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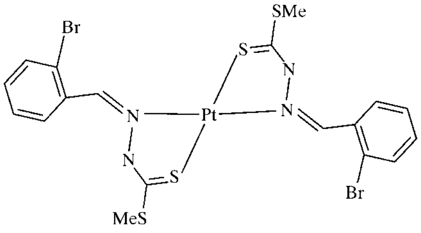
The Schiff base ligand in the title complex, $[Pt(C_9H_8BrN_2S_2)_2]$, is deprotonated from its tautomeric thiol form and coordinated to Pt^{II} *via* the mercapto S and β–N atoms. The configuration about Pt^{II} is a perfect square-planar, with two equivalent Pt—N [2.023 (3) Å] and Pt—S [2.293 (1) Å] bonds. The phenyl ring is twisted against the coordination moiety Pt1/N1/N1′/S2′/S2 by 31.8 (2)°, due to the steric hindrance induced by *ortho*-substituted bulky Br atom.

Comment

Organometallic compounds have recently received considerable attention as potential non-linear optical materials due to the various excited states present in these systems, as well as the ability to manipulate metal-organic ligand interactions (Long, 1995). Thiosemicabazones and their derivatives are known to coordinate readily with a variety of transition metal ions to afford stable metal complexes (Ali & Livingstone, 1974; Podhye & Kauffman, 1985). As part of our continuing studies on the syntheses and non-linear optical properties (including optical limiting) of Schiff base complexes containing mixed N,S donors (Tian *et al.*, 1997; Zhu, Chen *et al.*, 1999; Zhu, Liu *et al.*, 1999), we report herein the structure of title compound, (I), the Pt^{II} complex with a bidentate Schiff base ligand derived from *S*-methyl dithiocarbazate.



(I)

The molecular structure of $[Pt(C_9H_8BrN_2S_2)_2]$ consists of monomeric complex units. The Pt atom lies on a centre of symmetry with a perfect square-planar geometry with two equivalent Pt—N and Pt—S bonds; Pt^{II} is situated in the coordination plane. The bond lengths of Pt—N [2.023 (3) Å] and of Pt—S [2.2934 (12) Å] are normal (Clement *et al.*, 1996). The ligand has a *cis–cis* conformation, strictly resembling its analogues $[Pt\{N(CH_2Ph)NC(S)SMe\}_2]$ (Fares *et al.*, 1987) and $[Pt(PhL^1\text{-}2H)_2]$ (Dessy & Fares, 1980). The bond distances and bond angles are also not very different from those found in the analogues, the only significant difference being the Pt1—N1 distance [1.937 (4) and 1.966 (4) Å, respectively observed for the analogues] and related to the σ influence of the phenyl group. The Schiff base loses a proton from its tautomeric thiol form on cordination and acts as a singly charged bidentate ligand, coordinating to Pt^{II} *via* the mercapto–S and β–N atoms. The phenyl ring is twisted against the coordination moieties Pt1/N1/N1^{i}/S2/S2^{i} [symmetry code: (i) -*x*, 1-*y*, -*z*] by 31.8°, which is attributed to the steric hindrance induced by *ortho*-substituted bulky Br atom.

The *S*-methyldithiocarbazate, $N_2C(S)SMe$, group is planar with a maximum out-of-plane deviation of 0.013 (3) Å for N1. The Br atom deviates 0.043 (1) Å from the planarity of the phenyl ring.

Experimental

The title compound, $[Pt(C_9H_8BrN_2S_2)_2]$, was synthesized by refluxing an equivalent molar ratio of $PtCl_2$ and the Schiff-base ligand (prepared by condensation of 2-bromobenzaldehyde with *S*-methyl dithiocarbazate) in CH_3CN. Single crystals suitable for X-ray diffraction were obtained by evaporation of ether into a thf solution.

Crystal data

$[Pt(C_9H_8BrN_2S_2)_2]$
M_r = 771.50
Orthorhombic, *Pbca*
a = 7.9739 (1) Å
b = 14.1721 (2) Å
c = 20.3772 (2) Å
V = 2302.76 (5) Å^3
Z = 4
D_x = 2.23 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 2.00–28.34°
μ = 9.94 mm^{-1}
T = 293 (2) K
Slab, red
0.34 × 0.24 × 0.10 mm

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Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.070$, $T_{\max} = 0.370$
14 693 measured reflections
2865 independent reflections
2191 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 28.28°$
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 18$
$l = -27 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.084$
$S = 1.071$
2865 reflections
133 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 3.2007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.879$ e Å^{-3}
$\Delta\rho_{\min} = -2.062$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—N1	2.023 (3)	S2—C8	1.729 (5)
Pt1—S2	2.293 (1)	N1—C7	1.295 (5)
Br1—C6	1.898 (5)	N1—N2	1.411 (5)
S1—C8	1.751 (5)	N2—C8	1.293 (5)
S1—C9	1.803 (5)		
N1—Pt1—N1$^{\rm i}$	180.0 (1)	N1—Pt1—S2	83.2 (1)
N1—Pt1—S2$^{\rm i}$	96.8 (1)	N1$^{\rm i}$—Pt1—S2	96.8 (1)
N1$^{\rm i}$—Pt1—S2$^{\rm i}$	83.2 (1)	S2$^{\rm i}$—Pt1—S2	180.0 (1)

Symmetry codes: (i) $-x, 1-y, -z$.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. The temperature factors of C3, C4 and C5 are slightly higher. The highest peak and the deepest hole are located neat Pt atom.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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