(Dimethyl sulfoxide-*S*)methyl(1,10-phenanthroline-*N*,*N'*)platinum(II) Hexafluorophosphate

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Abstract

The title compound, $[Pt(CH_3)(C_2H_6OS)(C_{12}H_8N_2)]PF_6$, is composed of square-planar Pt^{II} complex cations and PF_6^- anions. The crystal packing is determined mainly by graphitic interactions between the phenanthroline rings, the mean planes of which are parallel and separated by 3.68 Å.

Comment

The crystal structure of (dimethyl sulfoxide)methyl-(1,10-phenanthroline)platinum(II)] hexafluorophosphate, (I), was determined as part of our interest in the *cis/trans* influence in square-planar platinum(II) compounds containing dimethyl sulfoxide and dimethyl sulfide ligands (Bruno, Bombieri, Alibrandi, Lanza & Romeo, 1982; Arena, Bruno, De Munno, Rotondo, Drommi & Faraone, 1993; Alibrandi, Bruno, Lanza, Minniti, Romeo & Tobe, 1987; Romeo, Arena, Monsù, Bruno, Nicolò & Plutino, 1995).

(I)
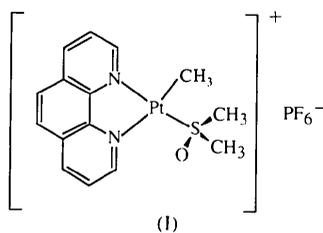
The crystal structure of the title compound is made up of discrete cationic complexes and hexafluorophosphate anions. Fig. 1 shows the ions with the atomic numbering scheme. The Pt atom shows its usual square-planar arrangement involving atoms N(1) and N(10) of the 1,10-phenanthroline ligand, the methyl group and the S atom of the dimethyl sulfoxide (DMSO) ligand. The 1,10-phenanthroline ligand is planar [maximum deviation from the best least-squares plane is 0.023 (5) Å] and coordinates to the Pt atom with a bite angle of 79.3 (2)°, determining large deviations from ideal square-planar geometry. The 1,10-phenanthroline

ligand makes an interplanar angle of 4.60 (9)° with the four atoms of the coordination plane, N(1), N(10), C(17) and S [maximum deviation from the best least-squares plane is −0.007 (6) Å for atom C(17)], from which the Pt atom is displaced by 0.026 (1) Å. The Pt—N bond distances are somewhat different, Pt—N(1) 2.135 (4) and Pt—N(10) 2.075 (4) Å, the former being at the top of the range of distances reported for Pt^{II} complexes in which electronic effects only are operating. It is comparable with the value of 2.140 (4) Å found in *cis*-[PtPh₂(CO)(py)] (Romeo, Arena, Monsù, Plutino, Bruno & Nicolò, 1994) and reflects the different *trans* influence exercised by the dimethyl sulfoxide and methyl groups. In the phenanthroline ligand, the N(1)···N(10) distance is 2.686 (7) Å, showing a shortening in comparison with free phenanthroline [average N···N is 2.735 Å for the corresponding values reported in the Cambridge Structural Database (1992)], leading to changes in both distances and angles. The complete structural features of the phenanthroline ligand correspond to previously reported values, both for the free molecule and when coordinated to various metal atoms. The Pt—C(17) bond distance of 2.056 (5) Å is comparable with the value of 2.049 (7) Å found in the neutral complex *trans*-[Pt(DMSO)₂(Me)Cl] (Romeo, Arena, Monsù, Bruno, Nicolò & Plutino, 1995), in which a Cl atom is *trans* to the methyl group.
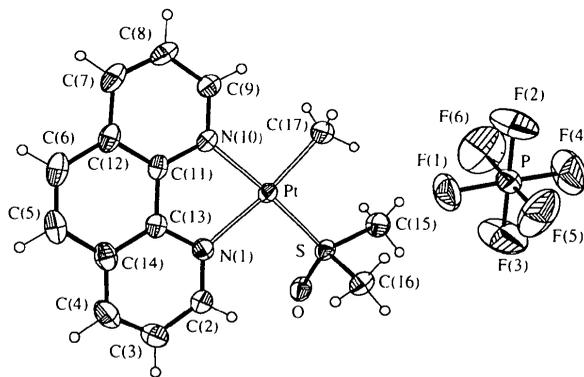
Fig. 1. A view of the title compound. Atoms are represented by displacement ellipsoids at the 35% probability level and the crystallographic numbering scheme is shown. The size of the H atoms is arbitrary.

As expected, the DMSO ligand is bonded through its S atom to the metal centre, with a Pt—S distance of 2.203 (1) Å, which is significantly shorter than those of 2.261 (2) and 2.257 (2) Å observed in the *trans*-[Pt(DMSO)₂(Me)Cl] complex. It is also shorter than the length of 2.248 (6) Å found in *cis*-[Pt(en)(DMSO)₂] (Bruno, Bombieri, Alibrandi, Lanza & Romeo, 1982). On the other hand, this distance agrees well with other Pt—S distances found in square-planar Pt^{II} complexes containing only one dimethyl sulfoxide moiety as an S-bonded ligand. The C(17)—Pt—S bond angle

[90.9 (2)°] and the other bond distances at the metal centre agree with those found for [(CH₃)ClPt(μ-Cl)(μ-Ph₂P)(py)Pt(CH₃)(DMSO)] (Arena, Bruno, De Munno, Rotondo, Drommi & Faraone, 1993). The S atom of the dimethyl sulfoxide ligand is in an approximately tetrahedral environment; the large difference between the Pt—S—C(15) [117.6 (2)°] and Pt—S—C(16) [108.4 (2)°] angles is determined by steric interaction with the C(17) atom of the methyl ligand σ-bonded to the metal [C(17)···C(15) 3.139 (8) Å]. The same steric interaction is also responsible for the lack of linearity and for the difference between the N(1)—Pt—C(17) and N(10)—Pt—S angles, which are 172.2 (2) and 175.7 (1)°, respectively. The other bond angles at the S atom, as well as the S—O [1.472 (3) Å] and S—C [mean value 1.773 (5) Å] bond distances, agree with the values reported for other Pt–DMSO complexes. The hexafluorophosphate anions have expected octahedral geometry [mean P—F bond distance 1.552 (4) Å]. The large anisotropic displacement parameters of the F atoms are evidence of a sensitive rotational disorder of the anion due to its spherical shape.

The crystal packing (Fig. 2) shows that pairs of cationic complexes, related by the inversion centre at $\frac{1}{2},\frac{1}{2},0$, are in a head-to-tail disposition. Such a disposition optimizes the graphitic interactions between the phenanthroline rings, whose mean planes are separated by 3.68 (1) Å; the metal–metal distance is 6.937 (1) Å. A Pt···Pt separation of 5.285 (1) Å is present between pairs of cationic complexes related by the inversion centre at $0,\frac{1}{2},0$ and disposed in a head-to-head orientation. The molecular packing, therefore, is constituted of layers of planar complex cations disposed as straight bands along the *b* axis, while the PF₆⁻ anions form parallel rows interconnected by hydrogen interactions involving the F and either methyl or phenanthroline H

atoms. There is also an intramolecular hydrogen bond involving the O atom of the dimethyl sulfoxide ligand [C(2)···O 3.090 (7), H(2)···O 2.340 (8) Å and C(2)—H(2)···O 137.5 (6)°] and this, together with the hindering effect of its two methyl groups, determines the DMSO orientation with respect to the mean plane of the complex.

Experimental

The title compound was prepared according to the procedure of Romeo, Arena, Monsù & Plutino (1995). Suitable yellow crystals were obtained from anhydrous methanol solution by slow evaporation. The density D_m was measured by flotation in CCl₄/CHBr₃.

Crystal data

[Pt(CH₃)(C₂H₆OS)-(C₁₂H₈N₂)]PF₆	Mo *K*α radiation
$M_r = 613.43$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 28
$P\bar{1}$	reflections
$a = 7.569 (1)$ Å	$\theta = 6.5–15°$
$b = 11.557 (2)$ Å	$\mu = 7.781$ mm⁻¹
$c = 12.158 (3)$ Å	$T = 293$ K
$\alpha = 61.84 (1)°$	Prismatic
$\beta = 88.74 (2)°$	$0.20 \times 0.15 \times 0.10$ mm
$\gamma = 84.59 (1)°$	Yellow
$V = 933.2 (3)$ Å³	
$Z = 2$	
$D_x = 2.183$ Mg m⁻³	
$D_m = 2.180$ Mg m⁻³	

Data collection

Siemens *R3m/V* diffractometer	3043 observed reflections
ω–2θ scans	$[F \geq 7\sigma(F)]$
Absorption correction:	$R_{int} = 0.0109$
ψ scan (Kopfmann & Huber, 1968)	$\theta_{max} = 26°$
$T_{min} = 0.584$, $T_{max} = 0.960$	$h = -10 \rightarrow 10$
	$k = -15 \rightarrow 15$
	$l = -1 \rightarrow 16$
4304 measured reflections	3 standard reflections
3684 independent reflections	monitored every 97
	reflections
	intensity decay: <3%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.66$ e Å⁻³
$R(F_o) = 0.0213$	$\Delta\rho_{min} = -0.63$ e Å⁻³
$wR(F_o^2) = 0.0497$	Extinction correction:
$S(F_o) = 1.017$	as free variable in the
3043 reflections	least-squares refinement
245 parameters	(*SHELXL*93; Sheldrick,
H atoms placed in calculated positions	1993)
$(U = 0.08$ Å²)	Extinction coefficient:
$w = 1/[\sigma^2(F_o^2) + 0.0109(F_o^2 + 2F_c^2)]$	$3 (2) \times 10^{-4}$
$(\Delta/\sigma)_{max} = 0.002$	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Fig. 2. A perspective view of the crystal packing down the *b* axis showing intermolecular hydrogen-bonding interactions (represented by dashed lines). The Pt atom of the complex cation is represented by a black ball, while the P atom of the PF₆⁻ anion is represented by a dotted sphere. Atomic sizes are arbitrary and depend on the element.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt	0.1904 (1)	0.2710 (1)	0.1268 (1)	0.035 (1)
N(1)	0.1528 (5)	0.4263 (4)	0.1756 (4)	0.041 (1)
C(2)	0.0969 (7)	0.4241 (5)	0.2802 (5)	0.051 (1)
C(3)	0.0895 (9)	0.5356 (7)	0.2991 (6)	0.067 (2)
C(4)	0.1431 (8)	0.6501 (6)	0.2087 (6)	0.068 (2)
C(5)	0.2617 (7)	0.7737 (6)	−0.0071 (6)	0.061 (2)
C(6)	0.3176 (7)	0.7733 (6)	−0.1126 (6)	0.059 (2)
C(7)	0.3753 (7)	0.6537 (6)	−0.2370 (5)	0.056 (1)
C(8)	0.3759 (7)	0.5392 (6)	−0.2421 (5)	0.057 (2)
C(9)	0.3223 (7)	0.4287 (5)	−0.1409 (5)	0.048 (1)
N(10)	0.2677 (5)	0.4280 (4)	−0.0358 (3)	0.038 (1)
C(11)	0.2663 (6)	0.5437 (5)	−0.0295 (4)	0.038 (1)
C(12)	0.3202 (6)	0.6588 (5)	−0.1273 (5)	0.048 (1)
C(13)	0.2069 (6)	0.5427 (5)	0.0832 (5)	0.040 (1)
C(14)	0.2045 (7)	0.6580 (5)	0.0953 (5)	0.051 (1)
S	0.1108 (2)	0.1130 (1)	0.3065 (1)	0.040 (1)
O	−0.0412 (5)	0.1525 (4)	0.3630 (3)	0.054 (1)
C(15)	0.0656 (8)	−0.0374 (6)	0.3118 (6)	0.061 (2)
C(16)	0.2941 (7)	0.0580 (5)	0.4130 (5)	0.051 (1)
C(17)	0.2448 (9)	0.1388 (6)	0.0593 (5)	0.061 (2)
P	0.6253 (2)	−0.2360 (2)	0.3590 (2)	0.056 (1)
F(1)	0.6194 (6)	−0.0844 (4)	0.3180 (4)	0.103 (2)
F(2)	0.7604 (7)	−0.2150 (6)	0.2540 (5)	0.129 (2)
F(3)	0.4985 (10)	−0.2536 (6)	0.4650 (6)	0.177 (3)
F(4)	0.6396 (9)	−0.3861 (5)	0.4037 (6)	0.144 (2)
F(5)	0.7882 (9)	−0.2551 (6)	0.4455 (5)	0.153 (2)
F(6)	0.4729 (7)	−0.2170 (7)	0.2700 (6)	0.165 (3)

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

Pt—C(17)	2.056 (5)	C(7)—C(12)	1.414 (8)
Pt—N(10)	2.075 (4)	C(8)—C(9)	1.379 (7)
Pt—N(1)	2.135 (4)	C(9)—N(10)	1.332 (6)
Pt—S	2.203 (1)	N(10)—C(11)	1.374 (6)
N(1)—C(2)	1.321 (6)	C(11)—C(12)	1.392 (7)
N(1)—C(13)	1.376 (6)	C(11)—C(13)	1.427 (7)
C(2)—C(3)	1.408 (8)	C(13)—C(14)	1.407 (7)
C(3)—C(4)	1.354 (9)	S—O	1.472 (3)
C(4)—C(14)	1.409 (8)	S—C(16)	1.772 (5)
C(5)—C(6)	1.343 (8)	S—C(15)	1.774 (5)
C(5)—C(14)	1.428 (8)	C(7)—C(8)	1.354 (8)
C(6)—C(12)	1.416 (8)		
C(17)—Pt—N(10)	93.1 (2)	C(11)—C(12)—C(6)	119.1 (5)
C(17)—Pt—N(1)	172.2 (2)	C(7)—C(12)—C(6)	123.6 (5)
N(10)—Pt—N(1)	79.3 (2)	N(1)—C(13)—C(14)	123.1 (4)
C(17)—Pt—S	90.9 (2)	N(1)—C(13)—C(11)	117.2 (4)
N(10)—Pt—S	175.7 (1)	C(14)—C(13)—C(11)	119.7 (5)
N(1)—Pt—S	96.6 (1)	C(13)—C(14)—C(4)	116.7 (5)
C(2)—N(1)—C(13)	117.8 (4)	C(13)—C(14)—C(5)	118.4 (5)
C(2)—N(1)—Pt	130.0 (4)	C(4)—C(14)—C(5)	124.9 (5)
C(13)—N(1)—Pt	112.0 (3)	O—S—C(16)	108.0 (2)
N(1)—C(2)—C(3)	122.5 (5)	O—S—C(15)	106.4 (3)
C(4)—C(3)—C(2)	120.0 (6)	C(16)—S—C(15)	100.7 (3)
C(9)—N(10)—C(11)	117.5 (4)	C(11)—N(10)—Pt	114.0 (3)
C(9)—N(10)—Pt	128.4 (3)		

The intensity data were evaluated by a peak-profile procedure (Diamond, 1969) and then corrected for Lp and absorption effects. The structure was solved by standard Patterson methods and subsequently completed by a combination of a least-squares technique and Fourier syntheses (*SHELXL93*; Sheldrick, 1993), and refined by a least-squares technique based on F^2. Neutral-atom scattering factors and anomalous-dispersion corrections were used (Stewart, 1970). The *SHELXTL-Plus* package (Sheldrick, 1991) was used for data reduction and producing the graphics, while the final geometrical calculations were carried out with a locally modified version of *PARST* (Nardelli, 1983) on a DEC MicroVAX/3400

computer of the Centro Interdipartimentale per la Diffrattometria a Raggi-X.

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Poly[*trans*-bis{trimethyltin(IV)}-μ-(2,2'-bipyridyl-4,4'-dicarboxylato-*O*:*O*':*O*'':*O*''')]. A Layered Structure Composed of Sheets Interconnected by Organometallic Moieties

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Abstract

In the solid state, the title compound, [Sn$_2$(C$_{12}$H$_6$N$_2$O$_4$)-(CH$_3$)$_6$], forms a two-dimensional polymer, which is developed parallel to the crystallographic 2$_1$ screw axis