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catena-Poly[[aquacopper(II)]-μ-hydroxido-μ-naphthalene-1-carboxylato-κ^2O:O']: effect of a bulky aromatic skeleton in self-assembly

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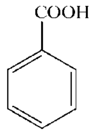
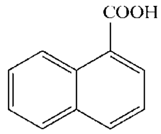
In the title coordination polymer, $[Cu(C_{11}H_7O_2)(OH)(H_2O)]_n$, the Cu^{II} center is five-coordinated by two O atoms from two different naphthalene-1-carboxylate (L) ligands, one O atom from one coordinated water molecule and two O atoms from two hydroxide anions. L ligands and hydroxide anions jointly bridge adjacent Cu^{II} centers to generate a one-dimensional chain along the b-axis direction. The results reveal that the steric bulk of the naphthalene ring system in L may play an important role in the formation of the title complex.

Comment

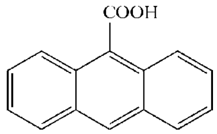
Metallo-supramolecular species assembled from transition metal and organic ligands have attracted much interest because of not only their intriguing structural diversities but also their potential uses as functional materials (Leininger *et al.*, 2000; Robin & Fromm, 2006; Steel, 2005). An effective and facile approach for the synthesis of such complexes is still the appropriate choice of well designed organic ligands as bridges or terminal groups (building blocks), with metal ions or metal clusters as nodes; this method, so far, has been at an evolutionary stage, with the current focus mainly on understanding the factors that determine the crystal packing as well as exploring relevant potential properties (Ye *et al.*, 2005). Among various ligands, the versatile carboxylic acid ligands exhibiting diverse coordination modes, especially the benzene-based carboxylic acids, have been used and well documented in the preparation of various carboxylate-containing Cu^{II} metal–organic complexes, for example, benzoic acid (HBA) (Bkouche-Waksman *et al.*, 1980; Kawata *et al.*, 1992; Koizumi *et al.*, 1963; Gavrilenko *et al.*, 2005) and benzene-1,4-dicarboxylic acid (Du *et al.*, 2005; Hu *et al.*, 2006).



HBA



HL



HACA

In comparison with the aforementioned benzene-based carboxylic acid ligands, however, the investigation of naph-

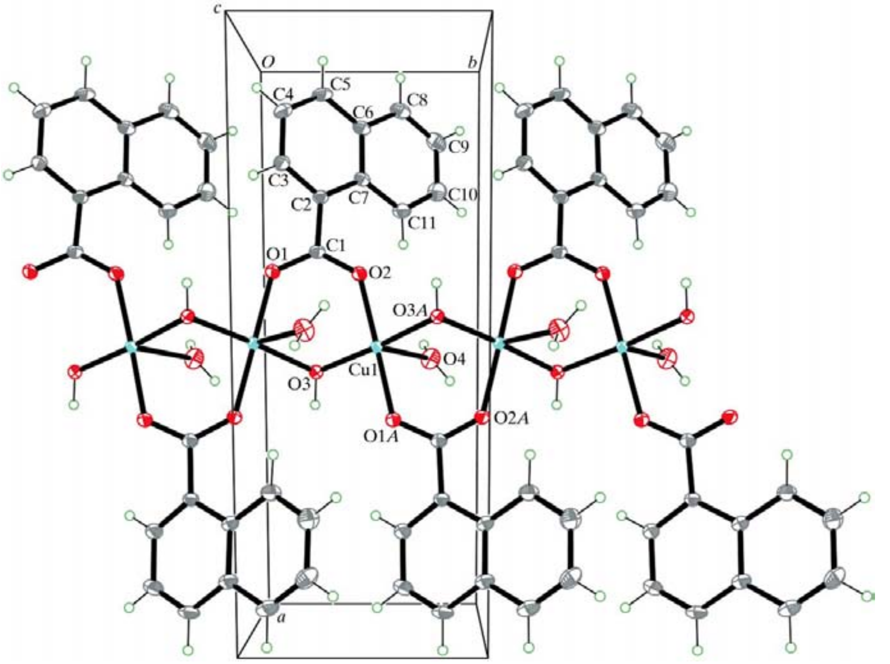


Figure 1
The one-dimensional molecular structure of the title compound, viewed along the b axis. Displacement ellipsoids are drawn at the 30% probability level and atoms labeled with the suffix A are generated by the symmetry operation $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$.

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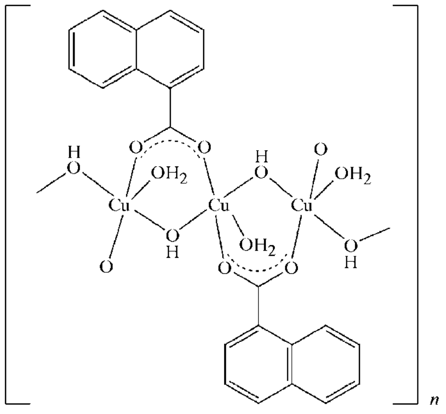
thalene- and anthracene-based carboxylic acids, such as naphthalene-1-carboxylic acid (H*L*) and anthracene-9-carboxylic acid (HACA), has been far less common. In general, such bulky aromatic carboxylic acid ligands have larger conjugated π-systems, and the steric hindrance of the bulky naphthalene and anthracene ring systems may affect the coordination abilities and modes of related carboxylate groups, leading to the formation of supramolecular structures that differ from those of related benzene-based carboxylic acid ligands. In our recent work, H*L* and HACA have been used successfully to construct a series of novel $\mathrm{Cu^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Mn^{II}}$ and $\mathrm{Cd^{II}}$ complexes having mononuclear, dinuclear, tetranuclear, one-dimensional and two-dimensional structures, and exhibiting interesting magnetic and luminescent properties (Liu *et al.*, 2006, 2007; Zou *et al.*, 2005).

To further explore the coordination architectures of ligand *L* bearing the bulky skeleton of the naphthalene ring system, in this research, a new $\mathrm{Cu^{II}}$ complex, (I), with H*L* was synthesized by taking advantage of the carboxylate bridging coordination abilities and the steric bulk of the naphthalene ring system. We report here the crystal structure of (I) and compare it with the structurally related benzene- and anthracene-based $\mathrm{Cu^{II}}$–carboxylate complexes whose crystal structures have been reported in the literature (Bkouche-Waksman *et al.*, 1980; Kawata *et al.*, 1992; Koizumi *et al.*, 1963; Liu *et al.*, 2007) .



(I)

Complex (I) consists of one-dimensional polymeric coordination chains containing only one kind of $\mathrm{Cu^{II}}$ coordination environment (Fig. 1). The asymmetric unit of (I) is composed of one $\mathrm{Cu^{II}}$ ion, one *L* ligand, one $\mathrm{OH^-}$ anion and one coordinated water molecule. Each $\mathrm{Cu^{II}}$ center is five-coordinated to two O atoms of carboxylate groups from two distinct *L* ligands and two O atoms from two $\mathrm{OH^-}$ anions in the equatorial plane, as well as to one O atom from the coordinated water molecule located at the axial position (Table 1). In general, several parameters are often used to define the coordination geometry of the five-coordinated metal center, and one of the most common parameters is the τ factor defined by Addison *et al.* (1984) (τ = 0 for regular square-pyramidal and τ = 1 for regular trigonal–bipyramidal geometry). The calculated τ value of (I) is 0.0432 for the $\mathrm{Cu^{II}}$ center, *i.e.* close to zero, indicating an almost ideal square-pyramidal coordination environment, and the $\mathrm{Cu^{II}}$ center deviates from the mean equatorial plane of the square pyramid [O1/O3/O1$^{\rm i}$/O3$^{\rm i}$; symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$] towards the apical O4 atom of the coordinated water molecule by *ca* 0.0718 Å. Moreover, *L* in (I) adopts a bidentate *syn–syn* bridging coordination mode using two O atoms of the carboxylate group, which further bridge adjacent $\mathrm{Cu^{II}}$ centers to generate a one-dimensional chain along the [010] direction (Fig. 1).

In the crystal structure of (I), adjacent one-dimensional $[\mathrm{Cu}L(\mathrm{OH})(\mathrm{H_2O})]_n$ chains are arranged into a two-dimensional network running parallel to the (100) plane by interchain O—H···O hydrogen-bonding interactions between the coordinated water molecules and the carboxylate O atoms of the *L* ligands (see Fig. 2 and Table 2).

The previously reported metal–organic coordination architectures constructed from benzene-based carboxylic acids include a one-dimensional $\mathrm{Cu^{II}}$–benzoate complex $[\mathrm{Cu(BA)](BA)(H_2O)_3}]_n$ (Koizumi *et al.*, 1963) and two dinuclear $\mathrm{Cu^{II}}$–benzoate complexes, $[\mathrm{Cu_2(BA)_4(CH_3OH)_2}]\cdot\mathrm{CH_3OH}$ (Bkouche-Waksman *et al.*, 1980) and $[\mathrm{Cu_2(BA)_4(HBA)_2}]$ (Kawata *et al.*, 1992). In this work, when we use H*L* instead of HBA to react with $\mathrm{Cu(NO_3)_2}$ under certain conditions, only one one-dimensional polymer, (I), was produced. When we further used HACA, with a larger bulky skeleton of aromatic rings, instead of H*L* to react with $\mathrm{Cu(NO_3)_2}$ under the same conditions, one dinuclear discrete structure analogous to that of copper acetate, $[\mathrm{Cu_2(ACA)_4(CH_3OH)_2}]\cdot\mathrm{CH_3OH}$, was obtained (Liu *et al.*, 2007). Thus, although the carboxylic acid coordination sites of H*L*, HACA and HBA are very similar, their coordination chemistry is obviously different, presumably as a result of the different skeletal bulk of the naphthalene, anthracene and benzene ring systems.

Our results, therefore, reveal that the steric bulk of different aromatic ring systems (naphthalene, anthracene or benzene) may play an important role in the formation of the related metal–organic complexes. From the viewpoint of ligand

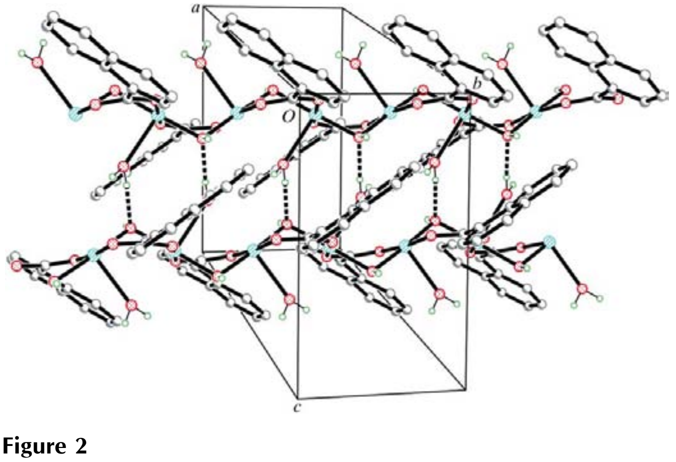


Figure 2
Part of the crystal packing, showing the two-dimensional network in the title compound formed by interchain O—H···O hydrogen-bond interactions (dashed lines). For the sake of clarity, only H atoms of water molecules and hydroxide ligands involved in the interactions are shown.

design, this fact may offer the means to construct coordination architectures with specific potential properties just by consideration of the steric bulk of the aromatic skeleton. Bulky carboxylate ligands containing naphthalene or anthracene ring systems might be generally used with different d^{10} transition metal ions, such as Ag, Zn and Cd, for constructing other metal–organic complexes with luminescence properties; research into this possibility is underway in our laboratory.

Experimental

A solution of H*L* (0.05 mmol) in CH_3OH (10 ml) in the presence of excess 2,6-dimethylpyridine (*ca* 0.05 ml for adjusting the pH value of the reaction system to basic conditions) was carefully layered on top of an aqueous solution (15 ml) of $Cu(NO_3)_2$ (0.1 mmol) in a test tube. Blue single crystals suitable for X-ray analysis appeared at the boundary between CH_3OH and H_2O after *ca* one month at room temperature (yield ~30% based on H*L*). Analysis calculated for $C_{11}H_{10}CuO_4$: C 48.98, H 3.74%; found: C 49.09, H 3.67%.

Crystal data

$[Cu(C_{11}H_7O_2)(OH)(H_2O)]$
$M_r = 269.73$
Monoclinic, $P2_1/c$
$a = 15.9395\ (7)$ Å
$b = 6.2397\ (2)$ Å
$c = 10.6094\ (6)$ Å
$\beta = 101.383\ (3)^\circ$
$V = 1034.43\ (8)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.11$ mm^{-1}
$T = 294\ (2)$ K
$0.16 \times 0.14 \times 0.12$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker,1998)
$T_{\min} = 0.729$, $T_{\max} = 0.786$
10552 measured reflections
2545 independent reflections
2010 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.084$
$S = 1.03$
2545 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O3	1.9232 (16)	Cu1—O4	2.3879 (19)
Cu1—O3$^{\rm i}$	1.9342 (16)	O1—Cu1$^{\rm ii}$	1.9923 (18)
Cu1—O2	1.9747 (18)	O3—Cu1$^{\rm ii}$	1.9342 (16)
Cu1—O1$^{\rm i}$	1.9923 (18)		
O3—Cu1—O3$^{\rm i}$	176.35 (5)	O2—Cu1—O1$^{\rm i}$	173.75 (8)
O3—Cu1—O2	91.80 (8)	O3—Cu1—O4	94.23 (7)
O3$^{\rm i}$—Cu1—O2	85.48 (7)	O3$^{\rm i}$—Cu1—O4	88.44 (7)
O3—Cu1—O1$^{\rm i}$	90.40 (8)	O2—Cu1—O4	94.71 (8)
O3$^{\rm i}$—Cu1—O1$^{\rm i}$	92.06 (8)	O1$^{\rm i}$—Cu1—O4	90.95 (8)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41···O3$^{\rm iii}$	0.85	1.88	2.725 (3)	169
O3—H31···O1$^{\rm i}$	0.85	2.48	2.779 (2)	102
O3—H31···O2$^{\rm ii}$	0.85	2.34	2.653 (2)	102

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

H atoms of the water molecules and hydroxide anions were located in difference maps and were allowed to ride on the parent atoms for refinement [with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm O})$]. The remaining H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms [C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3161). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Bkouche-Waksman, I., Bois, C., Popovitch, G. A. & L'Haridon, P. (1980). *Bull. Soc. Chim. Fr.* **1/2**, 69–75.
Bruker (1998). *SMART* (Version 5.051), *SAINT* (Version 5.01), *SADABS* (Version 2.03) and *SHELXTL* (Version 6.1). Bruker AXS Inc., Madison, Wisconsin, USA.
Du, M., Jiang, X.-J. & Zhao, X.-J. (2005). *Chem. Commun.* pp. 5521–5523.
Gavrilenko, K. S., Punin, S. V., Cador, O., Golhen, S., Ouahab, L. & Pavlishchuk, V. V. (2005). *J. Am. Chem. Soc.* **127**, 12246–12253.
Hu, T.-L., Li, J.-R., Liu, C.-S., Shi, X.-S., Zhou, J.-N., Bu, X.-H. & Ribas, J. (2006). *Inorg. Chem.* **45**, 162–173.
Kawata, T., Uekusa, H., Ohba, S., Furukawa, T., Tokii, T., Muto, Y. & Kato, M. (1992). *Acta Cryst.* B**48**, 253–261.
Koizumi, H., Osaki, K. & Watanabe, T. (1963). *J. Phys. Soc. Jpn*, **18**, 117–124.
Leininger, S., Olenyuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–907.
Liu, C.-S., Shi, X.-S., Li, J.-R., Wang, J.-J. & Bu, X.-H. (2006). *Cryst. Growth Des.* **6**, 656–663.
Liu, C.-S., Wang, J.-J., Yan, L.-F., Chang, Z., Bu, X.-H., Sañudo, E. C. & Ribas, J. (2007). *Inorg. Chem.* **46**, 6299–6310.
Robin, A. Y. & Fromm, K. M. (2006). *Coord. Chem. Rev.* **250**, 2127–2157.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Steel, P. J. (2005). *Acc. Chem. Res.* **38**, 243–250.
Ye, B.-H., Tong, M.-L. & Chen, X.-M. (2005). *Coord. Chem. Rev.* **249**, 545–565.
Zou, R.-Q., Liu, C.-S., Shi, X.-S., Bu, X.-H. & Ribas, J. (2005). *CrystEngComm*, **7**, 722–727.