Monoclinic
$P2_1/n$
$a = 9.510\,(2)$ Å
$b = 13.750\,(3)$ Å
$c = 13.410\,(2)$ Å
$\beta = 107.58\,(1)^\circ$
$V = 1671.7\,(5)$ Å^3
$Z = 4$
$D_x = 1.907$ Mg m^{-3}
D_m not measured

Cell parameters from 48 reflections
$\theta = 13.07\text{–}20.52^\circ$
$\mu = 5.692$ mm^{-1}
$T = 295$ K
Parallelepiped
0.39 × 0.34 × 0.21 mm
Blue–green

Data collection

Siemens *R3m/V* diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1991)
$T_{\min} = 0.10$, $T_{\max} = 0.31$
2463 measured reflections
2188 independent reflections

1340 reflections with $F > 6\sigma(F)$
$R_{\rm int} = 0.0581$
$\theta_{\max} = 22.5^\circ$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -14 \rightarrow 13$
3 standard reflections every 97 reflections intensity decay: 13.0%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.040$
$S = 1.16$
1340 reflections
173 parameters
H atoms placed in calculated positions; $U_{\rm H} = 0.15\,(2)$ Å^2

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}
Extinction correction: none
Scattering factors from Cromer & Waber (1974)

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

Se1—Co1	2.458 (2)	Co1—Cl2	2.259 (3)
Se2—Co1	2.472 (1)	Se1—C1	1.871 (8)
Co1—Cl1	2.277 (3)	Se2—C6	1.875 (10)
Co1—Se1—C1	100.4 (3)	Se2—Co1—Cl1	112.3 (1)
Co1—Se2—C6	99.3 (2)	Se1—Co1—Cl2	120.0 (1)
Se1—Co1—Se2	101.1 (1)	Se2—Co1—Cl2	107.5 (1)
Se1—Co1—Cl1	106.3 (1)	Cl1—Co1—Cl2	109.4 (1)

Data collection was stopped at $2\theta = 45^\circ$ due to the low percentage of observed data for high-order reflections, and due to the fact that the crystal had decayed significantly over the course of the 45° shell. A linear decay correction was applied to intensity data. The structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically, and H atoms were generated with ideal geometries (C—H = 0.96 Å) and refined with a group displacement parameter as riding groups.

Data collection: *P3 Diffractometer Program* (Siemens, 1976). Cell refinement: *P3 Diffractometer Program*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1302). Services for accessing these data are described at the back of the journal.

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π-Stacking of [Pt(2,2′-bipyridine)(ethylenediamine)]$^{2+}$ as its Hexafluorophosphate Salt

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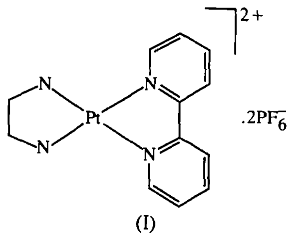
Abstract

The crystal structure of (2,2′-bipyridine-*N*,*N*′)(ethylenediamine-*N*,*N*′)platinum(II) bis(hexafluorophosphate), $[Pt(C_2H_8N_2)(C_{10}H_8N_2)](PF_6)_2$, $[Pt(bpy)(en)](PF_6)_2$, contains π-bpy-stacked columns of platinum complex cations. The bpy ligands are stacked keeping van der Waals contacts although the crystal exhibits essentially the same $^3\pi\text{–}\pi^*$ emission spectrum as that in dilute solution.

Comment

Square-planar platinum(II) complexes containing α-diimine ligands can form various stacking structures in the solid state which are controlled by metal–metal and/or ligand $\pi\text{–}\pi$ interactions (Kato *et al.*, 1996). Depending on the crystal structures and thus the intermolecular interactions, crystals of the platinum complexes show characteristic emission spectra which are considerably different from those for the monomeric forms in dilute solution. The perchlorate salt of $[Pt(bpy)(en)]^{2+}$, however, exhibits almost the same $^3\pi\text{–}\pi^*$(bpy) emission spectrum as that in dilute solution. Thus, it was suggested that the complex had a monomeric environment in the crystal (Miskowski & Houlding, 1989).

We report here a π-stacking structure for the crystal of $[Pt(bpy)(en)](PF_6)_2$, (I), which also shows essentially the same emission spectrum as that in dilute solution.



(I)

The complex cation (Fig. 1) has a crystallographic twofold axis passing through the Pt atom, the midpoint of the C5—C5′ bond of bpy and the midpoint of the C6—C6′ bond of en. The Pt atom is surrounded by a square-planar array of four N atoms and the bpy ligand is also located on almost the same plane. The deviations of all these atoms from their mean plane are within 0.03 Å. The monomer complexes are stacked on the bpy ligands in the crystal (Fig. 2). The coordination plane of each complex is not oriented exactly perpendicular to the stacking direction but inclined at *ca* 15° to the horizontal plane. The interplanar spacing is 3.528 (9) Å. Pt atoms are separated by more than 7 Å in the crystal. The PF_6^- counter anions are located near the ethylenediamine ligand of $[Pt(bpy)(en)]^{2+}$ suggesting weak hydrogen bonds between them [N2···F4(x, $-y$, $\frac{1}{2}+z$) 3.01 (1) and N2···F1(x, $-y$ $z+\frac{1}{2}$) 2.98 (1) Å]. The ethylenediamine chelate adopts a typical *gauche* conformation, which could prevent the Pt···Pt interactions sterically. As a result, the complex forms the π-stacked column. Analogous π-stacking structures are known for $[PtCl_2(bpy)]$ (Herber, Croft, Coyer, Bilash & Sahiner, 1994) and $[PtCl_2(i\text{-}biq)]$ (i-biq is 3,3′-biisoquinoline; Kato *et al.*, 1996). In the case of $[PtCl_2(i\text{-}biq)]$ with $^3\pi$–π^* emission, a remarkably red-shifted spectrum was observed compared with that of the monomeric complex in dilute solution and the phenomenon was ascribed to the electronic π–π interactions in the solid state. The effect of the π–π interactions on an emission state is not obvious for $[PtCl_2(bpy)]$ because the complex has a ligand-field (dd) emission (Miskowski & Houlding, 1989). The π-stacking structure of $[Pt(bpy)(en)](PF_6)_2$ is noteworthy in view of the fact that the $^3\pi$–π^* emission spectrum shows no shift in the solid state.

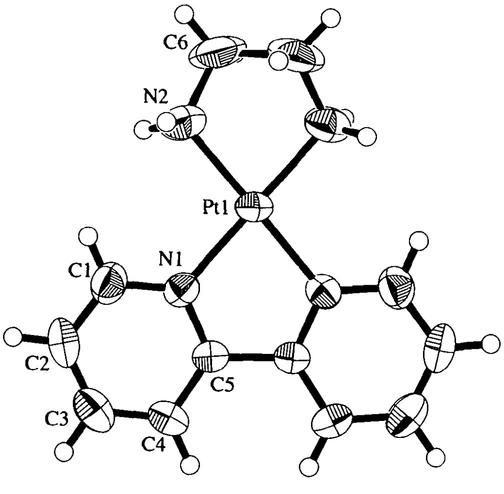


Fig. 1. The molecular structure of the $[Pt(bpy)(en)]^{2+}$ cation showing 50% probability displacement ellipsoids.

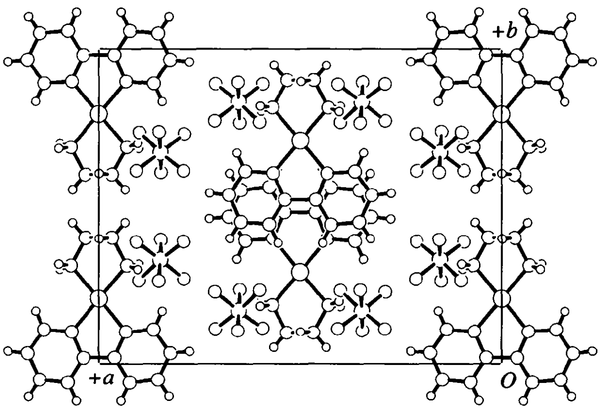


Fig. 2. Packing diagram viewed down the *c* axis.

Experimental

$[Pt(bpy)(en)]^{2+}$ was synthesized by heating an aqueous solution (50 ml) of $[PtCl_2(bpy)]$ (90 mg, 0.2 mmol) and an excess of ethylenediamine (*ca* 2 mmol) at 323 K for 18 h. After filtration, an excess of NH_4PF_6 (80 mg, 0.5 mmol) in water (5 ml) was added to the filtrate. Prismatic crystals were obtained from the concentrated solution.

Crystal data

$[Pt(C_2H_8N_2)(C_{10}H_8N_2)]$-$(PF_6)_2$
$M_r = 701.30$
Monoclinic
$C2/c$
$a = 18.848\ (4)$ Å
$b = 14.692\ (3)$ Å
$c = 7.333\ (2)$ Å
$\beta = 92.58\ (3)°$
$V = 2028.7\ (8)$ Å^3
$Z = 4$
$D_x = 2.296$ Mg m^{-3}
$D_m = 2.28$ Mg m^{-3}
D_m measured by flotation in dibromomethane/benzene

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.1$–$12.3°$
$\mu = 7.162$ mm^{-1}
$T = 293.2$ K
Prism
0.23 × 0.11 × 0.05 mm
Pale yellow

Data collection

Rigaku AFC-7*R* diffractometer

1824 reflections with $I > 3\sigma(I)$

ω–2θ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  $T_{min} = 0.592$, $T_{max} = 0.699$
3280 measured reflections
3065 independent reflections

$R_{int} = 0.0364$
$\theta_{max} = 30°$
$h = -26 \rightarrow 26$
$k = 0 \rightarrow 20$
$l = -10 \rightarrow 0$
3 standard reflections
  every 150 reflections
  intensity decay: 1.9%

Refinement

Refinement on F
$R = 0.0406$
$wR = 0.0511$
$S = 1.044$
1824 reflections
142 parameters
H atoms fixed with $U(\text{H}) = 1.2U_{eq}(\text{C})$

$w = 1/[\sigma^2(F_o) + 0.00087|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.083$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -1.15$ e Å^{-3} (close to Pt1)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pt1—N1	2.020 (7)	Pt1—N2	2.043 (8)
N1—Pt1—N1^{i}	80.9 (4)	N2—Pt1—N2^{i}	82.1 (5)
N1—Pt1—N2	98.5 (3)		

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

Table 2. *Contact distances (Å)*

N1···C3^{i}	3.61 (1)	C2···C3^{ii}	3.60 (1)
C1···C3^{i}	3.65 (1)	C4···C5^{ii}	3.55 (1)
C1···C4^{ii}	3.68 (1)	C5···C5^{iii}	3.61 (2)

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

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1995). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MITHRIL*90 (Gilmore, 1990). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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A Water-Bridged Dinuclear Complex of Cobalt(II), Pyridine and Stearic Acid

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Abstract

In the crystal structure of μ-aqua-1:2κ^2O-tetrapyridine-1κ^2N,2κ^2N-bis(μ-stearato)-1κ^2O:2κ^2O'-bis(stearato)-1κO,2κO-dicobalt(II), $[Co_2(C_{18}H_{35}O_2)_4(C_5H_5N)_4(H_2O)]$, hydrogen bonding [with an O···O distance of 2.564 (5) Å] between the H atoms of the bridging water and the non-metal-bonding O atoms of the monodentate stearic acid molecules, stabilizes the dimeric core complex and consequently limits chain packing and conformation options. The structure is a member of a rare class of compounds, the well crystallized metallic salts of long-chain fatty acids. The structure also bears a remarkable similarity to built-up Langmuir–Blodgett films of metal carboxylates.

Comment

During the course of a literature search investigation of the recrystallization methods for transition metal carboxylates or metallic soaps, early reports were found on the synthesis of long-chain metal soap complexes with pyridine (Koenig, 1914; Lawrence, 1939). Koenig synthesized an addition product of dry cobalt stearate and pyridine by cooling a heated saturated solution of the metal soap in pyridine. He reported that the precipitate consisted of rose-coloured crystalline plates containing stoichiometric amounts of pyridine, which effloresced slowly to a pink amorphous powder. The title compound, (I), was obtained during a repeat synthesis and its structure is reported here. The complex exhibits a dinuclear centre with the two hexacoordinated Co atoms bridged by an O atom from a water molecule and