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## Tetraphenylarsonium cis-bis[1,2-bis(tri-fluoromethyl)ethene-1,2-dithiolato]platinate(II)

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Received 29 May 2009; accepted 5 June 2009
Key indicators: single-crystal X-ray study; $T=150 \mathrm{~K}$; mean $\sigma(\mathrm{C}-\mathrm{C})=0.012 \AA$; disorder in main residue; $R$ factor $=0.054 ; w R$ factor $=0.156$; data-to-parameter ratio $=18.6$

In the title compound, $\left(\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{As}\right)\left[\mathrm{Pt}\left(\mathrm{C}_{4} \mathrm{~F}_{6} \mathrm{~S}_{2}\right)_{2}\right]$, the cation lies on a twofold rotation axis while the anion has crystallographic inversion symmetry. The $\mathrm{Pt}^{\mathrm{II}}$ ion is in a slightly distorted square-planar coordination environment. The F atoms of both unique $-\mathrm{CF}_{3}$ groups are disordered over two sets of sites, the ratios of refined occupancies being 0.677 (15):0.323 (15) and 0.640 (16):0.360 (16). The crystal structure is the first to date of a monoanionic $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{-}$species [tfd is 1,2-bis(trifluorometh-yl)ethene-1,2-dithiolate] with a non-redox-active cation.

## Related literature

For background information, see: Ray et al. (2005); Wang \& Stiefel (2001); Harrison et al. (2006). For related crystal structures, see: Kogut et al. (2006); Tang et al. (2009); Kasper \& Interrante (1976); Lim et al. (2001). For synthetic details, see: Davison et al. (1964). For the treatment of disordered solvent of crystallization, see: Spek (2009); Stähler et al. (2001); Cox et al. (2003); Mohamed et al. (2003); Athimoolam et al. (2005). For a detailed description of the electronic structure of metaldithiolene complexes, see: Kirk et al. (2004).


## Experimental

Crystal data
$\left(\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{As}\right)\left[\mathrm{Pt}\left(\mathrm{C}_{4} \mathrm{~F}_{6} \mathrm{~S}_{2}\right)_{2}\right]$
$M_{r}=1030.76$
Monoclinic, $C 2 / c$
$a=24.9649(10) \AA$
$b=7.3189$ (3) A
$c=23.6773(6) \AA$
$\beta=117.779$ (2) ${ }^{\circ}$

## Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
$T_{\text {min }}=0.341, T_{\text {max }}=0.471$

## Refinement

$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.054$
$w R\left(F^{2}\right)=0.156$
$S=1.09$
4282 reflections
230 parameters
$V=3827.6(2) \AA^{3}$
$Z=4$
Mo $K \alpha$ radiation
$\mu=4.82 \mathrm{~mm}^{-1}$
$T=150 \mathrm{~K}$
$0.24 \times 0.21 \times 0.16 \mathrm{~mm}$

13097 measured reflections 4282 independent reflections 3269 reflections with $I>2 \sigma(I)$ $R_{\text {int }}=0.051$

60 restraints
H -atom parameters constrained
$\Delta \rho_{\max }=4.18 \mathrm{e} \AA^{-3}$
$\Delta \rho_{\text {min }}=-2.83 \mathrm{e}^{-3}$

Data collection: COLLECT (Nonius, 2002); cell refinement: DENZO-SMN (Otwinowski \& Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2119).

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## supporting information

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# Tetraphenylarsonium cis-bis[1,2-bis(trifluoromethyl)ethene-1,2-dithiolato]platinate(II) 

Stephanie Hosking, Alan J. Lough and Ulrich FekI

## S1. Comment

Square-planar metal bisdithiolene compounds are of fundamental importance for our understanding of metal complexes containing non-innocent ligands (Ray et al., 2005). The nickel complex [ $\left.\mathrm{Ni}(\mathrm{tfd})_{2}\right]\left(\mathrm{tfd}=\mathrm{S}_{2} \mathrm{C}_{2}\left(\mathrm{CF}_{3}\right)_{2}\right)$ has received considerable attention due to its potential applicability in ethylene separation and purification (Wang \& Stiefel, 2001). The one-electron reduced form of the metal complex is involved in the mechanism of alkene binding (Harrison et al., 2006). In the course of our studies on the analogous platinum complexes we have crystallographically characterized $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{0}$ and $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{2-}$ (Kogut et al., 2006; Tang et al., 2009, respectively). These complexes contain square-planar platinum(II), and the tfd ligand is redox-active. While tfd is not fully reduced in the charge-neutral complex (and is only formally 1,2-perfluoromethylethene-1,2-dithiolate), tfd is fully reduced in the dianion. The $\mathrm{C}-\mathrm{C}$ bond in the chelate ring of the neutral complex shortens upon reduction (Tang et al., 2009).

We report here on the first crystal structure of monoanionic $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{-}$with a non-redox-active cation (Fig. 1). A report on a previous structural determination (Kasper \& Interrante, 1976) of the charge-transfer complex between tetrathiofulvalene and charge-neutral $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]$ has proposed that $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]$ is reduced by one electron and tetrathiovulvalene is oxidized to tetrathiafulvalinium; however, in order to reliably establish the structural properties of the one-electronreduced species, use of a non-redox-active cation is preferable. $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]$ in the title compound reported here is clearly monoanionic. The structure reported here completes structural characterization of the redox series $\left[\operatorname{Pt}(\mathrm{tfd})_{2}\right]^{0 / 1-/ 2-}$. Structural features of $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{-}$(Fig. 2) are intermediate with respect to those of $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{0}($ Kogut et al., 2006) and $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{2-}$ (Tang et al., 2009). The structural effects observed upon stepwise reduction of the neutral complex $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{0}$ to $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{-}$and $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{2-}$ are of varying statistical significance (significant within $2 \sigma$ for $\mathrm{Pt}-\mathrm{S}$, borderline significant for C-C). However, they confirm observations made by Lim et al. (2001) on an analogous nickel complex containing a non-fluorinated dithiolene, the redox series $\left[\mathrm{Ni}\left(\mathrm{S}_{2} \mathrm{C}_{2} \mathrm{Me}_{2}\right)_{2}\right]^{0,1-2-2}$. The combined evidence suggests that these effects are real. A relatively straightforward rationalization, in terms of resonance structures, is shown in Fig. 2. For a detailed description of the electronic structure of metal dithiolene complexes, see Kirk et al. (2004).

## S2. Experimental

The tetraphenylarsonium salt of $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{-}$was synthesized using a slightly modified literature procedure. The literature procedure uses acetone/ethanol as the reductant, followed by precipitation with tetraphenylarsonium chloride, (Davison et al., 1964) to obtain the product in $36 \%$ yield. We repeated that literature reaction and obtained $24 \%$ yield. We then decided to use water in THF to achieve reduction of $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]$, followed by addition of tetraphenylarsonium chloride. It was previously observed that water in polar solvents such as THF leads to reduction of the related nickel complex $\mathrm{Ni}\left[\left(\mathrm{S}_{2} \mathrm{C}_{2}\left(\mathrm{CF}_{3}\right)_{2}\right]_{2}\right.$ (Harrison et al., 2006). In a 10 ml vial, $24.9 \mathrm{mg}(0.0385 \mathrm{mmol})$ of $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]$ were dissolved in 1.0 ml ofTHF, leading to a dark greenish-blue solution. Addition of 0.3 ml of $\mathrm{H}_{2} \mathrm{O}$ induced a rapid colour change, to produce a
brownish-yellow solution. Solid tetraphenylarsonium chloride ( $25.3 \mathrm{mg}, 0.068 \mathrm{mmol}$ ) was added to the solution while stirring, followed by an additional 0.25 ml of THF, to produce a homogeneous solution. In order to lower the solubility of the salt again, an additional 0.4 ml of $\mathrm{H}_{2} \mathrm{O}$ were added, and the vial was storred at 278 K for three weeks. Crystals had not formed at that time, and crystallization was induced by scratching of the inner surface of the vial with a glass rod. After three additional weeks at $378 \mathrm{~K},\left[\mathrm{AsPh}_{4}\right]^{+}\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]$ had crystallized as dark yellow blocks. The crystals were removed from the supernatant and dried under vacuum. Yield: $26.6 \mathrm{mg}(0.0258 \mathrm{mmol}, 67 \%)$. Inspections of the crystals with a stereomicroscope showed them to be of excellent quality. One crystal was chosen for the single-crystal X-ray structure determination.

## S3. Refinement

H atoms were placed in calculated positions and treated as riding: $\mathrm{C}-\mathrm{H}=0.95 \AA$ with $U_{\mathrm{iso}}(\mathrm{H})=1.2 U_{\mathrm{iso}}(\mathrm{C})$. The F atoms of both unique $-\mathrm{CF}_{3}$ groups are disordered over two sets of sites with the ratio of refined occupancies being 0.677 (15):0.323 (15) for F1/F2/F3:F1A/F2A/F3A and 0.640 (16):0.360 (16) for F4/F5/F6:F4A/F5A/F6A. The SADI and EADP commands in the SHELXTL (Sheldrick, 2008) software were used to restrain the parameters of the disordered groups. During the refinement of the structure, electron density peaks were located that were believed to be highly disordered solvent molecules (possibly THF). Attempts made to model the solvent molecule were not successful. The SQUEEZE option in PLATON (Spek, 2009) indicated there was a solvent cavity of volume $130.0 \AA^{3}$ containing approximately 18 electrons. In the final cycles of refinement, this contribution to the electron density was removed from the observed data. The density, the $\mathrm{F}(000)$ value, the molecular weight and the formula are given without taking into account the results obtained with the SQUEEZE option PLATON (Spek, 2009). Similar treatments of disordered solvent molecules have been carried out in this manner (Stähler et al., 2001; Cox et al., 2003; Mohamed et al., 2003; Athimoolam et al., 2005).


Figure 1
A view of the molecular structure of the title compound. Displacement ellipsoids are drawn at the $30 \%$ probabilty level.
For the cation and anion, the primed labels are related by the symmetry operators $(-x, y,-z+1 / 2)$ and $(-x+1 / 2,-y+1 / 2$, $z+1$ ), respectively.
2.239(3)/2.252(3)/2.285(3)

1.70(1) /1.73(1)/1.75(1)


## Figure 2

Comparison of the structural features of $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{0}\left(\right.$ Kogut et al.,2006), $\left[\mathrm{Pt}(\mathrm{tfd})_{2}\right]^{-}$(this work) and $\left[\mathrm{Pt}(\mathrm{ffd})_{2}\right]^{2-}$ (Tang et al., 2009).

## Tetraphenylarsonium cis-bis[1,2-bis(trifluoromethyl)ethene-1,2-dithiolato]platinate(II)

## Crystal data

$\left(\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{As}\right)\left[\mathrm{Ptt}_{4}\left(\mathrm{C}_{4} \mathrm{~F}_{6} \mathrm{~S}_{2}\right)_{2}\right]$
$M_{r}=1030.76$
Monoclinic, C2/c
Hall symbol: - C 2yc
$a=24.9649$ (10) $\AA$
$b=7.3189$ (3) $\AA$
$c=23.6773$ (6) $\AA$
$\beta=117.779$ (2) ${ }^{\circ}$
$V=3827.6$ (2) $\AA^{3}$
$Z=4$

$$
\begin{aligned}
& F(000)=1980 \\
& D_{\mathrm{x}}=1.789 \mathrm{Mg} \mathrm{~m}^{-3} \\
& \text { Mo } K \alpha \text { radiation, } \lambda=0.71073 \AA \\
& \text { Cell parameters from } 13097 \text { reflections } \\
& \theta=2.9-27.5^{\circ} \\
& \mu=4.82 \mathrm{~mm}^{-1} \\
& T=150 \mathrm{~K} \\
& \text { Block, orange } \\
& 0.24 \times 0.21 \times 0.16 \mathrm{~mm}
\end{aligned}
$$

## Data collection

Nonius KappaCCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 9 pixels $\mathrm{mm}^{-1}$
$\varphi$ scans and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan
(SORTAV; Blessing, 1995)
$T_{\text {min }}=0.341, T_{\text {max }}=0.471$

## Refinement

Refinement on $F^{2}$
Least-squares matrix: full
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.054$
$w R\left(F^{2}\right)=0.156$
$S=1.09$
4282 reflections
230 parameters
60 restraints
Primary atom site location: structure-invariant direct methods

> 13097 measured reflections
> 4282 independent reflections
> 3269 reflections with $I>2 \sigma(I)$
> $R_{\text {int }}=0.051$
> $\theta_{\max }=27.5^{\circ}, \theta_{\min }=2.9^{\circ}$
> $h=-32 \rightarrow 25$
> $k=-8 \rightarrow 9$
> $l=-25 \rightarrow 30$

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H -atom parameters constrained
$w=1 /\left[\sigma^{2}\left(F_{\mathrm{o}}{ }^{2}\right)+(0.0976 P)^{2}+3.8529 P\right]$ where $P=\left(F_{0}^{2}+2 F_{\mathrm{c}}^{2}\right) / 3$
$(\Delta / \sigma)_{\text {max }}<0.001$
$\Delta \rho_{\text {max }}=4.18$ e $\AA^{-3}$
$\Delta \rho_{\text {min }}=-2.83$ e $\AA^{-3}$

## Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.
Refinement. Refinement of $F^{2}$ against ALL reflections. The weighted $R$-factor $w R$ and goodness of fit $S$ are based on $F^{2}$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^{2}$. The threshold expression of $F^{2}>\sigma\left(F^{2}\right)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^{2}$ are statistically about twice as large as those based on $F$, and $R$ - factors based on ALL data will be even larger.

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

|  | $x$ | $y$ | $z$ | $U_{\text {iso }} / U_{\text {eq }}$ | Occ. $(<1)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Pt1 | 0.2500 | 0.2500 | 0.5000 | $0.02912(17)$ |  |
| S1 | $0.22659(8)$ | $0.5216(3)$ | $0.44973(9)$ | $0.0371(4)$ |  |
| S2 | $0.30913(9)$ | $0.1915(3)$ | $0.45362(10)$ | $0.0408(5)$ |  |
| F1 | $0.2074(3)$ | $0.7827(10)$ | $0.3529(5)$ | $0.061(2)$ | $0.676(15)$ |
| F2 | $0.3033(3)$ | $0.8005(11)$ | $0.3897(5)$ | $0.061(2)$ | $0.676(15)$ |
| F3 | $0.2523(3)$ | $0.6463(10)$ | $0.3070(3)$ | $0.061(2)$ | $0.676(15)$ |
| F1A | $0.2129(6)$ | $0.680(3)$ | $0.3037(4)$ | $0.078(7)^{*}$ | $0.324(15)$ |
| F2A | $0.2298(8)$ | $0.795(2)$ | $0.3910(9)$ | $0.071(6)^{*}$ | $0.324(15)$ |
| F3A | $0.2988(6)$ | $0.796(2)$ | $0.3648(8)$ | $0.061(6)^{*}$ | $0.324(15)$ |
| F4 | $0.3847(4)$ | $0.2453(10)$ | $0.3995(4)$ | $0.062(2)$ | $0.638(16)$ |
| F5 | $0.3645(4)$ | $0.5234(10)$ | $0.3690(4)$ | $0.062(2)$ | $0.638(16)$ |
| F6 | $0.3084(3)$ | $0.3029(13)$ | $0.3109(3)$ | $0.062(2)$ | $0.638(16)$ |
| F6A | $0.2985(6)$ | $0.440(3)$ | $0.3141(6)$ | $0.092(7)^{*}$ | $0.362(16)$ |
| F4A | $0.3588(9)$ | $0.212(2)$ | $0.3578(12)$ | $0.137(12)^{*}$ | $0.362(16)$ |
| F5A | $0.3837(5)$ | $0.4871(18)$ | $0.3956(7)$ | $0.068(6)^{*}$ | $0.362(16)$ |
| C1 | $0.2649(3)$ | $0.5226(11)$ | $0.4045(3)$ | $0.0394(17)$ |  |


|  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| C2 | $0.3007(4)$ | $0.3803(12)$ | $0.4073(4)$ | $0.0438(19)$ |
| C3 | $0.2566(3)$ | $0.6806(13)$ | $0.3656(3)$ | $0.059(2)$ |
| C4 | $0.3370(3)$ | $0.3656(8)$ | $0.3723(3)$ | $0.059(2)$ |
| As1 | 0.0000 | $0.61646(13)$ | 0.2500 | $0.0248(2)$ |
| C11 | $0.0654(3)$ | $0.4612(9)$ | $0.2596(3)$ | $0.0261(13)$ |
| C12 | $0.0908(3)$ | $0.4759(10)$ | $0.2191(3)$ | $0.0367(16)$ |
| H12A | 0.0767 | 0.5658 | 0.1864 | $0.044^{*}$ |
| C13 | $0.1372(3)$ | $0.3578(12)$ | $0.2266(4)$ | $0.0415(19)$ |
| H13A | 0.1550 | 0.3674 | 0.1989 | $0.050^{*}$ |
| C14 | $0.1573(4)$ | $0.2281(10)$ | $0.2733(5)$ | $0.041(2)$ |
| H14A | 0.1892 | 0.1483 | 0.2781 | $0.049^{*}$ |
| C15 | $0.1313(4)$ | $0.2115(11)$ | $0.3144(4)$ | $0.0393(19)$ |
| H15A | 0.1455 | 0.1211 | 0.3469 | $0.047^{*}$ |
| C16 | $0.0849(3)$ | $0.3278(11)$ | $0.3071(3)$ | $0.0348(16)$ |
| H16A | 0.0665 | 0.3170 | 0.3341 | $0.042^{*}$ |
| C21 | $-0.0245(3)$ | $0.7717(8)$ | $0.1779(3)$ | $0.0254(14)$ |
| C22 | $0.0166(3)$ | $0.9043(10)$ | $0.1792(3)$ | $0.0302(15)$ |
| H22A | 0.0563 | 0.9104 | 0.2141 | $0.036^{*}$ |
| C23 | $-0.0014(3)$ | $1.0262(10)$ | $0.1288(3)$ | $0.0354(16)$ |
| H23A | 0.0260 | 1.1159 | 0.1286 | $0.042^{*}$ |
| C24 | $-0.0600(4)$ | $1.0162(11)$ | $0.0784(4)$ | $0.0425(18)$ |
| H24A | -0.0722 | 1.0999 | 0.0439 | $0.051^{*}$ |
| C25 | $-0.1002(3)$ | $0.8881(12)$ | $0.0776(3)$ | $0.0426(19)$ |
| H25A | -0.1401 | 0.8838 | 0.0430 | $0.051^{*}$ |
| C26 | $-0.0826(3)$ | $0.7638(9)$ | $0.1277(4)$ | $0.0333(17)$ |
| H26A | -0.1103 | 0.6744 | 0.1274 | $0.040^{*}$ |
|  |  |  |  |  |
|  |  |  |  |  |

Atomic displacement parameters $\left(\AA^{2}\right)$

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Pt1 | $0.0227(2)$ | $0.0289(2)$ | $0.0304(2)$ | $0.00284(14)$ | $0.00796(18)$ | $-0.00095(14)$ |
| S1 | $0.0276(9)$ | $0.0297(10)$ | $0.0446(10)$ | $0.0037(7)$ | $0.0090(8)$ | $0.0038(8)$ |
| S2 | $0.0384(11)$ | $0.0366(10)$ | $0.0520(12)$ | $0.0004(9)$ | $0.0248(9)$ | $-0.0049(9)$ |
| F1 | $0.053(3)$ | $0.061(3)$ | $0.075(4)$ | $0.007(2)$ | $0.035(3)$ | $0.029(3)$ |
| F2 | $0.053(3)$ | $0.061(3)$ | $0.075(4)$ | $0.007(2)$ | $0.035(3)$ | $0.029(3)$ |
| F3 | $0.053(3)$ | $0.061(3)$ | $0.075(4)$ | $0.007(2)$ | $0.035(3)$ | $0.029(3)$ |
| F4 | $0.056(4)$ | $0.080(5)$ | $0.066(4)$ | $0.015(3)$ | $0.042(3)$ | $0.001(3)$ |
| F5 | $0.056(4)$ | $0.080(5)$ | $0.066(4)$ | $0.015(3)$ | $0.042(3)$ | $0.001(3)$ |
| F6 | $0.056(4)$ | $0.080(5)$ | $0.066(4)$ | $0.015(3)$ | $0.042(3)$ | $0.001(3)$ |
| C1 | $0.034(4)$ | $0.036(4)$ | $0.037(4)$ | $-0.014(3)$ | $0.007(3)$ | $-0.001(3)$ |
| C2 | $0.047(4)$ | $0.040(5)$ | $0.045(4)$ | $-0.019(4)$ | $0.021(4)$ | $-0.014(4)$ |
| C3 | $0.056(6)$ | $0.062(6)$ | $0.056(6)$ | $-0.021(5)$ | $0.023(5)$ | $0.001(5)$ |
| C4 | $0.073(7)$ | $0.055(6)$ | $0.056(5)$ | $-0.009(5)$ | $0.036(5)$ | $-0.009(4)$ |
| As1 | $0.0215(5)$ | $0.0261(5)$ | $0.0256(5)$ | 0.000 | $0.0099(4)$ | 0.000 |
| C11 | $0.020(3)$ | $0.026(3)$ | $0.031(3)$ | $-0.001(3)$ | $0.010(3)$ | $-0.010(3)$ |
| C12 | $0.042(4)$ | $0.036(4)$ | $0.036(4)$ | $0.009(3)$ | $0.021(3)$ | $0.003(3)$ |
| C13 | $0.035(4)$ | $0.055(6)$ | $0.042(4)$ | $0.008(4)$ | $0.025(3)$ | $0.002(4)$ |
| C14 | $0.028(4)$ | $0.032(5)$ | $0.061(6)$ | $0.006(3)$ | $0.018(4)$ | $-0.010(3)$ |


|  |  |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C15 | $0.028(4)$ | $0.038(4)$ | $0.037(4)$ | $0.002(3)$ | $0.002(3)$ | $0.002(3)$ |
| C16 | $0.031(4)$ | $0.034(4)$ | $0.041(4)$ | $0.004(3)$ | $0.018(3)$ | $0.005(3)$ |
| C21 | $0.020(3)$ | $0.028(4)$ | $0.027(3)$ | $0.000(2)$ | $0.010(3)$ | $-0.002(2)$ |
| C22 | $0.026(3)$ | $0.033(4)$ | $0.027(3)$ | $-0.004(3)$ | $0.009(3)$ | $0.002(3)$ |
| C23 | $0.035(4)$ | $0.030(4)$ | $0.040(4)$ | $-0.001(3)$ | $0.016(3)$ | $0.011(3)$ |
| C24 | $0.054(5)$ | $0.039(5)$ | $0.037(4)$ | $0.007(4)$ | $0.023(4)$ | $0.009(3)$ |
| C25 | $0.031(4)$ | $0.054(5)$ | $0.031(4)$ | $0.008(4)$ | $0.004(3)$ | $0.009(4)$ |
| C26 | $0.019(3)$ | $0.043(5)$ | $0.034(4)$ | $0.003(3)$ | $0.009(3)$ | $0.005(3)$ |

Geometric parameters $\left(\AA,{ }^{\circ}\right)$

| $\mathrm{Pt} 1-\mathrm{S1}{ }^{\text {i }}$ | 2.2496 (18) | As1-C11 | 1.913 (6) |
| :---: | :---: | :---: | :---: |
| Pt1-S1 | 2.2496 (19) | C11-C12 | 1.378 (9) |
| $\mathrm{Pt} 1-\mathrm{S} 2^{\text {i }}$ | 2.254 (2) | C11-C16 | 1.394 (10) |
| Pt1-S2 | 2.254 (2) | C12-C13 | 1.390 (10) |
| S1-C1 | 1.737 (8) | C12-H12A | 0.9500 |
| S2-C2 | 1.715 (9) | C13-C14 | 1.364 (12) |
| F1-C3 | 1.346 (7) | C13-H13A | 0.9500 |
| F2-C3 | 1.355 (6) | C14-C15 | 1.402 (13) |
| F3-C3 | 1.365 (6) | C14-H14A | 0.9500 |
| F1A-C3 | 1.360 (7) | C15-C16 | 1.382 (11) |
| F2A-C3 | 1.372 (7) | C15-H15A | 0.9500 |
| F3A-C3 | 1.359 (7) | C16-H16A | 0.9500 |
| F4-C4 | 1.376 (6) | C21-C26 | 1.382 (10) |
| F5-C4 | 1.365 (6) | C21-C22 | 1.403 (9) |
| F6-C4 | 1.366 (6) | C22-C23 | 1.386 (10) |
| F6A-C4 | 1.371 (6) | $\mathrm{C} 22-\mathrm{H} 22 \mathrm{~A}$ | 0.9500 |
| F4A-C4 | 1.360 (6) | $\mathrm{C} 23-\mathrm{C} 24$ | 1.394 (11) |
| F5A-C4 | 1.362 (6) | C23-H23A | 0.9500 |
| $\mathrm{C} 1-\mathrm{C} 2$ | 1.353 (12) | C24-C25 | 1.368 (11) |
| C1-C3 | 1.432 (13) | C24-H24A | 0.9500 |
| C2-C4 | 1.489 (12) | C25-C26 | 1.394 (11) |
| As1-C21 ${ }^{\text {ii }}$ | 1.899 (7) | C25-H25A | 0.9500 |
| As1-C21 | 1.899 (7) | C26-H26A | 0.9500 |
| Asl-C11 ${ }^{\text {ii }}$ | 1.913 (6) |  |  |
| S1-Pt1-S1 | 180.00 (10) | C21ii-As1-C11 | 110.4 (3) |
| $\mathrm{S} 1^{\mathrm{i}}-\mathrm{Pt} 1-\mathrm{S} 2^{\mathrm{i}}$ | 88.73 (8) | C21-As1-C11 | 111.2 (3) |
| $\mathrm{S} 1-\mathrm{Pt} 1-\mathrm{S} 2{ }^{\text {i }}$ | 91.27 (8) | C11 ${ }^{\text {ii }}$-As1-C11 | 107.1 (4) |
| S 1 - $\mathrm{Pt} 1-\mathrm{S} 2$ | 91.27 (8) | C12-C11-C16 | 120.9 (6) |
| $\mathrm{S} 1-\mathrm{Pt} 1-\mathrm{S} 2$ | 88.73 (8) | C12-C11-As1 | 121.0 (5) |
| $\mathrm{S} 2{ }^{\text {i }}$ - $\mathrm{Pt} 1-\mathrm{S} 2$ | 180.000 (1) | C16-C11-As1 | 118.0 (5) |
| $\mathrm{C} 1-\mathrm{S} 1-\mathrm{Pt} 1$ | 104.3 (3) | C11-C12-C13 | 119.4 (7) |
| $\mathrm{C} 2-\mathrm{S} 2-\mathrm{Pt} 1$ | 104.2 (3) | C11-C12-H12A | 120.3 |
| $\mathrm{C} 2-\mathrm{C} 1-\mathrm{C} 3$ | 123.2 (7) | $\mathrm{C} 13-\mathrm{C} 12-\mathrm{H} 12 \mathrm{~A}$ | 120.3 |
| $\mathrm{C} 2-\mathrm{C} 1-\mathrm{S} 1$ | 120.5 (6) | C14-C13-C12 | 120.3 (7) |
| $\mathrm{C} 3-\mathrm{C} 1-\mathrm{S} 1$ | 116.3 (6) | C14-C13-H13A | 119.8 |
| C1-C2-C4 | 126.0 (7) | C12-C13-H13A | 119.8 |

supporting information

| C1-C2-S2 | $122.1(6)$ |
| :--- | :--- |
| C4-C2-S2 | $111.9(6)$ |
| F1-C3-F2 | $104.5(7)$ |
| F3A-C3-F1A | $102.9(8)$ |
| F1-C3-F3 | $104.1(7)$ |
| F2-C3-F3 | $101.0(6)$ |
| F3A-C3-F2A | $99.4(7)$ |
| F1A-C3-F2A | $99.5(7)$ |
| F1-C3-C1 | $115.9(7)$ |
| F2-C3-C1 | $114.5(7)$ |
| F1A-C3-C1 | $119.6(10)$ |
| F3-C3-C1 | $115.2(7)$ |
| F2A-C3-C1 | $99.6(11)$ |
| F4A-C4-F5A | $105.9(8)$ |
| F5-C4-F6 | $104.5(6)$ |
| F4A-C4-F6A | $104.3(8)$ |
| F5A-C4-F6A | $102.4(7)$ |
| F5-C4-F4 | $102.7(6)$ |
| F6-C4-F4 | $101.1(6)$ |
| F4A-C4-C2 | $128.2(13)$ |
| F5A-C4-C2 | $110.8(9)$ |
| F5-C4-C2 | $115.0(6)$ |
| F6-C4-C2 | $117.8(7)$ |
| F6A-C4-C2 | $102.1(10)$ |
| F4-C4-C2 | $113.8(7)$ |
| C21ii-As1-C21 | $106.5(4)$ |
| C21ii-As1-C11ii | $111.2(3)$ |
| C21-As1-C11ii | $110.4(3)$ |
|  |  |


| $\mathrm{C} 13-\mathrm{C} 14-\mathrm{C} 15$ | $120.6(7)$ |
| :--- | :--- |
| $\mathrm{C} 13-\mathrm{C} 14-\mathrm{H} 14 \mathrm{~A}$ | 119.7 |
| $\mathrm{C} 15-\mathrm{C} 14-\mathrm{H} 14 \mathrm{~A}$ | 119.7 |
| $\mathrm{C} 16-\mathrm{C} 15-\mathrm{C} 14$ | $119.4(8)$ |
| $\mathrm{C} 16-\mathrm{C} 15-\mathrm{H} 15 \mathrm{~A}$ | 120.3 |
| $\mathrm{C} 14-\mathrm{C} 15-\mathrm{H} 15 \mathrm{~A}$ | 120.3 |
| $\mathrm{C} 15-\mathrm{C} 16-\mathrm{C} 11$ | $119.3(7)$ |
| $\mathrm{C} 15-\mathrm{C} 16-\mathrm{H} 16 \mathrm{~A}$ | 120.3 |
| $\mathrm{C} 11-\mathrm{C} 16-\mathrm{H} 16 \mathrm{~A}$ | 120.3 |
| $\mathrm{C} 26-\mathrm{C} 21-\mathrm{C} 22$ | $120.8(6)$ |
| $\mathrm{C} 26-\mathrm{C} 21-\mathrm{As} 1$ | $121.1(5)$ |
| $\mathrm{C} 22-\mathrm{C} 21-\mathrm{As} 1$ | $117.9(5)$ |
| $\mathrm{C} 23-\mathrm{C} 22-\mathrm{C} 21$ | $119.1(6)$ |
| $\mathrm{C} 23-\mathrm{C} 22-\mathrm{H} 22 \mathrm{~A}$ | 120.5 |
| $\mathrm{C} 21-\mathrm{C} 22-\mathrm{H} 22 \mathrm{~A}$ | 120.5 |
| $\mathrm{C} 22-\mathrm{C} 23-\mathrm{C} 24$ | $119.5(7)$ |
| $\mathrm{C} 22-\mathrm{C} 23-\mathrm{H} 23 \mathrm{~A}$ | 120.2 |
| $\mathrm{C} 24-\mathrm{C} 23-\mathrm{H} 23 \mathrm{~A}$ | 120.2 |
| $\mathrm{C} 25-\mathrm{C} 24-\mathrm{C} 23$ | $121.3(7)$ |
| $\mathrm{C} 25-\mathrm{C} 24-\mathrm{H} 24 \mathrm{~A}$ | 119.4 |
| $\mathrm{C} 23-\mathrm{C} 24-\mathrm{H} 24 \mathrm{~A}$ | 119.4 |
| $\mathrm{C} 24-\mathrm{C} 25-\mathrm{C} 26$ | $119.8(7)$ |
| $\mathrm{C} 24-\mathrm{C} 25-\mathrm{H} 25 \mathrm{~A}$ | 120.1 |
| $\mathrm{C} 26-\mathrm{C} 25-\mathrm{H} 25 \mathrm{~A}$ | 120.1 |
| $\mathrm{C} 21-\mathrm{C} 26-\mathrm{C} 25$ | $119.5(7)$ |
| $\mathrm{C} 21-\mathrm{C} 26-\mathrm{H} 26 \mathrm{~A}$ | 120.2 |
| $\mathrm{C} 25-\mathrm{C} 26-\mathrm{H} 26 \mathrm{~A}$ | 120.2 |
|  |  |

Symmetry codes: (i) $-x+1 / 2,-y+1 / 2,-z+1$; (ii) $-x, y,-z+1 / 2$.

