Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

cis-(1,4-Dithiane-*S*,*S*′)diiodoplatinum(II)

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Received 2 February 2001
Accepted 12 February 2001
Online 28 February 2001

Key indicators

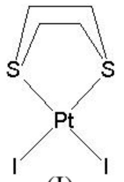
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
R factor = 0.026
wR factor = 0.049
Data-to-parameter ratio = 37.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, [$PtI_2(S_2C_4H_8)$], consists of a 1,4-dithiane and two iodo ligands coordinated to a Pt atom in a distorted square-planar *cis*-system with Pt on a twofold axis. The dithiane forms a bidentate chelate with Pt, bonding *via* the S atoms. The Pt—I bonds are 2.6035 (5) Å and the Pt—S bonds 2.2751 (16) Å. The Pt—S bond is influenced mainly by the *cis*-chelate effect and the Pt—I bond by the *trans*-influence of sulfur.

Comment

1,4-Dithiane [dit, $S(C_2H_4)_2S$] is the thioether analogue of the antitumor agent piperazine (Ciccarese *et al.*, 1998). Very few compounds with 1,4-dithiane as a bidentate ligand have been crystallographically characterized. The only metal–organic compound with a chelating dithiane found in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) is an osmium cluster (Adams *et al.*, 1995). Platinum halide compounds with thioether ligands have been investigated earlier and it is found that most of the chloro and bromo compounds structurally characterized adopt a *cis*-configuration, while the *trans*-configuration is mainly observed for iodo complexes (Lövqvist, 1996). Only two *cis*-platinum–iodo–thioether complexes are found in the CSD, both with chelating thioethers, diiodo[1,2-bis(phenylsulfanyl)ethane]platinum(II) (Marangoni *et al.*, 1995) and diiodo(1,3,5,7-tetramethyl-2,4,-6,8-tetrathiaadamantane)platinum(II) (Levy & Long, 1975).



(I)

The title compound, (I), crystallizes in the tetragonal space group $P4_32_12$ with the Pt atom on a twofold rotation axis. The dithiane forms a bidentate chelate with platinum(II), forcing the compound to adopt a *cis*-configuration with the two I atoms in *trans*-positions to the dithiane S atoms (Fig. 1). The dithiane molecule must assume the boat conformation to be able to bind as a bidentate ligand. Bond lengths and angles are shown in Table 1. The complex exhibits a distorted square-planar geometry with angles around Pt from 79.74 (8) to 93.76 (4)°. The S—C distances, 1.818 (7) and 1.810 (7) Å, and the S—C—C angles, 111.6 (5) and 112.9 (5)°, are close to those found in free dithiane, even though the free form adopts the chair conformation (Marsh, 1955). The C—C bond seems to

DOI: 101107/S1600536801002951

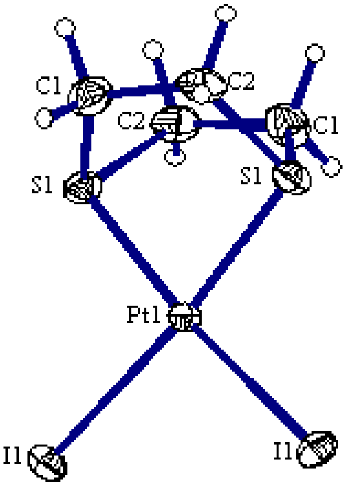


Figure 1
Numbering scheme with displacement ellipsoids (30% probability) for the title compound.

be elongated, 1.538 (10) *versus* 1.490 (18) Å, and the C—S—C angles become smaller, 97.4 (4) *versus* 99.0 (6)°, upon bidentate complexation with platinum. The closest contact between the complexes is S1···C1($-\frac{1}{2}+x$, $\frac{3}{2}-y$, $\frac{1}{4}-z$) of 3.729 (1) Å and the shortest Pt···Pt distance is 6.213 (1) Å.

In Table 2, *cis*- and *trans*-diiodoplatinum(II) compounds with thioethers from the literature are listed. There are only two *cis*-compounds found and they both have bidentate chelating thioethers. The Pt—I bond distance in the title compound, 2.6035 (5) Å, is close to those reported for the other *cis*-compound. The Pt—I distances in the *trans*-compounds show a wider range, 2.6039 (8) to 2.616 (1) Å.

The range of Pt—I bond distances *trans* to simple bidentate N-donor ligands with two C atoms between the N atoms in the CSD are 2.574 (2)–2.591 (2) Å (Casas *et al.*, 1998; Ciccarese *et al.*, 1998; Clark *et al.*, 1995; Connick & Gray, 1994; Fanizzi *et al.*, 1996; Mégnamisi-Bélombé & Endres, 1985) with one exception, 4,7-Ph$_2$-phen (phen = 1,10-phenanthroline), where the Pt—I distances are 2.558 (2) Å (Fanizzi *et al.*, 1996). In chelating bidentate ligand complexes *trans* to P atoms, the Pt—I bond distances are in the range 2.6480 (9)–2.662 (2) Å (Wilson *et al.*, 1994; Dahlenburg & Kurth, 1998). The differences in Pt—I bond length *trans* to S, N and P are thus consistent with the *trans*-influence series, where P > S > N (Greenwood & Earnshaw, 1997). The difference between P and S *trans*-influence is clearly shown in [PtI$_2$(PhPC$_6$H$_{12}$S)], where I is *trans* to both S and P, with Pt—I distances 2.598 (3) and 2.639 (2) Å, respectively.

In Table 2, the Pt—S distances in the above-mentioned thioether compounds are shown. In the *cis*-compounds the Pt—S bond distances are 2.265 (2) and 2.275 (2) Å. The Pt—S bond of 2.2751 (16) Å for [PtI$_2$(dit)] lies within the range for the above-mentioned values obtained from the literature. The average Pt—S bond distance for systems with S atoms *trans* to each other and *cis* to I is 2.305 (2) Å. These differences in the Pt—S bonds may be due to a *cis*-chelate effect, even though sulfur has a larger *trans*-influence than iodine. The *cis*-chelate effect is mainly referred to as a kinetic effect, but Marangoni *et al.* (1995) have performed comparative studies between Pt—S(thioether) bonds from both chelating and simple thioethers with the same atom in the *trans*-position for a number of different Pt$^{\rm II}$ compounds. The chelating compounds yield shorter bond lengths, independent of the atom in the *trans*-position and this is most probably due to electronic effects; the empty orbitals of sulfur are properly orientated towards the filled d$_{xy}$ orbitals of platinum, resulting in easier $\pi(d\text{–}d)$ back-donation.

The bite angle of the bidentate dithiane, 79.74 (8)°, is larger than the angle for *N*-methylpiperazine, 70.1 (7)° (Ciccarese *et al.*, 1998). This difference is probably due to the larger atomic radius of sulfur compared to nitrogen, but the bite angle for PhS(CH$_2$)$_2$SPh is larger than for both the others, 91.00 (8)°, as would be expected because only a one-carbon chain forms the chelating backbone in the latter (Marangoni *et al.*, 1995).

Experimental

PtI$_2$ (100 mg, 0.223 mmol) was added to an ethanol solution (5 ml) of 1,4-dithiane (30 mg, 0.245 mmol). The solution was stirred for 5 h at ambient temperature. The orange precipitate was filtered and washed with water (2 × 5 ml), ethanol (2 × 5 ml) and chloroform (3 × 5 ml) (yield 96 mg, 76%). Crystals of good quality were obtained by recrystallization from hot DMSO.

Crystal data

[PtI$_2$(C$_4$H$_8$S$_2$)]
$M_r = 569.11$
Tetragonal, $P4_32_12$
$a = 8.9850$ (13) Å
$c = 12.265$ (3) Å
$V = 990.2$ (3) Å^3
$Z = 4$
$D_x = 3.818$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4610 reflections
$\theta = 2.8\text{–}29.0°$
$\mu = 20.75$ mm^{-1}
$T = 293$ (2) K
Prism, orange
0.10 × 0.09 × 0.06 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: empirical using *SADABS* (Sheldrick, 1996)
$T_{\rm min} = 0.168$, $T_{\rm max} = 0.268$
10 493 measured reflections
1625 independent reflections
1387 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\rm max} = 32.0°$
$h = -13 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -13 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.049$
$S = 1.05$
1625 reflections
43 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 1.0607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 1.04$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.06$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00217 (15)
Absolute structure: Flack (1983)
Flack parameter = −0.009 (7)

Table 1
Selected geometric parameters (Å, °).

Pt—S1	2.2751 (16)	S1—C1	1.818 (7)
Pt—I1	2.6035 (5)	C1—C2^i	1.538 (10)
S1—C2	1.810 (7)		
S1—Pt—S1^i	79.74 (8)	C2—S1—Pt	100.7 (2)
S1—Pt—I1^i	173.50 (4)	C1—S1—Pt	98.8 (2)
S1^i—Pt—I1^i	93.76 (4)	C2^i—C1—S1	111.6 (5)
I1^i—Pt—I1	92.74 (2)	C1^i—C2—S1	112.9 (5)
C2—S1—C1	97.4 (4)		

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

Table 2
Comparative table of bond lengths and angles of structurally related PtI_2L/PtI_2L_2 (L = mono- or bidentate thioether ligands) complexes.

Complex	M—S	M—I	S—M—S	I—M—I
cis-[PtI_2(dit)]^a	2.2751 (16)	2.6035 (5)	79.74 (8)	92.74 (2)
cis-[$PtI_2\{PhS(CH_2)_2SPh\}$]^b	2.265 (2)	2.601 (1)	91.00 (8)	93.22 (2)
trans-[$PtI_2(SMe_2)_2$]^c	2.310 (2)	2.6039 (8)	180	180
trans-[$PtI_2(SOMe_2)_2$]^d	2.289 (2)	2.6111 (9)	180	180
trans-[$PtI_2(C_4H_8S)_2$]^e	2.309 (1) 2.310 (1)	2.606 (1) 2.616 (1)	180	180

Notes [no distances are reported for diiodo(1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane)platinum(II) (Levy & Long, 1975)]: (*a*) this study; (*b*) Marangoni *et al.* (1995); (*c*) Lövqvist *et al.* (1996); (*d*) Lövqvist (1996); (*e*) (C_4H_8S is tetrahydrothiophene) Oskarsson *et al.* (1990).

H atoms were refined with fixed individual displacement parameters [$U(H) = 1.2U_{eq}(C)$] using a riding model with C—H = 0.97 Å.

Data collection: *SMART* (Bruker, 1995); cell refinement: *SAINT* (Bruker, 1995); data reduction: *SAINT* (Bruker, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

Financial assistance of the South African National Research Fund, the Swedish Natural Science Research Council and The Crafoord Foundation is gratefully acknowledged. The efforts of Professors A. Roodt, Å. Oskarsson and L. I. Elding, who made the visit to Lund University for Hendrik Engelbrecht possible, are also gratefully acknowledged.

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