Syntheses, X-ray structures and AACVD studies of group 11 ditelluroimidodiphosphinate complexes[†]

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Reactions of Na(tmeda)[N(ⁱPr₂PTe)₂] with CuCl, AgI or AuCl (in the presence of PPh₃) in THF produced the coinage metal ditelluroimidodiphosphinate complexes {Cu[N(ⁱPr₂PTe)₂]}₃, (**5**), {Ag[N(ⁱPr₂PTe)₂]}₆ (**6**) and Au(PPh₃)[N(ⁱPr₂PTe)₂] (**7**), respectively. Complexes **5**, **6** and **7** were characterized in the solid state by X-ray crystallography. Complex **5** is trimeric and exhibits a highly distorted Cu₃Te₃ ring. In contrast, the Ag(I) complex **6** is a hexamer, and forms a twelve-membered Ag₆Te₆ ring. The replacement of the ⁱPr groups on phosphorus by Ph results in an intriguing structural change to a tetramer with a boat-shaped Ag₄Te₄ ring in {Ag[N(Ph₂PTe)₂]₄·2THF (**8**). The gold(I) complex **7** is monomeric. Aerosol-assisted chemical vapour deposition (AACVD) of compounds **5**, **6** and **7** yields CuTe, Ag₇Te₄, AuTe₂ and Au films, respectively. The films were grown at temperatures of 300–500 °C and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX).

Introduction

Binary metal tellurides have been shown to have interesting properties and many potential uses. Recent work has focused on the production of thin films or nanoparticles of group 12 (Zn, Cd, Hg)¹ or group 15 (Sb, Bi)² tellurides in view of their applications in photooptical and thermoelectric devices, respectively. The traditional syntheses of metal tellurides have involved either the high-temperature (500-600 °C) reaction between the elements³ or aqueous methods that employ the extremely toxic reagent H₂Te.⁴ As an alternative to these procedures the use of a single-source molecular precursor in which the metal and tellurium atoms are in close proximity has been investigated by various groups.^{5,6} To the best of our knowledge, there have been no reports of the generation of copper, silver or gold telluride thin films by this approach. Copper telluride thin films have been employed in various devices, including solar cells, photodetectors and microwave-shielding coatings.⁷⁻⁹ Silver tellurides find wide applications as thermoelectronic or magnetic materials as a result of their thermoelectric and magneto-resistive behaviour.¹⁰ The low-temperature phase of monoclinic silver telluride is a semiconductor with a narrow band gap, whereas the high-temperature phase is a superionic conductor. A recent paper by Zhang and co-workers describes the controlled hydrothermal synthesis of nanostructured thin films of Cu₂Te and Ag₂Te by the reaction of metal foils with Te powder in hydrazine.11

The dichalcogenoimidodiphosphinate anions 1 and 2 were first synthesized by Schmidpeter *et al.* in the 1960s (Chart 1).¹² In

† The HTML version of this article has been enhanced with colour images.



1995, Woollins and co-workers initiated the chemistry of the selenium analogue **3a**.¹³ Much of the early development of the coordination chemistry of these ligands with both main group¹⁴ and transition metals^{14,15} was focused on the phenyl derivatives. In 2004 it was demonstrated that metal complexes incorporating the more volatile *iso*-propyl ligand **3b** are excellent precursors for the production of a variety of binary metal selenides by CVD techniques.^{16,17} This method can also be employed for the generation of thin films of the important ternary material CuInSe₂ by thermal decomposition of a copper(I) complex of **3b** in the presence of a related indium precursor, In[N(¹Pr₂PSe)₂]Cl.¹⁸

The recent preparation of the ditelluroimidodiphosphinate anions **4a** and **4b** has paved the way for investigations of analogous tellurium systems.^{19–21} Simple metathesis reactions of the sodium salt of **4b** with metal halides have led to the synthesis of complexes of group 12 and 15 metals,²⁰ as well as a lanthanum(III) complex and a uranium(III) complex, the latter providing the first example of actinide–tellurium bonds.²² Interestingly, the reactions of **4b** with group 13 halides gives rise to a novel chalcogen-transfer process resulting in the formation of Ga₂Te₂ and In₃Te₃ rings.²³ Subsequent chemical vapour deposition studies demonstrated that several of these new tellurium-containing compounds can indeed act as single-source precursors for binary metal tellurides, including thin films of CdTe,²⁴ In₂Te₃,²⁵ and hexagonal Sb₂Te₃ nanoplates.²⁰

In this investigation we have synthesized the first ditelluroimidodiphosphinate group 11 complexes, for structural comparison

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with the analogous dithio and diseleno species, and evaluated their use as single-source precursors for the formation of copper, silver and gold telluride thin films.

Results and discussion

Syntheses and characterization of group 11 complexes

The ditelluroimidodiphosphinate complexes $\{Cu[N(^{i}Pr_2PTe)_2]\}_3$ (5) and $\{Ag[N(^{i}Pr_2PTe)_2]\}_6$ (6) (Chart 2) were readily prepared in good yield by the metathesis reactions of the reagent Na(tmeda)[N(ⁱPr_2PTe)_2]²⁰ with CuCl and AgI, respectively. In contrast, the reaction of AuCl with Na(tmeda)[N(ⁱPr_2PTe)_2] was very vigorous, immediately producing a dark red solution and a precipitate of gold metal, even at low temperatures.²⁶ However, the stable gold complex Au(PPh_3)[N(ⁱPr_2PTe)_2] (7) was prepared in good yield by treating the sodium complex of **4b** with a solution of (PPh_3)AuCl. The reaction of the sodium salt of **4a**, Na(tmeda)[N(Ph_2PTe)_2], with an equimolar quantity of AgI produced the homoleptic complex $\{Ag[N(Ph_2PTe)_2]\}_4$ (8) in 69% yield.



X-Ray crystal structures

The molecular structure of the copper(I) derivative **5** was determined by X-ray crystallography. Crystallographic data are summarized in Table 5. As indicated in Fig. 1, this complex is trimeric in the solid state. Selected bond distances and bond angles are given in Table 1. Complex **5** consists of three sixmembered $CuTe_2P_2N$ rings, which are linked together to form



Fig. 1 Molecular structure of $\{Cu[N(^{i}Pr_2PTe)_2]\}_3$ (5). Thermal ellipsoids are shown at 50%. Hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) and bond angles (°) for $\{Cu[N(^iPr_2PTe)_2]\}_3~(\textbf{5})$

Cu(1)–Te(1)	2.563(2)	Cu(1)–Te(2)	2.591(1)
Cu(1)–Te(5)	2.696(2)	Cu(1)–Te(6)	2.890(2)
Cu(2)–Te(2)	2.533(2)	Cu(3)–Te(4)	2.566(1)
Cu(2)–Te(3)	2.505(1)	Cu(3)–Te(5)	2.531(1)
Cu(2)–Te(4)	2.563(2)	Cu(3)–Te(6)	2.531(1)
Cu(1)–Cu(3)	2.637(2)	Cu(2)–Cu(3)	2.626(1)
$\begin{array}{l} Te(1)-Cu(1)-Te(2)\\ Te(1)-Cu(1)-Te(5)\\ Te(2)-Cu(1)-Te(5)\\ Te(2)-Cu(2)-Te(3)\\ Te(2)-Cu(2)-Te(4)\\ \end{array}$	113.16(5) 118.18(6) 99.94(5) 128.73(5) 107.50(5)	$\begin{array}{l} Te(3)-Cu(2)-Te(4)\\ Te(4)-Cu(3)-Te(5)\\ Te(4)-Cu(3)-Te(6)\\ Te(5)-Cu(3)-Te(6)\\ \end{array}$	123.71(5) 113.12(4) 134.10(5) 112.47(5)

two central, highly distorted Cu₃Te₃ rings. The distortion of these central rings results in surprisingly short copper-copper distances of 2.626(1) and 2.637(2) Å. Two of the ligands are equivalent with similar metrical parameters, each containing one tellurium which is complexed to one copper centre and one tellurium bridging two copper centres. The unique ligand Te(5)-P(5)-N(3)-P(6)-Te(6) can be viewed as asymmetrically bridging both Cu(1) and Cu(3) centres with significantly longer tellurium copper distances to Cu(1): Cu(1)-Te(6) 2.890(2) Å and Cu(1)-Te(5) 2.696(2) Å, *cf.* Cu(3)–Te(6) and Cu(3)–Te(5) = 2.531(1) Å. Cu(2) and Cu(3) display trigonal planar geometry (sum of bond angles around Cu are 359.9° and 359.7° , respectively). Disregarding the longer Cu(1)-Te(6) bond, the geometry of the Cu(1) center is highly distorted from trigonal planar (sum of bond angles around Cu(1) is 331.3°). This suggests a significant interaction with Te(6) and therefore the Cu(1) geometry is more accurately described as intermediate between tetrahedral and trigonal planar.

The analogous copper(I) complexes of the dithio and diseleno ligands **2b** and **3b**, respectively, are also trimeric and consist of a central six-membered Cu₃E₃ (E = S, Se) ring.^{18,27a} However, in contrast to complex **5**, both structures are considerably more open and there are no indications of metal–metal interactions [d(Cu–Cu) = 3.75–4.00 Å]. The longer, more labile copper–tellurium bonds in **5** may impart more flexibility to the structure, thus allowing one of the ligands to function in a doubly bridging mode, which brings two of the copper atoms in closer proximity than in the analogous sulfur or selenium complexes. We note, however, that the trimeric Cu(I) complex of the phenyl-substituted dithio ligand **2a** exhibits two short (2.637 and 2.625 Å) and one long (3.581 Å) Cu–Cu contacts.^{27b}

An X-ray structural determination of complex **6** revealed a novel arrangement consisting of six $Ag[N(Pr_2PTe)_2]$ units to give the hexamer $\{Ag[N(Pr_2PTe)_2]\}_6$ as shown in Fig. 2. The molecule lies on an inversion centre so the two halves of the hexamer are crystallographically equivalent. The silver centres are each bound to two tellurium centres from one ligand and one tellurium from an adjacent $Ag[N(Pr_2PTe)_2]$ moiety. Each silver centre is coordinated equally (Table 2) between two bridging tellurium centres of adjacent $[N(Pr_2PTe)_2]$ ligands forming a central twelvemembered Ag_6Te_6 ring. Two pairs of silver atoms in the twelvemembered ring have noticeably shorter metal–metal distances, Ag(2)-Ag(3A) 2.945(2) Å and Ag(3)-Ag(2A) 2.955(2), which are in the range for which metallophilic silver–silver interactions should be considered.^{28,29} However, the geometry at the metal

Table 2 Selected bond lengths (Å) and bond angles (°) for $\{Ag[N(^iPr_2PTe)_2]\}_6~(6)$

Ag(1)-Te(1) Ag(1)-Te(2) Ag(1)-Te(3)	2.725(1) 2.690(2) 2.724(1)	Ag(2)–Te(3) Ag(2)–Te(4) Ag(2)–Te(6A)	2.721(1) 2.692(1) 2.784(2)
Ag(3)-Te(6) Ag(3)-Te(5) Ag(2)-Ag(3A)	2.794(1) 2.725(1) 2.945(2)	Ag(3)–Te(1) Ag(3)–Ag(2A)	2.756(1) 2.955(2)
$\begin{array}{l} Te(1)-Ag(1)-Te(2)\\ Te(1)-Ag(1)-Te(3)\\ Te(2)-Ag(1)-Te(3)\\ Te(3)-Ag(2)-Te(4)\\ Te(3)-Ag(2)-Te(6A) \end{array}$	120.54(4) 111.47(4) 127.87(4) 119.16(5) 111.31(4)	Te(4)-Ag(2)-Te(6A) Te(1)-Ag(3)-Te(5) Te(1)-Ag(3)-Te(6) Te(5)-Ag(3)-Te(6)	129.53(4) 133.13(4) 108.44 116.34(4)



Fig. 2 Molecular structure of $\{Ag[N(Pr_2PTe)_2]\}_6$ (6). Thermal ellipsoids are shown at 50%. Hydrogen atoms and methyl groups have been omitted for clarity.

centres is nearly perfect trigonal planar in each case suggesting there is little interaction between the metal centres (sum of the bond angles: $Ag(2) 360.0^{\circ}$, $Ag(3) 357.9^{\circ}$). Thus it is not possible to establish if the proximity of the silver centres is a consequence of the bridging tellurium centres or due to a metallophilic interaction.

The analogous silver complex of the diseleno ligand **3b** is trimeric in the solid state and, as in the case of the copper complex of **3b**, no sign of metal–metal interaction is observed.¹⁸ Complex **6** is only the second example of a hexameric species formed by a metal complex of dichalcogenoimidodiphosphinate ligands. The sodium complex, $\{Na[N\{(PhO)_2PO\}_2]\}_6$ is also hexameric in the solid state,³⁰ presumably due to the spatial requirements of the phenoxy substituents on the phosphorus centres of the ligand. In the case of complex **6**, the large sizes of the metal and chalcogen are more likely to be the contributing factors.

In contrast to the *iso*-propyl-substituted silver complex **6**, Xray crystallography revealed **8** to be tetrameric in the solid state, $\{Ag[N(Ph_2PTe)_2]\}_4$ (Fig. 3). The molecule lies on an inversion centre, making the two halves of the molecule crystallographically equivalent. Selected bond lengths and bond angles for **8** are summarized in Table 3. The complex contains a central eightmembered Ag_4Te_4 ring. There are two distinct silver environments. The atoms Ag(1) and the crystallographic equivalent Ag(1A)

Table 3 Selected bond lengths (Å) and bond angles (°) for ${Ag[N(Ph_2PTe)_2]}_4$ (8)

$\begin{array}{l} Ag(1)-Te(1) \\ Ag(1)-Te(2) \\ Ag(1)-Te(3) \\ Ag(1)-Te(4) \end{array}$	2.880(1) 2.8901(9) 2.792(1) 2.816(1)	Ag(2)-Te(4) Ag(2)-Te(1A) Ag(2)-Te(2A) Ag(2)-Ag(2A) Ag(1)-Ag(2)	2.764(1) 2.827(1) 2.928(1) 2.992(2) 3.243(1)
Te(1)-Ag(1)-Te(2) Te(1)-Ag(1)-Te(3) Te(2)-Ag(1)-Te(3) Te(1A)-Ag(2)-Te(4) Te(2A)-Ag(2)-Te(4)	93.11(3) 124.08(3) 111.01(3) 151.02(3) 100.38(4)	Te(1)-Ag(1)-Te(4) Te(2)-Ag(1)-Te(4) Te(3)-Ag(1)-Te(4) Te(1A)-Ag(2)-Te(2A)	99.55(3) 116.10(3) 111.93(3) 93.42(3)



Fig. 3 Molecular structure of $\{Ag[N(Ph_2PTe)_2]\}_4$ (8). Thermal ellipsoids are shown at 50%. Hydrogen atoms and lattice molecules of THF have been omitted for clarity.

exhibit distorted tetrahedral geometry, each being coordinated to four tellurium centres. The other silver atoms, Ag(2) and Ag(2A), are each bound to three tellurium centres and display distorted trigonal planar geometry. These two silver centres are held 2.992(2) Å from each other, *cf.* 3.243(1) Å for Ag(1)–Ag(2), which is in the range for reported silver–silver interactions.²⁹ Although the close Ag \cdots Ag contact in **8** is similar in distance to those observed for **6**, the distortion of the geometry of these silver atoms towards pyramidal (sum of bond angles around Ag(2) is 344.8°) in **8**, in contrast to the trigonal planar geometry observed in **6**, is suggestive of a metallophilic interaction in the former.

Attention to gold–chalcogen chemistry has increased recently due to the interest in these compounds for chemotherapy.³¹ This has led to a number of gold selenide complexes being characterized and, in particular, a detailed study of gold complexes of ligand **3a** has been carried out, with examples of the metal centre being two, three or four coordinate.³²

An X-ray structural determination of Au(PPh₃)[N($^{i}Pr_{2}PTe_{2}$] (7) revealed a monomeric species (Fig. 4) with a trigonal planar gold(1) centre (sum of the bond angles around Au(1) is 359.4°) coordinated to one [N($^{i}Pr_{2}PTe_{2}$)₂]⁻ ligand and one molecule of triphenylphosphine. The gold centre is bound equally between the two tellurium centres of the ditelluroimidodiphosphinate ligand to form the six-membered AuTe₂P₂N metallacycle. The Au–Te bond distances are in the range of previously reported Au–Te bonds, 2.533–2.666 Å.³³ The six-membered ring has a twist conformation,



Fig. 4 Molecular structure of $Au(PPh_3)[N(^{1}Pr_2PTe)_2]$ (7). Thermal ellipsoids are shown at 50%. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–Te(1) 2.616(7), Au(1)–Te(2) 2.639(1), Au(1)–P(3), 2.309(2), Te(1)–Au(1)–Te(2) 118.63(2), Te(1)–Au(1)–P(3) 119.98(4), Te(2)–Au(1)–P(3), 120.78(4).

the gold centre lies in the same plane as the nitrogen and the tellurium centres with P(1) lying above (0.62 Å) and P(2) below (0.64 Å) this plane. Interestingly, structural characterization of the triphenylphosphine gold(1) complexes of ligands **2a** and **3a**, showed the gold centre to be asymmetrically bound between the two chalcogen centres,³² suggesting a weaker interaction with one side of the ligand, which is not observed in the case of complex **7**.

There are relatively few structurally characterized examples of gold–tellurium bonds, the majority of which involve binary $Au_x Te_y$ anions. Hence, the isolated molecular complex 7 can be considered a rare example of a gold(1) complex of a telluride ligand.³²

NMR characterization of group 11 complexes of 4

The iso-propyl-substituted complexes 5-7 each exhibit a single resonance (δ 23.2–26.8) in their respective ³¹P NMR spectra, indicating equivalence of the phosphorus centres in solution on the NMR time scale at room temperature. Consistently, one doublet $(\delta - 640 \text{ to } -770)$ is observed in each of the ¹²⁵Te NMR spectra of 5–7. The magnitudes of the ${}^{1}J_{\text{TeP}}$ (1290–1350 Hz) are comparable to those observed for covalent complexes of 4b with group 12 and group 15 metals (1282-1339 Hz).²⁰ In contrast to the homoleptic complexes of 4b with cadmium and mercury,²⁰ no coupling to the spin-active silver nuclei was observed in the ³¹P or ¹²⁵Te NMR spectra for compound 6 suggesting that this coinage-metal complex is fluxional in solution. The phenyl-substituted complex **8** exhibited a singlet at δ -14.4 with ${}^{1}J_{\text{TeP}} = 1361$ Hz but, as with complex 6 no coupling to spin-active silver nuclei was observed. We were unable to detect the ¹²⁵Te NMR resonance for 8 owing to low solubility.

Examination of the solid-state structures of complexes 5, 6 and 8 reveals that there is more than one tellurium environment in each of the structures. However, in each case only one signal is observed in the ³¹P and ¹²⁵Te NMR spectra. This suggests that the solid-state structures do not remain intact in solution, and a

fluxional process may be occurring to cause each tellurium centre to become equivalent on the NMR timescale. Low temperature NMR experiments were conducted on complexes **5**, **6** and **8**, however only singlets were observed in all cases.

Deposition of thin films

The chemical vapour deposition studies of compounds **5**, **6** and **7** were conducted in an aerosol-assisted (AA) CVD kit. The precursors have very high molecular masses ranging from 962–3668 g mol⁻¹ and would be unsuitable for use in conventional CVD experiments due to lack of thermal stability and volatility. However, the AACVD technique allows the transfer of aerosols to the reaction site where the aerosol droplets evaporate depositing the precursor on the glass substrate. The physical properties of compounds analysed by thermogravimetric analysis (TGA) indicates a single decomposition step between 208–297 °C for **5**, 210–355 °C for **6** and 206–317 °C for **7**. Prior to each deposition, the reactor was purged with argon for approx. 15 min at the deposition temperature in order to minimise the risk of producing oxidised films.

Copper telluride thin films were deposited from {Cu[N(i- $Pr_2PTe_{2}]_{3}$ (5) on glass substrates by AACVD. The copper precursor was dissolved in 20 mL toluene and the deposition process occurred over a period of 90 min in the temperature range 300 to 500 °C, with an argon flow rate of 160 sccm. The deposited grey films were non-adherent and could be easily wiped off the surface, indicating that the copper telluride particles were weakly adsorbed on the glass substrate. The XRD patterns of all the deposited films showed a mixture of orthorhombic CuTe (JCPDS 13-0258), hexagonal Te (JCPDS 36-1452) and phosphorus (JCPDS 25-0608) (Fig. 5). The unit cell parameters of the deposited films are compared with literature values in Table 4. There is some notable deviation for the films deposited at 300 °C as a consequence of phosphorus doping within the crystal lattice. The SEM studies revealed that the copper telluride particles have hexagonal shapes at 300 °C (Fig. 6). With an elevation in growth temperature to 350 °C, transparent individual sheets of CuTe along with CuTe spherical particles are observed. Stacking of sheets is observed at 400-500 °C. The tellurium rods are formed at all deposition temperatures. In all cases, EDAX analyses on the sheets indicate that they are copper rich (49-52%) along with phosphorus incorporation (5-12%). The high copper content may be due to the formation of individual tellurium rods, which reduces the availability of tellurium for the production of copper telluride sheets.

The deposition of silver telluride thin films was attempted from toluene solutions of $\{Ag[N(Pr_2PTe)_2]\}_6$ (6) on glass substrates in



Fig. 5 XRD pattern of CuTe films deposited at 400 °C. The additional diffraction peaks are identified as Te (*) and P (#).

Fable 4	A comparison between literature and observed unit cell parameters of deposited materials	
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$ \begin{cases} Cu[N(Pr,PTe)_2]\}, & 300 & CuTe + Te & a: 4.09; b: 6.95; c: 3.15 & a: 4.055(2); b: 7.046(5); c: 3.152(2) \\ a: 4.4579(3); c: 5.95270(6) & a: 4.4571(9); c: 5.919(3) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.4521(4); c: 3.146(4); c$	Precursor	Deposition temperature/°C	Materials deposited	Literature lattice constants/Å	Refined lattice constants/Å
$ \begin{cases} ar 4457(9); c: 59270(6) & ar 4457(9); c: 5919(3) \\ ar 44579(3); c: 59270(6) & ar 4488(5); br 6948(4); c: 5.146(3) \\ ar 44579(3); c: 59270(6) & ar 4485(4); c: 5.932(4) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.9273(7) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.9273(7) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.9273(7) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.9273(7) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.9270(7) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.9270(7) \\ ar 44559(3); c: 5.9270(6) & ar 4456(4); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4456(4); c: 5.919(2) \\ ar 44579(3); c: 5.9270(6) & ar 44579(3); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 44579(3); c: 5.9270(6) \\ ar 44579(3); c: 5.9270(6) & ar 44579(3); c: 5.917(3) \\ ar 44579(3); c: 5.9270(6) & ar 4457(3); c: 5.917(3) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.917(3) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.94(9) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.920(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.922(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.922(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.922(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.922(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.922(7) \\ ar 44579(3); c: 5.9270(6) & ar 4452(3); c: 5.922(7) \\ ar 44759(3); c: 5.9270(6) & ar 4452(3); c: 5.922(7) \\ ar 44759(3); c: 5.9270(6) & ar 4452(3); c: 10.15(7) \\ ar 4456(1); c: 5.923(1) \\ ar 40786 & ar 40786 \\ ar 40786 & ar 4078(7) \\ ar 40786 & ar 40778(5) \\ ar 40786 & ar 40778(5$	${Cu[N(^{i}Pr_{2}PTe)_{2}]}_{3}$	300	CuTe + Te	<i>a</i> : 4.09; <i>b</i> : 6.95; <i>c</i> : 3.15	<i>a</i> : 4.055(2); <i>b</i> : 7.046(5); <i>c</i> : 3.152(2)
$ \begin{cases} 350 & CuTe + Te & at .409; bt .657; ct .3.15 & at .4088(5); bt .6.948(4); ct .3.146(3) \\ 400 & CuTe + Te & at .44579(3); ct .5.9270(6) & at .4456(4); ct .5.932(4) \\ 450 & CuTe + Te & at .409; bt .657; ct .3.15 & at .4088(2); bt .6.950(3); ct .3.147(1) \\ at .44579(3); ct .5.9270(6) & at .4456(4); ct .5.927(7) \\ at .4455(4); ct .5.927(7) & at .4456(4); ct .5.927(7) \\ at .44579(3); ct .5.9270(6) & at .44560(5); ct .3.15 & at .4092(2); bt .6.950(3); ct .3.147(1) \\ at .44579(3); ct .5.9270(6) & at .44560(5); ct .3.15 & at .4092(2); bt .6.950(3); ct .3.147(1) \\ at .44579(3); ct .5.9270(6) & at .44560(5); ct .3.15 & at .4092(2); bt .6.950(3); ct .3.147(1) \\ at .44579(3); ct .5.9270(6) & at .44560(5); ct .5.9270(2) \\ at .44570(3); ct .5.9270(6) & at .44570(3); ct .5.920(2) \\ at .44570(3); ct .5.9270(6) & at .4457(2); ct .44570(3); ct .5.920(2) \\ at .44570(3); ct .5.9270(6) & at .4457(2); ct .4457(2) \\ at .44570(3); ct .5.9270(6) & at .4457(2); ct .4457(2) \\ at .44570(3); ct .5.9270(6) & at .4457(2); ct .4457(2) \\ at .44570(3); ct .5.9270(6) & at .4425(3); ct .5.946(4) \\ 450 & Ag; Te_4 + Te & at .13.457; ct .84564 & at .13.460(ct .8.473(3) \\ at .44570(3); ct .5.9270(6) & at .4425(3); ct .5.924(4) \\ at .44579(3); ct .5.9270(6) & at .4425(3); ct .5.924(4) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4455(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4457(2); at .44579(3); ct .5.923(1) \\ at .44579(3); ct .5.9270(6) & at .4457(2); at .4077(2) \\ at .445$				a: 4.4579(3); c: 5.9270(6)	<i>a</i> : 4.4571(9); <i>c</i> : 5.919(3)
$ \begin{cases} 400 & CuTe + Te & at .499; b; 6.95; c; 3.15 & at .4682(4); c; 5.932(4) \\ at .409; b; 6.95; c; 3.15 & at .4082(4); c; 5.927(5) \\ at .4456(4); c; 5.927(5) & at .4456(4); c; 5.927(7) \\ at .44579(3); c; 5.9270(6) & at .44560(3); c; 5.927(7) \\ at .44579(3); c; 5.9270(6) & at .44560(3); c; 5.927(7) \\ at .44579(3); c; 5.9270(6) & at .44560(3); c; 5.920(2) \\ at .44579(3); c; 5.9270(6) & at .44560(3); c; 5.920(2) \\ at .44579(3); c; 5.9270(6) & at .44560(3) \\ at .44579(3); c; 5.9270(6) & at .4456(3); c; 5.919(2) \\ at .44579(3); c; 5.9270(6) & at .4457(1); c; 5.919(2) \\ at .44579(3); c; 5.9270(6) & at .4457(1); c; 5.917(3) \\ at .44579(3); c; 5.9270(6) & at .4457(1); c; 5.917(3) \\ at .44579(3); c; 5.9270(6) & at .4457(1); c; 5.916(2) \\ at .44579(3); c; 5.9270(6) & at .4457(2); c; 5.946(4) \\ at .13457(c; 8.4564 & at .13.460(4); c; 8.473(3) \\ at .44579(3); c; 5.9270(6) & at .4455(3); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4455(3); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4455(3); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4455(3); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4455(3); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4455(3); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(5) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(1) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 5.922(1) \\ at .44579(3); c; 5.9270(6) & at .4456(1); c; 10.15(1) \\ at .45702(1); bt .440(5); c; 10.15(1) \\ at .45702(1); bt .440(5); c; 10.15(1) \\ at .45702(1); bt .440(5); c; 10.15(1) \\ at .4570$		350	CuTe + Te	<i>a</i> : 4.09; <i>b</i> : 6.95; <i>c</i> : 3.15	<i>a</i> : 4.088(5); <i>b</i> : 6.948(4); <i>c</i> : 3.146(3)
$ \begin{cases} 400 & CuTe + Te & x 4.09; b: 6.95; c: 3.15 & x 4.088(2); b: 6.942(3); c: 5.277(7) \\ x 4.4579(3); c: 5.9270(6) & x 4.463(4); c: 5.9275(7) \\ x 4.4579(3); c: 5.9270(6) & x 4.456(4); c: 5.925(1) \\ x 4.4579(3); c: 5.9270(6) & x 4.456(4); c: 5.926(1) \\ x 4.4579(3); c: 5.9270(6) & x 4.456(4); c: 5.920(2) \\ x 4.4563(9); c: 5.920(2) & x 4.4563(9); c: 5.920(2) \\ \end{cases} $				<i>a</i> : 4.4579(3); <i>c</i> : 5.9270(6)	<i>a</i> : 4.462(4); <i>c</i> : 5.932(4)
$ \begin{cases} ar 4.4579(3); c: 5.9270(6) & ar 4.4564(3); c: 5.5927(7) \\ ar 4.09(1); br 5.9(2); br 5.950(3); c: 3.147(1) \\ ar 4.09(1); br 5.9(2); br 5.950(3); c: 3.147(1) \\ ar 4.09(1); c: 5.9270(6) & ar 4.4560(5); c: 5.926(1) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.4560(5); c: 5.920(2) \\ ar 4.4561(5); c: 5.920(2) & ar 4.4561(5); c: 3.15 & ar 4.087(4); br 6.950(4); c: 3.150(2) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(4); br 6.950(4); c: 5.920(2) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(2); c: 5.919(2) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(2); c: 5.919(2) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(2); c: 5.919(2) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(2); c: 5.917(3) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(2); c: 5.917(3) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(3); c: 5.917(3) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.452(3); c: 5.927(6) \\ ar 4.452(3); c: 5.9270(6) & ar 4.457(3); c: 5.927(6) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(3); c: 5.927(6) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(3); c: 5.922(5) \\ 500 & Ag; Te_4 + Te & ar 13.457; c: 8.4564 & ar 13.460(4); c: 8.473(3) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(3); c: 5.922(5) \\ 500 & Ag; Te_4 + Te & ar 13.457; c: 8.4564 & ar 13.457(2); c: 8.467(2) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.457(3); c: 5.922(5) \\ 500 & Ag; Te_4 + Te & ar 13.457; c: 8.4564 & ar 13.457(2); c: 8.467(2) \\ ar 4.4579(3); c: 5.9270(6) & ar 4.4557(3); c: 5.923(1) \\ 400 & AuTe_2 & ar 8.76(1); b: 4.41(5); c: 10.15(1) & ar 8.75(2); b: 4.406(3); c: 10.157(9) \\ b; 125.200(2) & b; 125.20(2) \\ b; 125.10(1) \\ ar 8.770(3); b; 4.406(3); c: 10.16(1) \\ c: 10.779(5) & ar 4.0778(5) \\ ar 4.0778(5) & ar 4.0773(5) \\ ar 4.0778(5) & ar 4.0778(5) \\ ar 4.0778(5) & ar 4.0779(4) \\ ar 4.0786 & ar 4.0779(4) \\ ar 4.0786 & ar 4.0779(4) \\ ar 4.0778(5) & ar 4.0799(4) \\ \end{bmatrix}$		400	CuTe + Te	<i>a</i> : 4.09; <i>b</i> : 6.95; <i>c</i> : 3.15	<i>a</i> : 4.088(2); <i>b</i> : 6.942(3); <i>c</i> : 3.177(3)
$ \begin{cases} 450 & CuTe + Te & a: 4.09; (b; 5.65; c; 3.15) & a: 4.092(2); b: 5.65; 0: 5.2147(1) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.4550(5); c: 5.2920(1) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.4550(5); c: 5.2020(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.4550(5); c: 5.920(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.457(3); c: 5.9270(6) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.4577(9); c: 5.919(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.4577(9); c: 5.919(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.4577(9); c: 5.919(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.4577(9); c: 5.919(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.457(2); c: 8.467(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.457(2); c: 8.472(4) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(4); c: 8.472(4) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(6); c: 8.472(4) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(6); c: 8.472(4) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(6); c: 8.472(4) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(6); c: 5.922(5) \\ 500 Ag_{2}Te_{4} + Te & a: 13.457; c: 8.4564 & a: 13.457(c); c: 8.467(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(4); c: 5.922(5) \\ 500 Ag_{2}Te_{4} + Te & a: 13.457; c: 8.4564 & a: 13.457(c); c: 5.923(1) \\ \begin{cases} Au(PPh_{3})[N(Pr_{2}PTe)_{2]} & 300 & AuTe_{2} & a: 8.76(1); b: 4.41(5); c: 10.15(1) \\ a: 8.75(1); b: 4.403(2); c: 10.157(9) \\ \beta: 125.200(2) & \beta: 125.16(1) \\ a: 8.75(1); b: 4.403(2); c: 10.157(9) \\ \beta: 125.200(2) & \beta: 125.16(1) \\ a: 8.75(1); b: 4.403(2); c: 10.157(9) \\ \beta: 125.200(2) & a: 4.0778(3) \\ a: 4.0786 & a: 4.0778(3) \\ a: 4.0786 & a: 4.0778(3) \\ a: 4.0786 & a: 4.0778(5) \\ a: 4.0077(2) & a: 8.77(1); b: 4.403(2); c: 10.167(1) \\ \beta: 125.200(2) & \beta: 125.194(8) \\ a: 4.0786 & a: 4.0778(3) \\ a: 4.0786 & a: 4.0778(4) \\ a: 4.0786 & a: 4.0778(4) \\ a: 4.0786 & a: 4.0778(4) \\ a: 4.0786 & a: 4.0779(4) \\ a: 4.0786 & a: 4.0799(4) \\ \end{cases}$				<i>a</i> : 4.4579(3); <i>c</i> : 5.9270(6)	<i>a</i> : 4.4564(3); <i>c</i> : 5.9275(7)
$\begin{cases} Ag[N(Pr_2PTe)_2]_* & 300 & Ag, Te_4 + Te & a: 13, 457; c: 5, 8270(6) & a: 4, 4550(3); c: 5, 920(2) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 4550(3); c: 5, 920(2) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 457(4); c: 5, 919(2) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 457(1); c: 5, 919(2) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 457(1); c: 5, 919(2) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 457(1); c: 5, 919(2) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 457(1); c: 5, 919(2) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 457(1); c: 5, 917(3) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 457(1); c: 5, 917(3) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 457(1); c: 5, 917(3) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 455(1); c: 5, 917(3) \\ a: 4, 459(3); c: 5, 9270(6) & a: 4, 455(3); c: 5, 9270(6) \\ a: 4, 455(3); c: 5, 9270(6) & a: 4, 455(3); c: 5, 9270(6) \\ a: 4, 457(2); c: 5, 9270(6) & a: 4, 455(3); c: 5, 9270(6) \\ a: 4, 457(2); a: 5, 9270(6) & a: 4, 455(3); c: 5, 9270(6) \\ a: 4, 457(2); a: 5, 9270(6) & a: 4, 455(1); c: 5, 9270(6) \\ a: 4, 457(2); a: 5, 9270(6) & a: 4, 455(1); c: 5, 9220(1) \\ b: 125, 200(2) & a: 1, 13, 457(2); c: 8, 467(2) \\ a: 4, 4579(3); c: 5, 9270(6) & a: 4, 455(1); c: 5, 9220(1) \\ b: 125, 200(2) & a: 4, 457(2); a: 4, 405(3); c: 10.157(9) \\ f: 125, 200(2) & a: 4, 457(2); a: 4, 405(3); c: 10.157(9) \\ f: 125, 200(2) & a: 4, 0778(3) \\ a: 4, 0778(3) & a: 4, 0778(3) \\ a: 4, 0778(3) & a: 4, 0778(3) \\ a: 4, 0778(3) & a: 4, 0778(3) \\ a: 4, 0778(4) & a: 4, 0778(3) \\ a: 4, 0778(5) & a: 4, 407(3); c: 10.164(7) \\ f: 125, 200(2) & f: 125, 24(1) \\ a: 4, 0778(5) & a: 4, 407(3); c: 10.164(7) \\ f: 125, 200(2) & f: 125, 24(1) \\ a: 4, 0778(5) & a: 4, 00778(3) \\ a: 4, 0778(5) & a: 4, 07798(4) \\ a: 4, 0786 & a: 4, 0799(4) \\ b: 125, 200(2) & f: 125, 04(2) \\ a: 4, 0778(5) & a: 4, 0799(4) \\ b: 105, 000 & Au & a: 4, 0778(6) & a: 4, 0799(4) \\ b: 105, 000 & Au & a: 4$		450	CuTe + Te	<i>a</i> : 4.09; <i>b</i> : 6.95; <i>c</i> : 3.15	<i>a</i> : 4.092(2); <i>b</i> : 6.950(3); <i>c</i> : 3.147(1)
$ \begin{cases} S00 \\ CuTe + Te \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.4559(3); c: 5.920(2) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.4579(3); c: 5.920(6) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.4510(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.4510(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.4510(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.4510(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.4510(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.455(3); c: 5.9220(5) \\ a: 4.455(3); c: 5.9220(5) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.4579(3); c: 5.9270(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.4579(3); c: 5.9220(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.4579(3); c: 5.9220(6) \\ a: 4.456(1); c: 5.922(1) \\ a: 4.078(1); c: 4.01(3); c: 10.15(1) \\ a: 8.75(1); b: 4.40(3); c: 10.16(1) \\ f: 125.28(2) \\ a: 4.0786 \\ a: 4.0778(3) \\ a: 4.078(5) \\ a: 4.078(6) \\ a: 4.0799(4) \\ a: 4.078(5) \\ a: 4.0799($				<i>a</i> : 4.4579(3); <i>c</i> : 5.9270(6)	<i>a</i> : 4.4560(5); <i>c</i> : 5.926(1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		500	CuTe + Te	<i>a</i> : 4.09; <i>b</i> : 6.95; <i>c</i> : 3.15	<i>a</i> : 4.087(4); <i>b</i> : 6.950(4); <i>c</i> : 3.150(2)
$ \begin{cases} Ag[N(Pr_2PTe)_2]\}_{6} & 300 & Ag_{7}Te_{4} + Te & a: 13.457; c: 8.4564 & a: 13.444(5); c: 8.469(3) \\ a: 4.4577(3); c: 5.9270(6) & a: 4.4577(3); c: 5.919(2) \\ a: 4.4577(3); c: 5.9270(6) & a: 4.4571(3); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.451(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.451(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.452(3); c: 5.964(9) \\ a: 4.457(3); c: 5.9270(6) & a: 4.452(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.456(1); c: 10.15(1) \\ b: 125.15(1) & a: 8.75(1); b: 4.403(2); c: 10.157(9) \\ b: 125.100(2) & b: 125.15(1) \\ a: 8.75(1); b: 4.406(3); c: 10.16(1) \\ b: 125.200(2) & b: 125.15(1) \\ a: 8.776(8); b: 4.401(3); c: 10.16(1) \\ b: 125.194(8) & a: 4.0778(5) \\ a: 4.0786 & a: 4.0777(2) \\ a: 4.0786 & a: 4.0773(5) \\ a: 4.078(6) & a: 4.0778(3) \\ a: 4.0786(1); b: 4.41(5); c: 10.15(1) & a: 8.776(8); b: 4.409(2); c: 10.17(1) \\ b: 125.200(2) & b: 125.194(8) \\ a: 4.0786 & a: 4.0778(3) \\ a: 4.0786 & a: 4.0778(4) \\ b: 125.200(2) & b: 125.04(2) \\ b: 125.04(2) & b: 4.416(3); c: 10.15(1) \\ b: 125.04(2) & b: 4.416(3); c: 10.15(1)$				<i>a</i> : 4.4579(3); <i>c</i> : 5.9270(6)	<i>a</i> : 4.4563(9); <i>c</i> : 5.920(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\{Ag[N(^{i}Pr_{2}PTe)_{2}]\}_{6}$	300	$Ag_7Te_4 + Te$	<i>a</i> : 13.457; <i>c</i> : 8.4564	<i>a</i> : 13.444(5); <i>c</i> : 8.469(3)
$ \begin{cases} 350 & Ag_{7}Te_{4} + Te & a: 13.457; c: 8.4564 & a: 13.451(2); c: 8.467(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.451(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.451(1); c: 5.917(3) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.964(9) \\ 450 & Ag_{7}Te_{4} + Te & a: 13.457; c: 8.4564 & a: 13.4465(3); c: 5.922(5) \\ 500 & Ag_{7}Te_{4} + Te & a: 13.457; c: 8.4564 & a: 13.4465(3); c: 5.922(5) \\ 500 & Ag_{7}Te_{4} + Te & a: 13.457; c: 8.4564 & a: 13.4465(3); c: 5.922(5) \\ 500 & Ag_{7}Te_{4} + Te & a: 13.457; c: 8.4564 & a: 13.457(2); c: 8.467(2) \\ a: 4.4579(3); c: 5.9270(6) & a: 4.455(3); c: 5.922(5) \\ a: 4.455(3); c: 5.922(5) & a: 4.455(3); c: 5.922(5) \\ a: 4.455(3); c: 5.922(5) & a: 4.455(3); c: 5.922(5) \\ a: 4.4557(3); c: 5.9270(6) & a: 4.455(3); c: 5.923(1) \\ \begin{cases} Au(PPh_{3})[N(Pr_{2}PTe)_{2}] & 300 & AuTe_{2} & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.75(1); b: 4.403(2); c: 10.157(9) \\ \beta: 125.200(2) & \beta: 125.15(1) \\ 350 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.75(2); b: 4.406(3); c: 10.16(1) \\ \beta: 125.200(2) & \beta: 125.194(8) \\ a: 4.0786 & a: 4.0779(3) \\ 400 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.77(1); b: 4.409(2); c: 10.17(1) \\ \beta: 125.200(2) & \beta: 125.194(8) \\ a: 4.0786 & a: 4.0773(5) \\ a: 4.0786 & a: 4.0778(3) \\ 500 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.77(1); b: 4.409(2); c: 10.17(1) \\ \beta: 125.200(2) & \beta: 125.24(1) \\ a: 4.0786 & a: 4.0778(3) \\ 500 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.77(1); b: 4.409(2); c: 10.17(1) \\ \beta: 125.200(2) & \beta: 125.04(2) \\ a: 4.0786 & a: 4.0778(3) \\ 500 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.77(2); b: 4.416(3); c: 10.15(1) \\ a: 4.0786 & a: 4.0799(4) \\ \end{bmatrix}$			-	a: 4.4579(3); c: 5.9270(6)	a: 4.4577(9); c: 5.919(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		350	$Ag_7Te_4 + Te$	<i>a</i> : 13.457; <i>c</i> : 8.4564	a: 13.451(2); c: 8.467(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			-	a: 4.4579(3); c: 5.9270(6)	a: 4.451(1); c: 5.917(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		400	$Ag_7Te_4 + Te$	<i>a</i> : 13.457; <i>c</i> : 8.4564	a: 13.465(6); c: 8.472(4)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			-	a: 4.4579(3); c: 5.9270(6)	<i>a</i> : 4.425(3); <i>c</i> : 5.964(9)
$ \begin{cases} Au(PPh_3)[N(Pr_2PTe)_2) \\ Au(PPh_3)[N(Pr_2PTe)_2) \\ Au(PPh_3)[N(Pr_2PTe)_2) \\ Au(PPh_3)[N(Pr_2PTe)_2) \\ Bi \\ B$		450	$Ag_7Te_4 + Te$	<i>a</i> : 13.457; <i>c</i> : 8.4564	a: 13.460(4); c: 8.473(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			-	a: 4.4579(3); c: 5.9270(6)	<i>a</i> : 4.455(3); <i>c</i> : 5.922(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		500	$Ag_7Te_4 + Te$	<i>a</i> : 13.457; <i>c</i> : 8.4564	a: 13.457(2); c: 8.467(2)
$ \begin{cases} Au(PPh_3)[N({}^{1}Pr_{2}PTe)_{2}) & 300 & AuTe_{2} & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.75(1); b: 4.403(2); c: 10.157(9) \\ \beta: 125.200(2) & \beta: 125.15(1) \\ a: 8.75(2); b: 4.406(3); c: 10.16(1) \\ \beta: 125.200(2) & a: 4.0779(3) \\ 400 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.776(8); b: 4.401(3); c: 10.164(7) \\ \beta: 125.200(2) & a: 4.0778(3) \\ a: 4.0786 & a: 4.0779(3) \\ a: 4.0786 & a: 4.0773(5) \\ a: 4.0786 & a: 4.0777(2) \\ 450 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.77(1); b: 4.409(2); c: 10.17(1) \\ \beta: 125.200(2) & \beta: 125.24(1) \\ a: 4.0786 & a: 4.0778(3) \\ 500 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.77(1); b: 4.409(2); c: 10.17(1) \\ \beta: 125.200(2) & \beta: 125.24(1) \\ a: 4.0786 & a: 4.0778(3) \\ 500 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.77(2) \\ 450 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.77(1); b: 4.416(3); c: 10.15(1) \\ \beta: 125.200(2) & \beta: 125.24(1) \\ a: 4.0786 & a: 4.0786(2) \\ a: 4.0786 & a: 4.0778(3) \\ 500 & AuTe_{2} + Au & a: 8.76(1); b: 4.41(5); c: 10.15(1) & a: 8.74(2); b: 4.416(3); c: 10.15(1) \\ \beta: 125.200(2) & \beta: 125.04(2) \\ a: 4.0786 & a: 4.0799(4) \\ 500 & Au & a: 4.0786 & a: 4.0799(4) \\ \end{cases}$				<i>a</i> : 4.4579(3); <i>c</i> : 5.9270(6)	<i>a</i> : 4.456(1); <i>c</i> : 5.923(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\{Au(PPh_3)[N(^iPr_2PTe)_{2\}}$	300	AuTe ₂	<i>a</i> : 8.76(1); <i>b</i> : 4.41(5); <i>c</i> : 10.15(1)	<i>a</i> : 8.75(1): <i>b</i> : 4.403(2): <i>c</i> : 10.157(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			-	β: 125.200(2)	β: 125.15(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		350	$AuTe_2 + Au$	<i>a</i> : 8.76(1); <i>b</i> : 4.41(5); <i>c</i> : 10.15(1)	<i>a</i> : 8.75(2); <i>b</i> : 4.406(3); <i>c</i> : 10.16(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			-	β: 125.200(2)	β: 125.28(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				<i>a</i> : 4.0786	a: 4.0779(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		400	$AuTe_2 + Au$	<i>a</i> : 8.76(1); <i>b</i> : 4.41(5); <i>c</i> : 10.15(1)	a: 8.776(8); b: 4.401(3); c: 10.164(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				β: 125.200(2)	β: 125.194(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				a: 4.0786	<i>a</i> : 4.0773(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		400	Au	a: 4.0786	a: 4.0777(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		450	$AuTe_2 + Au$	<i>a</i> : 8.76(1); <i>b</i> : 4.41(5); <i>c</i> : 10.15(1)	<i>a</i> : 8.77(1); <i>b</i> : 4.409(2); <i>c</i> : 10.17(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				β : 125.200(2)	β : 125.24(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				<i>a</i> : 4.0786	<i>a</i> : 4.0786(2)
500AuTe2 + Au $a: 8.76(1); b: 4.41(5); c: 10.15(1)$ $a: 8.74(2); b: 4.416(3); c: 10.15(1)$ $\beta: 125.200(2)$ $\beta: 125.04(2)$ $a: 4.0786$ $a: 4.0799(4)$ 500Au $a: 4.0786$ $a: 4.0799(4)$		450	Au	<i>a</i> : 4.0786	<i>a</i> : 4.0778(3)
$\begin{array}{cccc} & & & & & & & & & & & & & & & & & $		500	$AuTe_2 + Au$	<i>a</i> : 8.76(1); <i>b</i> : 4.41(5); <i>c</i> : 10.15(1)	<i>a</i> : 8.74(2); <i>b</i> : 4.416(3); <i>c</i> : 10.15(1)
a: 4.0786 a: 4.0799(4) 500 Au a: 4.0786 a: 4.0799(4)				β: 125.200(2)	β: 125.04(2)
500 Au <i>a</i> : 4.0786 <i>a</i> : 4.0799(4)				<i>a</i> : 4.0786	<i>a</i> : 4.0799(4)
		500	Au	<i>a</i> : 4.0786	<i>a</i> : 4.0799(4)



Fig. 6 SEM images of copper telluride films deposited at (a) $300 \degree C$, (b) $350 \degree C$, (c) $400 \degree C$, (d) $450 \degree C$ and (e) $500 \degree C$.

the range 300–500 °C with a dynamic argon flow rate of 140 sccm for 60 min. Substrate temperatures below 300 °C were too low to initiate deposition. The XRD pattern of as-deposited samples indicated the formation of both Te (JCPDS 36-1452) and Ag₇Te₄ (JCPDS 18-1187) (Fig. 7). The presence of hexagonal Te was revealed by its characteristic diffraction peaks from the primary reflections of 2θ at 23.05°, corresponding to the (100) plane, and additional reflections of 2θ at 38.30, 40.45, 46.05, 49.8 and 57.05° for the (102), (110), (003), (201) and (202) planes, respectively. The observation of above-mentioned diffraction peaks at high deposition temperatures confirms the presence of Te. Two additional peaks at 2θ values of 27.05 and 43.45° correspond with both Te and Ag₇Te₄. The refined cell parameters of the deposited films indicate slight deviations from literature unit cell values as a consequence of phosphorus doping (Table 4). The presence of both Te and Ag₇Te₄ is supported by SEM/EDAX studies (Fig. 8). The SEM analysis shows heterogeneous growth occurring at 300 °C. The formation of micron-size tellurium tubes along with truncated hexagonal plates and spheres of Ag₇Te₄ is observed. The selected area electron diffraction (SAED) pattern embedded in Fig. 8(b) confirms the single crystallinity of the resulting hexagonal plates. The EDAX analysis on the tubes confirms the presence of only tellurium whereas EDAX on the plates and spheres shows 50% silver, 39% tellurium and 10% phosphorus.

As the deposition temperature is increased (350–450 °C), only spherical particles are observed in SEM (Fig. 8(c) and 8(d)). The EDAX indicates silver-deficient (~22%) and tellurium-rich (~72%) films with trace amounts of phosphorus (~6%). The phosphorus impurity could be due to incomplete decomposition of **6** at these deposition temperatures. At 450–500 °C, agglomerations of spheres with uneven surfaces are evident. Similarly, at 500 °C, EDAX analysis indicates high tellurium content within the films without any phosphorus contamination. The tellurium-rich films are a consequence of the formation of a mixture of both Te and Ag₇Te₄. The possible evaporation of silver from the surface of films at higher temperatures cannot be ruled out. At 500 °C, the absence of phosphorus contamination in the films is possibly due



Fig. 7 XRD pattern of Ag_7Te_4 films deposited at (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C and (e) 500 °C. The additional diffraction peaks are identified as Te (*) and Ag_7Te_4 and Te (\blacksquare).

to rupturing of P–Te bonds. The surface of the spheres can also be etched by treating the film deposited at 500 °C with 0.5 M HCl for 30 s. The compactness of the interior of the spheres is clearly evident. No obvious correlation between the sphere size and deposition temperatures is found. The calculated sphere sizes are $1.52 \,\mu\text{m} (300 \,^{\circ}\text{C}), 2.88 \,\mu\text{m} (350 \,^{\circ}\text{C}), 2.12 \,\mu\text{m} (400 \,^{\circ}\text{C}), 1.24 \,\mu\text{m} (450 \,^{\circ}\text{C})$ and 1.61 $\mu\text{m} (500 \,^{\circ}\text{C})$.

Gold telluride thin films are deposited from Au(PPh₃)- $[N(Pr_2PTe)_2]$ (7) on glass with an argon flow rate of 160 sccm between 300–500 °C for 60 min. At 300–350 °C, only grey films



Fig. 8 SEM images of Ag₇Te₄ films deposited at (a) and (b) 300 °C, (c) 350 °C, (d) 400 °C, (e) 450 °C and (f) 500 °C. The inset in (b) shows the SAED of truncated hexagonal plates. The inset in (f) shows the morphology of the film at 450 °C after etching.



Fig. 9 A typical XRD pattern of monoclinic AuTe $_2$ film deposited at 300 $^\circ\text{C}.$

were deposited, whereas at higher temperatures (400–500 °C), a mixture of grey and pinkish films was formed. All the films were found to be non-adherent to the substrate. The XRD studies of films grown at 300 °C exclusively show the formation of monoclinic AuTe₂ (Calaverite, JCPDS 75-1416) (Fig. 9). A mixture of monoclinic AuTe₂ and cubic Au (JCPDS 04-0784) was deposited at 350 °C as observed by XRD. At growth temperatures 400–500 °C, two types of deposits were observed: a mixture of monoclinic AuTe₂ and Au film closest to the precursor inlet (cooler part of the reactor) and only a cubic Au film further away from



Fig. 10 A typical XRD pattern of a gold film deposited at 450 °C.

the precursor inlet (Fig. 10). No appreciable difference is found in the calculated unit cell parameters of either the AuTe₂ or the Au films (Table 4). At deposition temperatures >350 °C, formation of individual gold particles along with AuTe₂ is due to the depletion of tellurium under CVD conditions. Also gold has a high affinity for tellurium due to its soft character, resulting in formation of AuTe₂ followed by Au particles. More recently, the AACVD technique has been employed for the fabrication of metallic gold nanoparticles as thin films from a colloidal gold precursor.³⁴

The SEM studies (Fig. 11) show that the films grown at 300 and 350 $^{\circ}\rm{C}$ have poor film coverage, consisting of granules with broad



Fig. 11 SEM images of (i) AuTe₂ films deposited at (a) 300 °C, (b) 350 °C; (ii) a mixture of AuTe₂ and Au particles formed at (c) 400 °C, (e) 450 °C, (g) 500 °C and (iii) pure Au particles deposited at (d) 400 °C, (f) 450 °C and (h) 500 °C. The inset in (f) shows the SAED pattern of gold nanoparticles at 400 °C.

distribution of sizes and morphologies. The EDAX analysis shows gold-deficient (~30-31%) and tellurium-rich (~68-69%) films with traces of phosphorus. At 400-500 °C, the films are comprised of micrometer-sized parallelepiped AuTe₂ along with anisotropic gold nanostructures. The gold films are composed of well-defined faceted crystals including triangular, cubic and polyhedral particles. Some gold particles seem to be agglomerates of two, three, or more smaller particles. In other places, two or more particles can be observed in close proximity but not conjointed. Bare glass substrate is also evident between the particles, indicating that less than one monolayer has been deposited. The SAED pattern of gold particles (inset in Fig. 11(f)) indicated a (102) spot which is generally not found in the face-centered cubic (FCC) system of gold. However, this extra reflection is expected for a hexagonal closed-packed (HCP) system of the metals. This can be attributed to the faulted regions arising from the dislocations caused by a slip in the (111) family of planes.³⁵ The EDAX analysis on AuTe₂ shows 32-37% gold and 63-68% tellurium depending on growth temperatures. The purity of the gold films was also confirmed by the EDAX.

It is well known that spherical gold nanoparticles exhibit a surface plasmon absorption band around at 520 nm.³⁶ Fig. 12 shows UV-Vis absorption spectra of the gold films at 400–500 °C, with a broad red shift at 554 nm, indicating high polydispersity, both in size and shape, which implies quite a broad range of possible resonance frequencies.



Fig. 12 UV-Vis spectra of gold thin films grown at (a) 400 $^{\circ}$ C, (b) 450 $^{\circ}$ C and 500 $^{\circ}$ C on glass using aerosol-assisted CVD.

Conclusions

Copper, silver and gold complexes of the ditelluroimidodiphosphinate ligand have been synthesized and structurally characterized. These are rare examples of coinage metal complexes of a telluride ligand. When compared to the corresponding dithio and diseleno ligands, the larger tellurium donors, and longer metal-tellurium bonds, impart a greater deal of flexibility to the structures that are observed. In particular, larger ring sizes are observed for the silver(1) complexes, also allowing both tellurium atoms of the ditelluro ligand to function in bridging modes. The coinage metal centers are brought closer together in the solid state and in the tetrameric silver complex **8**, this results in metallophilic $(d^{10}-d^{10})$ interactions. The compounds **5**, **6** and **7** have been used to deposit crystalline copper, silver, gold telluride and gold films by AACVD. As-deposited copper and silver telluride films are contaminated with tellurium and phosphorus, whereas, compound 7 yields $AuTe_2$ and Au films along with traces of phosphorus depending on the growth temperature. The deposited films show varied morphologies, namely hexagons and sheets for copper telluride films, truncated hexagons and spheres for silver telluride films, micrometre-sized parallelepiped gold telluride films and polydispersed gold nanoparticles.

Experimental

Reagents and general procedures

All reactions and the manipulations of products were performed under an argon atmosphere using standard Schlenk techniques or in an inert-atmosphere glove box. The solvent THF was dried by distillation over Na/benzophenone under a nitrogen atmosphere prior to use. The reagents Na[N(R₂PTe)₂](tmeda) (**4a**, R = Ph: **4b**, R = ⁱPr) were prepared by the literature procedures.^{19,20} The reagents CuCl, AgI, AuCl and PPh₃ were obtained from commercial sources and used as received.

Elemental analyses were performed by Analytical Services, Department of Chemistry, University of Calgary.

Spectroscopic methods

The ¹H, ³¹P and ¹²⁵Te NMR spectra were obtained in d₈-THF on a Bruker DRX 400 spectrometer operating at 399.592, 161.765 and 126.082 MHz, respectively. ¹H NMR spectra were referenced to the solvent signal and the chemical shifts are reported relative to Me₄Si. ³¹P NMR spectra were referenced externally to an 85% solution of H₃PO₄ and the chemical shifts are reported relative to H₃PO₄. The ¹²⁵Te NMR spectra were referenced externally to a saturated solution of H₆TeO₆ and the ¹²⁵Te chemical shifts are reported relative to Me₂Te [∂ (Me₂Te) = ∂ (H₆TeO₆) + 712].

Instrumentation

The TGA measurements were carried out by using a Seiko SSC/S200 model under a heating rate of 10 °C min⁻¹ under nitrogen. The XRD studies were carried out using Cu-K α radiation on a Bruker AXS D8 Advance diffractometer. The sample was mounted flat and was scanned between 10 to 80° in steps of 0.05 with a count time of 5.5 s. The films were carbon-coated using Edward's E306A coating system before carrying out SEM analyses. SEM analyses were performed using a Philips XL 30FEG instrument, whereas EDAX was carried out using a DX4 instrument. TEM analyses were conducted on a Philips CM200, 200KV DX4EDS. The sample was briefly sonicated in ethanol, which produces a suspension and then a drop of the suspension was placed on a TEM grid and allowed to dry.

Deposition of thin films

The precursor (0.10 g) was dissolved in toluene (10 to 20 mL) in a round-bottom flask and the deposition was carried out for 60 or 90 min. Argon was used as a carrier gas with flow rates

of 140 or 160 sccm for the deposition. The argon flow rate was controlled by a Platon flow gauge. Seven glass substrates (approx. 1×3 cm) were placed inside the reactor tube and they were annealed at the desired temperature for 15 min before carrying out the deposition. The precursor solution in a round-bottom flask was kept in a water bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (model no. 1077). The aerosol droplets of the precursor thus generated were transferred into the hot wall zone of the reactor by carrier gas. The reactor was cooled in a Carbolite furnace. After each CVD run, the reactor was cooled to room temperature under an inert atmosphere.

X-Ray crystallography

A suitable crystal of the complex was coated with Paratone oil, mounted on a thin glass fibre and frozen in the cold nitrogen stream of the goniometer. Data were collected at 173(2) K on a Nonius CCD-four circle Kappa FR540C diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) with φ and ω scans. The unit-cell parameters were calculated and refined from the full data set. Data reduction was performed by using Nonius HKL DENZO and SCALEPACK software.37 An absorption correction was applied to the data (SCALEPACK).37 The structures were solved by direct methods and Patterson (SHELXS-97)³⁸ and refined by a full-matrix least squares method based on F² using SHELXL-97.³⁹ Except as mentioned below, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated geometrically and were riding on their respective atoms. Thermal ellipsoid plots were generated using the program XSHELL (SHELXTL-97).39

In compound 9 there was a two-part disorder of the phenyl ring attached to P3 and the thermal parameters were best refined by using a 50:50 mixture and mild restraints. The structure includes two molecules of lattice THF for each tetramer. These were modeled over two positions, refining best as a 50:50 mixture.

Crystallographic data are summarized in Table 5.

CCDC reference numbers 612707–612711.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617429a

Synthesis of $\{Cu[N(Pr_2PTe)_2]\}_3$ (5). The reagent Na(tmeda)-[N(ⁱPr₂PTe)₂], (Na4b), was prepared by using a modification of the literature procedure.²⁰ A solution of Na4b (1.286 g, 2.00 mmol) in THF (15 mL) was added slowly to a suspension of CuCl (0.200 g, 2.00 mmol) in THF (10 mL) at -78 °C. The mixture was stirred for 1 h to give a bright yellow cloudy reaction mixture. The precipitate was removed by filtration, and the solvent was removed in vacuo. The resulting yellow solid was washed with cold hexane (5 mL) and dried in vacuo (0.842 g, 1.48 mmol, 74%). X-Ray quality crystals were grown from a concentrated solution in hexane. Mp 73 °C (dec.), 134-136 °C melts to a red oil. NMR data (300 MHz, 23 °C, C₄D₈O): ¹H δ 2.12–2.05 (m, 2 H, -CH(CH₃)₂), 1.29–1.16 (m, 12 H, -CH(CH₃)₂); ³¹P δ 26.8 (s, ¹J_{P-Te} 1310 Hz); ¹²⁵Te δ –686 (d, ¹J_{P-Te} 1315 Hz). Analytical data were obtained on a sample that was recrystallized from THF. Anal. Calc. (%) for C₄₄H₁₀₀Cu₃N₃P₆O₂Te₆: C 28.64, H 5.46, N 2.28. Found: C 28.56, H 5.61, N 2.57.

Synthesis of {**Ag**[**N**('**Pr**₂**PTe**)₂]}₆ (6). A clear yellow solution of (Na4b) (1.929 g, 3.00 mmol) in THF (20 mL) was added slowly to a suspension of AgI (0.702 g, 3.00 mmol) in THF (20 mL), wrapped in foil, at 23 °C. The mixture was stirred for 1 h to give a clear pale yellow solution. The solvent was removed *in vacuo* and the resulting yellow solid was redissolved in toluene (20 mL). The NaI by-product was removed by filtration. The clear yellow solution was reduced to dryness *in vacuo* and diethyl ether (10 mL) was added. Removal of the diethyl ether *in vacuo* yielded a yellow crystalline solid (1.243 g, 2.03 mmol, 68%). Mp 134 °C (dec.), 152–154 °C melts to a red oil. NMR data (300 MHz, 23 °C, C₇D₈): 'H δ 1.96–1.84 (m, 2 H, -CH(CH₃)₂), 1.23–1.12 (m, 12 H, -CH(CH₃)₂); ³¹P δ 26.2 (s, ¹J_{P-Te} 1294 Hz); ¹²⁵Te δ –771 (d, ¹J_{P-Te} 1290 Hz). Anal. Calc. (%) for C₇₂H₁₆₈Ag₆N₆P₁₂Te₁₂: C 23.57, H 4.62, N 2.29. Found: C 23.71, H 4.20, N 2.49.

Table 5 Selected crystal data, data collection and refinement parameters for complexes 5-8

	5	6	7	8	
Formula	C36H84Cu3N3P6Te6	$C_{72}H_{168}Ag_6N_6P_{12}Te_{12}$	$C_{30}H_{43}AuNP_{3}Te_{2}$	$C_{104}H_{96}Ag_4N_4O_2P_8Te_8$	
Formula weight	1701.10	3668.18	962.73	3133.89	
Space group	$\bar{P}1$	$\overline{P}1$	P2(1)/n	$\overline{P}1$	
a/Å	14.007(3)	14.514(3)	8.656(2)	10.580(2)	
b/Å	14.424(3)	14.799(3)	43.228(9)	15.079(3)	
c/Å	16.538(3)	16.306(3)	9.907(2)	17.761(4)	
$a/^{\circ}$	83.97(3)	72.73(3)	90	98.44(3)	
β/°	76.89(3)	67.47(3)	113.36(3)	100.97(3)	
y/°	62.51(3)	69.23(3)	90	103.11(3)	
$V/Å^3$	2886.8(13)	2972.1(13)	3403(1)	2655.3(11)	
Ζ	2	1	4	1	
$d_{\rm calc}/{\rm g~cm^{-3}}$	1.957	2.049	1.879	1.960	
μ/mm^{-1}	4.260	4.053	6.164	3.050	
F(000)	1620	1728	1832	1488	
Reflections collected	55172	54940	33665	18045	
Independent reflections (R_{int})	10186 (0.0407)	10470 (0.0692)	5774 (0.070)	9349 (0.0257)	
R	0.0511	0.0457	0.0387	0.0359	
wR	0.1445	0.0956	0.1117	0.0971	

Synthesis of Au(PPh₃)[N(ⁱPr₂PTe)₂] (7). A solution of PPh₃ (0.262 g, 1.00 mmol) in THF (10 mL) was added to a stirred suspension of AuCl (0.232 g, 1.00 mmol) in THF (10 mL) at 23 °C. The yellow suspension immediately became a clear colourless solution. The solution was cooled to -78 °C and added dropwise to a stirred yellow solution of (Na4b) (0.643 g, 1.00 mmol) in THF (20 mL), also cooled to -78 °C, over 30 min. The resulting clear orange solution was stirred at -78 °C for 1 h. The reaction solution was warmed slowly to 23 °C over 1 h and changed to a dark red colour. The solvent was removed in vacuo to give an oily red solid. The product was dissolved in diethyl ether (30 mL) and filtered to remove NaCl. The solution was reduced in volume to ca. 20 mL and stored at -18 °C for 24 h, yielding a yellow crystalline solid. The solution was decanted and the product was washed with cold *n*-hexane $(1 \times 5 \text{ mL}) (0.620 \text{ g})$ 0.64 mmol, 64%). X-Ray quality crystals were grown from a diethyl ether solution at 23 °C. Mp 148-150 °C. NMR data (300 MHz, 23 °C, C₇D₈): ¹H δ 7.62–7.69 (m, 6 H, -P(C₆H₅)₃), 7.02–7.00 (m, 9 H, -P(C₆H₅)₃), 1.77–1.71 (m, 4 H, -CH(CH₃)₂), 1.21–1.08 (m, 24 H, -CH(CH₃)₂); ³¹P δ 23.2 (s, ¹J_{P-Te} 1348 Hz, ⁱPr₂PTe), 37.5 (broad s, *PPh*₃); 125 Te δ –642 (d, ${}^{1}J_{P-Te}$ 1353 Hz). Anal. Calc. (%) for C₃₀H₄₃AuNP₃Te₂: C 37.43, H 4.50, N 1.45. Found C 36.84, H 4.58, N 1.46.

Synthesis of $\{Ag[N(Ph_2PTe)_2]\}_4$ (8). A yellow solution of (Na4a) (0.778 g, 1 mmol) in THF (20 mL) was added dropwise to a stirred suspension of AgI (0.235 g, 1 mmol) in THF (10 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h resulting in a bright orange solution. A small amount of precipitate was formed which was removed by filtration through Celite, to give a clear orange solution. Reduction in volume of the solvent (approx. 5 mL) under vacuum, addition of hexane (5 mL) and storage at 23 °C for 24 h, resulted in a crop of bright orange crystals (0.540 g, 69%). Mp dec. at 163 °C; brown oil formed at 235 °C. NMR data (300 MHz, 23 °C, C₄D₈O): ¹H δ 7.81–7.74 (m, 8 H, -P(C₆H₅)₂), 7.24–7.22 (m, 12 H, -P(C₆H₅)₂), 3.63–3.60 (m, 2 H, -C₄H₈O), 1.79–1.75 (m, 2 H, $-C_4H_8O$; ³¹P δ –14.4 (s, ¹J_{P-Te} 1361 Hz). Carbon analyses were consistently low by 2-3% possibly due to partial loss of lattice THF molecules.

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