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## **Tetrakis[pyridine-2(1*H*)-thione- $\kappa$ S]platinum(II) dichloride**

**Mina Mizota, Yoshimi Yokoyama and Ken Sakai**

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Tetrakis[pyridine-2(1*H*)-thione- $\kappa$ S]platinum(II) dichlorideMina Mizota,<sup>a</sup> Yoshimi Yokoyama<sup>b</sup> and Ken Sakai<sup>b\*</sup><sup>a</sup>Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan, and <sup>b</sup>Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan

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## Key indicators

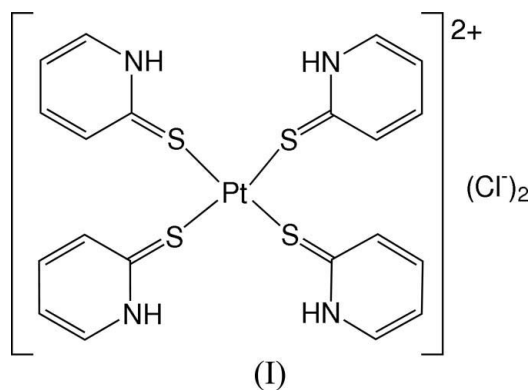
Single-crystal X-ray study  
 $T = 296\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$   
 $R$  factor = 0.019  
 $wR$  factor = 0.041  
Data-to-parameter ratio = 18.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $[\text{Pt}(\text{C}_5\text{H}_5\text{NS})_4]\text{Cl}_2$ , the  $\text{Pt}^{\text{II}}$  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) and  $2.3444$  (7)  $\text{\AA}$ ]. The  $\text{Cl}^-$  ion positioned at each axial site of the  $\text{Pt}^{\text{II}}$  ion [ $\text{Pt}\cdots\text{Cl} = 3.5171$  (8)  $\text{\AA}$ ] is hydrogen-bonded to the N—H units of the ligands [ $\text{Cl}\cdots\text{N} = 3.103$  (3) and  $3.125$  (3)  $\text{\AA}$ ].

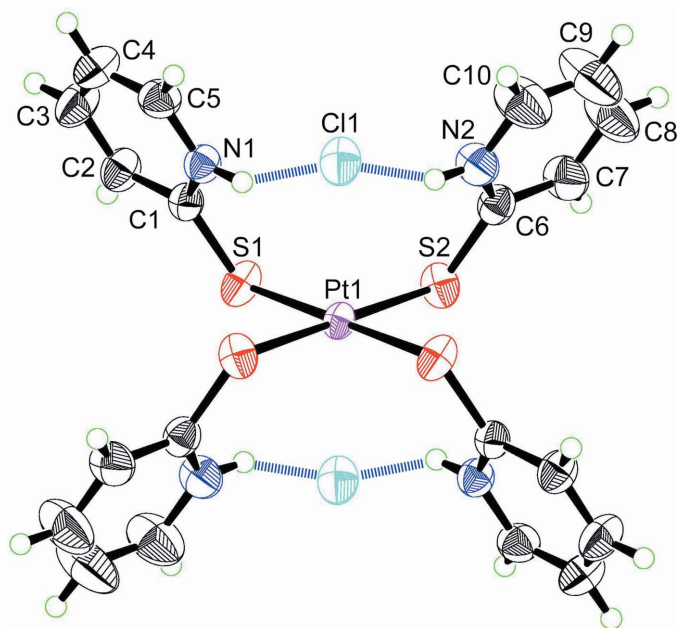
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## Comment

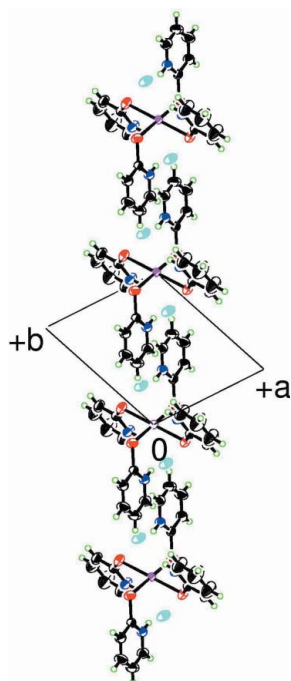
Metal–metal interactions often give rise to exceptionally reactive metal centres, leading to the activation of small molecules. In this context, we have long been interested in the evolution of  $\text{H}_2$  from  $\text{H}_2\text{O}$  catalyzed by amidate-bridged *cis*-diammineplatinum(II) dimers,  $[\text{Pt}^{\text{II}}_2(\text{NH}_3)_4(\mu\text{-amidato})_2]^{2+}$  (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,  $[\text{Pt}(\text{pyridine-2-thione})_4]\text{Cl}_2$ , (I).



Complex (I) was prepared as a precursor for one of our target molecules, *viz.* a trinuclear platinum(II) chain complex,  $[\text{LPt}(\mu\text{-}B)_2\text{Pt}(\mu\text{-}B)_2\text{PtL}]^{2+}$  [ $L = 2,2'$ -bipyridine,  $(\text{NH}_3)_2$ , *etc.*;  $B = \text{pyridine-2-thionate}$ ], even though the preparation of such a trimer has been unsuccessful to date. Although an almost analogous complex involving 4-methylpyridine-2-thione,  $[\text{Pt}(4\text{-methylpyridine-2-thione})_4]\text{Cl}_2\cdot\text{MeOH}$  [hereinafter (II)], was previously prepared from the reaction of  $\text{K}_2\text{PtCl}_4$  and 4-methylpyridine-2-thione in toluene (Nishioka *et al.*, 1992), the preparation of (I) according to that method has been unsuccessful to date, presumably due to the difference in the solubilities of the two analogous systems. In the present study, compound (I) was found to be produced in good yield based on our synthetic strategy (see *Experimental*).



**Figure 1**  
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator  $(-x, -y, -z)$ . Broken lines indicate hydrogen bonds.



**Figure 2**  
A view showing the manner in which the molecules of (I) stack along the [110] direction.

As shown in Fig. 1, atom Pt1 of (I) is located at an inversion centre. Therefore, the Pt<sup>II</sup> ion possesses a crystallographically imposed planar geometry. The shortest Pt $\cdots$ Cl 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 $\cdots$ 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)<sub>4</sub>]Cl<sub>2</sub>·MeOH (Nishioka *et al.*, 1992), [Pd(pyridine-2-thione)<sub>4</sub>]Cl<sub>2</sub> (Umakoshi *et al.*, 1990) and [Pt(1-methyl-4-imidazoline-2-thione)<sub>4</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O (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  $\pi$  back-donation from  $d\pi(\text{Pt})$  to the  $\pi^*(\text{C}=\text{S})$  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)%. In each pyridine ring, the C–C unit directly attached to the S atom clearly has a longer distance than the rest of the C–C units (Table 1), indicating that it has a higher single-bond character in comparison with the remaining bonds. The thione tautomerism is also obvious from the N–H $\cdots$ Cl hydrogen-bonding geometries summarized in Table 2 (see also Fig. 1).

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  $\pi$ -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*-PtCl<sub>2</sub>(DMSO)<sub>2</sub> (0.10 mmol, 0.042 g; Price *et al.*, 1972; DMSO is dimethyl sulfoxide) and pyridine-2(1*H*)-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 PtS<sub>4</sub>Cl<sub>2</sub>N<sub>4</sub>C<sub>20</sub>H<sub>20</sub>: C 33.80, H 2.84, N 7.88%; found: C 33.82, H 2.82, N 7.88%. IR (KBr, cm<sup>-1</sup>): 2863 (*br*), 1608 (*m*), 1570 (*s*), 1560 (*m*), 1492 (*m*), 1436 (*m*), 1139 (*s*), 1132 (*s*), 1082 (*w*), 748 (*s*), 727 (*m*).

### Crystal data

[Pt(C<sub>5</sub>H<sub>5</sub>NS)<sub>4</sub>]Cl<sub>2</sub>  
 $M_r$  = 710.63  
 Triclinic, *P*1  
 $a$  = 8.3372 (8) Å  
 $b$  = 9.0754 (8) Å  
 $c$  = 10.1261 (9) Å  
 $\alpha$  = 99.709 (1)°  
 $\beta$  = 114.142 (1)°  
 $\gamma$  = 104.871 (1)°  
 $V$  = 642.4 (1) Å<sup>3</sup>

$Z$  = 1  
 $D_x$  = 1.837 Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5806 reflections  
 $\theta$  = 2.4–28.2°  
 $\mu$  = 6.01 mm<sup>-1</sup>  
 $T$  = 296 (2) K  
 Plate, yellow  
 0.44 × 0.23 × 0.11 mm

## Data collection

Bruker SMART APEX CCD area-detector diffractometer	2632 independent reflections
$\omega$ scans	2629 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian (XPREP in SAINT; Bruker, 2001)	$R_{\text{int}} = 0.058$
$T_{\text{min}} = 0.162$ , $T_{\text{max}} = 0.535$	$\theta_{\text{max}} = 26.4^\circ$
7352 measured reflections	$h = -10 \rightarrow 10$
	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 12$

## Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.019$	$w = 1/[\sigma^2(F_o^2) + (0.0093P)^2]$
$wR(F^2) = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2632 reflections	$\Delta\rho_{\text{max}} = 0.98 \text{ e } \text{\AA}^{-3}$
142 parameters	$\Delta\rho_{\text{min}} = -0.70 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Pt1—S2	2.3439 (7)	C2—C3	1.379 (5)
Pt1—S1	2.3444 (7)	C3—C4	1.404 (5)
S1—C1	1.731 (3)	C4—C5	1.367 (5)
S2—C6	1.729 (3)	C6—C7	1.414 (4)
N1—C5	1.364 (4)	C7—C8	1.381 (5)
N1—C1	1.367 (4)	C8—C9	1.384 (6)
N2—C10	1.365 (4)	C9—C10	1.356 (6)
C1—C2	1.417 (4)		
C2...C4 <sup>i</sup>	3.534 (4)		
S2—Pt1—S1	88.47 (3)	C1—S1—Pt1	109.05 (9)
S2—Pt1—S1 <sup>ii</sup>	91.53 (3)	C6—S2—Pt1	109.67 (10)
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 ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A...C11	0.86	2.35	3.125 (3)	150
N2—H2A...C11	0.86	2.32	3.103 (3)	152

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; 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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