Data collection

Siemens *P*4 diffractometer	$R_{int} = 0.027$
$2\theta/\omega$ scans	$\theta_{max} = 25.04°$
Absorption correction:	$h = -1 \rightarrow 13$
ψ scan (North *et al.*,	$k = -1 \rightarrow 12$
1968)	$l = -15 \rightarrow 14$
$T_{min} = 0.562, T_{max} = 0.595$	3 standard reflections
3254 measured reflections	every 197 reflections
2505 independent reflections	intensity decay: 13.6%
1821 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{max} = 0.262$ e Å^{-3}
$wR(F^2) = 0.091$	$\Delta\rho_{min} = -0.278$ e Å^{-3}
$S = 1.024$	Extinction correction: none
2504 reflections	Scattering factors from
225 parameters	*International Tables for*
All H-atom parameters	*Crystallography* (Vol. C)
refined	

$$w = 1/[\sigma^2(F_o^2) + (0.0330P)^2 + 0.2173P]$$
where $P = (F_o^2 + 2F_c^2)/3$

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

Ni1—N3	1.864 (3)	N1—C1	1.336 (5)
Ni1—N4	1.924 (3)	N2—C1	1.331 (4)
Ni1—S1	2.143 (1)	N2—N3	1.385 (4)
Ni1—Cl1	2.173 (1)	N3—C2	1.307 (4)
S1—C1	1.741 (4)		
N3—Ni1—N4	83.86 (13)	N4—Ni1—Cl1	97.26 (10)
N3—Ni1—S1	87.08 (10)	S1—Ni1—Cl1	91.80 (5)
N4—Ni1—S1	170.93 (9)	Cl—S1—Ni1	95.54 (14)
N3—Ni1—Cl1	178.85 (10)	Cl—N1—H1N*B*	121 (3)

All H atoms were found from a difference map and refined isotropically; C—H distances are in the range 0.87 (4)–0.97 (4) Å.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*. Geometric calculations: *PARST* (Nardelli, 1983).

References

Duan, C. Y., Wu, B.-M. & Mak, T. C. W. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3485–3490.
Liberta, A. E. & West, D. X. (1992). *Biometals*, pp. 121–127.
Liu, M. C., Lin, T. S., Penketh, P. & Sratorelli, A. C. (1995). *J. Med. Chem.* **38**, 4234–4241.
Liu, Z. H., Duan, C. Y., Hu, J. & You, Y. Z. (1999). *Inorg. Chem.* **38**, 1719–1724.
Long, N. J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 21–38.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Podhye, S. & Kauffman, G. B. (1985). *Coord. Chem. Rev.* **63**, 127–164.
Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *SHELXTL.* Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tian, Y.-P., Duan, C.-Y., Zhao, C.-Y., You, X.-Z., Mak, T. C. W. & Zhang, Z.-Y. (1997). *Inorg. Chem.* **36**, 1247–1252.
West, D. X., Liberta, A. E., Rajendran, K. G. & Hall, I. H. (1993). *Anticancer Drugs*, **4**, 241–246.

Tris[3,6-bis(2-pyridyl)pyridazine-N^1,N^6]-nickel(II) diperchlorate 0.11-hydrate

Jau-Shuenn Wang, Chou-Fu Sheu and Jung-Si Lee

Department of Chemistry, Tamkang University, Tamsui 25137, Taiwan. E-mail: jslee@mail.tku.edu.tw

Abstract

The structure of the title complex, $[Ni(C_{14}H_{10}N_4)_3]$-$(ClO_4)_2 \cdot 0.11H_2O$, consists of well separated mononuclear tris[3,6-bis(2-pyridyl)pyridazine]nickel(II) cations and perchlorate anions. There are two crystallographically independent cations, in which the Ni atoms are surrounded in a distorted octahedral arrangement by three bulky organic ligands, with four possible N-donor atoms each, acting as bidentate chelates. The Ni—N distances range from 2.045 (4) to 2.094 (3) Å and the bite angles range from 77.6 (1) to 78.4 (1)°. The lattice water molecule is hydrogen bonded to two perchlorate anions.

Comment

Ligands that contain a delocalized π system and which can serve as molecular bridges between metal centres give inorganic chemists access to a wide variety of transition metal complexes with various structures. One such ligand is 3,6-bis(2-pyridyl)pyridazine (dppa), which has been used to synthesize many mono-, bi- and polynuclear complexes, *e.g.* mononuclear $[RuCl_2(CO)_2(dppa)]$ (De Munno *et al.*, 1988), $[Cu(dppa)_2Cl]Cl \cdot 5H_2O$ (Lanfredi *et al.*, 1982) and $[Mn(dppa)_2(NO_3)_2]$ (Andrew *et al.*, 1975), binuclear $[Cu_2Cl_4(H_2O)(dppa)]$ (De Munno & Bruno, 1984) and $[Ni_2(dppa)_2(H_2O)_4](ClO_4)_4$ (Ball & Blake, 1969), and polynuclear $\{[Cu_2(dppa)Cl_2(H_2O)(OH)]-Cl\}_n \cdot 2nH_2O$ (Dapporto *et al.*, 1983). We report here

the crystal structure of tris[3,6-bis(2-pyridyl)pyridazine-N^1,N^6]nickel(II) diperchlorate 0.11-hydrate, (I). To our knowledge, this is the first example of a mononuclear complex that contains three of the rather bulky dppa ligands.

(I)

·2ClO$_4^-$·0.11H$_2$O
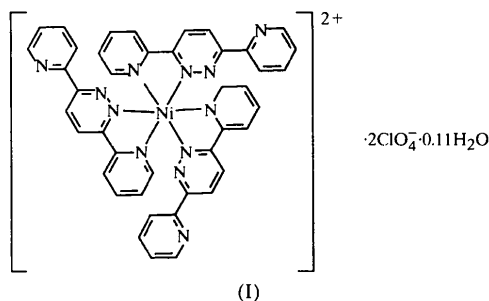
Complex (I) consists of two crystallographically in-dependent [Ni(dppa)$_3$]$^{2+}$ cations (Fig. 1) and four ClO$_4^-$ anions, together with some lattice water molecules. The ions are well separated and no close intermolecular con-tacts were found in the structure. In both cations, the Ni atoms are surrounded in a distorted octahedral ar-rangement by three independent four-N-donor organic ligands acting as bidentate chelates. The Ni—N dis-tances range from 2.045 (4) to 2.094 (3) Å. These dis-tances are similar to those found in the binuclear Ni complex of the similar ligand 2,5-bis(2-pyridyl)pyrazine (bppz), i.e. [Ni$_2$(bppz)(H$_2$O)$_8$](SO$_4$)$_2$·2H$_2$O, where the Ni—N distances are in the range 2.047 (4)–2.086 (4) Å (Neels et al., 1997), but they are slightly shorter than those observed in the polymeric {[Ni$_2$(bppz)(H$_2$O)$_2$-(CH$_3$OH)$_2$]Cl$_2$}$_n$ [2.103 (9)–2.132 (10) Å; Neels et al., 1997]. We notice that the mean Ni—N$_{pyridine}$ distance of 2.083 (9) Å is slightly longer than the mean Ni—N$_{pyridazine}$ distance [2.064 (12) Å] in the present com-pound.

The six bite angles in (I) range from 77.6 (1) to 78.4 (1)°. In each ligand, the two pyridyl N atoms are on opposite sides with respect to the N—N bond of the pyridazine ring, to minimize the conflict between peripheral H atoms. Similar situations have also been found in mononuclear metal–dppa compounds, e.g. [RuCl$_2$(CO)$_2$(dppa)] (De Munno et al., 1988) and [Cu-(dppa)$_2$Cl]Cl·5H$_2$O (Lanfredi et al., 1982). However, in polynuclear complexes such as [Cu$_2$Cl$_4$(H$_2$O)(dppa)] (De Munno & Bruno, 1984) and {[Cu$_2$(dppa)Cl$_2$(H$_2$O)-(OH)]Cl}$_n$·2nH$_2$O (Dapporto et al., 1983), the two pyridyl N atoms of each dppa ligand are on the same side with respect to the N—N bond of the pyridazine ring.

None of the six dppa ligands in the two indepen-dent [Ni(dppa)$_3$]$^{2+}$ cations are planar, although all six-membered rings in the ligands are flat. In each of the three dppa ligands of the Ni1 cation, the dihe-dral angle between the coordinated pyridine ring and

the central pyridazine ring is larger than that between the non-coordinated pyridine ring and the central pyri-dazine ring [10.8 (1) > 4.4 (2)°, 8.0 (3) > 7.0 (4)° and 7.9 (3) > 4.5 (3)°]. On the contrary, in each ligand of the Ni2 cation, the former dihedral angle is smaller than the latter [4.8 (3) < 18.1 (3)°, 7.3 (1) < 15.0 (2)° and 13.9 (2) < 22.4 (2)°]. These differences are presumably due to a combination of intramolecular steric and pack-ing effects.

The perchlorate anions have the expected tetrahedral geometry, with an average Cl—O bond distance of
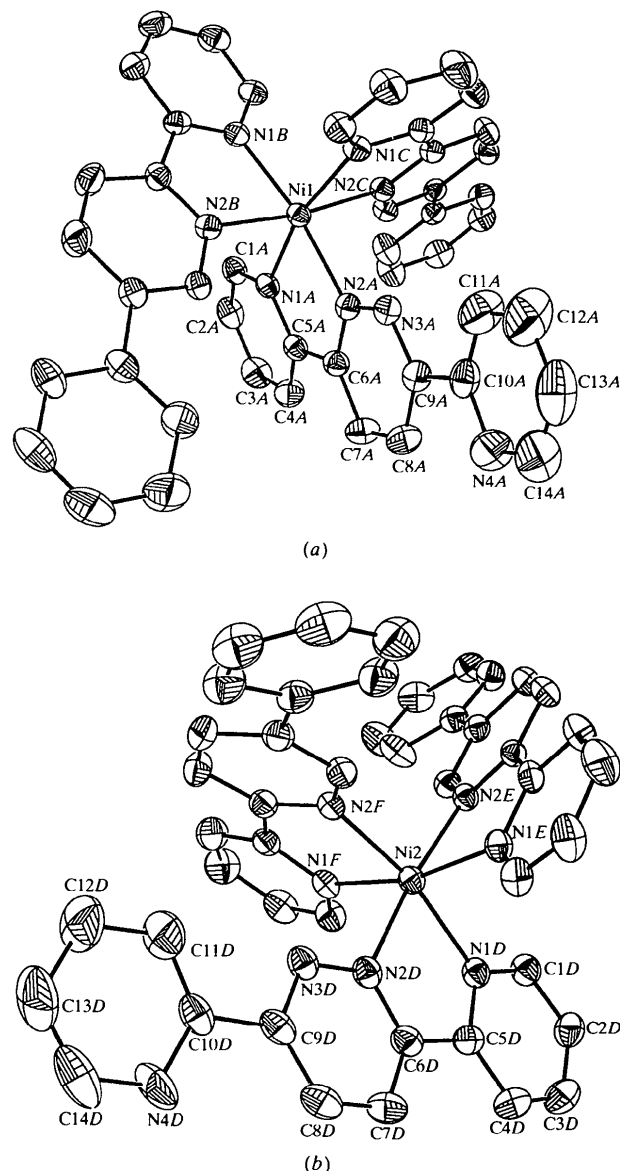

Fig. 1. Perspective views, (a) and (b), of the two crystallographically independent cations of (I) with the atomic numbering schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

1.388 (8) Å and an average O—Cl—O bond angle of 109.4 (7)°. The shorter-than-normal Cl—O bond length and the very large anisotropic displacements associated with some O atoms, as observed in $[Co(CN_5O_2)_2\text{-}(NH_3)_4]ClO_4$ (Morosin et al., 1997), suggest that the ClO_4^- ions may indeed be disordered. Hydrogen bonds involving the lattice water molecule and perchlorate O atoms [O5···O1B 2.87 (3), O5···O1C 2.93 (3) Å and O1B···O5···O1C = 105.8 (8)°] are present.

Experimental

The title compound was synthesized by mixing $Ni(ClO_4)_2$·-$6H_2O$ with dppa in a 1:3 stoichiometric ratio in acetonitrile and methanol (1:2 v/v). The resulting solution was left at room temperature and allowed to evaporate slowly. Dark orange crystals of (I) suitable for X-ray diffraction studies were obtained.

Crystal data

$[Ni(C_{14}H_{10}N_4)_3](ClO_4)_2$·-	Mo $K\alpha$ radiation
$0.11H_2O$	$\lambda = 0.71073$ Å
$M_r = 962.43$	Cell parameters from 25
Triclinic	reflections
$P\bar{1}$	$\theta = 5.94\text{--}12.50°$
$a = 16.249 (2)$ Å	$\mu = 0.657$ mm^{-1}
$b = 16.3338 (12)$ Å	$T = 293 (2)$ K
$c = 17.414 (3)$ Å	Block
$\alpha = 81.362 (10)°$	$0.75 \times 0.65 \times 0.20$ mm
$\beta = 87.180 (12)°$	Orange
$\gamma = 67.335 (9)°$	
$V = 4216.2 (9)$ Å^3	
$Z = 4$	
$D_x = 1.516$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.020$
$2\theta/\omega$ scans	$\theta_{max} = 25°$
Absorption correction:	$h = 0 \rightarrow 18$
empirical via ψ scans	$k = -17 \rightarrow 19$
(North et al., 1968)	$l = -20 \rightarrow 20$
$T_{min} = 0.706$, $T_{max} = 0.877$	3 standard reflections
15 335 measured reflections	every 97 reflections
14 758 independent	intensity decay: 5.35%
reflections	
9987 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.001$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$\Delta\rho_{max} = 0.89$ e Å^{-3}
$wR(F^2) = 0.168$	$\Delta\rho_{min} = -0.54$ e Å^{-3}
$S = 1.046$	Extinction correction: none
14748 reflections	Scattering factors from
1181 parameters	International Tables for
H atoms riding	Crystallography (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0774P)^2$	
$+ 4.0452P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (Å, °)

Ni1—N1A	2.084 (3)	Ni2—N1D	2.083 (4)
Ni1—N1B	2.070 (4)	Ni2—N1E	2.094 (3)
Ni1—N1C	2.092 (3)	Ni2—N1F	2.073 (3)
Ni1—N2A	2.063 (3)	Ni2—N2D	2.077 (4)
Ni1—N2B	2.071 (3)	Ni2—N2E	2.057 (3)
Ni1—N2C	2.071 (3)	Ni2—N2F	2.045 (4)
N1A—Ni1—N1C	166.04 (14)	N1D—Ni2—N1E	92.26 (14)
N1B—Ni1—N1A	97.92 (14)	N1F—Ni2—N1D	99.99 (14)
N1B—Ni1—N1C	92.31 (14)	N1F—Ni2—N1E	166.01 (15)
N1B—Ni1—N2B	78.04 (14)	N1F—Ni2—N2D	94.22 (14)
N1B—Ni1—N2C	95.92 (14)	N2D—Ni2—N1D	77.60 (14)
N2A—Ni1—N1A	78.08 (14)	N2D—Ni2—N1E	95.01 (14)
N2A—Ni1—N1B	171.09 (14)	N2E—Ni2—N1D	99.57 (14)
N2A—Ni1—N1C	93.03 (14)	N2E—Ni2—N1E	78.39 (14)
N2A—Ni1—N2B	94.25 (13)	N2E—Ni2—N1F	92.81 (13)
N2A—Ni1—N2C	92.17 (13)	N2E—Ni2—N2D	172.78 (14)
N2B—Ni1—N1A	94.77 (13)	N2F—Ni2—N1D	167.23 (14)
N2B—Ni1—N1C	96.63 (13)	N2F—Ni2—N1E	91.43 (14)
N2C—Ni1—N1A	91.45 (13)	N2F—Ni2—N1F	78.09 (14)
N2C—Ni1—N1C	78.01 (13)	N2F—Ni2—N2D	89.91 (14)
N2C—Ni1—N2B	171.86 (13)	N2F—Ni2—N2E	93.15 (13)

The H atoms were positioned with idealized geometry (C—H = 0.93 Å) and refined using a riding model, with displacement parameters equal to $1.2U_{eq}$ of the parent atom. Late in the refinement, a comparatively large peak in the difference map was observed, at a reasonable distance for a water molecule with hydrogen bonds to O1B and O1C. The peak was modelled as a lattice water molecule with a site occupancy of 0.11 (1) per Ni. No H atoms were placed on the water molecules. It was apparent that the perchlorate anions undergo considerable thermal motion and may indeed be disordered; the largest residual peaks (0.89 e Å^{-3}) in the difference Fourier map are primarily associated with this ClO_4^- disorder. Examination of the map, however, did not reveal any meaningful disordered model.

Data collection: XSCANS (Siemens, 1994a). Cell refinement: XSCANS. Data reduction: SHELXTL (Siemens, 1994b). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.
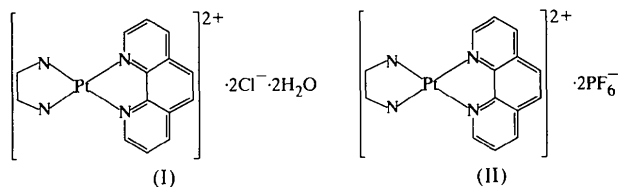
References

Andrew, J. E., Blake, A. B. & Fraser, L. R. (1975). J. Chem. Soc. Dalton Trans. pp. 800–805.
Ball, P. W. & Blake, A. B. (1969). J. Chem. Soc. A, pp. 1415–1422.
Dapporto, P., De Munno, G., Bruno, G. & Romeo, M. (1983). Acta Cryst. C39, 718–720.
De Munno, G. & Bruno, G. (1984). Acta Cryst. C40, 2022–2024.
De Munno, G., Denti, G., De Rosa, G. & Bruno, G. (1988). Acta Cryst. C44, 1193–1196.
Lanfredi, A. M. M., Tiripicchio, A., Ghedini, M. & De Munno, G. (1982). Acta Cryst. B38, 1165–1168.
Morosin, B., Dunn, R. G., Assink, R., Massis, T. M., Fronabarger, J. & Duesler, E. N. (1997). Acta Cryst. C53, 1609–1611.
Neels, A., Neels, B. M., Stoeckli-Evans, H., Clearfield, A. & Poojary, D. M. (1997). Inorg. Chem. 36, 3402–3409.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994a). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994b). *SHELXTL.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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*

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 nonplanar 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.
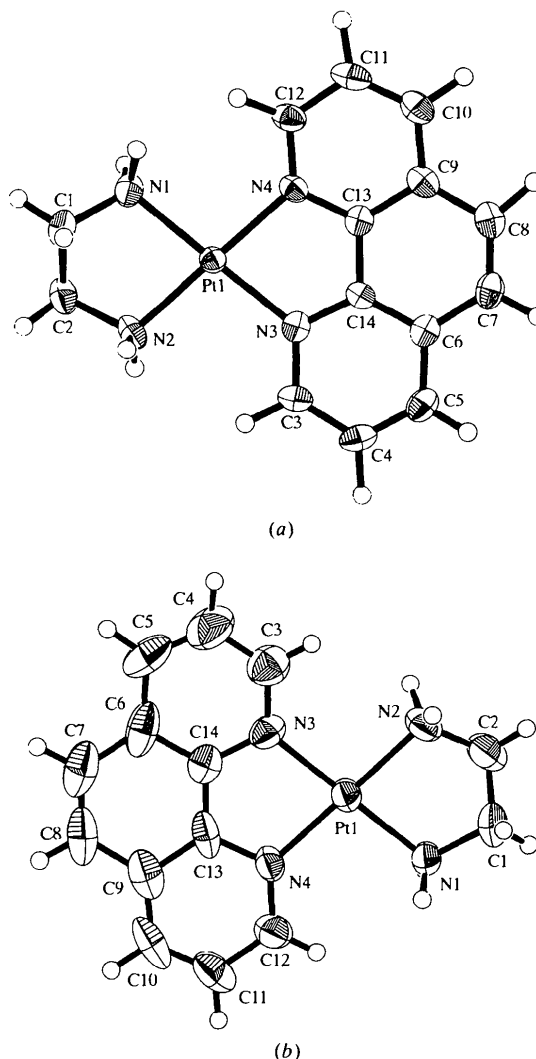
(I)   (II)

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.