Monoclinic
$P2_1/c$
$a = 18.168$ (2) Å
$b = 7.867$ (2) Å
$c = 21.908$ (3) Å
$\beta = 125.58$ (4)°
$V = 2546$ (2) Å^3
$Z = 4$
$D_x = 1.56$ (5) Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.991$ mm^{-1}
$T = 294$ K
Prismatic
0.35 × 0.30 × 0.20 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4467 measured reflections
2862 independent reflections
2607 reflections with $I > 3\sigma(I)$

$R_{\rm int} = 0.055$
$\theta_{\rm max} = 24°$
$h = -20 \rightarrow 19$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 21$
2 standard reflections
frequency: 60 min
intensity decay: 0.79%

Refinement

Refinement on F
$R = 0.075$
$wR = 0.098$
$S = 3.208$
2607 reflections
334 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\rm max} = 0.025$
$\Delta\rho_{\rm max} = 0.90$ e Å^{-3}
$\Delta\rho_{\rm min} = 0.56$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Cu—O1	1.983 (6)	Cu—N3	2.059 (5)
Cu—N1	2.089 (8)	Cu—N4	2.234 (7)
Cu—N2	2.021 (5)		
O1—Cu—N1	168.6 (3)	N1—Cu—N3	94.3 (3)
O1—Cu—N2	88.8 (2)	N1—Cu—N4	96.3 (3)
O1—Cu—N3	87.3 (2)	N2—Cu—N3	170.8 (3)
O1—Cu—N4	94.7 (2)	N2—Cu—N4	93.4 (2)
N1—Cu—N2	87.9 (3)	N3—Cu—N4	95.2 (2)

In compound (1), the H atoms of the O1 and O2 water molecules were located by difference Fourier synthesis and the remaining H atoms of both structures were introduced at idealized positions. In complex (2), the F atoms of the PF_6^- anion are disordered, but it was not possible to resolve them into several sites. The displacement parameters of these atoms are therefore high and not significant. Correction for absorption was considered unnecessary on the basis of ψ scans which did not show significant variation.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *BEGIN* in *SDP* (Frenz, 1985); program(s) used to solve structures: *MULTAN*80 (Main *et al.*, 1980); program(s) used to refine structures: *LSFM* in *SDP*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 562-565

Arene–Arene Stacking in *cis*-Bis[2-(2-thienyl-C^3)pyridine-*N*]platinum(II)

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(*Received 14 August 1996; accepted 3 December 1996*)

Abstract

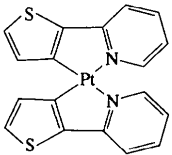
In the crystal structure of the title complex, $[Pt(C_9H_6NS)_2]$, although the aromatic ligands are coordinated to a central heavy metal atom, T-shaped and shifted

π-stacked arrangements of the aromatic moieties are preferred, leading to a sandwich herring-bone type of crystal-packing motif. The crystal structure is therefore consistent with the view that the arene–arene interactions are determined by electrostatics (multipole–multipole).

Comment

Transition metal complexes with organic ligands have been investigated with increasing interest over recent decades, since these complexes exhibit an enormous potential for the discovery of new physical, biological and chemical properties and applications. For example, photoredox processes for solar-energy conversion, information storage systems, new laser materials and biosensors have already been explored or are under current investigation. Most of the possible applications are related to the properties of the lowest excited electronic states and these depend crucially on both the molecular structure and the environment of the chromophore (Yersin, Schützenmeier, Wiedenhofer & von Zelewsky, 1993; Yersin, Humbs & Strasser, 1997). Analyzing crystal-packing patterns is one approach to developing a better understanding of non-covalent intermolecular interactions, which are important for the molecular recognition and self-assembly processes leading to molecular aggregates.

The title compound, *cis*-bis[2-(2-thienyl)pyridine]-platinum(II), [Pt(2-thpy)$_2$], (I), which belongs to a relatively new class of *ortho*-metalated compounds (Chassot & von Zelewsky, 1987; Maestri, Balzani, Deuschel-Cornioley & von Zelewsky, 1992; Balzani *et al.*, 1987), exhibits a series of very interesting electronic and vibronic properties which have only recently been explored (Wiedenhofer, Schützenmeier, von Zelewsky & Yersin, 1995). The determination of the crystal structure of (I) is therefore an important addition to the knowledge of this compound.



(I)

The molecular structure of [Pt(2-thpy)$_2$] is shown in Fig. 1. Both the geometry of the ligand and the coordination sphere of the Pt atom are in agreement with related Pt^{II} and Pt^{IV} cyclometalated complexes (Giordano & Rasmussen, 1975; von Zelewsky, Suckling & Stoeckli-Evans, 1993; Stückl, Klement & Range, 1993; Allen & Kennard, 1993). The mean Pt—C and Pt—N bond lengths, and the ligand bite angles of the five characterized compounds reported in the literature are 2.00 (3), 2.15 (6) Å and 79.8 (1)° (standard deviation of the mean given), respectively, while we have found averages of 1.989 (6), 2.160 (5) Å and 79.3 (2)° (standard deviation of the sample given).

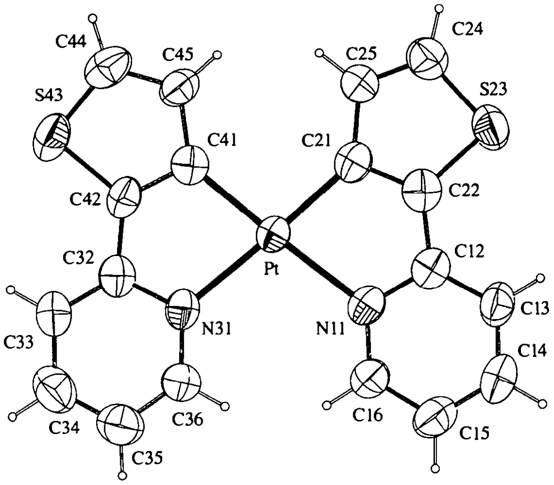


Fig. 1. The molecular structure of [Pt(2-thpy)$_2$] showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

As observed for the related cyclometalated compound *cis*-bis(2-phenylpyridine)platinum(II), [Pt(phpy)$_2$] (Chassot, Müller & von Zelewsky, 1984), the mutual steric influences of the H atoms on C16/C36 and C25/C45 cause the ligands to be slightly distorted in a bowlike manner. The C16 and C25 atoms are displaced by −0.019 (8) and −0.136 (7) Å, respectively, below the plane defined by the Pt, N11, C21, N31 and C41 atoms, while the C36 and C45 atoms are pushed above this plane by 0.092 (7) and 0.172 (7) Å, respectively.

The thienyl and pyridine rings are planar, the maximum deviations from the four least-squares planes being 0.011 (6), 0.009 (6), 0.030 (5) and 0.005 (5) Å for the C12, C21, N31 and C45 atoms, respectively. The dihedral angles between the thienyl and pyridine rings in the ligands are 5.6 (3) and 10.6 (4)° for rings N11–C16/C21–C25 and N31–C36/C41–C45, respectively, while the angles between the phenyl and pyridine rings are 17.81 and 19.51° in the case of the less planar [Pt(phpy)$_2$].

Similar to what was observed for [Pt(phpy)$_2$], the packing of [Pt(2-thpy)$_2$] comprises 'dimeric' units, the two molecules of a 'dimer' being related to one another by a center of inversion. The Pt$\cdots$Pt^{i} distance [3.7547 (9) Å], however, is even longer than in [Pt(phpy)$_2$] (3.53 Å), implying no dominant bonding interaction between the two metal centers [symmetry code: (i) $-x$, $2-y$, $-z$]. Furthermore, the molecules in the 'dimer' unit are shifted parallel to the planes of the molecules by 1.604 Å (Fig. 2), indicating that the interaction is controlled by so-called 'π–π' interactions. This shifted π-stacked arrangement and the short distances from the ring centroids to the parallel aromatic planes (3.430–3.627 Å; see Fig. 2) are in agreement with this view. Recent experimental (Cozzi, Cinquini, Annuziata & Siegel, 1993; Hunter, 1993) and simulation (Jorgensen & Severance, 1990) work shows that most 'π–π' interactions are dominated by electrostatics (multipole–multipole). The inherent polarity of aromatic systems stems from the electron-rich core being surrounded by an electron-poor torus of H atoms. This electrostatic description accounts for the energetic preference for T-shaped and shifted π-stacked arrangements leading to herring-bone and/or π-stacked crystal-packing motifs (Desiraju & Gavezzotti, 1989) depending on the relative size of the surface areas with the opposite sign of molecular electrostatic potential (MEP).

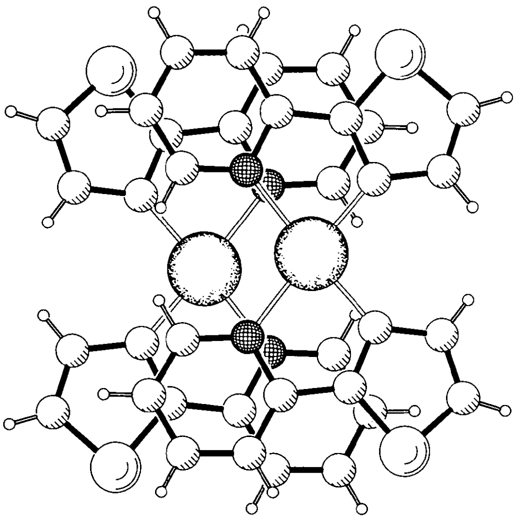


Fig. 2. The shifted π-stack arrangement of the molecules in the 'dimer'.

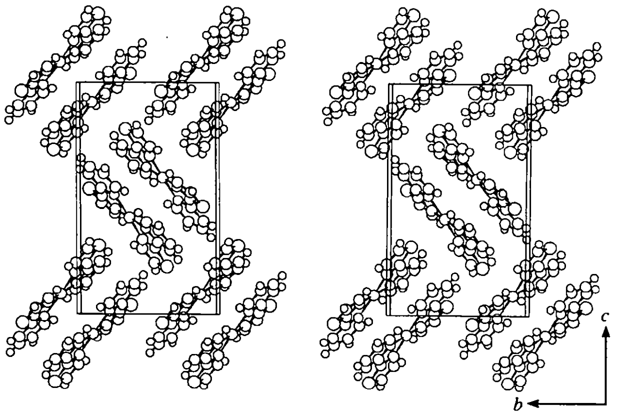


Fig. 3. The crystal packing of [Pt(2-thpy)$_2$] viewed down the a axis, showing the herring-bone-like arrangement and the 'dimer' columns running along **b**.

The crystal packing of [Pt(2-thpy)$_2$] displays a herring-bone motif (Fig. 3). Along the b axis, 'dimers' are built into columns, again with a staggered parallel stacking of ligands. The molecules in the adjacent pile are oriented almost perpendicularly yielding a T-shaped contact.

Even though the aromatic heterocycles are coordinated to the heavy metal, the crystal packing is in accordance with the usual packing patterns of aromatic compounds, which are determined by electrostatic interactions.

Experimental

cis-Bis[2-(2-thienyl)pyridine]platinum(II) was synthesized according to the method of Chassot & von Zelewsky (1987). Suitable single crystals were obtained by recrystallization from acetone by slow evaporation.

Crystal data

[Pt(C$_9$H$_6$NS)$_2$]
$M_r = 515.52$
Monoclinic
$P2_1/c$
$a = 9.320\,(2)$ Å
$b = 9.9726\,(14)$ Å
$c = 17.203\,(4)$ Å
$\beta = 104.831\,(15)°$
$V = 1545.7\,(5)$ Å^3
$Z = 4$
$D_x = 2.215$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 1808 reflections
$\theta = 3.05–24.72°$
$\mu = 9.35$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.24 × 0.20 × 0.14 mm
Brown

Data collection

Stoe IPDS diffractometer
Rotation scans
Absorption correction: numerical from crystal shape (Stoe & Cie, 1996)
4454 measured reflections
2052 independent reflections

1840 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0341$
$\theta_{\rm max} = 24.72°$
$h = -10 \rightarrow 10$
$k = -7 \rightarrow 11$
$l = -13 \rightarrow 19$

Refinement

Refinement on F^2
$R(F) = 0.0265$
$wR(F^2) = 0.0714$
$S = 1.118$
2052 reflections
208 parameters
H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.735$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.197$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pt—N11	2.159 (5)	S43—C42	1.727 (7)
Pt—N31	2.161 (5)	S43—C44	1.662 (8)
Pt—C21	1.986 (6)	N11—C12	1.362 (8)
Pt—C41	1.992 (6)	N11—C16	1.341 (9)
S23—C22	1.708 (7)	N31—C32	1.360 (8)
S23—C24	1.713 (8)	N31—C36	1.337 (8)

N11—Pt—N31	103.30 (18)	N11—C12—C22	112.9 (5)
N11—Pt—C21	79.1 (2)	N11—C16—C15	123.1 (7)
N11—Pt—C41	177.3 (2)	Pt—C21—C22	115.3 (5)
N31—Pt—C21	176.5 (2)	Pt—C21—C25	136.9 (5)
N31—Pt—C41	79.4 (2)	S23—C22—C12	125.5 (5)
C21—Pt—C41	98.2 (3)	S23—C22—C21	115.2 (5)
C22—S23—C24	89.7 (4)	S23—C24—C25	112.6 (6)
C42—S43—C44	90.9 (3)	N31—C32—C33	122.5 (7)
Pt—N11—C12	113.0 (4)	N31—C32—C42	111.4 (5)
Pt—N11—C16	130.0 (5)	N31—C36—C35	124.5 (7)
C12—N11—C16	116.9 (6)	Pt—C41—C42	113.7 (5)
Pt—N31—C32	113.5 (4)	Pt—C41—C45	137.3 (5)
Pt—N31—C36	130.3 (4)	S43—C42—C32	124.7 (5)
C32—N31—C36	116.1 (6)	S43—C42—C41	113.7 (5)
N11—C12—C13	122.0 (6)	S43—C44—C45	113.2 (5)

H atoms were calculated in their ideal positions and refined using a riding model, with a C—H distance of 0.93 Å and isotropic displacement parameters set to 1.2 times the equivalent isotropic parameters of the atoms to which they are attached.

Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990) and *INSIGHT*II (Biosym Technologies, 1993). Software used to prepare material for publication: *PLATON*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KA1218). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). **C53**, 565–568

Molecular Adducts of Inorganic Salts. VII. Cadmium Tetraoxorhenium Hexakis(thiourea) Hydrate

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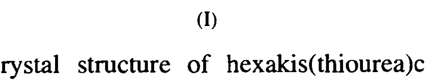
Abstract

The title compound, $[Cd(CH_4N_2S)_6](ReO_4)_2.H_2O$, is built up of isolated centrosymmetric $[Cd\{SC(NH_2)_2\}_6]^{2+}$ octahedra, ReO_4^- tetrahedra and water molecules packed most densely in the *ac* plane. Two of the three non-equivalent thiourea molecules are almost parallel and the third one is perpendicular to the *ac* plane. The structural units are held together by a complex network of intra- and intercluster hydrogen bonds.

Comment

In the system $Cd(ReO_4)_2$–tu–H_2O (tu is thiourea), several different $Cd(ReO_4).n(tu)$ adducts, with $n = 2$, 4 and 6, have been found. For $n = 2$, two polymorphic phases have been identified (Petrova, Angelova & Macíček, 1996). One of them is built up of infinite kröhnkite-type chains (Hawthorne & Ferguson, 1975), while in the other, the chains consist of CdS_3O_3 octahedra linked by alternating double ReO_4 and tu bridges. The crystal structure of $Cd(ReO_4)_2.4tu$ is built up of isolated *trans*-[*M*(ReO_4)$_2$tu$_4$] clusters (Petrova, Angelova, Bakardjieva & Macíček, 1996). In this paper, we discuss the coordination of the Cd atom and the cation–anion packing when $n = 6$, (I).



(I)

The crystal structure of hexakis(thiourea)cadmium tetraoxorhenium monohydrate consists of isolated centrosymmetric $[Cd(tu)_6]^{2+}$ cations, $ReO_4{}^-$ anions and

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