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Key indicators

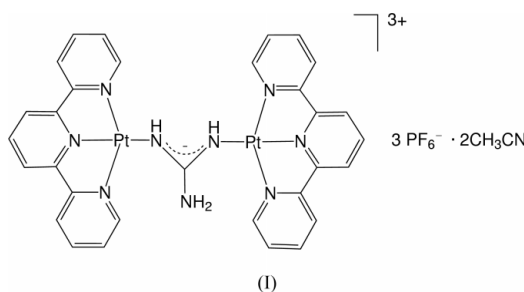
Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.020$ Å
 R factor = 0.058
 wR factor = 0.174
Data-to-parameter ratio = 13.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>. μ -Guanidinido-bis[(terpyridine)platinum(II)]
tris(hexafluorophosphate) acetonitrile solvate

The title cationic complex μ -guanidinido-bis[(2,2':6',2''-terpyridine)platinum(II)], $[\text{Pt}_2(\text{C}_{15}\text{H}_{11}\text{N}_3)_2(\text{CH}_4\text{N}_3)]^{3+}$, has a twofold axis and shows a stacked dinuclear structure with a short $\text{Pt}\cdots\text{Pt}$ distance of $3.0749(6)$ Å. The complexes are further stacked to form a columnar structure in the crystal of the title compound.

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Comment

The complex cation, $[\text{Pt}_2(\text{gua})(\text{tpy})_2]^{3+}$ (tpy is 2,2':6',2''-terpyridine and gua is guanidinide), has a stacked dinuclear structure of the Pt-tpy moiety bridged by a guanidine anion (Fig. 1), (I).



There exists a crystallographic twofold axis through the C16–N5 bond of the guanidinide ligand. The Pt-tpy moiety is almost planar and the deviations of the atoms are within 0.13 Å of the least-squares plane. The two Pt-tpy planes in the dinuclear complex are not parallel, but slightly tilted, with a dihedral angle of $16.4(1)^\circ$, clearly because of the repulsion between the π systems of tpy. The $\text{Pt}\cdots\text{Pt}$ distance is $3.0749(6)$ Å, which is short for divalent platinum, enabling the metal atoms to interact with each other electronically. In fact, the complex exhibits a very intense luminescence at around 630 nm, originating from the $^3\text{MMLCT}$ (metal-metal-to-ligand charge transfer) state, both in solution and in the solid state, even at room temperature. The structure is essentially the same as that of the corresponding perchlorate salt (Yip *et al.*, 1992), although the latter has a lower symmetry than that of the PF_6^- salt. As shown in Fig. 2, the dinuclear complexes are stacked to form a columnar structure along the c axis. The adjacent dinuclear complexes in the column are related by an inversion center, and thus the adjacent Pt-tpy planes are completely parallel to each other, with an interplanar spacing of $3.48(1)$ Å. The Pt atoms in adjacent complexes in the column are separated by a distance of $4.725(1)$ Å. The acetonitrile solvate molecule is linked to the guanidinide ligand by a hydrogen bond.

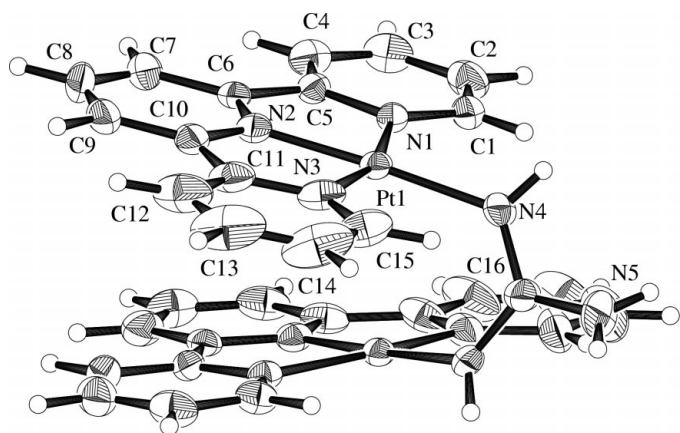


Figure 1

A perspective view of the title cation, showing the atom-numbering scheme, with displacement ellipsoids plotted at the 30% probability level.

Experimental

[PtCl(tpy)]Cl was prepared according to the literature method (Howe-Grant & Lippard, 1980). The complex cation [Pt₂(gua)(tpy)₂]³⁺ was synthesized in a similar way to that reported by Yip *et al.* (1992). A mixture of [PtCl(tpy)]Cl·2H₂O (54 mg, 0.1 mmol) and guanidine carbonate (9 mg, 0.05 mmol) in water was refluxed for 24 h. An excess of NH₄PF₆ was added to the red solution. The resulting red precipitate was recrystallized from acetonitrile/ethanol to give red crystals of (I).

Crystal data

[Pt ₂ (C ₁₅ H ₁₁ N ₃) ₂ (CH ₄ N ₃)](PF ₆) ₃ ·2C ₂ H ₃ N	$D_x = 2.087 \text{ Mg m}^{-3}$
$M_r = 1431.78$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 24 reflections
$a = 17.000 (5) \text{ \AA}$	$\theta = 14.9\text{--}15.0^\circ$
$b = 20.351 (4) \text{ \AA}$	$\mu = 6.33 \text{ mm}^{-1}$
$c = 13.915 (4) \text{ \AA}$	$T = 296.2 \text{ K}$
$\beta = 108.87 (2)^\circ$	Plate, red
$V = 4555 (1) \text{ \AA}^3$	$0.60 \times 0.50 \times 0.08 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-7R diffractometer	$R_{\text{int}} = 0.038$
ω - 2θ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$h = -2 \rightarrow 22$
$T_{\text{min}} = 0.418$, $T_{\text{max}} = 0.999$	$k = 0 \rightarrow 26$
6172 measured reflections	$l = -18 \rightarrow 17$
5243 independent reflections	3 standard reflections
3897 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: 5.6%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.136P)^2]$
$wR(F^2) = 0.174$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.002$
3897 reflections	$\Delta\rho_{\text{max}} = 2.69 \text{ e \AA}^{-3}$
299 parameters	$\Delta\rho_{\text{min}} = -3.42 \text{ e \AA}^{-3}$

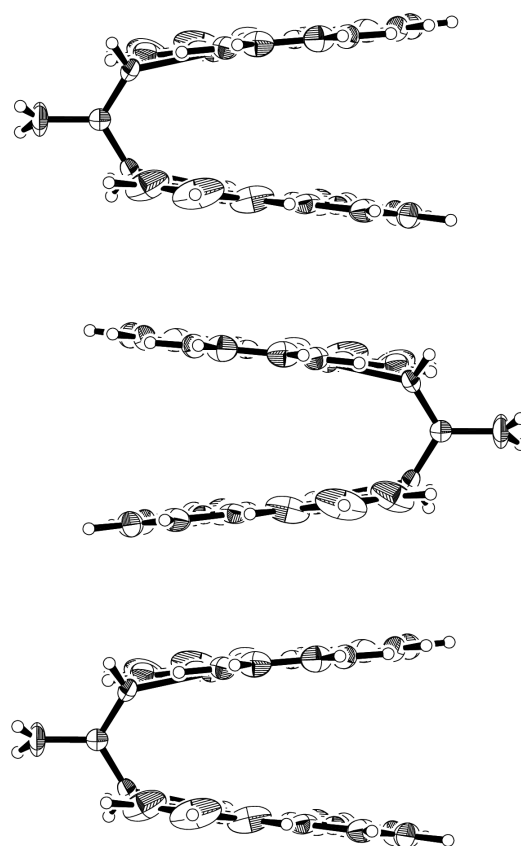


Figure 2

The stacking arrangement of the [Pt₂(gua)(tpy)₂]³⁺ complex cations.

Table 1

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

Pt1—N1	2.024 (7)	Pt1—N4	1.987 (7)
Pt1—N2	1.922 (7)	N4—C16	1.34 (1)
Pt1—N3	2.018 (9)	N5—C16	1.35 (2)
N1—Pt1—N2	82.0 (3)	N2—Pt1—N4	177.1 (4)
N1—Pt1—N3	162.1 (3)	N3—Pt1—N4	98.4 (4)
N1—Pt1—N4	99.4 (3)	N4—C16—N4 ⁱ	119 (1)
N2—Pt1—N3	80.3 (3)	N4—C16—N5	120.5 (6)
Pt1...Pt1 ⁱ	3.0749 (6)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N4—H13...F1	0.88	2.41	3.14 (1)	140
N5—H14...N6 ⁱⁱ	0.87	3.00	3.16 (2)	93
N5—H14...F8 ⁱⁱⁱ	0.87	2.65	3.21 (1)	123

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} + y, z$.

The data collection was successfully performed by using a crystal in a sealed capillary. Atoms for the acetonitrile solvent molecule were refined isotropically, because their large displacement parameters suggested disorder, but the anisotropic ellipsoids were featureless,

showing no particular characteristics that might suggest the direction of the disorder or the existence of disordered sites.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1995); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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