g cm⁻³; 98 992 reflections collected; 16 736 unique ($R_{int} = 0.0513$); giving $R_1 = 0.0278$, $wR_2 = 0.0516$ for 13 604 data with [$I > 2\sigma(I)$] and $R_1 = 0.0413$, $wR_2 = 0.0566$ for all 16 736 data. Residual electron density (e⁻ Å⁻³) max/min: 1.547/-1.421.

An arbitrary sphere of data were collected on a tablet-like crystal, having approximate dimensions of $0.32 \times 0.19 \times 0.09$ mm, on a Bruker Kappa X8-APEX-II diffractometer using a combination of ω -and φ -scans of 0.3° . Data were corrected for absorption and polarisation effects and analysed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.2 × for all C–H).

Three locations for solvent molecules (modelled as dichloromethane) were observed in the asymmetric unit. Two sites are near each other and represent a full molecule of solvent disordered over two sites, the third site is located on a centre of symmetry. Initially all site occupancies were refined independently leading to occupancies of 0.71, 0.29 and 0.51. Subsequently the two close sites (which initially refined to 0.71 and 0.29 occupancy) were then refined with occupancies summed to unity. The remaining site was refined with an occupancy fixed at 0.5. The thermal parameter of the minor component solvent carbon atom was refined isotropically, all other non-hydrogen atoms were refined with anisotropic thermal parameters.

3.11. X-ray structure determination on [PtQ(PPh₃)₂]BPh₄ 6

Crystals were obtained from dichloromethane-diethyl ether.

Crystal data for $C_{75}H_{62}BNOP_2Pt$; $M_r = 1261.10$; Triclinic; space group $P\bar{1}$; a = 12.5329(18) Å; b = 14.574(2) Å; c = 19.111(3) Å; $\alpha = 68.500(2)^\circ$; $\beta = 88.726(2)^\circ$; $\gamma = 65.029(2)^\circ$; V = 2907.6(7) Å³; Z = 2; T = 120(2) K; λ (Mo K α) = 0.71073 Å; μ (Mo K α) = 2.516 mm⁻¹; $d_{calc} = 1.440$ g cm⁻³; 39 711 reflections collected; 11 849 unique ($R_{int} = 0.0343$); giving $R_1 = 0.0240$, $wR_2 = 0.0489$ for 10 784 data with [$I > 2\sigma(I)$] and $R_1 = 0.0285$, $wR_2 = 0.0538$ for all 11 849 data. Residual electron density (e⁻Å⁻³) max/min: 0.912/-0.564.

An arbitrary sphere of data were collected on a pale yellow block-like crystal, having approximate dimensions of $0.23 \times 0.15 \times 0.14$ mm, on a Bruker APEX-II diffractometer using a combination of ω - and φ -scans of 0.3° . Data were corrected for absorption and polarisation effects and analysed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix leastsquares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded ($1.2 \times$ for all others).

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Appendix A. Supplementary material

CCDC 812347 and 812346 contain the supplementary crystallographic data for (3b) and (6). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary_data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.05.014.

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