North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994*a*). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994*b*). *SHELXTL.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). C**55**, 1809–1812

Anion-controlled π-stacks of (ethylenediamine-*N*,*N*′)(1,10-phenanthroline-*N*,*N*′)platinum(II)

Masako Kato[a] and Junko Takahashi[b]

[a]*Department of Material Science, Graduate School of Human Culture, Nara Women's University, Nara 630-8506, Japan, and 'State and Transformation' PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi 332-0012, Japan, and* [b]*Department of Chemistry, Graduate School of Human Culture, Nara Women's University, Nara 630-8506, Japan. E-mail: kato@cc.nara-wu.ac.jp*

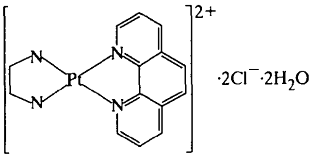
(*Received 4 May 1999; accepted 29 June 1999*)

Abstract

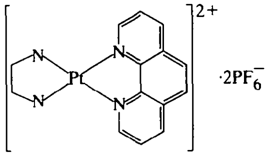
Two salts of (ethylenediamine-*N*,*N*′)(1,10-phenanthroline-*N*,*N*′)platinum(II), namely the dichloride dihydrate, $[Pt(C_2H_8N_2)(C_{12}H_8N_2)]Cl_2\cdot 2H_2O$, (I), and the bis(hexafluorophosphate), $[Pt(C_2H_8N_2)(C_{12}H_8N_2)](PF_6)_2$, (II), have π-phenanthroline-stacked structures. The interplanar spacings of the π–π stacks, however, are quite different in the two salts, being 3.38 (1) and 3.40 (1) Å for (I), and 3.60 (5) and 3.56 (5) Å for (II). These are controlled by the anions located on the aliphatic sites.

Comment

Square-planar platinum(II) complexes have a tendency to stack in the crystalline state. However, when a non-planar ligand such as ethylenediamine (en) is included in the complex, the column structure becomes disadvantageous. In the case of $[Pt(bpy)(en)](PF_6)_2$ (bpy is 2,2′-bipyridine), we have previously reported a π-bpy-stacked structure (Kato *et al.*, 1997). In the present study, we have determined the crystal structures of $[Pt(en)(phen)]Cl_2\cdot 2H_2O$, (I), and $[Pt(en)(phen)](PF_6)_2$ (phen is 1,10-phenanthroline), (II), and found that the interplanar spacings of the π–π stacks are quite different for the two salts.



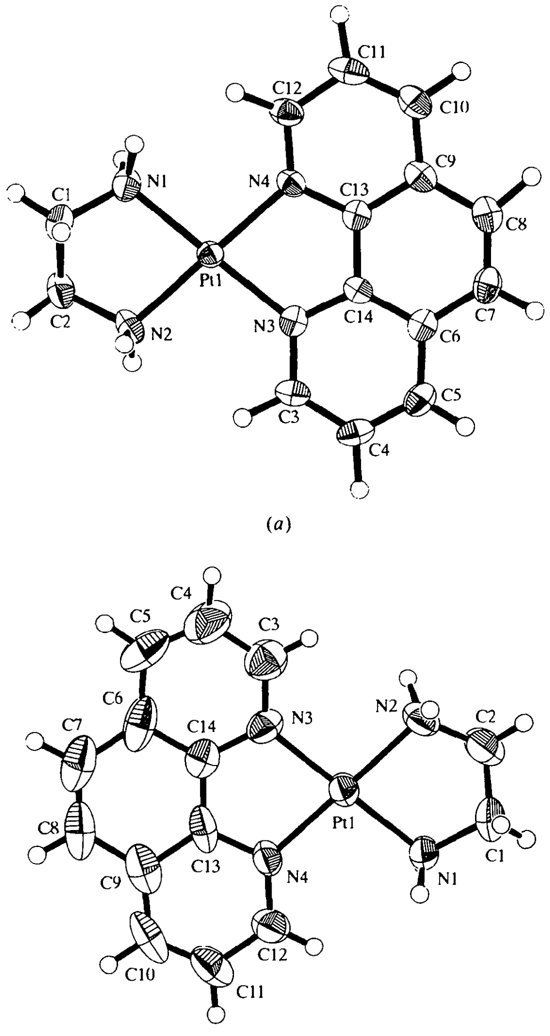
(I)



(II)

The molecular structures of the $[Pt(en)(phen)]^{2+}$ cations in (I) and (II) are very similar (Fig. 1). Fig. 2 shows a packing diagram of (I) viewed down the *a* axis.

The phen ligands in the π-stack, which are almost planar, have a good overlap and are completely parallel because they are related through inversion centres. The interplanar spacings are 3.38 (1) and 3.40 (1) Å. On the



(*a*)

(*b*)

Fig. 1. The molecular structure of the $[Pt(en)(phen)]^{2+}$ cation in (*a*) (I) and (*b*) (II), showing the atom-numbering scheme and displacement ellipsoids plotted at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

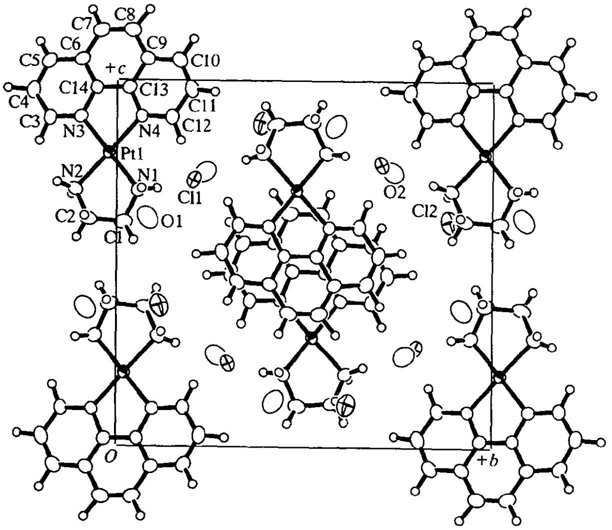


Fig. 2. Packing diagram of (I) viewed down the *a* axis.

other hand, the π-phen stack of (II) is considerably different from that of (I), as shown in Fig. 3. The phen ligands are not parallel but are a little inclined, as the complexes in the π-phen stack are related through glide planes along **a**. The dihedral angle between neighbouring phen ligands is 2.16° and the interplanar spacings are 3.60 (5) and 3.56 (5) Å. These spacings are clearly larger than those found for (I), although the values for (II) have large s.u.'s because of the inclined stack. The difference is due to the anions, which are located near the en ligands, making close hydrogen bonds in both salts. Thus, the interplanar spacings of the π-stacks seem to be dependent on the size of the anions. Fig. 4 shows the stacking structure of (II) viewed along the *c* axis; it resembles a ladder. On both sides of the π-phen stack, the PF_6^- anions connect the en ligands on every other step. In the case of (I), however, the hydrogen-bonding chains consisting of en, Cl^- and H_2O molecules are flexible and thus could not affect the π-phen stack.

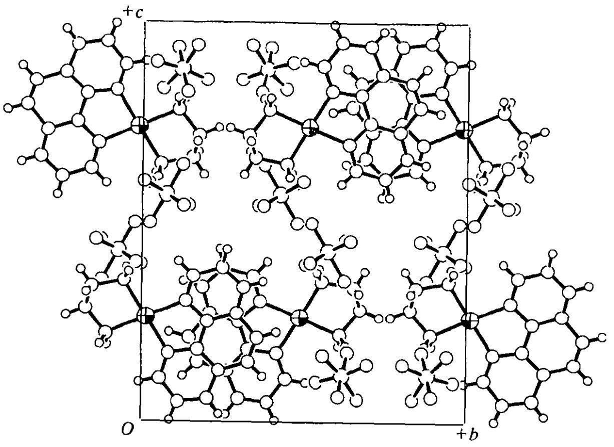


Fig. 3. Packing diagram of (II) viewed down the *a* axis.

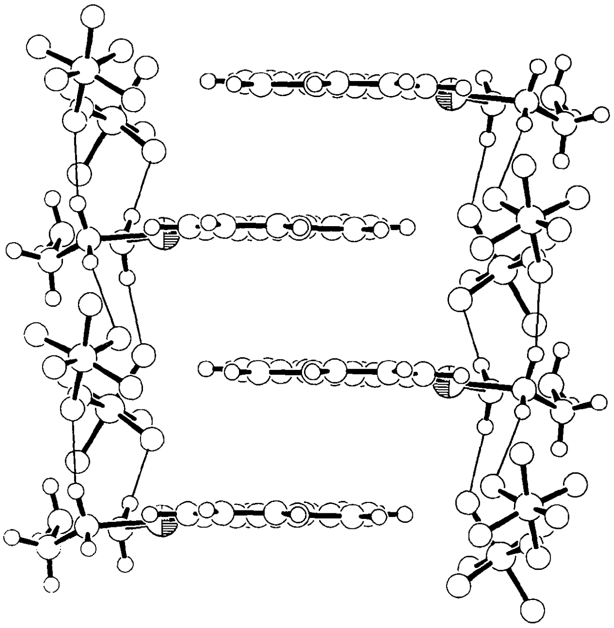


Fig. 4. Diagram showing the ladder-type stacking of (II) along **c**.

The π–π stacking structures could be main routes for energy and electron transfer. The present results indicate the importance of the anions for controlling the π–π interactions.

Experimental

$[PtCl_2(phen)]$ was prepared by the reaction of $K_2[PtCl_4]$ (1.02 g, 2.5 mmol) with 1,10-phenanthroline (phen; 0.49 g, 2.5 mmol) in acidic hot water (50 ml). The resulting yellow precipitate was recrystallized from dimethylformamide. An aqueous suspension of $[PtCl_2(phen)]$ (0.54 g, 1.2 mmol in 50 ml) containing a few drops of ethylenediamine (en) was refluxed for 3 h. The resulting clear reaction solution was evaporated and recrystallization of the residue from methanol gave pale-yellow crystals of (I). A white precipitate of (II) was obtained from the reaction solution by adding an excess amount of NH_4PF_6 solution. Recrystallization from water gave pale-yellow crystals of (II). Spectroscopic analysis for (I): ^1H NMR (DMSO-d_6, δ, p.p.m.): 2.75 (*s*, 4H, CH_2), 7.15 (*s*, 4H, NH_2), 8.28 (*dd*, 2H, phen), 8.36 (*s*, 2H, phen), 9.16 (*d*, 2H, phen), 9.25 (*d*, 2H, phen). Spectroscopic analysis for (II): ^1H NMR (DMSO-d_6, δ, p.p.m.): 2.76 (*s*, 4H, CH_2), 6.94 (*s*, 4H, NH_2), 8.28 (*dd*, 2H, phen), 8.38 (*s*, 2H, phen), 9.15 (*d*, 2H, phen), 9.17 (*d*, 2H, phen); IR (KBr, cm^{-1}): 833, 562 (νPF_6).

Compound (I)

Crystal data

$[Pt(C_2H_8N_2)(C_{12}H_8N_2)]Cl_2 \cdot 2H_2O$
$M_r = 542.33$
Monoclinic
$P2_1/n$
$a = 7.357\,(2)$ Å
$b = 15.528\,(2)$ Å
$c = 15.137\,(2)$ Å
$\beta = 94.68\,(2)°$
$V = 1723.6\,(4)$ Å^3
$Z = 4$
$D_x = 2.090$ Mg m^{-3}
$D_m = 2.095$ Mg m^{-3}
D_m measured by flotation in dibromomethane/benzene

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 14.8\text{–}15.0°$
$\mu = 8.432$ mm^{-1}
$T = 293.2$ K
Needle
$0.80 \times 0.05 \times 0.04$ mm
Pale yellow

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.604$, $T_{\max} = 0.726$
4431 measured reflections
4123 independent reflections
3233 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.013$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 0$
$k = 0 \rightarrow 20$
$l = -19 \rightarrow 19$
3 standard reflections every 150 reflections intensity decay: 0.09%

Refinement

Refinement on F^2
$R(F) = 0.026$
$wR(F^2) = 0.080$
$S = 0.929$
3967 reflections
209 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 0.00001(F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.065$

$\Delta\rho_{\max} = 1.17$ e Å^{-3}
$\Delta\rho_{\min} = -1.42$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.0031 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pt1—N1	2.044 (4)	Pt1—N3	2.018 (4)
Pt1—N2	2.037 (4)	Pt1—N4	2.030 (4)
N1—Pt1—N2	82.9 (2)	N2—Pt1—N3	97.8 (2)
N1—Pt1—N3	176.9 (1)	N2—Pt1—N4	178.7 (1)
N1—Pt1—N4	98.2 (2)	N3—Pt1—N4	81.1 (1)

Compound (II)

Crystal data

$[Pt(C_2H_8N_2)(C_{12}H_8N_2)](PF_6)_2$
$M_r = 725.33$
Monoclinic
$P2_1/a$
$a = 7.483\,(4)$ Å
$b = 15.061\,(4)$ Å
$c = 18.836\,(5)$ Å
$\beta = 99.70\,(4)°$
$V = 2092\,(1)$ Å^3
$Z = 4$
$D_x = 2.302$ Mg m^{-3}
$D_m = 2.290$ Mg m^{-3}
D_m measured by flotation in dibromomethane/CCl_4

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 14.9\text{–}15.0°$
$\mu = 6.948$ mm^{-1}
$T = 295.2$ K
Needle
$0.80 \times 0.05 \times 0.04$ mm
Pale yellow

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.685$, $T_{\max} = 0.767$
6852 measured reflections
6342 independent reflections
3512 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.050$
$\theta_{\max} = 30.02°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 21$
$l = -26 \rightarrow 26$
3 standard reflections every 150 reflections intensity decay: −3.61%

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.127$
$S = 1.306$
4061 reflections
299 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} = 0.042$

$\Delta\rho_{\max} = 2.67$ e Å^{-3}
$\Delta\rho_{\min} = -2.80$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.0005 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pt1—N1	2.039 (7)	Pt1—N3	2.005 (8)
Pt1—N2	2.050 (8)	Pt1—N4	2.017 (7)
N1—Pt1—N2	82.2 (3)	N2—Pt1—N3	98.0 (3)
N1—Pt1—N3	178.0 (3)	N2—Pt1—N4	179.7 (3)
N1—Pt1—N4	98.2 (3)	N3—Pt1—N4	81.7 (3)

H atoms were fixed with $U(\mathrm{H}) = 1.2U_{\rm eq}(\mathrm{C})$. In the final difference Fourier map, small peaks were found close to Pt1 in both (I) and (II).

For both compounds, data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1995); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1998); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 11640566 and 11136234) from the Ministry of Education, Science, Sports and Culture, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1091). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kato, M., Kosuge, C., Yano, S. & Kimura, M. (1997). *Acta Cryst.* C**53**, 838–840.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1418.
Molecular Structure Corporation (1998). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.9. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Rigaku (1995). *Rigaku/AFC Diffractometer Control Software*. Version 5.32b. Rigaku Corporation, Tokyo, Japan.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1999). C**55**, 1812–1813

endo-{6,6′-Diethoxy-2,2′-[(*R*)-propane-1,2-diylbis(nitrilomethylidene)]diphenolato-*O*,*N*,*N*′,*O*′}oxovanadium(IV)

Gakuse Hoshina, Masanobu Tsuchimoto and Shigeru Ohba

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan. E-mail: ohba@chem.keio.ac.jp

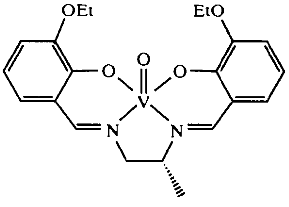
(*Received 6 April 1999; accepted 29 June 1999*)

Abstract

In the title mononuclear oxovanadium(IV) complex, [VO($C_{21}H_{24}N_2O_4$)], the methyl group of the central diamine moiety in the Schiff base ligand is directed opposite to the oxo ligand. This *endo* isomer elutes more slowly than the *exo* isomer when subjected to high-performance liquid reversed-phase chromatography using CH_3CN–H_2O (1:1 *v*/*v*) as the eluent. Crystals of both the *endo* and *exo* isomers decompose at 473 K, with no solid-state isomerization from *endo* to *exo* or *vice versa*.

Comment

The solid-state thermal isomerization of Schiff base–oxovanadium(IV) complexes has been investigated previously by Kojima *et al.* (1994) and Hoshina, Ohba *et al.* (1999). However, the mechanism of isomerization is still unclear at present. Thus, the title complex, (I), was prepared and studied by X-ray crystallography and the results are presented here.



(I)

There are two possible geometrical isomers for (I), *exo* and *endo*, which are defined as having the substituted group (the methyl on C18) of the central diamine moiety in the Schiff base ligand directed outside or inside the $O_{oxo}N_2$ plane (O2, N7 and N8) of the VN_2O_3 square pyramid, respectively. In the present study, the slower eluate by high-performance liquid reversed-phase chromatography was determined to be the *endo* isomer. The methyl on C18 is in an axial position, almost antiparallel to the V1═O2 bond axis. This is in contrast to the equatorial methyl orientation of the sal-(*R*)(*S*)-pn ligand (sal = salicylidene; pn = 1,2-propylenediamine) in crystals of *endo*-(chlorotriphenylstannyloxy)[*N*,*N*′-1,2-propylenebis(salicylideneamino)]vanadium(IV) (Cashin *et al.*, 1989).

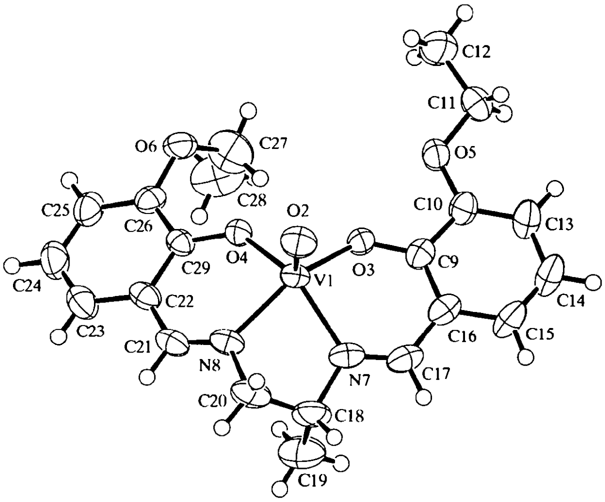


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I) showing the atom-numbering scheme and 50% probability ellipsoids. H atoms are drawn as spheres of arbitrary radii.

Although Schiff base–oxovanadium(IV) complexes with two ethoxy substituents at the 3-positions have a tendency to connect with a water molecule for crystallization *via* two bifurcated hydrogen bonds (Zamian *et al.*, 1995; Kasahara *et al.*, 1996; Hoshina *et al.*, 1998; Hoshina, Tsuchimoto & Ohba, 1999), the title crystal is an exception as it is unhydrated. The O6 ethoxy group is directed perpendicular to the salicylidene moiety, which may be due to the packing efficiency.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999