

**cis-Dichloridobis(diethyl sulfide- κ S)
platinum(II) at 295 and 150 K**

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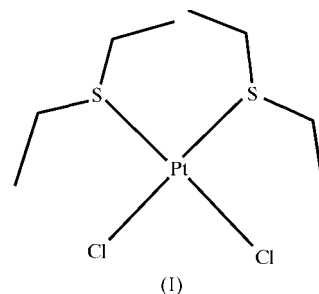
The title compound, *cis*-[PtCl₂(C₄H₁₀S)₂], crystallizes in the space group *P*2₁/*n* with pseudo-square-planar coordination geometry. The orientation of the ethyl groups on the S atoms is staggered with respect to the coordination plane, giving the complex approximate C_{2v} symmetry. The complex does not form dimeric packing units with short Pt...S intradimeric distances as seen in some related complexes, but instead displays C—H...Cl interactions in three dimensions. These C—H...Cl—Pt contacts are compared with those of related compounds reported in the Cambridge Structural Database, which show a frequency maximum in the range 120–170° for the C—H...Cl angle.

Comment

In the solid state, the complex *cis*-PtCl₂(Me₂S)₂ (Horn *et al.*, 1990) has one dimethyl sulfide (dms) ligand in a staggered and one in an eclipsed orientation with respect to the PtCl₂S₂ coordination plane. A similar situation has been observed in *cis*-PtCl₂(tx)₂ (tx = 1,4-thioxane, SC₄H₈O; Bugarcic *et al.*, 1993). Both structures form centrosymmetric dimeric units with Pt...S distances of 3.58 and 3.59 Å for the dimers [*cis*-PtCl₂(tx)₂]₂ and [*cis*-PtCl₂(Me₂S)₂]₂, respectively. On the other hand, the complex *cis*-PtCl₂(Ph₂S)₂ (Johansson *et al.*, 2001) does not form a centrosymmetric unit with a short Pt...S distance but is stabilized by C—H...Cl interactions. In order to gain more information on the formation of dimeric packing units with a short Pt...S distance, the title complex *cis*-PtCl₂(Et₂S)₂, (I), has been examined.

The title complex possesses a pseudo-square-planar coordination geometry, with angles around the Pt atom in the range 87.40 (4)–91.43 (5)° at 295 K and 87.90 (3)–90.75 (4)° at 150 K. Selected bond distances and angles for the 150 K structure are shown in Table 1. Both diethyl sulfide ligands are orientated in a staggered manner with one ethyl group above and one beneath the coordination plane. The organic groups of the two sulfide ligands are directed away from each other and the complex adopts approximately C_{2v} symmetry (Fig. 1).

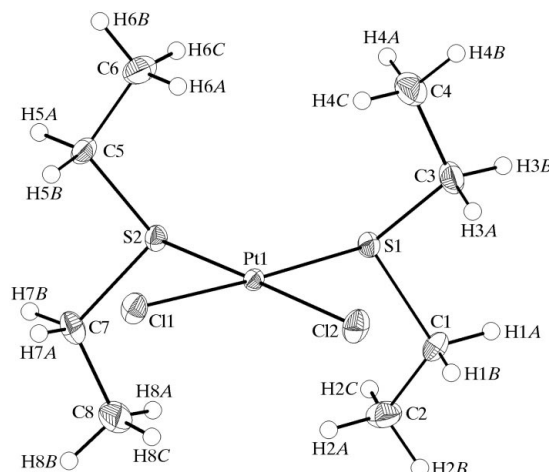
The packing arrangement of the complex may be described as consisting of layers of complexes in the (101) plane formed by C—H...Cl interactions with H...Cl distances in the range



2.78–2.90 Å and C—H...Cl angles in the range 135–157° at 150 K (Table 2 and Fig. 2). However, if the interval is extended to 3.20 Å, it is seen that the layers are connected by four additional Cl...H contacts to form a three-dimensional network. Two of these interactions between the layers have C—H...Cl angles in the range 108–110°, whereas the other two are in the same range as the interactions within the layers.

With the exception of the molecules that straddle 0 0 $\frac{1}{2}$, which have a short H7A...H7Aⁱⁱ contact of 2.31 Å, the symmetry centres create voids of different sizes (symmetry codes are given in Tables 1 and 2). Four molecules form a ring around 0 0 0 with H1A...Cl2ⁱⁱⁱ and H2B...Cl2^{iv} contacts of 2.90 and 3.12 Å, respectively. Dimers are formed around 0 $\frac{1}{2}$ 0, with a H4B...Cl2^v distance of 3.10 Å. A ring of four molecules is formed around $\frac{1}{2}$ 0 0, with contacts H1A...Cl1ⁱⁱⁱ and H5A...Cl2^{vi} having H...Cl distances of 2.80 and 2.78 Å, respectively. The Pt...S²ⁱ distance across the ring is 5.3822 (10) Å.

There are no significant differences between the Pt—Cl or Pt—S bond lengths of *cis*-PtCl₂(Me₂S)₂ and the title compound. The S—Pt—S angle at 150 K is 87.90 (3)° in the diethyl sulfide complex and 94.75° in the complex with dms ligands, probably reflecting the different ways in which the two ligands orientate around the Pt^{II} ion. Since one of the dms ligands has one methyl group placed in the coordination plane,

**Figure 1**

The numbering scheme for (I) at 150 K. The displacement ellipsoids are drawn at the 30% probability level.

the ligand demands more space and thus the S—Pt—S angle becomes larger, mostly at the expense of the neighbouring S—Pt—Cl angle. The sulfide ligands in the *trans* isomer of $\text{PtCl}_2(\text{Et}_2\text{S})_2$ (Skvortsov *et al.*, 1994) are staggered with respect to the coordination plane and the complex possesses C_i symmetry.

The title compound does not form dimeric packing units of the type seen in *cis*- $\text{PtCl}_2(\text{Me}_2\text{S})_2$ and *cis*- $\text{PtCl}_2(\text{tx})_2$. A dimerization with short Pt...S interactions requires a reorientation of one of the thioether ligands. The cost in energy for this must be compensated by the combined effect of the dimerization and the energy of packing the dimers. There seems to be a delicate balance between these factors since *cis*- $\text{PtCl}_2(\text{Me}_2\text{S})_2$ and *cis*- $\text{PtCl}_2(\text{tx})_2$ form dimers with short Pt...S interactions while *cis*- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ and *cis*- $\text{PtCl}_2(\text{Ph}_2\text{S})_2$ do not. It may be possible for *cis*- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ to form more C—H...Cl contacts in three dimensions than *cis*- $\text{PtCl}_2(\text{Me}_2\text{S})_2$, since more H atoms are present, and the formation of C—H...Cl interactions probably stabilizes the packing of the title compound. This is supported by data in the Cambridge Structural Database (CSD, Version 5.28, November 2006 release; Allen, 2002) which has been searched using *ConQuest* software (Bruno *et al.*, 2002). Most Pt^{II} —Cl complexes in the CSD have C—H...Cl angles in the range 120–170°. C—H(methyl)...Cl and C—H(methylene)...Cl angles have means of 141 and 139°, respectively, for a H...Cl cut-off distance of 3.2 Å. A cut-off distance of 3.0 Å increases the mean values to 150 and 145° for C—H(methyl)...Cl and C—H(methylene)...Cl, respectively (see deposited material).

The complexes $[\text{PtCl}_3(\text{Me}_2\text{S})]^-$ (Kukushkin *et al.*, 1994), *cis*/*trans*- $\text{PtCl}_2(\text{Me}_2\text{S})_2$ (Horn *et al.*, 1990; Hansson *et al.*, 2006) and $[\text{PtCl}(\text{Me}_2\text{S})_3]^+$ (Hansson *et al.*, 2003) make up a series of complexes with dms and chloride ligands in different ratios. Dimeric units with a short Pt...S interaction have been found in *cis*- $\text{PtCl}_2(\text{Me}_2\text{S})_2$ (as discussed above) and $[\text{PtCl}(\text{Me}_2\text{S})_3]^+$, but not in the other complexes in the series.

Most of the 13 Pt^{II} complexes with one or more diethyl sulfide ligands in the CSD (Allen, 2002) contain diethyl sulfide

molecules in which the orientation of the ethyl groups is similar to that seen in the title compound, but exceptions do occur. The complex (8-methoxynaphthyl)platinum chloride bis(diethyl sulfide) (Wehman *et al.*, 1988) contains one diethyl sulfide ligand with ethyl groups in staggered orientation, and one which is turned so that one methylene carbon is approximately in the coordination plane, *i.e.* a similar orientation to that seen in *cis*- $\text{PtCl}_2(\text{Me}_2\text{S})_2$. However, this orientation is probably governed by the steric demand of the 8-methoxynaphthyl ligand.

The so-called Kitaigorodsky packing index (KPI), *i.e.* the ratio between occupied volume and the total unit-cell volume, has been calculated using the VOID option in *PLATON* (Spek, 2003) for the title compound at 295 and 150 K, and for the related complexes *cis*- $\text{PtCl}_2(\text{Me}_2\text{S})_2$, *cis*- $\text{PtCl}_2(\text{Ph}_2\text{S})_2$, *cis*- $\text{PtCl}_2(\text{tx})_2$ and their *trans* counterparts (Table 3). No H-atom positions were reported for *trans*- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ and *cis*/*trans*- $\text{PtCl}_2(\text{tx})_2$, so H atoms had to be added to the structures before the KPI could be calculated. The observed range of KPI, *viz.* 0.65–0.73, is within the interval proposed for organic molecules of 0.65–0.77 (Kitaigorodsky, 1973). The KPI of *cis*- $\text{PtCl}_2(\text{Me}_2\text{S})_2$ is larger than the KPI of the title compound, indicating that the former complex is able to pack more efficiently.

When comparing *cis* and *trans* isomers of compounds with the general formula $\text{PtCl}_2(\text{S-donor})_2$, it is observed that the *trans* isomer often seems to be more densely packed than the corresponding *cis* isomer (Table 3). However, the differences are small, <3%. The difference in density for the title compound at 295 and 150 K is 3.5%, and the volume expansion coefficient ($1/V \text{ d}V/\text{d}T$) is $2.3 \times 10^{-4} \text{ K}^{-1}$, indicating that thermal expansion properties are very important for these types of compounds, and no general conclusion about packing efficiency between *cis* and *trans* complexes can be drawn.

Experimental

K_2PtCl_4 (0.506 g, 1.21 mmol) was dissolved in 20 ml water. Diethyl sulfide (3.7 ml, 34.3 mmol) was added, giving a dark-yellow precipitate. The reaction mixture was stirred for 24 h. The yellow precipitate which formed was filtered off and dried. Recrystallization from acetone gave yellow-green crystals suitable for X-ray diffraction experiments.

Compound (I) at 295 K

Crystal data

$[\text{PtCl}_2(\text{C}_4\text{H}_{10}\text{S})_2]$
 $M_r = 446.35$
 Monoclinic, $P2_1/n$
 $a = 10.7928$ (2) Å
 $b = 11.4223$ (2) Å
 $c = 12.2417$ (2) Å
 $\beta = 100.6190$ (10)°

$V = 1483.30$ (5) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 10.07 \text{ mm}^{-1}$
 $T = 295$ (1) K
 $0.24 \times 0.11 \times 0.06 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur3
 diffractometer
 Absorption correction: analytical
 (*CrysAlis RED*; Oxford
 Diffraction, 2006)
 $T_{\text{min}} = 0.257$, $T_{\text{max}} = 0.618$

14809 measured reflections
 5157 independent reflections
 3266 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

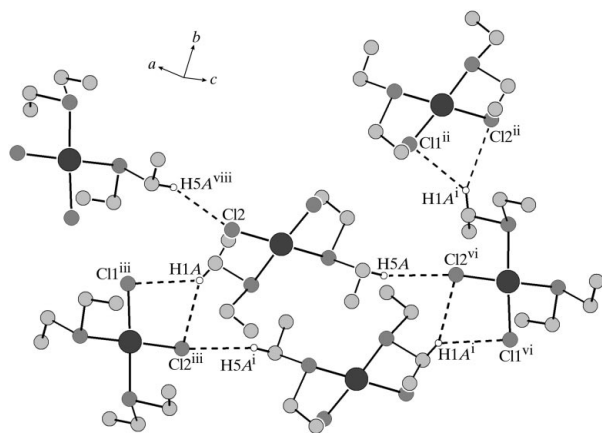


Figure 2

The hydrogen-bonded layer (101). Dashed lines indicate C—H...Cl interactions. [Symmetry code (viii) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; other symmetry codes are as given in Table 2.]

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	122 parameters
$wR(F^2) = 0.076$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\max} = 1.72 \text{ e } \text{\AA}^{-3}$
5157 reflections	$\Delta\rho_{\min} = -1.09 \text{ e } \text{\AA}^{-3}$

Compound (I) at 150 K

Crystal data

$[\text{PtCl}_2(\text{C}_4\text{H}_{10}\text{S})_2]$	$V = 1435.00 (11) \text{ \AA}^3$
$M_r = 446.35$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.7598 (5) \text{ \AA}$	$\mu = 10.40 \text{ mm}^{-1}$
$b = 11.1976 (5) \text{ \AA}$	$T = 150 (1) \text{ K}$
$c = 12.1559 (5) \text{ \AA}$	$0.24 \times 0.11 \times 0.06 \text{ mm}$
$\beta = 101.536 (4)^\circ$	

Data collection

Oxford Diffraction Xcalibur3 diffractometer	14202 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	5054 independent reflections
$T_{\min} = 0.222$, $T_{\max} = 0.635$	4061 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	122 parameters
$wR(F^2) = 0.080$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\max} = 3.61 \text{ e } \text{\AA}^{-3}$
5054 reflections	$\Delta\rho_{\min} = -1.19 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I) at 150 K.

Pt1—S2	2.2699 (9)	S1—C3	1.815 (4)
Pt1—S1	2.2736 (9)	S1—C1	1.820 (4)
Pt1—Cl2	2.3105 (10)	S2—C5	1.812 (4)
Pt1—Cl1	2.3159 (9)	S2—C7	1.820 (5)
Pt1...S2 ⁱ	5.3822 (10)	H7A...H7A ⁱⁱ	2.31
S2—Pt1—Cl2	177.68 (4)	C1—S1—Pt1	107.90 (16)
S1—Pt1—Cl1	177.30 (3)	C5—S2—Pt1	107.00 (16)
C3—S1—Pt1	108.43 (15)	C7—S2—Pt1	107.47 (15)

Symmetry codes: (i) $-x + 1, -y, -z + 2$; (ii) $-x + 1, -y + 1, -z + 2$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I) at 150 K.

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
C1—H1A...Cl1 ⁱⁱⁱ	0.97	2.80	3.5504 (48)	135
C1—H1A...Cl2 ⁱⁱⁱ	0.97	2.90	3.7967 (46)	154
C2—H2B...Cl2 ^{iv}	0.96	3.12	3.5602 (46)	110
C4—H4B...Cl2 ^v	0.96	3.10	3.9963 (50)	157
C5—H5A...Cl2 ^{vi}	0.97	2.78	3.5868 (52)	141
C6—H6B...Cl1 ^{vii}	0.96	3.07	3.4968 (50)	108
C8—H8B...Cl1 ⁱⁱ	0.96	3.20	3.9659 (61)	139

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

H-atom positions were calculated as riding on the adjacent C atoms (methyl C—H = 0.96 \AA and methylene C—H = 0.97 \AA), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$ and $1.2U_{\text{eq}}(\text{methylene C})$. At 150 K, the highest peak in the final difference map is situated 1.94 \AA from C8 and 3.01 \AA from C2, while the lowest peak is 0.68 \AA from Pt1.

Table 3

Density and KPI for four thioether *cis/trans* complexes.

Compound formula	Density (Mg m^{-3})	KPI
<i>cis</i> -PtCl ₂ (Me ₂ S) ₂ ^a	2.52	0.698
<i>cis</i> -PtCl ₂ (Et ₂ S) ₂ (295 K) ^b	2.00	0.654
<i>cis</i> -PtCl ₂ (Et ₂ S) ₂ (150 K) ^b	2.07	0.676
<i>cis</i> -PtCl ₂ (Ph ₂ S) ₂ ^c	1.81	0.666
<i>cis</i> -PtCl ₂ (tx) ₂ ^d	2.39	0.728
<i>trans</i> -PtCl ₂ (Me ₂ S) ₂ ^e	2.60	0.726
<i>trans</i> -PtCl ₂ (Et ₂ S) ₂ ^f	2.06	0.675
<i>trans</i> -PtCl ₂ (Ph ₂ S) ₂ ^c	1.83	0.674
<i>trans</i> -PtCl ₂ (tx) ₂ ^d	2.37	0.730

Notes: (a) Horn *et al.* (1990); (b) this paper; (c) Johansson *et al.* (2001); (d) Bugarcic *et al.* (1993); (e) Hansson *et al.* (2006); (f) Skvortsov *et al.* (1994).

For both determinations, 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: SQ3085). Services for accessing these data are described at the back of the journal.

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