Correspondence to:

Professor W. Henderson,

Chemistry,

School of Science,

University of Waikato,

Private Bag 3105,

Hamilton 3240,

New Zealand

e-mail w.henderson@waikato.ac.nz

Reactivity of the metalloligand [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] towards tellurium(II) thiourea complexes; synthesis and structural characterisation of the ditellurium(I) derivative [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$

Ryland G. Fortney-Zirker,[a] William Henderson[a,*] and Edward R. T. Tiekink[b]

[a] Chemistry, School of Science, University of Waikato, Private Bag 3105, Hamilton, New Zealand 3240

[b] Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

1

Abstract

Reaction of the platinum(II) sulfide metalloligand [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with the tellurium(II) source TeCl$_2$(tu)$_2$ (tu = thiourea) is dependent on reaction conditions employed. In the presence of added acid, the dominant species observed in the Electrospray Ionisation (ESI) mass spectrum is the tetraplatinum species [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$. This contains the Te$_2$$^{2+}$ moiety and is related to the previously reported tellurium(I) dithiophosphinate analogue [(Ph$_2$PS$_2$)$_2$Te$_2$]. However, in the absence of acid, considerable degradation of the {Pt$_2$S$_2$} metalloligand occurs as evidenced by the formation of the mononuclear complex [Pt{SC(NH$_2$)NH}(PPh$_3$)$_2$]$^+$ containing a deprotonated thiourea ligand, together with other thiourea-containing ions, identified by ESI MS. Likewise, attempted use of a fully-substituted thiourea, *viz.* Me$_2$NC(S)NMe$_2$ (tmtu) in TeCl$_2$(tmtu)$_2$, also resulted in degradation of the {Pt$_2$S$_2$} core and detection of the known complex [(Ph$_3$P)$_2$PtCl{SC(NMe$_2$)$_2$}]$^+$. The [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$ cation was isolated with several anions, and unequivocal confirmation of the structure of the complex was obtained by an X-ray structure determination on the BF$_4$$^-$ salt, which shows the presence of the Te$_2$$^{2+}$ unit, with the Te–Te bond bridged by two {Pt$_2$S$_2$} metalloligands.

Keywords: Platinum complexes; Sulfide ligands; ESI mass spectrometry; Tellurium; Coordination complex

1. Introduction

As part of ongoing investigations into the chemistry of the enigmatic metalloligand [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] **1**,[1] we recently described the reactivity of **1** and the selenide analogue [Pt$_2$(μ-Se)$_2$(PPh$_3$)$_4$] towards a variety of chalcogen sources (including the elemental chalcogens S$_8$ and Se, as well as diaryl dichalcogenides R$_2$E$_2$, where E = S, Se and Te) with the intention of synthesising complexes containing mixed-chalcogenide ligands.[2] In this contribution, we now describe investigations into the reactivity of **1** towards tellurium(II) sources. The oxidation state of tellurium in compounds with sulphur ligands is commonly II and IV,[3] with Te(II) being preferred, typically having four-coordinate square planar,[4] T-shaped,[5] and trapezoidal planar geometries. Tellurium(II) is known to form a wide range of complexes with bidentate chelating sulphur and selenium ligands such as dithiocarboxylates [6], dithiocarbamates [7,8] and [R$_2$P(E)NP(E)R'$_2$]$^-$ (E = S, Se) [5,9,10] Accordingly, we reasoned that [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$], being a well-known bidentate sulphur metalloligand, should also form complexes with Te(II).
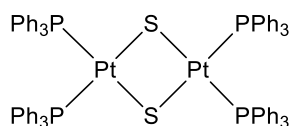
1

Our methodology of choice uses Electrospray Ionisation Mass Spectrometry (ESI MS) [11] as a convenient and sensitive tool for the identification of reaction products of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] **1**. We have previously used ESI MS to explore the chemistry of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] and the related selenide complex, and our investigations in this area have been summarised in a review.[12] In this work we extend this methodology to the identification and subsequent synthesis and characterisation of the interesting tellurium(I) complex [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$.

2. Results and discussion

*2.1 Reactivity of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] **1** towards TeCl$_2$(tu)$_2$ in acidic solution*

The thiourea complex TeCl$_2$(tu)$_2$ was used as a convenient source of Te(II) in these experiments, which were initially explored on a micro-scale, with reaction monitoring using positive-ion ESI MS. In this work, the ligand abbreviation tu represents a neutral, non-deprotonated thiourea ligand, SC(NH$_2$)$_2$. Tellurium(II) thiourea complexes, particularly [Te(tu)$_4$]Cl$_2$, have been used as precursors for the preparation of coordination complexes of the Te(II) centre.[Novosad615,Birdsall435,Necas124,13,14]

When [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] **1** was reacted with TeCl$_2$(tu)$_2$ in neutral solution, relatively complex spectra were obtained, *vide infra*. However, when reactions were carried out in the presence of added acid (either acetic acid or hydrochloric acid), which is known to protonate [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$],[15] reactions with TeCl$_2$(tu)$_2$ proceeded much more smoothly, giving a single dominant product species. Thus, addition of hydrochloric acid to a light-orange suspension of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] **1** in methanol gave a transparent yellow solution, which was reacted with TeCl$_2$(tu)$_2$, immediately effecting formation of a clear red solution. The solution was examined by ESI MS (Fig. 1) and showed a dominant dicationic species at *m/z* 1630.88, which was assigned on the basis of the *m/z* value and isotope pattern matching (Fig. 1 inset) to the ditellurium species [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$ **2**.

Addition of NaBPh$_4$ or NH$_4$PF$_6$ to filtered reaction solutions containing the [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$ ion gave precipitates of the BPh$_4^-$ and PF$_6^-$ salts. However, all attempts at growing single crystals of these compounds suitable for an X-ray diffraction study resulted in the formation of very fine needles. Using **NaBF$_4$** as the precipitating agent in place of NaBPh$_4$

successfully precipitated the salt [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$][N(SO$_2$C$_2$F$_5$)$_2$]$_2$ as a red powder, which gave satisfactory elemental analytical data. The ^{31}P{^{1}H} NMR spectrum showed the expected features, namely a single ^{31}P NMR resonance at δ 20.9 with satellites due to coupling to ^{195}Pt, [^{1}*J*(PtP) 2959 Hz] however the peaks were surprisingly somewhat broader than are normally obtained with diamagnetic adducts of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$].

Vapour diffusion of diethyl ether into an acetone solution of the NaBF$_4^-$ salt gave dark brown prismatic crystals suitable for an X-ray diffraction study. The X-ray structure determination unequivocally confirms the identity of the cation as [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$ **2**. The structure of the cation is shown in Fig. 2.
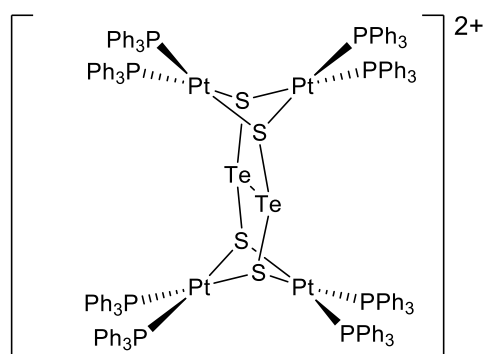
2

The structure contains two bidentate [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] metalloligands spanning the Te–Te bond of a formally Te$_2^{2+}$ unit. The dication is disposed about a point of symmetry 22. Thus, both Te atom lies on a 2-fold axis and the Te–Te vector is bisected by a second 2-fold axis perpendicular to the original axis. This implies the crystallographic asymmetric unit comprises one quarter of a dication as indicated in the top view of Fig. 2. The Te–Te bond length is 2.7978(16) Å and, from symmetry, there is a unique Te–S1 bond length of 2.676(3) Å. The resultant Te$_2$S$_4$ rectangle is close to planar and the Te atom has a T-shaped coordination geometry defined by a S$_2$Te donor set. As neither the Pt nor S1 atoms lie on an axis, there are two independent but, similar Pt–S1, S1^i bond lengths, i.e. 2.343(2) and 2.339(2) Å; symmetry

operation i: ½ - x, y, ½ - z. The Pt_2S_2 atoms adopt a folded configuration with the dihedral angle between the two S_2Pt residues being 44.16(10)°. The Pt atom coordination geometry is completed by two Ph_3P ligands and the resulting cis-P_2S_2 donor set defines an approximate square planar geometry.

Related Te(I) complexes with Te–Te bonds and sulphide ligands have been previously described in the literature, and the chemistry of tellurium complexes with sulphur donor ligands has been reviewed.[16] These complexes predominantly have a T-shaped coordination geometry, with long range contacts or secondary bonds sometimes found at an axial position where a square-planar ligand would be; such secondary bonds are common in tellurium chemistry.[ref 8,,17] The compound [$Te_2(S_2PPh_2)_2$] **3** is a close analogue of complex **2**; complex **3** was originally prepared (and crystallized as the benzene solvate) by reduction of TeO_2 with Ph_2PS_2H.[18] This compound has a Te_2^{2+} group spanned by two bidentate, bridging diphenyldithiophosphinate anions, although the ligand binds the two Te centres somewhat asymmetrically. The same compound has also been prepared by reaction of the tellurium(II) complex [$Te(tu)_4$]Cl_2 with $Ph_2P(S)NC(S)pip$ (pip = piperidyl) and KO^tBu.[19] In the solid state **3** forms long range intermolecular Te···Te contacts in the benzene solvate,[Newton] or in the unsolvated compound (crystallised from CH_2Cl_2-hexane), Te···S contacts resulting in long intermolecular chains.[Novosad2861] The structural chemistry of this system has been summarised by Bandeira *et al*, who carried out a computational study (using DFT) on the nature of Te···Te interactions in such species.[20]
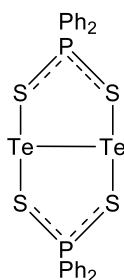
3

Complex **2** also pays a resemblance to the silver(I) [21, 22, 23] and gold(I) [24,Fong1986] complexes **4**, where two d^{10} metal ions are spanned by two $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ metalloligands, and a significant interaction is proposed to occur between the metals in them.
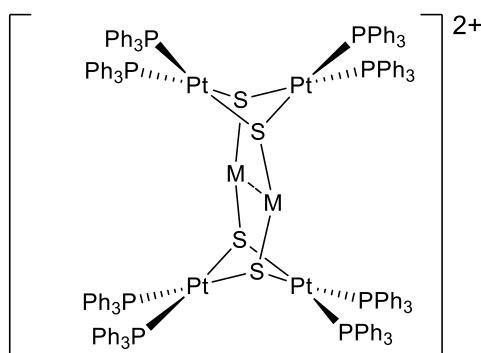

4, M = Ag or Au

Detailed characterization of $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2][N(SO_2C_2F_5)_2]_2$ has been carried out using ESI MS, specifically with a view to exploring the fragmentation of the complex cation. Fig. 3 shows spectra of the compound at a range of capillary exit voltages. At a relatively low voltage (120 V, Fig. 3a) the spectrum is dominated by the parent $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2]^{2+}$ cation at m/z 1630.95, together with two partly overlapping ions around m/z 1502. An expansion of these is shown in the top inset to Fig. 3, which shows the observed isotope patterns, together with the excellent agreement with an mMass-modelled pattern comprising $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_3Te_2]^+$ in a 7:1 ratio. The major ion $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]^+$ is formed by oxidation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, and represents one of the fragment ions of **2**. This ion has been observed as a fragment ion previously, for example in the fragmentation of cobalt(III) [25] and iron(III) [26] derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, where the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ centre undergoes oxidation, with concomitant reduction and loss of the Fe or Co. It is noteworthy that non-redox active adducts such as indium(III) derivatives [Clarke] do not show the same behaviour. The observation of this ion in the current tellurium(I) system

is therefore suggestive of possible electron transfer forming reduced tellurium-containing species. Indeed, the other observed ion, $[Pt_2(\mu\text{-}S)_2(PPh_3)_3Te_2]^+$, formally contains tellurium in the +0.5 oxidation state (i.e. reduction from Te in the +1 oxidation state in **2**, to +0.5), as well as being formed by loss of a PPh_3 ligand. At higher capillary exit voltages of 150 and 180 V (Fig. 3), the parent ion undergoes successively more complete fragmentation to $[Pt_2(\mu\text{-}S)_2\text{-}(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_3Te_2]^+$. However, there is an additional fragmentation process operating under these conditions, which is elucidated by examination of the high-resolution isotope patterns of the *m/z* 1631 ion, shown in the lower inset to Fig. 3. At a relatively low voltage of 150 V, the observed isotope pattern (spectrum β_1) shows good agreement with the calculated pattern for $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2]^{2+}$ (spectrum β_{1a}). On increasing the capillary exit voltage, the isotope pattern progressively changes (through spectrum β_2 at 165 V and spectrum β_3 at 174 V) to spectrum β_4 at 180 V, which can be modelled as an overlap of $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2]^{2+}$ with the mono-tellurium species $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Te]^+$ (which would nominally have the same *m/z* value) in a 3:1 ratio. This latter ion is formed by homolytic fragmentation of the dimer $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2]^{2+}$.

*2.2 Investigation of the effect of added acetic acid on the reaction between [Pt$_2$(µ-S)$_2$(PPh$_3$)$_4$] **1** and TeCl$_2$(tu)$_2$*

When TeCl$_2$(tu)$_2$ is reacted, in the absence of added acid, with a stirred, light-orange suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** in methanol, a clear red solution was immediately formed, which after stirring for 24 h had changed from red to a clear, very dark-green solution. A trace amount of dark insoluble residue (possibly elemental tellurium) was present. To assess the effect of added acetic acid on the reaction between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and TeCl$_2$(tu)$_2$ three simultaneous microscale reactions of **1** and TeCl$_2$(tu)$_2$ in methanol were carried out and analysed by ESI MS (Fig. 4). A reaction solution without acetic acid (Fig. 4a) was compared

with reaction solutions containing 0.05 mL (Fig. 4b) and 0.15 mL (Fig. 4c) of glacial acetic acid respectively. The spectra were acquired after mixing for 12 h at room temperature, and a very low capillary exit voltage of 20 V was employed to minimise fragmentation. It can be observed that in the absence of acid, a significant ion at m/z 794.15 is observed, assigned as $[(Ph_3P)_2Pt\{SC(=NH_2)NH\}]^+$ **5** (calculated m/z 794.15), while in the presence of acid, this ion is less significant. Complex **5** has been reported on two previous occasions,[27,28] and contains an *N,S*-chelated thiourea monoanion. Other ions containing a deprotonated thiourea ligand are the trinuclear species $[Pt_3(\mu_3\text{-}S)_2(PPh_3)_5\{SC(=NH_2)NH\}]^+$ (m/z 2035.65) together with the thiourea-substituted ion $[(Ph_3P)Pt\{SC(=NH_2)NH\}(tu)]^+$ at m/z 608.08. These ions, together with dications at m/z 1018.13, assigned as $[Pt_3(\mu_3\text{-}S)_2(PPh_3)_5(tu)]^{2+}$ (calculated m/z 1018.15) and m/z 925.12, assigned as $[Pt_3(\mu_3\text{-}S)_2(PPh_3)_4(tu)_2]^{2+}$ (calculated m/z 925.11) with neutral thiourea ligands, are clearly indicative of substantial degradation of the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ core.
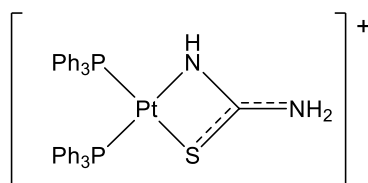
5

The reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** towards $TeCl_2(tu)_2$ in neutral solution was explored by following the reaction over time using ESI MS, at a capillary exit voltage of 150 V. After *ca* 5 min. the spectrum displayed a prominent base peak at m/z 1503.13, which is indicative of an incomplete reaction. The assignment of this ion as the oxidised parent complex $[\mathbf{1}]^+$ was made after a close examination of the isotope pattern, as described previously.[ref] After 12 h, the now -reen reaction solution gave a similar spectrum, but with some notable changes. The base peak of the spectrum was now m/z 794.16, due to **5**, and the mono-oxidised ion $[\mathbf{1}]^+$ is of significant relative intensity at m/z 1503.25 with partial overlapping with $[Pt_2(\mu\text{-}S)_2(PPh_3)_3Te_2]^+$ (m/z 1495.97). Low mass ions at m/z 532.07 and m/z 608.08 due to $[(Ph_3P)Pt\{SC(=NH_2)NH\}]^+$ (calculated m/z 532.06) and $[(Ph_3P)Pt\{SC(=NH_2)NH\}(tu)]^+$

(calculated m/z 608.07), respectively, were also observed. Several low intensity cations are also observed: $[Pt_3(\mu_3-S)_2(PPh_3)_5(tu)]^{2+}$ (m/z 1018.17) with a similar monocationic relative at m/z 2035.30 with thiourea in the deprotonated form (calculated m/z 2035.30). $[Pt_3(\mu_3-S)_2(PPh_3)_5(tu)]^{2+}$ fragments through PPh_3 loss to give a dication at m/z 887.13 (calculated m/z 887.11). The PPh_3-displaced triplatinum aggregate structurally proposed as $[Pt_3(\mu_3-S)_2(PPh_3)_5]^{2+}$ is assigned to a peak at m/z 980.17 (calculated m/z 980.15), with its PPh_3-loss dication $[Pt_3(\mu_3-S)_2(PPh_3)_4]^{2+}$ detected at m/z 849.12 (calculated m/z 849.10). At m/z 1044.62 is a dication formulaically assigned as the trinuclear species $[Pt_2(\mu_3-S)_2(PPh_3)_5PtTe]^{2+}$ (calculated m/z 1044.60). An ion at m/z 1600.18 is assigned as $[Pt_2(\mu-S)(\mu-Te)(PPh_3)_4]^+$ (calculated m/z 1600.17), a mixed core species, observed as its oxidised ion, while an ion at m/z 1663.14 is tentatively assigned as the trinuclear $[Pt_3(\mu_3-S)_2(PPh_3)_3(tu)_2\{SC(=NH_2)NH\}]^+$ (calculated m/z 1663.13), with two neutral thiourea ligands and one anionic thiourea. Finally, at m/z 1675.18 is an ion assigned as $[Pt_2(\mu-S)(\mu-Te)(PPh_3)_4\{SC(=NH_2)NH\}]^+$ (calculated m/z 1675.17), a mixed core complex with one deprotonated thiourea ligand. The observation of these ions confirms substantial degradation of the $\{Pt_2S_2\}$ core, ultimately resulting in the mononuclear thiourea complex **5**.

After 24 h, the mass spectrum showed a prominent base peak due to **5** with no ions observed above m/z 780. Two lower intensity ions $[(Ph_3P)Pt\{SC(=NH_2)NH\}]^+$ and $[(Ph_3P)Pt(tu)\{SC(=NH_2)NH\}]^+$ are still present at m/z 532.07 and m/z 608.08, respectively.

2.3 Reaction of [Pt₂(μ-S)₂(PPh₃)₄] and TeCl₂(tmtu)₂ (tmtu = tetramethylthiourea)

Another approach at minimising attack of platinum by liberated thiourea explored using a more protected thiourea with a decreased tendency to coordinate anionically; tetramethylthiourea (tmtu) was chosen due to the absence of NH protons which are readily deprotonated. Using a similar methodology to the previous reactions, 0.05 mL of glacial acetic acid was added to a suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ **1** in methanol and stirred for 10 min.

Upon addition of TeCl$_2$(tmtu)$_2$, the reaction solution immediately turned clear red and the ESI mass spectrum of the reaction solution acquired was after one hour. Using gentle ionisation conditions (capillary exit voltage 20 V), a clean spectrum was observed with a base peak at *m/z* 887.16 assigned as the mononuclear complex [(Ph$_3$P)$_2$PtCl{SC(NMe$_2$)$_2$}]$^+$ (**6**, calculated *m/z* 887.19), whose isotope pattern agreed closely with the calculated pattern. This complex has been previously synthesised and structurally characterised, and a study by ESI MS indicated that the tmtu ligand was easily lost, predicating the necessity for a low capillary exit voltage for its successful observation.[29] No further investigations were carried out using tmtu-Te complexes.

6
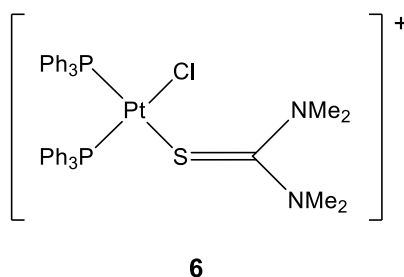
Conclusions

The tellurium(II) complex TeCl$_2$(tu)$_2$ acts as a convenient source of low-valent inorganic tellurium, and gives the formally tellurium(I) complex [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$ on reaction with [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$]. Fragmentation of the {Pt$_2$S$_2$} core by thiourea leads to the formation of the mononuclear platinum(II) thiourea complex [(Ph$_3$P)$_2$Pt{SC(=NH$_2$)NH}]$^+$, however this was successfully suppressed by addition of acid to the reaction mixture. The tetra-platinum complex [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$ has a similar structure to the known dithiophosphinate-bridged tellurium(I) species [Te$_2$(S$_2$PPh$_2$)$_2$] and to the silver(I) and gold(I) adducts [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$M$_2$]$^{2+}$.

3. Experimental

3.1 Instrumentation

Mass spectra were obtained using a high-resolution Bruker MicrOTOF spectrometer that was periodically calibrated with methanolic sodium formate. For reaction solutions, a drop of the reaction mixture was diluted to *ca.* 1.5 mL with methanol. Solutions were centrifuged prior to analysis, and the sample introduced by a microlitre syringe and syringe pump. Typically a *Capillary Exit* voltage of 150 V and a *Skimmer 1* voltage of 50 V were used, though this was varied to investigate fragmentation behaviour of observed ions (see text). Ions were assigned by *m/z* value and comparison of experimental and theoretical isotope patterns. Theoretical patterns were obtained using Bruker instrument-based software, and mass spectrometry data were further analysed and prepared for presentation with the open-source mass spectrometry tool mMass.[30,31]

Elemental analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker AVIII-400 spectrometer in $CDCl_3$ solution.

3.2 Materials

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** was prepared by the literature procedure.[32] Tetramethylthiourea (tmtu, Aldrich) and glacial acetic acid were used as supplied. $TeCl_2(tu)_2$ was from either a commercial source (Aldrich) or was prepared by a literature procedure.[33] $TeCl_2(tmtu)_2$ was prepared by the literature procedure.[34] $NaBPh_4$ (Aldrich), NH_4PF_6 (Aldrich) and $Li[N(SO_2C_2F_5)_2]$ (3M) were used as obtained. Other chemicals were at least of reagent grade.

3.3 Synthesis of $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2][N(SO_2C_2F_5)_2]_2$

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (101.8 mg, 0.067 mmol) was suspended in methanol (25 mL) and 37% aqueous HCl (0.1 mL) added, and the mixture stirred at room temperature for 3 h. The resulting clear yellow solution was filtered to remove a trace amount of insoluble matter, and

to the resulting filtrate was added $TeCl_2(tu)_2$ (23.6 mg, 0.067 mmol). The clear red solution was stirred at room temperature for 10 min., filtered to remove insoluble matter, and the filtrate examined by ESI MS. To the filtrate was added excess $Li[N(SO_2C_2F_5)_2]$ (150 mg, 0.387 mmol) and the red solution stirred for 30 min. resulting in the formation of a dark red precipitate. The solid was collected by vacuum filtration, washed with water (10 mL x 2) and diethyl ether (5 mL), and dried under vacuum to give 29.3 mg (21.7 %) of product as a red powder. Anal. Found: C, 45.65; H, 3.05; N, 0.86. $C_{152}H_{120}F_{20}N_2O_8P_8Pt_4S_8Te_2$ requires: C, 45.39; H, 3.00; N, 0.70%. $^{31}P\{^1H\}$ NMR (162 MHz), δ 20.9 [br s, ^1J(PtP) 2959 Hz]. ESI MS (capillary exit voltage 45 V) m/z 1630.88 $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2]^{2+}$ (100%).

3.4 Reaction of [Pt₂(μ-S)₂(PPh₃)₄] *1* with TeCl₂(tu)₂ in methanol

*3.4 Reaction of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] **1** with TeCl$_2$(tu)$_2$ in methanol*

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (49 mg, 0.033 mmol) was suspended in methanol (20 mL) with $TeCl_2(tu)_2$ (6 mg, 0.017 mmol) and the clear red mixture was stirred at room temperature for 24 h, with monitoring by positive-ion ESI MS. After 24 h a clear, dark green solution was observed.

*3.5 Comparison of reactions of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] **1** with TeCl$_2$(tu)$_2$ in methanol with varying amounts of acetic acid*

In three parallel reaction vessels, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (20 mg, 0.0133 mmol) was suspended in methanol (10 mL) and stirred. Reaction (a): the orange mixture was stirred at room temperature for 10 min. Reaction (b): same as (a), with glacial acetic acid (0.05 mL) added. Reaction (c): same as (a) with glacial acetic acid (0.15 mL) added. After 10 min., $TeCl_2(tu)_2$ (4.7 mg, 0.0134 mmol) was added to each reaction, with the resulting clear red mixtures stirred at room temperature for 12 h. Reaction (a): the dark green solution was filtered to remove insoluble matter and the filtrate analysed by ESI MS. Reactions (b,c): the clear red

solutions were filtered to remove any insoluble matter and the filtrates were analysed by ESI MS.

3.6 X-ray crystal structure determination of [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$][BF$_4$]$_2$

Dark-brown prismatic crystals of the complex suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into an acetone solution of the complex. Intensity data were measured at T = 100(2) K on a SuperNova Dual AtlasS2 diffractometer fitted with Cu Kα radiation so that θ_{max} was 73.8°. Data reduction, including analytical absorption correction, was accomplished with CrysAlisPro [35]. Of the 29343 measured reflections, 6512 were unique (R$_{int}$ = 0.057) and of these, 4621 data satisfied the $I \geq 2\sigma(I)$ criterion of observability. The structure was solved by direct-methods [36] and refined (anisotropic displacement parameters, C-bound H atoms in the riding model approximation, and a weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.086P^2 + 82.709P]$ where $P = (F_o^2 + 2F_c^2)/3$) on F^2 [37]. For charge balance, half a BF$_4^-$ anion is required. However, this assignment was quite ambiguous. While a possible position for the B atom was found, being located on a site of symmetry *222* implied multiple positions for the F atoms which were not resolved in the X-ray experiment. Accordingly, the routine SQUEEZE [38] was employed to model the unresolved electron density due to the BF$_4^-$ anions. Even with this treatment, it is noted that there was considerable atomic motion in the structure despite the low temperature of the X-ray experiment. Based on the refinement of 324 parameters, the final values of R and wR (all data) were 0.070 and 0.207, respectively. The molecular structure diagram was generated with DIAMOND [39].

Crystal data for C$_{144}$H$_{120}$B$_2$F$_8$P$_8$Pt$_4$S$_4$Te$_2$: M = 3435.57, orthorhombic space group *Pnnn*, a = 18.4717(2), b = 18.5907(3), c = 19.0659(3) Å, V = 6547.26(16) Å^3, Z = 2, D_x = 1.743 g cm^{-3}, F(000) = 3332, μ = 13.276 mm^{-1}. CCDC deposition number: 1578001.
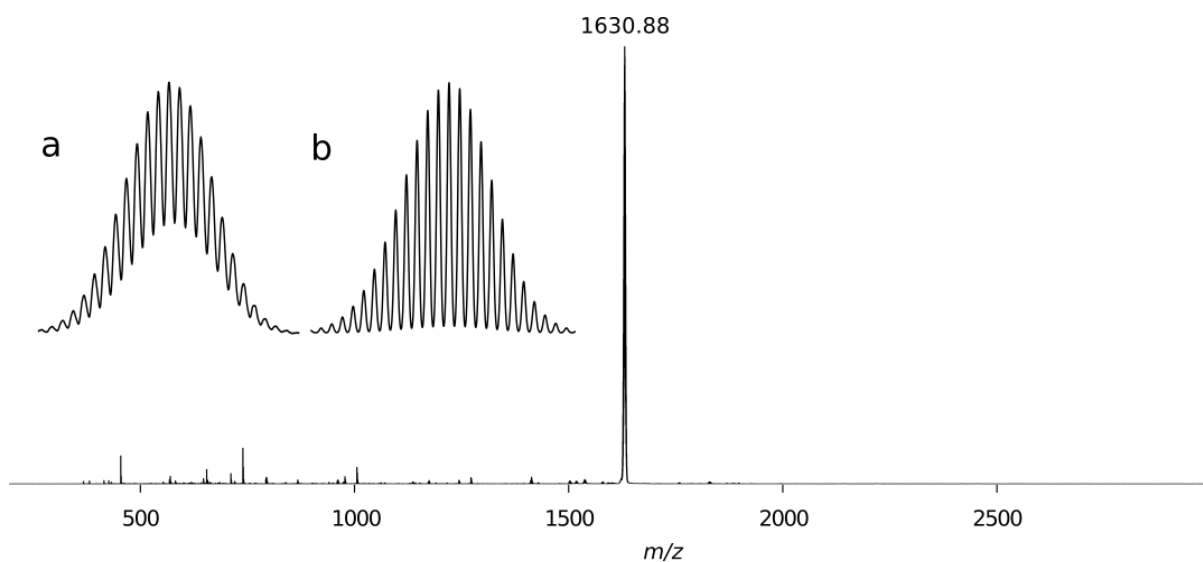
Acknowledgements

Fig. 1. The ESI mass spectrum of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** and $TeCl_2(tu)_2$ in methanol with added HCl, after 10 min. The inset shows an isotope pattern comparison of (a) the observed dication at m/z 1630.88 and (b) the calculated isotope pattern for $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2]^{2+}$ (m/z 1631.14).
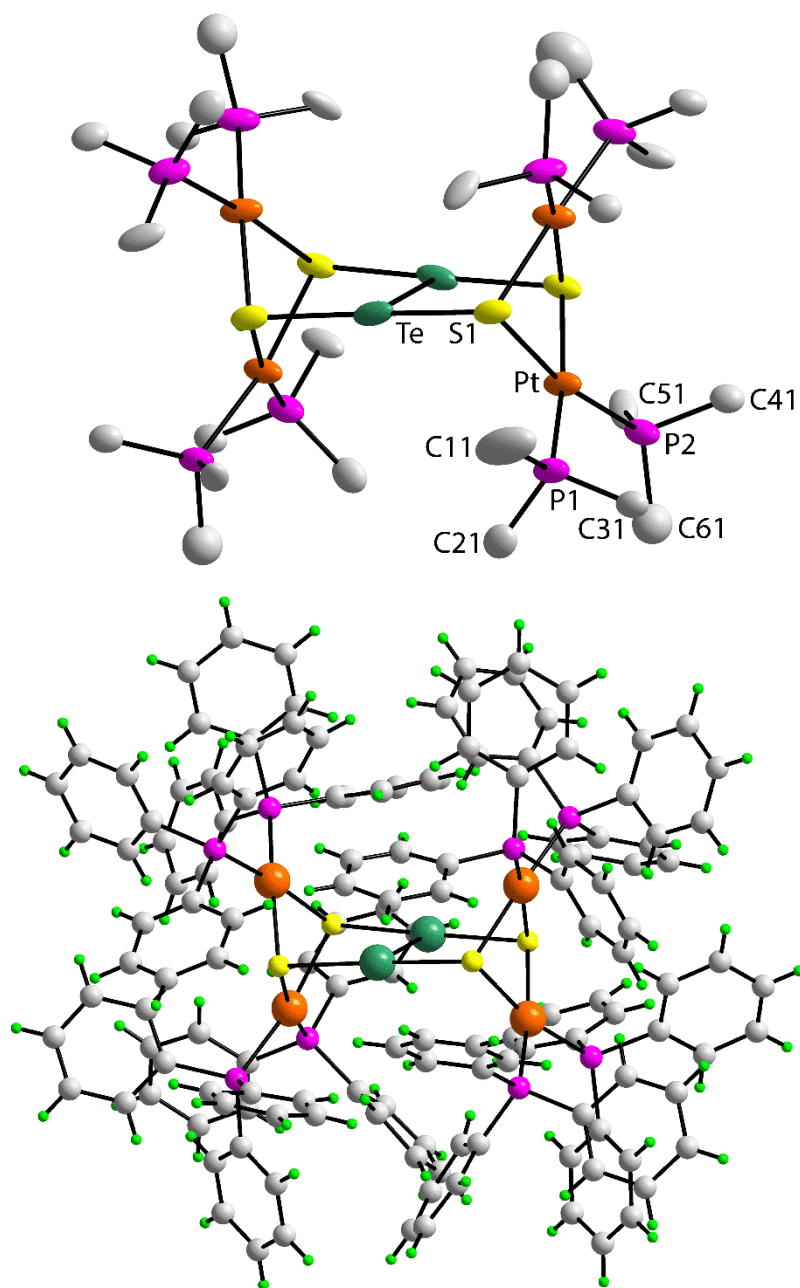
Fig. 2. Two views of $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Te_2]^{2+}$ (**2**) in its BF_4^- salt, showing the core structure (all but the ipso-C atoms of the phenyl groups being removed) with atom labelling and displacement ellipsoids at the 35% probability level (upper view) and the full dication, showing idealised spheres (lower view).
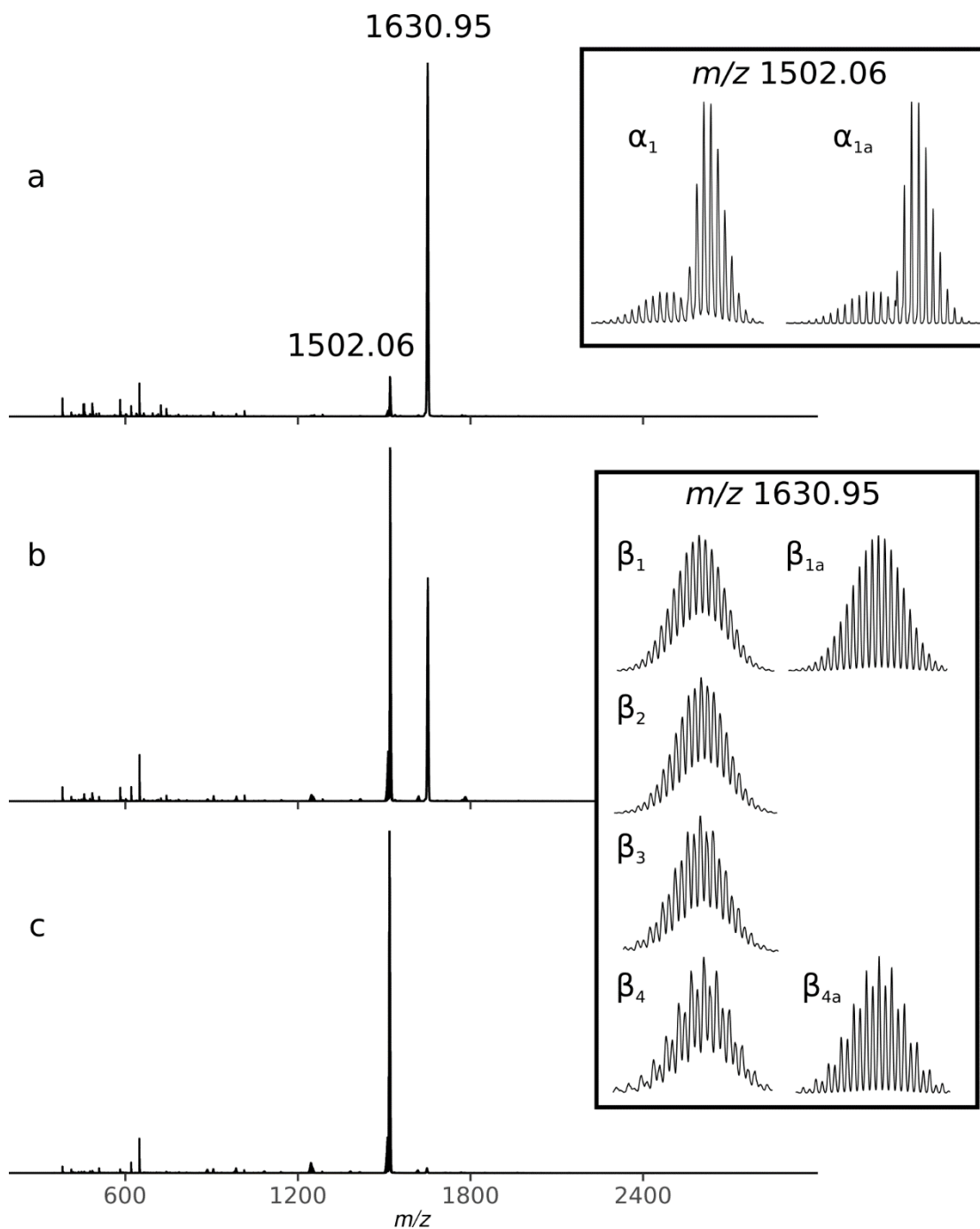
Fig. 3. A comparison of ESI mass spectra of [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$][N(SO$_2$C$_2$F$_5$)$_2$]$_2$ showing fragmentation at increasing capillary exit voltages of (a) 120 V, (b) 150 V, and (c) 180 V. The top inset is an isotope pattern comparison of (α_1) the observed peak at *m/z* 1502.06 and (α_{1a}) an mMass-modelled peak of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$]$^+$: [Pt$_2$(μ-S)$_2$(PPh$_3$)$_3$Te$_2$]$^+$ 7:1 (*m/z* 1502.24). The lower inset follows the isotope pattern of [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$ at capillary exit voltages of (β_1) 150 V, (β_2) 165 V, (β_3) 174 V, and (β_4) 180 V. (β_{1a}) is a calculated isotope pattern for [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$ (*m/z* 1631.14). (β_{4a}) is a modelled isotope pattern for [{Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$}$_2$Te$_2$]$^{2+}$: [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Te]$^+$ 3:1 (*m/z* 1631.14).
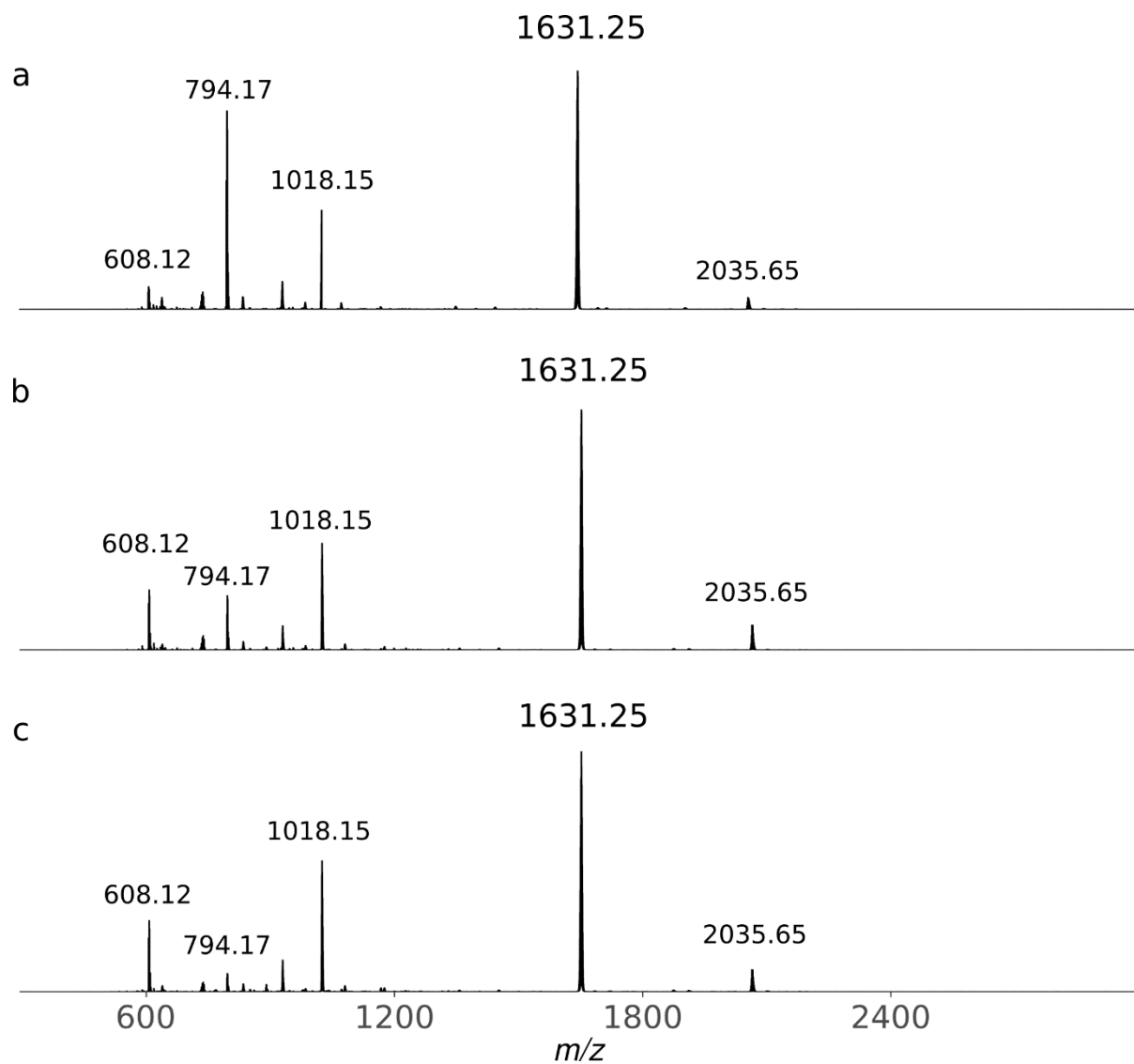
Fig. 4. A comparison of reaction solutions of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] **1** and TeCl$_2$(tu)$_2$ in methanol containing (a) no glacial acetic acid, (b) one drop (*ca* 0.05 mL) glacial acetic acid and (c) 3 drops (*ca* 0.15 mL) glacial acetic acid. Spectra were acquired after mixing 12 h at room temperature. Capillary exit voltage 20 V.

References

[1]   S.-W.A. Fong, T.S.A. Hor, J. Chem. Soc., Dalton Trans. (1999) 639.

[2]   R.G. Fortney-Zirker, W. Henderson and E.R.T. Tiekink, Inorg. Chim. Acta, in press.

[3]   S. Husebye, Phosphorus, Sulfur, Silicon Related Elem. 136 (1998) 377.

[4]   a) P. Sekar, J.A. Ibers, Inorg. Chem. 42 (2003) 6294; b) P.W.C. Barnard, J.D. Donaldson, R.M.A. Grimsey, G. Dennes, U. Russo, S. Calogero, Inorg. Chim. Acta 51 (1981) 217.

[5]   J. Novosad, S.V. Lindeman, J. Marek, J.D. Woollins, S. Husebye, Heteroat. Chem. 9 (1998) 615.

[6]   S. Kato, K. Tani, M. Ishida, J. Nonogaki, M. Ebihara, S. Hayashi, W. Nakanishi, O. Niyomura, F. Ando, J. Koketsu, Dalton Trans. 40 (2011) pp. 8156.

[7]   P.C. Srivastava, S. Bajpai, R. Lath, R. Kumar, V. Singh, S. Dwivedi, R.J. Butcher, S. Hayashi, W. Nakanishi, Polyhedron 27 (2008) 835.

[8]   E.R.T. Tiekink, J. Zukerman-Schpector, Coord. Chem. Rev. 254 (2010) 46.

[9]   M. Necas, J. Novosad, S. Husebye, J. Organomet. Chem. 623 (2001) 124.

[10]   D.J. Birdsall, J. Novosad, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2000) pp. 435.

[11]   W. Henderson, J.S. McIndoe, Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds – Tools-Techniques-Tips, John Wiley & Sons (2005).

[12]   W. Henderson, T.S.A. Hor, Inorg. Chim. Acta 411 (2014) 199.

[13]   C.A. Dodds, A.R. Kennedy, J. Reglinski, M.D. Spicer, Inorg. Chem. 43 (2004) 394.

[14]   P. Sekar, J.A. Ibers, Inorg. Chem. 42 (2003) 6294.

[15]   S.-W.A. Fong, W.T. Yap, J.J. Vittal, T.S.A. Hor, W. Henderson, A.G. Oliver, C.E.F. Rickard, J. Chem. Soc., Dalton Trans. (2001) pp. 1986.

[16]   I. Haiduc, R.B. King, M.G. Newton, Chem. Rev. 94 (1994) 301.

[17] A. Silvestru, Phosphorus, Sulfur, Silicon Related Elem. 136 (1998) 617.

[18] M.G. Newton, R.B. King, I. Haiduc, A. Silvestru, Inorg. Chem. 32 (1993) 3795.

[19] J. Novosad, K.W. Törnroos, M. Necas, A.M.Z. Slawin, J.D. Woollins, S. Husebye, Polyhedron 18 (1999) 2861.

[20] N.A.G. Bandeira, L.F. Veiros, M.J. Calhorda, J. Novosad, Inorg. Chim. Acta 356 (2003) 319.

[21] C.E. Briant, T.S.A. Hor, N.D. Howells, D.M.P. Mingos, J. Organomet. Chem. 256 (1983) C15.

[22] H. Liu, A.L. Tan, C.R. Cheng, K.F. Mok, T.S.A. Hor, Inorg. Chem. 36 (1997) 2916.

[23] B.H. Aw, K.K. Looh, H.S.O. Chan, K.L. Tan, T.S.A. Hor, J. Chem. Soc., Dalton Trans. (1994) 3177.

[24] Z. Li, K.F. Mok, T.S.A. Hor, J. Organomet. Chem. 682 (2003) 73.

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

[26] W. Henderson, A.G. Oliver, M.M. Turnbull, Inorg. Chem. Commun. 27 (2013) 142.

[27] S. Okeya, Y. Fujiwara, S. Kawashima, Y. Hayashi, K. Isobe, Y. Nakamura, H. Shimomura, Y. Kushi, Chem. Lett. (1992) 1823.

[28] L. Battan, S. Fantasia, M. Manassero, A. Pasini, M. Sansoni, Inorg. Chim. Acta 358 (2005) 555.

[29] W. Henderson, B.K. Nicholson, R.G. Fortney-Zirker, S. Patel, J.R. Lane, M.J. Wyllie, E.R.T. Tiekink, Inorg. Chim. Acta 425 (2015) 154.

[30] http://www.mmass.org

[31] M. Strohalm, M. Hassman, B. Košata, M. Kodíček, Rapid Commun. Mass Spectrom. 22 (2008) 905.

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

[33] K.J. Lushington, H.J. Gysling, U.S. (1997) US 5677120 A 19971014.

[34]   S. Husebye, K.W. Törnroos, H. Zhu, Z. Anorg. Allg. Chem. 627 (2001) 1921.

[35]   CrysAlis PRO, Rigaku Oxford Diffraction, Tokyo, Japan, 2015.

[36]   G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.

[37]   G.M. Sheldrick, Acta Crystallogr., Sect. C 71 (2015) 3.

[38]   A.L. Spek, Acta Crystalllogr. Sect. D 65 (2009) 148.

[39]   K. Brandenburg, DIAMOND, Crystal Impact GbR, Bonn, Germany, 2006.