

Takashi Fujihara,^{a*} Atsuo Kobayashi,^b Miho Iwai^b and Akira Nagasawa^a^aDepartment of Chemistry, Faculty of Science, Saitama University, Shimo-Okubo 255, Sakuraku, Saitama 338-8570, Japan, and ^bKojima Chemicals Co. Ltd, 337-26 Kashiwabara, Sayama, Saitama 350-1335, Japan

Correspondence e-mail: fuji@chem.saitama-u.ac.jp

Key indicators

Single-crystal X-ray study
 $T = 173\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
H-atom completeness 89%
Disorder in solvent or counterion
 R factor = 0.026
 wR factor = 0.073
Data-to-parameter ratio = 15.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.***cis*-Bis(2,2'-bipyridine-4,4'-dicarboxylic acid- κ^2N,N')dichlororuthenium(II) monohydrate**

The crystal structure of the title compound, $[\text{RuCl}_2(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4)_2]\cdot\text{H}_2\text{O}$, which is a precursor of the dye for dye-sensitized solar cells, is composed of a ruthenium(II) complex molecule containing 2,2'-bipyridine-4,4'-dicarboxylic acid (H_2dcbpy) as a ligand and an uncoordinated water molecule. The overlapped arrangement and the separation of 3.34 (7) Å suggest π - π stacking between parallel H_2dcbpy ligands in neighboring complex molecules. A three-dimensional network is formed by intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds and π - π stacking between neighboring complex molecules.

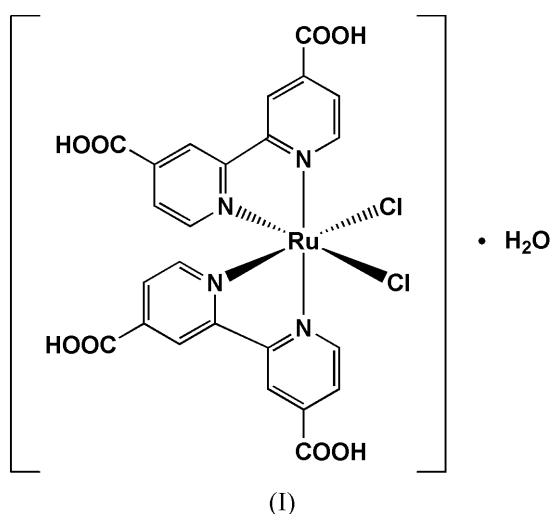
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Comment

Ruthenium complexes containing 2,2'-bipyridine-4,4'-dicarboxylic acid (H_2dcbpy) have received much attention as a photosensitizer for dye-sensitized solar cells (DSC; Grätzel, 2003). The molecular structures of these complexes have been reported (Shklover *et al.*, 1997, 1998). The title compound, (I), is one of the important precursors of those dyes. As a part of a systematic investigation of the properties of these dyes, we reported very recently the crystal and molecular structures of $(\text{Et}_4\text{N}^+)_2(\text{dcbpy}^{2-})\cdot 4\text{H}_2\text{O}$, which contains a dianion component of the dye (Fujihara *et al.*, 2004). It is also important from the chemical and materials scientific points of view to elucidate the structural features of (I). We report here its crystal structure.



The molecular structure of (I) is illustrated in Fig. 1. The compound is isomorphous with the dibromo analogue *cis*- $[\text{RuBr}_2(\text{H}_2\text{dcbpy})_2]\cdot\text{H}_2\text{O}$, (II) (Eskelinen *et al.*, 2000). The central Ru^{2+} ion has an octahedral coordination geometry formed by two chloride ions and two H_2dcbpy ligands.

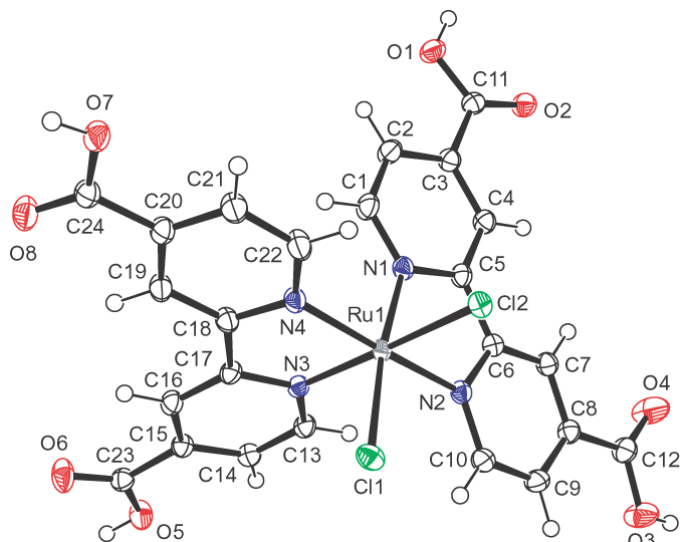


Figure 1
A view of the complex molecule in (I), with 50% probability displacement ellipsoids and the atom-numbering scheme.

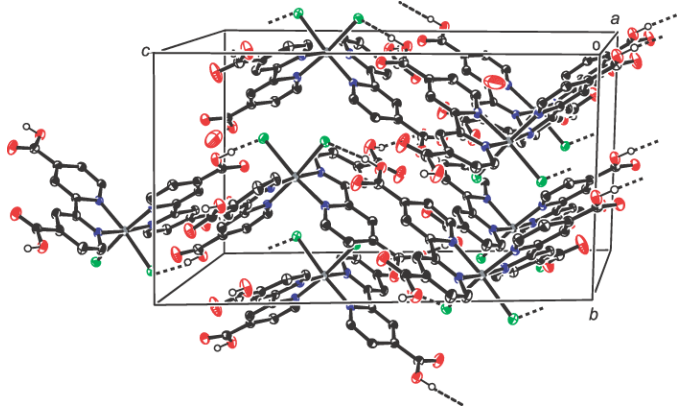


Figure 2
A molecular packing diagram of (I). The dashed lines indicate hydrogen bonds.

Selected bond lengths and angles are given in Table 1. The average Ru—Cl bond length of 2.421 (9) Å is comparable to that for the bipyridine (bpy) analogue *cis*-[RuCl₂(bpy)₂] [2.426 (1) Å, (III) (Eggleston *et al.*, 1985), which indicates that the electronic influence of the carboxylate substituents at the 4- and 4'-positions is not so strong. The Ru—N bond lengths for the N atom *trans* to the N atom of the other H₂dcbpy ligand [Ru—N2 = 2.0419 (14) Å and Ru—N4 = 2.0426 (14) Å] are nearly the same as the value of 2.054 (2) Å observed in (III). The Ru—N bond lengths for the N atom *trans* to the chloride ion [Ru—N1 = 2.0063 (14) Å and Ru—N3 = 2.0295 (14) Å] are significantly shorter than those *trans* to another H₂dcbpy N atom. These notable structural features for (I) are similar to those observed in (III). The bond lengths and angles for the H₂dcbpy ligands are almost the same as for the free ligand (dcbpy²⁻; Fujihara *et al.*, 2004). The average dihedral angle between pyridine planes is 9 (2)°, slightly larger than that for (III) (1.3°). The average dihedral angle between the pyridine ring and the carboxyl group (C/O/O) is 3.5 (9)°,

which is slightly smaller than that for free dcbpy²⁻ [8.2 (3)°; Fujihara *et al.*, 2004]. An overlapped arrangement of parallel H₂dcbpy ligands in neighboring complex molecules is observed in the crystal structure (Fig. 2). The H₂dcbpy ligands in (I), related by symmetry transformation ($x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$), are separated by 3.34 (7) Å. This finding suggests the existence of a π - π stacking interaction between H₂dcbpy ligands. Carboxylate atoms O1, O3, O5 and O7 act as hydrogen-bond donors, forming intermolecular hydrogen bonds with the nearest neighbor *cis*-[RuCl₂(H₂dcbpy)₂] molecules (Fig. 2 and Table 2). The above-mentioned π - π stacking interactions and the intermolecular hydrogen bonds permit the formation of a three-dimensional network in the crystal structure.

Experimental

The compound (I) was synthesized according to a literature method (Liska *et al.*, 1988). Single crystals of (I) suitable for X-ray diffraction were grown from a dimethylformamide–water solution (4:1) by diffusion of acetone vapor at room temperature in the dark to avoid possible *trans* isomerization. Analysis found: C 42.37, H 2.75, N 8.38%; calculated for C₂₄H₁₈Cl₂N₄O₉Ru: C 42.49, H 2.67, N 8.26%.

Crystal data

[RuCl₂(C₁₂H₈N₂O₄)₂] \cdot H₂O
M_r = 678.39
 Monoclinic, *P*2₁/*n*
a = 12.2172 (7) Å
b = 11.0152 (7) Å
c = 19.5064 (12) Å
 β = 106.999 (1)°
V = 2510.4 (3) Å³
Z = 4

D_x = 1.795 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 5415 reflections
 θ = 2.3–27.9°
 μ = 0.90 mm⁻¹
T = 173 (2) K
 Block, black
 0.26 \times 0.23 \times 0.21 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.800, *T_{max}* = 0.833
 17 958 measured reflections

5983 independent reflections
 5466 reflections with *I* > 2 σ (*I*)
R_{int} = 0.021
 θ_{max} = 27.9°
h = -16 \rightarrow 15
k = -14 \rightarrow 14
l = -19 \rightarrow 25

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.026
wR(*F*²) = 0.073
S = 1.05
 5983 reflections
 387 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 1.3308P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.68 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.43 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cl2—Ru1	2.4299 (4)	N2—Ru1	2.0426 (14)
Cl1—Ru1	2.4123 (4)	N3—Ru1	2.0295 (14)
N1—Ru1	2.0063 (14)	N4—Ru1	2.0419 (14)
O2—C11—O1	123.86 (16)	N1—Ru1—N2	79.37 (6)
O6—C23—O5	123.49 (17)	N4—Ru1—N2	173.90 (6)
O4—C12—O3	123.94 (18)	N1—Ru1—Cl1	173.21 (4)
O8—C24—O7	124.54 (16)	N3—Ru1—Cl2	174.04 (4)
N3—Ru1—N4	79.16 (6)	Cl1—Ru1—Cl2	86.420 (16)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H52 \cdots O6 ⁱ	0.87 (3)	1.80 (3)	2.6634 (19)	174 (3)
O1—H51 \cdots Cl1 ⁱⁱ	0.89 (3)	2.06 (3)	2.9355 (14)	168 (2)
O7—H54 \cdots O2 ⁱⁱⁱ	0.84 (3)	1.83 (3)	2.6564 (18)	168 (3)
O5—H53 \cdots Cl2 ^{iv}	0.85 (3)	2.22 (3)	3.0404 (14)	164 (2)

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

H atoms of the carboxyl groups in H₂dc bpy were located in difference Fourier maps and refined isotropically. Other H atoms in H₂dc bpy were placed in calculated positions, with C—H = 0.95 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$. The positions of the water molecule were found to be affected by disorder and the occupancies at both sites were allowed to refine with their sum constrained to unity. This resulted in final occupancies of 0.710 (5) and 0.290 (5). No attempt was made to find or to place geometrically the H atoms on the water molecule.

Data collection: *SMART-W2K/NT* (Bruker, 2003); cell refinement: *SAINT-W2K/NT* (Bruker, 2003); data reduction: *SAINT-W2K/NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 2003); program(s) used to refine structure: *SHELXTL-NT*; molecular

graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT*.

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