Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Aqua[*N*-(6-carboxylato-κ*O*-pyridine-2-carbonyl-κ*N*)-L-histidinato-κ^2*N*,*N*′]copper(II)

Takayuki Kato,[a]* Kunihisa Sugimoto[b] and Mikio Yamasaki[b]

[a]Department of Industrial Chemistry, Ashikaga Institute of Technology, 268-1 Omae-cho, Ashikaga, Tochigi 326-8558, Japan, and [b]X-Ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan
Correspondence e-mail: tkato@ashitech.ac.jp

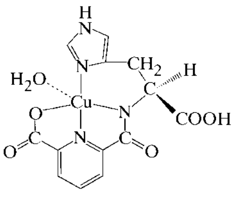
Received 22 May 2001
Accepted 30 July 2001

The title compound, [Cu($C_{13}H_{10}N_4O_5$)(H_2O)], is an asymmetric and pentacoordinated square-pyramidal copper(II) complex, with a water molecule occupying an apical position. It consists of *syn* and *anti* isomers of the apical water molecule with respect to the metal-free carboxyl group on the equatorial ligand. The crystal structure of this complex is a rare example of conformational isomerization, in which the two isomers cocrystallize in a 1:3 ratio of *syn* to *anti* molecules in the same lattice.

Comment

In the context of a study on the characteristic ligancy of asymmetric metal complexes, we have focused on the molecular and crystal structures of asymmetric copper(II) complexes. We report here the characteristic molecular conformation and crystal structure of the title compound, (I).

The atoms and atom groups of the equatorial tetradentate ligand in (I) are almost coplanar, except for the methylene group, the inclined imidazole ring and the metal-free carboxyl group. The six-membered chelate ring formed by the imidazole ring and the amide group as they coordinate to the metal has a twisted half-chair conformation, in accordance with the axial preference of the carboxyl substituent (Ertan & Csoregh, 1995; Uehara *et al.*, 1999).



(I)

The apical water molecule has *syn* and *anti* coordination modes with respect to the axial carboxyl group. It is noteworthy that the unit cell consists of the isomers with a 1:3 ratio of *syn* to *anti* molecules (Fig. 2). The best mean basal plane of the first *anti* isomer, defined by O1, N1, N2 and N4, is planar to within 0.02 (3) Å, and atom Cu1 is displaced by 0.17 (3) Å toward the apical water molecule from this basal plane. For the Cu2 and Cu3 complexes, the corresponding values of the best mean basal planes are 0.04 (5) and 0.04 (5) Å, respectively, and the displacements of the Cu atoms are 0.16 (5) and 0.17 (5) Å, respectively.

The coordination geometry around the Cu atom of the *syn* isomer is almost the same as those of the *anti* isomers, except for the situation of the apical water molecule. The best mean basal plane of the *syn* isomer, defined by O19, N13, N14 and N16, is planar to within 0.06 (6) Å, and atom Cu4 is displaced by 0.12 (6) Å toward the apical water molecule. The equatorial conformation of the *syn* isomer is basically the same as those of the *anti* isomers, but with a somewhat different inclination angle between the imidazole ring and the basal plane. The inclined angle (25°) of the imidazole ring to the basal plane of the *syn* isomer is larger than those of the *anti* isomers, which are in the range 3.6 (6)–5.7 (6)°.

The distances between each apical water molecule and the respective Cu atom of the *anti* isomers are 2.347 (2), 2.296 (2) and 2.275 (3) Å, and that of the *syn* isomer is 2.333 (2) Å.

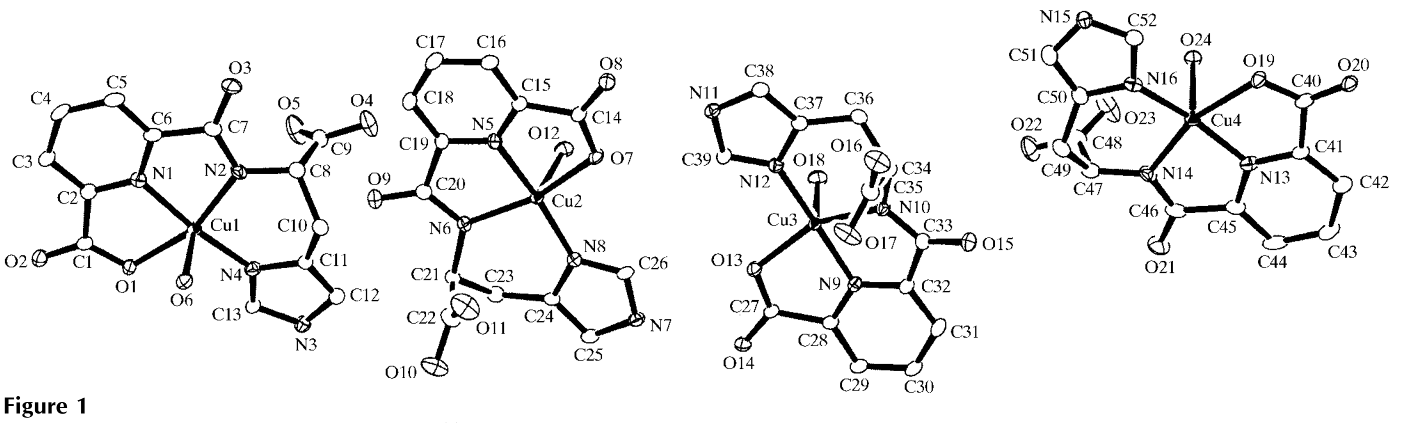


Figure 1
The molecular structure of the four isomers in (I), showing the atom-numbering schemes with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

These bond lengths are comparable with the corresponding distances in analogous pentacoordinated copper(II) complexes, *viz.* 2.2681 (18) Å for the glycolate complex (Medina *et al.*, 2000), 2.309 (3) Å for the propanediaminate complex (Arıcı *et al.*, 1999), 2.355 (4) Å for the glycinate complex (Alvarez-Larena *et al.*, 1995) and 2.294 (6) Å for the L-glutamate complex (Antorini *et al.*, 1983).

The O23···O24 distance in the *syn* isomer indicates the existence of a significant O—H···O hydrogen-bonding interaction between the apical water molecule and the carboxyl group. Therefore, the O24—Cu4—N14 angle of the *syn* isomer [95.9 (1)°] is smaller than the corresponding angles of the *anti* isomers [98.45 (9)–106.43 (9)°].

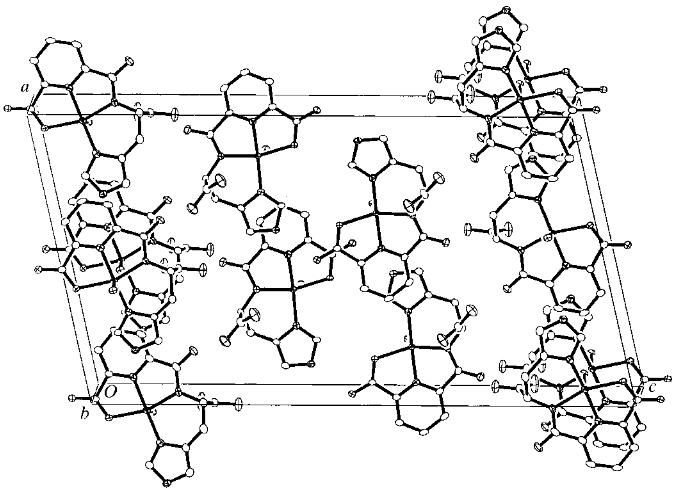


Figure 2
The packing of the molecules of (I).

The C=C distances in the oxalic acid moieties of the *syn* and *anti* isomers are in the range 1.507 (4)–1.520 (4) Å. These distances are similar to the value of 1.526 Å observed for the C=C distance in [Cu($C_{21}H_{17}N_3O_5$)(H_2O)] (Ertan & Csoregh, 1995), in which the oxalic acid moieties coordinate to the Cu^{II} atom.

The O3···O16 and O4···O9 distances are 2.553 (3) and 2.538 (3) Å, respectively, and indicate the existence of a significant O—H···O hydrogen-bonding interaction between each *anti* isomer.

Experimental

A solution of L-histidine (20 mmol) in 0.5 *M* NaOH solution (50 ml) and a 2 *M* NaOH solution (30 ml) were added dropwise to a suspension of 2,6-pyridinedicarbonyl dichloride (20 mmol) in CH_2Cl_2 (50 ml) with stirring over a period of 30 min. The mixture was then stirred for an additional 3 h at room temperature. 6 *M* HCl was added to the separated water phase until a pH of 4 was reached. $CuSO_4 \cdot 5H_2O$ (18 mmol) was added to the resultant reaction mixture. Compound (I) precipitated as blue crystals after several days. Crystals of (I) suitable for single-crystal X-ray analysis were obtained from a high-performance liquid chromatographic purification on an ODS column (ODS is octadecasilane-covered silica gel) followed by slow evaporation of the solvent at room temperature.

Crystal data

[Cu($C_{13}H_{10}N_4O_5$)(H_2O)]
M_r = 383.81
Monoclinic, $P2_1$
a = 15.983 (1) Å
b = 6.5095 (4) Å
c = 29.068 (1) Å
β = 102.2801 (5)°
V = 2955.0 (3) $Å^3$
Z = 8

D_x = 1.725 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9082 reflections
θ = 3.1–27.5°
μ = 1.52 mm^{-1}
T = 123 (1) K
Plate, blue
0.2 × 0.2 × 0.1 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.731, T_{max} = 0.859
21 831 measured reflections

7102 independent reflections (plus 5197 Friedel-related reflections)
11 052 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.076
θ_{max} = 27.5°
$h = -20 \rightarrow 19$
$k = -8 \rightarrow 7$
$l = -37 \rightarrow 37$

Refinement

Refinement on F^2
$R(F)$ = 0.032
$wR(F^2)$ = 0.074
S = 1.34
12 299 reflections
902 parameters
H-atom parameters constrained

$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.90 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.03 e $Å^{-3}$
Absolute structure: Flack (1983)
Flack parameter = 0.015 (7)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	2.065 (2)	Cu3—O13	2.076 (2)
Cu1—O6	2.347 (2)	Cu3—O18	2.275 (3)
Cu1—N1	1.917 (3)	Cu3—N9	1.920 (2)
Cu1—N2	1.976 (3)	Cu3—N10	1.974 (3)
Cu1—N4	1.928 (3)	Cu3—N12	1.930 (2)
Cu2—O7	2.073 (2)	Cu4—O19	2.067 (2)
Cu2—O12	2.296 (2)	Cu4—O24	2.333 (2)
Cu2—N5	1.920 (2)	Cu4—N13	1.917 (3)
Cu2—N6	1.975 (3)	Cu4—N14	1.993 (3)
Cu2—N8	1.926 (2)	Cu4—N16	1.922 (3)
O1—Cu1—O6	89.71 (9)	O13—Cu3—O18	86.75 (8)
O1—Cu1—N1	79.5 (1)	O13—Cu3—N9	79.48 (9)
O6—Cu1—N1	94.95 (11)	O18—Cu3—N9	96.72 (9)
O1—Cu1—N2	159.8 (1)	O13—Cu3—N10	157.44 (9)
O6—Cu1—N2	98.45 (9)	O18—Cu3—N10	106.43 (9)
N1—Cu1—N2	81.36 (12)	N9—Cu3—N10	80.8 (1)
O1—Cu1—N4	101.62 (11)	O13—Cu3—N12	102.43 (9)
O6—Cu1—N4	96.87 (9)	O18—Cu3—N12	91.3 (1)
N1—Cu1—N4	168.13 (12)	N9—Cu3—N12	171.83 (12)
N2—Cu1—N4	95.74 (12)	N10—Cu3—N12	95.6 (1)
O7—Cu2—O12	86.75 (8)	O19—Cu4—O24	88.53 (9)
O7—Cu2—N5	79.86 (9)	O19—Cu4—N13	79.5 (1)
O12—Cu2—N5	96.3 (1)	O24—Cu4—N13	97.2 (1)
O7—Cu2—N6	157.80 (9)	O19—Cu4—N14	160.9 (1)
O12—Cu2—N6	105.88 (9)	O24—Cu4—N14	95.9 (1)
N5—Cu2—N6	80.6 (1)	N13—Cu4—N14	81.47 (11)
O7—Cu2—N8	102.45 (9)	O19—Cu4—N16	102.61 (11)
O12—Cu2—N8	91.3 (1)	O24—Cu4—N16	93.19 (11)
N5—Cu2—N8	172.25 (12)	N13—Cu4—N16	169.46 (13)
N6—Cu2—N8	95.6 (1)	N14—Cu4—N16	95.74 (12)

Table 2
Contact distances (Å).

O3···O16^{i}	2.553 (3)	O23···O24	2.692 (3)
O4···O9^{ii}	2.538 (3)		

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

The H atoms of the H_2O and COOH groups were not fixed because they could not be found from the difference Fourier map. All other H atoms were refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2001); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1998); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

We thank Dr Shinji Masuda of the Ashikaga Institute of Technology for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1117). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1998). *J. Appl. Cryst.* **32**, 115–119.

Alvarez-Larena, A., Brianso-Penalva, J. L. & Piniella, J. F. (1995). *Acta Cryst.* C**51**, 852–854.

Antorini, L., Marcotrigiano, G. & Pellacani, G. C. (1983). *Inorg. Chem.* **22**, 141–145.

Arıcı, C., Ercan, F., Atakol, O. & Cakırer, O. (1999). *Acta Cryst.* C**55**, 1654–1655.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Ertan, A. & Csoregh, I. (1995). *Acta Cryst.* C**51**, 385–392.

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

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Medina, G., Gasque, L. & Bernes, S. (2000). *Acta Cryst.* C**56**, 766–768.

Rigaku (2001). *CrystalClear* (Version 1.3) and *CrystalStructure* (Version 2.00). Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.

Uehara, F., Sato, M., Kaneko, C. & Kurihara, H. (1999). *J. Org. Chem.* **64**, 1436–1441.

Watkin, D. J., Prout, C. K., Carruthers, J. R. & Betteridge, P. W. (1996). *CRYSTALS*. Issue 10. Chemical Crystallography Laboratory, University of Oxford, England.