Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hexafluorophosphates of chlorotris(dimethyl sulfide)platinum(II) and bromotris(dimethyl sulfide)platinum(II)

Christian Hansson,[a]* Vadim Yu. Kukushkin,[b] Karin Lövqvist,[a]† Shen Yong[a]‡ and Åke Oskarsson[a]

[a]Inorganic Chemistry, Centre for Chemistry and Chemical Engineering, Lund University, PO Box 124, SE-221 00 Lund, Sweden, and [b]Department of Chemistry, St Petersburg State University, 198904 Stary Petorgraf, St Petersburg, Russia
Correspondence e-mail: christian.hansson@inorg.lu.se

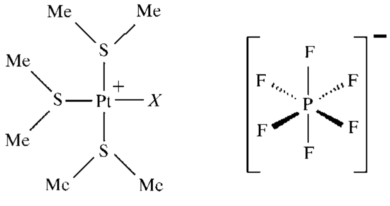
Received 27 June 2003
Accepted 11 September 2003
Online 11 October 2003

The title compounds, chlorotris(dimethyl sulfide-κ*S*)platinum(II) hexafluorophosphate, $[PtCl(C_2H_6S)_3]PF_6$, and bromotris(dimethyl sulfide-κ*S*)platinum(II) hexafluorophosphate, $[PtBr(C_2H_6S)_3]PF_6$, are isomorphous and are composed of $[PtX(dms)_3]^+$ complex cations (X = Cl and Br, and dms is dimethyl sulfide) and PF_6^- anions. The Pt atom is coordinated by three S atoms and one X atom in a pseudo-square-planar coordination, with Pt—S distances in the range 2.293 (1)–2.319 (2) Å. Two dms ligands have a staggered conformation with respect to the coordination plane, while the third is rotated by ~90° compared with the orientation of the other two. The packing can be described as consisting of $[PtX(dms)_3]_2(PF_6)_2$ units with a centre of symmetry. In this description, the Pt^{II} atom has a pseudo-octahedral coordination, with four normal bonds and two long weak interactions. Density-functional theory calculations show that a conformation in which one dms ligand is not staggered is less favourable than having all three dms ligands staggered.

Comment

The observed geometry of a metal complex in the solid state is often discussed in terms of intramolecular forces alone, thus neglecting packing effects (Belsky *et al.*, 1990). The influence of the environment on shape and dimensions can be investigated by studying a particular complex in different crystallographic environments, *i.e.* by the study of crystal structures with more than one molecule in the asymmetric unit (Lövqvist, 1996), of polymorphs (Kapoor *et al.*, 1996), of different solvates (Johansson *et al.*, 2000) or of a charged complex with different counter-ions (Ericson *et al.*, 1992). We explore here the conformational space in the gas phase, using density-functional theory (DFT) calculations, and compare geometry-optimized structures (global minimum as well as local minima) with the geometry observed in the crystal structure.

The structures of $[PtX(dms)_3]PF_6$ (X = Cl and Br, and dms is dimethyl sulfide), (I) and (II), are isomorphous. The Pt atom is coordinated by three dms molecules and one halide molecule in a distorted pseudo-square-planar configuration (Fig. 1). The S atoms bind to the metal through one of the lone pairs, the Pt—S—C angles being in the range 103.4 (2)–112.0 (3)°. Two of the dms ligands are oriented in a staggered conformation with respect to the coordination plane, while the third is rotated by ~90° and has both methyl groups on the same side of the coordination plane (Fig. 1). The Pt—S distances for the two staggered dms ligands are shorter than that of the third ligand in both compounds (Tables 1 and 2). The $[PtX(dms)_3]^+$ complex ions are packed as dimers around a centre of symmetry, with intermolecular Pt···S distances of 3.643 (2) Å in both compounds (Fig. 2). The lone pair on this S atom points approximately towards the Pt atom in the neighbouring complex cation, the Pt—S···Pt angles being in the range 97.7 (2)–98.6 (2)°. The anions are located in 'pockets' on the surface of the dimers, the shortest Pt···F distance being 3.772 (8) Å for (I) and 3.781 (8) Å for (II). The Pt^{II} atom thus has a pseudo-octahedral geometry, with four normal bonds and two long bonds. In this description, the structure is built from electrically neutral $[PtX(dms)_3]_2(PF_6)_2$ units, with a centre of symmetry; space group $P2_1/c$ is adequate for close packing in such specimens (Kitaigorodsky, 1973). Similar dimers have been observed for [chlorotris(1,4-oxathiane-*S*)platinum(II)]trifluoromethanesulfonate (Lövqvist, 1996) and for the neutral complexes *cis*-bis(dimethyl sulfoxide-*S*)dinitratopalladium(II) and *cis*-bis(1,4-oxathiane-*S*)-dinitratopalladium(II) (Johansson & Oskarsson, 2001).



(I) X = Cl
(II) X = Br

DFT calculations on (I) and (II) in the gas phase show two distinct energy minima, both with the dms molecules in a staggered conformation with respect to the coordination plane. There is a local minimum for which all dms molecules have a paddle-wheel-like arrangement, *i.e.* all dms molecules point in the same direction, as in $[Pd(dms)_4]^{2+}$ (Johansson & Oskarsson, 2002). For the global minimum, however, the two dms molecules in *cis* positions with respect to the X atom both

---

† Current address: Solid State Analysis, AstraZeneca R&D, SE-431 83 Mölndal, Sweden.

‡ On leave from Zhongshan University, Guangzhou, People's Republic of China.

DOI: 10.1107/S0108270103020225

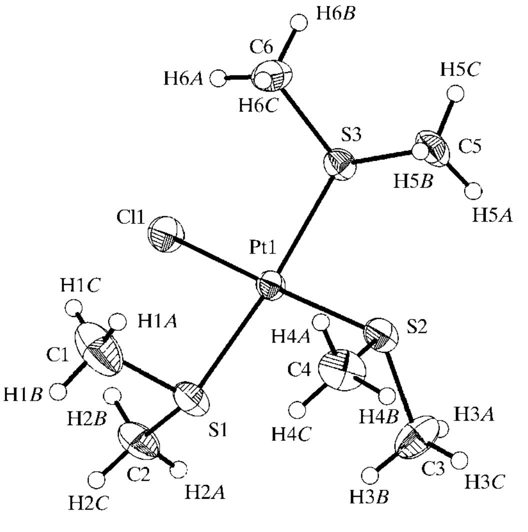


Figure 1

The numbering scheme for the complex cation in (I) and (II). Displacement ellipsoids are drawn at the 30% probability level.

have their methyl groups pointing towards the halide, *i.e.* one of the dms molecules in the *cis* position is rotated by 180° between the local and the global minimum, and the difference in energy between these conformers is 21.5 kJ mol^{-1}. The observed geometry in the solid state is intermediate between these conformers and is thus not at an energy minimum for a single molecule in the gas phase. In both compounds, the observed Pt—S distance for the non-staggered dms molecule is longer than that for the other two molecules; the difference is small but probably significant, namely 0.024 (2) and 0.020 (3) Å for (I) and (II), respectively. The longer Pt—S distance for this dms molecule may be the result of intramolecular forces, but it may also be due to the formation of dimers, *i.e.* an interaction between the S atom in this ligand and the Pt atom in the neighbouring complex ion. A single-point calculation of the $[PtX(dms)_3]_2(PF_6)_2$ packing unit as observed in the crystal structure shows a very small electron density between the Pt atom and the S atom in the neighbouring complex ion (~0.008 a.u. in both compounds; Fig. 2), which is not regarded as significant. Johansson & Oskarsson (2001) calculated ROP (reduced overlap population) values at the EH level for the Pd···O bonds in the similar neutral dimers *cis*-bis(dimethyl sulfoxide-*S*)dinitratopalladium(II) and *cis*-bis(1,4-oxathiane-*S*)dinitratopalladium(II). The reported ROP values are 0.011 and 0.000 for the sulfoxide and 1,4-oxathiane complexes, respectively, and a value as small as 0.011 is hardly significant enough to indicate a covalent interaction. Another plausible explanation for the formation of dimers is, at least in the title compounds, electrostatic interaction between neighbouring complex ions, since the Mulliken charges are −0.54 and 0.35 for the Pt^{II} and S atoms in (I) and are similar in (II) (–0.48 and 0.36). A fairly strong interaction between the Pt^{II} atom and an S atom in the neighbouring complex ion is further corroborated by the U_{eq} value for this atom, *viz*. 0.0430 (2) and 0.0423 (4) Å^2 in (I) and (II), respectively, compared with the range 0.0515 (4)–0.0550 (3) Å^2 for the other S atoms.

It is thus concluded that: (i) the observed geometry of the metal complex in the solid state is not close to an energy minimum of the complex in the gas phase but is rather at a higher energy between two minima; (ii) the observed geometry is thus a consequence of the formation of dimers, but this formation is not due to covalent but rather to electrostatic interactions between two complex ions; and (iii) the packing unit in the solid state is $[PtX(dms)_3]_2(PF_6)_2$, with a centre of symmetry and Pt···F distances of 3.772 (8) and 3.781 (8) Å in (I) and (II), respectively. The coordination geometry for the Pt^{II} atom can thus be described as octahedral, with four short and two long bonds.

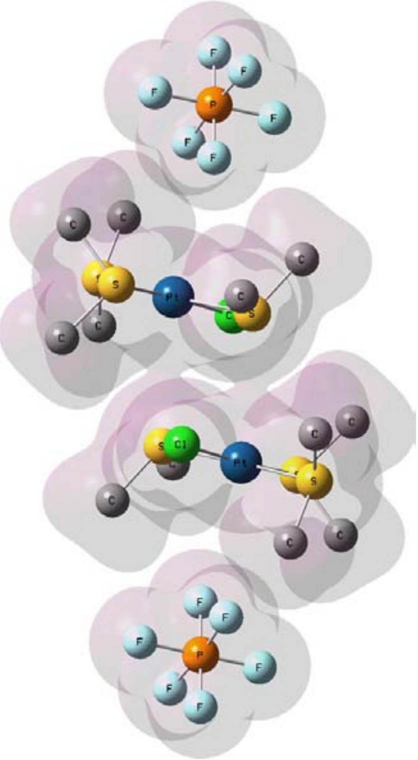


Figure 2

The $[PtCl(dms)_3]_2(PF_6)_2$ packing unit, showing the charge density at the 0.008 a.u. level.

Experimental

For the preparation of (I), dms (5.0 ml) was added to a solution of $K_2[PtCl_4]$ (1.015 g) in water (40 ml). The resulting precipitate was filtered off after 24 h and HPF_6 (0.40 ml, 60% in water) was added to the filtrate. A white precipitate of the desired product was formed, and recrystallization from a 1:1 mixture of acetone and toluene gave pale-yellow crystals (yield 17%). For the preparation of (II), KBr (1.008 g) was added to a solution of $K_2[PtCl_4]$ (0.490 g) in water (20 ml), and dms (2.5 ml) was added after 30 min. The procedure adopted for the preparation of (I) was then followed (yield 22%).

Compound (I)

Crystal data

$[PtCl(C_2H_6S)_3]PF_6$
$M_r = 561.89$
Monoclinic, $P2_1/c$
$a = 8.3027$ (17) Å
$b = 24.083$ (5) Å
$c = 8.5884$ (17) Å
$\beta = 103.92$ (3)°
$V = 1666.8$ (6) Å^3
$Z = 4$

$D_x = 2.239$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6410 reflections
$\theta = 1.7$–33.2°
$\mu = 9.09$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.35 × 0.15 × 0.08 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.223$, $T_{max} = 0.483$
17 196 measured reflections

5511 independent reflections
3939 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 33.2°$
$h = -12 \rightarrow 12$
$k = -36 \rightarrow 35$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.081$
$S = 1.02$
5511 reflections
164 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.51$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00133 (17)

Table 1

Selected geometric parameters (Å, °) for (I).

Pt1—S2	2.2934 (13)	S3—C6	1.862 (5)
Pt1—S1	2.2945 (12)	S2—C4	1.802 (6)
Pt1—Cl1	2.3133 (13)	S2—C3	1.839 (6)
Pt1—S3	2.3175 (12)	S1—C2	1.727 (5)
S3—C5	1.750 (5)	S1—C1	1.867 (8)
S2—Pt1—S1	89.22 (5)	C6—S3—Pt1	104.6 (2)
S2—Pt1—Cl1	176.12 (5)	C4—S2—C3	99.4 (3)
S1—Pt1—Cl1	93.26 (5)	C4—S2—Pt1	109.5 (2)
S2—Pt1—S3	95.39 (4)	C3—S2—Pt1	109.66 (19)
S1—Pt1—S3	174.93 (5)	C2—S1—C1	98.5 (3)
Cl1—Pt1—S3	82.25 (5)	C2—S1—Pt1	109.4 (2)
C5—S3—C6	102.3 (3)	C1—S1—Pt1	103.4 (2)
C5—S3—Pt1	110.82 (18)		

Compound (II)

Crystal data

$[PtBr(C_2H_6S)_3]PF_6$
$M_r = 606.35$
Monoclinic, $P2_1/c$
$a = 8.5981$ (4) Å
$b = 23.9384$ (10) Å
$c = 8.3852$ (3) Å
$\beta = 104.235$ (1)°
$V = 1672.89$ (12) Å^3
$Z = 4$

$D_x = 2.408$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4313 reflections
$\theta = 1.7$–31.7°
$\mu = 11.29$ mm^{-1}
$T = 293$ (2) K
Needle, yellow
0.30 × 0.09 × 0.03 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.336$, $T_{max} = 0.713$
16 670 measured reflections

5170 independent reflections
3275 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 31.7°$
$h = -12 \rightarrow 10$
$k = -35 \rightarrow 34$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.096$
$S = 1.01$
5170 reflections
163 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.34$ e Å^{-3}
$\Delta\rho_{min} = -1.20$ e Å^{-3}

Table 2

Selected geometric parameters (Å, °) for (II).

Pt1—S2	2.2937 (17)	S3—C6	1.815 (7)
Pt1—S1	2.3030 (18)	S2—C3	1.773 (8)
Pt1—S3	2.3186 (17)	S2—C4	1.797 (8)
Pt1—Br1	2.4265 (8)	S1—C2	1.787 (8)
S3—C5	1.798 (7)	S1—C1	1.804 (10)
S2—Pt1—S1	90.24 (7)	C6—S3—Pt1	104.6 (3)
S2—Pt1—S3	93.50 (6)	C3—S2—C4	100.5 (4)
S1—Pt1—S3	175.83 (7)	C3—S2—Pt1	110.6 (3)
S2—Pt1—Br1	176.16 (6)	C4—S2—Pt1	106.5 (3)
S1—Pt1—Br1	91.74 (6)	C2—S1—C1	99.8 (5)
S3—Pt1—Br1	84.63 (5)	C2—S1—Pt1	111.4 (3)
C5—S3—C6	99.3 (4)	C1—S1—Pt1	103.8 (3)
C5—S3—Pt1	112.0 (3)		

In both compounds, the maximum and minimum electron densities are within 1 Å of the Pt^{II} atom. H atoms were placed geometrically after each cycle.

For both compounds, data collection: *SMART* (Bruker, 1995); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000).

Financial assistance from the Crafoord Foundation, the Swedish National Research Council and Lund University (for a scholarship to SY) are gratefully acknowledged. The efforts of Professor L. I. Elding, who made the visit to Lund University for VYK possible, are also gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1144). Services for accessing these data are described at the back of the journal.

References

Belsky, V. K., Konovalov, V. E., Kukushkin, V. Y. & Moiseev, A. I. (1990). *Inorg. Chim. Acta*, **169**, 101–107.
Brandenburg, K. (2000). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (1995). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1998). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Ericson, V., Lövqvist, K., Noren, B. & Oskarsson, Å. (1992). *Acta Chem. Scand.* **46**, 854–860.
Johansson, M. H. & Oskarsson, Å. (2001). *Acta Cryst.* C**57**, 1265–1267.
Johansson, M. H. & Oskarsson, Å. (2002). *Acta Cryst.* C**58**, m102–m104.
Johansson, M. H., Otto, S., Roodt, A. & Oskarsson, Å. (2000). *Acta Cryst.* B**56**, 226–233.
Kapoor, P., Kukushkin, V. Y., Lövqvist, K. & Oskarsson, Å. (1996). *J. Organomet. Chem.* **517**, 71–79.
Kitaigorodsky, A. I. (1973). In *Molecular Crystals and Molecules*. New York/London: Academic Press.
Lövqvist, K. (1996). PhD thesis, Lund University, Sweden.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.