Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

A two-dimensional coordination polymer containing copper(II): poly[[(1*H*-benzimidazole-κN^3)copper(II)]-μ_3-3-carboxylatophenoxyacetato-$\kappa^4 O,O':O'':O'''$]

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 12 November 2004
Accepted 18 November 2004
Online 27 November 2004

In the title two-dimensional coordination polymer, $[Cu(C_9H_6O_5)(C_7H_6N_2)]_n$, each Cu^{II} atom exists in a distorted square-pyramidal coordination environment, defined by one N atom from the terminal benzimidazole molecule and four carboxyl O atoms derived from three different 3-carboxylatophenoxyacetate (3-CPOA) dianions. The tetradentate 3-CPOA ligand forms three bonds to adjacent Cu atoms to form chains that are linked to neighboring chains, *via* a fourth Cu—O bond, so as to form a layer structure that is further stabilized by hydrogen bonds.

Key indicators

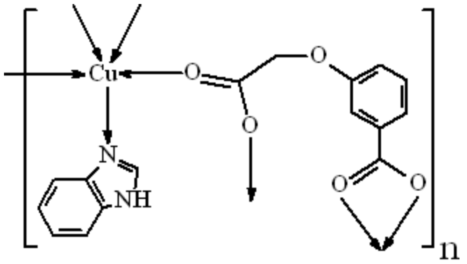
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.041
wR factor = 0.102
Data-to-parameter ratio = 15.3

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

Comment

A rational synthetic strategy to manipulate the assembly of bridging ligands and metal centers to generate desired topologies is still one of the great challenges facing chemists working in crystal engineering. These polymeric architectures can be influenced by the degree of deprotonation, the coordination modes and capabilities of the ligands, and the coordination sphere of the metal centers (Kawata *et al.*, 1997; Castillo *et al.*, 2000). In this sense, carboxyphenoxyacetic acids (*i.e.* n-$HO_2CCH_2OC_6H_4CO_2H$ for n = 2, 3 and 4) could be regarded as a family of excellent bridging ligands, with both rigid and flexible parts, that could be exploited for the construction of coordination polymers because of their versatile coordination modes and high structural stability. Previously, we have reported the structures of a mononuclear Co^{II} complex (Li *et al.*, 2004) and two one-dimensional Ni^{II} and Mn^{II} polymers (Gu, Gao, Huo *et al.*, 2004; Gu, Gao, Zhao *et al.*, 2004) based on 3- or 4-$CPOAH_2$ ligands, in which the carboxylate groups act variously as monodentate, tridentate and tetradentate ligands. However, there is limited structural information on high-dimensional polymers derived from these ligands. The hydrothermal reaction technique offers a powerful synthetic route for the preparation of polymeric solids with multi-dimensional structure and thereby complements traditional solution techniques such as evaporation, diffusion and cooling. On the basis of the above, the two-dimensional title complex, [Cu(1*H*-benzimidazole)(3-CPOA)]$_n$, (I), has been synthesized, employing hydrothermal methods.

As shown in Fig. 1, the fundamental building unit of complex (I) comprises a five-coordinate Cu^{II} center, one benzimidazole molecule and one 3-$CPOA^{2-}$ ligand. The copper(II) ion is in a square-pyramidal coordination environment. The basal plane is formed by the N1 atom from the benzimidazole molecule and three carboxyl O atoms [O1, $O4^{ii}$ and $O5^{ii}$] of two different 3-$CPOA^{2-}$ ligands [symmetry code: (ii) $x - \frac{1}{4}, -y + \frac{1}{4}, z + \frac{3}{4}$]. The coordination sphere of the Cu^{II} atom is completed by an apical O atom from another carboxylate group, and the axial Cu—O1^{i} [symmetry code: (i) $x, y, z + 1$] bond distance of 2.289 (3) Å is longer, as expected, than those of the basal Cu—O bonds [1.938 (3)–2.040 (3) Å] as a result of the Jahn–Teller effect. The basal plane is not perfectly planar, with an r.m.s. deviation of 0.11 (3) Å, and the Cu atom is displaced by 0.06 (3) Å from the mean basal plane towards the apical site. The dihedral angle between the benzimidazole molecule and aromatic ring of the 3-CPOA^{2-} ligand is 77.2 (3)°. The dihedral angles between the two carboxyl groups and the aromatic ring are 78.5 (4) (O1—C8—02) and 16.9 (4)° (O4—C16—04), respectively, and the oxyacetate group is twisted out of the aromatic ring plane, the C10—O3—C9—C8 torsion angle being 85.0 (4)°].



(I)

The carboxylate groups in the 3-CPOA^{2-} ligand display two different coordination modes. One acts in a bidentate bridging coordination mode through atoms O1 and O2, whilst the other binds to the Cu^{II} atom in a chelating mode through atoms O4 and O5, forming a four-membered ring. As described, the 3-CPOA^{2-} ligand simultaneously adopts a monodentate mode through atom O1 and a bidentate mode through atoms O4 and O5 to bridge two copper(II) centers, forming a one-dimensional chain structure running along the *a* axis and adopting a corrugated arrangement (Fig. 2). In the polymeric chain, the Cu1$\cdots$Cu1^{iv} distance is 10.862 (3) Å [symmetry code: (iv) $x + \frac{1}{4}, -y + \frac{1}{4}, z - \frac{3}{4}$]. The benzimidazole molecules reside alternately on opposite sides of the polymeric chain. The polymeric chains are cross-linked by Cu—O2 bonds to form a two-dimensional open layer with a square grid-like structure parallel to the crystallographic *ac* plane (Fig. 3). The Cu1$\cdots$Cu1^{iii} and Cu1$^{iii}\cdots$Cu1^{iv} separations are 4.784 (3) and 7.605 (3) Å, respectively [symmetry code: (iii) $x, y, z - 1$]. The coordinated benzimidazole molecule engages in hydrogen bonding with the adjacent carboxyl O atoms (Table 2 and Fig. 4), contributing to the stabilization of the crystal structure.

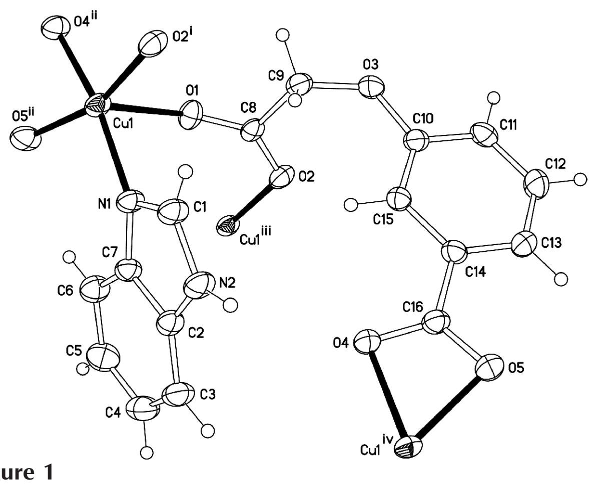


Figure 1
An *ORTEP* (Johnson, 1976) plot of the title complex, with displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $x, y, z + 1$; (ii) $x - \frac{1}{4}, -y + \frac{1}{4}, z + \frac{3}{4}$; (iii) $x, y, z - 1$; (iv) $x + \frac{1}{4}, -y + \frac{1}{4}, z - \frac{3}{4}$].

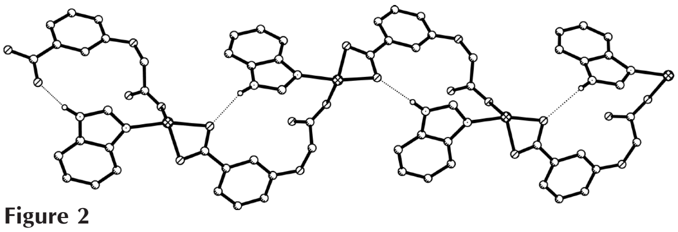


Figure 2
The one-dimensional chain structure of the title complex, with the carbon-bound H atoms omitted; hydrogen bonding is shown as dashed lines.

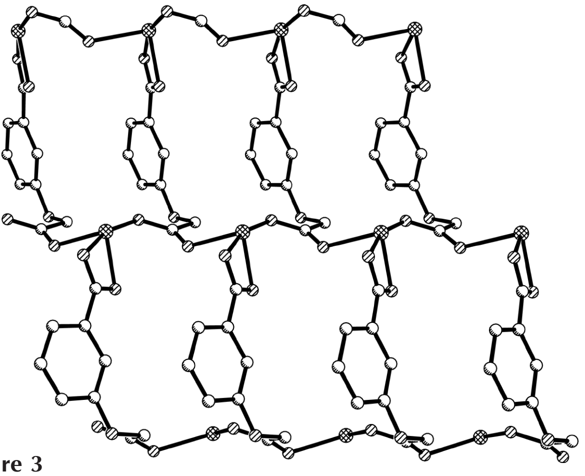


Figure 3
The two-dimensional layer structure of the title complex; benzimidazole molecules and H atoms have been omitted for clarity.

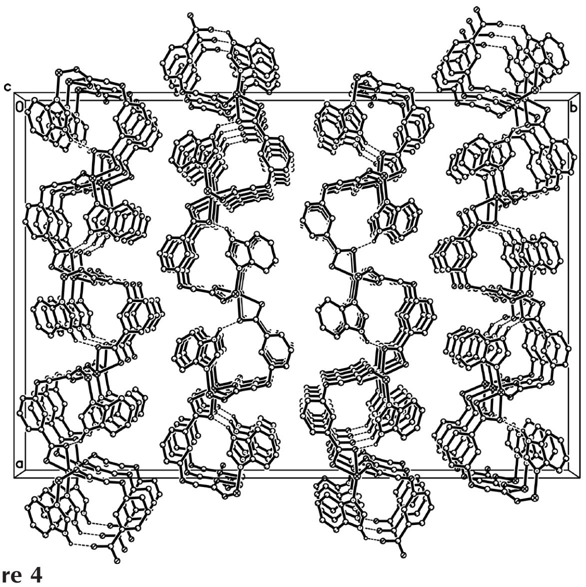


Figure 4
The packing of the title complex; H-bonding is shown as dashed lines and carbon-bound H atoms are omitted for clarity.

Acta Cryst. (2004). E**60**, m1936–m1938 Shan Gao *et al.* • [Cu(C$_9$H$_6$O$_5$)(C$_7$H$_6$N$_2$)] **m1937**

Experimental

The title complex was prepared by the addition of a stoichiometric amount of $Cu(OAc)_2 \cdot H_2O$ (2.00 g, 10 mmol) and benzimidazole (1.17 g, 10 mmol) to an aqueous solution of 3-$CPOAH_2$ (1.96 g, 10 mmol); the pH was then adjusted to 7 with 0.1 *M* NaOH. The mixture was sealed in a 25 ml Teflon-lined stainless steel bomb and held at 423 K for 5 d. The bomb was cooled naturally to room temperature, and blue prismatic crystals were obtained over several days. Analysis calculated for $C_{16}H_{12}CuN_2O_5$: C 51.13, H 3.22, N 7.45%; found: C 51.30, H 3.27, N 7.41%.

Crystal data

$[Cu(C_9H_6O_5)(C_7H_6N_2)]$
$M_r = 375.83$
Orthorhombic, *Fdd*2
$a = 29.0545$ (14) Å
$b = 42.7251$ (15) Å
$c = 4.784$ (1) Å
$V = 5938.7$ (13) Å^3
$Z = 16$
$D_x = 1.681$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 649 reflections
$\theta = 3.4$–27.5°
$\mu = 1.50$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.37 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.644$, $T_{\max} = 0.764$
12 860 measured reflections
3313 independent reflections
2841 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 27.6°$
$h = -37 \rightarrow 37$
$k = -51 \rightarrow 54$
$l = -6 \rightarrow 5$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.102$
$S = 1.03$
3313 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 8.324P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.69$ e Å^{-3}
Absolute structure: Flack (1983), 1386 Friedel pairs
Flack parameter = 0.013 (18)

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.964 (3)	O1—C8	1.226 (4)
Cu1—O1	2.289 (3)	O2—C8	1.267 (4)
Cu1—O2$^{\rm i}$	1.938 (3)	O4—C16	1.255 (4)
Cu1—O4$^{\rm ii}$	2.040 (3)	O5—C16	1.263 (4)
Cu1—O5$^{\rm ii}$	1.982 (3)		
N1—Cu1—O1	88.66 (13)	O2$^{\rm i}$—Cu1—O4$^{\rm ii}$	101.58 (11)
N1—Cu1—O4$^{\rm ii}$	165.18 (12)	O2$^{\rm i}$—Cu1—O5$^{\rm ii}$	162.63 (12)
N1—Cu1—O5$^{\rm ii}$	100.99 (12)	O4$^{\rm ii}$—Cu1—O1	88.25 (11)
O2$^{\rm i}$—Cu1—N1	93.14 (12)	O5$^{\rm ii}$—Cu1—O1	95.00 (12)
O2$^{\rm i}$—Cu1—O1	95.38 (11)	O5$^{\rm ii}$—Cu1—O4$^{\rm ii}$	64.87 (11)

Symmetry codes: (i) $x, y, 1 + z$; (ii) $x - \frac{1}{4}, \frac{1}{4} - y, \frac{3}{4} + z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H17···O1$^{\rm v}$	0.86	2.09	2.911 (4)	159
N2—H17···O4	0.86	2.64	3.088 (5)	114

Symmetry codes: (v) $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$.

H atoms on C and N atoms were placed in calculated positions, with C—H = 0.93–0.97 Å, N—H = 0.86 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}$(C,N), and were refined in the riding-model approximation.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 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 (1054 G036) and Heilongjiang University for supporting this study.

References

Castillo, O., Luque, A., Iglesias, S., Vitoria, P. & Rományan, P. (2000). *New J. Chem.* **24**, 771–775.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gu, C. S., Gao, S., Huo, L. H., Zhu, Z. B., Zhao, H. & Zhao, J. G. (2004). *Chin. J. Inorg. Chem.* **20**, 843–846.
Gu, C. S., Gao, S., Zhao, J. G., Zhu, Z. B., Zhao, H. & Huo, L. H. (2004). *Chin. J. Struct. Chem.* **23**, 1073–1076.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Li, S. J., Gu, C. S, Gao, S., Zhao, H., Zhao, J. G. & Huo, L. H. (2004). *Chin. J. Struct. Chem.* **20**, 835–838.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.
Kawata, S., Breeze, S. R., Wang, S., Greedan, J. E. & Raju, N. P. (1997). *Chem. Commun.* pp. 717–718.
Rigaku Corporation (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.

m1938 Shan Gao *et al.* • $[Cu(C_9H_6O_5)(C_7H_6N_2)]$ *Acta Cryst.* (2004). E**60**, m1936–m1938