

# Cation–anion interactions in triphenyl telluronium salts. The crystal structures of $(\text{Ph}_3\text{Te})_2[\text{MCl}_6]$ ( $\text{M} = \text{Pt}, \text{Ir}$ ), $(\text{Ph}_3\text{Te})[\text{AuCl}_4]$ , and $(\text{Ph}_3\text{Te})(\text{NO}_3)\cdot\text{HNO}_3$

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## Abstract

Triphenyltelluronium hexachloroplatinate (**1**), hexachloroiridate (**2**), tetrachloroaurate (**3**), and tetrachloroplatinate (**4**) were prepared from  $\text{Ph}_3\text{TeCl}$  and potassium salts of the corresponding anions. Upon recrystallization of **4** from concentrated nitric acid,  $\text{K}_2[\text{PtCl}_6]$  and  $(\text{Ph}_3\text{Te})(\text{NO}_3)\cdot\text{HNO}_3$  (**5**) were obtained. The crystal structures of **1–3** and **5** are reported. Compounds **1** and **2** are isostructural. They are triclinic,  $P\bar{1}$ ,  $Z = 2$  (the asymmetric unit contains two formula units). Compound **1**:  $a = 10.7535(2)$ ,  $b = 17.2060(1)$ ,  $c = 21.4700(3)$  Å,  $\alpha = 78.9731(7)^\circ$ ,  $\beta = 77.8650(4)^\circ$ ,  $\gamma = 78.8369(4)^\circ$ . Compound **2**:  $a = 10.7484(2)$ ,  $b = 17.1955(2)$ ,  $c = 21.4744(2)$  Å,  $\alpha = 78.834(1)^\circ$ ,  $\beta = 77.649(1)^\circ$ ,  $\gamma = 78.781(1)^\circ$ . Compound **3** is monoclinic,  $P2_1/c$ ,  $Z = 4$ ,  $a = 8.432(2)$ ,  $b = 14.037(3)$ ,  $c = 17.306(3)$  Å,  $\beta = 93.70(3)^\circ$ . Compound **5** is monoclinic.  $P2_1/n$ ,  $Z = 4$ ,  $a = 9.572(2)$ ,  $b = 14.050(3)$ ,  $c = 13.556(3)$  Å,  $\beta = 90.76(3)^\circ$ . The primary bonding in the  $\text{Ph}_3\text{Te}^+$  cation in each salt is a trigonal  $\text{AX}_3\text{E}$  pyramid with Te–C bond lengths in the range 2.095(8)–2.14(2) Å and the bond angles 94.1(6)–100.9(5)°. The weak  $\text{Te}\cdots\text{Cl}$  (**1–3**) and  $\text{Te}\cdots\text{O}$  (**5**) secondary interactions expand the coordination sphere. In **1** and **2** the cation shows a trigonal bipyramidal  $\text{AX}_3\text{YE}$  coordination with one primary Te–C bond and the shortest secondary  $\text{Te}\cdots\text{Cl}$  contact in axial positions and the two other Te–C bonds and the lone-pair in equatorial positions. The cation in **3** shows a distorted octahedral  $\text{AX}_3\text{Y}_3\text{E}$  environment and that in **5** is a more complex  $\text{AX}_3\text{Y}_3\text{Y}'_2$  arrangement. In both latter salts the structure is a complicated three-dimensional network of cations and anions. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Triphenyltelluronium; Tetrachloroaurate; Tetrachloroplatinate; Hexachloroplatinate; Hexachloroiridate; Crystal structures

## 1. Introduction

Organotelluronium salts,  $\text{R}_3\text{TeX}$ , have been known for over a century [1]. In recent years they have attracted considerable interest because of their role in organic synthetic chemistry. For example, it has been reported that the telluronium salts are precursors for telluronium ylides that react with the carbonyl compounds forming a variety of products like oxiranes and secondary alcohols [2].

The X-ray structure determinations of several organotelluronium salts (for some representative examples, see Refs. [3–14]) have established that in the solid state the structural features are governed by weak secondary

tellurium–anion interactions [15] that expand the  $\text{AX}_3\text{E}$  ( $\text{X}$  = bonding pair,  $\text{E}$  = lone pair) trigonal pyramidal geometry around tellurium into a five- or six-coordinate entity. In the absence of these secondary interactions, simple ionic structures are expected [16]. Christian et al. [17] and Collins et al. [13] have discussed the nature of the secondary bonding and rationalized the structures in terms of the coordination geometry around tellurium. It has also been shown that solid-state  $^{125}\text{Te}$ -NMR spectroscopy is a sensitive tool for identification of covalent secondary bonding interactions between the cations and anions [13].

The present study is concerned with the structure and bonding of  $\text{Ph}_3\text{Te}^+$  cation with relatively large counterions. Octahedral hexachloroplatinate  $[\text{PtCl}_6]^{2-}$  and -iridate  $[\text{IrCl}_6]^{2-}$  as well as square planar  $[\text{AuCl}_4]^-$  and  $[\text{PtCl}_4]^{2-}$  were chosen to establish the effect of the

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geometry and the charge of the anion on the cation–anion interactions.

## 2. Experimental

### 2.1. Syntheses

#### 2.1.1. General

The preparation of  $\text{Ph}_3\text{TeCl}$  was carried out as described in the literature [18].  $\text{K}[\text{AuCl}_4]$ ,  $\text{K}_2[\text{PtCl}_6]$  and  $\text{K}_2[\text{IrCl}_6]$  (Aldrich) were used without further purification.  $\text{K}_2[\text{PtCl}_4]$  was prepared by reducing  $\text{K}_2[\text{PtCl}_6]$  with  $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$  [19].

#### 2.1.2. $(\text{Ph}_3\text{Te})_2[\text{PtCl}_6]$ (**1**) and $(\text{Ph}_3\text{Te})_2[\text{IrCl}_6]$ (**2**)

$\text{Ph}_3\text{TeCl}$  (162 mg, 0.42 mmol) in 5 ml of EtOH was added into 5 ml of a hot aqueous solution containing 100 mg (0.21 mmol) of  $\text{K}_2[\text{PtCl}_6]$  or  $\text{K}_2[\text{IrCl}_6]$  resulting in the immediate formation of an orange–yellow or brown precipitate, respectively. The precipitates were filtered, washed with water and EtOH, and dried. Upon recrystallization from nitric acid, orange crystals of  $[\text{Ph}_3\text{Te}]_2[\text{PtCl}_6]$  or dark red crystals of  $[\text{Ph}_3\text{Te}]_2[\text{IrCl}_6]$  were obtained. Yield: **1**, 205 mg (88%); **2**, 165 mg (71%). Anal. Found: C, 38.47; H, 2.56. Calc. for  $\text{C}_{36}\text{H}_{30}\text{Cl}_6\text{PtTe}_2$  (**1**): C, 38.41; H, 2.69%. Anal. Found: C, 38.54; H, 2.55. Calc. for  $\text{C}_{36}\text{H}_{30}\text{Cl}_6\text{IrTe}_2$  (**2**): C, 38.51; H, 2.69%.

#### 2.1.3. $(\text{Ph}_3\text{Te})[\text{AuCl}_4]$ (**3**)

$\text{Ph}_3\text{TeCl}$  (50 mg, 0.13 mmol) in 5 ml of EtOH was added into 5 ml of an ethanolic solution containing 48 mg (0.13 mmol) of  $\text{K}[\text{AuCl}_4]$ . The potassium chloride precipitate was removed by filtration. Upon standing for 3 days in 4 °C, yellow crystals of  $(\text{Ph}_3\text{Te})[\text{AuCl}_4]$  were obtained from the filtrate. Yield: 74 mg (85%). Anal. Found: C, 31.12; H, 2.14. Calc. for  $\text{C}_{18}\text{H}_{15}\text{AuCl}_4\text{Te}$  (**3**): C, 31.00; H, 2.17%.

#### 2.1.4. $(\text{Ph}_3\text{Te})_2[\text{PtCl}_4]$ (**4**)

$\text{Ph}_3\text{TeCl}$  (212 mg, 0.55 mmol) in 5 ml of water was added into 5 ml of a hot aqueous solution containing 112 mg (0.27 mmol) of  $\text{K}_2[\text{PtCl}_4]$ . A pale brown precipitate was obtained almost immediately. The precipitate was filtered, washed with water and  $\text{Et}_2\text{O}$ , and dried. Yield: 155 mg (55%). Anal. Found: C, 40.63; H, 2.63. Calc. for  $\text{C}_{36}\text{H}_{30}\text{Cl}_4\text{PtTe}_2$ : C, 41.00; H, 2.87%.

The recrystallization of **4** from nitric acid with the addition of  $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$  afforded both yellow and colourless crystals. Yellow crystals turned out to be  $\text{K}_2[\text{PtCl}_6]$  and the colourless crystals  $(\text{Ph}_3\text{Te})\cdot(\text{NO}_3)\cdot\text{HNO}_3$  (**5**). Anal. Found: C, 43.94; H, 3.28; N, 5.60. Calc. for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_6\text{Te}$  (**5**): C, 44.67; H, 3.33; N, 5.79%.

### 2.2. X-ray diffraction

Diffraction data for **1–3** and **5** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073$  Å) by recording 360 frames via  $\phi$ -rotation ( $\Delta\phi = 1^\circ$ ; two times 10–20 s per frame). Crystal data and the details of the structure determinations are given in Table 1. All structures were solved by direct methods using SHELXS-97 [20] and refined using SHELXL-97 [21]. After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms in **1–3** were placed in calculated positions in the aromatic rings ( $\text{C–H} = 0.93$  Å). In the final refinement the hydrogen atoms were riding with the carbon atom they were bonded to. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon atom. In the case of **5**, the aromatic hydrogen atoms were treated as described above. The acidic hydrogen atom of the nitric acid molecule, however, could be located in the difference Fourier map after anisotropic refinement of all non-hydrogen atoms. Its position could be refined involving an isotropic thermal parameter.

The scattering factors for the neutral atoms were those incorporated with the programs. Fractional coordinates of all atoms, anisotropic thermal parameters, and the full listing of bond parameters are available as supplementary material.

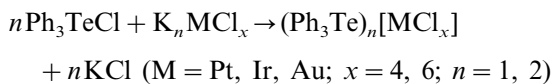
### 2.3. NMR spectroscopy

The  $^{125}\text{Te}$  spectra were recorded on a Bruker DPX400 spectrometer operating at 126.24 MHz. The spectral width was 101.522 kHz, the pulse width was 10.0  $\mu\text{s}$  corresponding to the nuclear tip angle of  $45^\circ$ , and the pulse delay was 1.6 s. Saturated solution of  $\text{H}_6\text{TeO}_6$  (aq.) was used as an external reference. The spectrum was recorded unlocked. Chemical shifts are reported relative to neat  $\text{Me}_2\text{Te}$ . [ $\delta(\text{Me}_2\text{Te}) = \delta(\text{H}_6\text{TeO}_6) + 712$ ].

## 3. Results and discussion

### 3.1. General

The formation of the salts **1–4** is a straightforward metathesis reaction:



$(\text{Ph}_3\text{Te})_2[\text{PtCl}_6]$  (**1**) and  $(\text{Ph}_3\text{Te})_2[\text{IrCl}_6]$  (**2**) are only slightly soluble in water and in ethanol and precipitate

Table 1

Details of the structure determination of (Ph<sub>3</sub>Te)<sub>2</sub>[PtCl<sub>6</sub>] (**1**), (Ph<sub>3</sub>Te)<sub>2</sub>[IrCl<sub>6</sub>] (**2**), (Ph<sub>3</sub>Te)[AuCl<sub>4</sub>] (**3**), and (Ph<sub>3</sub>Te)(NO<sub>3</sub>)·HNO<sub>3</sub> (**5**)

| Compound                                                             | (Ph <sub>3</sub> Te) <sub>2</sub> [PtCl <sub>6</sub> ] ( <b>1</b> ) | (Ph <sub>3</sub> Te) <sub>2</sub> [IrCl <sub>6</sub> ] ( <b>2</b> ) | (Ph <sub>3</sub> Te)[AuCl <sub>4</sub> ] ( <b>3</b> ) | (Ph <sub>3</sub> Te)(NO <sub>3</sub> )·HNO <sub>3</sub> ( <b>5</b> ) |
|----------------------------------------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------|----------------------------------------------------------------------|
| Empirical formula                                                    | C <sub>36</sub> H <sub>30</sub> Cl <sub>6</sub> PtTe <sub>2</sub>   | C <sub>36</sub> H <sub>30</sub> Cl <sub>6</sub> IrTe <sub>2</sub>   | C <sub>18</sub> H <sub>15</sub> Cl <sub>4</sub> TeAu  | C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>6</sub> Te     |
| Relative molecular mass                                              | 1125.59                                                             | 1122.70                                                             | 697.67                                                | 483.98                                                               |
| Crystal system                                                       | Triclinic                                                           | Triclinic                                                           | Monoclinic                                            | Monoclinic                                                           |
| Space group                                                          | <i>P</i> $\bar{1}$                                                  | <i>P</i> $\bar{1}$                                                  | <i>P</i> 2 <sub>1</sub> / <i>c</i>                    | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                   |
| <i>a</i> (Å)                                                         | 10.7535(2)                                                          | 10.7484(2)                                                          | 8.432(2)                                              | 9.572(2)                                                             |
| <i>b</i> (Å)                                                         | 17.2060(1)                                                          | 17.1955(2)                                                          | 14.037(3)                                             | 14.050(3)                                                            |
| <i>c</i> (Å)                                                         | 21.4700(3)                                                          | 21.4744(2)                                                          | 17.306(3)                                             | 13.556(3)                                                            |
| $\alpha$ (°)                                                         | 78.9731(7)                                                          | 78.834(1)                                                           |                                                       |                                                                      |
| $\beta$ (°)                                                          | 77.8650(4)                                                          | 77.649(1)                                                           | 93.70(3)                                              | 90.76(3)                                                             |
| $\gamma$ (°)                                                         | 78.8369(4)                                                          | 78.781(1)                                                           |                                                       |                                                                      |
| <i>V</i> (Å <sup>3</sup> )                                           | 3763.0(1)                                                           | 3754.9(1)                                                           | 2044.1(7)                                             | 1822.9(6)                                                            |
| <i>Z</i>                                                             | 4 <sup>a</sup>                                                      | 4 <sup>a</sup>                                                      | 4                                                     | 4                                                                    |
| $\rho_{\text{calc}}$ (g cm <sup>-3</sup> )                           | 1.987                                                               | 1.986                                                               | 2.267                                                 | 1.763                                                                |
| <i>T</i> (K)                                                         | 293                                                                 | 293                                                                 | 150                                                   | 150                                                                  |
| <i>F</i> (000)                                                       | 2120                                                                | 2116                                                                | 1288                                                  | 952                                                                  |
| $\mu$ (Mo–K $\alpha$ ) (mm <sup>-1</sup> )                           | 5.700                                                               | 5.531                                                               | 9.117                                                 | 1.670                                                                |
| Crystal size (mm)                                                    | 0.40 × 0.35 × 0.10                                                  | 0.25 × 0.20 × 0.10                                                  | 0.20 × 0.10 × 0.10                                    | 0.30 × 0.30 × 0.20                                                   |
| Number of reflections collected                                      | 26 868                                                              | 34 934                                                              | 12 770                                                | 12 787                                                               |
| Number of unique reflections                                         | 13 567                                                              | 13 809                                                              | 4989                                                  | 3569                                                                 |
| Number of observed reflections [ <i>I</i> > 2 <i>s</i> ( <i>I</i> )] | 10 894                                                              | 11 536                                                              | 4521                                                  | 3077                                                                 |
| <i>R</i> <sub>int</sub>                                              | 0.0237                                                              | 0.0284                                                              | 0.0353                                                | 0.0862                                                               |
| <i>R</i> <sub>1</sub> <sup>b</sup>                                   | 0.0383                                                              | 0.0634                                                              | 0.0267                                                | 0.0374                                                               |
| <i>wR</i> <sub>2</sub> <sup>b</sup>                                  | 0.0837                                                              | 0.1529                                                              | 0.0568                                                | 0.0914                                                               |
| <i>R</i> <sub>1</sub> (all data) <sup>b</sup>                        | 0.0533                                                              | 0.0758                                                              | 0.0326                                                | 0.0455                                                               |
| <i>wR</i> <sub>2</sub> (all data) <sup>b</sup>                       | 0.0892                                                              | 0.1570                                                              | 0.0589                                                | 0.0964                                                               |

<sup>a</sup> The asymmetric unit contains two independent (Ph<sub>3</sub>Te)<sub>2</sub>[MCl<sub>6</sub>] (M = Pt, Ir) units.<sup>b</sup> *R*<sub>1</sub> =  $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$ , *wR*<sub>2</sub> =  $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2}$ .

immediately upon mixing of the reagents. Single crystals that are suitable for the X-ray structure determination were obtained by recrystallization from concentrated nitric acid. (Ph<sub>3</sub>Te)[AuCl<sub>4</sub>] (**3**) is soluble in ethanol and X-ray quality crystals were obtained upon prolonged standing at a temperature slightly below the ambient temperature.

The recrystallization of the ale brown precipitate of (Ph<sub>3</sub>Te)<sub>2</sub>[PtCl<sub>6</sub>] (**4**) by evaporating a concentrated nitric acid solution with the prior addition of N<sub>2</sub>H<sub>4</sub>·2HCl afforded a mixture of yellow and colourless crystals. The unit cell parameters and the space group of the yellow crystals indicated them to be K<sub>2</sub>[PtCl<sub>6</sub>].<sup>1</sup> The colourless crystals were shown to be (Ph<sub>3</sub>Te)(NO<sub>3</sub>)·HNO<sub>3</sub> (**5**) by X-ray crystallography.

### 3.2. NMR spectra

The <sup>125</sup>Te-NMR spectra of the compounds **1–4** were recorded in nitric acid. Only one resonance at 754 ppm appears in every solution. The <sup>125</sup>Te-NMR spectrum of (Ph<sub>3</sub>Te)[AuCl<sub>4</sub>] was also recorded in ethanol and exhibited one resonance at 788 ppm. The resonance of Ph<sub>3</sub>TeCl was observed at 754 and 788 ppm in nitric acid and ethanol, respectively. The <sup>125</sup>Te chemical shifts

of the Me<sub>3</sub>Te<sup>+</sup>, Bu<sub>2</sub>PhTe<sup>+</sup>, and MePh<sub>2</sub>Te<sup>+</sup> cations in CDCl<sub>3</sub> have been reported to be 418, 543, and 675 ppm, respectively [2]. The resonance is shifted upfield in an almost linear fashion as the number of phenyl groups in the cation increases. It can be concluded that <sup>125</sup>Te-NMR spectroscopy has confirmed the existence of discrete Ph<sub>3</sub>Te<sup>+</sup> cations in all solutions.

### 3.3. Crystal structures

The crystal structures of (Ph<sub>3</sub>Te)<sub>2</sub>[MCl<sub>6</sub>] [M = Pt (**1**) and Ir (**2**)] are shown in Fig. 1. Those of (Ph<sub>3</sub>Te)[AuCl<sub>4</sub>] (**3**) and (Ph<sub>3</sub>Te)(NO<sub>3</sub>)·HNO<sub>3</sub> (**5**) are shown in Figs. 2 and 3, respectively. All compounds are composed of discrete ions.

The selected bond parameters of **1–3** are shown in Table 2 and those for **5** in Table 3. The Te–C distances span ranges of 2.095(8)–2.131(8) Å in **1**, 2.09(2)–2.14(2) Å in **2**, 2.112(4)–2.122(4) Å in **3**, and 2.117(3)–2.120(3) Å in **5**. These values are quite normal and compare well with those in related aromatic telluronium salts, as exemplified by the mean Te–C<sub>aryl</sub> bond lengths of 2.13(2) and 2.130(4) Å in (Ph<sub>3</sub>Te)(NCS) [7] and Ph<sub>3</sub>TeCl [8], respectively. The bond parameters of the cations in several telluronium salts reported by Collins et al. [13] are also consistent with those of the present salts. The primary Te–C bonds expectedly de-

<sup>1</sup> Cubic, *a* = 9.743(1) Å, space group *Fm*3*m* {c.f. 9.751(5) Å [22]}.

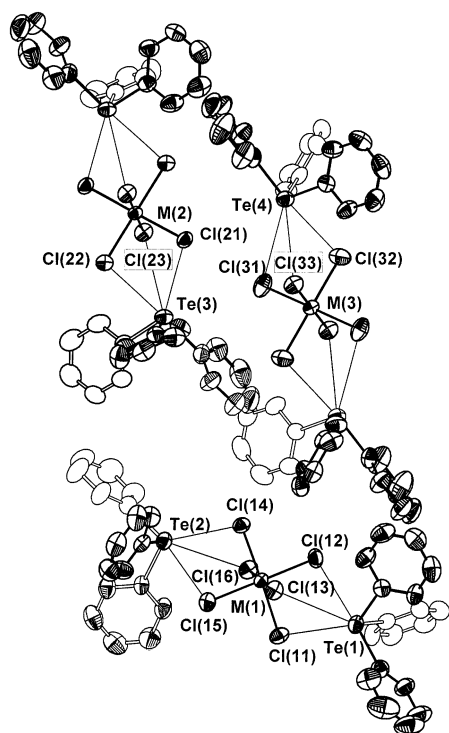


Fig. 1. The molecular structure of  $(\text{Ph}_3\text{Te})_2[\text{MCl}_6]$  [ $\text{M} = \text{Pt}$  (1),  $\text{Ir}$  (2)] indicating the numbering of the atoms. The thermal ellipsoids are drawn at 50% probability level. The atom M(1) occupies a general position with six independent  $\text{Cl}^-$  ligands. The atoms M(2) and M(3) occupy a special position with three independent  $\text{Cl}^-$  ligands. The octahedra are completed by symmetry. Hydrogen atoms have been omitted for clarity.

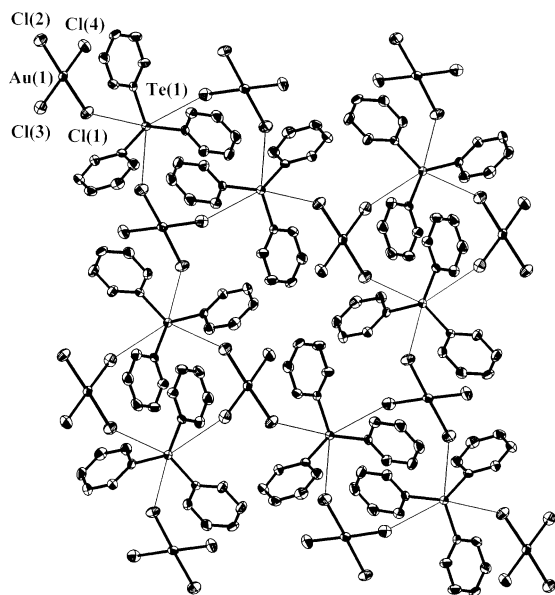


Fig. 2. The molecular structure of  $(\text{Ph}_3\text{Te})[\text{AuCl}_4]$  (3) indicating the numbering of the atoms. The thermal ellipsoids are drawn at 50% probability level. The secondary bonding expands the coordination around tellurium to a distorted  $\text{AX}_3\text{Y}_3\text{E}$  octahedron. Hydrogen atoms have been omitted for clarity.

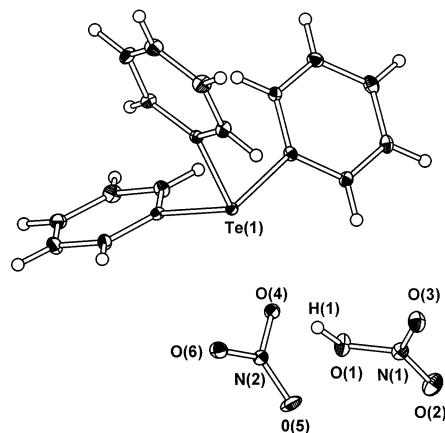


Fig. 3. The molecular structure of  $(\text{Ph}_3\text{Te})(\text{NO}_3)(\text{HNO}_3)$  (5) indicating the numbering of the atoms. The thermal ellipsoids are drawn at 50% probability level.

present a  $\text{AX}_3\text{E}$  trigonal pyramid with the  $\text{C}-\text{Te}-\text{C}$  angles varying between  $93.5(3)$  and  $100.9(3)^\circ$  (mean value  $96.8^\circ$ ) in 1,  $94.1(6)$  and  $100.9(5)^\circ$  (mean value  $96.9^\circ$ ) in 2,  $96.5(1)$  and  $98.7(1)^\circ$  in 3, and  $96.3(1)$  and  $98.0(1)^\circ$  (mean value  $97.0^\circ$ ) in 5. These values are also quite typical (see also Refs. [2–14]).

The orientation of the phenyl rings in the cations can be defined in terms of the angles between the rings and the two opposite  $\text{Te}-\text{C}$  bonds as shown in Fig. 4. Many phenyl rings show a tendency to be approximately parallel with one of the two  $\text{Te}-\text{C}$  bonds and perpendicular to the other. This is consistent with the earlier observation that in aromatic dichalcogenides the planes of the aromatic groups tend to be either parallel or perpendicular to the chalcogen–chalcogen bonds [23]. In the absence of steric effects the orientation of the ring seems to depend on its electron-withdrawing nature. In the present salts, however, the packing interactions cause deviations from the coplanarity.

The bond parameters in the anions of 1–3 are quite normal. The three crystallographically independent  $[\text{MCl}_6]^{2-}$  anions in both 1 and 2 are almost regular octahedra with the bond lengths in the range  $2.317(2)$ – $2.334(2)$  Å in 1 and  $2.322(4)$ – $2.342(4)$  Å in 2. The tetrachloroaurate anion in 3 is also a virtually regular square-plane with the  $\text{Au}-\text{Cl}$  bond lengths of  $2.273(1)$ – $2.294(1)$  Å.

The lattice of 5 incorporates both a nitrate ion and a free nitric acid molecule. The nitrate ions and nitric acid molecules are bound together with a strong, almost symmetric  $\text{O}(1)-\text{H}(1)\cdots\text{O}(4)$  hydrogen bond arrangement (see Table 3). The  $\text{H}(1)-\text{O}(1)$  bond shows a length of  $1.18(7)$  Å and the  $\text{H}(1)\cdots\text{O}(4)$  distance is  $1.32(7)$  Å. The  $\text{O}(1)-\text{H}(1)\cdots\text{O}(4)$  angle is  $159(6)^\circ$ . The resulting  $\text{O}(1)\cdots\text{O}(4)$  distance of  $2.455(4)$  Å indicates a very strong interaction. The  $\text{N}(1)-\text{O}(1)$  and  $\text{N}(2)-\text{O}(4)$  bonds that are involved in the hydrogen bonding are expectedly somewhat longer [ $1.320(4)$  and  $1.318(4)$  Å,

Table 2

Selected bond lengths (Å) and angles (°) in the  $\text{Ph}_3\text{Te}^+$  cation of  $(\text{Ph}_3\text{Te})_2[\text{PtCl}_6]$  (**1**),  $(\text{Ph}_3\text{Te})_2[\text{IrCl}_6]$  (**2**), and  $(\text{Ph}_3\text{Te})[\text{AuCl}_4]$  (**3**)(a)  $(\text{Ph}_3\text{Te})_2[\text{PtCl}_6]$  (**1**) and  $(\text{Ph}_3\text{Te})_2[\text{IrCl}_6]$  (**2**)

|              | <b>1</b> | <b>2</b> |                     | <b>1</b> | <b>2</b> |
|--------------|----------|----------|---------------------|----------|----------|
| Te(1)–C(111) | 2.116(7) | 2.13(1)  | C(111)–Te(1)–C(121) | 99.4(3)  | 98.7(5)  |
| Te(1)–C(121) | 2.110(7) | 2.11(1)  | C(111)–Te(1)–C(131) | 96.4(3)  | 96.2(6)  |
| Te(1)–C(131) | 2.131(8) | 2.14(2)  | C(121)–Te(1)–C(131) | 95.1(3)  | 94.9(6)  |
| Te(2)–C(211) | 2.099(7) | 2.09(2)  | C(211)–Te(2)–C(221) | 99.8(3)  | 100.4(6) |
| Te(2)–C(221) | 2.115(8) | 2.12(1)  | C(211)–Te(2)–C(231) | 95.1(3)  | 95.1(6)  |
| Te(2)–C(231) | 2.130(8) | 2.14(2)  | C(221)–Te(2)–C(231) | 94.8(3)  | 94.7(6)  |
| Te(3)–C(311) | 2.095(8) | 2.09(2)  | C(311)–Te(3)–C(321) | 97.6(3)  | 97.7(6)  |
| Te(3)–C(321) | 2.123(8) | 2.11(1)  | C(311)–Te(3)–C(331) | 98.8(3)  | 99.2(6)  |
| Te(3)–C(331) | 2.101(8) | 2.12(1)  | C(321)–Te(3)–C(331) | 95.1(4)  | 94.6(6)  |
| Te(4)–C(411) | 2.116(7) | 2.10(1)  | C(411)–Te(4)–C(421) | 100.9(3) | 100.9(5) |
| Te(4)–C(421) | 2.120(8) | 2.12(1)  | C(411)–Te(4)–C(431) | 95.5(3)  | 95.7(6)  |
| Te(4)–C(431) | 2.124(8) | 2.13(2)  | C(421)–Te(4)–C(431) | 93.5(3)  | 94.1(6)  |

(b)  $(\text{Ph}_3\text{Te})[\text{AuCl}_4]$  (**3**)

|              |          |                     |         |
|--------------|----------|---------------------|---------|
| Te(1)–C(111) | 2.112(4) | C(111)–Te(1)–C(121) | 96.5(1) |
| Te(1)–C(121) | 2.122(4) | C(111)–Te(1)–C(131) | 98.7(1) |
| Te(1)–C(131) | 2.114(4) | C(121)–Te(1)–C(131) | 98.7(1) |

respectively] than the N–O bonds not involved in the hydrogen bonding [1.209(3)–1.232(3) Å].

### 3.4. Packing

The packing of ions in the lattice depends on the geometry of the anions. In **1** and **2** each crystallographically independent  $[\text{MCl}_6]^{2-}$  show close contacts to two  $\text{Ph}_3\text{Te}^+$  cations on the opposite trigonal faces of the octahedra (see Fig. 1). The resulting three  $\text{Te}\cdots\text{Cl}$  close contacts range 3.331(2)–3.843(2) and 3.313(4)–3.783(4) Å in **1** and **2**, respectively. The shortest distances are clearly shorter than the sums of the van der Waals' radii of tellurium and chlorine of 4.01 Å [24]. The shortest  $\text{Te}\cdots\text{Cl}$  secondary bonding interactions depict an approximate trigonal bipyramidal  $\text{AX}_3\text{YE}$  (Y = a secondary bonding pair) bonding arrangement with the lone-pair and two primary  $\text{Te}-\text{C}$  bonds occupying the equatorial positions. The third  $\text{Te}-\text{C}$  bond and the  $\text{Te}\cdots\text{Cl}$  secondary interactions occupy the axial positions. As seen in Table 4, the axial  $\text{Te}-\text{C}$  bond in each  $\text{Ph}_3\text{Te}^+$  cation is expectedly somewhat longer than the two equatorial bonds. The effect is very small and has barely statistical significance, but is quite consistent. This trend is in agreement with the *trans*-relationships between the secondary and primary bonding discussed by Christian et al. [17].

The discrete  $\text{Ph}_3\text{Te}\cdots\text{MCl}_6\cdots\text{TePh}_3$  units are further joined together by weak hydrogen bonds involving phenyl hydrogen atoms from the cation and chlorine atoms of the anion.

In  $(\text{Ph}_3\text{Te})[\text{AuCl}_4]$  (**3**) the cation and the anion form a continuous network as shown in Fig. 2. Three  $\text{Te}\cdots\text{Cl}$  close contacts of 3.064(4)–3.400(1) Å from three different  $[\text{AuCl}_4]^-$  anions result in the octahedral coordination around tellurium and indicate a  $\text{AX}_3\text{Y}_3\text{E}$

secondary bonding arrangement with  $\text{Cl}(1)\cdots\text{Te}(1)-\text{C}(11)$ ,  $\text{Cl}(2)\cdots\text{Te}(1)-\text{C}(31)$ , and  $\text{Cl}(3)\cdots\text{Te}(1)-\text{C}(21)$  angles of 171.6, 159.0, and 162.7°, respectively.

The packing arrangements and the geometry around tellurium due to the secondary bonding can be compared to those observed in  $\text{Ph}_3\text{TeCl}$  [11] and  $\text{Ph}_3\text{TeCl}\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$  [12]. In the former the ions combine to form discrete dimers. The  $\text{Te}\cdots\text{Cl}$  distances range

Table 3

Selected bond lengths (Å) and angles (°) in  $(\text{Ph}_3\text{Te})(\text{NO}_3)\cdot(\text{HNO}_3)$  (**5**)

| Bond lengths        |          |                |          |
|---------------------|----------|----------------|----------|
| Te(1)–C(111)        | 2.117(3) | N(2)–O(4)      | 1.318(4) |
| Te(1)–C(121)        | 2.120(3) | N(2)–O(5)      | 1.209(4) |
| Te(1)–C(131)        | 2.118(4) | N(2)–O(6)      | 1.232(3) |
| N(1)–O(1)           | 1.320(4) | H(1)–O(1)      | 1.18(7)  |
| N(1)–O(2)           | 1.210(4) | H(1)–O(4)      | 1.32(7)  |
| N(1)–O(3)           | 1.222(4) |                |          |
| Bond angles         |          |                |          |
| C(111)–Te(1)–C(121) | 96.3(1)  | O(4)–N(2)–O(5) | 119.2(3) |
| C(111)–Te(1)–C(131) | 98.0(1)  | O(4)–N(2)–O(6) | 116.2(3) |
| C(121)–Te(1)–C(131) | 96.6(1)  | O(5)–N(2)–O(6) | 124.6(3) |
| O(1)–N(1)–O(2)      | 116.9(3) | N(1)–O(1)–H(1) | 103(3)   |
| O(1)–N(1)–O(3)      | 117.8(3) | N(2)–O(4)–H(1) | 108(3)   |
| O(2)–N(1)–O(3)      | 125.2(3) | O(1)–H(1)–O(4) | 159(6)   |

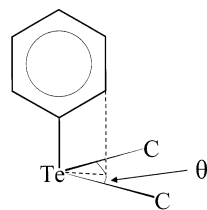


Fig. 4. The orientation of the phenyl ring with respect to the two opposite  $\text{Te}-\text{C}$  bonds.

Table 4

The trigonal bipyramidal  $AX_3YE$  geometry of tellurium in  $(Ph_3Te)_2[PtCl_6]$  (**1**) and  $(Ph_3Te)_2[IrCl_6]$  (**2**)

| $(Ph_3Te)_2[PtCl_6]$ ( <b>1</b> ) |        |             |          |               | $(Ph_3Te)_2[IrCl_6]$ ( <b>2</b> ) |          |               |
|-----------------------------------|--------|-------------|----------|---------------|-----------------------------------|----------|---------------|
|                                   |        | Cl...Te (Å) | Te–C (Å) | Cl...Te–C (°) | Cl...Te (Å)                       | Te–C (Å) | Cl...Te–C (°) |
| Cl(12)...Te(1)                    | C(111) | 3.411(2)    | 2.116(7) | 80.5          | 3.382(4)                          | 2.13(1)  | 80.7          |
| Cl(12)...Te(1)                    | C(121) | 3.411(2)    | 2.110(7) | 90.3          | 3.382(4)                          | 2.11(1)  | 90.1          |
| Cl(12)...Te(1)                    | C(131) | 3.411(2)    | 2.131(8) | 174.1         | 3.382(4)                          | 2.14(2)  | 174.5         |
| Cl(15)...Te(2)                    | C(211) | 3.348(2)    | 2.099(7) | 74.1          | 3.328(4)                          | 2.09(2)  | 74.9          |
| Cl(15)...Te(2)                    | C(221) | 3.348(2)    | 2.115(8) | 81.9          | 3.328(4)                          | 2.12(1)  | 82.4          |
| Cl(15)...Te(2)                    | C(231) | 3.348(2)    | 2.130(8) | 167.8         | 3.328(4)                          | 2.14(2)  | 168.7         |
| Cl(22)...Te(3)                    | C(311) | 3.416(2)    | 2.095(8) | 73.9          | 3.384(4)                          | 2.09(2)  | 74.6          |
| Cl(22)...Te(3)                    | C(321) | 3.416(2)    | 2.123(8) | 171.3         | 3.384(4)                          | 2.11(1)  | 172.0         |
| Cl(22)...Te(3)                    | C(331) | 3.416(2)    | 2.101(8) | 87.8          | 3.384(4)                          | 2.12(1)  | 88.2          |
| Cl(32)...Te(4)                    | C(411) | 3.331(2)    | 2.116(7) | 84.3          | 3.313(4)                          | 2.10(1)  | 84.6          |
| Cl(32)...Te(4)                    | C(421) | 3.331(2)    | 2.120(8) | 79.0          | 3.313(4)                          | 2.12(1)  | 79.5          |
| Cl(32)...Te(4)                    | C(431) | 3.331(2)    | 2.124(8) | 172.2         | 3.313(4)                          | 2.13(2)  | 173.4         |

3.142(1)–3.234(1) Å and the coordination around tellurium is a distorted trigonal bipyramid with an  $AX_3Y_2E$  arrangement. In contrast the cations and anions in the solvated salt form a tetrameric structural unit with two different environments around tellurium. One shows an octahedral  $AX_3Y_3E$  arrangement and the other a five-coordinated  $AX_3Y_2E$  arrangement with one vacant secondary bond position blocked by a phenyl group [12].

The structure of  $(Ph_3Te)(NO_3) \cdot HNO_3$  (**5**) consists of two rows of  $Ph_3Te^+$  cations that are bound together by nitrate ions and nitric acid molecules, as shown in Fig. 5. The environment around tellurium is rather complex. There are five Te...O contacts, two of which are due to the nitric acid molecule and three due to two nitrate ions, one oxygen atom acting as a bridge between two  $Ph_3Te^+$  cations. The distances involving nitric acid oxygen atoms O(2) and O(3) [3.550(3) and 3.482(3) Å, respectively] are longer than those involving the nitrate oxygen atoms O(1) and the bridging O(4) [3.083(3) and 3.087(3)–3.119(3), respectively]. Since the angles  $\angle C(131)-Te(1) \cdots O(2)$ ,  $\angle C(121)-Te(1) \cdots O(4)$ , and  $\angle C(111)-Te(1) \cdots O(6)$  are approximately  $180^\circ$  (168.8, 174.3, and 167.9, respectively), the bonding arrangement can best be described as  $AX_3Y_3Y_2E$ . A similar environment around tellurium has been observed for  $(TeF_3)_2(SO_4)$  [17].

#### 4. Conclusions

In this paper we have reported the preparation of four triphenyltelluronium salts  $(Ph_3Te)_n[MCl_x]$  ( $M = Pt, Ir, Au$ ;  $x = 4, 6$ ;  $n = 1, 2$ ) (**1–4**) in order to study the effect of the size, geometry, and charge of a rather bulky anion on the cation–anion interactions. The recrystallization of  $(Ph_3Te)_2[PtCl_4]$  (**4**) resulted in the formation of  $K_2[PtCl_6]$  and  $(Ph_3Te)(NO_3) \cdot HNO_3$  (**5**).

The X-ray structures of **1–3**, and **5** have shown that the cation–anion interactions are significant in governing the coordination geometry around tellurium and the overall structural features. The primary bonding in the  $Ph_3Te^+$  cation in each salt is a trigonal  $AX_3E$  pyramid. The weak secondary interactions expand the coordination sphere. In  $(Ph_3Te)_2[MCl_6]$  ( $M = Pt$  (**1**),  $Ir$  (**2**)) the cation shows a trigonal bipyramidal  $AX_3YE$  coordination with one primary Te–C bond and the shortest

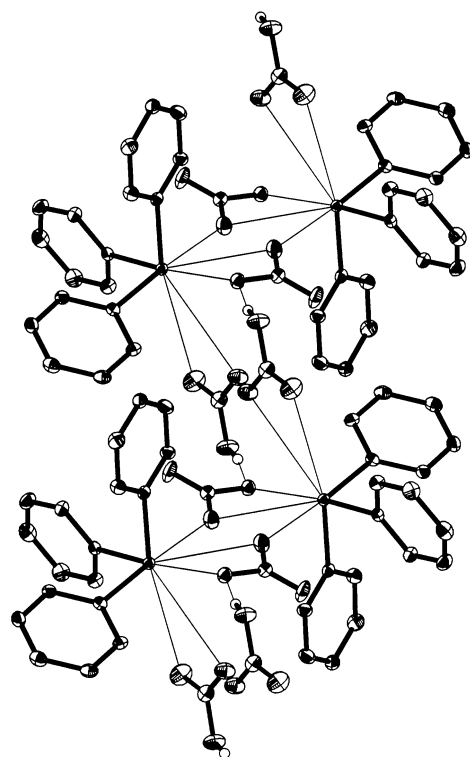


Fig. 5. The packing of the ions in the lattice of  $(Ph_3Te)(NO_3)(HNO_3)$  (**5**). The secondary bonding expands the coordination around tellurium to an  $AX_3Y_3Y_2E$  arrangement. Hydrogen atoms have been omitted for clarity.

secondary Te...Cl contact occupying the axial positions and the two other Te–C bonds and the lone-pair occupying the equatorial positions. Both compounds show discrete  $\text{Ph}_3\text{Te}\cdots[\text{MCl}_6]\cdots\text{TePh}_3$  that are joined together by hydrogen bonds. The cation in  $(\text{Ph}_3\text{Te})[\text{AuCl}_4]$  (**3**) shows a distorted octahedral  $\text{AX}_3\text{Y}_3\text{E}$  environment and that in  $(\text{Ph}_3\text{Te})(\text{NO}_3)\cdot\text{HNO}_3$  (**5**) is a more complex  $\text{AX}_3\text{Y}_3\text{Y}'_2$  arrangement. In both latter salts the structure is a complicated three-dimensional network of cations and anions.

## 5. Supplementary material

Crystallographic information for compounds **1–3** and **5** has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 163383–163386. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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