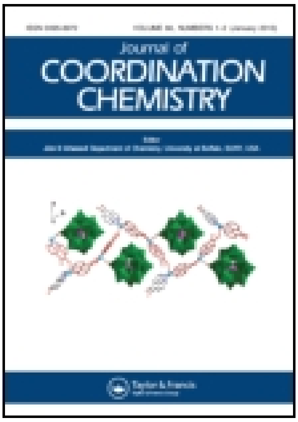
This article was downloaded by: [Chongqing University]
On: 14 February 2014, At: 13:26
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

A study of zinc complexes of the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ of the type $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL]^+$ (L = bidentate chelating ligand)

William Henderson[a], Scott H. Robertson[a] & Brian K. Nicholson[a]
[a] Department of Chemistry, University of Waikato, Hamilton, New Zealand

Accepted author version posted online: 05 Sep 2013.Published online: 22 Oct 2013.

To cite this article: William Henderson, Scott H. Robertson & Brian K. Nicholson (2013) A study of zinc complexes of the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ of the type $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL]^+$ (L = bidentate chelating ligand), Journal of Coordination Chemistry, 66:19, 3412-3422, DOI: 10.1080/00958972.2013.840883

To link to this article: http://dx.doi.org/10.1080/00958972.2013.840883

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry, 2013
Vol. 66, No. 19, 3412–3422, http://dx.doi.org/10.1080/00958972.2013.840883

Taylor & Francis
Taylor & Francis Group

A study of zinc complexes of the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ of the type $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL]^+$ (L = bidentate chelating ligand)

WILLIAM HENDERSON*, SCOTT H. ROBERTSON and BRIAN K. NICHOLSON

Department of Chemistry, University of Waikato, Hamilton, New Zealand

(*Received 14 April 2013; accepted 5 August 2013*)

Reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with zinc acetate and an ancillary chelating ligand L (HL = 8-hydroxyquinoline, 8-tosylaminoquinoline or maltol) with added trimethylamine in methanol give new cationic platinum–zinc sulfide aggregates $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL]^+$, isolated as their BF_4^- salts. The complexes were characterized by NMR spectroscopy, ESI mass spectrometry, microelemental analysis, and an X-ray structure determination of the tosylamidoquinoline derivative $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(TAQ)]BF_4$, which showed a distorted tetrahedral coordination geometry at zinc. Additional examples, containing picolinate, dithiocarbamate, or dithiophosphinate ligands were also synthesized and partly characterized in order to demonstrate a wider range of available derivatives.

Keywords: Platinum complexes; Zinc complexes; Sulfide ligand; Metalloligand; Crystal structure; Electrospray ionization mass spectrometry

1. Introduction

The platinum(II) sulfide complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) possesses a rich metalloligand coordination chemistry as a result of the two electron-rich bridging sulfides [1]. Complexes with many main group and transition elements have been reported in the literature, with a tendency for a wide range of stable complexes to be formed with softer metal ions, as expected. We have been using the technique of electrospray ionization mass spectrometry (ESI MS) [2] as a powerful screening tool for extending the coordination chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ [3]. This technique is efficient in terms of sample quantity required, effective (because products are often cationic and produce strong ion signals in the mass spectrum), and can be used to identify novel species for subsequent macroscopic synthesis and characterization [4].

In this contribution, we report further studies on coordination chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards zinc centers with ancillary bidentate chelating ligands. A limited number of zinc complexes of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ have been previously reported. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $ZnCl_2$ gave a simple tetrahedral adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnCl_2]$ (**2**), while reaction with $ZnSO_4$ instead gave a dimeric structure $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnSO_4\}_2]$

---

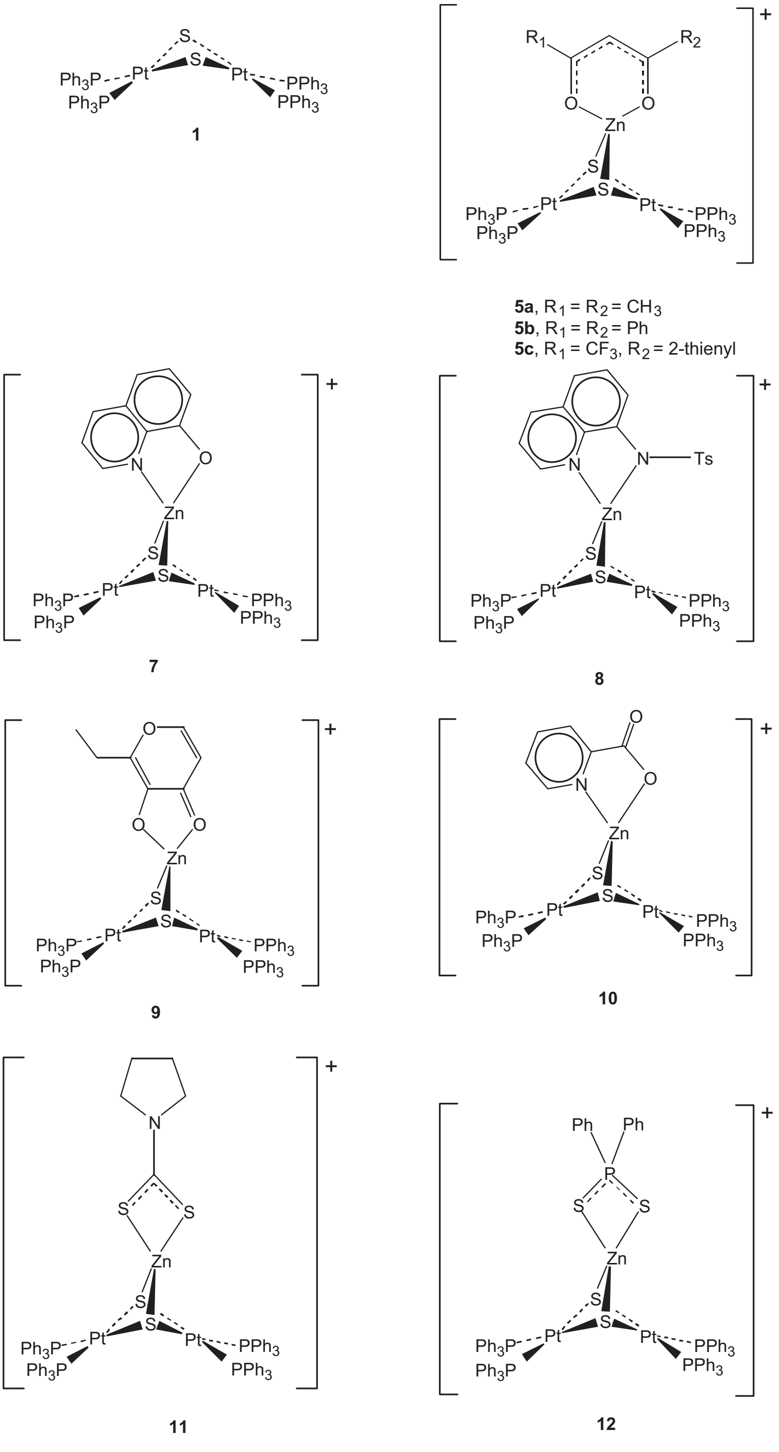
*Corresponding author. Email: w.henderson@waikato.ac.nz

(**3**) containing an eight-membered {$Zn_2S_2O_4$} ring with two bridging sulfates, with each Zn also coordinated to a bidentate [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] metalloligand [5]. The bis adduct [{$Pt_2(\mu\text{-}S)_2(PPh_3)_4$}$_2$Zn]$^{2+}$ (**4**) is also known from the reaction of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] with Zn ($ClO_4$)$_2$ in a 2 : 1 M ratio [4]. Some examples of complexes with ancillary ligands have also been prepared. The reaction of [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] with zinc β-diketonate complexes ZnL_2 [L = $CH_3COCHCOCH_3$, PhCOCHCOPh, or $CF_3COCHCO$(2-thienyl)] gave cationic four-coordinate zinc adducts [$Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL$]$^+$ (**5a–c**) [6]. However, the products were invariably contaminated with [$PtL(PPh_3)_2$]$^+$ as a result of fragmentation of the {$Pt_2(\mu\text{-}S)_2$} core effected by liberated L^-. A five-coordinate zinc adduct [$Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnCl$(bipy)]$^+$ (**6**) (bipy = 2,2′-bipyridine) is also known [7]. Finally, related {Pt_2S_2Zn} complexes with other phosphine or arsine ligands have been prepared by reactions of [$Pt_2(\mu\text{-}S)_2(dppe)_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) with $Zn(ClO_4)_2$ or [$Pt_2(\mu\text{-}S)_2(dpae)_2$] (dpae = $Ph_2AsCH_2CH_2AsPh_2$) with $ZnCl_2$ to give [{$Pt_2(\mu\text{-}S)_2(L)_2$}$_2$Zn]$^{2+}$ {L = dppe [8] or dpae [9]}.

2. Results and discussion

In this work, we employed a 'one-pot' approach to the synthesis of cationic complexes [$Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL$]$^+$, where L is a mono-anionic bidentate ligand. The reactions between [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$], zinc acetate, and one mole equivalent of an ancillary bidentate ligand were investigated in methanol solution with additional base (trimethylamine solution) also added. The bidentate ligands used were 8-hydroxyquinoline (HQ), 8-tosylaminoquinoline (HTAQ), and maltol (Hmalt), which chelate metal ions as mono-anionic ligands; zinc complexes of Q^- [10] and TAQ^- [11] (and closely related analogs) have attracted considerable interest, in particular, for their photophysical characteristics. Maltolato complexes of zinc, e.g. Zn(malt)$_2$, are also known [12]. The initial reaction between [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] and Zn ($OAc)_2$•$2H_2O$ produced a cream suspension, which was not further characterized. Addition of the ancillary HL and Me_3N, followed by filtration, gave yellow (Q) or pale yellow (TAQ, malt) reaction mixtures that were shown by ESI MS to contain the desired cationic adducts [$Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL$]$^+$ **7** (L = Q), **8** (L = TAQ), and **9** (L = malt), in addition to byproduct ions [$PtL(PPh_3)_2$]$^+$, which were most significant in the case of **7** and **9**, but only of low intensity for **8**. The mixtures were filtered to remove a significant quantity of unidentified cream-colored precipitate and the cationic products were isolated in low yields from the filtrate as BF_4^- salts by successive addition of excess $NaBF_4$ and water. Structures of the isolated complexes are shown in scheme 1.

ESI mass spectra of the isolated solids **7**•BF_4, **8**•BF_4, and **9**•BF_4 showed them to be pure, with the precipitation step eliminating [$PtL(PPh_3)_2$]$^+$. Spectra obtained under gentle ionization conditions showed the parent [$Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL$]$^+$ as the base peak in the spectra, and in all cases there was excellent agreement between observed and calculated isotope patterns, as shown in figure 1 for [$Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnQ$]$BF_4$. Increasing fragmentation (with increasing capillary exit voltage) was investigated for **7** and **9**. For **7**, no significant fragmentation was observed until the capillary exit voltage exceeded 220 V. The most significant fragment ions at 250 V were formed by loss of PPh_3, e.g. [$Pt_2(\mu\text{-}S)_2(PPh_3)_3ZnQ$]$^+$ (observed *m/z* 1450.18) and [$Pt_2(\mu\text{-}S)_2(PPh_3)_2ZnQ$]$^+$ (observed *m/z* 1188.07), while a minor ion at *m/z* 1154.09 is formed by loss of H_2S (34 Da) from [$Pt_2(\mu\text{-}S)_2(PPh_3)_2ZnQ$]$^+$. Analogous fragment ions were observed for **9**. The UV–vis spectra of the pale yellow **7** and **8** show a broad absorption centered at 380 nm, while the corresponding band in the maltolate complex **9** was at <350 nm and could not be resolved due to the cutoff range of the



1

5a, $R_1 = R_2 = CH_3$
5b, $R_1 = R_2 = Ph$
5c, $R_1 = CF_3$, $R_2 =$ 2-thienyl

7

8

9

10

11

12

Scheme 1. Structures of new complexes with $\{Pt_2S_2Zn\}$ cores reported herein.

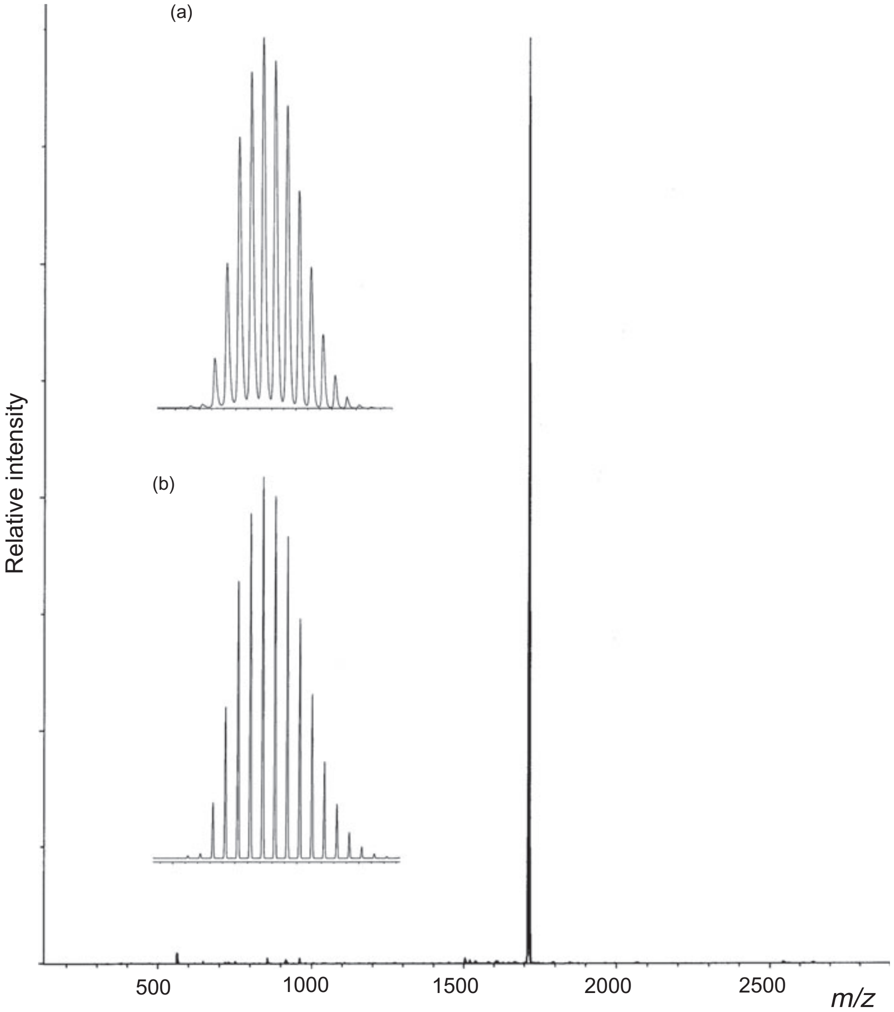


Figure 1. Positive-ion ESI mass spectrum of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnQ]BF_4$ **7**•BF_4 (methanol, capillary exit 150 V) showing the high purity of the complex; the insets show the experimental (upper, a) and the calculated (lower, b) isotope patterns of the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnQ]^+$ ion (Calcd *m/z* 1712.212).

instrument. The infrared spectra of **7–9** provided little useful characterization data, being dominated by CH, C–C (aryl), and B–F absorptions, with medium intensity S=O bands tentatively identified at 1324 and 1144 cm^{-1} in **8**.

The complexes show a single central resonance in their $^{31}P\{^1H\}$ NMR spectra, with (typically) two closely spaced sets of satellites from coupling to ^{195}Pt, from two PPh_3 environments arising from the asymmetric ligand coordination at zinc. For example, **9** shows a central resonance at δ 21.5 with similar $^1J(PtP)$ coupling constants of 3129 and 3089 Hz. Similar observations have been found in related complexes with asymmetric ligands, e.g. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4CoQ_2]^+$ [13].

Single crystals of the tosylamidoquinoline (TAQ) complex **8**•BF_4 were readily obtained from dichloromethane–diethyl ether and in order to fully characterize its geometric features, an X-ray structure determination was carried out. The structure of the core of **8** is shown in figure 2 and selected bond lengths and angles are given in table 1. The structure determination confirms the complex as the expected trinuclear $\{Pt_2ZnS_2\}$ aggregate, with the zinc coordinated by two sulfides as well as the chelating TAQ bonded to zinc through the quinoline nitrogen [Zn(1)–N(1) 2.094(4) Å] and the deprotonated sulfonamide nitrogen through a rather shorter bond [Zn(1)–N(2) 2.004(4) Å]. There has been one previous structural determination of a zinc complex of the TAQ ligand, $Zn(TAQ)_2$ [14], where the zinc quinoline nitrogen bond distances [2.047(1) and 1.981(1) Å] and the zinc–sulfonamide distances [1.972(9) and 1.931(1) Å] are somewhat shorter than in **8**. The lengthening of the Zn–N bonds in **8** is most likely due to the strong electron donation and significant steric bulk of the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ metalloligand. The zinc–sulfonamidoquinoline unit of **8** is planar.

The acetylacetonato (acac) complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(acac)]^+$ (**5a**) [6] provides a useful comparison with **8**, since the ancillary acac is also a mono-anionic chelating ligand, allowing the effects changing from an O donor to an N donor to be elucidated. The TAQ of **8** has a N(1)–Zn(1)–N(2) bite angle of 80.47(17)°, whereas in **5a** the bite angle of acac ligand is larger at 95.96(15)°, a consequence of the presence of a six- *vs.* five-member ring. The Zn–S bond distances of **8** are similar [Zn(1)–S(1) 2.3661(14) and Zn(1)–S(2) 2.3576 (15) Å] and are slightly longer than the Zn–S bond distances in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(acac)]^+$ (**5a**) [2.3459(12) and 2.3398(12) Å] [6], presumably due to the presence of more strongly donating N donors in **8**. The Zn–S bonds of **8** are considerably shorter than in the chloro complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnCl_2]$ (**2**) [2.418(2) Å] [5] and in the five-coordinate complex

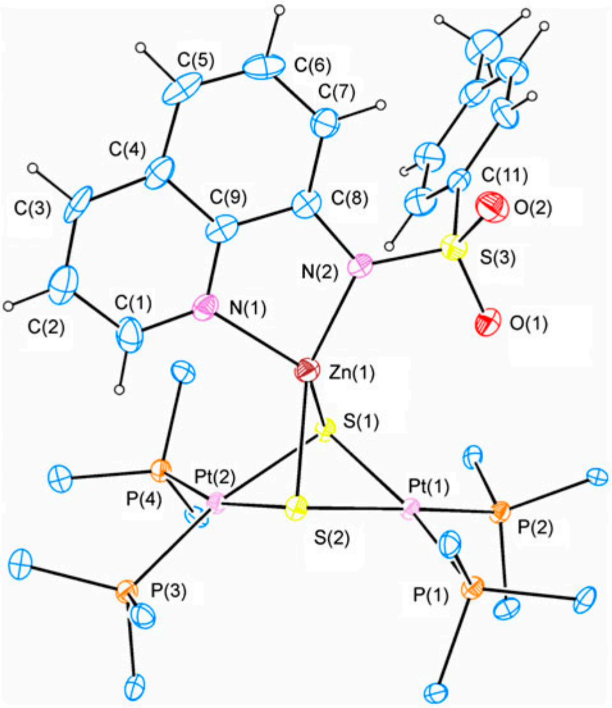


Figure 2. X-ray structure of the core of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(TAQ)]^+$ (**8**) (as its BF_4^- salt) showing the atom numbering scheme; triphenylphosphine carbons other than *ipso* carbons are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(TAQ)]BF_4$ [**8**$\cdot BF_4\cdot CH_2Cl_2\cdot Et_2O$].

Pt(1)–S(1)	2.3671(13)	Pt(1)–S(2)	2.3723(12)
Pt(2)–S(1)	2.3856(13)	Pt(2)–S(2)	2.3630(13)
Zn(1)–S(1)	2.3661(14)	Zn(1)–S(2)	2.3576(15)
Zn(1)–N(1)	2.094(4)	Zn(1)–N(2)	2.004(4)
S(3)–O(1)	1.444(4)	S(3)–O(2)	1.435(4)
S(3)–N(2)	1.593(4)	S(3)–C(11)	1.773(6)
N(2)–Zn(1)–N(1)	80.47(17)	N(2)–Zn(1)–S(2)	141.17(14)
N(1)–Zn(1)–S(2)	108.47(13)	N(2)–Zn(1)–S(1)	124.23(14)
N(1)–Zn(1)–S(1)	128.65(12)	S(2)–Zn(1)–S(1)	80.43(5)
Zn(1)–S(1)–Pt(1)	79.07(4)	Zn(1)–S(1)–Pt(2)	79.32(4)
Zn(1)–S(2)–Pt(2)	79.95(4)	Zn(1)–S(2)–Pt(1)	79.14(4)
Pt(1)–S(1)–Pt(2)	89.27(5)	Pt(2)–S(2)–Pt(1)	89.69(4)
P(2)–Pt(1)–P(1)	100.81(5)	P(2)–Pt(1)–S(1)	93.37(5)
P(1)–Pt(1)–S(2)	85.80(5)	S(1)–Pt(1)–S(2)	80.11(4)
P(3)–Pt(2)–P(4)	103.51(5)	P(3)–Pt(2)–S(2)	90.26(5)
P(4)–Pt(2)–S(1)	86.95(5)	S(2)–Pt(2)–S(1)	79.92(4)
O(2)–S(3)–O(1)	117.2(2)	O(2)–S(3)–N(2)	112.0(2)
O(1)–S(3)–N(2)	105.6(2)	O(2)–S(3)–C(11)	107.5(3)
O(1)–S(3)–C(11)	107.0(3)	N(2)–S(3)–C(11)	107.1(3)

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnCl(bipy)]^+$ (**6**) [average 2.494(2) Å] [7]. The bite angle of the $\{Pt_2S_2\}$ metalloligand at zinc S(2)–Zn(1)–S(1) is 80.43(5)° in **8**, compared to 83.91(4)° in $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(acac)]^+$ (**5a**), consistent with the presence of slightly longer Zn–S bonds in **8**.

The coordination geometry at zinc is significantly distorted from tetrahedral, which can be quantified by means of the τ_4 parameter developed by Houser *et al.* [15], which for **8** is 0.64; by reference a regular tetrahedron has $\tau_4 = 1$ and a regular square-plane has $\tau_4 = 0$. This indicates that the geometry at zinc is best described as see-saw. In a perfect tetrahedron, the zinc–amidoquinoline unit should be coplanar with the two platinum centers, but in **8** it is twisted (the angle between the Pt_2Zn and Zn-amidoquinoline least-squares planes is 19.06°). The zinc–TAQ unit is also tilted towards one platinum [Pt(2)]. This can be further quantified by (a) the non-bonding Pt…N distances [Pt(2)…N(1) 3.855(4) Å shorter than Pt(1)…N(2) 4.349(4) Å] and (b) the S–Zn–N bond angles [N(1)–Zn(1)–S(2), on the side of Pt(2) is 108.47(13)°, while N(2)–Zn(1)–S(2) on the side of Pt(1) is 141.17(14)°]. However, for sulfide S(1), the corresponding bond angles N(2)–Zn(1)–S(1) [124.23(14)°] and N(1)–Zn(1)–S(1) [128.65(12)°] are more similar. The Zn–S–Pt bond angles lie within a narrow range [79.07(4)°–79.95(4)°], indicating that the distortion lies in the zinc-amidoquinoline. These distortions are presumably to accommodate the significant steric bulk of the tosyl group; the SO_2 group is directed into a pocket bounded by aromatic rings, such that the Pt(1)…O(1) non-bonding distance is 3.457(4) Å. The $\{Pt_2S_2\}$ butterfly core has a dihedral angle between the two platinum least-squares coordination planes of 131.17°, which can be compared to a value of 131.42(3)° in **5a** [6]. The long platinum–zinc distances of **8** [Pt(1)–Zn(1) 3.0130(6), Pt(2)–Zn(1) 3.0328(6) Å] are, as expected, non-bonding.

We have also undertaken partial syntheses of several other derivatives to demonstrate the general applicability of the method. Thus, analogous reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, Zn $(OAc)_2\cdot 2H_2O$, and ligand L^- (generated from HL with added Me_3N if necessary) gave the additional complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnL]^+$ **10** (L = picolinate), **11** ($L = S_2CN(CH_2)_4$), and **12** ($L = S_2PPh_2$), scheme 1. In each case, the crude reaction mixture contained a significant quantity of the mono-platinum decomposition product $[PtL(PPh_3)_2]^+$, which was removed by precipitation of the desired product using $NaBF_4$. The isolated complexes were partially characterized by ESI MS (giving single product cations at the expected *m/z* values) and $^{31}P\{^1H\}$ NMR spectroscopy.

In conclusion, a number of new zinc adducts of the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ have been synthesized by a simple one-pot process. The investigations reported herein further extend the wide range of metalloderivatives of the enigmatic $\{Pt_2S_2\}$ core. While the zinc adducts show typical coordination behavior of the $\{Pt_2S_2\}$ metalloligand, the results suggest that a range of other metal/ligand combinations should be accessible from analogous one-pot procedures, to further extend the versatile coordination chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards metals with a richer, more diverse chemistry.

3. Experimental

3.1. *Materials and instrumentation*

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was prepared by the literature procedure from *cis*-$[PtCl_2(PPh_3)_2]$ and $Na_2S{\bullet}9H_2O$ (Aldrich) in benzene suspension following the literature procedure [16, 17]. The following compounds were used as supplied from commercial sources: zinc acetate dihydrate (BDH), 8-tosylaminoquinoline (Aldrich), 8-hydroxyquinoline (Riedel de Häen), picolinic acid (Aldrich), diphenyl dithio phosphinic acid (Aldrich), ammonium tetramethylene dithiocarbamate (BDH), sodium tetrafluoroborate (Aldrich), aqueous trimethylamine solution (BDH), and maltol (Aldrich). Reactions were carried out in LR grade methanol, without regard for the exclusion of light, air, or moisture. Water was singly distilled.

NMR spectra were recorded in $CDCl_3$ using a Bruker Avance DRX300 spectrometer using XWIN-NMR software version 3.0. $^{31}P\{^1H\}$ spectra were referenced relative to external H_3PO_4 and ^1H spectra were referenced relative to the residual $CHCl_3$ signal. Coupling constants (J) are in Hz. Elemental analyzes were obtained from the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Melting points were determined on a Reichert-Jung hotstage apparatus and are uncorrected. IR spectra were recorded as KBr disks on a Perkin-Elmer Spectrum100 spectrometer. UV–vis spectra were recorded in dichloromethane solution using a Perkin-Elmer Lambda 11 spectrophotometer.

Positive-ion ESI mass spectra were recorded on a Bruker MicrOTOF mass spectrometer that was periodically calibrated using an aqueous sodium formate solution. Samples for analysis were prepared by dissolving a small quantity of solid (*ca*. 0.1 mg) in a few drops of dichloromethane, followed by dilution with 1.5 mL of methanol. Solutions were centrifuged prior to analysis. Spectra were routinely recorded using a capillary exit voltage of 150 V, which was varied in order to investigate fragmentation pathways. Ion identification was assisted by comparison of observed and calculated isotope patterns, the latter was obtained using proprietary instrument-based software or an internet program [18]. The reported *m/z* values are for the most intense isotopomer in the overall isotopic envelope of the ion.

3.2. *Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4ZnQ]BF_4$ ($7{\bullet}BF_4$)*

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (363 mg, 0.242 mmol) and $Zn(OAc)_2{\bullet}2H_2O$ (55 mg, 0.251 mmol) in methanol (40 mL) was stirred for 15 min. to give a cream solution/suspension. 8-Hydroxyquinoline (HQ, 37 mg, 0.255 mmol) was added and the reaction mixture immediately went more yellow. Aqueous trimethylamine solution (five drops, excess) was added with no significant change. The reaction mixture was stirred for 1 h and filtered through glass fiber filter paper to give a clear yellow solution. Sodium tetrafluoroborate (200 mg, large excess) was added, followed by water (60 mL) to give a yellow precipitate. This was filtered, washed with water (2 × 10 mL), and dried under vacuum to give **7**•BF_4 (194 mg, 45%) as a pale yellow solid. Found: C, 54.00; H, 3.71; N, 1.53. $C_{81}H_{66}BF_4NOP_4Pt_2S_2Zn$ (M_r 1798.92) requires C, 54.03; H, 3.70; N, 0.78%. M.p. > 213 °C (decomp.). UV–vis (CH_2Cl_2) λ_{max} 380 nm. IR (ν_{max} cm^{-1}) 3054, 1577, 1497, 1461, 1435, 1387, 1328, 1095, 1084, 1059, 743, 693, 537, 524 and 514. ESI MS, capillary exit 150 V: *m/z* 1712.27 [$Pt_2(\mu$-$S)_2(PPh_3)_4ZnQ]^+$ (Calcd *m/z* 1712.21). Capillary exit 250 V: *m/z* 1450.18 [$Pt_2(\mu$-$S)_2(PPh_3)_3ZnQ]^+$, *m/z* 1188.07 [$Pt_2(\mu$-$S)_2(PPh_3)_2ZnQ]^+$, *m/z* 1154.09 [$Pt_2(\mu$-$S)_2(PPh_3)_2ZnQ - H_2S]^+$. $^{31}P\{^1H\}$ NMR, δ 20.7 (s), ^1J(PtP) 3114 and 3079. ^1H NMR, δ 8.81 (s, Q), 8.45 [d, Q, J(HH) 8.0], 7.66 (br t, Q), 7.39–7.06 (m, Q and PPh_3).

3.3. *Synthesis of [$Pt_2(\mu$-$S)_2(PPh_3)_4Zn(TAQ)]BF_4$ (8•BF_4)*

A suspension of [$Pt_2(\mu$-$S)_2(PPh_3)_4$] (278 mg, 0.185 mmol) and $Zn(OAc)_2$•$2H_2O$ (43 mg, 0.196 mmol) in methanol (40 mL) was stirred for 15 min. to give a cream solution/suspension. 8-Tosylaminoquinoline (HTAQ, 58 mg, 0.195 mmol) was added with no significant change. Aqueous trimethylamine solution (five drops, excess) was added and the mixture was stirred for 1 h. Filtration through glass fiber filter paper yielded a clear light yellow solution. Sodium tetrafluoroborate (200 mg, large excess) followed by water (60 mL) were added, giving a pale yellow precipitate which was filtered, washed with water (2 × 10 mL), and dried under vacuum to give **8**•BF_4 as a cream solid (81 mg, 22%). Found: C, 53.14; H, 3.67; N, 1.18. $C_{88}H_{73}BF_4N_2O_2P_4Pt_2S_3Zn$ (M_r 1951.94) requires C, 54.10; H, 3.77; 1.43%. M.p. > 247 °C (decomp.). UV–vis (CH_2Cl_2) λ_{max} 380 nm. IR (ν_{max} cm^{-1}) 3550, 3479, 3416, 3053, 1637, 1618, 1502, 1481, 1435, 1380, 1324, 1285, 1190, 1144, 1117, 1094, 1085, 1059, 999, 745, 693, 536, 524 and 514. ESI MS, capillary exit 150 V: *m/z* 1865.32 [$Pt_2(\mu$-$S)_2(PPh_3)_4Zn(TAQ)]^+$ (Calcd *m/z* 1865.24). Capillary exit 250 V: *m/z* 1603.23 [$Pt_2(\mu$-$S)_2(PPh_3)_3Zn(TAQ)]^+$, *m/z* 1341.13 [$Pt_2(\mu$-$S)_2(PPh_3)_2Zn(TAQ)]^+$, *m/z* 1307.13 [$Pt_2(\mu$-$S)_2(PPh_3)_2Zn(TAQ) - H_2S]^+$. $^{31}P\{^1H\}$ NMR, δ 20.2 (s, br), ^1J(PtP) 3046.

3.4. *Synthesis of [$Pt_2(\mu$-$S)_2(PPh_3)_4Zn(malt)]BF_4$ (9•BF_4)*

A suspension of [$Pt_2(\mu$-$S)_2(PPh_3)_4$] (302 mg, 0.201 mmol) and $Zn(OAc)_2$•$2H_2O$ (48 mg, 0.219 mmol) in methanol (40 mL) was stirred for 15 min. to give a cream solution/suspension. Maltol (Hmalt, 28 mg, 0.222 mmol) and aqueous trimethylamine (5 drops) were added, and the mixture was stirred for 1 h. Filtration through glass fiber filter paper produced a light yellow filtrate. Sodium tetrafluoroborate (200 mg, large excess) was added, followed by water (60 mL), giving a cream precipitate. This was filtered, washed with water (2 × 5 mL), and dried under vacuum to give **9**•BF_4 as a cream solid (73 mg, 20%). Found: C, 52.02; H, 3.62; N, 0.00. $C_{78}H_{65}BF_4O_3P_4Pt_2S_2Zn$ (M_r 1779.89) requires C, 52.59; H, 3.68; N, 0.00%. M.p. > 240 °C (decomp.). UV–vis (CH_2Cl_2) λ_{max} < 350 nm. IR (ν_{max} cm^{-1}) 3551, 3478, 3415, 3054, 1637, 1618, 1569, 1481, 1459, 1435, 1283, 1095, 1060, 999, 742, 693, 537, 524, 513 and 498. ESI MS, capillary exit voltage 150 V: *m/z* 1693.28 [$Pt_2(\mu$-$S)_2(PPh_3)_4Zn(malt)]^+$ (Calcd *m/z* 1693.19). $^{31}P\{^1H\}$ NMR, δ 21.5 (s), ^1J(PtP) 3129 and 3089.

3.5. *Synthesis of additional derivatives*

Following the general procedures for **7–9**, the following derivatives were also prepared and partially characterized:

3.5.1. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(pic)]BF_4$ (10•BF_4). $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (50 mg, 0.033 mmol), $Zn(OAc)_2$•$2H_2O$ (7.4 mg, 0.034 mmol), and picolinic acid (Hpic, 4.1 mg, 0.033 mmol) gave a yellow solution, which with $NaBF_4$ (150 mg, 1.36 mmol) gave **10**•BF_4 as a pale brown solid (31 mg, 52%). M.p. > 209 °C (decomp.). ESI MS *m/z* 1690.23 $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(pic)]^+$ (Calcd *m/z* 1690.19). $^{31}P\{^1H\}$ NMR, δ 20.0 (s), $^1J(PtP)$ 3088, and 3053.

3.5.2. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn\{S_2CN(CH_2)_4\}]BF_4$ (11•BF_4). In this synthetic procedure, no trimethylamine solution was used. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (50 mg, 0.033 mmol), $Zn(OAc)_2$•$2H_2O$ (7.4 mg, 0.034 mmol), and $NH_4\{S_2CN(CH_2)_4\}$ (5.8 mg, 0.035 mmol) gave an orange–yellow solution, which with $NaBF_4$ (150 mg, 1.36 mmol) gave **11**•BF_4 as a light brown solid (16 mg, 27%). M.p. > 203 °C (decomp.). ESI MS *m/z* 1714.21 $[Pt_2(\mu\text{-}S)_2Zn\{S_2CN(CH_2)_4\}]^+$ (Calcd *m/z* 1714.18). $^{31}P\{^1H\}$ NMR, δ 20.5, $^1J(PtP)$ 3125, and 3089.

3.5.3. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(S_2PPh_2)]BF_4$ (12•BF_4). $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (50 mg, 0.033 mmol), $Zn(OAc)_2$•$2H_2O$ (7.4 mg, 0.034 mmol), diphenylthiophosphinic acid (8.3 mg, 0.033 mmol) gave a pale yellow solution, which with $NaBF_4$ (150 mg, 1.36 mmol) gave **12**•BF_4 as an off-white solid (21 mg, 33%). M.p. > 176 °C (decomp.). ESI MS *m/z* 1816.80 $[Pt_2(\mu\text{-}S)_2Zn(S_2PPh_2)]^+$ (Calcd *m/z* 1817.16). $^{31}P\{^1H\}$ NMR, δ 20.5 (s) PPh_3, $^1J(PtP)$ 3125 and 63.7 (s), Ph_2PS_2.

Table 2. Crystal and refinement details for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(TAQ)]BF_4$ CH_2Cl_2•Et_2O [**8**•BF_4•CH_2Cl_2•Et_2O].

Empirical formula	$C_{93}H_{85}BCl_2F_4N_2O_3P_4Pt_2S_3Zn$
Formula weight	2111.95
Temperature	95(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 17.4537(3) Å
	b = 19.7214(3) Å
	c = 24.6490(4) Å
Volume	8484.5(2) Å
Z, Calcd density	4, 1.653 g cm^{-3}
Absorption coefficient	3.843 mm^{-1}
$F(0\ 0\ 0)$	4200
Theta range for data collection	1.32°–27.95°
Reflections collected/unique	61,848/20,276 [R_{int} = 0.0589]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6998 and 0.3549
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	20,276/0/1039
Flack x parameter	−0.009(4)
Goodness-of-fit on F^2	0.913
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0384, wR_2 = 0.0654
R indices (all data)	R_1 = 0.0590, wR_2 = 0.0716
Largest diff. peak and hole	1.357 and −0.767 e $Å^{-3}$

3.6. *X-ray structure determination on [$Pt_2(\mu\text{-}S)_2(PPh_3)_4Zn(TAQ)]BF_4$ (8•BF_4)*

Pale yellow crystals of the complex were obtained by vapor diffusion of diethyl ether into a dichloromethane solution at room temperature; a crystal of dimensions *ca.* 0.34 mm × 0.20 mm × 0.10 mm was selected for the study. The complex crystallizes with one molecule of CH_2Cl_2 and one diethyl ether per formula unit.

Data were obtained on a Bruker SMART CCD diffractometer at the University of Auckland and were corrected for absorption using a multiscan method [19]. The structure was solved by direct methods of SHELXS-97 [20] to give the location of platinum. All other non-hydrogen atoms were located from a series of different maps. Full-matrix least-squares refinement (SHELXL-97) [21] was based on F_o^2 with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. Crystal and refinement details are summarized in table 2.

Supplementary material

Crystallographic data for **8**•BF_4 have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 933343. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk or www: www.ccdc.cam.ac.uk/data_request/cif).

Acknowledgments

We thank the University of Waikato for financial support of this work, Pat Gread and Wendy Jackson for mass spectrometry assistance and technical support, and Dr Tania Groutso (University of Auckland) for collection of the X-ray data-set. WH thanks Professor Paul Low (University of Durham, UK) for provision of facilities for the writing of this manuscript.

References

[1] For a review see: S.-W.A. Fong, T.S.A. Hor. *J. Chem. Soc., Dalton Trans.*, 639 (1999).

[2] W. Henderson, J.S. McIndoe. *Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds.*, Wiley, Chichester (2005).

[3] For selected examples see: (a) copper: S.M. Devoy, W. Henderson, B.K. Nicholson, J. Fawcett, T.S.A. Hor. *Dalton Trans.*, 2780 (2005); (b) platinum and palladium: S.-W.A. Fong, T.S.A. Hor, S.M. Devoy, B.A. Waugh, B.K. Nicholson, W. Henderson. *Inorg. Chim. Acta*, **357**, 2081 (2004); (c) thallium: S.L. Rose, W. Henderson, B.K. Nicholson, T.S.A. Hor. *Inorg. Chim. Acta*, **362**, 5237 (2009); (d) molybdenum: W. Henderson, B.K. Nicholson, J.H. Bridson, J.T. Kueh, T.S.A. Hor. *Inorg. Chim. Acta*, **375**, 142 (2011).

[4] For an example of this synthetic approach see: S.-W.A. Fong, K. Evans, W. Henderson, B.K. Nicholson, T.S.A. Hor. *Inorg. Chim. Acta*, **363**, 301 (2010).

[5] Z. Li, W. Zheng, H. Liu, K.F. Mok, T.S.A. Hor. *Inorg. Chem.*, **42**, 8481 (2003).

[6] J.H. Bridson, W. Henderson, B.K. Nicholson, T.S.A. Hor. *Inorg. Chim. Acta*, **359**, 680 (2006).

[7] Z. Li, Z.-H. Loh, S.-W.A. Fong, Y.-K. Yan, W. Henderson, K.F. Mok, T.S.A. Hor. *J. Chem. Soc., Dalton Trans.*, 1027 (2000).

[8] M. Capdevila, Y. Carrasco, W. Clegg, R.A. Coxall, P. González-Duarte, A. Lledós, J.A. Ramírez. *J. Chem. Soc., Dalton Trans.*, 3103 (1999).

[9] F. Novio, R. Mas-Ballesté, I. Gallardo, P. González-Duarte, A. Lledós, N. Vila. *Dalton Trans.*, 2742 (2005).

[10] For a selection see: (a) N. Khaorapapong, M. Ogawa. *J. Phys. Chem. Solids*, **69**, 941 (2008); (b) T.A. Hopkins, K. Meerholz, S. Shaheen, M.L. Anderson, A. Schmidt, B. Kippelen, A.B. Padias, H.K. Hall

Jr., N. Peyghambarian, N.R. Armstrong. *Chem. Mater.*, **8**, 344 (1996); (c) H.-C. Pan, F.-P. Liang, C.-J. Mao, J.-J. Zhu, H.-Y. Chen. *J. Phys. Chem. B*, **111**, 5767 (2007); (d) X. Wang, M. Shao, L. Liu. *Synth. Met.*, **160**, 718 (2010); (e) K. Sokołowski, I. Justyniak, W. Śliwiński, K. Sołtys, A. Tulewicz, A. Kornowicz, R. Moszyński, J. Lipkowski, J. Lewiński. *Chem. Eur. J.*, **18**, 5637 (2012); (f) N. Khaorapapong, P. Pimchana, M. Ogawa. *Dalton Trans.*, 5964 (2011).

[11] See for example: (a) M.G. Kapliunov, S.S. Krasnikova, I.O. Balashova, I.K. Yakushchenko. *Mol. Cryst. Liq. Cryst.*, **535**, 212 (2011); (b) L.E. da Silva, A.C. Joussef, L.K. Pacheco, D.G.da Silva, M. Steindel, R.A. Rebelo. *Bioorg. Med. Chem.*, **15**, 7553 (2007); (c) M.G. Kaplunov, S.S. Krasnikova, I.O. Balashova, I.K. Yakushchenko. *Mol. Cryst. Liq. Cryst.*, **535**, 212 (2011); (d) J.F. García-Reyes, P. Ortega-Barrales, A. Molina-Díaz. *Anal. Sci.*, **23**, 1179 (2007); (e) P. Jiang, L. Chen, J. Lin, Q. Liu, J. Ding, X. Gao, Z. Guo. *Chem. Commun.*, 1424 (2002).

[12] S.I. Ahmed, J. Burgess, J. Fawcett, S.A. Parsons, D.R. Russell, S.H. Laurie. *Polyhedron*, **19**, 129 (2000); T. Moniz, M.J. Amorim, R. Ferreira, A. Nunes, A. Silva, C. Queirós, A. Leite, P. Gameiro, B. Sarmento, F. Remião, Y. Yoshikawa, H. Sakurai, M. Rangel. *J. Inorg. Biochem.*, **105**, 1675 (2011).

[13] H.M. Clarke, W. Henderson, B.K. Nicholson. *Inorg. Chim. Acta*, **376**, 446 (2011).

[14] B. Macías, I. García, M.V. Villa, J. Borrás, A. Castiñeiras, F. Sanz. *Z. Anorg. Allg. Chem.*, **629**, 255 (2003).

[15] L. Yang, D.R. Powell, R.P. Houser. *Dalton Trans.*, 955 (2007).

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

[17] W. Henderson, S. Thwaite, B.K. Nicholson, T.S.A. Hor. *Eur. J. Inorg. Chem.*, 5119 (2008).

[18] http://fluorine.ch.man.ac.uk/research/tools.php

[19] R.H. Blessing. *Acta Crystallogr., Sect. A*, **51**, 33, (1995).

[20] G.M. Sheldrick. *SHELXS97 – Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).

[21] G.M. Sheldrick. *SHELXL97 – Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).