Tetrakis[pyridine-2(1H)-thione-κS]platinum(II) dichloride
Mina Mizota, Yoshimi Yokoyama and Ken Sakai
In the title compound, \([\text{Pt}(\text{C}_5\text{H}_5\text{NS})_4]\text{Cl}_2\), the Pt^{II} ion is located at a crystallographic inversion centre, with each S-donor ligand in its thione tautomeric form \([\text{Pt}–\text{S} = 2.3439 (7)\text{ Å}\) and 2.3444 (7) Å\]. The Cl\(^{-}\) ion positioned at each axial site of the Pt^{II} ion \([\text{Pt}···\text{Cl} = 3.5171 (8)\text{ Å}\)] is hydrogen-bonded to the N–H units of the ligands \([\text{Cl}···\text{N} = 3.103 (3)\text{ and } 3.125 (3)\text{ Å}\)]

Comment

Metal–metal interactions often give rise to exceptionally reactive metal centres, leading to the activation of small molecules. In this context, we have long been interested in the evolution of H\(_2\) from H\(_2\)O catalyzed by amidate-bridged cis-diammineplatinum(II) dimers, \([\text{Pt}^{II}_2(\text{NH}_3)_4(\mu-\text{amidato})_2]^{2+}\) (amidate = acetamidate, 2-fluoroacetamidate, \(\alpha\)-pyridonate, \(\alpha\)-pyrrolidinonate, etc.) (Sakai et al., 1993). As extended studies on the catalysis of such dinuclear systems, efforts have also been made to develop new electronic systems having unusual reactivity. Here, we report the synthesis and crystal structure of the title complex, \([\text{Pt}((\text{pyridine}-2\text{-thione})_4)\text{Cl}_2]\), (I).
As shown in Fig. 1, atom Pt1 of (I) is located at an inversion centre. Therefore, the PtII ion possesses a crystallographically imposed planar geometry. The shortest Pt−C1/C1 distance [3.5171 (8) Å] corresponds to the sum of the van der Waals radii of Pt and Cl (1.72–1.75 Å for Pt and ca 1.75 Å for Cl; Bondi, 1964), and is slightly shorter than that reported for (II) [Pt−Cl = 3.612 (6) Å]. The ligand is found to serve as a monodentate S-donor ligand in its thione tautomeric form, as illustrated in the scheme. This is a general trend which has been observed thus far for this series of complexes, e.g. [Pt(4-methylpyridine-2-thione)4]Cl2·MeOH (Nishioka et al., 1992), [Pd(pyridine-2-thione)4]Cl2 (Umakoshi et al., 1990) and [Pt(1-methyl-4-imidazoline-2-thione)4]Cl2·2H2O (Birker et al., 1982).

The C=S bond distances in (I) [1.729 (3) and 1.731 (3) Å] are slightly longer than those reported for the free or uncoordinated thione molecule [1.692 (2)–1.698 (2) Å; Ohms et al., 1982], which must be caused by a slight decrease in its bond order due to the formation of π back-donation from dπ(Pt) to the π*(C=S) orbital. As described in an earlier structure report on 2-thiopyridone, the extent of double-bond character for the C−S bond may be estimated using the linear relationship between the order and length of C−S (Penfold, 1953). If we adopt the reported correlation (Penfold, 1953), the double-bond character of the C−S groups in (I) can be estimated to be ca 40 (5)%.

The two 2-thiopyridone planes, defined by S1/N1/C1–C5 and S2/N2/C6–C10, are tilted with respect to the Pt coordination plane by 65.47 (7) and 64.71 (14)°, respectively. Only one of the two pyridine-2-thione ligands forms a π-stack to a neighbouring molecule through an inversion centre, leading to the establishment of one-dimensional chains propagating along the [110] direction (Fig. 2). The plane-to-plane separation between the stacked pyridyl planes is estimated at 3.527 (2) Å.

**Experimental**

A solution of cis-PtCl2(DMSO)2 (0.10 mmol, 0.042 g; Price et al., 1972; DMSO is dimethyl sulfoxide) and pyridine-2(1H)-thione (1.0 mmol, 0.111 g) in methanol (20 ml) was refluxed for 12 h. After cooling the solution to room temperature, it was evaporated to a total volume of ca 7 ml until a small amount of yellow precipitate started to deposit. Leaving the solution to stand in air at room temperature overnight afforded (I) as yellow plates (yield 70%). Analysis calculated for PtS4Cl2N4C20H20: C 33.80, H 2.84, N 7.88%; found: C 33.82, H 2.82, N 7.88%. IR (KBr, cm−1): 2863 (br), 1608 (m), 1570 (s), 1560 (m), 1492 (m), 1436 (m), 1139 (s), 1132 (s), 1082 (w), 748 (s), 727 (m).
Data collection
Bruker SMART APEX CCD area-detector diffractometer
\( \omega \) scans
Absorption correction: Gaussian (XPREP in SAINT; Bruker, 2001)
\( T_{\text{min}} = 0.162, T_{\text{max}} = 0.535 \)
2632 independent reflections
2629 reflections with \( I > 2\sigma(I) \)
\( R_{\text{int}} = 0.058 \)
\( \theta_{\text{max}} = 26.4^\circ \)
\( h = -10 \rightarrow 10 \)
\( k = -11 \rightarrow 11 \)
\( l = -12 \rightarrow 12 \)
7352 measured reflections

Refinement
Refinement on \( F^2 \)
\( R[F^2 > 2\sigma(F^2)] = 0.019 \)
\( wR(F^2) = 0.041 \)
\( S = 1.02 \)
2632 reflections
142 parameters

\( \Delta \rho_{\text{max}} = 0.98 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.70 \text{ e Å}^{-3} \)

Table 1
Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th></th>
<th>Pt1—S2</th>
<th>C2—C3</th>
<th>1.379 (5)</th>
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<tr>
<td>Pt1—S1</td>
<td>2.3439 (7)</td>
<td>C3—C4</td>
<td>1.404 (5)</td>
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<td>S1—C1</td>
<td>1.731 (3)</td>
<td>C4—C5</td>
<td>1.367 (5)</td>
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<td>S2—C6</td>
<td>1.729 (3)</td>
<td>C6—C7</td>
<td>1.414 (4)</td>
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<td>N1—C5</td>
<td>1.364 (4)</td>
<td>C7—C8</td>
<td>1.381 (5)</td>
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<tr>
<td>N1—C1</td>
<td>1.367 (4)</td>
<td>C8—C9</td>
<td>1.384 (6)</td>
</tr>
<tr>
<td>N2—C10</td>
<td>1.365 (4)</td>
<td>C9—C10</td>
<td>1.356 (6)</td>
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<tr>
<td>C1—C2</td>
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<tr>
<td>C2—C4</td>
<td>3.534 (4)</td>
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<tr>
<td>S2—Pt1—S1</td>
<td>88.47 (3)</td>
<td>C1—S1—Pt1</td>
<td>109.05 (9)</td>
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<tr>
<td>S2—Pt1—S1( ^a )</td>
<td>91.53 (3)</td>
<td>C6—S2—Pt1</td>
<td>109.67 (10)</td>
</tr>
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</table>

Pt1—S1—C1—N1 3.6 (2) Pt1—S2—C6—N2 −5.8 (3)

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

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

<table>
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<tr>
<th>D—H—A</th>
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<tr>
<td>N1—H1A—C1</td>
<td>0.86</td>
<td>2.35</td>
<td>3.125 (3)</td>
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<tr>
<td>N2—H2A—C1</td>
<td>0.86</td>
<td>2.32</td>
<td>3.103 (3)</td>
<td>152</td>
</tr>
</tbody>
</table>

All H atoms were placed at their idealized positions as riding atoms, with \( C—H = 0.93 \text{ Å} \) for aromatic rings and \( N—H = 0.86 \text{ Å} \) for thioamide groups, and included in the refinement in a riding-model approximation, with \( U_{eq}(H) = 1.2U_{eq}(\text{carrier atom}) \).

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: KENX (Sakai, 2004); software used to prepare material for publication: SHELXL97, TEXSAN (Molecular Structure Corporation, 2001), KENX and ORTEP (Johnson, 1976).

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References