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cis–trans Isomers of PtX_4L_2 (X = halogen and L = neutral ligand): *trans*-bis(dimethyl sulfide)tetraiodidoplatinum(IV)

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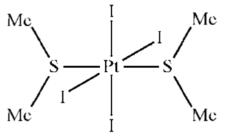
The octahedral title complex, [$PtI_4(C_2H_6S)_2$] or *trans*-$PtI_4(dms)_2$ (dms is dimethyl sulfide), crystallizes in the monoclinic space group $P2_1/n$ (Z = 2), with molecular symmetry C_i, which is the most frequently occurring point group for *trans*-PtX_4L_2 {56%, 28 structures in the Cambridge Structural Database (CSD) [Allen (2002). *Acta Cryst.* B**58**, 380–388]}, followed by C_1 (22%, 11 structures). The complexes form a puckered pseudo-hexagonal layer in the $(10\overline{1})$ plane, and the layers are stacked with an interplanar distance of 7.10 Å. Density functional theory (DFT) calculations on an isolated complex with the observed parameters as a starting structure converged to C_{2h}. Constraints to C_i on the observed geometry give 3–4 kJ mol^{-1} higher energy compared with C_{2h}. DFT calculations on [$PtCl_4(PzH)_2$] (PzH is pyrazole), reported in the CSD in both the *cis* and *trans* forms, show an energy difference of 21 kJ mol^{-1} in favour of the *trans* complex. A CSD search for PtX_4L_2-type complexes, where X is a halogen and L is a ligand with a donor atom from group 14, 15 or 16, indicated a preferred *trans* geometrical arrangement, with a total fraction of 68%. The dominating crystal packing operators for the *trans* complexes are an inversion centre combined with a screw axis/glide plane (48%), followed by an inversion centre alone (28%).

Comment

The principal nonzero oxidation states of Pt are II and IV. *cis/trans*- Pt$^{II}X_2L_2$ complexes, where X is a halogen and L a ligand with a donor atom from group 14, 15 or 16, have been extensively studied in the solid state, with 316 entries in the Cambridge Structural Database (CSD; Allen, 2002). Data for Pt$^{IV}X_4L_2$ are scarce, and we report here the structure of the title compound, *trans*-$PtI_4(dms)_2$ (dms is dimethyl sulfide), (I), together with data mining for this class of compounds in the CSD (2006 release), with emphasis on the following: (i) is there a preference for *cis* or *trans* complexes in the solid state? (ii) what molecular symmetries are retained in the solid state? (iii) which are the dominating crystal packing operators?



(I)

The title compound crystallizes in the monoclinic space group $P2_1/n$ (Z = 2), with molecular symmetry C_i (Fig. 1). The Pt—I distances (Table 1) are slightly larger than those observed in *cis*-[$PtI_4(net)_2$] [net is ethylamine, NC_2H_5; Pt—I = 2.65 Å for I atoms in *trans* positions and 2.61 Å for I atoms *trans* to N (Thiele *et al.*, 1999)]. Geometry optimization of the title compound, using density functional theory (DFT) calculations with the observed parameters as a starting structure, converged to C_{2h}. Constraints to C_i on the observed geometry give 3–4 kJ mol^{-1} higher energy compared with C_{2h}, which would require a space group that hampers close packing, indicating that intermolecular forces determine the point group for the complex. There is good agreement between the calculated and observed geometry (Table 2), and the deviation from 90° of the I—Pt—S angle observed in the crystal structure is even larger in the calculated structure, suggesting that it is the result of an intramolecular effect.

The geometries of isostructural *trans*-PtX_4(dms)$_2$ (X= Cl, Br or I) are given in Table 2. The Pt—S distances are about the same for X = Cl and Br (2.36 Å), but significantly larger for X = I [2.390 (2) 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°, which further supports the idea that this is an intramolecular effect. The intermolecular $X\cdots X$ contact of 3.92 (6) Å is on the short side for X = I and on the long side for X = Cl and Br. However I···I contacts as short as 3.48 Å have been observed in *cis*-[$PtI_4(net)_2$].

trans-PtX_4(dms)$_2$ forms a puckered pseudo-hexagonal close-packed layer in the $(10\overline{1})$ plane, with four I···I contacts [3.92 (1) Å] and two S···S contacts [3.69 (1) Å; Fig. 2]. Halogen–halogen interactions are known for stabilizing supramolecular structures (Desiraju, 1995). The stacking layers are parallel-displaced, resulting in a pseudo-close

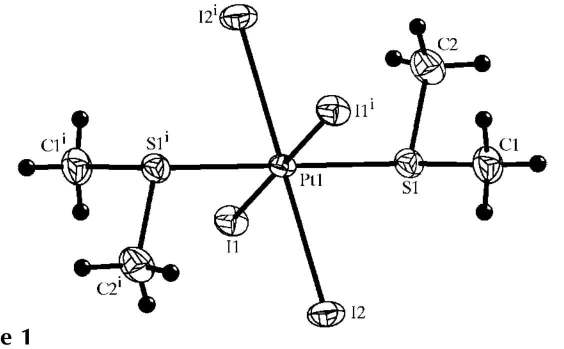


Figure 1
A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) 2 − x, −y, 2 − z.]

packing with an inter-layer distance of 7.10 Å, with notable inter-layer contacts (H···I = 3.23 Å and C—H···I = 153°) and also some soft H···H contacts (2.86 Å). For the isostructural compounds, the distortion from an ideal close packing is about the same for the bromide but much more severe for the chloride, as manifested by the Pt···Pt···Pt angles within a layer, which are close to 120° for both the iodide and bromide but only about 100° for the chloride.

The CSD was searched using *ConQuest* (Bruno *et al.*, 2002) for *cis*/*trans*-PtX_4L_2 complexes, where X is a halogen and L a ligand containing a donor atom from group 14, 15 or 16. Simple solvates are included, but no chelates or structures with no coordinates, obscure connectivity or disorder. The majority of these 50 complexes (68%) preferred the *trans* configuration (Tables A and B, deposited), compared with 50% in the system *trans*-PtX_2L_2 (Hansson *et al.*, 2006). The complex [$PtCl_4(PzH)_2$] (PzH is pyrazole, $N_2C_3H_4$) is reported in the CSD as both the *cis* and the *trans* isomers (Khripun *et al.*, 2006). DFT calculations on these complexes show a difference between the *cis* and *trans* isomers of 21 kJ mol^{-1} in favour of the *trans* complex in the gas phase, also indicating a preference for the *trans* configuration.

Complexes *trans*-PtX_4L_2 may adopt the molecular point groups C_1, C_i, C_s, C_2, C_{2v} and C_{2h}. C_i is retained in 56% of cases, followed by C_1 (22%), C_s (12%), C_2 (8%) and C_{2h} (2%), with no representatives for C_{2v} (Table C, deposited); the order of preference is C_i (78%), C_1 (16%), C_2 (11%) and C_{2h} (2%) for *trans*-PtX_2L_2 (Hansson *et al.*, 2006). C_{2v} is not represented in any of the systems and C_{2h} has very low frequency, in accordance with Kitaigorodsky's (1973) rule that C_{2v} requires space groups that hamper close packing and C_{2h} may adopt maximal density in the space group $C2/m$, which is actually observed in both systems.

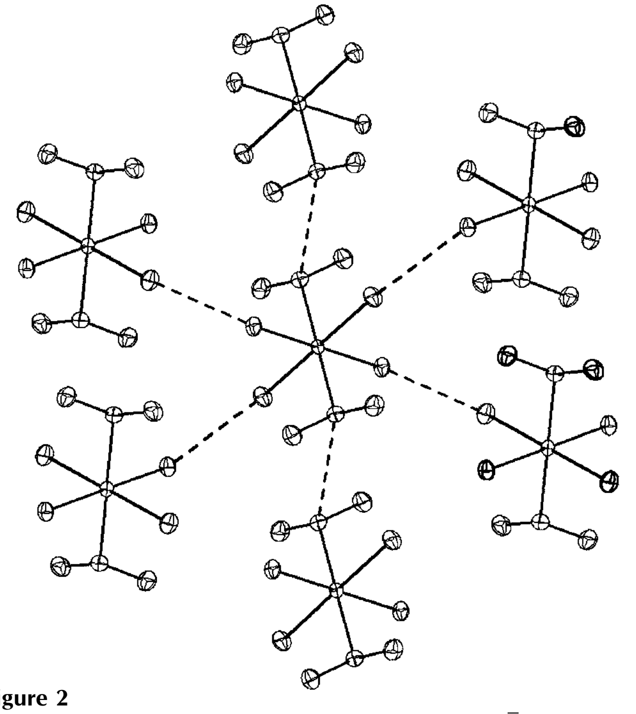


Figure 2
A view of the pseudo-hexagonal close-packed layer, $(10\overline{1})$; the b axis is vertical. Dashed lines represent the positions of short contacts. Displacement ellipsoids are drawn at the 30% probability level.

The dominating crystal packing operator is an inversion centre as the sole packing operator in 28% of cases (neglecting pure translations which are always present), an inversion centre together with a screw axis/glide plane in 48% and an inversion centre in combination with other operators in 6% (Table C, deposited). It is interesting to note that $P2_1$ and $P2_12_12_1$ only represent 6% of cases, in contrast to the situation for organic molecules, where these space groups are relatively frequent (Brock & Dunitz, 1994; Oskarsson, 2007).

Experimental

The title compound was obtained during an attempted synthesis of *trans*-$PtI_2(dms)_2$, by recrystallization of *trans*-$PtI_2(dms)_2$ in diphenyl sulfide. It is known that triodide and iodine formed by air oxidation of iodide may oxidize Pt^{II} to Pt^{IV} (Olsson, 1986). The synthesis of *trans*-$PtI_2(dms)_2$ was performed according to a literature procedure, with a few modifications (Roulet & Barbey, 1973). [K_2PtCl_4] (100 mg, 0.241 mmol) was dissolved in water (20 ml). To this, KI (1.5 equivalents, 60 mg, 0.361 mmol) was added. The solution was stirred for 30 min, an excess of dimethyl sulfide (0.45 ml, 6.03 mmol) was added and the mixture was left to stir. After 2 h, the complex *trans*-$PtI_2(dms)_2$ was filtered off (yield 93 mg, 71%). *trans*-$PtI_2(dms)_2$ (50 mg, 0.087 mmol) was dissolved in diphenyl sulfide (8 ml) and left in a freezer. From this, *trans*-$PtI_4(dms)_2$ crystallized out as red rods. DFT calculations were performed at the s-VWN level with the basis sets def-TZVPP for Pt and I, TZVPP for Cl, and 6–31G* for C, H and N atoms, using the software *TURBOMOLE 5.5* (Alrichs *et al.*, 1989).

Crystal data

[$PtI_4(C_2H_6S)_2$]
M_r = 826.95
Monoclinic, $P2_1/n$
a = 7.5635 (15) Å
b = 7.4984 (15) Å
c = 13.346 (3) Å
β = 102.06 (3)°
V = 740.2 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 18.06 mm^{-1}
T = 293 (2) K
0.17 × 0.05 × 0.03 mm

Data collection

Bruker SMART 1K CCD diffractometer
Absorption correction: multi-scan *SADABS* (Bruker, 2004)
T_{min} = 0.149, T_{max} = 0.613 (expected range = 0.142–0.582)
6602 measured reflections
1774 independent reflections
1479 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.065
S = 1.06
1774 reflections
54 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.07 e Å^{-3}
$\Delta\rho_{min}$ = −0.95 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—S1	2.3904 (18)	S1—C1	1.793 (8)
Pt1—I1	2.6918 (7)	S1—C2	1.805 (7)
Pt1—I2	2.7070 (8)		
S1—Pt1—I1	84.26 (4)	C1—S1—C2	98.2 (4)
S1—Pt1—I2	83.23 (5)	C1—S1—Pt1	111.6 (3)
I1—Pt1—I2	89.38 (2)	C2—S1—Pt1	110.4 (3)

Acta Cryst. (2008). C**64**, m40–m42 Janse van Rensburg *et al.* • [$PtI_4(C_2H_6S)_2$] **m41**

Table 2
Comparative geometric data (Å, °) for *trans* $\mathrm{Pt^{IV}}X_4(\mathrm{dms})_2$ compounds.

X	Pt—X1	Pt—X2	Pt—S	S—C1	S—C2	X1—Pt—S	X2—Pt—S	X1—Pt—X2	$X1\cdots X2$	$\mathrm{S}\cdots\mathrm{S}$
Cl[i]	2.313 (3)	2.32 (3)	2.363 (10)	1.78 (5)	1.794 (6)	95.68 (5)	83.43 (4)	90.42 (5)	3.759 (2)	3.58 (1)
Br[ii]	2.475 (1)	2.467 (1)	2.364 (2)	1.76 (1)	1.804 (13)	96.05 (7)	83.75 (6)	90.57 (4)	3.922 (2)	3.57 (1)
I[iii]	2.6918 (7)	2.7070 (8)	2.3904 (18)	1.793 (8)	1.805 (7)	96.77 (5)	83.23 (5)	89.38 (1)	3.92 (6)	3.69 (1)
I[iv]	2.70	2.70	2.36	1.79	1.79	98.8	81.1	89.7	–	–

Notes: (i) Toffoli *et al.* (1987); (ii) Skvortsov *et al.* (1994); (iii) this work; (iv) DFT results.

H atoms were positioned geometrically with fixed C—H distances of 0.96 Å [$U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$]. The highest residual peak is 0.68 Å from I2 and the deepest hole is 0.69 Å from Pt1. A Hirshfeld test failure appeared in the structure validation, with the U values of two iodine sites being large in relation to the Pt centre. Suspecting compositional disorder, from chlorine in the starting material, a disordered model was introduced using the PART instruction in *SHELXL97* (Sheldrick, 1997), thus refining the U values of a possible Cl atom at an occupancy value of 0.02. Although the Hirshfeld test was passed, given that the occupancy is so small the values were considered unreliable and the disorder model was not adopted. A similar problem was previously reported in the crystal structure of $[\mathrm{PtI_2(C_9H_{21}P)_2}]$ (Constable *et al.*, 2006).

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3105). Services for accessing these data are described at the back of the journal.

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m42 Janse van Rensburg *et al.* • $[\mathrm{PtI_4(C_2H_6S)_2}]$ *Acta Cryst.* (2008). C**64**, m40–m42