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cis-Bis(acetato-*κO*)bis(dimethyl sulfide-*κS*)platinum(II)

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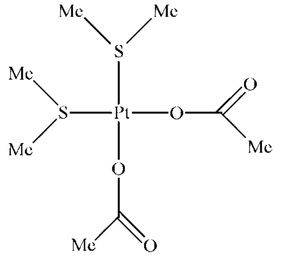
The title compound, *cis*-$[Pt(CH_3COO)_2(C_2H_6S)_2]$, crystallizes in the $P2_1/c$ space group with a pseudo-square-planar coordination geometry. The complex forms centrosymmetric dimeric packing units, with C—H···O—Pt interactions and a short Pt···Pt distance [3.5868 (2) Å]. The coordination mode of the acetate ligands is monodentate and they are oriented almost perpendicular to the coordination plane. Cambridge Structural Database [Allen (2002). *Acta Cryst.* B**58**, 380–388] data show a preferred staggered conformation with respect to the coordination plane for Me_2S in complexes with Pt^{II}.

Comment

No diacetatoplatinum(II) complex with sulfur donor ligands has previously been reported to the Cambridge Structural Database (CSD; Version 5.28 of November 2006; Allen, 2002). Out of 13 acetatoplatinum(II) complexes found in the CSD, eight contain acetate ligands that bridge two platinum(II) ions (in one case one acetate ligand coordinates to three platinum ions), two are *cis* and two *trans* complexes, and one complex contains a single acetate ligand. Only one diacetatoplatinum(II) complex with nonbridging acetate ligands and identical nonchelating neutral ligands is reported, *viz.* *trans*-$[Pt(CH_3COO)_2(PPh_3)_2]$ (Basato *et al.*, 2003). Acetate and nitrate ions are topologically related, and the structure of *cis*-$[Pt(NO_3)_2(Me_2S)_2]$ has recently been reported (Hansson & Oskarsson, 2007). We report here the crystal structure of the title compound with emphasis on: (i) the coordination mode of the acetate ion compared with the nitrate ion; (ii) the packing of the title compound in relation to other $[PtX_2L_2]$ compounds, X being a ligand with a −1 charge and L being a neutral ligand; and (iii) the coordination mode of dimethyl sulfide (dms) in relation to other $[Pt^{II}A_{4-n}(Me_2S)_n]$ (where A is any ligand and n = 1–4) complexes.

cis-$[Pt(CH_3COO)_2(Me_2S)_2]$, (I), has a pseudo-square-planar coordination geometry (Fig. 1). The Pt—O and Pt—S bonds (Table 1) illustrate the different *trans* influence of the O and S atoms, which was previously observed in *cis*-$[Pt(NO_3)_2(Me_2S)_2]$ (Hansson & Oskarsson, 2007). The Pt—O distances are elongated by ~0.04 Å compared with those in $[Pt(NO_3)_4]^{2-}$ (Elding & Oskarsson, 1985) and the Pt—S distances are shortened by ~0.06 Å compared with $[Pt(Me_2S)_4]^{2+}$ (Bugarcic *et al.*, 1991)



(I)

The two acetate ligands coordinate in a monodentate fashion *via* one of the O atoms, as shown by the differences in the Pt1—O1/Pt1—O2 and Pt1—O3/Pt1—O4 distances being more than 1 Å and thus fulfilling the criterion of a difference of more than 0.6 Å suggested by Kleywegt *et al.* (1985) for monodentate nitrate ligands. This is further supported by the differences in the C5—O1/C5—O2 and C7—O3/C7—O4 distances, which are approximately 0.1 Å (Table 1). Both acetate ligands are oriented almost perpendicular to the coordination plane, as shown by the torsion angles S2—Pt1—O1—C5 [−81.8 (3)°] and S1—Pt1—O3—C7 [79.9 (3)°], and the noncoordinated atoms O2 and O4 are both on the same side of the coordination plane. In the corresponding *cis*-$[Pt(NO_3)_2L_2]$ complexes, seven have nitrate ions on opposite sides, five on the same side and two in the plane (Hansson & Oskarsson, 2007). The most striking difference in behaviour between acetate and nitrate in these systems is the greater tendency of the acetate ion to form bridging polynuclear complexes compared with the nitrate ion.

The dms ligands are oriented similarly and coordinate to platinum in a semi-staggered conformation, with C—S1—Pt1—S2 and C—S2—Pt1—O1 torsion angles of ~79 and ~−27°.

The packing of the title compound features centrosymmetric dimers (Fig. 2) across ($\frac{1}{2}$, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), which are held together by C—H···O—Pt interactions ($H2B—O1^{i}$ = 2.58 Å and $H4B—O3^{i}$ = 2.60 Å; all symmetry codes as in

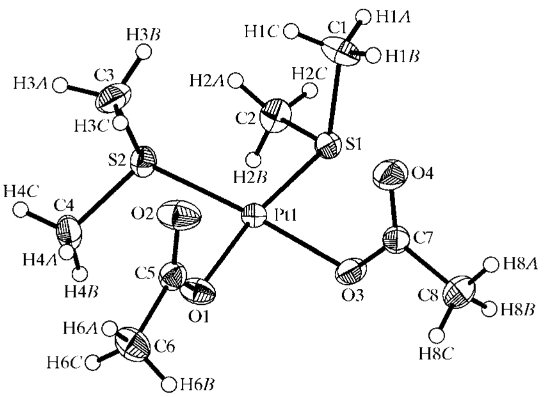


Figure 1
The atom-numbering scheme for the title compound. Displacement ellipsoids are drawn at the 30% probability level.

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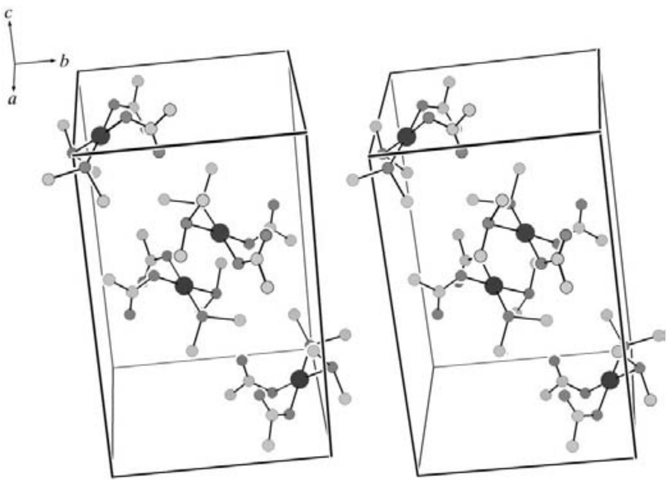

Figure 2
A stereoscopic view of the packing of the title compound. One centrosymmetric dimeric pair of complexes is visible at the centre of the cell.

Table 2). The Pt1···Pt1^{i} distance is 3.5868 (2) Å, which probably also represents an attractive interaction, since the stabilizing energy of the dimer is 57 kJ (mol monomer)$^{-1}$ according to density functional theory (DFT) calculations. The centres of gravity of the dimers form an *I*-centred monoclinic unit cell (easily seen after a suitable unit-cell transformation), *i.e.* each dimer is surrounded by 14 others. It is interesting to note that such a packing is common for centrosymmetric *trans*-[PtX_2L_2] compounds (Hansson *et al.*, 2006). The four carbonyl O atoms point towards neighbouring dimers and are directed along the *c* axis. These atoms take part in C—H···O═C interactions (H2*A*—O4^{ii} = 2.50 Å, H4*C*—O2^{iii} = 2.62 Å and H3*A*—O2^{iii} = 2.65 Å; Table 2). Voids are formed at (0, 0, 0), (0, 0, $\frac{1}{2}$) and ($\frac{1}{2}$, 0, $\frac{1}{2}$). Six-membered rings are formed around the voids *via* C—H···O interactions.

A *ConQuest* (Bruno *et al.*, 2002) search of the CSD for Pt^{II} compounds with one or more dms molecules coordinated to the metal centre resulted in 44 complexes of the type [Pt$^{II}A_{4-n}$(Me$_2$S)$_n$] (where *A* is any ligand), containing in total 79 dms ligands (see deposited material). Complexes with bridging dms ligands and compounds without atomic coordinates reported in the database were excluded. The angle between the two Me—S bonds and the coordination plane was estimated using the C—S—Pt—*A* torsion angle (where *A* is *cis* to the Me$_2$S ligand and n = 1–4). Three different behaviours are observed. Four Me$_2$S (5%) ligands have both methyl groups on the same side of the coordination plane, and 15 (19%) are close to eclipsed with one torsion angle in the range 2–12°. However, the staggered conformation, with torsion angles of 35–55°, dominates strongly (69% of the 79 reported Me$_2$S ligands).

Experimental

Pt(Me$_2$S)$_2$I$_2$ (0.317 g, 0.554 mmol) was dissolved in acetone (15 ml). Ag(CH$_3$COO) (0.192 g, 1.15 mmol) was added and the reaction mixture stirred for 90 min. Solid AgI was removed by filtration. The pale-yellow acetone solution was left to evaporate slowly, which resulted in a yellow solid. Crystals suitable for X-ray diffraction experiments were obtained by recrystallization from a diethyl ether–ethanol mixture (2:1 *v*/*v*). DFT calculations were performed at the s-VWN level with the basis sets def-TZVPP for Pt, TZVPP for S and O, and 6–31G* for C and H atoms, using the software *TURBOMOLE 5.5* (Alrichs *et al.*, 1989).

Crystal data

[Pt(C$_2$H$_3$O$_2$)$_2$(C$_2$H$_6$S)$_2$]
M_r = 437.43
Monoclinic, $P2_1/c$
a = 8.7306 (5) Å
b = 10.3274 (5) Å
c = 15.5205 (9) Å
β = 105.623 (3)°
V = 1347.69 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 10.71 mm^{-1}
T = 295 (1) K
0.28 × 0.12 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur3 diffractometer
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min}$ = 0.115, $T_{\max}$ = 0.629
12845 measured reflections
4530 independent reflections
3389 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.073
S = 0.97
4530 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.71 e Å^{-3}
$\Delta\rho_{\min}$ = −1.15 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—O1	2.032 (3)	Pt1—S2	2.2559 (10)
Pt1—O3	2.043 (3)	Pt1—S1	2.2633 (10)
Pt1···Pt1^{i}	3.5868 (2)		
O1—Pt1—O3	84.94 (13)	O3—Pt1—S1	88.61 (9)
O1—Pt1—S2	92.04 (10)	S2—Pt1—S1	94.21 (4)
O3—Pt1—S2	176.24 (9)	C5—O1—Pt1	124.8 (3)
O1—Pt1—S1	171.97 (9)	C7—O3—Pt1	120.4 (3)

Symmetry code: (i) $-x+1, -y, -z+2$.

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2*B*···O1^{i}	0.96	2.58	3.216 (5)	124
C4—H4*B*···O3^{i}	0.96	2.60	3.392 (6)	139
C2—H2*A*···O4^{ii}	0.96	2.50	3.425 (6)	163
C4—H4*C*···O2^{iii}	0.96	2.62	3.479 (6)	150
C3—H3*A*···O2^{iii}	0.96	2.65	3.552 (7)	156
C1—H1*B*···S2^{iv}	0.96	3.12	3.996 (6)	153

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

H atoms were positioned geometrically and treated as riding on the adjacent C atom [C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C)].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*;

molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *CRYSTALS* (Betteridge *et al.*, 2003) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3114). Services for accessing these data are described at the back of the journal.

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