Low-temperature redetermination of *trans*-tetrabromidobis(dimethyl sulfide-*κS*)platinum(IV)

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The octahedral molecule of the title compound, $[PtBr_4(C_2H_6S)_2]$, lies on an inversion centre [Pt—Br = 2.4654 (4) and 2.4761 (4) Å; Pt—S = 2.3624 (9) Å]. A similar set of bond distances is predicted by density functional theory.

Related literature

For the original room-temperature structure, see: Skvortsov *et al.* (1994). For the isostructural chlorido analogue, see: Toffoli *et al.* (1987). For the iodido analogue, see: Janse van Rensburg *et al.* (2007). For background literature, see: Muller *et al.* (2006); Otto (2000); Otto *et al.* (2001); Roodt *et al.* (2003).
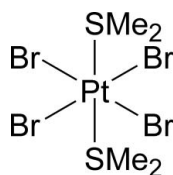
Experimental

Crystal data

$[PtBr_4(C_2H_6S)_2]$
$M_r = 638.99$
Monoclinic, $P2_1/n$
$a = 7.1993$ (2) Å
$b = 7.0922$ (2) Å
$c = 12.6033$ (3) Å
$\beta = 100.674$ (1)°

$V = 632.38$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 24.01$ mm^{-1}
$T = 100$ (2) K
$0.14 \times 0.07 \times 0.06$ mm

Data collection

Bruker Kappa APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.098$, $T_{max} = 0.239$

12836 measured reflections
1577 independent reflections
1503 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.048$
$S = 1.25$
1577 reflections
54 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -2.31$ e Å^{-3}

Table 1
Comparison of geometric parameters (Å, °) for trans-$[PtX_4(dms)_2]$.

X	Pt—$X1$	Pt—$X2$	Pt—S	$X1$—Pt—S	$X2$—Pt—S	$X1$—Pt—$X2$
Cl^a	2.313 (3)	2.319 (33)	2.363 (10)	95.68 (5)	83.43 (4)	90.42 (5)
Br^b	2.475 (1)	2.467 (1)	2.364 (2)	96.05 (7)	83.75 (6)	90.57 (4)
Br^c	2.4654 (4)	2.4761 (4)	2.3624 (9)	96.02 (2)	83.48 (2)	90.607 (12)
Br^d	2.558	2.558	2.440	96.88	83.30	89.89

Notes: (a) Toffoli *et al.* (1987); (b) Skvortsov *et al.* (1994); (c) this work, observed; (d) this work, calculated.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2369).

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supplementary materials

Low-temperature redetermination of *trans*-tetrabromidobis(dimethyl sulfide-*κS*)platinum(IV)

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Comment

As part of an ongoing investigation (Muller *et al.*, 2006; Roodt *et al.*, 2003; Otto, 2001; Otto *et al.*, 2000) into determining which factors govern a disordered packing mode in symmetrical square-planar complexes of Rh, Ir, Pd and Pt we set out to synthesize the starting compound *trans*-[PtBr$_2$(dms)$_2$], however we formed *trans*-[PtBr$_4$(dms)$_2$].

The current redetermination of the structure (Skvortsov *et al.*, 1994) is accompanied by a DFT calculation to determine the optimum structure in the gas phase, similar to what we reported previously for square planar Rh complexes (Muller *et al.*, 2006).

The title compound *trans*-[PtBr$_4$(dms)$_2$] (dms = SMe$_2$), (I), crystallizes in the monoclinic space group P2(1)/n (*Z* = 2) and lies on an inversion centre (Figure 1). Selected geometrical data are given in Table 2. The Pt—Br distances of the current low temperature study are slightly smaller than the previously reported, room temperature, structure (Skvortsov *et al.*, 1994; data extracted from the Cambridge Structural Database; Version 5.27, update of August 2006), as is to be expected. No short intermolecular contacts were observed. A packing diagram is given in Figure 2.

Geometry optimization of the title compound using Density Functional Theory (DFT) calculations with the observed parameters as a starting structure converged to similar geometry. A good agreement between the calculated and observed geometry (Table 3) was found (r.m.s. deviation of all non-H atoms = 0.1684 Å). The overlay of the calculated and experimental structures is shown in Figure 3.

The geometries of *trans*-[PtX_4(dms)$_2$] (X = Cl, Br, I) which are isostructural are given in Table 3. The Pt—S distances are about the same for X = Cl and Br, 2.36 Å. The X—Pt—X angles are close to 90° for all complexes and the X—Pt—S angles are 5–7° off the 'ideal' 90°. Recently (Janse van Rensburg *et al.*, 2007) the iodo complex has been described as being suspended by I···I contacts, and we refer to their discussion of these contacts.

Experimental

The title compound was formed during an attempted synthesis of *trans*-[PtBr$_2$(dms)$_2$]. [K$_2$PtCl$_4$] (1.00 g, 2.41 mmol) was dissolved in water (50 ml). To this 5 equivalents of LiBr (g, mmol) was added. The solution was stirred for 30 min and an excess of dimethyl sulfide (4.5 ml, 60 mmol) was added and left to stir. After 3 h the complex was filtered off, washed with water and left to dry. Recrystallization from CH$_2$Cl$_2$ gave red cuboids.

DFT calculations were performed at the B3LYP level with the LANL2DZ basis set for platinum and the 6–311 G(*d*) basis set for bromine, sulfur, carbon and hydrogen atoms, using the Gaussian03 software package. Minima were verified *via* frequency analysis of the stationary point.

supplementary materials

Refinement

The methyl protons were placed in geometrically idealized positions and constrained to ride on their parent atoms with $U_{iso}(H) = 1.5$, with torsion angles refined from the electron density.

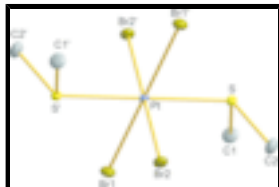The final difference Fourier map had a large peak near Pt1.

Figures

Fig. 1. The structure (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. Primed atoms were generated by symmetry ($-x$, $-y + 1$, $-z$).
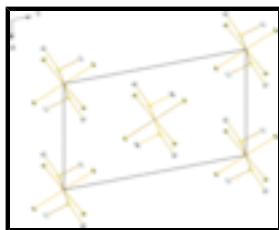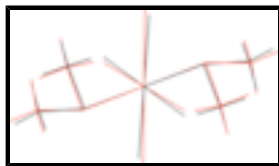

Fig. 2. Packing diagram of (I).

Fig. 3. Overlay of calculated and observed structures of (I)

trans-tetrabromidobis(dimethyl sulfide-κ*S*)platinum(IV)

Crystal data

$[PtBr_4(C_2H_6S)_2]$	$F_{000} = 572$
$M_r = 638.99$	$D_x = 3.356$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 7741 reflections
$a = 7.1993$ (2) Å	$\theta = 3.0–28.3°$
$b = 7.0922$ (2) Å	$\mu = 24.01$ mm^{-1}
$c = 12.6033$ (3) Å	$T = 100$ (2) K
$\beta = 100.674$ (1)°	Cuboid, red
$V = 632.38$ (3) Å^3	$0.14 \times 0.07 \times 0.06$ mm
$Z = 2$	

Data collection

Bruker X8 APEXII 4K Kappa CCD	1577 independent reflections

diffractometer

Monochromator: graphite	1503 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3 pixels mm^{-1}	$R_{int} = 0.037$
$T = 100(2)$ K	$\theta_{max} = 28.3°$
φ and ω scans	$\theta_{min} = 3.0°$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$h = -9 \rightarrow 9$
$T_{min} = 0.098$, $T_{max} = 0.239$	$k = -8 \rightarrow 9$
12836 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2 + 0.9733P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.019$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.048$	$\Delta\rho_{max} = 0.60$ e Å^{-3}
$S = 1.25$	$\Delta\rho_{min} = -2.31$ e Å^{-3}
1577 reflections	Extinction correction: none
54 parameters	

Special details

Experimental. The intensity data was collected on a Bruker X8 Apex II 4 K Kappa CCD diffractometer using an exposure time of 20 s/frame. A total of 2528 frames were collected with a frame width of 0.5° covering up to $\theta = 28.3°$ with 100% completeness accomplished.

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Pt	0	0.5	0	0.00571 (7)
Br1	0.12665 (5)	0.42300 (6)	−0.16361 (3)	0.01208 (10)
Br2	0.26367 (5)	0.32209 (5)	0.10955 (3)	0.01170 (9)
S	0.14169 (12)	0.80085 (13)	0.02722 (7)	0.00895 (18)
C1	0.2075 (6)	0.8796 (6)	−0.0964 (3)	0.0152 (8)
H1A	0.2529	1.0099	−0.0878	0.023*
H1B	0.0974	0.8733	−0.1551	0.023*
H1C	0.308	0.7984	−0.1136	0.023*
C2	0.3716 (5)	0.7772 (6)	0.1094 (3)	0.0162 (8)
H2A	0.4487	0.6927	0.0737	0.024*
H2B	0.3599	0.7246	0.1797	0.024*
H2C	0.4323	0.9012	0.1196	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt	0.00420 (10)	0.00743 (12)	0.00574 (11)	0.00062 (7)	0.00159 (7)	0.00040 (6)
Br1	0.01282 (18)	0.0146 (2)	0.01001 (18)	0.00212 (15)	0.00527 (14)	−0.00004 (14)
Br2	0.00882 (18)	0.01303 (19)	0.01265 (18)	0.00292 (14)	0.00047 (14)	0.00183 (13)
S	0.0078 (4)	0.0087 (4)	0.0109 (4)	−0.0010 (3)	0.0033 (3)	−0.0007 (3)
C1	0.018 (2)	0.015 (2)	0.0149 (19)	−0.0038 (16)	0.0078 (16)	0.0043 (16)
C2	0.0117 (18)	0.018 (2)	0.018 (2)	−0.0045 (16)	−0.0012 (15)	−0.0021 (16)

Geometric parameters (Å, °)

Pt—S	2.3624 (9)	S—C1	1.799 (4)
Pt—S^i	2.3624 (9)	C1—H1A	0.98
Pt—Br1^i	2.4654 (4)	C1—H1B	0.98
Pt—Br1	2.4654 (4)	C1—H1C	0.98
Pt—Br2	2.4761 (4)	C2—H2A	0.98
Pt—Br2^i	2.4761 (4)	C2—H2B	0.98
S—C2	1.790 (4)	C2—H2C	0.98
S—Pt—S^i	180	C2—S—C1	99.6 (2)
S—Pt—Br1^i	83.98 (2)	C2—S—Pt	109.11 (15)
S^i—Pt—Br1^i	96.02 (2)	C1—S—Pt	109.30 (14)
S—Pt—Br1	96.02 (2)	S—C1—H1A	109.5
S^i—Pt—Br1	83.98 (2)	S—C1—H1B	109.5
Br1^i—Pt—Br1	180	H1A—C1—H1B	109.5
S—Pt—Br2	96.52 (2)	S—C1—H1C	109.5
S^i—Pt—Br2	83.48 (2)	H1A—C1—H1C	109.5
Br1^i—Pt—Br2	90.607 (12)	H1B—C1—H1C	109.5
Br1—Pt—Br2	89.393 (12)	S—C2—H2A	109.5
S—Pt—Br2^i	83.48 (2)	S—C2—H2B	109.5
S^i—Pt—Br2^i	96.52 (2)	H2A—C2—H2B	109.5
Br1^i—Pt—Br2^i	89.393 (12)	S—C2—H2C	109.5
Br1—Pt—Br2^i	90.607 (12)	H2A—C2—H2C	109.5
Br2—Pt—Br2^i	180	H2B—C2—H2C	109.5
Br1^i—Pt—S—C2	91.04 (15)	Br1^i—Pt—S—C1	−161.04 (15)
Br1—Pt—S—C2	−88.96 (15)	Br1—Pt—S—C1	18.96 (15)
Br2—Pt—S—C2	1.11 (15)	Br2—Pt—S—C1	109.04 (15)
Br2^i—Pt—S—C2	−178.89 (15)	Br2^i—Pt—S—C1	−70.96 (15)

Symmetry codes: (i) −*x*, −*y*+1, −*z*.

Table 1
Comparison of geometric parameters (Å, °) for trans-[PtX$_4$(dms)$_2$].

X	Pt—X1	Pt—X2	Pt—S	X1—Pt—S	X2—Pt—S	X1—Pt—X2

Cl (i)	2.313 (3)	2.319 (33)	2.363 (10)	95.68 (5)	83.43 (4)	90.42 (5)
Br (ii)	2.475 (1)	2.467 (1)	2.364 (2)	96.05 (7)	83.75 (6)	90.57 (4)
Br (iii)	2.4654 (4)	2.4761 (4)	2.3624 (9)	96.02 (2)	83.48 (2)	90.607 (12)
Br (iv)	2.558	2.558	2.440	96.88	83.30	89.89

(i) Toffoli *et al.* (1987); (ii) Skvortsov *et al.* (1994); (iii) this work, observed; (iv) this work, calculated.
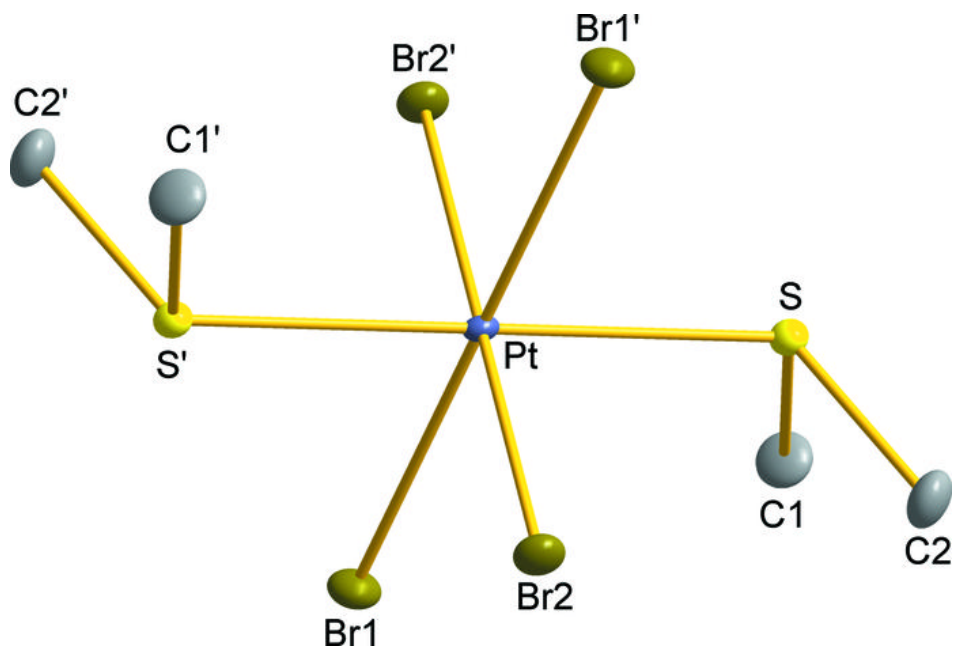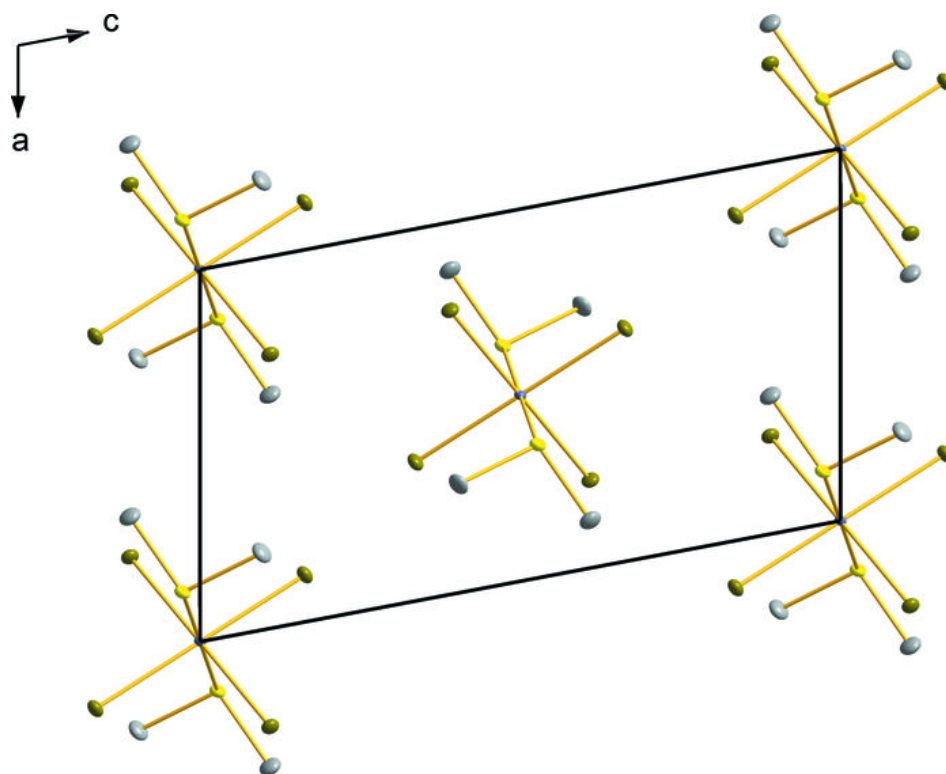
Fig. 1

Fig. 2

Fig. 3