Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(μ-3-carboxylatophenoxyacetato)bis[(1*H*-imidazole)copper(II)] dihydrate

Shan Gao,* Chang-Sheng Gu, Li-Hua Huo, Ji-Wei Liu and Jing-Gui Zhao

School of Chemistry and Materials Science,
Heilongjiang University, Harbin 150080,
People's Republic of China

Correspondence e-mail:
shangao67@yahoo.com

Received 5 November 2004
Accepted 17 November 2004
Online 27 November 2004

Key indicators

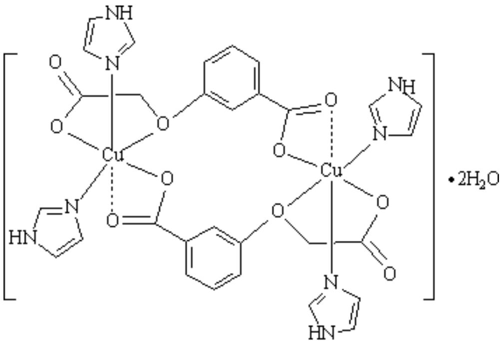
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.099
Data-to-parameter ratio = 16.5

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

In the title centrosymmetric dinuclear complex, $[Cu_2(3\text{-}CPOA)_2(C_3H_4N_2)_4]\cdot 2H_2O$ (3-CPOA^{2-} is the 3-carboxylatophenoxyacetate dianion, $C_9H_6O_5$), each Cu^{II} ion is coordinated by three carboxyl O atoms, one ether O atom from two 3–CPOA^{2-} groups and two N atoms from two imidazole co-ligands, displaying an elongated square-pyramidal coordination geometry with a based capped by one very long semicoordinate Cu—O$_{carboxyl}$ bond [2.8191 (15) Å]. The two Cu^{II} ions are bridged by 3–CPOA^{2-} ligands, generating a macrocyclic ring motif, with a Cu$\cdots$Cu separation of 6.879 (3) Å. The dinuclear motifs are further linked into a two-dimensional supramolecular network *via* hydrogen-bonding interactions.

Comment

The design and construction of supramolecular complexes with extended architectures utilizating non-covalent linkages, such as hydrogen-bond interactions, has been a rapidly developing research area in recent years (Iglesias *et al.*, 2003; Burrows *et al.*, 1997). Hydrogen-bonding interactions between ligands are specific and directional, and have little dependence on the properties of metal ions; they play a critical role in the structures and functions of the products. In this sense, 3-carboxyphenoxyacetic acid (3-CPOAH$_2$) is an excellent candidate for the construction of supramolecular complexes, since it not only has multiple coordination modes but also can form regular hydrogen bonds by functioning as both hydrogen-bond donor and acceptor (Gu *et al.*, 2004). However, the coordination chemistry of 3-carboxyphenoxyacetic acid has received little attention to date.



(I)

We have previously reported the structures of mononuclear Ni^{II} and Co^{II} complexes (Gao *et al.*, 2004; Li *et al.*, 2004) based on this ligand, in which intermolecular hydrogen bonds result in a supramolecular network structure. We describe here a dinuclear Cu^{II} complex with an extended two-dimensional

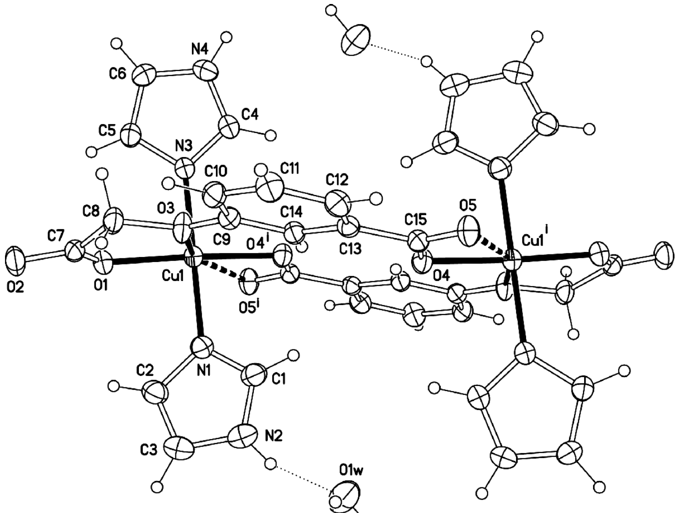


Figure 1
*ORTEP*II plot (Johnson, 1976) of the title complex, shown with 30% probability ellipsoids. Hydrogen bonds are shown as dashed and dotted lines. Symmetry code (i) as in Table 1.

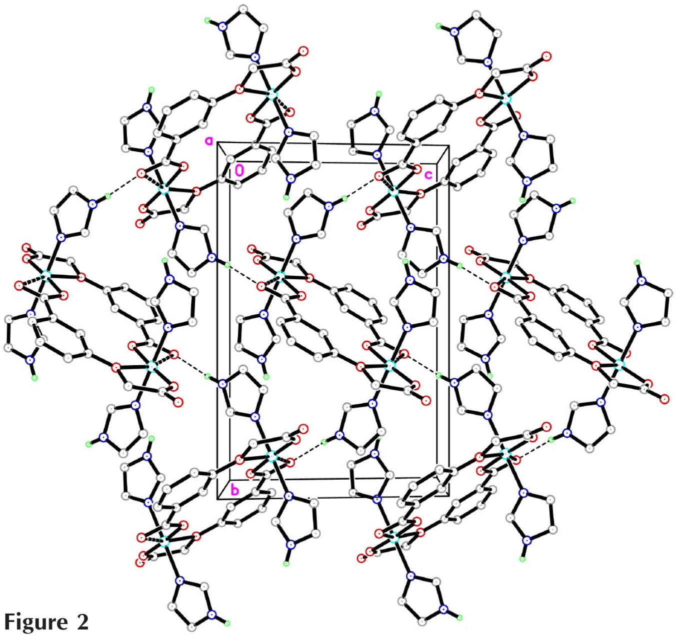


Figure 2
The two-dimensional hydrogen-bonding (dashed lines) in the title complex. The H atoms on C atoms and of water molecules have been omitted.

hydrogen-bonding supramolecular architecture, $[Cu_2(3\text{-}CPOA)_2(C_3H_4N_2)_4]\cdot 2H_2O$ (3-CPOA^{2-} is the 3-carboxylatophenoxyacetate dianion), (I), obtained by the reaction of 4-carboxyphenoxyacetic acid, imidazole and copper diacetate monohydrate in an aqueous solution.

As illustrated in Fig. 1, the title complex consists of a neutral centrosymmetric dinuclear Cu^{II} complex, $[Cu_2(3\text{-}CPOA)_2(C_3H_4N_2)_4]$, and two water molecules. The unique water molecule (O1*W*) forms an intermolecular hydrogen bond with the uncoordinated imidazole N2 atom, with an N$\cdots$O bond length of 2.712 (3) Å and an N—H$\cdots$O bond angle of 158°. Each Cu^{II} ion is coordinated by three carboxylate O atoms and one ether O atom from two 3-CPOA^{2-} groups and by two N atoms from two imidazole co-ligands, and the local coordination geometry around the Cu^{II} ion can be described as elongated square-pyramidal with a based capped by one long semicoordinate Cu—O5^{i} bond [symmetry code: (i) $-x, 1-y, 1-z$] of 2.8191 (15) Å (Sieroń *et al.*, 2002). The basal plane is defined by atoms O1, O4^{i}, N1 and N3, with an r.m.s. deviation of 0.02 (3) Å. The Cu^{II} ion is displaced from the mean basal plane by 0.02 (3) Å. Atom O3 occupies the apical site, with a Cu—O distance of 2.3814 (18) Å. The Cu—O distances fall in the range 1.9513 (16)–2.8191 (15) Å, within which the Cu—O1(oxycarboxyl) distance is considerably shorter (Table 1).

The 3-CPOA^{2-} group exhibits interesting coordination modes with the metal ion. The carboxyl group is in a monodentate mode through atom O4, while the oxyacetate group combines with the Cu^{II} center through ether atom O3 and carboxyl atom O1 to give one five-membered chelate ring (O1/C7/C8/O3/Cu); the r.m.s. deviation for the five atoms is 0.06 (3) Å. The O1—C7 and O4—C15 distances are somewhat longer than the O2—C7 and O5—C15 distances, in accord with greater double-bond character of the latter bonds. The oxyacetate group and benzene ring are not coplanar, the torsion angle being −164.43 (19)° (C9—O3—C8—C7). The dihedral angles between the benzene ring and the imidazole co-ligands are 76.6 (8) and 88.2 (8)°. The dihedral angles between the imidazole co-ligands is 17.9 (7)°.

Two Cu^{II} ions are linked together by two independent 3-CPOA^{2-} groups, generating a macrocyclic ring motif, the center of which lies on a crystallographic center of symmetry. The intramolecular Cu$\cdots$Cu separation is 6.879 (3) Å.

The dinuclear motifs are further linked into a two-dimensional layer structure *via* an N—H$\cdots$O hydrogen bond, with an N$\cdots$O distance of 2.812 (3) Å and an N—H$\cdots$O angle of 171°. The layers are futher connected through other intermolecular hydrogen bonds involving the uncoordinated water molecules and the carboxylate O atoms, resulting in the formation of a two-dimensional supramolecular network (Table 2 and Fig. 2).

Experimental

The title complex was prepared by the addition of stoichiometric amounts of $Cu(OAc)_2\cdot H_2O$ (2.00 g, 10 mmol), NaOH (0.80 g, 20 mmol) and imidazole (1.36 g, 20 mmol) to a hot aqueous solution of 3-CPOAH$_2$ (1.96 g, 10 mmol), with subsequent filtration. Blue crystals were obtained at room temperature over several days. Analysis; calculated for $C_{30}H_{32}Cu_2N_8O_{12}$: C 43.74, H 3.92, N 13.60%; found: C 43.58, H 4.00, N 13.56%.

Crystal data

$[Cu_2(C_9H_6O_5)_2(C_3H_4N_2)_4]\cdot 2H_2O$
M_r = 823.74
Monoclinic, $P2_1/c$
a = 9.997 (2) Å
b = 16.422 (3) Å
c = 10.857 (2) Å
β = 98.20 (3)°
V = 1764.2 (6) Å^3
Z = 2

D_x = 1.551 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 849 reflections
θ = 3.1–27.4°
μ = 1.28 mm^{-1}
T = 293 (2) K
Prism, blue
0.35 × 0.26 × 0.19 mm

m1934 Shan Gao et al. • $[Cu_2(C_9H_6O_5)_2(C_3H_4N_2)_4]\cdot 2H_2O$ Acta Cryst. (2004). E60, m1933–m1935

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.663$, $T_{\max} = 0.793$
16 077 measured reflections
3982 independent reflections
3319 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 27.4°$
$h = -12 \rightarrow 12$
$k = -21 \rightarrow 21$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.099$
$S = 1.04$
3982 reflections
241 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.5757P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.994 (2)	Cu1—O5$^{\rm i}$	2.8191 (15)
Cu1—N3	1.9837 (19)	O1—C7	1.266 (3)
Cu1—O1	1.9513 (16)	O2—C7	1.238 (3)
Cu1—O3	2.3814 (18)	O4—C15	1.273 (3)
Cu1—O4$^{\rm i}$	1.9810 (15)	O5—C15	1.243 (3)
N1—Cu1—O3	90.76 (7)	O4$^{\rm i}$—Cu1—N3	91.72 (7)
N3—Cu1—N1	179.65 (8)	O4$^{\rm i}$—Cu1—O3	107.31 (6)
N3—Cu1—O3	89.02 (7)	O5$^{\rm i}$—Cu1—N1	88.52 (7)
O1—Cu1—N1	89.07 (8)	O5$^{\rm i}$—Cu1—N3	91.83 (7)
O1—Cu1—N3	90.62 (8)	O5$^{\rm i}$—Cu1—O1	125.82 (7)
O1—Cu1—O3	75.39 (6)	O5$^{\rm i}$—Cu1—O3	158.76 (6)
O1—Cu1—O4$^{\rm i}$	176.45 (7)	O5$^{\rm i}$—Cu1—O4$^{\rm i}$	51.45 (6)
O4$^{\rm i}$—Cu1—N1	88.60 (8)		

Symmetry code: (i) $-x, 1-y, 1-z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H16$\cdots$O1W	0.86	1.90	2.712 (3)	158
N4—H17$\cdots$O5$^{\rm ii}$	0.86	1.96	2.812 (3)	171
O1W—H1W1$\cdots$O5$^{\rm iii}$	0.85 (2)	1.96 (3)	2.802 (3)	168 (4)
O1W—H1W2$\cdots$O2$^{\rm iv}$	0.85 (2)	1.84 (3)	2.691 (3)	172 (4)

Symmetry codes: (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$.

The H atoms attached to C and N atoms were placed in calculated positions, with C—H = 0.93 (aromatic) or 0.97 Å (aliphatic) and N—H = 0.86 Å (imidazole), and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,N), and were refined in the riding-model approximation. The water H atoms were located in a difference Fourier map and refined with an O—H distance restraint of 0.85 (1) Å and with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

The authors thank the National Natural Science Foundation of China (No. 20101003), Heilongjiang Province Natural Science Foundation (No. B0007), the Scientific Fund of Remarkable Teachers of Heilongjiang Province (1054G036), and Heilongjiang University for supporting this study.

References

Burrows, A. D., Menzer, S., Mingos, D. M. P., White, A. J. P. & Williams, D. J. (1997). *J. Chem. Soc. Dalton Trans.* pp. 4237–4240.

Gao, S., Li, J. R., Liu, J. W., Gu, C. S. & Huo, L. H. (2004). *Acta Cryst.* E**60**, m22–m23.

Gu, C. S., Liu, J. W., Huo, L. H., Zhao, H., Zhao, J. G. & Gao, S. (2004). *Acta Cryst.* E**60**, o760–o761.

Li, S. J., Gu, C. S., Gao, S., Zhao, H., Zhao, J. G. & Huo, L. H. (2004). *Chin. J. Struct. Chem.* **20**, 835–838.

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

Iglesias, S., Castillo, O., Luque, A. & Romaán, P. (2003). *Inorg. Chim. Acta*, **349**, 273–278.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

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

Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Sieroń, L., Bukowska-Strzyzewska, M., Korabik, M. & Mroziński, J. (2002). *Polyhedron*, **24**, 2473–2479.

Acta Cryst. (2004). E**60**, m1933–m1935 Shan Gao *et al.* • $[Cu_2(C_9H_6O_5)_2(C_3H_4N_2)_4]\cdot 2H_2O$ **m1935**