Chlorido(dimethyl sulfoxide-κS)[2-(2-pyridyl)phenyl-κ2N1,C1]platinum(II)

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Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.007 Å; R factor = 0.024; wR factor = 0.064; data-to-parameter ratio = 17.3.

In the title compound, [Pt(C11H8N)Cl(C2H6OS)], the S atom of dimethyl sulfoxide is trans to the pyridyl N atom [Pt–S = 2.2181 (11) Å] and the chlorido ligand is trans to the carbon donor of 2-(2-pyridyl)phenyl [Pt–Cl = 2.4202 (10) Å]. The [2-(2-pyridyl)phenyl]platinum(II) unit forms a one-dimensional stack along the c axis with two independent interplanar separations of 3.44 (9) and 3.50 (2) Å.

Related literature

For background information, see: Herber et al. (1994); Mdleleni et al. (1995); Newman et al. (2007); Ozawa et al. (2006, 2007); Sakai & Ozawa (2007); Sakai et al. (1993); Ozawa & Sakai (2007); Kobayashi et al. (2008).

Experimental

Crystal data

\[
[\text{Pt(C}_1\text{H}_8\text{N})\text{Cl(C}_2\text{H}_6\text{OS})]
\]

\begin{align*}
M_r &= 462.85 \\
&\text{Monoclinic, } C2/c \\
a &= 22.414 (3) \text{ Å} \\
b &= 10.0205 (16) \text{ Å} \\
c &= 14.057 (2) \text{ Å} \\
\beta &= 124.512 (2)°
\end{align*}

\[
V = 2601.6 (7) \text{ Å}^3
\]

\[Z = 8\]

Mo Kα radiation

\[
\mu = 11.14 \text{ mm}^{-1}
\]

\[T = 100 (2) \text{ K}
\]

\[0.09 \times 0.08 \times 0.04 \text{ mm}
\]

Data collection

Bruker SMART APEXII CCD-detector diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

\[T_{\text{min}} = 0.486, \ T_{\text{max}} = 0.640\]

\[2448 \text{ reflections with } I > 2\sigma (I)\]

\[R_{\text{int}} = 0.018\]

Refinement

\[R[F^2 > 2\sigma(F^2)] = 0.023\]

\[wR(F^2) = 0.064\]

\[S = 1.11\]

\[2850 \text{ reflections}\]

\[165 \text{ parameters}\]

H-atom parameters constrained

\[\Delta \rho_{\text{max}} = 2.05 \text{ e Å}^{-3}\]

\[\Delta \rho_{\text{min}} = -1.43 \text{ e Å}^{-3}\]

Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2; data reduction: SAINT (Bruker, 2004); program(s) used to solve structure: SHELXL97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: KENX (Sakai, 2004); software used to prepare material for publication: SHELXL97, TEXSAN (Molecular Structure Corporation, 2001), KENX and ORTEPII (Johnson, 1976).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2633).

References


supplementary materials
Chlorido(dimethyl sulfoxide-κS)[2-(2-pyridyl)phenyl-κ2N1,C1]platinum(II)

M. Kobayashi, S. Masaoka and K. Sakai

Comment

Interests over many years have concentrated on the molecular catalysis of Pt\textsuperscript{II} complexes in photochemical hydrogen production from water (Sakai \textit{et al.}, 1993; Ozawa \textit{et al.}, 2006; Sakai & Ozawa, 2007; Ozawa, Yokoyama \textit{et al.}, 2007). The results obtained so far suggest that destabilization of the HOMO, which generally corresponds to the filled Pt\textsuperscript{II} d\textsubscript{z}\textsuperscript{2} orbital, gives rise to the higher H\textsubscript{2}-evolving activity of the complexes (Sakai & Ozawa, & Sakai, 2007). It has also been ascertained that the mononuclear Pt\textsuperscript{II} complexes possessing a \textit{cis}-PtCl\textsubscript{2} unit, such as \textit{cis}-PtCl\textsubscript{2}(NH\textsubscript{3})\textsubscript{2}, PtCl\textsubscript{2}(4,4'-dicarboxy-2,2'-bipyridine), and PtCl\textsubscript{2}(2,2'-bipyrimidine), exhibit considerably higher H\textsubscript{2}-evolving activity in comparison with those only having the amine or pyridyl type of neutral ligands, such as [Pt(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} and [Pt(bpy)\textsubscript{2}]\textsuperscript{2+} (Ozawa, Yokoyama \textit{et al.}, 2007). In this context, the 2-phenylpyridinate (ppy) ligand was selected because of the well known strong σ-donating character of the C(ppy) donor, expecting the higher energy level of the HOMO for the Pt\textsuperscript{II}(ppy) complexes. As a result, the first water-soluble salt of [Pt(ppy)Cl\textsubscript{2}]\textsuperscript{-}, that is, [K(18-crown-6)][Pt(ppy)Cl\textsubscript{2}]\textsubscript{0.5}H\textsubscript{2}O (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) [abbreviated as compound (II)], was recently prepared in our group and its catalytic activity in photochemical hydrogen production from water was examined in detail (Kobayashi \textit{et al.}, in submission). The title compound, Pt(ppy)Cl(DMOS-S) (DMSO = dimethyl sulfoxide) [abbreviated as compound (I)], was first prepared from recrystallization of (II) from DMSO, but an improved synthetic route is reported in this work (see Experimental Section). It has been ascertained that the H\textsubscript{2}-evolving activity of (I) is much lower than that of (II), the reason for which remains ambiguous at the moment.

The donor atoms, except for the sulfur atom S1, comprise a planar geometry and the Pt atom (Pt1) does not deviate from this plane at all. The four-atom r.m.s. deviation, given in the best-plane calculation for the plane defined by atoms N1, C11, C1, and Pt1, was negligible (0.0003). Hereafter, this plane is defined as the Pt coordination plane. The sulfur atom (S1) and the oxygen atom (O1) of DMSO are only slightly shifted out of this plane by 0.067 (5) and 0.045 (8) Å, respectively. The torsion angles given by C11—Pt1—S1—O1 = 2.4 (2) and Cl1—Pt1—S1—O1 = -177.83 (17)° also reveal that the oxygen atom of DMSO is not largely shifted out of the coordination plane. Thus, it can be considered that (I) adopts a pseudo mirror symmetry. The benzene ring consisting of atoms C6—C11 is nearly coplanar with the coordination plane, where the dihedral angle between the benzene and the coordination planes is calculated as 0.7 (2)°. The pyridyl plane defined by atoms N1 and C1—C5 is slightly declined with respect to the coordination plane by 2.8 (2)°. The dihedral angle between the two aromatic rings is 2.5 (2)°.

The ppy ligand in compound (I, Fig. 1) does not suffer from any disorder problem. Indeed, there is a clear difference in the bond lengths of Pt—N(ppy) and Pt—C(ppy); Pt1—N1 = 2.069 (3) and Pt1—C11 = 2.002 (4) Å. Because of the strong \textit{trans} influence originated by the C(ppy) donor, Pt1—C11 distance [2.4202 (10) Å] is longer than those reported for PtCl\textsubscript{2}(2,2'-bipyridine) [2.281 (4) - 2.306 (2) Å; Herber \textit{et al.}, 1994]. Th Pt1—C11 distance is comparable to the value reported for Pt(ppy)(Hppy)Cl [2.4145 (23) Å; Mdleleni \textit{et al.}, 1995]. In addition, the Pt1—S1 bond distance [2.2181 (11) Å, in the
position trans to the N(ppy) donor, is comparable to those previously reported for Pt(2-(4-fluorophenyl)pyridine)Cl(DMSO) [2.2161 (16) Å; Newman et al., 2007].

On the other hand, compound (I) forms a one-dimensional stack along the c axis based on the π-π stacking interactions between the phenylpyridinatoplatinum(II) units (see Fig. 2). The separation between the two adjacent planes is estimated as 3.44 (9) Å for the stack shown in Fig. 4 and 3.50 (2) Å for that in Fig. 5. In the former (Fig. 4), atoms C1\textsuperscript{i}, C5\textsuperscript{i}, N1\textsuperscript{i}, and Pt1\textsuperscript{i} have an interaction to the phenylpyridinate moiety originally located and therefore shifts of these atoms from the best plane defined by atoms N1 and C1—C11 are used to calculate the separation of the two stacked planes at this geometry. In the latter (Fig. 5), atoms N1\textsuperscript{ii}, C1\textsuperscript{ii}, C2\textsuperscript{ii}, C5\textsuperscript{ii}, C6\textsuperscript{ii}, C10\textsuperscript{ii}, C11\textsuperscript{ii}, and Pt1\textsuperscript{ii} are involved in the π-stacking association and their shifts from the best plane defined by atoms N1 and C1—C11 are similarly used to calculate the separation at this geometry. In these geometries, strong d-π interactions also contribute to the stabilization of stacking associations [Pt1—C4\textsuperscript{i} = 3.525 (4) Å and Pt1—C4\textsuperscript{ii} = 3.523 (4) Å; symmetry codes: (i) -x, y, 0.5 - z; (ii) -x, 1 - y, 1 - z]. Finally, it must be noted that metal-metal interactions are unimportant in this crystal [Pt1—Pt1\textsuperscript{i} = 5.9946 (8) Å and Pt1—Pt1\textsuperscript{ii} = 5.4225 (9) Å], where the symmetry operations are same to those given in Fig. 4 and Fig. 5.

**Experimental**

A mixture of cis-PtCl\textsubscript{2}(DMSO)\textsubscript{2} (0.21 g, 0.50 mmol) and 2-phenylpyridine (0.078 g, 0.50 mmol) in methanol (10 ml) was sealed in a pressure-resistant vial and was stirred at 393 K for 3 h. After the solution was cooled down to room temperature, the yellow precipitate of compound (I) was filtrated and dried in vacuo (Caution! Do not open the vial while it is hot, since the solution splashes out because of the violent boiling phenomenon upon a sudden decrease in pressure). Yield: 0.14 g (60%). Analysis calculated for C\textsubscript{13}H\textsubscript{14}ClNOPtS: C 33.73, H 3.05, N 3.03. Found: C 33.95, H 2.99, N 3.02. \textsuperscript{1}H NMR (300.53 MHz, acetone-d\textsubscript{6}), p.p.m.: δ 9.63 [d, J = 5.97 Hz, \textsuperscript{3}J\textsuperscript{195}Pt-\textsuperscript{1}H = 17.8 Hz, 1H], 8.37 [d, J = 6.81 Hz, \textsuperscript{3}J\textsuperscript{195}Pt-\textsuperscript{1}H = 22.8 Hz, 1H], 8.16–8.06 (m, 2H), 7.25 (d, J = 6.46 Hz), 7.48 (t, J = 6.43 Hz), 7.20–7.11 (m, 2H), 3.63 [s, \textsuperscript{3}J\textsuperscript{195}Pt-\textsuperscript{1}H = 12.2 Hz, 6H]. A good quality single-crystal was prepared by diffusion of methanol into a DMSO solution of (I).

**Refinement**

All H atoms were placed in idealized positions (methyl C—H = 0.98 Å and aromatic C—H = 0.95 Å), and included in the refinement in a riding-model approximation, with \textit{U}_{iso}(H) = 1.5\textit{U}_{eq}(methyl C) and \textit{U}_{iso}(H) = 1.2\textit{U}_{eq}(aromatic C). In the final difference Fourier map, the highest peak was located 0.83 Å from atom Pt1. The deepest hole was located 1.07 Å from atom H9.

**Figures**

Fig. 1. The molecular structure of (I) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 2. Views down the c axis, showing the manner how the phenylpyridinatoplatinum(II) units are stacked along the c axis to give a one-dimensional network. Hydrogen atoms are omitted for clarity.

Fig. 3. Views down the b axis, showing the manner how the phenylpyridinatoplatinum(II) units are stacked along the c axis to give a one-dimensional network. Hydrogen atoms are omitted for clarity.

Fig. 4. Views perpendicular to the aromatic systems that are stacked at two independent geometries [Symmetry code: (i) -x, y, 0.5 - z].

Fig. 5. Views perpendicular to the aromatic systems that are stacked at two independent geometries [Symmetry code: (ii) -x, 1 - y, 1 - z].

Chlorido(dimethyl sulfoxide-κS)[2-(2-pyridyl)phenyl-κ²N,C²]platinum(II)

Crystal data

[Pt(C₁₁H₈N)Cl(C₂H₆OS)]

$F_{000} = 1744$

$D_\text{m} = 2.363 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ Å}$

Cell parameters from 3936 reflections

$\theta = 2.5^{\circ}-27.9^{\circ}$

$\mu = 11.14 \text{ mm}^{-1}$

$T = 100 (2) \text{ K}$

Prisms, yellow

$0.09 \times 0.08 \times 0.04 \text{ mm}$
supplementary materials

Data collection

Bruker SMART APEX CCD-detector diffractometer 2850 independent reflections
Radiation source: rotating anode with a mirror focusing unit 2448 reflections with \( I > 2\sigma(I) \)
Monochromator: graphite \( R_{\text{int}} = 0.018 \)
\( T = 100(2) \) K \( 0_{\text{max}} = 27.1^\circ \)
\( \varphi \) and \( \omega \) scans \( 0_{\text{min}} = 2.2^\circ \)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
\( T_{\text{min}} = 0.486, T_{\text{max}} = 0.640 \)
7004 measured reflections \( h = -28 \rightarrow 28 \)

Refinement

Refinement on \( F^2 \) Secondary atom site location: difference Fourier map
Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
\( R[F^2 > 2\sigma(F^2)] = 0.023 \) H-atom parameters constrained
\( wR(F^2) = 0.064 \) where \( P = (F_o^2 + 2F_c^2)/3 \)
\( S = 1.11 \) \( \Delta\rho_{\text{max}} = 2.05 \) e Å\(^{-3} \)
2850 reflections \( \Delta\rho_{\text{min}} = -1.42 \) e Å\(^{-3} \)
165 parameters Primary atom site location: structure-invariant direct methods

Special details

Experimental. The first 50 frames were rescanned at the end of data collection to evaluate any possible decay phenomenon. Since it was judged to be negligible, no decay correction was applied to the data.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Least-squares planes (\( x,y,z \) in crystal coordinates) and deviations from them (* indicates atom used to define plane)

\[-14.3368 (0.0269) x - 0.3580 (0.0127) y + 13.9887 (0.0034) z = 5.0906 (0.0091)\]

\[* 0.0000 (0.0001) N1 * -0.0003 (0.0009) C11 * -0.0002 (0.0007) C11 * 0.0004 (0.0015) Pt1 - 0.0669 (0.0049) S1 - 0.0453 (0.0077)\]

O1

Rms deviation of fitted atoms = 0.0003

\[-15.0609 (0.0266) x - 0.5670 (0.0181) y + 13.9054 (0.0039) z = 4.9585 (0.0082)\]

Angle to previous plane (with approximate e.s.d.) = 2.77 (0.16)
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\* -0.0032 (0.0026) N1 * 0.0072 (0.0030) C1 * -0.0025 (0.0030) C2 * -0.0058 (0.0029) C3 * 0.0096 (0.0029) C4 * -0.0052 (0.0027) C5 - 0.1020 (0.0055) Pt1

Rms deviation of fitted atoms = 0.0061

-14.3427 (0.0315) x - 0.4723 (0.0194) y + 13.9812 (0.0035) z = 5.0095 (0.0158)

Angle to previous plane (with approximate e.s.d.) = 2.52 (0.18)

\* -0.0053 (0.0030) C6 * 0.0050 (0.0034) C7 * 0.0011 (0.0036) C8 * -0.0071 (0.0033) C9 * 0.0068 (0.0030) C10 * -0.0006 (0.0029) C11 0.0196 (0.0064) Pt1

Rms deviation of fitted atoms = 0.0050

-14.3368 (0.0269) x - 0.3580 (0.0127) y + 13.9887 (0.0034) z = 5.0906 (0.0091)

Angle to previous plane (with approximate e.s.d.) = 0.66 (0.17)

\* 0.0000 (0.0001) N1 * -0.0003 (0.0009) C11 * -0.0002 (0.0007) C11 * 0.0004 (0.0015) Pt1 - 0.0669 (0.0049) S1 - 0.0453 (0.0077) O1

Rms deviation of fitted atoms = 0.0003

-14.6775 (0.0205) x - 0.4790 (0.0073) y + 13.9524 (0.0028) z = 4.9852 (0.0045)

Angle to previous plane (with approximate e.s.d.) = 1.36 (0.14)

\* 0.0328 (0.0031) N1 * 0.0226 (0.0035) C1 * -0.0212 (0.0037) C2 * -0.0380 (0.0034) C3 * -0.0016 (0.0037) C4 * 0.0177 (0.0038) C5 * 0.0052 (0.0039) C6 * 0.0303 (0.0041) C7 * 0.0139 (0.0042) C8 * -0.0215 (0.0039) C9 * -0.0223 (0.0033) C10 * -0.0180 (0.0035) C11 - 3.4480 (0.0042) N1_S1 - 3.3136 (0.0062) C11_S1 - 3.5267 (0.0045) C5_S1 - 3.4606 (0.0029) Pt1_S1

Rms deviation of fitted atoms = 0.0228

-14.6775 (0.0205) x - 0.4790 (0.0073) y + 13.9524 (0.0028) z = 4.9852 (0.0045)

Angle to previous plane (with approximate e.s.d.) = 0.00 (0.12)

\* 0.0328 (0.0031) N1 * 0.0226 (0.0035) C1 * -0.0212 (0.0037) C2 * -0.0380 (0.0034) C3 * -0.0016 (0.0037) C4 * 0.0177 (0.0038) C5 * 0.0052 (0.0039) C6 * 0.0303 (0.0041) C7 * 0.0139 (0.0042) C8 * -0.0215 (0.0039) C9 * -0.0223 (0.0033) C10 * -0.0180 (0.0035) C11 3.4700 (0.0040) N1_S2 3.4803 (0.0050) C11_S2 3.5240 (0.0050) C2_S2 3.4851 (0.0048) C5_S2 3.4977 (0.0053) C6_S2 3.5252 (0.0047) C10_S2 3.5209 (0.0046) C11_S2 3.5174 (0.0022) Pt1_S2

Rms deviation of fitted atoms = 0.0228

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > σ(F^2) is used only for calculating R-factors etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

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Atomic displacement parameters (Å$^2$)
Geometric parameters (Å, °)

Pt1—C11  2.002 (4)  C3—H3  0.9500  0.9500
Pt1—N1  2.069 (3)  C4—H4  0.9500  0.9500
Pt1—S1  2.2181 (11)  C5—C6  1.464 (6)  1.464 (6)
Pt1—Cl1  2.4202 (10)  C6—C7  1.400 (6)  1.400 (6)
S1—O1  1.474 (3)  C6—C11  1.413 (6)  1.413 (6)
S1—C12  1.782 (5)  C7—C8  1.386 (6)  1.386 (6)
S1—C13  1.788 (5)  C7—H7  0.9500  0.9500
N1—C5  1.355 (6)  C8—C9  1.392 (6)  1.392 (6)
N1—C1  1.359 (6)  C8—H8  0.9500  0.9500
C1—C2  1.377 (6)  C9—C10  1.393 (6)  1.393 (6)
C2—C3  1.392 (6)  C9—H9  0.9500  0.9500
C3—C4  1.384 (6)  C10—C11  1.393 (6)  1.393 (6)
C4—C5  1.385 (6)  C10—H10  0.9500  0.9500
Pt1—C4  3.525 (4)  C12—H12A  0.9800  0.9800
Pt1—C4  3.523 (4)  C12—H12B  0.9800  0.9800
Pt1—Pt1  5.9946 (8)  C12—H12C  0.9800  0.9800
Pt1—Pt1  5.4225 (9)  C13—H13A  0.9800  0.9800
Pt1—Pt1  5.4225 (9)  C13—H13B  0.9800  0.9800
C1—H1  0.9500  C13—H13C  0.9800  0.9800
C2—H2  0.9500  C1—C2—C3  119.5 (4)
C11—Pt1—N1  80.28 (16)  C7—C6—C11  121.5 (4)
C11—Pt1—S1  177.97 (10)  C7—C6—C5  122.1 (4)
C11—Pt1—Cl1  173.26 (12)  C8—C7—C6  116.3 (4)
N1—Pt1—C11  98.69 (12)  C8—C7—H7  121.0 (4)
N1—Pt1—C11  98.69 (12)  C6—C7—H7  121.0 (4)
N1—Pt1—C11  98.69 (12)  C7—C8—C9  119.9 (4)
N1—Pt1—C11  98.69 (12)  C7—C8—H8  120.0 (4)
N1—Pt1—C11  98.69 (12)  C9—C8—H8  120.0 (4)
N1—Pt1—C11  98.69 (12)  C8—C9—C10  120.0 (4)
N1—Pt1—C11  98.69 (12)  C8—C9—H9  120.0 (4)
N1—Pt1—C11  98.69 (12)  C9—C10—C11  120.0 (4)
N1—Pt1—C11  98.69 (12)  C9—C10—H10  119.0 (4)
N1—Pt1—C11  98.69 (12)  C10—C11—C6  116.7 (4)
N1—Pt1—C11  98.69 (12)  C10—C11—Pt1  129.1 (3)
N1—Pt1—C11  98.69 (12)  C11—C10—Pt1  114.2 (3)
N1—Pt1—C11  98.69 (12)  S1—C12—H12A  109.5
N1—Pt1—C11  98.69 (12)  S1—C12—H12B  109.5
N1—Pt1—C11  98.69 (12)  H12A—C12—H12B  109.5

supplementary materials
supplementary materials

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Symmetry codes: (i) −x, y, −z+1/2; (ii) −x, −y+1, −z+1.
supplementary materials

Fig. 1
supplementary materials

Fig. 2
Fig. 3
supplementary materials

Fig. 4
Fig. 5