[μ-2,3,5,6-Tetrakis(2-pyridyl)pyrazine]bis[chloroplatinum(II)] bis[trichloro(dimethyl sulfoxide-κS)platinate(II)]

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[μ-2,3,5,6-Tetrakis(2-pyridyl)pyrazine]bis-[chloroplatinum(II)] bis[trichloro(dimethyl sulfoxide-κS)platinate(II)]

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A reaction of *cis*-PtCl$_2$(DMSO)$_2$ (DMSO = dimethyl sulfoxide, C$_2$H$_6$OS) with 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tpp, C$_{24}$H$_{16}$N$_6$) gave the title salt, [Pt$_2$Cl$_2$(μ-tpp)][PtCl$_3$(DMSO)]$_2$. The compound consists of a dinuclear Pt cation, [Pt$_2$Cl$_2$(μ-tpp)]$^{2+}$, and two [PtCl$_3$(DMSO)]$^-$ anions. The two Pt atoms within the cation are separated by a distance of 6.4792 (17) Å, and their coordination planes are canted at an angle of 19.6 (9)°. The shortest intermolecular Pt···Pt distance is 4.5726 (16) Å. Metal–metal interactions are unimportant in the crystal structure, and the packing is stabilized by extensive π–π interactions between the tpp moieties, in addition to ionic interactions.

Comment

Attempts have been made thus far to develop new types of one-dimensional platinum compounds in our laboratory (Sakai *et al.*, 2002). We were hoping to obtain systems involving relatively large aromatic systems and recently started exploring the coordination chemistry of platinum and 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tpp). The title compound was obtained during efforts to synthesize tetravalent dinuclear cations of hexadentate tpp, such as [Pt$_2$(NH$_3$)$_2$(μ-tpp)]$^{4+}$, even though the preparation of such compounds has been unsuccessful so far. Here we report on the crystal structure of a novel salt obtained for the Pt-tpp family, [Pt$_2$Cl$_2$(μ-tpp)][PtCl$_3$(DMSO)]$_2$, (I).

(I)
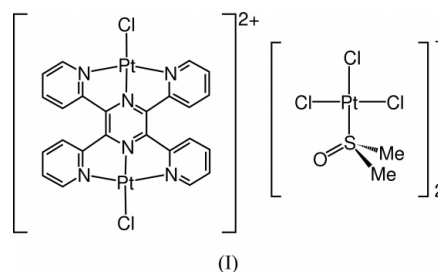
Until now, at least 34 tpp complexes have been structurally analysed by X-ray diffraction (Cambridge Structural Database; Allen, 2002), and at least eight kinds of coordination modes have been characterized. These compounds involve mono-, di-, and trinuclear complexes, but no structures of mixed-metal complexes have been determined. Among them, 12 complexes possess a structure in which tpp bridges two metal centers with two tridentate moieties in a *mer* fashion. As for Pt, only one compound, namely [Pt$_2$(PEt$_3$)$_2$Cl$_2$(μ-tpp)][Pt(SnCl$_3$)$_4$(PEt$_3$)] (Teles *et al.*, 2000), has been structurally characterized, where tpp binds to two Pt atoms with two
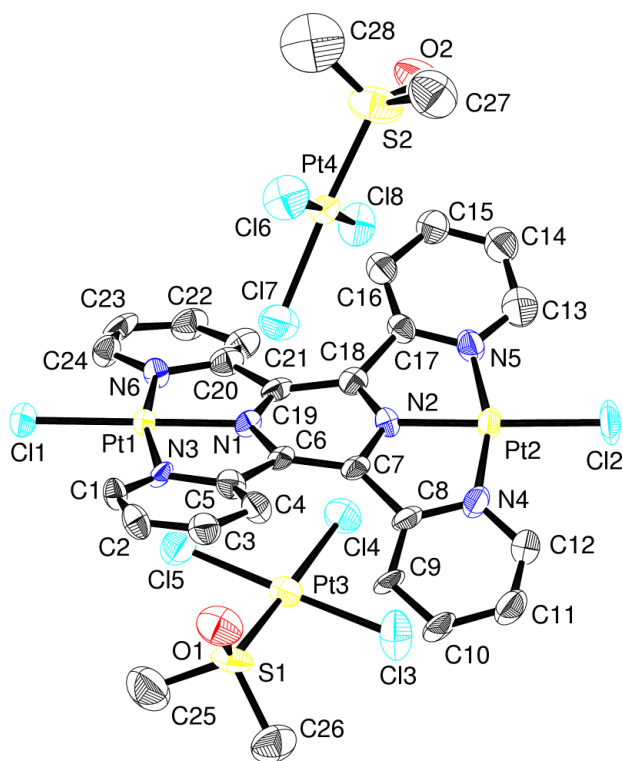
Figure 1
The structures of the three independent complex ions in (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.
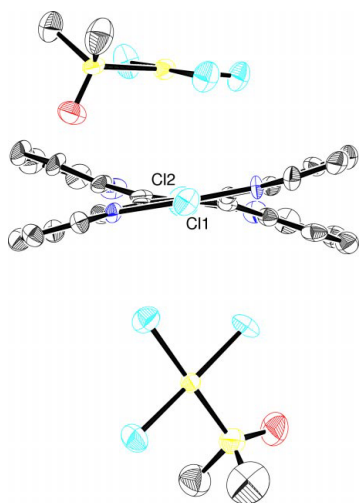
Figure 2
A view along the Cl1—Pt1···Pt2—Cl2 axis, showing the twist of the tpp ligand.

bidentate moieties while the two N donors of the pyrazine ring do not take part in the coordination. In this context, this is the first example of a Pt–tpp complex in which tpp bridges two Pt centers in a fully ligated form, with two chelates in a *mer* fashion.

As shown in Fig. 1, a dinuclear cation and two mononuclear anions are found in the asymmetric unit of (I). Displacement parameters of DMSO C and O atoms are relatively large, reflecting the rotational flexibility about the Pt—S axes. The

tpp ligand is severely distorted from planarity to avoid steric contacts between the H atoms at the 3-position of pyridyl moieties. The twist in the tpp ligand is estimated to be $\omega(\text{tpp}) = 26.7\,(2)°$, based on the least-squares-plane calculations performed for two halves of the ligand (see Fig. 2), where 15-atom r.m.s. deviations are 0.102 and 0.117 Å. The twist angle, based on the dihedral cant between two Pt coordination planes, is $\omega(\text{Pt1}/\text{Pt2}) = 19.6\,(9)°$, where four-atom r.m.s. deviations are 0.008 and 0.014 Å. These values are quite similar to those reported for $[\text{Pd}_2(\text{NO}_3)_2(\mu\text{-tpp})]$-$(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ [$\omega(\text{tpp}) = 29.1°$ and $\omega(\text{Pd1}/\text{Pd2}) = 21.9°$; Yamada *et al.*, 2000]. On the other hand, Ni complexes are reported to have relatively large twists compared to those discussed above [$\omega(\text{tpp}) = 38.3°$ and $\omega(\text{Ni1}/\text{Ni2}) = 31.9°$ for $[\text{Ni}_2(\text{acetato})_4(\text{H}_2\text{O})_2(\mu\text{-tpp})] \cdot \text{CH}_2\text{O}$ (Koman *et al.*, 1998), and $\omega(\text{tpp}) = 34.6°$ and $\omega(\text{Ni1}/\text{Ni2}) = 25.1°$ for $[\text{Ni}_2(\text{H}_2\text{O})_6(\mu\text{-tpp})](\text{NO}_3)_4 \cdot 2.5\text{H}_2\text{O}$ (Graf *et al.*, 1997)].

The displacements of atoms Pt1 and Pt2 from their coordination planes are 0.020 (8) and 0.003 (9) Å, respectively. The former is clearly relevant to the effective d–π interaction achieved between the Pt atom and the neighboring tpp moiety [$\text{Pt1}—\text{C24}^{\text{ii}} = 3.40\,(3)$ Å; symmetry code: (ii) $-x, 1-y, 1-z$]. However, face-to-face interactions between the tpp ligands appear to dominate the stabilization of the crystal packing of (I). The intermolecular Pt···Pt distances listed in Table 1 indicate that Pt···Pt interactions are not significant in this system.

Finally, it should be noted that the Pt—Cl distances within the cation [2.278 (7) and 2.268 (7) Å] are effectively shorter than those in $[\text{PtCl}_3(\text{DMSO})]^-$ [2.294 (8)–2.320 (7) Å], presumably due to the relatively strong back-donation promoted by the tpp ligand.

Experimental

A solution of tpp (0.050 mmol, 0.020 g; Goodwin & Lions, 1959) and *cis*-$\text{PtCl}_2(\text{DMSO})_2$ (0.10 mmol, 0.042 g; Price *et al.*, 1972) in methanol (15 ml) was reacted within a pressure-resistant sealed tube at 393 K for 12 h. After the solution was cooled down to room temperature, orange prisms of (I) were collected by filtration.

Crystal data

$[\text{Pt}_2\text{Cl}_2(\text{C}_{24}\text{H}_{16}\text{N}_6)]$-$[\text{PtCl}_3(\text{C}_2\text{H}_6\text{OS})]_2$	$Z = 2$
$M_r = 1608.64$	$D_x = 2.639$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.0868\,(11)$ Å	Cell parameters from 818
$b = 12.9476\,(14)$ Å	reflections
$c = 16.5057\,(19)$ Å	$\theta = 2.5$–$19.1°$
$\alpha = 94.085\,(2)°$	$\mu = 14.45$ mm^{-1}
$\beta = 105.321\,(2)°$	$T = 296\,(1)$ K
$\gamma = 100.954\,(2)°$	Plate, orange
$V = 2024.3\,(4)$ Å^3	$0.08 \times 0.04 \times 0.02$ mm

Data collection

Bruker SMART APEX CCD-detector diffractometer	5638 independent reflections
ω scans	3198 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian (*XPREP* in *SAINT*; Bruker, 2001)	$R_{\text{int}} = 0.088$
	$\theta_{\max} = 23.3°$
	$h = -11 \rightarrow 11$
	$k = -14 \rightarrow 14$
$T_{\min} = 0.511$, $T_{\max} = 0.868$	$l = -18 \rightarrow 18$
9820 measured reflections	

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.079$
$wR(F^2) = 0.117$
$S = 0.91$
5638 reflections
455 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.55$ e Å^{-3}
$\Delta\rho_{min} = -1.15$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—N1	1.95 (2)	Pt4—Cl8	2.276 (7)
Pt1—N6	2.008 (18)	Pt4—Cl7	2.292 (7)
Pt1—N3	2.017 (19)	Pt4—Cl6	2.310 (8)
Pt1—Cl1	2.278 (7)	Pt1···Pt2	6.4792 (17)
Pt2—N2	1.92 (2)	Pt1···Pt3	4.5726 (16)
Pt2—N5	1.99 (2)	Pt2···Pt2^i	4.662 (2)
Pt2—N4	1.99 (2)	Pt1···Pt1^{ii}	4.760 (2)
Pt2—Cl2	2.268 (7)	Pt2···Pt3	5.2396 (16)
Pt3—S1	2.212 (7)	Pt2···Pt2^{iii}	5.758 (2)
Pt3—Cl5	2.294 (8)	Pt2···Pt4	5.9359 (16)
Pt3—Cl3	2.300 (8)	Pt1···Pt4	5.9778 (16)
Pt3—Cl4	2.320 (7)	Pt1···C24^{ii}	3.40 (3)
Pt4—S2	2.184 (8)		
N1—Pt1—N6	81.2 (8)	S1—Pt3—Cl5	90.6 (3)
N1—Pt1—N3	83.4 (8)	S1—Pt3—Cl3	91.6 (3)
N6—Pt1—N3	164.6 (8)	Cl5—Pt3—Cl3	177.7 (3)
N1—Pt1—Cl1	178.6 (6)	S1—Pt3—Cl4	177.3 (3)
N6—Pt1—Cl1	97.6 (6)	Cl5—Pt3—Cl4	89.0 (3)
N3—Pt1—Cl1	97.8 (6)	Cl3—Pt3—Cl4	88.7 (3)
N2—Pt2—N5	80.5 (9)	S2—Pt4—Cl8	91.7 (3)
N2—Pt2—N4	82.1 (9)	S2—Pt4—Cl7	176.6 (4)
N5—Pt2—N4	162.5 (9)	Cl8—Pt4—Cl7	87.0 (3)
N2—Pt2—Cl2	179.0 (6)	S2—Pt4—Cl6	90.9 (3)
N5—Pt2—Cl2	99.1 (7)	Cl8—Pt4—Cl6	176.5 (3)
N4—Pt2—Cl2	98.4 (7)	Cl7—Pt4—Cl6	90.6 (3)

Symmetry codes: (i) $-1-x, 1-y, -z$; (ii) $-x, 1-y, 1-z$; (iii) $-x, 1-y, -z$.

All H atoms were located at their idealized positions as riding atoms (C—H = 0.96 Å for the methyl H atoms of DMSO and C—H = 0.93 Å for the aromatic H atoms of tpp). In the final difference Fourier synthesis, 33 residual peaks in the range 1.0–1.55 e Å^{-3} were observed within *ca* 1.3 Å of the Pt atoms. The deepest hole is 1.36 Å from H27*C*. Initially, data were collected to θ_{max} of 27.5°, but upon inspection, the data above θ_{max} of 23.3° were essentially unobserved. The data above 23.3° were discarded for the refinement of the structure. This resulted in 57% of the unique data having having $I > 2\sigma(I)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL*97, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* and *ORTEP*II (Johnson, 1976).

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