Bis(2,2'-bipyridine-κ²N,N')(1,10-phenanthroline-κ²N,N')ruthenium(II) tetracyanoplatinate(II)

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Bis(2,2’-bipyridine-κ²N,N’)(1,10-phenanthroline-κ²N,N’)-ruthenium(II) tetracyanoplatinate(II)

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Received 24 November 2003
Accepted 22 December 2003
Online 31 January 2004

In the title compound, [Ru(C₁₀H₈N₂)₂(C₁₂H₈N₂)][Pt(CN)₄]₂, 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 photocatalytic H₂ 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)]¹⁺ derivatives and platinum complexes. Our aim has been to develop water-insoluble crystals involving both the photosensitizing and the H₂-evolving centers. Visible-light-induced water splitting into H₂ and O₂ 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]₂, (I) (phen is 1,10-phenanthroline).

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,
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, \([\text{Pt(NH}_3\text{)}_4][\text{PtCl}_4]\) (Atoji \textit{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 \([\text{Pt(CN)}_4]^{2-}\) units alternate along the \(a\) axis (see Figs. 2–4). As shown in Fig. 3, the phen and tetracyanoplatinate planes are not co-planar 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 \(\pi-\pi\) associations between the phen units. As shown in Fig. 4, two neighboring phen units form a \(\pi-\pi\) stack through an inversion center. From the average shift of atoms C6ii–C9ii [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 \(\pi-\pi\) attractive forces are enhanced in the crystal structure of (I), the Pt\textsuperscript{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 \textit{et al.} (2004), it has been ascertained in our laboratory that double salts containing \([\text{Ru(bpy)}_2]^{2+}\) (which may be classified as homo-ligand systems) tend to form two-dimensional cationic/porous layers \(i.e.\) two-dimensional \(\{[\text{Ru(bpy)}_2]\}_n\) layers) in the crystal structure. For instance, the crystal structures of \([M^{II}(\text{bpy})_3][\text{Pt(oxalato)}_2]\) \((M^{II}=\text{Ni}^{II},\text{Fe}^{II}\) and \(\text{Ru}^{II})\) have been ascertained to comprise very similar two-dimensional cationic/porous layers in which the pores are occupied by the \([\text{Pt(oxalato)}_2]^{2-}\) 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**

\(K_2[\text{Pt(CN)}_4]_3\cdot3\text{H}_2\text{O}\) (Kojima Chemicals Co. Ltd) was used as received. \textit{cis-RuCl}_2(bpy)_2\cdot2\text{H}_2\text{O} was prepared as described previously (Sullivan \textit{et al.}, 1978). \([\text{Ru(bpy)}_2(\text{phen})]\text{Cl}_2\) was previously reported as a trihydrated salt (Baggott \textit{et al.}, 1983) but has been prepared as a heptahydrate. \([\text{Ru(bpy)}_2(\text{phen})]\text{Cl}_2\cdot7\text{H}_2\text{O}\) by the following method. A mixture of \textit{cis-RuCl}_2(bpy)_2\cdot2\text{H}_2\text{O} (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 \(C_{38}H_{36}Cl_2N_8O\cdot\text{Ru}:\) C 48.61, H 4.84, N 10.63%; found: C 48.58, H 4.67, N 10.65%. Diffraction-quality single
was a pentahydrated salt. Analysis calculated for \(\text{C}_{36}\text{H}_{34}\text{N}_{10}\text{O}_{5}\text{PtRu}\) 

room temperature. Elemental analysis showed that the major product 

rapidly lost water, giving an amorphous material on exposure to air at 

orange crystals, was found to be unstable in air, since the crystals 

stand at 293 K for a few days. The major product, in the form of 

simultaneously, to zones 1 and 3, respectively. The solution was left to 

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 \(\text{K}_2\text{[Pt(CN)_{4}]}\) 

Cl\(_2\) (0.015 mmol) in water (1.5 ml) and of \(\text{[Ru(bpy)_{2}(phen)\text{-C}_{3}\text{H}_{7}\text{H}_{2}O}\) (0.015 mmol) in water (1.5 ml) were added dropwise, 

S\(_{b}\) = 12.7842 (15) Å\(^{3}\) 

re£ections. The solution was left to 

crystals of (I) were prepared using the following unique diffusion 

absorption correction: Gaussian 

Bruker SMART APEX CCD area-

data, 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 \(U_{eq}(\text{C})\) 

values equal to 1.2\(U_{eq}(\text{C})\). 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 Rul.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: KENX (Sakai, 2002); software used to prepare material for publication: SHELXL97, TEXSAN (Molecular Structure Corporation, 2001), KENX and ORTEPII (Johnson, 1976).

This work was supported by Grants-in-Aid for Scientific Research on Priority Areas (Nos. 10149248, 11136246 and 12023247 ‘Metal-assembled Complexes’) from the Ministry of Education, Science, Sports and Culture of Japan, and was partly supported by a Grant-in-Aid for Scientific Research (No. 14340223) from the Ministry of Education, Science, Sports and Culture of Japan.

Table 1

<table>
<thead>
<tr>
<th>Selected geometric parameters (Å, °).</th>
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<tbody>
<tr>
<td>Pt1—C33</td>
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<tr>
<td>Pt1—C34</td>
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<tr>
<td>Pt1—C35</td>
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<tr>
<td>Pt1—C36</td>
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<tr>
<td>Ru1—N1</td>
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Table 2

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<tr>
<th>Observed short contacts (Å).</th>
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<tr>
<td>N9—C8</td>
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<tr>
<td>N9—C7</td>
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<tr>
<td>C3—Pt1</td>
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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 (C5A/C6A and C5B/C6B). 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, 

C5A, C6A and C7 were very weakly restrained to have similar 

values; the displacement parameters of atoms C26, C25, C26B 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 \(U_{eq}(\text{H})\) 

values equal to 1.2\(U_{eq}(\text{C})\). 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 Rul.
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.

References