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Bis(2,2′-bipyridine-κ^2N,N')(1,10-phenanthroline-κ^2N,N')ruthenium(II) tetracyanoplatinate(II)

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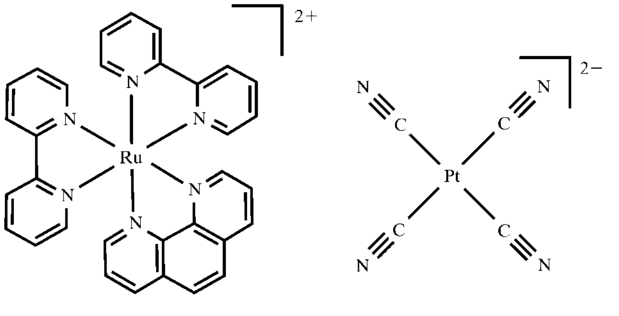
In the title compound, $[Ru(C_{10}H_8N_2)_2(C_{12}H_8N_2)][Pt(CN)_4]$, cations and anions alternate along the *a* axis to afford a one-dimensional network. The one-dimensional character arises from the π–π stacking as well as from the electrostatic interactions formed between the phen (1,10-phenanthroline) and $[Pt(CN)_4]^{2-}$ units. Two adjacent one-dimensional chains form further stacks based on the π–π stacking interactions between the phen moieties, where the interplanar spacing is 3.50 (1) Å.

Comment

Homogeneous catalysis of platinum(II) complexes in photochemical H_2 production from water have been examined in our laboratory by utilizing a well known photosystem consisting of $[Ru(bpy)_3]^{2+}$ (bpy is 2,2′-bipyridine) and methylviologen (usually *N*,*N*′-dimethyl-4,4′-bipyridinium dichloride; Sakai & Matsumoto, 1990; Sakai *et al.*, 1993). In this context, we began five years ago to explore the chemistry of double salts consisting of $[Ru(bpy)_3]^{2+}$ derivatives and platinum complexes. Our aim has been to develop water-insoluble crystals involving both the photosensitizing and the H_2-evolving centers. Visible-light-induced water splitting into H_2 and $\frac{1}{2}O_2$ might be promoted under dispersion in aqueous media of such hybrid crystals, including their doped systems. As a part of these studies, we report here the crystal structure of the title compound, *viz*. $[Ru(bpy)_2(phen)][Pt(CN)_4]$, (I) (phen is 1,10-phenanthroline).



(I)

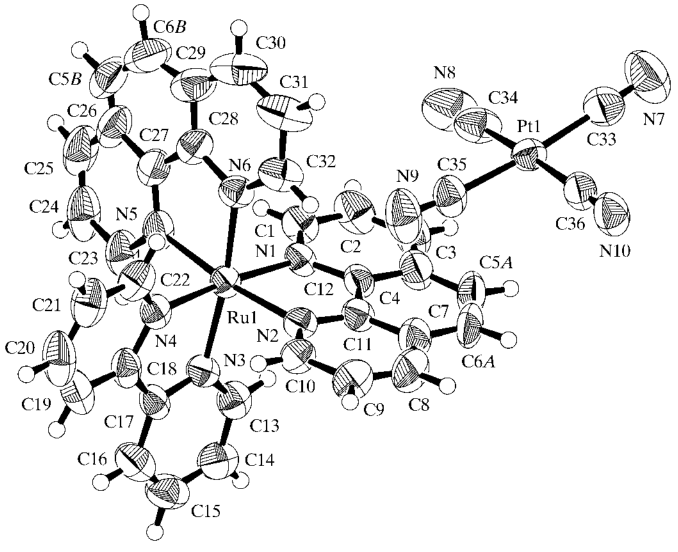


Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. There is positional disorder of the phen ligand, and the site-occupation factors of atoms C5*A*/C6*A* and C5*B*/C6*B* are 75.2 (5) and 24.8 (5)%, respectively.

The asymmetric unit of (I) consists of an $[Ru(bpy)_2(phen)]^{2+}$ cation and a $[Pt(CN)_4]^{2-}$ anion (Fig. 1). The phen ligand of the cation is disordered over two sites. For simplicity,

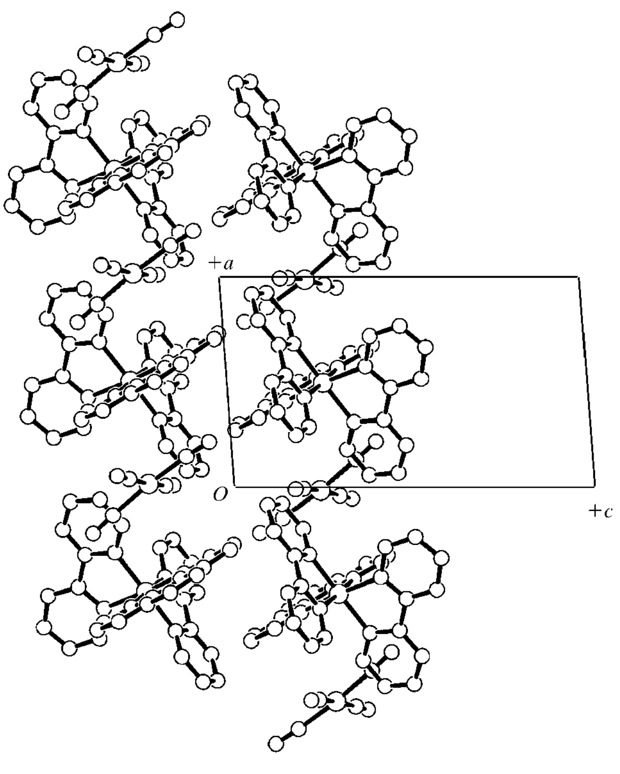


Figure 2
The crystal packing of (I), viewed along the *b* axis, showing two adjacent one-dimensional chains. Atoms C5*B* and C6*B* and all H atoms have been omitted for clarity.

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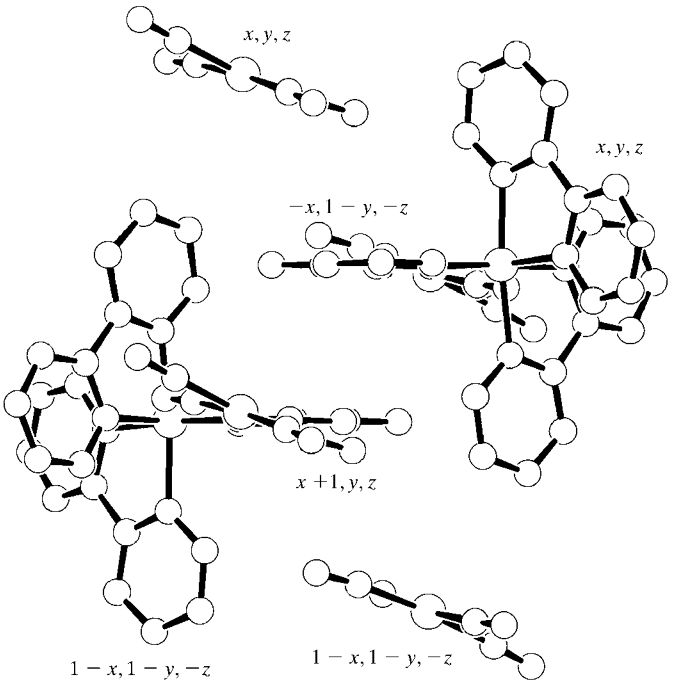

Figure 3
A view of (I), parallel to the phen plane including atoms C5*A* and C6*A*, showing how the $[Pt(CN)_4]^{2-}$ anions and the major phen units stack along the *a* axis. Atoms C5*B* and C6*B* and all H atoms have been omitted for clarity.

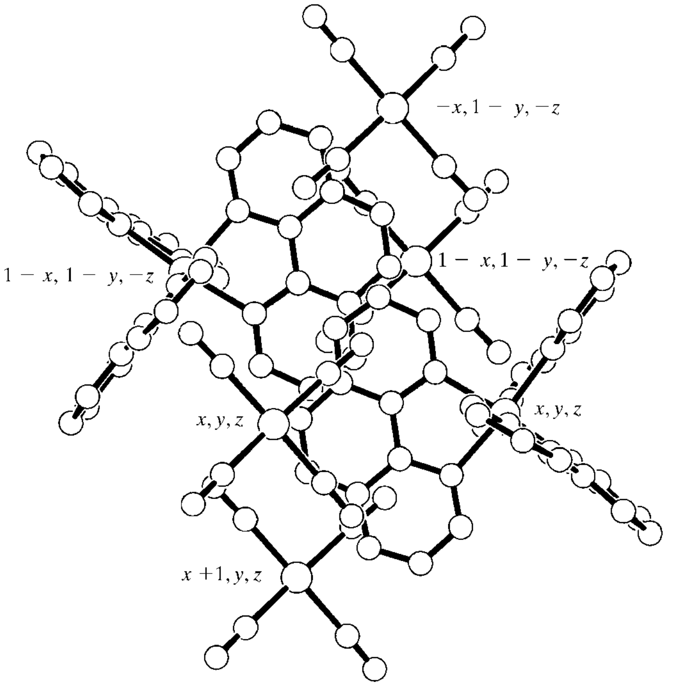

Figure 4
A view of (I), perpendicular to the phen plane including atoms C5*A* and C6*A*, showing how the $[Pt(CN)_4]^{2-}$ anions and the major phen units stack along the *a* axis. Atoms C5*B* and C6*B* and all H atoms have been omitted for clarity.

only the structure containing the major phen component, which has an occupancy of 75.2 (5)%, will be discussed below. The cations and anions stack along the *a* axis in an alternating fashion (Fig. 2), which is, in a sense, similar to that reported for the so-called Magnus green salt, $[Pt(NH_3)_4][PtCl_4]$ (Atoji *et al.*, 1957). The phen unit, having an aromatic system that is slightly larger than the bpy unit, seems to play an important role in stabilizing the one-dimensional network in (I). Thus, a more appropriate description is that the phen and $[Pt(CN)_4]^{2-}$ units alternate along the *a* axis (see Figs. 2–4). As shown in Fig. 3, the phen and tetracyanoplatinate planes are not coplanar and are inclined by 21.9 (2)° to one another. The observed short contacts are listed in Table 2. In addition, two adjacent chains are stacked as a result of π–π associations between the phen units. As shown in Fig. 4, two neighboring phen units form a π–π stack through an inversion center. From the average shift of atoms $C6^{ii}$–$C9^{ii}$ [symmetry code: (ii) $1 - x$, $1 - y$, $-z$] from the mean plane of the phen molecule, defined by atoms N1/N2/C1–C12, the interplanar separation is estimated as 3.50 (1) Å. Some relevant C···C contacts are also given in Table 2.

Because the electrostatic and π–π attractive forces are enhanced in the crystal structure of (I), the Pt^{II} ion shows a relatively large distortion towards a tetrahedral geometry, in which the Pt1/C33/C36 and Pt1/C34/C35 planes are inclined at an angle of 7.2 (3)°. Selected distances and angles in (I) are listed in Table 1.

As recently reported by Sakai, Uchida *et al.* (2004), it has been ascertained in our laboratory that double salts containing $[Ru(bpy)_3]^{2+}$ (which may be classified as homo-ligand systems) tend to form two-dimensional cationic/porous layers (*i.e.* two-dimensional $\{[Ru(bpy)_3]\}_n^{2n+}$ layers) in the crystal structure. For instance, the crystal structures of $[M^{II}(bpy)_3][Pt(oxalato)_2]$ (M^{II} = Ni^{II}, Fe^{II} and Ru^{II}) have been ascertained to comprise very similar two-dimensional cationic/porous layers in which the pores are occupied by the $[Pt(oxalato)_2]^{2-}$ anions (unpublished results), even though structure determinations of the tetracyanoplatinate derivatives have been unsuccessful thus far because of the difficulty in the crystallization of the materials. At the moment, we think that the one-dimensionality achieved in the crystal structure of (I) is relevant to the lower symmetry in the present mixed-ligand system.

Experimental

$K_2[Pt(CN)_4]\cdot3H_2O$ (Kojima Chemicals Co. Ltd) was used as received. *cis*-$RuCl_2(bpy)_2\cdot2H_2O$ was prepared as described previously (Sullivan *et al.*, 1978). $[Ru(bpy)_2(phen)]Cl_2$ was previously reported as a trihydrated salt (Baggott *et al.*, 1983) but has been prepared as a heptahydrate, $[Ru(bpy)_2(phen)]Cl_2\cdot7H_2O$, by the following method. A mixture of *cis*-$RuCl_2(bpy)_2\cdot2H_2O$ (0.26 g, 0.5 mmol) and phen (0.099 g, 0.55 mmol) in ethanol (25 ml) was refluxed overnight. After the solution had been filtered to remove insoluble materials, the filtrate was evaporated to a total volume of 5–10 ml. The solution was added gradually to diethyl ether (80 ml) with stirring. The deposited orange precipitate was collected by suction filtration and air dried (yield 80%). The compound was recrystallized from hot water before use. Analysis calculated for $C_{32}H_{38}Cl_2N_6O_7Ru$: C 48.61, H 4.84, N 10.63%; found: C 48.58, H 4.67, N 10.65%. Diffraction-quality single crystals of (I) were prepared using the following unique diffusion method, as reported for $[Pt(bpy)(2\text{-aminopyridine})_2][Pt(oxalato)_2]\cdot 2H_2O$ (Sakai *et al.*, 2003) and $[Pt(bpy)(2\text{-aminopyridine})_2][Pt(CN)_4]\cdot 2H_2O$ (Sakai, Mizota *et al.*, 2004). A petri dish, having a diameter of ~60 mm and a depth of ~15 mm, was divided into three zones using filter papers, the central zone (zone 2) being sandwiched between the other two zones (zones 1 and 3). Zones 1 and 2 (and zones 2 and 3) were separated by two or three pieces of filter paper, while contact between zones 1 and 3 was avoided. Water (6 ml) was added to the petri dish, filling all three zones. Finally, solutions of $K_2[Pt(CN)_4]\cdot 3H_2O$ (0.015 mmol) in water (1.5 ml) and of $[Ru(bpy)_2(phen)]Cl_2\cdot 7H_2O$ (0.015 mmol) in water (1.5 ml) were added dropwise, simultaneously, to zones 1 and 3, respectively. The solution was left to stand at 293 K for a few days. The major product, in the form of orange crystals, was found to be unstable in air, since the crystals rapidly lost water, giving an amorphous material on exposure to air at room temperature. Elemental analysis showed that the major product was a pentahydrated salt. Analysis calculated for $C_{36}H_{34}N_{10}O_5PtRu$: C 43.99, H 3.49, N 14.25%; found: C 43.91, H 3.40, N 14.36%. On the other hand, the title compound, (I), which deposited as the minor product in the form of red prisms, was found to be very stable, as it is an anhydrous salt. Since the product yield was quite low, elemental analysis of (I) could not be carried out. It was considered possible that (I) might be contaminated with $[Ru(bpy)_3]^{2+}$, since the disorder phenomena observed around the phen moiety might also be elucidated with a model in which the $[Ru(bpy)_2(phen)]^{2+}$ cations are partly replaced by the $[Ru(bpy)_3]^{2+}$ cations. However, such a possibility can be ruled out because the purity of both $[Ru(bpy)_2(phen)]Cl_2\cdot 7H_2O$ and *cis*-$RuCl_2(bpy)_2\cdot 2H_2O$ was checked carefully by ^{1}H NMR analysis in our laboratory. Consequently, the model described is judged to be valid.

Crystal data

$[Ru(C_{10}H_8N_2)_2(C_{12}H_8N_2)][Pt(CN)_4]$
$M_r = 892.81$
Triclinic, $P\overline{1}$
$a = 8.6251\ (10)$ Å
$b = 12.7842\ (15)$ Å
$c = 14.7039\ (17)$ Å
$\alpha = 94.557\ (2)^\circ$
$\beta = 94.063\ (2)^\circ$
$\gamma = 92.637\ (2)^\circ$
$V = 1610.0\ (3)$ Å^3
$Z = 2$
$D_x = 1.842$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5196 reflections
$\theta = 2.7\text{–}27.2^\circ$
$\mu = 4.85$ mm^{-1}
$T = 296\ (2)$ K
Prism, red
0.38 × 0.22 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: Gaussian (*XPREP* in *SAINT*; Bruker, 2001)
$T_{\min} = 0.262$, $T_{\max} = 0.512$
8622 measured reflections
5785 independent reflections
4934 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.037$
$\theta_{\max} = 25.4^\circ$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 15$
$l = -17 \rightarrow 8$
154 standard reflections
frequency: 330 min
intensity decay: 0,0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.068$
$S = 1.00$
5785 reflections
452 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.88$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—C33	1.959 (6)	Ru1—N2	2.057 (3)
Pt1—C34	2.000 (5)	Ru1—N3	2.062 (3)
Pt1—C35	1.988 (6)	Ru1—N4	2.049 (4)
Pt1—C36	1.983 (5)	Ru1—N5	2.061 (3)
Ru1—N1	2.068 (3)	Ru1—N6	2.052 (3)
C33—Pt1—C36	90.0 (2)	N4—Ru1—N5	90.28 (14)
C36—Pt1—C35	90.79 (19)	N6—Ru1—N5	78.52 (15)
C33—Pt1—C34	91.2 (2)	N4—Ru1—N3	78.32 (15)
C35—Pt1—C34	88.4 (2)	N2—Ru1—N3	88.60 (13)
C36—Pt1—C34	175.32 (19)	N5—Ru1—N3	97.14 (15)
C33—Pt1—C35	174.5 (2)	N6—Ru1—N1	86.90 (14)
N4—Ru1—N6	96.40 (14)	N2—Ru1—N1	79.84 (14)
N4—Ru1—N2	95.37 (14)	N5—Ru1—N1	94.72 (14)
N6—Ru1—N2	96.17 (14)	N3—Ru1—N1	98.71 (14)

Table 2
Observed short contacts (Å).

N9···C8	3.495 (8)	C5*A*···C36$^{\rm i}$	3.676 (9)
N9···C7	3.611 (8)	C8···C7$^{\rm ii}$	3.595 (8)
C3···Pt1$^{\rm i}$	3.888 (6)	C9···C6*A*$^{\rm ii}$	3.597 (10)

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

The phen C atoms at the 5- and 6-positions were found to be disordered over two sites (C5*A*/C6*A* and C5*B*/C6*B*). In other words, the phen ligand and one of the bpy ligands (involving atoms N5 and N6) are partly replaced by one another. The validity of this model has been checked by examination of the difference Fourier maps generated by *PLATON* (Spek, 2003). The occupancies of sites *A* and *B* converged at 75.2 (5) and 24.8 (5)%, respectively. The anisotropic displacement parameters of atoms C4, C5*A*, C6*A* and C7 were very weakly restrained to have similar values; the displacement parameters of atoms C26, C5*B*, C6*B* and C29 were also weakly restrained to have similar values. All H atoms, except those attached to the disordered bpy units, were placed at idealized positions (C—H = 0.93 Å for bpy), and included in the refinement in a riding-motion approximation, with $U_{\text{iso}}(\text{H})$ values equal to $1.2U_{\text{eq}}(\text{C})$. H atoms at the 3- and 3′-positions of the disordered bpy units were not located. The highest electron-density peak was 0.95 Å from atom Pt1, while the deepest hole was 0.85 Å from atom Ru1.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL*97, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* and *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1157). Services for accessing these data are described at the back of the journal.

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