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## Bis(tetraphenylarsonium) Hexafluoridotechnetate(IV) Dihydrate: Preparation, Structure and Spectroscopic Analysis

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# Bis(tetraphenylarsonium) hexafluoridotechnetate(IV) dihydrate: preparation, structure and spectroscopic analysis

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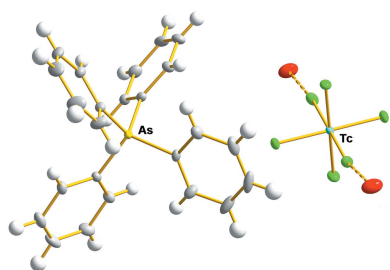
**CCDC reference:** 1962597

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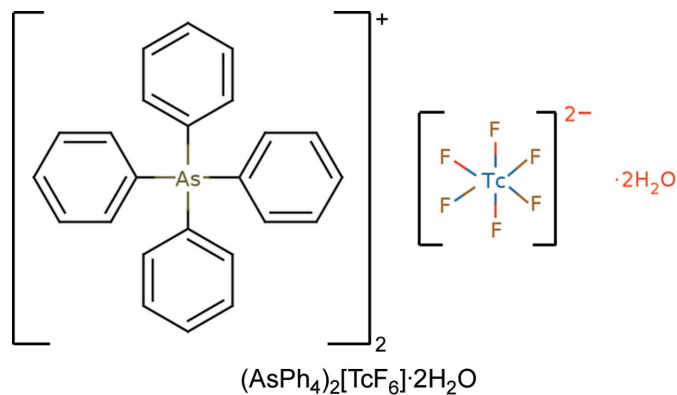
Reports of quadrivalent transition-metal fluoride salts containing bulky organic cations are limited. In this context, we prepared the bis(tetraphenylarsonium) hexafluoridotechnetate(IV) dihydrate salt,  $(C_{24}H_{20}As)_2[TcF_6] \cdot 2H_2O$ , by a cation metathesis reaction of  $(NH_4)_2[TcF_6]$  in water. This is the first report of an arsonium salt of the hexafluoridotechnetate(IV) dianion.  $(AsPh_4)_2[TcF_6] \cdot 2H_2O$  crystallizes in the triclinic space group  $P\bar{1}$ . The  $[TcF_6]^{2-}$  anion adopts a slightly distorted octahedral geometry with an average Tc–F bond length of 1.933 Å. The cyclic voltammogram of  $(AsPh_4)_2[TcF_6] \cdot 2H_2O$  in  $CH_3CN$  shows a one-electron reversible oxidation wave at 1.496 V.

## 1. Introduction

In technetium fluoride chemistry, the first studies focused on the higher oxidation state, binary fluoride, and oxo complexes (Selig *et al.*, 1961; Edwards *et al.*, 1968, 1970; Mercier & Schrobilgen, 1993; LeBlond & Schrobilgen, 1996; Casteel *et al.*, 1998; LeBlond *et al.*, 2000*a,b*; LeBlond & Schrobilgen, 2001; Drews *et al.*, 2006; Supel *et al.*, 2007). In the intermediate oxidation state, salts of hexafluoridotechnetate(IV) have been known for almost 50 years, whereas the binary fluoride, *i.e.*  $Tc^{IV}F_4$ , has been predicted recently by first-principles calculations (Weck *et al.*, 2009). A quadrivalent technetium fluoride salt,  $K_2[TcF_6]$ , was first prepared by the solid-state melt reaction of  $K_2[TcBr_6]$  with  $KHF_2$ , followed by aqueous work-up (Schwochau & Herr, 1963). Alberto & Anderegg (1985) reported an improved procedure for the preparation of  $K_2[TcF_6]$  by the treatment of  $K_2[TcBr_6]$  with HF (40%) and AgF. The first reported crystallographic information on a  $[TcF_6]^{2-}$  salt is a powder X-ray diffraction study of  $K_2[TcF_6]$  (Schwochau & Herr, 1963), while other alkali metal salts of  $[TcF_6]^{2-}$  have been reported occasionally and do not contain any details of these compounds (Schwochau, 1964). The re-investigation of the preparation, spectroscopic and solid-state structures of hexafluoridotechnetate(IV) was reported recently, however, its structural chemistry is limited to alkali metals, ammonium, and tetramethylammonium salts (Balasekaran *et al.*, 2013). These  $Tc^{IV}$  salts were obtained by metathesis reactions or by reduction of pertechnetate with sodium dithionate or zinc dust in the presence of  $HF_{(aq)}$ . The structures of  $M_2[TcF_6]$  ( $M = NH_4, Na, K, Rb,$  and  $Cs$ ) display the trigonal space group  $P\bar{3}m1$ , and that of  $(NMe_4)_2[TcF_6]$  is rhombohedral  $R\bar{3}$ . These solid-state structures are stabilized by cation and anion interactions, which are also the reason for their solubility being limited to only water and aqueous HF.



Tchnetium precursors known in the form of tetraphenylarsonium salts are  $\text{AsPh}_4[\text{TcO}_4]$  (Bandoli *et al.*, 1982),  $\text{AsPh}_4[\text{TcOCl}_4]$  (Baldas & Colmanet, 1989),  $\text{AsPh}_4[\text{TcNCl}_4]$  (Figgis *et al.*, 1996),  $\text{AsPh}_4[\text{TcNBr}_4]$  (Baldas *et al.*, 1985), and  $(\text{AsPh}_4)_2[\text{TcCl}_6]$  (Baldas *et al.*, 1984). Baldas *et al.* (1984) determined the crystal structure of the salt tetraphenylarsonium hexachlorotechnetate(IV), which crystallized in the triclinic space group  $P\bar{1}$ . Quadrivalent transition-metal fluoride salts containing bulky organic cations are limited to  $(\text{PPh}_4)[\text{MF}_6] \cdot 2\text{H}_2\text{O}$  ( $M = \text{Zr, Re, Ir, and Os}$ ) (Pedersen *et al.*, 2014, 2016, 2017). These salts were prepared by the cation metathesis reaction of highly water-soluble  $(\text{NH}_4)_2[\text{MF}_6]$  ( $M = \text{Zn and Re}$ ) or  $\text{Na}_2[\text{MF}_6]$  ( $M = \text{Ir and Os}$ ) with  $\text{PPh}_4\text{Cl}$  in water. In this context, we prepared the tetraphenylarsonium salt of  $[\text{TcF}_6]^{2-}$  and characterized it in the solid state by single-crystal X-ray diffraction (SCXRD) and in solution by UV–Vis spectroscopy and cyclic voltammetry.



## 2. Experimental

**Caution!**  $^{99}\text{Tc}$  is a  $\beta^-$  emitter ( $E_{\text{max}} = 0.29 \text{ MeV}$ ). All operations relating to the synthesis of this sample were performed in a licensed radiochemical laboratory. Appropriate shielding was employed during all manipulations for the loading of samples into containers for examination.

Ammonium bifluoride, tetraphenylarsonium chloride, acetonitrile, and hydrobromic acid (48%) were purchased from Sigma–Aldrich and used without further purification. This work was performed in a well-ventilated fume hood due to the corrosive nature of bifluoride.  $(\text{NH}_4)_2[\text{TcBr}_6]$  was prepared as described in the literature (Dalziel *et al.*, 1958) and the detailed syntheses of  $(\text{NH}_4)_2[\text{TcF}_6]$  and  $(\text{AsPh}_4)_2[\text{TcF}_6] \cdot 2\text{H}_2\text{O}$  are described below.

### 2.1. Synthesis and crystallization

**2.1.1. Preparation of  $(\text{NH}_4)_2[\text{TcF}_6]$ .**  $(\text{NH}_4)_2[\text{TcF}_6]$  was prepared by melting  $(\text{NH}_4)_2[\text{TcBr}_6]$  (612 mg, 1 mmol) with an excess of  $\text{NH}_4\text{HF}_2$  (2 g, 0.35 mol) in a nickel crucible at 573 K for 20 min in a box furnace. The resulting pale-pink–grey solid product which formed was allowed to cool to room temperature and was washed with MeOH (10  $\times$  10 ml). Subsequently, the product was washed with several aliquots of an  $\text{H}_2\text{O}/\text{MeOH}$  mixture (3  $\times$  5 ml, 1:4 v/v) and centrifuged. The resulting pink solid was dissolved in warm water (5 ml) and

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	$(\text{C}_{24}\text{H}_{20}\text{As})_2[\text{TcF}_6] \cdot 2\text{H}_2\text{O}$
$M_r$	1010.64
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
$a, b, c$ (Å)	10.043 (2), 11.036 (2), 21.159 (4)
$\alpha, \beta, \gamma$ (°)	75.991 (3), 77.963 (3), 71.388 (3)
$V$ (Å <sup>3</sup> )	2134.3 (7)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.94
Crystal size (mm)	0.36 $\times$ 0.18 $\times$ 0.11
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Numerical (SADABS; Krause <i>et al.</i> , 2015; Bruker, 2017)
$T_{\text{min}}, T_{\text{max}}$	0.40, 0.82
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	30509, 10713, 9659
$R_{\text{int}}$	0.027
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.061, 1.07
No. of reflections	10713
No. of parameters	532
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.85, -1.28

Computer programs: APEX2 (Bruker, 2017), SAINT (Bruker, 2017), SHELXT2014 (Sheldrick, 2015a), SHELXL2016 (Sheldrick, 2015b), shelXle (Hübschle *et al.*, 2011) and DIAMOND (Brandenburg & Putz, 2005).

the solution evaporated slowly at room temperature. Colorless crystals of  $(\text{NH}_4)_2[\text{TcF}_6]$  were obtained (yield: 175 mg, 0.7 mmol, 70%).

**2.1.2. Preparation of  $(\text{AsPh}_4)_2[\text{TcF}_6] \cdot 2\text{H}_2\text{O}$ .** A saturated aqueous solution of  $\text{AsPh}_4\text{Cl}$  (188 mg, 0.45 mmol) was added to a saturated aqueous solution of  $(\text{NH}_4)_2[\text{TcF}_6]$  (50 mg, 0.2 mmol). The resulting mixture was left to stand for 24 h to give  $(\text{AsPh}_4)_2[\text{TcF}_6] \cdot 2\text{H}_2\text{O}$  (yield: 176 mg, 0.175 mmol, 88%). UV–Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda = 230$  ( $\epsilon = 26820 \text{ M}^{-1} \text{ cm}^{-1}$ ), 259 ( $\epsilon = 8314 \text{ M}^{-1} \text{ cm}^{-1}$ ), 264 ( $\epsilon = 10240 \text{ M}^{-1} \text{ cm}^{-1}$ ), 271 ( $\epsilon = 8376 \text{ M}^{-1} \text{ cm}^{-1}$ ), and 352 nm ( $\epsilon = 250 \text{ M}^{-1} \text{ cm}^{-1}$ ).

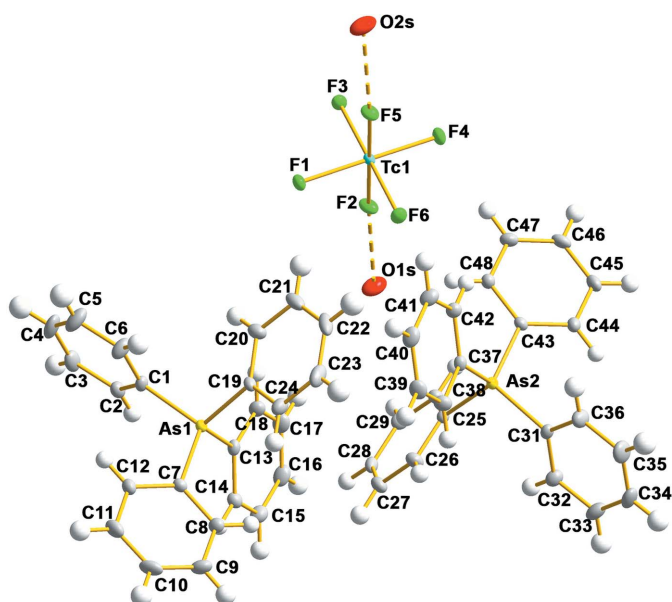
### 2.2. Refinement

Crystal data, data collection and structure refinement details for  $(\text{AsPh}_4)_2[\text{TcF}_6] \cdot 2\text{H}_2\text{O}$  are summarized in Table 1. The aromatic H atoms were refined using a riding model, with  $\text{C}–\text{H} = 0.95 \text{ Å}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The H atoms of the water molecules were not located and were therefore not included in the refinement.

## 3. Results and discussion

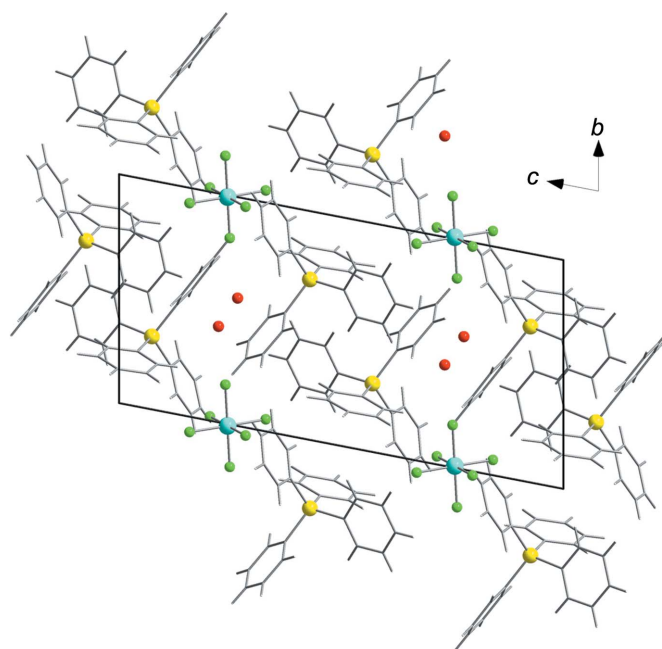
### 3.1. Crystal structure analysis

The title compound,  $(\text{AsPh}_4)_2[\text{TcF}_6] \cdot 2\text{H}_2\text{O}$ , is the first reported arsonium salt of the hexafluorotechnetate(IV) dianion. Colorless crystals were obtained in a day from an aqueous solution mixture of  $(\text{NH}_4)_2[\text{TcF}_6]$  and  $\text{AsPh}_4\text{Cl}$  at room temperature.  $(\text{AsPh}_4)_2[\text{TcF}_6] \cdot 2\text{H}_2\text{O}$  crystallizes in the


**Figure 1**

The molecular structure of the cation and anion in  $(\text{AsPh}_4)_2[\text{TcF}_6]\cdot 2\text{H}_2\text{O}$ , with displacement ellipsoids drawn at the 50% probability level. Color key: Tc turquoise, F green, O red, As yellow, C grey, and H white.

triclinic crystal space group  $P\bar{1}$ . The asymmetric unit consists of two independent  $(\text{AsPh}_4)^+$  cations, one  $[\text{TcF}_6]^{2-}$  anion, and two cocrystallized water molecules. The molecular structure of  $(\text{AsPh}_4)_2[\text{TcF}_6]\cdot 2\text{H}_2\text{O}$  is shown in Fig. 1 and the packing of the structural units in the unit cell in Fig. 2. Selected bond lengths and angles are given in Table 2. The  $[\text{TcF}_6]^{2-}$  anion exhibits a slightly distorted octahedral geometry, with Tc–F bond lengths varying from 1.9266 (10) to 1.9487 (10) Å and an average Tc–F distance of 1.933 Å. This value is very similar to those observed in  $M_2[\text{TcF}_6]$  ( $M = \text{Rb}$  and  $\text{Cs}$ ) and slightly longer than those observed in  $A_2[\text{TcF}_6]$  ( $A = \text{Na}$ ,  $\text{K}$ ,  $\text{NH}_4$ , and  $\text{NMe}_4$ ) (Balasekaran *et al.*, 2013). The angles around the Tc atom are close to octahedral values (Table 2).

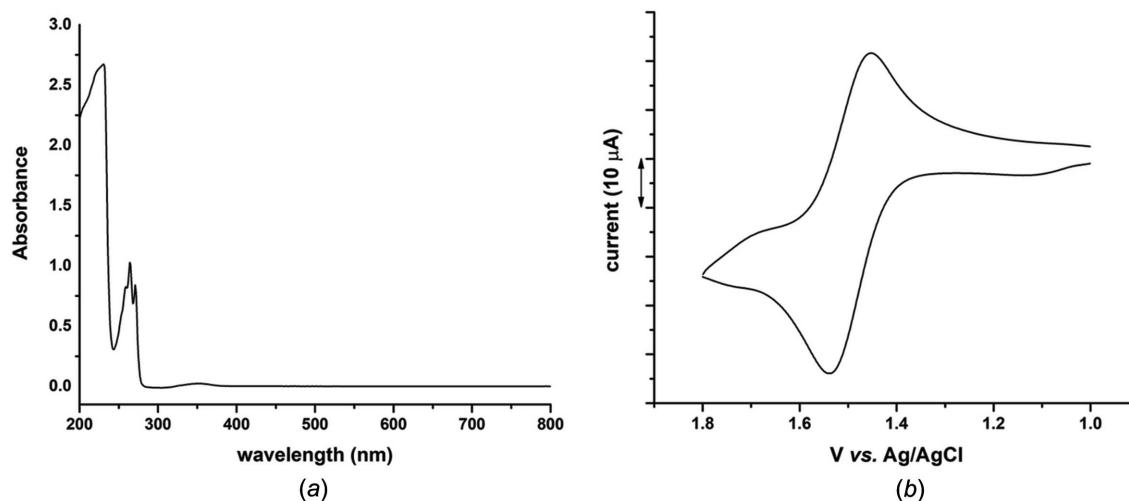

**Figure 2**

Unit-cell representation of  $(\text{AsPh}_4)_2[\text{TcF}_6]\cdot 2\text{H}_2\text{O}$ .

The  $[\text{AsPh}_4]^+$  cation adopts a distorted tetrahedral configuration in which the phenyl groups are attached asymmetrically (Fig. 1). The As–C bond lengths (Table 2) are similar to those reported for  $(\text{AsPh}_4)[\text{TcCl}_6]$  (Baladas *et al.*, 1984),  $(\text{AsPh}_4)_2[\text{ReBr}_6]$  (Kochel, 2007) and  $(\text{AsPh}_4)_2[\text{ZrCl}_6]$  (Borjas *et al.*, 2018). The tetragonal distortion of the As atom in the  $[\text{AsPh}_4]^+$  cation is less severe, with only a  $2.5^\circ$  difference between the C–As–C angles.

### 3.2. Spectroscopic analysis

The UV–Vis spectrum of  $(\text{AsPh}_4)_2[\text{TcF}_6]\cdot 2\text{H}_2\text{O}$  (Fig. 3a) was recorded in  $\text{CH}_3\text{CN}$  and exhibits the bands listed in §2.1.2. The band at 352 nm was also reported for  $M_2[\text{TcF}_6]$  ( $M = \text{K}$ ,


**Figure 3**

(a) UV–Vis spectrum of  $(\text{AsPh}_4)_2[\text{TcF}_6]\cdot 2\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$ . (b) Cyclic voltammogram of  $(\text{AsPh}_4)_2[\text{TcF}_6]\cdot 2\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}/n\text{-Bu}_4\text{NPF}_6$  solution ( $100 \text{ mV s}^{-1}$ ). Potentials are referenced to  $\text{Ag}/\text{AgCl}$ .

**Table 2**  
Selected geometric parameters (Å, °).

Tc1—F1	1.9312 (9)	Tc1—F6	1.9266 (10)
Tc1—F2	1.9487 (10)	As1—C1	1.9053 (15)
Tc1—F3	1.9282 (9)	As1—C7	1.9046 (15)
Tc1—F4	1.9233 (9)	As1—C13	1.9077 (15)
Tc1—F5	1.9414 (10)	As1—C19	1.9041 (15)
F4—Tc1—F6	90.13 (4)	F6—Tc1—F2	88.85 (4)
F4—Tc1—F3	90.21 (4)	F3—Tc1—F2	91.42 (4)
F6—Tc1—F3	179.56 (4)	F1—Tc1—F2	89.71 (4)
F4—Tc1—F1	179.36 (4)	F5—Tc1—F2	179.51 (4)
F6—Tc1—F1	89.85 (4)	C19—As1—C7	109.81 (7)
F3—Tc1—F1	89.81 (4)	C19—As1—C1	108.65 (7)
F4—Tc1—F5	90.53 (4)	C7—As1—C1	110.07 (7)
F6—Tc1—F5	90.69 (4)	C19—As1—C13	109.00 (7)
F3—Tc1—F5	89.03 (4)	C7—As1—C13	111.30 (7)
F1—Tc1—F5	90.11 (4)	C1—As1—C13	107.96 (7)
F4—Tc1—F2	89.65 (4)		

Rb, and Cs) (Balasekaran *et al.*, 2013). The electrochemical properties of (AsPh<sub>4</sub>)<sub>2</sub>[TcF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O were investigated by cyclic voltammetry in acetonitrile and compared with those of (*n*-Bu<sub>4</sub>N)[TcX<sub>6</sub>] (*X* = Cl and Br) (Trop *et al.*, 1979).

For [TcX<sub>6</sub>]<sup>2−</sup> (*X* = Cl and Br) it has been shown that one irreversible oxidation wave at +1.88 (*X* = Cl<sup>−</sup>) and +1.70 V (*X* = Br<sup>−</sup>) versus SCE corresponding to Tc<sup>4+</sup> → Tc<sup>5+</sup>, and one irreversible reduction corresponding to Tc<sup>4+</sup> → Tc<sup>3+</sup> at −0.34 and −0.27 V, respectively (Trop *et al.*, 1979). The cyclic voltammogram of (AsPh<sub>4</sub>)<sub>2</sub>[TcF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O exhibits a reversible one-electron oxidation wave (*E*<sub>1/2</sub> = 1.496 V versus Ag/AgCl) (Fig. 3*b*) corresponding to the formation of Tc<sup>5+</sup>. In the [TcX<sub>6</sub>]<sup>2−</sup> (*X* = F, Cl, and Br) series, the oxidation potentials are in the order Cl > Br > F and indicate that the fluorinated species is less oxidative than the heavier halogens.

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### References

Alberto, R. & Anderegg, G. (1985). *Polyhedron*, **4**, 1067.  
Balasekaran, S. M., Molski, M., Spandl, J., Hagenbach, A., Alberto, R. & Abram, U. (2013). *Inorg. Chem.* **52**, 7094–7099.  
Baldas, J., Bonnyman, J., Samuels, D. L. & Williams, G. A. (1984). *Acta Cryst.* **C40**, 1343–1346.  
Baldas, J., Bonnyman, J. & Williams, G. A. (1985). *Aust. J. Chem.* **38**, 215–219.

Baldas, J. & Colmanet, S. F. (1989). *Aust. J. Chem.* **42**, 1155–1159.  
Bandoli, G., Clemente, D. A., Mazzi, U. & Roncari, E. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1381–1384.  
Borjas, R., Mariappan Balasekaran, S. & Poineau, F. (2018). *IUCrData*, **3**, x180528.  
Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
Bruker (2017). *APEX2, SAINT, and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Casteel, W. J., Dixon, D. A., LeBlond, N., Mercier, H. P. A. & Schrobilgen, G. J. (1998). *Inorg. Chem.* **37**, 340–353.  
Dalziel, J., Gill, N. S., Nyholm, R. S. & Peacock, R. D. (1958). *J. Chem. Soc.* pp. 4012–4016.  
Drews, T., Supel, J., Hagenbach, A. & Seppelt, K. (2006). *Inorg. Chem.* **45**, 3782–3788.  
Edwards, A. J., Jones, G. R. & Sills, R. J. C. (1968). *Chem. Commun.* pp. 1177–1178.  
Edwards, A. J., Jones, G. R. & Sills, R. J. C. (1970). *J. Chem. Soc. A*, pp. 2521–2523.  
Figgis, B. N., Reynolds, P. A., Larsen, F. K., Williams, G. A. & Delfs, C. D. (1996). *Aust. J. Chem.* **49**, 633–637.  
Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). *J. Appl. Cryst.* **44**, 1281–1284.  
Kochel, A. (2007). *Acta Cryst.* **E63**, m596–m597.  
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.  
LeBlond, N., Dixon, D. A. & Schrobilgen, G. J. (2000*a*). *Inorg. Chem.* **39**, 2473–2487.  
LeBlond, N., Mercier, H. P. A., Dixon, D. A. & Schrobilgen, G. J. (2000*b*). *Inorg. Chem.* **39**, 4494–4509.  
LeBlond, N. & Schrobilgen, G. J. (1996). *Chem. Commun.* pp. 2479–2480.  
LeBlond, N. & Schrobilgen, G. J. (2001). *Inorg. Chem.* **40**, 1245–1249.  
Mercier, H. P. A. & Schrobilgen, G. J. (1993). *Inorg. Chem.* **32**, 145–151.  
Pedersen, K. S., Bendix, J., Tressaud, A., Durand, E., Weihe, H., Salman, Z., Morsing, T. J., Woodruff, D. N., Lan, Y., Wernsdorfer, W., Mathonière, C., Piligkos, S., Klokishner, S. I., Ostrovsky, S., Ollefs, K., Wilhelm, F., Rogalev, A. & Clérac, R. (2016). *Nat. Commun.* **7**, 12195.  
Pedersen, K. S., Sigrist, M., Sørensen, M. A., Barra, A.-L., Weyhermüller, T., Piligkos, S., Thuesen, C. A., Vinum, M. G., Mutka, H., Weihe, H., Clérac, R. & Bendix, J. (2014). *Angew. Chem. Int. Ed.* **53**, 1351–1354.  
Pedersen, K. S., Woodruff, D. N., Singh, S. K., Tressaud, A., Durand, E., Atanasov, M., Perlepe, P., Ollefs, K., Wilhelm, F., Mathonière, C., Neese, F., Rogalev, A., Bendix, J. & Clérac, R. (2017). *Chem. Eur. J.* **23**, 11244–11248.  
Schwochau, K. (1964). *Z. Naturforsch. Teil A*, **19**, 1237–1238.  
Schwochau, K. & Herr, W. (1963). *Angew. Chem.* **75**, 95.  
Selig, H., Chernick, C. L. & Malm, J. G. (1961). *J. Inorg. Nucl. Chem.* **19**, 377.  
Sheldrick, G. M. (2015*a*). *Acta Cryst.* **A71**, 3–8.  
Sheldrick, G. M. (2015*b*). *Acta Cryst.* **C71**, 3–8.  
Supel, J., Abram, U., Hagenbach, A. & Seppelt, K. (2007). *Inorg. Chem.* **46**, 5591–5595.  
Trop, H. S., Davison, A., Carey, G. H., DePamphilis, B. V., Jones, A. G. & Davis, M. A. (1979). *J. Inorg. Nucl. Chem.* **41**, 271–272.  
Weck, P. F., Kim, E., Poineau, F., Rodriguez, E. E., Sattelberger, A. P. & Czerwinski, K. R. (2009). *Inorg. Chem.* **48**, 6555–6558.

## supporting information

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## Bis(tetraphenylarsonium) hexafluoridotechnetate(IV) dihydrate: preparation, structure and spectroscopic analysis

**Samundeeswari Mariappan Balasekaran and Frederic Poineau**

### Computing details

Data collection: *APEX2* (Bruker, 2017); cell refinement: *SAINTE* (Bruker, 2017); data reduction: *SAINTE* (Bruker, 2017); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *shelXle* (Hübschle *et al.*, 2011) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015b).

(I)

### Crystal data

(C<sub>24</sub>H<sub>20</sub>As)<sub>2</sub>[TcF<sub>6</sub>]·2H<sub>2</sub>O

*M<sub>r</sub>* = 1010.64

Triclinic, *P* $\bar{1}$

*a* = 10.043 (2) Å

*b* = 11.036 (2) Å

*c* = 21.159 (4) Å

$\alpha$  = 75.991 (3)°

$\beta$  = 77.963 (3)°

$\gamma$  = 71.388 (3)°

*V* = 2134.3 (7) Å<sup>3</sup>

*Z* = 2

*F*(000) = 1014

*D<sub>x</sub>* = 1.573 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 9852 reflections

$\theta$  = 2.3–28.4°

$\mu$  = 1.94 mm<sup>-1</sup>

*T* = 100 K

Rectangular box, translucent colourless  
0.36 × 0.18 × 0.11 mm

### Data collection

Bruker D8 QUEST  
diffractometer

Radiation source: sealed tube

Curved graphite monochromator

Detector resolution: 8.3333 pixels mm<sup>-1</sup>

' $\varphi$  and  $\omega$  scans'

Absorption correction: numerical

(SADABS; Krause *et al.*, 2015; Bruker, 2017)

*T<sub>min</sub>* = 0.40, *T<sub>max</sub>* = 0.82

30509 measured reflections

10713 independent reflections

9659 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.027

$\theta_{\max}$  = 28.4°,  $\theta_{\min}$  = 2.0°

*h* = -13→13

*k* = -14→14

*l* = -28→28

### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.024

*wR*(*F*<sup>2</sup>) = 0.061

*S* = 1.07

10713 reflections

532 parameters

0 restraints

Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

*w* = 1/[ $\sigma^2(F_o^2) + (0.0277P)^2 + 1.0558P$ ]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.85 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.28 \text{ e } \text{\AA}^{-3}$$

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Tc1	0.00388 (2)	1.00821 (2)	0.24427 (2)	0.00949 (4)
F1	0.06365 (10)	0.94725 (9)	0.33028 (4)	0.01526 (18)
F2	0.02023 (10)	0.82987 (9)	0.23933 (5)	0.0195 (2)
F3	-0.19139 (9)	1.03518 (9)	0.28472 (4)	0.01655 (19)
F4	-0.05545 (10)	1.06694 (9)	0.15857 (4)	0.01763 (19)
F5	-0.01067 (10)	1.18549 (9)	0.24916 (5)	0.01773 (19)
F6	0.19929 (10)	0.98174 (10)	0.20439 (5)	0.0195 (2)
As1	0.45214 (2)	0.29894 (2)	0.42956 (2)	0.01042 (4)
C1	0.31552 (16)	0.31567 (15)	0.50669 (7)	0.0145 (3)
C2	0.25079 (17)	0.21702 (16)	0.53425 (8)	0.0180 (3)
H2	0.270344	0.144717	0.513462	0.022*
C3	0.15713 (19)	0.22550 (19)	0.59257 (8)	0.0252 (4)
H3	0.112918	0.15837	0.61218	0.03*
C4	0.1284 (2)	0.3323 (2)	0.62208 (9)	0.0311 (4)
H4	0.064797	0.337471	0.662098	0.037*
C5	0.1909 (2)	0.4311 (2)	0.59403 (10)	0.0328 (4)
H5	0.169211	0.504327	0.614389	0.039*
C6	0.28562 (19)	0.42354 (18)	0.53600 (9)	0.0249 (4)
H6	0.329448	0.491	0.516558	0.03*
C7	0.63893 (16)	0.23460 (15)	0.45270 (7)	0.0133 (3)
C8	0.75427 (17)	0.19724 (16)	0.40462 (8)	0.0171 (3)
H8	0.739633	0.198641	0.361485	0.02*
C9	0.89073 (18)	0.15802 (17)	0.42096 (9)	0.0232 (4)
H9	0.970448	0.132401	0.388921	0.028*
C10	0.91017 (19)	0.15639 (18)	0.48434 (10)	0.0258 (4)
H10	1.003751	0.131673	0.494923	0.031*
C11	0.7956 (2)	0.19013 (17)	0.53225 (9)	0.0240 (4)
H11	0.810651	0.185851	0.575696	0.029*
C12	0.65851 (18)	0.23031 (16)	0.51665 (8)	0.0175 (3)
H12	0.579173	0.254536	0.549104	0.021*
C13	0.41533 (16)	0.18399 (15)	0.38534 (7)	0.0136 (3)
C14	0.51153 (17)	0.06344 (15)	0.37946 (8)	0.0159 (3)
H14	0.597658	0.036331	0.397584	0.019*
C15	0.48039 (19)	-0.01725 (17)	0.34670 (8)	0.0208 (3)
H15	0.545441	-0.099905	0.342352	0.025*
C16	0.35423 (19)	0.02311 (18)	0.32038 (8)	0.0220 (3)

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H16	0.332796	-0.032548	0.298466	0.026*
C17	0.25931 (18)	0.14417 (18)	0.32588 (8)	0.0216 (3)
H17	0.173761	0.171602	0.307258	0.026*
C18	0.28901 (17)	0.22513 (17)	0.35848 (8)	0.0180 (3)
H18	0.223976	0.307933	0.362513	0.022*
C19	0.42920 (17)	0.46563 (14)	0.37366 (7)	0.0138 (3)
C20	0.29201 (18)	0.54734 (16)	0.36844 (8)	0.0209 (3)
H20	0.212525	0.522818	0.394932	0.025*
C21	0.2730 (2)	0.66473 (17)	0.32415 (9)	0.0276 (4)
H21	0.1801	0.721214	0.320059	0.033*
C22	0.3898 (2)	0.69940 (17)	0.28589 (9)	0.0314 (5)
H22	0.376542	0.779325	0.255134	0.038*
C23	0.5249 (2)	0.61913 (18)	0.29202 (9)	0.0302 (4)
H23	0.604154	0.644727	0.265928	0.036*
C24	0.54654 (19)	0.50076 (16)	0.33610 (8)	0.0212 (3)
H24	0.639744	0.445191	0.340361	0.025*
As2	0.55665 (2)	0.68116 (2)	0.07390 (2)	0.01046 (4)
C25	0.54993 (16)	0.51924 (14)	0.13106 (7)	0.0127 (3)
C26	0.66485 (17)	0.44428 (16)	0.16335 (8)	0.0189 (3)
H26	0.746711	0.473571	0.157309	0.023*
C27	0.65974 (18)	0.32639 (16)	0.20449 (8)	0.0205 (3)
H27	0.738632	0.274216	0.226184	0.025*
C28	0.53936 (18)	0.28513 (15)	0.21381 (7)	0.0179 (3)
H28	0.535333	0.205071	0.242423	0.021*
C29	0.42462 (18)	0.36006 (16)	0.18159 (8)	0.0195 (3)
H29	0.342506	0.330943	0.188121	0.023*
C30	0.42918 (16)	0.47766 (15)	0.13974 (8)	0.0159 (3)
H30	0.350939	0.52888	0.117399	0.019*
C31	0.70622 (16)	0.65070 (15)	0.00237 (7)	0.0143 (3)
C32	0.77080 (17)	0.52649 (17)	-0.01108 (8)	0.0191 (3)
H32	0.743372	0.453872	0.016242	0.023*
C33	0.87638 (18)	0.50972 (19)	-0.06515 (9)	0.0252 (4)
H33	0.921224	0.425261	-0.075043	0.03*
C34	0.91586 (18)	0.6157 (2)	-0.10438 (8)	0.0266 (4)
H34	0.987199	0.603818	-0.141495	0.032*
C35	0.8525 (2)	0.7397 (2)	-0.09023 (9)	0.0304 (4)
H35	0.881084	0.812019	-0.117231	0.036*
C36	0.74738 (19)	0.75739 (18)	-0.03654 (9)	0.0242 (4)
H36	0.703742	0.841754	-0.026361	0.029*
C37	0.59785 (16)	0.79474 (15)	0.11746 (7)	0.0133 (3)
C38	0.73209 (17)	0.75814 (16)	0.13698 (8)	0.0190 (3)
H38	0.800909	0.680258	0.127557	0.023*
C39	0.76318 (18)	0.83735 (17)	0.17031 (8)	0.0214 (3)
H39	0.853665	0.813048	0.184239	0.026*
C40	0.66342 (19)	0.95157 (18)	0.18345 (8)	0.0216 (3)
H40	0.685521	1.005174	0.206385	0.026*
C41	0.53122 (18)	0.98773 (17)	0.16313 (8)	0.0210 (3)
H41	0.463401	1.066574	0.171884	0.025*



C42	0.49717 (17)	0.90955 (15)	0.13006 (8)	0.0161 (3)
H42	0.406498	0.934187	0.116276	0.019*
C43	0.37895 (16)	0.75799 (14)	0.04174 (7)	0.0124 (3)
C44	0.37396 (17)	0.76662 (15)	-0.02462 (7)	0.0156 (3)
H44	0.458803	0.740707	-0.053936	0.019*
C45	0.24319 (18)	0.81363 (16)	-0.04729 (8)	0.0189 (3)
H45	0.238014	0.81983	-0.092327	0.023*
C46	0.12020 (18)	0.85148 (16)	-0.00393 (8)	0.0200 (3)
H46	0.030845	0.881727	-0.019405	0.024*
C47	0.12591 (17)	0.84575 (16)	0.06197 (8)	0.0187 (3)
H47	0.041092	0.874463	0.090795	0.022*
C48	0.25579 (16)	0.79800 (15)	0.08558 (7)	0.0149 (3)
H48	0.260763	0.792664	0.130562	0.018*
O1S	0.10019 (15)	0.58106 (13)	0.22377 (7)	0.0309 (3)
O2S	-0.11068 (15)	1.44144 (14)	0.26691 (8)	0.0337 (3)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Tc1	0.00933 (6)	0.00945 (6)	0.00997 (6)	-0.00266 (4)	-0.00292 (4)	-0.00103 (4)
F1	0.0179 (4)	0.0167 (4)	0.0122 (4)	-0.0048 (4)	-0.0066 (3)	-0.0008 (3)
F2	0.0235 (5)	0.0115 (4)	0.0265 (5)	-0.0032 (4)	-0.0117 (4)	-0.0045 (4)
F3	0.0107 (4)	0.0216 (5)	0.0165 (4)	-0.0053 (4)	-0.0011 (3)	-0.0019 (4)
F4	0.0189 (5)	0.0217 (5)	0.0126 (4)	-0.0059 (4)	-0.0066 (3)	0.0000 (4)
F5	0.0205 (5)	0.0114 (4)	0.0232 (5)	-0.0053 (4)	-0.0076 (4)	-0.0017 (4)
F6	0.0117 (4)	0.0272 (5)	0.0181 (4)	-0.0042 (4)	-0.0004 (3)	-0.0046 (4)
As1	0.01032 (7)	0.01117 (7)	0.00962 (7)	-0.00359 (6)	-0.00147 (5)	-0.00088 (5)
C1	0.0129 (7)	0.0191 (8)	0.0112 (6)	-0.0062 (6)	0.0002 (5)	-0.0017 (6)
C2	0.0171 (8)	0.0190 (8)	0.0164 (7)	-0.0063 (6)	-0.0024 (6)	0.0010 (6)
C3	0.0211 (8)	0.0336 (10)	0.0188 (8)	-0.0138 (7)	0.0002 (6)	0.0047 (7)
C4	0.0242 (9)	0.0532 (13)	0.0169 (8)	-0.0159 (9)	0.0070 (7)	-0.0101 (8)
C5	0.0318 (10)	0.0442 (12)	0.0285 (10)	-0.0167 (9)	0.0095 (8)	-0.0219 (9)
C6	0.0260 (9)	0.0289 (9)	0.0239 (8)	-0.0150 (7)	0.0071 (7)	-0.0119 (7)
C7	0.0135 (7)	0.0124 (7)	0.0143 (7)	-0.0036 (6)	-0.0043 (5)	-0.0013 (5)
C8	0.0158 (7)	0.0193 (8)	0.0168 (7)	-0.0034 (6)	-0.0038 (6)	-0.0054 (6)
C9	0.0144 (8)	0.0239 (9)	0.0311 (9)	-0.0008 (6)	-0.0029 (7)	-0.0116 (7)
C10	0.0188 (8)	0.0222 (9)	0.0389 (10)	0.0010 (7)	-0.0158 (7)	-0.0095 (8)
C11	0.0291 (9)	0.0213 (8)	0.0236 (8)	-0.0018 (7)	-0.0151 (7)	-0.0051 (7)
C12	0.0211 (8)	0.0167 (7)	0.0140 (7)	-0.0035 (6)	-0.0054 (6)	-0.0019 (6)
C13	0.0157 (7)	0.0163 (7)	0.0108 (6)	-0.0078 (6)	-0.0015 (5)	-0.0021 (5)
C14	0.0173 (7)	0.0147 (7)	0.0164 (7)	-0.0059 (6)	-0.0039 (6)	-0.0009 (6)
C15	0.0246 (9)	0.0171 (8)	0.0218 (8)	-0.0074 (7)	-0.0002 (6)	-0.0060 (6)
C16	0.0263 (9)	0.0271 (9)	0.0201 (8)	-0.0171 (7)	0.0000 (7)	-0.0085 (7)
C17	0.0174 (8)	0.0312 (9)	0.0207 (8)	-0.0120 (7)	-0.0038 (6)	-0.0056 (7)
C18	0.0144 (7)	0.0219 (8)	0.0189 (7)	-0.0051 (6)	-0.0030 (6)	-0.0054 (6)
C19	0.0193 (7)	0.0100 (7)	0.0116 (6)	-0.0035 (6)	-0.0039 (6)	-0.0004 (5)
C20	0.0205 (8)	0.0171 (8)	0.0248 (8)	-0.0020 (6)	-0.0081 (7)	-0.0037 (7)
C21	0.0397 (11)	0.0156 (8)	0.0260 (9)	0.0036 (7)	-0.0177 (8)	-0.0054 (7)

C22	0.0627 (14)	0.0131 (8)	0.0145 (8)	-0.0051 (8)	-0.0083 (8)	-0.0004 (6)
C23	0.0463 (12)	0.0207 (9)	0.0196 (8)	-0.0138 (8)	0.0094 (8)	-0.0023 (7)
C24	0.0235 (8)	0.0180 (8)	0.0192 (8)	-0.0066 (7)	0.0041 (6)	-0.0031 (6)
As2	0.00984 (7)	0.01133 (7)	0.00975 (7)	-0.00323 (5)	-0.00131 (5)	-0.00092 (5)
C25	0.0144 (7)	0.0119 (7)	0.0106 (6)	-0.0026 (6)	-0.0009 (5)	-0.0019 (5)
C26	0.0167 (8)	0.0172 (8)	0.0227 (8)	-0.0043 (6)	-0.0072 (6)	-0.0002 (6)
C27	0.0241 (8)	0.0166 (8)	0.0188 (8)	-0.0014 (6)	-0.0086 (6)	-0.0006 (6)
C28	0.0259 (8)	0.0124 (7)	0.0119 (7)	-0.0039 (6)	0.0004 (6)	-0.0006 (6)
C29	0.0194 (8)	0.0173 (8)	0.0214 (8)	-0.0082 (6)	0.0012 (6)	-0.0022 (6)
C30	0.0135 (7)	0.0159 (7)	0.0172 (7)	-0.0034 (6)	-0.0030 (6)	-0.0011 (6)
C31	0.0117 (7)	0.0187 (8)	0.0122 (7)	-0.0051 (6)	0.0001 (5)	-0.0028 (6)
C32	0.0173 (8)	0.0205 (8)	0.0209 (8)	-0.0077 (6)	0.0009 (6)	-0.0065 (6)
C33	0.0181 (8)	0.0320 (10)	0.0262 (9)	-0.0051 (7)	0.0028 (7)	-0.0148 (8)
C34	0.0162 (8)	0.0449 (11)	0.0171 (8)	-0.0089 (8)	0.0040 (6)	-0.0079 (8)
C35	0.0290 (10)	0.0353 (11)	0.0221 (9)	-0.0148 (8)	0.0057 (7)	0.0033 (8)
C36	0.0258 (9)	0.0204 (8)	0.0213 (8)	-0.0076 (7)	0.0041 (7)	0.0006 (7)
C37	0.0140 (7)	0.0159 (7)	0.0114 (6)	-0.0070 (6)	-0.0016 (5)	-0.0014 (5)
C38	0.0148 (7)	0.0193 (8)	0.0234 (8)	-0.0047 (6)	-0.0043 (6)	-0.0040 (6)
C39	0.0174 (8)	0.0281 (9)	0.0227 (8)	-0.0111 (7)	-0.0065 (6)	-0.0028 (7)
C40	0.0245 (9)	0.0266 (9)	0.0203 (8)	-0.0150 (7)	-0.0014 (6)	-0.0081 (7)
C41	0.0202 (8)	0.0216 (8)	0.0243 (8)	-0.0082 (7)	0.0002 (6)	-0.0098 (7)
C42	0.0138 (7)	0.0179 (8)	0.0173 (7)	-0.0052 (6)	-0.0019 (6)	-0.0040 (6)
C43	0.0128 (7)	0.0112 (7)	0.0133 (7)	-0.0036 (5)	-0.0044 (5)	-0.0002 (5)
C44	0.0187 (8)	0.0143 (7)	0.0126 (7)	-0.0031 (6)	-0.0024 (6)	-0.0022 (6)
C45	0.0247 (8)	0.0163 (8)	0.0162 (7)	-0.0026 (6)	-0.0104 (6)	-0.0019 (6)
C46	0.0175 (8)	0.0155 (7)	0.0269 (8)	-0.0002 (6)	-0.0115 (6)	-0.0026 (6)
C47	0.0134 (7)	0.0174 (8)	0.0239 (8)	-0.0016 (6)	-0.0037 (6)	-0.0044 (6)
C48	0.0152 (7)	0.0159 (7)	0.0134 (7)	-0.0044 (6)	-0.0025 (6)	-0.0022 (6)
O1S	0.0309 (7)	0.0214 (7)	0.0416 (8)	-0.0102 (6)	0.0060 (6)	-0.0141 (6)
O2S	0.0284 (7)	0.0273 (7)	0.0465 (8)	-0.0096 (6)	0.0086 (6)	-0.0187 (6)

*Geometric parameters (Å, °)*

Tc1—F1	1.9312 (9)	C23—C24	1.392 (2)
Tc1—F2	1.9487 (10)	C23—H23	0.95
Tc1—F3	1.9282 (9)	C24—H24	0.95
Tc1—F4	1.9233 (9)	As2—C43	1.9048 (15)
Tc1—F5	1.9414 (10)	As2—C31	1.9069 (15)
Tc1—F6	1.9266 (10)	As2—C37	1.9082 (15)
As1—C1	1.9053 (15)	As2—C25	1.9123 (15)
As1—C7	1.9046 (15)	C25—C26	1.389 (2)
As1—C13	1.9077 (15)	C25—C30	1.392 (2)
As1—C19	1.9041 (15)	C26—C27	1.389 (2)
C1—C2	1.391 (2)	C26—H26	0.95
C1—C6	1.394 (2)	C27—C28	1.384 (2)
C2—C3	1.390 (2)	C27—H27	0.95
C2—H2	0.95	C28—C29	1.387 (2)
C3—C4	1.388 (3)	C28—H28	0.95

C3—H3	0.95	C29—C30	1.391 (2)
C4—C5	1.380 (3)	C29—H29	0.95
C4—H4	0.95	C30—H30	0.95
C5—C6	1.390 (2)	C31—C32	1.387 (2)
C5—H5	0.95	C31—C36	1.391 (2)
C6—H6	0.95	C32—C33	1.393 (2)
C7—C12	1.395 (2)	C32—H32	0.95
C7—C8	1.398 (2)	C33—C34	1.380 (3)
C8—C9	1.390 (2)	C33—H33	0.95
C8—H8	0.95	C34—C35	1.389 (3)
C9—C10	1.390 (3)	C34—H34	0.95
C9—H9	0.95	C35—C36	1.385 (2)
C10—C11	1.383 (3)	C35—H35	0.95
C10—H10	0.95	C36—H36	0.95
C11—C12	1.390 (2)	C37—C42	1.390 (2)
C11—H11	0.95	C37—C38	1.398 (2)
C12—H12	0.95	C38—C39	1.387 (2)
C13—C14	1.389 (2)	C38—H38	0.95
C13—C18	1.395 (2)	C39—C40	1.385 (3)
C14—C15	1.392 (2)	C39—H39	0.95
C14—H14	0.95	C40—C41	1.387 (2)
C15—C16	1.389 (3)	C40—H40	0.95
C15—H15	0.95	C41—C42	1.390 (2)
C16—C17	1.387 (3)	C41—H41	0.95
C16—H16	0.95	C42—H42	0.95
C17—C18	1.385 (2)	C43—C44	1.395 (2)
C17—H17	0.95	C43—C48	1.399 (2)
C18—H18	0.95	C44—C45	1.390 (2)
C19—C24	1.387 (2)	C44—H44	0.95
C19—C20	1.395 (2)	C45—C46	1.388 (2)
C20—C21	1.386 (2)	C45—H45	0.95
C20—H20	0.95	C46—C47	1.393 (2)
C21—C22	1.386 (3)	C46—H46	0.95
C21—H21	0.95	C47—C48	1.391 (2)
C22—C23	1.376 (3)	C47—H47	0.95
C22—H22	0.95	C48—H48	0.95
F4—Tc1—F6	90.13 (4)	C21—C22—H22	119.7
F4—Tc1—F3	90.21 (4)	C22—C23—C24	120.59 (18)
F6—Tc1—F3	179.56 (4)	C22—C23—H23	119.7
F4—Tc1—F1	179.36 (4)	C24—C23—H23	119.7
F6—Tc1—F1	89.85 (4)	C19—C24—C23	118.62 (17)
F3—Tc1—F1	89.81 (4)	C19—C24—H24	120.7
F4—Tc1—F5	90.53 (4)	C23—C24—H24	120.7
F6—Tc1—F5	90.69 (4)	C43—As2—C31	110.01 (7)
F3—Tc1—F5	89.03 (4)	C43—As2—C37	111.36 (7)
F1—Tc1—F5	90.11 (4)	C31—As2—C37	106.19 (7)
F4—Tc1—F2	89.65 (4)	C43—As2—C25	107.84 (6)

F6—Tc1—F2	88.85 (4)	C31—As2—C25	109.62 (7)
F3—Tc1—F2	91.42 (4)	C37—As2—C25	111.82 (6)
F1—Tc1—F2	89.71 (4)	C26—C25—C30	120.63 (14)
F5—Tc1—F2	179.51 (4)	C26—C25—As2	120.04 (12)
C19—As1—C7	109.81 (7)	C30—C25—As2	119.33 (11)
C19—As1—C1	108.65 (7)	C27—C26—C25	119.80 (15)
C7—As1—C1	110.07 (7)	C27—C26—H26	120.1
C19—As1—C13	109.00 (7)	C25—C26—H26	120.1
C7—As1—C13	111.30 (7)	C28—C27—C26	119.81 (15)
C1—As1—C13	107.96 (7)	C28—C27—H27	120.1
C2—C1—C6	120.97 (15)	C26—C27—H27	120.1
C2—C1—As1	119.11 (12)	C27—C28—C29	120.35 (15)
C6—C1—As1	119.88 (12)	C27—C28—H28	119.8
C3—C2—C1	119.19 (16)	C29—C28—H28	119.8
C3—C2—H2	120.4	C28—C29—C30	120.31 (15)
C1—C2—H2	120.4	C28—C29—H29	119.8
C4—C3—C2	119.83 (16)	C30—C29—H29	119.8
C4—C3—H3	120.1	C29—C30—C25	119.09 (15)
C2—C3—H3	120.1	C29—C30—H30	120.5
C5—C4—C3	120.85 (16)	C25—C30—H30	120.5
C5—C4—H4	119.6	C32—C31—C36	120.96 (15)
C3—C4—H4	119.6	C32—C31—As2	121.20 (12)
C4—C5—C6	119.99 (18)	C36—C31—As2	117.84 (12)
C4—C5—H5	120.0	C31—C32—C33	119.10 (16)
C6—C5—H5	120.0	C31—C32—H32	120.5
C5—C6—C1	119.15 (17)	C33—C32—H32	120.5
C5—C6—H6	120.4	C34—C33—C32	120.01 (17)
C1—C6—H6	120.4	C34—C33—H33	120.0
C12—C7—C8	121.23 (14)	C32—C33—H33	120.0
C12—C7—As1	119.37 (12)	C33—C34—C35	120.76 (16)
C8—C7—As1	119.35 (11)	C33—C34—H34	119.6
C9—C8—C7	118.90 (15)	C35—C34—H34	119.6
C9—C8—H8	120.6	C36—C35—C34	119.65 (17)
C7—C8—H8	120.6	C36—C35—H35	120.2
C8—C9—C10	119.78 (16)	C34—C35—H35	120.2
C8—C9—H9	120.1	C35—C36—C31	119.51 (17)
C10—C9—H9	120.1	C35—C36—H36	120.2
C11—C10—C9	121.14 (16)	C31—C36—H36	120.2
C11—C10—H10	119.4	C42—C37—C38	121.00 (15)
C9—C10—H10	119.4	C42—C37—As2	121.11 (11)
C10—C11—C12	119.81 (16)	C38—C37—As2	117.89 (12)
C10—C11—H11	120.1	C39—C38—C37	118.95 (15)
C12—C11—H11	120.1	C39—C38—H38	120.5
C11—C12—C7	119.10 (15)	C37—C38—H38	120.5
C11—C12—H12	120.5	C40—C39—C38	120.54 (15)
C7—C12—H12	120.5	C40—C39—H39	119.7
C14—C13—C18	120.81 (14)	C38—C39—H39	119.7
C14—C13—As1	121.23 (12)	C39—C40—C41	120.01 (16)

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C18—C13—As1	117.96 (12)	C39—C40—H40	120.0
C13—C14—C15	119.28 (15)	C41—C40—H40	120.0
C13—C14—H14	120.4	C40—C41—C42	120.54 (16)
C15—C14—H14	120.4	C40—C41—H41	119.7
C16—C15—C14	119.98 (16)	C42—C41—H41	119.7
C16—C15—H15	120.0	C41—C42—C37	118.96 (15)
C14—C15—H15	120.0	C41—C42—H42	120.5
C17—C16—C15	120.41 (16)	C37—C42—H42	120.5
C17—C16—H16	119.8	C44—C43—C48	121.50 (14)
C15—C16—H16	119.8	C44—C43—As2	118.90 (11)
C18—C17—C16	120.11 (16)	C48—C43—As2	119.51 (11)
C18—C17—H17	119.9	C45—C44—C43	119.10 (15)
C16—C17—H17	119.9	C45—C44—H44	120.4
C17—C18—C13	119.40 (16)	C43—C44—H44	120.4
C17—C18—H18	120.3	C46—C45—C44	119.80 (15)
C13—C18—H18	120.3	C46—C45—H45	120.1
C24—C19—C20	121.14 (15)	C44—C45—H45	120.1
C24—C19—As1	120.19 (12)	C45—C46—C47	120.93 (15)
C20—C19—As1	118.55 (12)	C45—C46—H46	119.5
C21—C20—C19	119.25 (17)	C47—C46—H46	119.5
C21—C20—H20	120.4	C48—C47—C46	120.00 (15)
C19—C20—H20	120.4	C48—C47—H47	120.0
C22—C21—C20	119.79 (17)	C46—C47—H47	120.0
C22—C21—H21	120.1	C47—C48—C43	118.64 (14)
C20—C21—H21	120.1	C47—C48—H48	120.7
C23—C22—C21	120.61 (17)	C43—C48—H48	120.7
C23—C22—H22	119.7		

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