Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis[2-mercaptopyridine *N*-oxide(1–)-κ^2*N*,*O*]-platinum(II)

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The title complex, $[Pt(C_5H_4NOS)_2]$, shows a *trans*-S_2O_2 square-planar coordination geometry for the Pt^{II} centre. The molecule self-assembles into a two-dimensional layer through weak intermolecular C—H···O/S/N interactions.

Received 8 December 2004
Accepted 15 December 2004
Online 24 December 2004

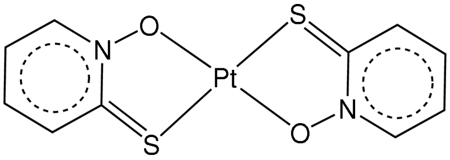
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.017 Å
R factor = 0.048
wR factor = 0.112
Data-to-parameter ratio = 14.7

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

Comment

A large number of metal complexes with pyridine *N*-oxide and its derivatives have been reported for their interesting coordination chemistry in recent decades (Karayannis *et al.*, 1973, 1976; Landers & Phillips, 1982; Casellato *et al.*, 1983; Scarrow *et al.*, 1985; Lobana & Singh, 1995). However, metal complexes of pyridine *N*-oxide derivatives with donor atoms in the 2-position, such as 2-hydroxypyridine *N*-oxide (Landers & Phillips, 1981) and 2-mercaptopyridine *N*-oxide (mpo) (Robinson, 1964; Davidson *et al.*, 1983; Chen *et al.*, 1991; Shi *et al.*, 1997; Lobana & Verma, 1999; Lobana *et al.*, 2003) have been rarely been studied. However, the synthesis of $Pt(mpo)_2$ has been reported (Davidson *et al.*, 1983; Lobana & Verma, 1999; Lobana *et al.*, 2003). These studies suggest that the Pt atom is in a square-planar environment of two mpo ligands, but little work has been carried out on the X-ray crystal structure determination. We report here the X-ray crystal structure of $Pt(mpo)_2$, (I).



(I)

The title complex has a square-planar geometry around the central Pt atom, which is coordinated by two mpo ligands (Fig. 1 and Table 1). The two S atoms are in a *trans* configuration. The whole molecule is nearly planar, with a maximum derivation of 0.201 (5) Å for atom S1. The average Pt—S bond distance of 2.270 (3) Å is shorter than those reported for *cis*-[Pt(η^1-S-pyridine-2-thione)$_2$(dppe)] [2.358 (3) Å; dppe is 1,2-bis(diphenylphosphino)ethane; Lobana *et al.*, 2000] and *cis*-[Pt(η^1-s-pyridine-2-thione)$_2$(dppen)] [2.351 (2) Å; dppen is *cis*-1,2-bis(diphenylphosphino)ethene; Lobana *et al.*, 2000]. The average Pt—O and Pt—S bond distances of 2.007 (7) and 2.270 (3) Å, respectively, in (I) are comparable with those found in complexes with a PtS_2O_2 core, *e.g.* *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)platinum(II) [2.021 (6) and 2.232 (2) Å; Sacht *et al.*, 2000], *cis*-bis(*N*,*N*′-di-*n*-butyl-*N*′-benzoylthioureato)platinum(II) [2.022 (4) and 2.232 (2) Å; Irving *et al.*, 1993] and *trans*-bis(*N*-naphthoyl-*N*′,*N*′-dibutyl-

doi:10.1107/S1600536804033264

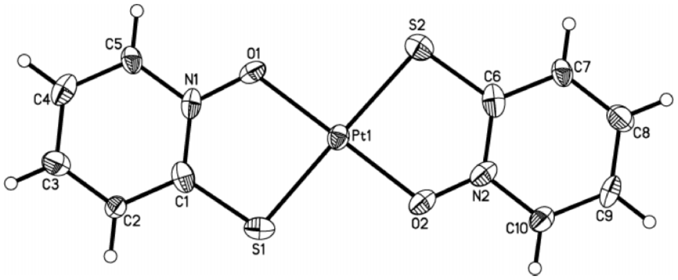


Figure 1
The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

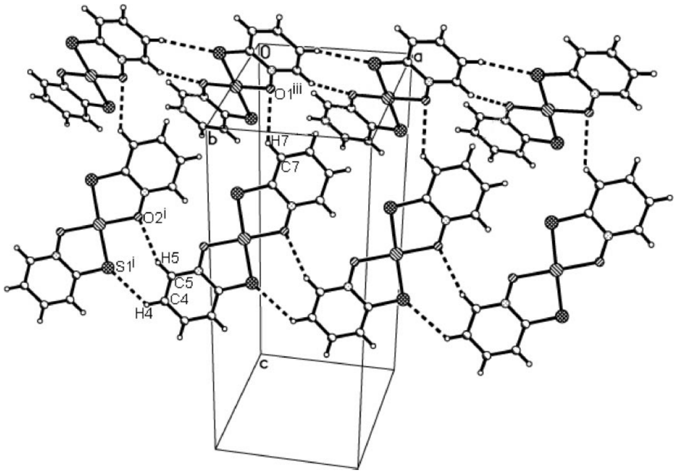


Figure 2
The intermolecular weak interactions (dashed lines) of the title compound [symmetry codes: (i) $x - 1, y, z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$].

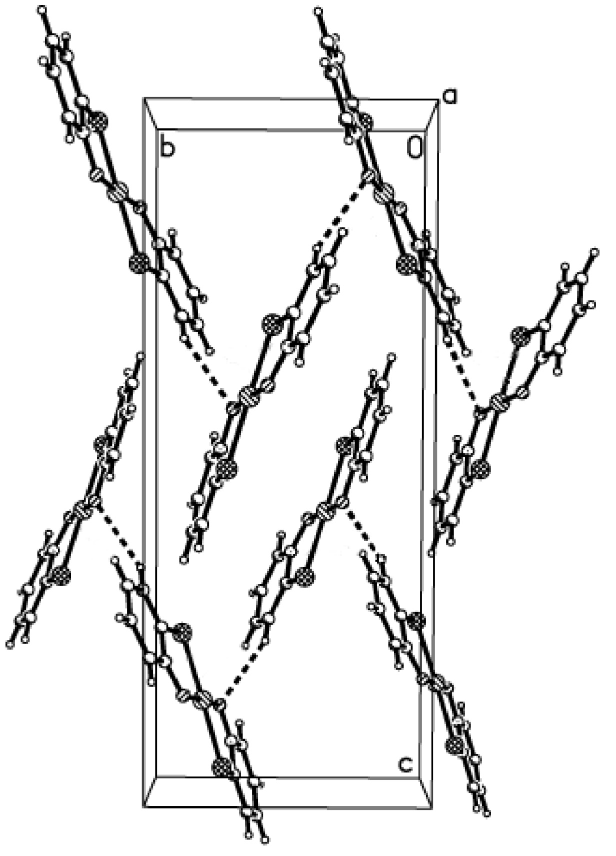


Figure 3
The two-dimensional layer structure of the title compound. Dashed lines indicate weak intermolecular interactions

thioureato-κ^2S,O)platinum(II) [1.98 (1) and 2.250 (4) Å; Koch *et al.*, 1994].

There are three weak intermolecular C—H···O/S interactions in the crystal structure, as shown in Fig. 2. Chains of molecules are formed along the *a* axis through two weak intermolecular interactions (C5—H5···O2^{i} and C4—H4···S1^{i}) (symmetry codes are as in Table 2) between neighboring molecules. Neighboring chains of molecules are connected through another weak intermolecular interaction (C7—H7···O1^{ii}), resulting in a layer structure (Fig. 3).

Experimental

To a suspension of K_2PtCl_6 (0.062 g, 0.15 mmol) in methanol (20 ml) was added a solution of Na(mpo) (0.054 g, 0.30 mmol) in H_2O (4 ml) with stirring. The resulting mixture was refluxed for 6 h and filtered. Brown plate-shaped crystals suitable for X-ray structure analysis were obtained by recrystallizing the yellow precipitate from CH_3CN (71% yield). Analysis calculated for $C_{10}H_8N_2O_2PtS_2$: C 26.83, H 2.05, N 6.13%; found: C 26.85, H 1.80, N 6.26%; IR (KBr, cm^{-1}): 3085 [*w*, (=C—H)], 3059 [*w*, (=C—H)], 3028 [*w*, (=C—H)], 1603 [*m*, (C=C)], 1543 [*s*, (=C—H)], 1459 [*vs*, (=C—H)], 1416 [*s*, (=C—H)], 1269 [*w*, (=C—H)], 1251 [*s*, (=C—H)], 1167 [*w*, (C=S)], 1153 [*m*, (C=S)], 1136 [*vs*, (C=S)], 1090 [*s*, (N—O)], 1040 [*w*, (=C—H)], 1027 [*w*, (=C—H)], 814 [*m*, γ (=C—H)], 781 [*s*, γ (=C—H)], 750 [*s*, γ (=C—H)], 711 [*s*, γ (=C—H)], 675 [*m*, γ (=C—H)].

Crystal data

$[Pt(C_5H_4NOS)_2]$
$M_r = 447.39$
Monoclinic, $P2_1/c$
$a = 7.535$ (1) Å
$b = 7.935$ (1) Å
$c = 19.368$ (3) Å
$\beta = 95.03$ (4)°
$V = 1153.6$ (3) Å^3
$Z = 4$

$D_x = 2.576$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 392 reflections
$\theta = 2.7$–16.2°
$\mu = 12.51$ mm^{-1}
$T = 293$ (2) K
Flake, brown
0.30 × 0.15 × 0.05 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.118$, $T_{\max} = 0.531$
6065 measured reflections

2261 independent reflections
1836 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 26.0$°
$h = -9 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -20 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.112$
$S = 1.05$
2261 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 1.22P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.00$ e Å^{-3}
$\Delta\rho_{\min} = -2.90$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—O2	1.994 (7)	S1—C1	1.729 (12)
Pt1—O1	2.019 (7)	S2—C6	1.724 (12)
Pt1—S1	2.266 (3)	N1—O1	1.300 (11)
Pt1—S2	2.274 (3)	N2—O2	1.273 (12)
O2—Pt1—O1	178.0 (3)	O1—N1—C5	116.8 (9)
O2—Pt1—S1	93.1 (2)	O2—N2—C6	122.7 (9)
O1—Pt1—S1	86.4 (2)	O2—N2—C10	117.2 (9)
O2—Pt1—S2	85.8 (2)	N1—O1—Pt1	115.7 (6)
O1—Pt1—S2	94.7 (2)	N2—O2—Pt1	117.3 (6)
S1—Pt1—S2	178.70 (11)	N1—C1—S1	117.7 (8)
C1—S1—Pt1	96.8 (4)	C2—C1—S1	122.3 (9)
C6—S2—Pt1	96.4 (4)	C7—C6—S2	122.4 (9)
O1—N1—C1	123.2 (9)	N2—C6—S2	117.6 (8)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O2^{i}	0.93	2.65	3.458 (14)	145
C4—H4···S1^{i}	0.93	2.86	3.511 (13)	128
C7—H7···O1^{ii}	0.93	2.61	3.322 (13)	134

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

The H atoms were positioned geometrically and refined as riding, with C—H distances of 0.93 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The highest peak and deepest hole are located 0.69 Å from C2 and 0.53 Å from Pt1, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by a Measurement Grant of Nanjing University (grant No. 0205001333).

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