

trans-Diaquabis(3-hydroxybenzoato- κ O¹)bis(nicotinamide- κ N¹)copper(II)

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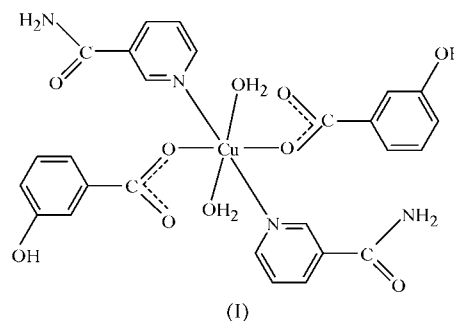
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The title compound, [Cu(C₇H₅O₃)₂(C₆H₆N₂O)₂(H₂O)₂], is a two-dimensional hydrogen-bonded supramolecular complex. The Cu^{II} ion resides on a centre of symmetry and is in an octahedral coordination environment comprising two pyridine N atoms, two carboxylate O atoms and two O atoms from water molecules. Intermolecular N—H...O and O—H...O hydrogen bonds produce R₂²(4), R₂²(8) and R₂²(15) rings which lead to one-dimensional polymeric chains. An extensive two-dimensional network of N—H...O and O—H...O hydrogen bonds and C—H... π interactions are responsible for crystal stabilization.

Comment

Investigation of coordination polymers has attracted increasing interest over the past decade (Moulton & Zaworotko, 2001) because of the intriguing structural motifs of these compounds and their potential applications in catalysis, host-guest chemistry and magnetism (Leininger *et al.*, 2000; Feng & Xu, 2001; Yuan *et al.*, 2002). The rational design and synthesis of coordination polymers have focused on the use of benzene di- and polycarboxylates as rigid bridging spacers (Li *et al.*, 1999; Chui *et al.*, 1999). The utilization of aliphatic α,ω -dicarboxylates to construct supramolecular aggregates is also of growing interest (Rao *et al.*, 2004; Kitagawa *et al.*, 2004). Recent research has concentrated on the construction of coordination polymers with specific topologies based on co-bridging of rigid 4,4'-bipyridine (bipy) and α,ω -dicarboxylates (Zheng *et al.*, 2004; Zheng & Ying, 2005). Some interesting coordination polymers assembled with bipy have been reported, showing various structural motifs, including two-dimensional layers (Carlucci *et al.*, 1997; Tong *et al.*, 1998) and three-dimensional nets (Lu *et al.*, 1998; Hagrman *et al.*, 1998; Kondo *et al.*, 1999; Zhang *et al.*, 1999; Greve *et al.* 2003; Şahin *et al.*, 2007). We report here the structure of the title compound, (I), in which hydrogen bonds and C—H... π

interactions lead to a two-dimensional supramolecular network.



The molecular structure of (I) and the atom-labelling scheme are shown in Fig. 1. The compound crystallizes in the space group $P2_1/c$ with $Z' = \frac{1}{2}$. The Cu^{II} atom is located on a centre of symmetry and is coordinated by two O atoms from two equivalent carboxylate groups, two O atoms from aqua ligands and two pyridyl N atoms. The geometry around the Cu^{II} ion (Table 1) is that of a distorted octahedron, the equatorial plane of which (O2/O5/O2^{iv}/O5^{iv}) is formed by two carboxylate O atoms (O2 and O2^{iv}) and two aqua O atoms (O5 and O5^{iv}) [symmetry code: (iv) $1 - x, 1 - y, 1 - z$]. The axial positions are occupied by two pyridyl N atoms (N1 and N1^{iv}). The significant difference between the Cu—L bond distances in the equatorial plane [Cu—O2/O2^{iv} = 1.9714 (12) Å and Cu—O5/O5^{iv} = 2.569 (2) Å] and those in the axial positions [Cu—N1/N1^{iv} = 2.0117 (14) Å] has also been observed in other copper complexes (Uçar *et al.*, 2005). The Cu—O5 distance is longer than the corresponding distances in related structures (Wen *et al.*, 2004; Lu *et al.*, 2006). This elongation can be attributed to the static Jahn–Teller effect. Carboxylate atom O3 is pendant, with a longer

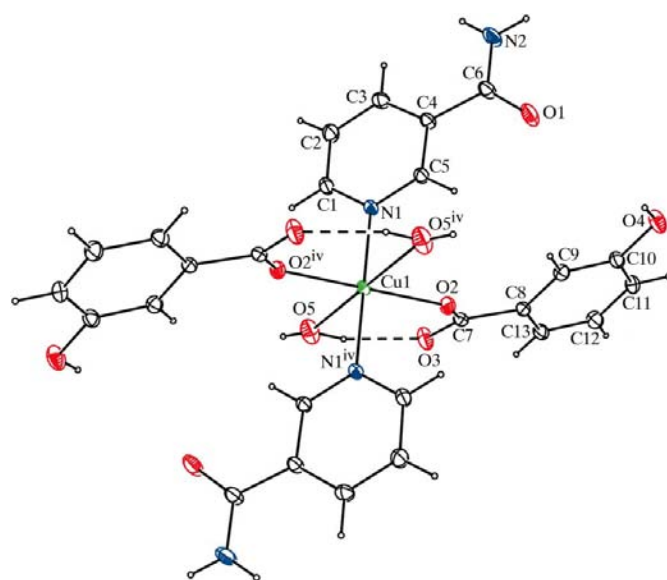


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines. [Symmetry code: (iv) $1 - x, 1 - y, 1 - z$.]

Cu1...O3 distance [3.161 (2) Å] and larger Cu1—O2—C7 angle, consistent with the absence of bonding between atoms Cu1 and O3. The carboxylate group is not coplanar with the attached benzene ring, the dihedral angle between the planes being 15.8 (2)°.

Molecules are linked by intermolecular hydrogen bonding, and we employ graph-set notation (Bernstein *et al.*, 1995) to describe the patterns formed. Molecules of (I) are linked into sheets by a combination of O—H...O and N—H...O hydrogen bonds (Table 2). Thus, the O5—H5A...O3 hydrogen bond produces an $S(6)$ motif (Fig. 1). Amino atom N2 in the reference molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H2A, to O1 in the molecule at $(-x + 3, -y + 1, -z + 2)$, so forming a $C(12)[R_2^2(8)]$ chain of rings running parallel to the [201] direction and a centrosymmetric $R_2^2(8)$ ring centred at $(-\frac{1}{2}, \frac{1}{2}, 0)$ (Fig. 2). Fig. 3 shows the way in which hydroxyl atom O4, a water ligand and carboxylate atom O3 are involved in intermolecular hydrogen-bonding interactions. Water atom O5 in the reference molecule at (x, y, z)

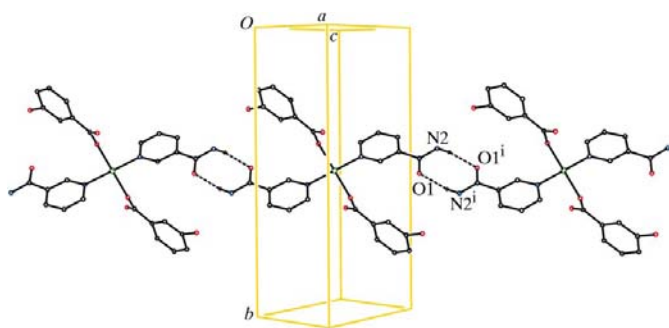


Figure 2
Part of the crystal structure of (I), showing the formation of a centrosymmetric $R_2^2(8)$ ring centred at $(-\frac{1}{2}, \frac{1}{2}, 0)$. Dashed lines indicate hydrogen bonds. H atoms not involved in these interactions have been omitted for clarity. [Symmetry code: (i) $-x + 3, -y + 1, -z + 2$.]

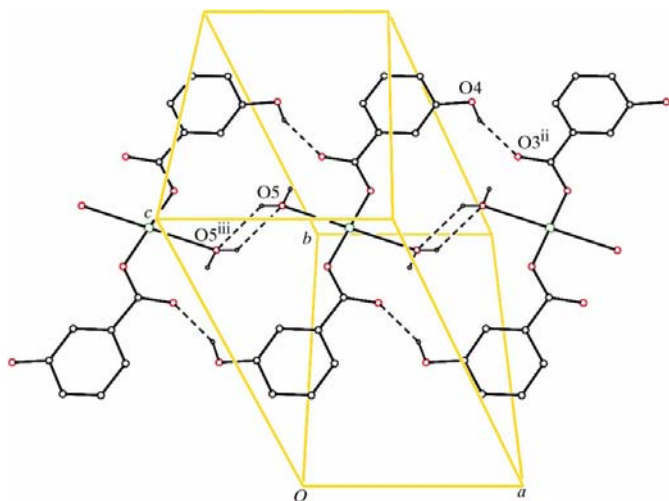


Figure 3
Part of the crystal structure of (I), showing the formation of $R_2^2(4)$ and $R_2^2(15)$ rings. H atoms not involved in these interactions have been omitted for clarity. [Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x, -y + 1, -z + 1$.]

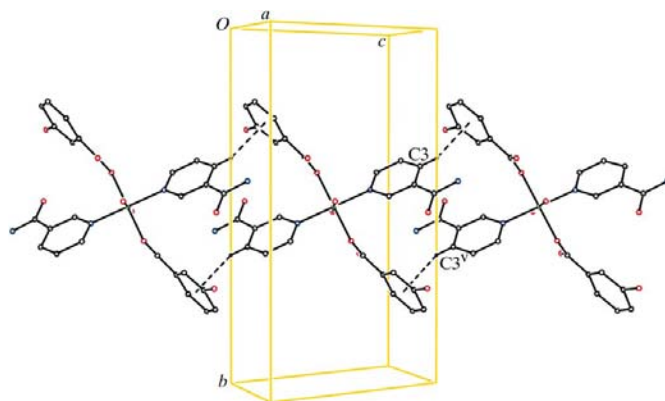


Figure 4
Part of the crystal structure of (I), showing the formation of a chain along [101] generated by the C—H... π interaction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry code: (v) $2 - x, 1 - y, 2 - z$.]

acts as a hydrogen-bond donor, *via* atom H5B, to atom O5 in the molecule at $(-x, -y + 1, -z + 1)$, so forming a $C(4)[R_2^2(4)]$ chain of rings running parallel to the [100] direction and centrosymmetric $R_2^2(4)$ rings centred at $(0, \frac{1}{2}, \frac{1}{2})$. At the same time, atom O4 in the reference molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H4, to atom O3 of the molecule at $(x + 1, y, z)$, so forming a $C(7)$ chain running parallel to the [100] direction. The combination of the $C(4)$ and $C(7)$ chains along [100] generates a chain of edge-fused $R_2^2(15)$ rings (Fig. 3).

In the structure of (I), there is also a strong C—H... Cg^v interaction [symmetry code: (v) $2 - x, 1 - y, 2 - z$] between C3—H3 (of a pyridine ring) and the centroid Cg of a benzene ring. Interlinked C3—H3... Cg^v and C3^v—H3^v... Cg interactions define an $R_2^2(20)$ ring pattern (Fig. 4). The C—H... Cg^v contact distance between the centroid of a benzene ring and the H atoms of the nearest pyridine ring is 2.63 Å. The perpendicular distance between atom H3 and the centre of the benzene ring is 2.616 Å and the C—H... Cg^v angle is 153°. This C—H... π interaction produces a chain running parallel to the [101] direction.

These intermolecular interactions, namely an extensive network of hydrogen bonds and π -ring interactions, play a key role in assembling the supramolecular structure of (I).

Experimental

The preparation of *p*-hydroxybenzoate complexes was carried out as follows. First, sodium 3-hydroxybenzoate was prepared according to the equation: $3\text{-hba} + 2\text{NaHCO}_3 \rightarrow 2\text{Na(3-hba)} + 2\text{CO}_2 + 2\text{H}_2\text{O}$ (3-hba is 3-hydroxybenzoic acid). In the second step, Cu^{II}(3-hba) salts were synthesized from the Na(3-hba) salt by the substitution reaction: $2\text{Na(3-hba)} + \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{Cu(3-hba)}_2 \cdot n\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$. The Cu(3-hba)₂·*n*H₂O salts were prepared in aqueous media. The synthesis of the mixed-ligand complexes was carried out as follows. A solution of na (nicotinamide, 2 mmol) in distilled water (30 ml) was added dropwise with stirring to a solution of Cu(3-hba)₂·*n*H₂O (1 mmol) in hot distilled water (50 ml). The solution was heated to 323 K in a temperature-controlled bath and stirred for 4 h, then cooled to room temperature and left for 10–12 d for crystallization.

The crystals which formed were filtered off, washed with cold water and acetone, and dried *in vacuo*. The mixed-ligand complexes were prepared according to the equation: $\text{Cu}(\text{3-hba})_2 \cdot n\text{H}_2\text{O} + 2\text{na} \rightarrow \text{Cu}(\text{3-hba})_2(\text{na})_2(\text{H}_2\text{O})_2$.

Crystal data

$[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$	$V = 1281.2 (2) \text{ \AA}^3$
$M_r = 618.05$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.2667 (7) \text{ \AA}$	$\mu = 0.92 \text{ mm}^{-1}$
$b = 17.8020 (14) \text{ \AA}$	$T = 296 \text{ K}$
$c = 10.8166 (10) \text{ \AA}$	$0.74 \times 0.52 \times 0.40 \text{ mm}$
$\beta = 113.706 (7)^\circ$	

Data collection

Stoe IPDSII diffractometer	8248 measured reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	2562 independent reflections
$T_{\min} = 0.413$, $T_{\max} = 0.563$	2296 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	
$S = 1.03$	$\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
2562 reflections	$\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$
193 parameters	
4 restraints	

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1—Cu1	2.0117 (14)	O5—Cu1	2.569 (2)
O2—Cu1	1.9714 (12)		
C7—O2—Cu1	124.08 (12)	O2—Cu1—O5	98.86 (6)
O2—Cu1—N1	88.61 (5)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2A \cdots O1 ⁱ	0.86	2.08	2.928 (2)	168
O4—H4 \cdots O3 ⁱⁱ	0.82	1.98	2.709 (2)	148
O5—H5A \cdots O3	0.83 (3)	1.90 (3)	2.702 (2)	162 (3)
O5—H5B \cdots O5 ⁱⁱⁱ	0.78 (3)	2.33 (3)	2.883 (4)	129 (3)

Symmetry codes: (i) $-x + 3, -y + 1, -z + 2$; (ii) $x + 1, y, z$; (iii) $-x, -y + 1, -z + 1$.

H atoms bonded to C and N atoms were included in their expected positions and allowed to ride, with C—H and N—H distances constrained to 0.93 and 0.86 \AA , respectively. Water H atoms were located in difference maps and refined subject to a restraint of O—H = 0.83 (2) \AA . H atoms were assigned a $U_{\text{iso}}(\text{H})$ value of $1.2U_{\text{eq}}$ of the parent atom. The H atom of the hydroxy group (O4) was allowed for with a fixed O—H distance of 0.82 \AA [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$ (parent)].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3124). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi, A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1801–1803.
- Chui, S. S.-Y., Lo, S. M.-F., Charmant, J. P. H., Orpen, A. G. & Williams, I. D. (1999). *Science*, **283**, 1148–1150.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Feng, S. H. & Xu, R. R. (2001). *Acc. Chem. Res.* **34**, 239–247.
- Greve, J., Jess, I. & Näther, C. (2003). *J. Solid State Chem.* **175**, 328–340.
- Hagman, D., Hammond, R. P., Haushalter, R. & Zubieta, J. (1998). *Chem. Mater.* **10**, 2091–2094.
- Kitagawa, S., Kitaura, R. & Noro, S.-I. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.
- Kondo, M., Shimamura, M., Noro, S. I., Yoshitomi, T., Minakoshi, S. & Kitagawa, S. (1999). *Chem. Lett.* pp. 285–286.
- Leininger, S., Olenyuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–908.
- Li, H., Eddaoudi, M., O'Keeffe, M. & Yaghi, O. M. (1999). *Nature (London)*, **402**, 276–279.
- Lu, J., Yu, C., Niu, T. Y., Paliwala, T., Crisci, G., Somosa, F. & Jacobson, A. J. (1998). *Inorg. Chem.* **37**, 4637–4640.
- Lu, L.-P., Yao, S.-Q. & Zhu, M.-L. (2006). *Acta Cryst.* **C62**, m220–m222.
- Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.
- Rao, C. N. R., Natarajan, S. & Vaidyanathan, R. (2004). *Angew. Chem. Int. Ed.* **43**, 1466–1568.
- Şahin, O., Büyükgüngör, O., Köse, D. A., Ozturkkan, E. F. & Necefoglu, H. (2007). *Acta Cryst.* **C63**, m243–m245.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (2002). *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.
- Tong, M. L., Cai, J. W., Yu, X. L., Che, X. M., Ng, S. W. & Mak, T. C. W. (1998). *Aust. J. Chem.* **51**, 637–641.
- Uçar, I., Bulut, A. & Büyükgüngör, O. (2005). *Acta Cryst.* **C61**, m218–m220.
- Wen, Y.-H., Qin, Y.-Y., Zhang, J., Li, Z.-J., Cheng, J.-K., Kang, Y. & Yao, Y.-G. (2004). *Acta Cryst.* **C60**, m371–m372.
- Yuan, M., Li, Y. G., Wang, E. B., Lu, Y., Hu, C. W., Hu, N. H. & Jia, H. Q. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2916–2920.
- Zhang, Y. S., Enright, G. D., Breeze, S. R. & Wang, S. (1999). *New J. Chem.* **23**, 625–628.
- Zheng, Y.-Q., Lin, J.-L. & Kong, Z.-P. (2004). *Inorg. Chem.* **43**, 2590–2596.
- Zheng, Y.-Q. & Ying, E.-B. (2005). *Polyhedron*, **24**, 397–406.