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Reactivity of the metalloligand $[Pt_2(\mu-S)_2(PPh_3)_4]$ toward tellurium(II) thiourea complexes: synthesis and structural characterization of the ditellurium(I) derivative $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$

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Reactivity of the metalloligand $[Pt_2(\mu-S)_2(PPh_3)_4]$ toward tellurium(II) thiourea complexes: synthesis and structural characterization of the ditellurium(I) derivative $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$

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ABSTRACT

Reaction of the platinum(II) sulfide metalloligand $[Pt_2(\mu S_{2}(PPh_{3})_{4}$ 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 ionization (ESI) mass spectrum is the tetraplatinum species $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$. This contains the Te₂²⁺ moiety and is related to the previously reported tellurium(I) dithiophosphinate analog [(Ph₂PS₂)₂Te₂]. However, in the absence of acid, considerable degradation of the {Pt₂S₂} 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. Me₂NC(S)NMe₂ (tmtu) in TeCl₂(tmtu)₂, also resulted in degradation of the {Pt₂S₂} core and detection of the known complex $[(Ph_3P)_2PtCl{SC(NMe_2)_2}]^+$. The $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ 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 {Pt₂S₂} metalloligands. Density functional theory was used to further probe the Te_2^{2+} bonding interactions in [{Pt}_2(\mu- $S_{2}(PPh_{3})_{4}^{2}Te_{2}^{2+}$ and the previously reported [$(Ph_{2}PS_{2})_{2}Te_{2}$].

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Supplemental Material

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1. Introduction

The platinum(II) sulfido complex $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) has been known for many years, yet continues to offer surprises: it is a potent metalloligand, and coordinates to metal centers across the Periodic Table [1]. In contrast to the well-developed coordination chemistry with metals, adducts with non-metals or semi-metals are far less well-described. As part of our ongoing investigations into the chemistry of 1 we recently described the reactivity of 1 and the selenide analogue $[Pt_2(\mu-Se)_2(PPh_3)_4]$ toward a variety of chalcogen sources (including the elemental chalcogens S₈ and Se, as well as diaryl dichalcogenides R₂E₂, where E = S, Se and Te) with the intention of synthesizing complexes containing mixed-chalcogenide ligands [2].

In this contribution, we describe investigations into the reactivity of **1** toward tellurium(II) sources, with the intention of synthesizing complexes containing Te–S bonds. The oxidation states of tellurium in compounds with sulfur ligands are 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) forms a wide range of complexes with bidentate chelating sulfur and selenium ligands such as dithiocarboxylates [6], dithiocarbamates [7, 8] and $[R_2P(E)NP(E)R'_2]^-$ (E = S, Se) [5, 9, 10]. In this way, tellurium is acting as a *pseudo*-metal showing coordination chemistry-like behavior. Accordingly, we reasoned that $[Pt_2(\mu-S)_2(PPh_3)_4]$, being a well-known bidentate sulfur metalloligand, should also form complexes with Te(II). Although such compounds are not expected to find any practical applications, they are of fundamental interest in developing the *pseudo*-metallic chemistry of tellurium, and provide a comparison with the known complexes of $[Pt_2S_2(PPh_3)_4]$ with neighboring metalloidal elements in the Periodic Table; although there are no antimony adducts, its heavier analogue bismuth provides a number of examples [11–13].

Our methodology of choice uses Electrospray Ionization Mass Spectrometry (ESI MS) [14] as a convenient and sensitive tool for identification of reaction products of **1**. We have previously used ESI MS to explore the chemistry of $[Pt_2(\mu-S)_2(PPh_3)_4]$ and the related selenide complex, and our investigations in this area have been summarized in a review [15]. In this study, we extend this methodology to the identification and subsequent synthesis and characterization of the interesting tellurium(I) complex [$\{Pt_2(\mu-S)_2(PPh_3)_4\}_2Te_2\}^{2+}$. The structures of the compounds described in this article are shown in Scheme 1.



4, M = Ag or Au

Scheme 1. Structures of compounds described herein.

2. Results and discussion

2.1. Reactivity of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) toward $TeCl_2(tu)_2$ 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 microscale, with reaction monitoring using positive-ion ESI MS. In this study, the ligand abbreviation tu represents a neutral, non-deprotonated thiourea ligand, viz. $SC(NH_2)_2$. Tellurium(II) thiourea complexes, particularly $[Te(tu)_4]Cl_2$, have been used as precursors for preparation of coordination complexes containing the Te(II) center [5, 9, 10, 16, 17].

When $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) was reacted with TeCl₂(tu)₂ in neutral solution, 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 protonate $[Pt_2(\mu-S)_2(PPh_3)_4]$ [18], reactions with TeCl₂(tu)₂ proceeded much more smoothly, giving a single dominant product. Thus, addition of hydrochloric acid to a light-orange suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) in methanol gave a transparent yellow solution, which was reacted with TeCl₂(tu)₂, immediately forming a clear red solution. The solution was examined by ESI MS (Figure 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 (Figure 1 inset) to the ditellurium species $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ (2). This species, and its isolated salts described below, are air stable both as solids and in solution.

Addition of NH₄PF₆ or Li[N(SO₂C₂F₅)₂] to filtered reaction solutions containing the [{Pt₂(μ -S)₂(PPh₃)₄}₂Te₂]²⁺ ion gave precipitates of the respective salts as red powders. [{Pt₂(μ -S)₂(PPh₃)₄}₂Te₂][N(SO₂C₂F₅)₂]₂ gave satisfactory elemental analytical data. The ³¹P{¹H} NMR spectrum of the [N(SO₂C₂F₅)₂]⁻ salt showed the expected features, namely



Figure 1. The positive-ion ESI mass spectrum of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (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 $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ (m/z 1631.14).

a single ³¹P NMR resonance at δ 20.9 with satellites due to coupling to ¹⁹⁵Pt [¹J(PtP) 2959 Hz], however, the peaks were surprisingly somewhat broader than are normally obtained with diamagnetic adducts of [Pt₂(μ -S)₂(PPh₃)₄]. Although the ³¹P NMR parameters of the starting [Pt₂S₂(PPh₃)₄] (1) do not appear to have been reported, due to its insolubility in all common solvents, and reactivity with chlorinated solvents, the closely-related complex [Pt₂S₂(P(*p*-tolyl)₃)₄] is soluble in C₆D₆, giving δ ³¹P 27.3 and ¹J(PtP) 2795 Hz [19]. The larger ¹J(PtP) in [{Pt₂(μ -S)₂(PPh₃)₄]₂Te₂]²⁺ is consistent with coordination of sulfur to tellurium producing a concomitant decrease in *trans*-influence of the sulfido ligands.

All attempts at growing single crystals of the PF_6^- or $[N(SO_2C_2F_5)_2]^-$ salts suitable for an X-ray diffraction study were unsuccessful. The BF_4^- salt was obtained in an analogous method using NaBF₄, and vapor diffusion of diethyl ether into an acetone solution gave dark brown prismatic crystals suitable for X-ray diffraction. The X-ray structure determination unequivocally confirms the identity of the cation as $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ (2). The structure of the cation is shown in Figure 2.

The structure contains two bidentate $[Pt_2(\mu-S)_2(PPh_3)_4]$ metalloligands spanning the Te–Te bond of a formally Te₂²⁺ unit. The dication is disposed about a point of symmetry 22. Thus, both Te atoms lie 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 Figure 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 Te₂S₄ rectangle is close to planar and the Te atom has a T-shaped coordination geometry defined by a S₂Te donor set, the S1–Te–S1ⁱ angle being 175.56(10)°; symmetry operation i: x, 1/2 - y, 1/2 - z.

As neither the Pt nor S1 atoms lie on an axis, there are two independent but, similar Pt–S1, S1ⁱ bond lengths, i.e. 2.343(2) and 2.339(2) Å; symmetry operation i: 1/2 - x, y, 1/2 - z. The Pt₂S₂ atoms adopt a folded configuration with the dihedral angle between the two S₂Pt residues being 44.16(10)°. The Pt coordination geometry is completed by two Ph₃P ligands and the resulting *cis*-P₂S₂ donor set defines an approximate square planar geometry.



Figure 2. Two views of $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ (2) as its BF₄⁻ salt, showing the core structure (all but the *ipso*-C atoms of the phenyl groups being removed) with atom labeling and displacement ellipsoids at the 35% probability level (upper view) and the full dication, showing idealized spheres (lower view). Selected bond lengths (Å) and angles (°): Pt–S1 2.343(2), Pt–S1ⁱ 2.339(2), Te–S1 2.676(3), Pt–P1 2.281(3), Pt–P2 2.303(3), Te–Te 2.7978(16), S1–Pt–P1 91.3(1), S1–Pt–P2 167.1(1), S1–Pt–S1ⁱ 80.3(1), P1–Pt–P2 100.1(1), P1–Pt–S1ⁱ 171.5(1), P2–Pt–S1ⁱ 88.4(1), S1–Te–S1ⁱⁱ 175.6(1), Pt–S1–Ptⁱ 90.2(1), Te–S1–Ptⁱ 107.0(1).

Related Te(I) complexes with Te–Te bonds and sulfide ligands have been previously described in the literature, and the chemistry of tellurium complexes with sulfur donor ligands has been reviewed [20]. 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 [8, 21]. [(Ph₂PS₂)₂Te₂] (**3**) is a close analogue of **2**; complex **3** was originally prepared (and crystallized as the benzene solvate) by reduction of TeO₂ with Ph₂PS₂H [22]. This compound has a Te₂²⁺ group spanned by



Figure 3. A comparison of ESI mass spectra of $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2][N(SO_2C_2F_5)_2]_2$ 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-modeled peak of $[Pt_2(\mu-S)_2(PPh_3)_4]^{+:}$ $[Pt_2(\mu-S)_2(PPh_3)_3Te_2]^+$ 7:1 (*m/z* 1502.24). The lower inset follows the isotope pattern of $[\{Pt_2(\mu-S)_2(PPh_3)_4\}_2Te_2]^{2+}$ 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 $[\{Pt_2(\mu-S)_2(PPh_3)_4\}_2Te_2]^{2+}$ (*m/z* 1631.14). (β_{4a}) is a modeled isotope pattern for $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+:} [Pt_2(\mu-S)_2(PPh_3)_4Te]^+ 3:1 (m/z 1631.14).$

two bidentate, bridging diphenyldithiophosphinate anions, although the ligand binds the two Te centers somewhat asymmetrically. The same compound has also been prepared by reaction of the tellurium(II) complex [Te(tu)₄]Cl₂ with Ph₂P(S)NC(S)pip (pip = piperidyl) and KO^tBu [23]. In the solid-state **3** forms long-range intermolecular Te...Te contacts in the benzene solvate [22] or in the unsolvated compound (crystallized from CH₂Cl₂-hexane); Te···S contacts result in long intermolecular chains [23]. The structural chemistry of this system has been summarized by Bandeira et al. [24] who carried out a computational study (using DFT) on the nature of Te...Te interactions in such species. In the case of the formal Te_2^{2+} species reported herein, it is possible that reduction of Te(II) to Te(I) is facilitated by oxidation of the thiourea [to the

formamidine disulfide cation, $(H_2N)_2CSSC(NH_2)_2]^{2+}$] [25, 26]. No attempts were made to identify such oxidized thiourea by-products.

Complex **2** also resembles silver(I) [27–29] and gold(I) [18, 30] complexes **4**, where two d^{10} metal ions are spanned by two [Pt₂(µ-S)₂(PPh₃)₄] metalloligands, and a significant interaction is proposed to occur between the metals in them.

Detailed characterization of $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2][N(SO_2C_2F_5)_2]_2$ has been carried out using ESI MS, specifically with a view to exploring the fragmentation of the complex cation. Figure 3 shows spectra of the compound at a range of capillary exit voltages. At a relatively low voltage (120 V, Figure 3a) the spectrum is dominated by the parent $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ 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 Figure 3, which shows the observed isotope patterns, together with the excellent agreement with an mMass-modeled pattern comprising $[Pt_2(\mu-S)_2(PPh_3)_4]^+$ and $[Pt_2(\mu-S)_2(PPh_3)_4]^+$ S)₂(PPh₃)₃Te₂]⁺ in a 7:1 ratio. The major ion $[Pt_2(\mu-S)_2(PPh_3)_4]^+$ is formed by oxidation of $[Pt_2(\mu-S)_2(PPh_3)_4]$ 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) [31] and iron(III) [32] derivatives of $[Pt_2(\mu-S)_2(PPh_3)_4]$, where the $[Pt_2(\mu-S)_2(PPh_3)_4]$ center 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 [31] do not show the same behavior. 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, $[Pt_2(\mu-S)_2(PPh_3)_3Te_2]^+$, formed by loss of a PPh₃ ligand, formally contains tellurium in the +0.5 oxidation state (i.e. reduction from Te in the +1 oxidation state in **2**, to +0.5). At higher capillary exit voltages of 150 and 180 V (Figure 3b and 3c, respectively), the parent ion undergoes successively more complete fragmentation to $[Pt_2(\mu-S)_2(PPh_3)_4]^+$ and $[Pt_2(\mu-S)_2(PPh_3)_3Te_2]^+$. 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 Figure 3. At a relatively low voltage of 150 V, the observed isotope pattern (spectrum β_1) shows good agreement with the calculated pattern for $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ (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 modeled (spectrum β_{4a}) as an overlap of $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ with the mono-tellurium species $[Pt_2(\mu-S)_2(PPh_3)_4]_2Te_2]^{2+}$ $S_2(PPh_3)_4Te^{-1}$ (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 $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$.

2.2. Investigation of the effect of added acetic acid on the reaction between $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) and $TeCl_2(tu)_2$

As described in the preceding section, added acid was found to promote the formation of the ditellurium complex $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ when $[Pt_2(\mu-S)_2(PPh_3)_4]$ is reacted with TeCl₂(tu)₂. Accordingly, we have carried out a detailed investigation of the effect of different amounts of added acid on the product speciation using ESI MS to monitor reactions.



Figure 4. A comparison of reaction solutions of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (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) three drops (ca 0.15 mL) glacial acetic acid. Spectra were acquired after mixing 12 h at room temperature. Capillary exit voltage 20 V.

When TeCl₂(tu)₂ is reacted, in the *absence* of added acid, with a stirred, light-orange suspension of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) in methanol, a clear red solution was immediately formed, which after stirring for 24 h 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 different amounts of added acetic acid on the reaction between $[Pt_2(\mu-S)_2(PPh_3)_4]$ and $TeCl_2(tu)_2$ three parallel microscale reactions of 1 and $TeCl_2(tu)_2$ in methanol were carried out and analyzed by ESI MS (Figure 4). A reaction solution without acetic acid (Figure 4a) was compared with reaction solutions containing 0.05 mL (Figure 4b) and 0.15 mL (Figure 4c) of glacial acetic acid. 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 minimize fragmentation. 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 [33, 34] and contains an N,Schelated thiourea monoanion. Thus, the effect of added acetic acid appears to be to suppress the deprotonation of thiourea, and hence reduce its nucleophilicity.

Other detected ions containing a deprotonated thiourea ligand are the trinuclear species $[Pt_3(\mu_3-S)_2(PPh_3)_5[SC(=NH_2)NH]^+$ (m/z 2035.65) together with the thiourea-substituted ion $[(Ph_3P)Pt{SC(=NH_2)NH}(tu)]^+$ at m/z 608.12. These ions, together with

dications at m/z 1018.15, assigned as $[Pt_3(\mu_3-S)_2(PPh_3)_5(tu)]^{2+}$ and m/z 925.12, assigned as $[Pt_3(\mu_3-S)_2(PPh_3)_4(tu)_2]^{2+}$ with neutral thiourea ligands, are clearly indicative of substantial degradation of the $[Pt_2(\mu-S)_2(PPh_3)_4]$ core.

The reactivity of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) toward $TeCl_2(tu)_2$ 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/z1503.13, which is indicative of an incomplete reaction. The assignment of this ion as the oxidized parent complex [1]⁺ was made after a close examination of the isotope pattern, as described previously [15]. After 12 h, the now green 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-oxidized ion [1]⁺ is of significant relative intensity at m/z 1503.25 with partial overlapping with $[Pt_2(\mu-S)_2(PPh_3)_3Te_2]^+$ (m/z1495.97). 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. 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/z532.07 and m/z 608.08, respectively.

2.3. Reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ and $TeCl_2(tmtu)_2$ (tmtu = tetramethylthiourea)

Another approach at minimizing attack of platinum by liberated thiourea used 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 TeCl₂(tmtu)₂, the reaction solution immediately turned clear red and the ESI mass spectrum of the reaction solution was acquired after 1 h. Using gentle ionization 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 $[(Ph_3P)_2PtCl{SC(NMe_2)_2}]^+$ (6, calculated m/z 887.19), whose isotope pattern agreed closely with the calculated pattern. This complex has been previously synthesized and structurally characterized, 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 [35]. Despite the absence of deprotonatable N-H groups, it is likely that the strong sulfur-based nucleophilicity of the tmtu ligand is responsible for its inability to suppress degradation of the {Pt₂S₂} core. No further investigations were carried out using tmtu–Te complexes.

2.4. Computational investigation of $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ and $[(Ph_2PS_2)_2Te_2]$

To further investigate the unusual Te_2^{2+} unit, density functional theory (DFT) calculations were undertaken for $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ and $[(Ph_2PS_2)_2Te_2]$ using the corresponding structures determined from X-ray crystallography. The resulting electron densities were analyzed using the density overlap regions indicator (DORI) [36, 37] to simultaneously elucidate areas of covalent and non-covalent character. As DORI is



Figure 5. A DORI contour map of the $\{(\mu-S)_2Te_2(\mu-S)_2\}$ core of $[\{Pt_2(\mu-S)_2(PPh_3)_4\}_2Te_2]^{2+}$ in the *xz* plane. Values in the range from 0 (blue) to 1 (red).



Figure 6. A DORI contour map of the Te_2^{2+} unit of $[\{Pt_2(\mu-S)_2(PPh_3)_4\}_2\text{Te}_2]^{2+}$ in the *yz* plane. Values in the range from 0 (blue) to 1 (red).

related to the geometric deformation of electron density, it is worth noting the volume of a DORI isosurface does not necessarily correspond to the strength of a particular interaction. DORI contour maps (Figures 5 and 6) of the Te–Te axis display overlap regions of electron density mapped from 0 (blue, at the nuclei and far from the molecule) to 1 (red, strong overlap of electron density). The Te–Te axis is bisected by a red lenticular region with small noticeable blue areas either side on the tellurium atomic boundaries. Comparisons can be made with DORI contour plots of both O_2 and F_2 [36], the latter being a very weak covalent interaction [38]. The four Te–S interactions, which display a more compressed shape to the Te–Te interaction, are merged with the larger atomic regions of tellurium.



Figure 7. DORI =0.97 isosurfaces of $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ using a blue-green-red color map of $-0.08 < sign(\lambda_2)\rho < 0.08$. Phenyl rings of triphenylphosphine ligands omitted for clarity.



Figure 8. DORI =0.97 isosurface of $[(Ph_2PS_2)_2Te_2]$ using a blue-green-red color map of $-0.08 < sign(\lambda_2)\rho < +0.08$.

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As DORI itself provides no information on the attractive/repulsive nature or strength of the bonding interaction, the electron density Laplacian $(\nabla^2 \rho)$ can be used in combination to reveal such properties [36]. Specifically, the sign $(\lambda_2)\rho$ scalar field was used to color-map (blue–green–red) a DORI isosurface (s=0.97) (Figure 7) with negative (blue) and positive (red) magnitudes corresponding to attractive and repulsive interactions, respectively.

The isosurfaces between { Pt_2S_2 } rings and Te–Te–S–Pt–S cycles can now be identified as regions of mild repulsion; non-covalent interactions typical for loci of cyclic systems [39]. The blue–green lenticular isosurface bisecting the Te–Te axis is indicative of a bonding interaction with covalent character, with the four isosurfaces in the Te–S regions less cylindrical and greener in color suggesting weaker bonding interactions. The blue isosurfaces around the square–planar platinum centers show the stronger valence interfaces of the coordinated sulfides.

A DORI examination of a similar complex with a Te_2^{2+} unit, $[(Ph_2PS_2)_2Te_2]$ [23] (Figure 8), reveals a similar blue–green lenticular isosurface bisecting the Te–Te axis which is slightly separated from the atomic Te regions. Interestingly, there is noticeable asymmetry in the molecular geometry and accordingly two distinct Te–S bonding interactions can be identified, one strong bonding interaction and *trans* to this a much weaker bonding interaction.

Overall, the areas of electron density overlap in $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ as revealed by DORI support the expected bonding interactions. The unusual separation of some DORI isosurfaces displayed has been described as a numerical artifact attributed to the nonphysical behavior of finite atomic orbital basis set expansion in areas of fringe electronic density [36, 40].

3. Conclusion

The tellurium(II) complex TeCl₂(tu)₂ is a convenient source of low-valent inorganic tellurium and gives the formally tellurium(I) complex $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ on reaction with $[Pt_2(\mu-S)_2(PPh_3)_4]$. Fragmentation of the ${Pt_2S_2}$ core by thiourea leads to formation of the mononuclear platinum(II) thiourea complex $[(Ph_3P)_2Pt{SC(=NH_2)NH}]^+$, however, this was successfully suppressed by addition of acid to the reaction mixture. The tetra-platinum complex $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2]^{2+}$ has a similar structure to the known dithiophosphinate-bridged tellurium(I) species $[Te_2(S_2PPh_2)_2]$ and to the silver(I) and gold(I) adducts $[{Pt_2(\mu-S)_2(PPh_3)_4}_2M_2]^{2+}$.

4. Experimental

4.1. 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 microliter 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 behavior 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 analyzed and prepared for presentation with the open-source mass spectrometry tool mMass [41, 42].

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 CDCl₃ solution.

4.2. Materials

 $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) was prepared by the literature procedure [43]. Tetramethylthiourea (tmtu, Aldrich) was used as supplied. $TeCl_2(tu)_2$ was from either a commercial source (Aldrich) or was prepared by a literature procedure [44]. $TeCl_2(tmtu)_2$ was prepared by the literature procedure [45]. NH_4PF_6 (Aldrich), $NaBF_4$ (Aldrich) and $Li[N(SO_2C_2F_5)_2]$ (3M) were used as obtained. Other chemicals were at least of reagent grade.

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

[Pt₂(μ-S)₂(PPh₃)₄] (1) (101.8 mg, 0.067 mmol) was suspended in methanol (25 mL), 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 TeCl₂(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(SO₂C₂F₅)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 ×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. C₁₅₂H₁₂₀F₂₀N₂O₈P₈Pt₄S₈Te₂ requires: C, 45.39; H, 3.00; N, 0.70%. ³¹P{¹H} NMR (162 MHz), δ 20.9 [br s, ¹J(PtP) 2959 Hz]. ESI MS (capillary exit voltage 45 V) *m/z* 1630.88 [{Pt₂(μ-S)₂(PPh₃)₄}₂Te₂]²⁺ (100%).

The other salts containing PF_6^- or BF_4^- ions were prepared by analogous procedures, substituting Li[N(SO₂C₂F₅)₂] by excess NaBF₄ or NH₄PF₆.

4.4. Reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) with $TeCl_2(tu)_2$ in methanol

 $[Pt_2(\mu-S)_2(PPh_3)_4]$ (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.

4.5. Comparison of reactions of $[Pt_2(\mu-S)_2(PPh_3)_4]$ (1) with $TeCl_2(tu)_2$ in methanol with varying amounts of acetic acid

In three parallel reaction vessels, $[Pt_2(\mu-S)_2(PPh_3)_4]$ (20 mg, 0.0133 mmol) was suspended in methanol (10 mL) and stirred. Reaction (a): the orange mixture was stirred

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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, $\text{TeCl}_2(\text{tu})_2$ (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 analyzed by ESI MS. Reactions (b, c): the clear red solutions were filtered to remove any insoluble matter and the filtrates were analyzed by ESI MS.

4.6. X-ray crystal structure determination of [{Pt₂(μ-S)₂(PPh₃)₄}₂Te₂][BF₄]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 K α radiation so that θ_{max} was 73.8°. Data reduction, including analytical absorption correction, was accomplished with CrysAlisPro [46]. Of the 29,343 measured reflections, 6512 were unique (R_{int} =0.057) and of these, 4621 data satisfied the $l \ge 2\sigma(l)$ criterion of observability. The structure was solved by direct methods [47] 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 $P = (F_0^2 + 2F_c^2)/3)$ on F^2 [48]. For charge balance, half a BF₄⁻ 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 [49] was employed to model the unresolved electron density due to the $BF_4^$ anions. Even with this treatment, there was considerable atomic motion in the structure despite the low temperature of the X-ray experiment. In keeping with this, the C61–C66 phenyl ring was found to be badly disordered and was modeled isotropically as an idealized phenyl ring with C–C bond lengths fixed at 1.39 Å. Despite the difficulties encountered in the refinement, the molecular structure of the cation has been determined unambiguously. 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 [50].

Crystal data for $C_{144}H_{120}B_2F_8P_8Pt_4S_4Te_2$: M = 3435.57, orthorhombic space group *Pnnn*, a = 18.4717(2), b = 18.5907(3), c = 19.0659(3) Å, V = 6547.26(16) Å³, Z = 2, $D_x = 1.743$ g cm⁻³, F(000) = 3332, $\mu = 13.276$ mm⁻¹. CCDC deposition number: 1811863.

4.7. Computational details

Single point energy DFT calculations were performed using molecular geometry obtained from crystal structures of $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Te_2](BF_4)_2$ and $[(Ph_2PS_2)_2Te_2]$ [23] with the Q-Chem 4.2 [51] software package using the ω B97X [52] functional with DFT-D3 long-range dispersion correction by Grimme *et al.* [53]. The LANL2DZ [54] effective core potential and basis set was used for platinum and tellurium atoms, the Dunning double- ζ augmented correlation-consistent polarized basis set aug-cc-pV(D + d)Z [55] used for sulfur atoms, and the Pople double- ζ polarized basis set 6-31G(d) [56] used

for the treatment of all other atoms. Wave function analysis was performed using Multiwfn [57]. Visual Molecular Dynamics [58] and Tachyon [59] ray tracer were used to render isosurfaces and Python was used to generate contour images.

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Supplementary material

CCDC 1811863 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. Supplementary data to this article can be found online.

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