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[(1*R*,2*R*)-1,2-Diaminocyclohexane-κ^2N,N'](α-diimine-κ^2N,N')platinum(II) bis(hexafluorophosphate), where α-diimine is 2,2′-bipyridine and 1,10-phenanthroline

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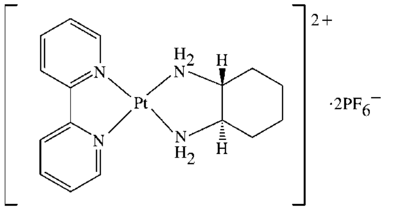
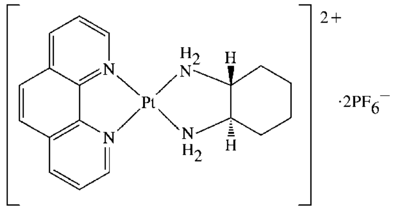
The title Pt^{II} complexes, *viz*. (2,2′-bipyridine-κ^2N,N')[(1*R*,2*R*)-1,2-diaminocyclohexane-κ^2N,N']platinum(II) bis(hexafluorophosphate), [Pt($C_6H_{14}N_2$)($C_{10}H_8N_2$)](PF_6)$_2$, and [(1*R*,2*R*)-1,2-diaminocyclohexane-κ^2N,N'](1,10-phenanthroline-κ^2N,N')platinum(II) bis(hexafluorophosphate), [Pt($C_6H_{14}N_2$)($C_{12}H_8N_2$)](PF_6)$_2$, containing an aromatic α-diimine and a non-planar diaminocyclohexane, both form a ladder-type structure, which is constructed *via* loose π–π stacking on the α-diimine ligands and hydrogen bonding between the cyclic amines and the counter-anions. In the former compound, there are two independent complex cations, both of which have a twofold axis through the Pt atom.

Comment

Square-planar Pt^{II} complexes containing α-diimine ligands, such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen), form various stacking structures based on Pt···Pt and/or π–π interactions. For example, [PtCl$_2$(bpy)] is known to form two columnar stacking structures, *viz*. the red form with a Pt···Pt linear chain (Osborn & Rogers, 1974; Connick *et al.*, 1996) and the yellow form with a π–π stack (Herber *et al.*, 1994). However, complexes containing a non-planar ligand, such as ethylenediamine (en), should have difficulty in forming a columnar structure because of the steric effect of the en ligand and the positive charge of the complex. We have previously reported that the [Pt(α-diimine)(en)]$^{2+}$ ions (α-diimine is bpy and phen) form a ladder-type stacking structure, which is constructed *via* π–π stacking of the α-diimine ligands and hydrogen bonding between the en ligand and the counter-anion (Kato & Takahashi, 1999). In order to expand the structural chemistry of this type of platinum complex, we have synthesized new Pt^{II} complexes containing a more bulky chiral ligand, namely (1*R*,2*R*)-1,2-diaminocyclohexane (*RR*-chxn). In this paper, the crystal structures of [Pt(bpy)(*RR*-chxn)](PF_6)$_2$, (I), and [Pt(phen)(*RR*-chxn)](PF_6)$_2$, (II), are reported.



(I)



(II)

Fig. 1 shows the molecular structure of one of the two independent [Pt(bpy)(*RR*-chxn)]$^{2+}$ ions in (I). This ion has a twofold axis through the Pt atom, intersecting the bpy and *RR*-chxn ligands. The coordination geometry is almost planar, including the bpy ligand, while the cyclohexane ring adopts a stable chair conformation. The geometries of the two independent complexes (Table 1) are very similar to one another, being related by a pseudo-center of symmetry, except that the diaminocyclohexane ligand has an *RR* configuration. The bpy ligands of the complex cations are stacked, and the PF_6^- ions are located near the *RR*-chxn ligands, as shown in Fig. 2. The crystal structure is similar to that of the corresponding en complex [Pt(bpy)(en)](PF_6)$_2$ (Kato *et al.*, 1997). As shown in Fig. 3, the geometry of the platinum complex in (II) (Table 3) is very similar to that in (I), although the crystal packing is somewhat different.

In the crystal structures of both (I) and (II), ladder-type structures similar to those found in the corresponding en complexes are formed. Fig. 4 shows the ladder-type stacking in (II). The dihedral angles and the interplanar spacings between

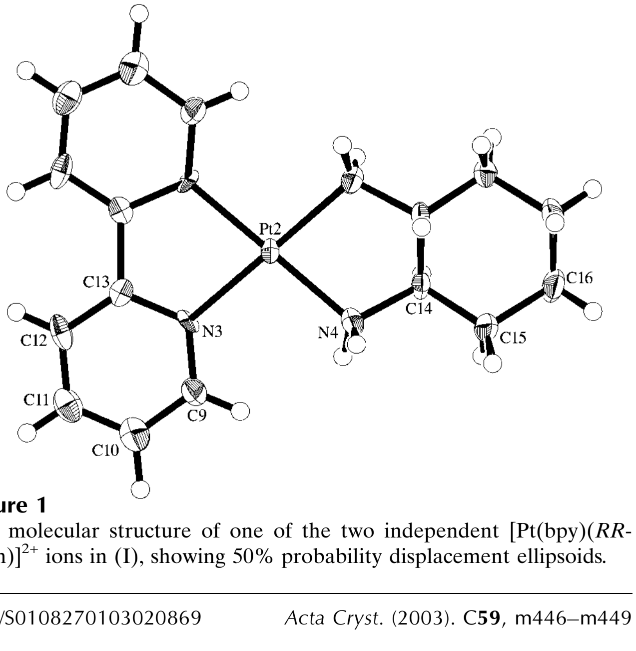


Figure 1
The molecular structure of one of the two independent [Pt(bpy)(*RR*-chxn)]$^{2+}$ ions in (I), showing 50% probability displacement ellipsoids.

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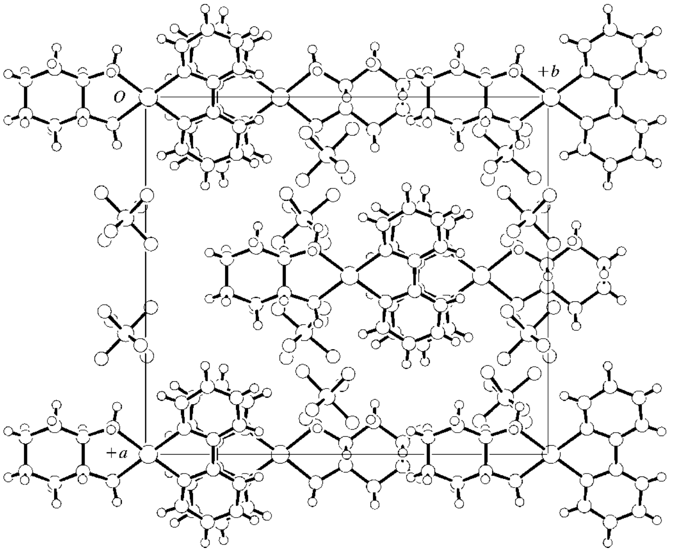

Figure 2
The packing structure of (I), viewed along the *c* axis.

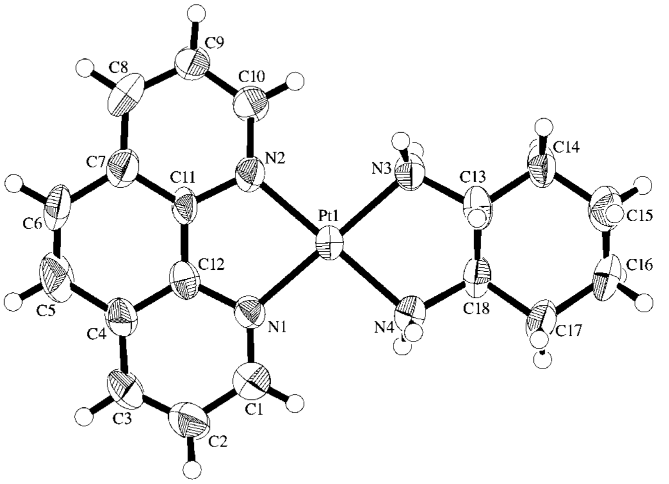

Figure 3
The molecular structure of the [Pt(phen)(*RR*-chxn)]$^{2+}$ ion in (II), showing 50% probability displacement ellipsoids.

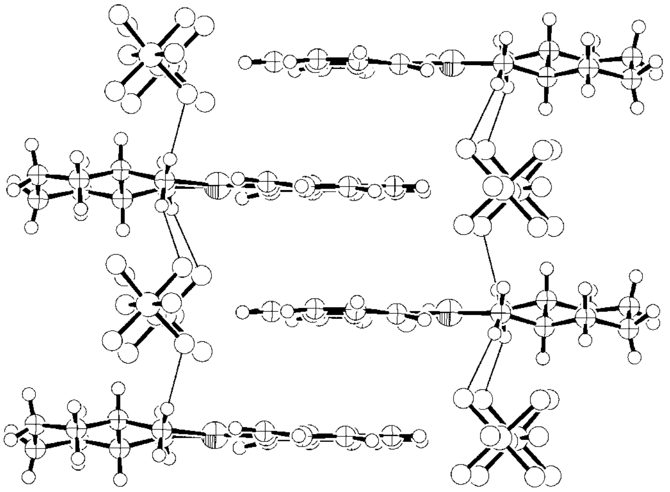

Figure 4
The ladder-type stacking of (II) along the *a* axis.

neighboring bpy and phen ligands are, respectively, 0.5 (1)° and 3.53 (1) Å for (I), and 1.8 (2)° and 3.66 (2) Å for (II). Such a loose π–π stacking would be controlled by the counter-anion. In fact, we found that the larger anion, PF_6^-, expanded the interplanar spacing between the phen ligands in the ladder structure of the [Pt(en)(phen)]$^{2+}$ complex compared with the spacing in the complex containing the smaller anion, Cl^- (Kato & Takahashi, 1999). The PF_6^- anions form hydrogen bonds with the *RR*-chxn ligands (Tables 2 and 4), thus linking the Pt^{II} complexes on every other step. As a remarkable characteristic, we reported that [Pt(bpy)(en)]$^{2+}$ acts as a host molecule and takes up free phen preferentially, thus forming a tight integrated stack (Kato *et al.*, 2001). Complexes containing the bulky *RR*-chxn ligand are expected to include larger guests, because (I) and (II) have more space between the complexes in the stack than complexes containing the en ligand.

Experimental

[$PtCl_2$(bpy)] was prepared according to the method reported by Morgan & Burstall (1934). [$PtCl_2$(phen)] was prepared in a similar manner, using phen as a starting material. The resulting yellow precipitates of [$PtCl_2$(bpy)] and [$PtCl_2$(phen)] were recrystallized from acetone and *N*,*N*-dimethylformamide, respectively. An aqueous suspension of [$PtCl_2$(bpy)] (0.33 g, 0.78 mmol) containing (1*R*,2*R*)-1,2-diaminocyclohexane (0.089 g, 0.78 mmol) was refluxed for 3 h. To the resulting clear yellow solution was added an aqueous solution of an excess amount of NH_4PF_6 (0.30 g, 1.8 mmol). The solution was left to stand at room temperature and pale-yellow needle-shaped crystals of (I) were produced (yield 52%). Complex (II) was obtained in a similar manner, using [$PtCl_2$(phen)] instead of [$PtCl_2$(bpy)]. Recrystallization from methanol/acetone gave pale-yellow needle-shaped crystals (yield 57%). For (I), ^{1}H NMR (DMSO-d_6): δ 1.19 (5, 2H, CH_2), 1.39 (4, 2H, CH_2), 1.58 (*d*, 2H, CH_2), 2.05 (*s*, 2H, CH_2), 2.57 (*s*, 2H, CH), 6.36 (*t*, 2H, NH_2), 6.90 (*d*, 2H, NH_2), 7.97 (*t*, 2H, bpy), 8.57 (*t*, 2H, bpy), 8.76 (*d*, 4H, bpy); IR (KBr, cm^{-1}): 892.19, 563.28 (νPF_6). For (II), ^{1}H NMR (DMSO-d_6): δ 1.22 (*d*, 2H, CH_2), 1.45 (*d*, 2H, CH_2), 1.61 (*d*, 2H, CH_2), 2.11 (*d*, 2H, CH_2), 6.55 (*d*, 2H, NH_2), 7.15 (*d*, 2H, NH_2), 8.31 (*dd*, 2H, phen), 8.37 (*s*, 2H, phen), 9.19 (*d*, 4H, bpy); IR (KBr, cm^{-1}): 861.32, 557.50 (νPF_6).

Compound (I)

Crystal data

[$Pt(C_6H_{14}N_2)(C_{10}H_8N_2)](PF_6)_2$
M_r = 755.40
Monoclinic, *C*2
a = 15.534 (1) Å
b = 17.448 (2) Å
c = 8.2424 (7) Å
β = 93.256 (4)°
V = 2230.4 (3) Å^3
Z = 4
D_x = 2.249 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4092 reflections
θ = 3.1–27.5°
μ = 6.52 mm^{-1}
T = 173.2 K
Needle, pale yellow
0.68 × 0.20 × 0.16 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.254, T_{max} = 0.713
8699 measured reflections
5075 independent reflections
4820 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°
$h = -17 \rightarrow 20$
$k = -22 \rightarrow 22$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R(F) = 0.032$
$wR(F^2) = 0.077$
$S = 1.04$
5075 reflections
317 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 6.5862P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.024$
$\Delta\rho_{\max} = 1.63$ e Å^{-3}
$\Delta\rho_{\min} = -2.16$ e Å^{-3}
Absolute structure: Flack (1983), 2446 Friedel pairs
Flack parameter = 0.04 (2)

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

Pt1—N1	2.005 (11)	Pt2—N3	2.033 (9)
Pt1—N2	2.052 (10)	Pt2—N4	2.037 (12)
N1—Pt1—N1^{i}	80.1 (6)	N3—Pt2—N3^{ii}	80.8 (5)
N1—Pt1—N2	98.7 (4)	N3—Pt2—N4	98.8 (4)
N1—Pt1—N2^{i}	176.5 (4)	N3—Pt2—N4^{ii}	178.8 (4)
N2—Pt1—N2^{i}	82.7 (6)	N4—Pt2—N4^{ii}	81.7 (7)

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

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H5$\cdots$F2	1.03	2.61	3.26 (1)	120
N2—H5$\cdots$F4	1.03	2.06	3.03 (1)	155
N2—H6$\cdots$F5^{iii}	0.87	2.88	3.14 (1)	100
N2—H6$\cdots$F7	0.87	2.63	3.46 (1)	159
N2—H6$\cdots$F12	0.87	2.36	3.11 (1)	146
N4—H17$\cdots$F6^{iv}	0.95	2.20	3.06 (1)	151
N4—H17$\cdots$F11^{v}	0.95	2.96	3.26 (1)	100
N4—H16$\cdots$F8^{iv}	0.96	2.65	3.25 (1)	120
N4—H16$\cdots$F10^{iv}	0.96	2.06	2.97 (1)	156

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

Compound (II)

Crystal data

$[Pt(C_6H_{14}N_2)(C_{12}H_8N_2)](PF_6)_2$
$M_r = 779.42$
Orthorhombic, $P2_12_12_1$
$a = 7.3142$ (5) Å
$b = 18.2738$ (5) Å
$c = 18.4925$ (5) Å
$V = 2471.7$ (2) Å^3
$Z = 4$
$D_x = 2.094$ Mg m^{-3}
$D_m = 2.01$ (2) Mg m^{-3}
D_m measured by flotation in bromoform/CCl$_4$ at 303 K
Mo $K\alpha$ radiation
Cell parameters from 9155 reflections
$\theta = 3.1$–27.5°
$\mu = 5.91$ mm^{-1}
$T = 293.2$ K
Needle, pale yellow
0.70 × 0.14 × 0.10 mm

Table 3
Selected geometric parameters (Å, °) for (II).

Pt1—N1	2.015 (5)	Pt1—N3	2.042 (6)
Pt1—N2	2.008 (6)	Pt1—N4	2.046 (6)
N1—Pt1—N2	81.6 (2)	N2—Pt1—N3	97.9 (2)
N1—Pt1—N3	178.8 (5)	N2—Pt1—N4	178.1 (6)
N1—Pt1—N4	97.7 (2)	N3—Pt1—N4	82.8 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H9$\cdots$F1	0.86	2.15	2.97 (1)	158
N3—H9$\cdots$F12	0.86	3.03	3.331 (7)	103
N3—H10$\cdots$F2^{vi}	0.84	2.14	2.95 (1)	161
N4—H11$\cdots$F7^{vii}	0.83	2.45	3.24 (1)	158
N4—H11$\cdots$F9^{vii}	0.83	2.85	3.58 (2)	147
N4—H11$\cdots$F11^{vii}	0.83	2.39	3.11 (1)	145

Symmetry codes: (vi) $x-1, y, z$; (vii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Data collection

Rigaku/MSC Mercury CCD diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
$T_{\min} = 0.514$, $T_{\max} = 0.782$
26 208 measured reflections
5570 independent reflections
5485 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 23$
$l = -23 \rightarrow 24$

Refinement

Refinement on F^2
$R(F) = 0.047$
$wR(F^2) = 0.105$
$S = 1.26$
5570 reflections
334 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 5.6317P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.034$
$\Delta\rho_{\max} = 1.81$ e Å^{-3}
$\Delta\rho_{\min} = -0.79$ e Å^{-3}
Absolute structure: Flack (1983), 2413 Friedel pairs
Flack parameter = 0.21 (2)

H atoms were positioned geometrically and fixed [$U_{\rm iso}(H) = U_{\rm eq}$(parent atom)]. The *PLATON*/*ADDSYM* (Spek, 2003) results suggested the existence of a pseudo-center of symmetry for both crystal structures. The pseudo-space groups of (I) and (II) are $C2/c$ and $Pnma$, respectively. However, these were rejected because both structures contain the chiral ligand. The absolute structures of (I) and (II) were assigned based on the known chirality of the (1*R*,2*R*)-1,2-diaminocyclohexane ligand and led to Flack (1983) values of 0.04 (2) and 0.21 (2), respectively, in the refinements. The crystal structure of (II) has voids of 42 Å^3 without detectable electron density (> 0.5 e Å^{-3}). The D_m value for (II) is consistent with the crystal containing no solvent molecules.

For both compounds, data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation/Rigaku, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1141). Services for accessing these data are described at the back of the journal.

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