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Aqua(cyclobutane-1,1-dicarboxylato-κ^2O,O')(di-2-pyridylamine-κ^2N,N')copper(II) trihydrate

Masahiro Yodoshi, Mari Mototsuji and Nobuo Okabe*

Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashiosaka, Osaka 577-8502, Japan

Correspondence e-mail:
okabe@phar.kindai.ac.jp

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In the title complex, $[Cu(C_6H_6O_2)(C_{10}H_9N_3)(H_2O)]\cdot 3H_2O$, the Cu atom has a distorted *cis*-square-pyramidal geometry formed by two O atoms of a bidentate cyclobutane-1,1-dicarboxylate anion, two N atoms of a bidentate di-2-pyridylamine (bpa) molecule and a water O atom. In the crystal structure, the complex molecules are connected by hydrogen bonds through the water molecules, and by π–π stacking interactions between bpa ligands.

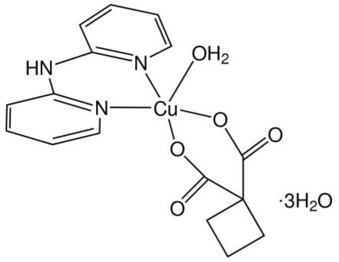
Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.021
wR factor = 0.060
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

cis-Diamminedichloroplatinum(II) (cisplatin) and *cis*-diammmine(cbdca)platinum(II) (carboplatin), where cbdca is cyclobutane-1,1-dicarboxylate, are well known therapeutic anticancer drugs. The Pd(II) analogues have been used as good models for studies of their coordination chemistry. We have synthesized and determined the crystal structures of some *cis*-coordinated Pd complexes with heterocyclic ligands such as 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and di-2-pyridylamine (bpa) (Muranishi & Okabe, 2004; Okabe *et al.*, 2006). In recent years, studies on the interaction of transition metal complexes with nucleic acids have been actively advanced (Li *et al.*, 2005). A number of ternary Cu^{II} complexes with various kinds of ligand species have been synthesized and the interaction of these complexes with DNA has been investigated (Antolini *et al.*, 1985; Wang & Okabe, 2005; Liu *et al.*, 2006). In the present study, we have characterized the ternary Cu^{II} complex, (I), with a heterocyclic ligand, bpa, and cbdca.



(I)

The Cu atom in (I) (Fig. 1 and Table 1) has a distorted *cis*-square-pyramidal geometry formed by two O atoms of a bidentate cbdca anion, two N atoms of a bidentate bpa ligand and a water O atom in the apical position. The coordination geometry in (I) resembles those of [Pd(bpy)(cbdca)], [Pd(phen)(cbdca)] and [Pd(bpa)(cbdca)] (Muranishi & Okabe, 2004; Okabe *et al.*, 2006). The Cu atom deviates by 0.2123 (7) Å from the mean plane through atoms N1, N2, O1 and O3. The dihedral angle between the Cu1/N1/N2 and Cu1/O1/O3 planes is 18.7 (1)°. The two pyridine rings in the bpa ligand are not coplanar, with a dihedral angle of 23.15 (8)°.

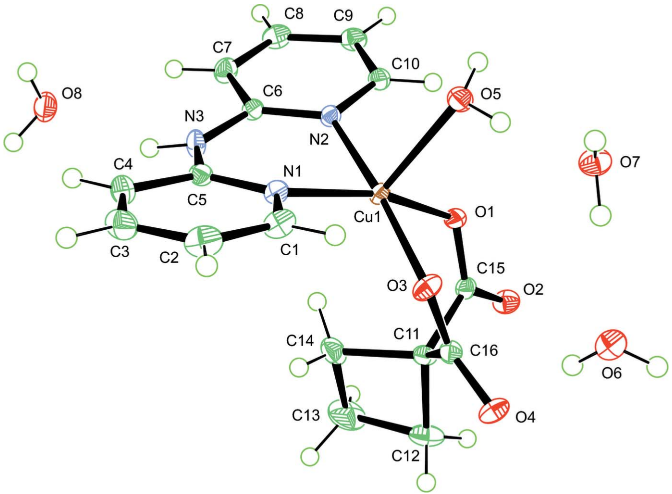


Figure 1
The structure of the cationic complex of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

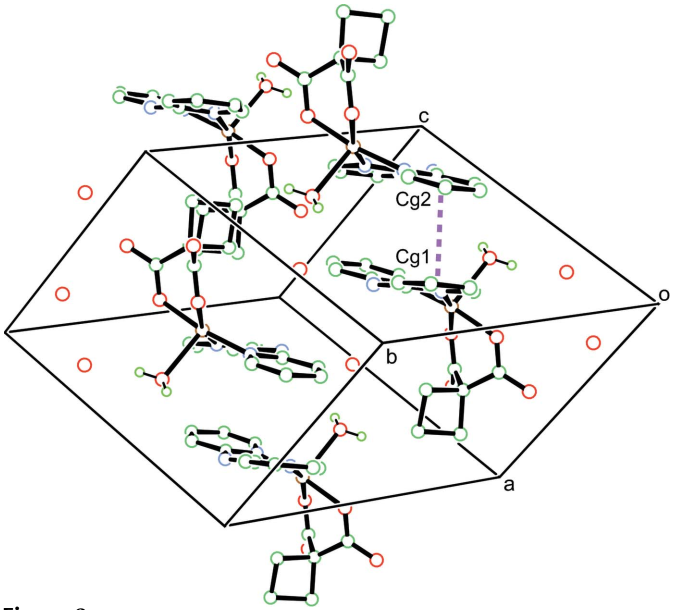


Figure 2
A view of the π–π stacking interaction in (I). *Cg*1 is the centroid of the N1/C1–C5 pyridine ring and *Cg*2 is the centroi of N3/C6–C10 at (x, $1 - y$, $1 - z$). H atoms, except those of coordinated water, have been omitted.

The Cu1—N bond distances are slightly longer than those in Cu(bpa)Cl_2 [1.948 (6) Å; Spodine *et al.*, 1996]. The Cu1—O1/O3/O5 distances are also slightly longer than the respective Cu—O distances of 1.947 (4), 1.904 (4) and 2.299 (4) Å reported for the analogous ternary complex [Cu(lactate)(phen)(OH_2)] (Carballo *et al.*, 2001). By contrast, longer Cu—N [2.119 (12) Å] and Cu—O [2.002 (11) and 2.325 (3) Å] bond distances are observed in [Cu(tmen)(cdbca)], where tmen is tetramethylethylenediamine (Pajunen *et al.*, 1979). The longest Cu—O bond length is explained by the well known Jahn–Teller effect.

The crystal structure is stabilized by all of the available O—H···O-type hydrogen bonds between carbonyl atoms of cbdca and the water molecules, and N—H···O hydrogen bonds between the imino group of bpa and a solvent water molecule (Table 2). There are also π–π stacking interactions present between bpa ligands, which also contribute to the stabilization of the crystal packing (Fig. 2). The distance between the centroids of the pyridine rings, *Cg*1 (N1/C1–C5) and *Cg*2 (N2/C6–C10) at (x, $1 - y$, $1 - z$) is 3.808 (4) Å (Spek, 2003).

Experimental

A 1:1 molar ration of bpa (10.0 mg) dissolved in dimethylformamide (DMF, 5 ml) was reacted with $CuCl_2 \cdot 2H_2O$ (9.96 mg), dissolved in DMF (1 ml), for 5 min at room temperature. This was followed by the addition of cbdca (8.42 mg) dissolved in distilled water (1 ml), and reacted for 1 h at room temperature. The reaction mixture was left to stand at room temperature and after several days blue prismatic crystals of (I) appeared from the mother liquor.

Crystal data

$[Cu(C_6H_6O_2)(C_{10}H_9N_3)(H_2O)] \cdot 3H_2O$
$M_r = 448.92$
Triclinic, $P\overline{1}$
$a = 8.810\ (9)$ Å
$b = 11.19\ (1)$ Å
$c = 11.203\ (9)$ Å
$\alpha = 70.31\ (3)°$
$\beta = 80.18\ (3)°$
$\gamma = 67.11\ (3)°$
$V = 957.0\ (15)$ Å^3
$Z = 2$
$D_x = 1.558$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.19$ mm^{-1}
$T = 123$ K
Prism, blue
0.30 × 0.30 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.712$, $T_{max} = 0.789$
9508 measured reflections
4401 independent reflections
4099 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.011$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.060$
$S = 1.08$
4401 reflections
278 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 0.4273P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O1	1.962 (2)	Cu1—N1	1.999 (2)
Cu1—O3	1.957 (1)	Cu1—N2	1.983 (1)
Cu1—O5	2.254 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H9···O8	0.86	2.00	2.799 (2)	154
O5—H16···O7	0.81	1.93	2.734 (2)	168
O5—H17···O2^{i}	0.81	2.01	2.811 (3)	173 (1)
O6—H18···O4^{ii}	0.79	2.04	2.818 (3)	164 (2)
O6—H19···O4	0.82	2.00	2.810 (2)	173
O7—H20···O6	0.81	1.93	2.734 (3)	178
O7—H21···O2^{iii}	0.81	1.96	2.756 (2)	164 (1)
O8—H22···O5^{iv}	0.81	2.05	2.852 (3)	172 (1)
O8—H23···O7^{v}	0.81	2.07	2.848 (3)	161 (2)

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

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All H atoms were located in difference Fourier maps and refined in the riding-model approximation, with C—H = 0.93–0.97, N—H = 0.86 and O—H = 0.85 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N) or 1.5$U_{\rm eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *CrystalStructure*.

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References

Antolini, L., Marcotrigiano, G., Menabue, L., Pellacani, G. C., Saladini, M. & Sola, M. (1985). *Inorg. Chem.* **24**, 3621–3626.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Carballo, R., Covelo, B., Balvoa, S., Castineiras, A. & Niclos, J. (2001). *Z. Anorg. Allg. Chem.* **627**, 948–954.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Li, H., Le, X.-Y., Pang, D.-Y., Deng, H., Xu, Z.-H. & Lin, Z.-H. (2005). *J. Inorg. Biochem.* **99**, 2240–2247.

Liu, F. Q., Wang, Q. X., Jiao, K., Jian, F. F., Liu, G. Y. & Li, R. X. (2006). *Inorg. Chim. Acta*, **359**, 1524–1530.

Muranishi, Y. & Okabe, N. (2004). *Acta Cryst.* C**60**, m47–m50.

Okabe, N., Mizubayashi, Y. & Odoko, M. (2006). *Acta Cryst.* E**62**, m2747–m2749.

Pajunen, A. & Pajunen, S. (1979). *Acta Cryst.* B**35**, 2401–2403.

Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2005). *CrystalStructure*. Version 3.7. Rigaku/MSC, The Woodlands, Texas, USA.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Spodine, E., Atria, A. M., Baggio, R. & Garland, M. T. (1996). *Acta Cryst.* C**52**, 1407–1410.

Wang, Y. & Okabe, N. (2005). *Inorg. Chim. Acta*, **358**, 3407–3416.

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