

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1191). Services for accessing these data are described at the back of the journal.

## References

- Boschmann, E., Nypaver, G. A., Major, J. P., Ealy, S. M. & Vanhorn, M. (1978). *J. Coord. Chem.* **7**, 141–147.
- Boschmann, E., Weinstock, L. & Carmack, M. (1974). *Inorg. Chem.* **13**, 1297–1300.
- Childers, L. S., Foltz, K., Merritt, L. Jr & Streib, W. E. (1975). *Acta Cryst.* **B31**, 924–926.
- Choi, S.-N., Kwon, M. A., Kim, Y., Bereman, R. D., Singh, P., Knight, B. & Seff, K. (1995). *J. Coord. Chem.* **34**, 241–252.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Fraencl, G., Appleman, B. & Ray, J. G. (1974). *J. Am. Chem. Soc.* **96**, 5113–5119.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- 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.
- Togni, A., Rihs, G., Pregosin, P. S. & Ammann, C. (1990). *Helv. Chim. Acta*, **73**, 723–732.
- Wroblewski, J. T. & Long, G. J. (1977). *Inorg. Chem.* **16**, 704–709.

*Acta Cryst.* (1998). **C54**, 1584–1586

## *cis*-(2,2'-Bipyridyl-*N,N'*)carbonyl(methanato-*C*)( $\eta^2$ -2,2':6',2''-terpyridyl-*N,N'*)-ruthenium(II) Hexafluorophosphate

DOROTHY H. GIBSON, BRADLEY A. SLEADD, MARK S. MASHUTA AND JOHN F. RICHARDSON

Department of Chemistry and, Center for Chemical Catalysis, University of Louisville, Louisville, KY 40292, USA. E-mail: dhgibs01@homer.louisville.edu

(Received 17 February 1998; accepted 5 May 1998)

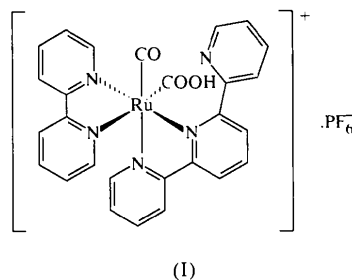
## Abstract

The title compound, [Ru(CHO<sub>2</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(C<sub>15</sub>H<sub>11</sub>-N<sub>3</sub>)(CO)]PF<sub>6</sub> or *cis*-[Ru(bpy)( $\eta^2$ -tpy)(CO)(COOH)]PF<sub>6</sub> (where bpy is 2,2'-bipyridyl and tpy is 2,2':6',2''-terpyridyl), has distorted octahedral geometry about the Ru atom, a bidentate terpyridyl ligand and a fully chelated bipyridyl ligand. The terminal carbonyl and carboxyl groups are *cis*. The Ru—C—O angle (terminal carbonyl) is distorted from linearity [173.7 (4)°] by the pendant pyridyl group of the *N,N'*-bound tpy ligand, which is hydrogen bonded to the hydroxyl proton of the carboxyl group.

## Comment

In spite of their importance as intermediates in water-gas shift (WGS) reactions (Ford, 1993) and in metal-catalyzed carbon dioxide conversions (Sutin *et al.*, 1997), only two metallocarboxylic acids, MCOOH, have been structurally characterized. The platinum complexes, *trans*-[Pt(Ph)(PEt<sub>3</sub>)<sub>2</sub>(COOH)] (Bennett *et al.*, 1988) and [Pt(COOH){C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-2,6}] (Bennett *et al.*, 1993) exist as dimers, resulting from hydrogen bonding involving the carboxyl groups. A ruthenium complex, *cis*-[Ru(bpy)<sub>2</sub>(CO)(COOH)](CF<sub>3</sub>SO<sub>3</sub>) (Toyohara *et al.*, 1996), showed hydrogen bonding of the carboxyl protons of two molecules of the acid to the oxygen of a bridging water molecule.

We prepared the title compound, (I), because of the importance of such ruthenium complexes in catalytic conversions of carbon dioxide (Sutin *et al.*, 1997).



Compound (I) exists as a monomer with distorted octahedral geometry about the Ru atom. Its formulation as a metallocarboxylic acid follows from its IR spectral

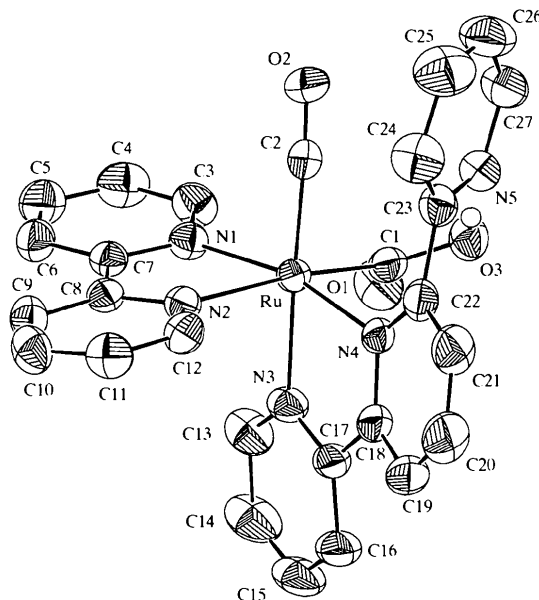


Fig. 1. ORTEPII (Johnson, 1976) plot of the title complex (cation only) showing 50% probability displacement ellipsoids. H atoms (with the exception of HO3) have been omitted for clarity.

properties (see *Experimental*) and from the unequal carboxylate C—O bond distances [C1—O1 1.220(5) and C1—O3 1.360(5) Å]. The longest Ru—N bond is that to N2, which is *trans* to the  $\sigma$ -donating carboxyl group. This bond-lengthening effect has been observed in other octahedral ruthenium–polypyridyl complexes bearing carboxyl groups (Haukka *et al.*, 1995; Tanaka *et al.*, 1993; Toyohara *et al.*, 1996). However, all of the Ru—N bonds in (I) are longer than their counterparts in the acid with two bpy ligands (Toyohara *et al.*, 1996). The hydroxyl proton in (I) is weakly hydrogen bonded to the N5 atom of the pendant pyridyl group of the tpy ligand; the O3...N5 distance is 1.94(5) Å. The resultant twisting of the pendant pyridyl group leads to steric crowding of the terminal carbonyl ligand (C2—O2) and distortion of the Ru—C2—O2 angle from linearity [173.7(4)°]. The unit cell for (I) contains pairs of enantiomers related by the crystallographic center of symmetry.

## Experimental

The synthesis of the title complex was carried out by reaction of *cis*-[Ru(bpy)( $\eta^2$ -tpy)(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (Thomas & Fischer, 1990) in CH<sub>3</sub>CN with aqueous Na<sub>2</sub>CO<sub>3</sub> over a period of 1.5 h at 273 K. The solvent was evaporated and the residue extracted with CH<sub>3</sub>CN. The solvent was again evaporated and the product crystallized by slow diffusion of ether into a solution of the compound in CH<sub>3</sub>CN. The product showed  $\nu_{\text{CO}}$ (DRIFTS) at 1628 and 1060 cm<sup>-1</sup>.

### Crystal data

[Ru(CHO<sub>2</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-  
(C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>)(CO)]PF<sub>6</sub>  
M<sub>r</sub> = 708.52  
Monoclinic  
C2/c  
a = 30.229 (15) Å  
b = 13.009 (3) Å  
c = 14.157 (7) Å  
β = 102.42 (4)°  
V = 5437 (4) Å<sup>3</sup>  
Z = 8  
D<sub>x</sub> = 1.731 Mg m<sup>-3</sup>  
D<sub>m</sub> not measured

Mo K $\alpha$  radiation  
λ = 0.7107 Å  
Cell parameters from 25  
reflections  
θ = 15–18°  
μ = 0.718 mm<sup>-1</sup>  
T = 296 (2) K  
Block  
0.41 × 0.33 × 0.33 mm  
Dark yellow

### Data collection

Enraf–Nonius CAD-4  
diffractometer  
ω/2θ scans  
Absorption correction:  
empirical ψ scans (333  
scans of 9 reflections;  
North *et al.*, 1968)  
T<sub>min</sub> = 0.726, T<sub>max</sub> = 0.789  
5201 measured reflections  
5093 independent reflections

4074 reflections with  
I > 1.5σ(I)  
R<sub>int</sub> = 0.032  
θ<sub>max</sub> = 25°  
h = -35 → 35  
k = -15 → 0  
l = -16 → 0  
3 standard reflections  
frequency: 60 min  
intensity decay: < 0.5%

### Refinement

Refinement on F  
R = 0.040  
wR = 0.044  
S = 2.76  
4074 reflections  
402 parameters  
H atoms: see below  
Weighting scheme based  
on measured s.u.'s;  
w = 1/σ<sup>2</sup>(F)

(Δ/σ)<sub>max</sub> = 0.027  
Δρ<sub>max</sub> = 0.77 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.61 e Å<sup>-3</sup>  
Extinction correction:  
Zachariasen (1967) type  
2 Gaussian isotropic  
Extinction coefficient:  
1.77 (8) × 10<sup>-7</sup>  
Scattering factors from  
Cromer & Waber (1974)

Table 1. Selected geometric parameters (Å, °)

Ru—N1	2.096 (3)	Ru—C2	1.848 (4)
Ru—N2	2.178 (3)	O1—C1	1.220 (5)
Ru—N3	2.113 (3)	O2—C2	1.153 (5)
Ru—N4	2.118 (3)	O3—C1	1.360 (5)
Ru—C1	2.053 (4)	HO3—N5	1.94 (5)
N1—Ru—N2	77.4 (1)	Ru—C1—O3	120.7 (3)
N3—Ru—N4	78.3 (1)	O1—C1—O3	114.8 (4)
N4—Ru—C2	102.6 (2)	Ru—C2—O2	173.7 (4)
Ru—C1—O1	124.4 (3)		

Atomic scattering factors were taken from Cromer & Waber (1974) and corrections for anomalous dispersion effects were made. H atoms were located on ΔF maps and included in fixed positions, with the exception of the HO3 atom, for which coordinates were refined. The disorder in the PF<sub>6</sub><sup>-</sup> anion was modeled with three isotropically refined groups of F atoms (F1a–F6a, F1b–F6b and F1c–F6c), all with site occupancies of 33% bonded to a full-occupancy P atom. F1ab and F2ab are common to two groups. No solvent molecules are present.

Data collection: *CAD-4 Manual* (Schagen *et al.*, 1989). Cell refinement: *CAD-4 Manual*. Data reduction: *DIRDIF94* (Beurskens *et al.*, 1994). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1994). Software used to prepare material for publication: *TEXSAN*.

Support of this work by the United States Department of Energy, Division of Chemical Sciences (Office of Basic Energy Sciences), is gratefully acknowledged. The X-ray equipment was purchased with assistance from the National Science Foundation (grant No. CHE-9016978).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1398). Services for accessing these data are described at the back of the journal. A displacement ellipsoid plot of the disordered anion has also been deposited.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.  
Bennett, M. A., Jin, H. & Willis, A. C. (1993). *J. Organomet. Chem.* **451**, 249–256.  
Bennett, M. A., Robert, G. B., Rokicki, A. & Wickramasinghe, W. A. (1988). *J. Am. Chem. Soc.* **110**, 7098–7105.  
Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1994). *The DIRDIF94 Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 72–98. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Ford, D. C. (1993). *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, edited by B. P. Sullivan, pp. 68–93. Amsterdam: Elsevier.
- Haukka, M., Kiviaho, J., Ahlgren, M. & Pakkanen, T. A. (1995). *Organometallics*, **14**, 825–833.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1994). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3700 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Schagen, J. D., Straver, L., van Meurs, F. & Williams, G. (1989). *CAD-4 Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Sutin, N., Creutz, C. & Fujita, E. (1997). *Comments Inorg. Chem.* **19**, 67–92.
- Tanaka, H., Tzeng, B.-C., Nagao, H., Peng, S.-M. & Tanaka, K. (1993). *Inorg. Chem.* **32**, 1508–1512.
- Thomas, N. C. & Fischer, J. (1990). *Coord. Chem.* **21**, 119–128.
- Toyohara, K., Nagao, H., Adachi, T., Yoshida, T. & Tanaka, K. (1996). *Chem. Lett.* pp. 27–28.
- Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

*Acta Cryst.* (1998). **C54**, 1586–1588

### Bis(acetato- $\kappa^2$ O,O')(di-2-pyridyl- $\kappa$ N-amine)copper(II) Dihydrate

SUJITRA YOUNGME,<sup>a</sup> CHAVENG PAKAWATCHAI,<sup>b</sup> HOONG-KUN FUN<sup>c</sup>† AND KANDASAMY CHINNAKALI<sup>c</sup>‡

<sup>a</sup>Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, <sup>b</sup>Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai 90112, Thailand, and <sup>c</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: sujitra@kku1.kku.ac.th

(Received 3 December 1997; accepted 5 May 1998)

#### Abstract

The copper(II) ion in the title complex, [Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>-(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)]·2H<sub>2</sub>O, is coordinated unsymmetrically to each of the two bidentate acetate ligands and to the N atoms of the di-2-pyridylamine (dpyam) ligand. The copper(II) ion is surrounded by a distorted square-based arrangement of the two dpyam pyridyl N atoms at dis-

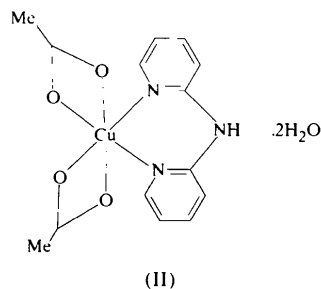
† On sabbatical leave at: The Department of Chemistry, Prince of Songkla University, Hat Yai, Thailand.

‡ On leave from: Department of Physics, Anna University, Chennai 600 025, India.

tances of 1.974 (2) and 1.995 (2) Å, and by two acetate O atoms at distances of 1.965 (1) and 1.967 (1) Å. The second O atom from each acetate group is involved in weak coordination in the tetragonal positions, at longer Cu—O distances of 2.482 (2) and 2.690 (2) Å, completing the six-coordination. The overall geometry at the copper(II) ion is best described as distorted octahedral with elongated axial bonds.

#### Comment

The local molecular stereochemistries of the [Cu(chelate)(OXO)(OYO)] complexes, where chelate is ethylenediamine (en) or 2,2'-bipyridyl (bipy), and OXO and OYO are oxyanions, were characterized by electron-spin resonance (ESR) and electronic spectra (Procter *et al.*, 1972). Mononuclear or polynuclear complexes with axially elongated octahedral stereochemistries were suggested from this stoichiometry. In order to investigate this postulation, the crystal structures of complexes containing the di-2-pyridylamine (dpyam) and other related chelate ligands have been reported. The complexes [Cu(tmen)(NO<sub>3</sub>)<sub>2</sub>], where tmen is *N,N,N',N'*-tetramethylethylenediamine (Pavkovic & Miller, 1977), [Cu(DMAEP)(NO<sub>3</sub>)<sub>2</sub>], where DMAEP is 2-(2-dimethylaminoethyl)pyridine (Lewis & Hodgson, 1973), [Cu(bipy)(NO<sub>2</sub>)<sub>2</sub>] (Stephens, 1969) and [Cu(dpyam)(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>].H<sub>2</sub>O [(I); Munoz *et al.*, 1993] are mononuclear, whereas a polynuclear chain structure is known to exist for the corresponding complexes [Cu(dpyam)(CH<sub>3</sub>CO<sub>2</sub>)(ClO<sub>4</sub>)].H<sub>2</sub>O (Ray *et al.*, 1982), [Cu(dpyam)(CH<sub>3</sub>CO<sub>2</sub>)(NO<sub>3</sub>)] (Aduldecha & Hathaway, 1991) and [Cu(dpyam)(CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>)(NO<sub>3</sub>)] (Youngme *et al.*, 1998). In a search for additional examples containing this type of stoichiometry with the dpyam chelate ligand, the crystal structure of [Cu(dpyam)(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>].2H<sub>2</sub>O, (II), has been determined and compared with the known structures of relevant complexes.



The crystal structure of (II) is composed of discrete monomeric molecules with an irregular (4+2) coordination polyhedron about copper. This arrangement consists of two dpyam N atoms and two acetate O atoms forming a tetrahedrally distorted square base. A second O atom from each acetate group then occupies the tetragonal position above and below the CuN<sub>2</sub>O<sub>2</sub> basal