metal-organic papers

[2-Acetylpyridine 1,1-(hexane-1,6-diyl)thiosemicarbazone-κ^3N,N',S]chloroplatinum(II)

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In the title compound, [Pt(C$_{14}$H$_{19}$N$_4$S)Cl], the azepane ring is partially disordered over two sites. The Pt atom coordination adopts a slightly distorted square-planar geometry. The 2-acetylpyridine thiosemicarbazone moiety is very close to planar. The azepane ring has a ($-sc$, $+sc$)$_3$, $+sp$ conformation (sc is synclinal and sp is synperiplanar) and, for the minor disorder component, a ($-sc$, $+sc$)$_3$, $-sp$ conformation. The computed bond valences for the Pt centre are $v_{\text{Pt}-\text{N}}$ = 0.467 and 0.587, $v_{\text{Pt}-\text{S}}$ = 0.60, and $v_{\text{Pt}-\text{Cl}}$ = 0.48 v.u. (valence units), and thus the computed valence of the Pt atom is 2.13 v.u. π–π stacking interactions give rise to π-bonded dimers.

Comment

Heterocyclic thiosemicarbazones are important because of their potentially beneficial biological activity (Scovill *et al.*, 1982). 2-Acetylpyridine 1,1-(hexane-1,6-diyl)thiosemicarbazone (Achexim) has been screened for medicinal use against HSV-1, HSV-2 and leukaemia P388 (Easmon *et al.*, 1989; Klayman, Scovill, Bartosevich & Bruce, 1983; Klayman, Scovill, Mason *et al.*, 1983). The AcheximPdCl and AcheximPdBr complexes also show cytostatic activity in *in vitro* tests (Kovala-Demertzi *et al.*, 1997). Here, we present the structure of the title platinum complex with Achexim, AcheximPtCl, (I).

(I)
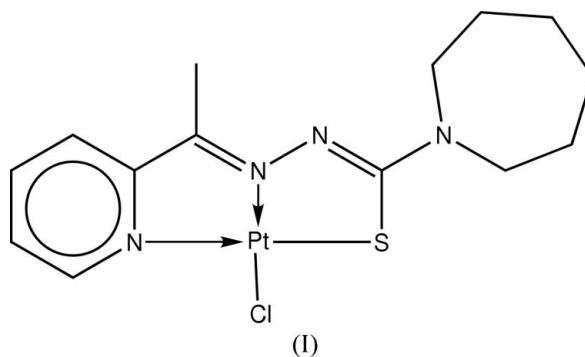
Compound (I) is isomorphous and isostructural with AcheximPdCl (Kovala-Demertzi *et al.*, 1998) and Achexim-CuBr (Butcher & West, 1993). Atoms C11 and C12 of the azepane ring are disordered over two positions (Fig. 1), with occupancy factors 0.63 (4):0.37 (4). The coordination of the Pt atom has distorted square-planar geometry. The 2-acetyl-pyridine thiosemicarbazone moiety is very close to planar; the maximum deviation (from the mass-weighted least-squares plane calculated for all 2-acetylpyridine thiosemicarbazone atoms) is 0.054 (7) Å for atom C7. Atom Pt1 is 0.065 (4) Å from this plane, in the same direction as atoms N1 and S1.

Therefore, atom Pt1 lies in this plane, within experimental error. This ligand plane makes an angle of 4.40 (13)° with the Pt coordination plane. The azepane ring has $(-sc, +sc)_3, +sp$ and $(-sc, +sc)_3, -sp$ conformations (sc is syn-clinal and sp is syn-periplanar), the latter being for the minor disorder component.

It has been stated that the correlation between bond length and bond valence represents a measure of bond strength independent of atomic size (Brown, 1994). The application of this correlation allows us to compare the relative importance of Pt—N, Pt—S and Pt—Cl bonds in (I) and to check the valence-sum rule for coordinated atoms (Brown, 2002). The valence-sum rule states that the sum of the valences of the bonds formed by an atom is equal to the valence (formal oxidation state) of the atom (Brown, 2002). The bond valences in (I) were computed as $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ (Brown, 1992, 1997; O'Keeffe & Brese 1991), where R_{ij} is the bond-valence parameter. The values of R_{Pt-N}, R_{Pt-S} and R_{Pt-Cl} were taken as 1.770, 2.08 and 2.05, respectively (Brese & O'Keeffe, 1991). The computed bond valences of Pt are $v_{Pt-N1} = 0.467$, $v_{Pt-N2} = 0.587$, $v_{Pt-S1} = 0.60$ and $v_{Pt-Cl1} = 0.48$ v.u. (valence units). Thus, the computed valence of atom Pt1 is 2.13 v.u. Although this computed valence is larger than the formal oxidation state of +2, this is much less than the error of 0.25–0.30 (Palenik, 2003) which indicates mistakes in the interpretation of the structure. These can arise from omission or addition of weak hydrogen bonds or from inappropriate crystallographic constraints (Wagner & O'Keeffe, 1988). According to bond-valence calculations, it can be stated that the Pt1—N1 and Pt1—Cl1 bonds have comparable strength and they are distinctly weaker than the Pt1—N2 and Pt1—S1 bonds, which are of almost the same strength.

In the crystal structure of (I), π–π stacking interactions (Hunter & Sanders, 1990) exist between pyridine rings [second ring related by symmetry code $(-x, -y, -z + 1)$] to create π-bonded dimers. The distance between ring centroids is 4.551 (14) Å, the perpendicular distance between rings is 3.463 (14) Å, the angle between the vector linking the ring centroids and the normal to one of the planes is 44.4 (10)°, and the offset is 2.953 (15) Å.

Experimental

The title compound was prepared according to the method of Kovala-Demertzi et al. (1997). The crystals used for data collection were grown from a dimethylsulfoxide solution by slow evaporation.

Crystal data

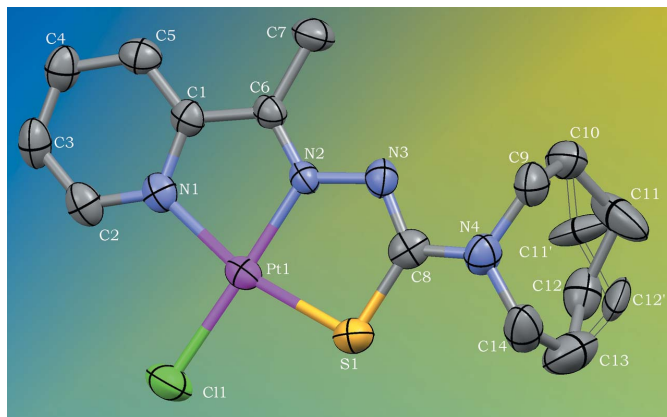|	
[Pt(C14H19N4S)Cl]	$D_x = 2.064$ Mg m^{-3}
$M_r = 505.93$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4615
$a = 7.2976$ (11) Å	reflections
$b = 24.999$ (2) Å	$\theta = 2$–20°
$c = 9.2074$ (14) Å	$\mu = 8.91$ mm^{-1}
$\beta = 104.272$ (13)°	$T = 291.0$ (3) K
$V = 1627.9$ (4) Å^3	Prism, red
$Z = 4$	$0.24 \times 0.12 \times 0.06$ mm

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Atoms of the minor disorder component are primed.

Data collection

Kuma KM-4 CCD area-detector diffractometer	2900 independent reflections
	2556 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.087$
Absorption correction: numerical	$\theta_{max} = 25.1°$
(X-RED; Stoe & Cie, 1999)	$h = -8 \rightarrow 8$
$T_{min} = 0.109$, $T_{max} = 0.596$	$k = -29 \rightarrow 29$
16639 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$+ 11.6759P]$
$wR(F^2) = 0.086$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.21$	$(\Delta/\sigma)_{max} < 0.001$
2900 reflections	$\Delta\rho_{max} = 1.11$ e Å^{-3}
207 parameters	$\Delta\rho_{min} = -0.99$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Pt1—N2	1.967 (7)	C6—N2	1.314 (11)
Pt1—N1	2.052 (8)	N2—N3	1.378 (10)
Pt1—S1	2.271 (3)	N3—C8	1.328 (11)
Pt1—Cl1	2.322 (3)	C8—N4	1.342 (12)
C1—C6	1.468 (12)	C8—S1	1.789 (10)
N2—Pt1—N1	80.9 (3)	N2—C6—C1	115.8 (8)
N2—Pt1—S1	85.2 (2)	C6—N2—N3	120.4 (7)
N1—Pt1—S1	166.0 (2)	C6—N2—Pt1	116.6 (6)
N2—Pt1—Cl1	176.3 (2)	N3—N2—Pt1	122.8 (5)
N1—Pt1—Cl1	96.8 (2)	C8—N3—N2	113.5 (8)
S1—Pt1—Cl1	97.18 (10)	N3—C8—S1	123.6 (7)
N1—C1—C6	114.4 (8)	C8—S1—Pt1	94.8 (3)
N4—C9—C10—C11	−62.2 (9)	C14—N4—C9—C10	87.4 (11)
C9—C10—C11—C12	62.2 (12)	N4—C9—C10—C11'	−28 (2)
C10—C11—C12—C13	−78 (2)	C9—C10—C11'—C12'	−45 (4)
C11—C12—C13—C14	57 (3)	C10—C11'—C12'—C13	87 (6)
C12—C13—C14—N4	9 (2)	C11'—C12'—C13—C14	−64 (5)
C13—C14—N4—C9	−75.0 (14)	C12'—C13—C14—N4	46 (3)

All carbon-bound H atoms were placed in calculated positions and refined as riding on the parent C atom, with C—H = 0.93–0.97 Å and with U_{iso}(H) = $1.2U_{eq}$(C) or $1.5U_{eq}$(methyl C). The methyl groups were allowed to rotate about their local threefold axis. The highest peak is located 1.50 Å from atom Pt1.

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