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catena-Poly[[(1,10-phenanthroline-κ^2N,N')copper(II)]-μ-(dihydrogen benzene-1,2,4,5-tetracarboxylato)-κ^2O^1:O^4]

Mao-Lin Hu,* Hong-Ping Xiao, Shun Wang and Xin-Hua Li

Department of Chemistry and Material Science, Wenzhou Normal College, Wenzhou 325027, People's Republic of China
Correspondence e-mail: hml64@sohu.com

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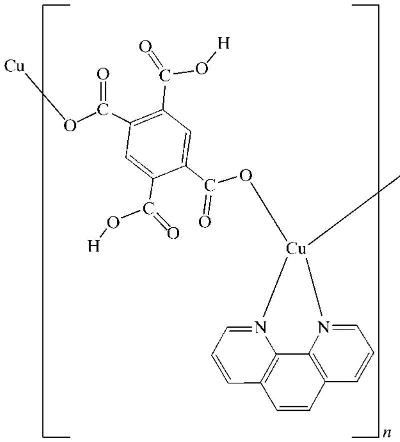
In the title compound, $[Cu(C_{10}H_4O_8)(C_{12}H_8N_2)]_n$, the Cu^{II} cation has a four-coordination environment completed by two N atoms from one 1,10-phenanthroline (phen) ligand and two O atoms belonging to two dihydrogen benzene-1,2,4,5-tetracarboxylate anions (H_2TCB^{2-}). There is a twofold axis passing through the Cu^{II} cation and the centre of the phen ligand. The $[Cu(phen)]^{2+}$ moieties are bridged by H_2TCB^{2-} anions to form an infinite one-dimensional coordination polymer with a zigzag chain structure along the *c* axis. A double-chain structure is formed by hydrogen bonds between adjacent zigzag chains. Furthermore, there are π–π stacking interactions between the phen ligands, with an average distance of 3.64 Å, resulting in a two-dimensional network structure.

Comment

In recent years, intense research activity has been directed toward the assembly of coordination polymers, due to their potential application in gas adsorption, catalysis and opto-electronic devices (Fujita *et al.*, 1994; Sato *et al.*, 1996). The key step in the design of coordination polymers is to select suitable multidentate bridging ligands and spacers. Accordingly, benzene-1,2,4,5-tetracarboxylic acid (H_4TCB) has a very versatile coordination behaviour, since it can form bridges between metallic centres, generating varied and sometimes surprising molecular architectures. Therefore, numerous complexes with the H_4TCB ligand have been extensively studied (Cheng *et al.*, 2001; Chu *et al.*, 2001; Wang *et al.*, 2000), although the construction of complexes from H_4TCB, 1,10-phenanthroline (phen) and Cu^{II} building blocks is still limited (Shi *et al.*, 2001; Zou *et al.*, 1998). To the best of our knowledge, only a one-dimensional double-chain polymer, $[Cu_2(TCB)(phen)_2]_n\cdot nH_2O$, has been reported to date (Shi *et al.*, 2001). We report here the hydrothermal synthesis and structure of the title one-dimensional zigzag chain polymer, $[Cu(phen)(H_2TCB)]_n$, (I). It is entirely possible to prepare $[Cu_2(TCB)(phen)_2]$ and $[Cu(phen)(H_2TCB)]$ separately. The compositions of the complexes can be controlled by using different molar ratios of the reactants and different H-atom receptors, such as phen alone, phen and NaOH, *etc.*



(I)

In (I), the Cu^{II} cation is coordinated by two N atoms from one phen ligand and two O atoms from two H_2TCB^{2-} anions (Fig. 1 and Table 1). There is a twofold axis passing through the Cu^{II} cation and the centre of the phen ligand. An infinite one-dimensional coordination polymer with a zigzag chain structure is formed by the Cu^{II} cations, the μ_2-bridging H_2TCB^{2-} anions and the terminal phen ligands.

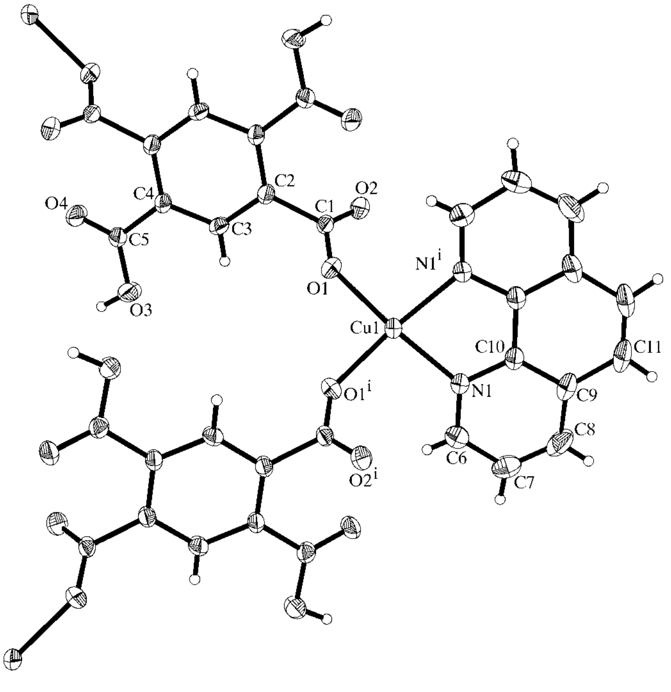


Figure 1
The coordination environment of the Cu^{II} cation in (I), with the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $2 - x, y, \frac{1}{2} - z$.]

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The Cu—O bond lengths are 1.9363 (19) Å, which is within the normal range for $Cu—O_{carboxylate}$ distances (1.927–2.010 Å; Zou *et al.*, 1998), while the Cu—N distance of 2.006 (2) Å is longer than that in $[Cu_2(TCB)(phen)_2]_n{\cdot}nH_2O$ [1.984 (4) Å]. The bond angles around the Cu^{II} cation are characteristic of a distorted square-planar geometry.

An O3—H1···O2($\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) hydrogen bond (Table 2) is formed between neighbouring one-dimensional zigzag chains. This leads to a one-dimensional double-chain structure and the two chains interweave with each other (Fig. 2). Furthermore, there are π–π stacking interactions between the aromatic rings of the phen ligands and the H_2TCB^{2-} anions of two neighbouring chains, with an average distance of 3.64 Å, which is different from the interactions between phen ligands observed in $[Cu_2(TCB)(phen)_2]_n{\cdot}nH_2O$ and which results in a two-dimensional network structure.

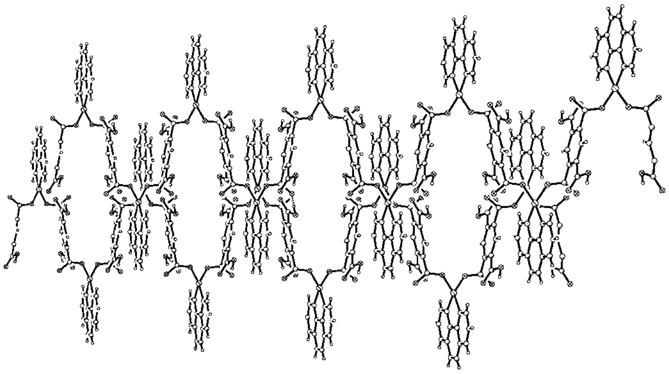

Figure 2
The double-chain structure in (I).

Experimental

The title compound was synthesized by a hydrothermal method from a mixture of benzene-1,2,4,5-tetracarboxylic acid (1 mmol, 0.25 g), $CuSO_4{\cdot}5H_2O$ (1 mmol, 0.25 g), 1,10-phenanthroline (3 mmol, 0.54 g) and water (20 ml) in a 30 ml Teflon-lined stainless steel reactor. The solution was heated at 433 K for 3 d. After slow cooling of the reaction system to room temperature, blue prism-shaped crystals of (I) were collected and washed with distilled water.

Crystal data

$[Cu(C_{10}H_4O_8)(C_{12}H_8N_2)]$
$M_r = 495.88$
Monoclinic, $C2/c$
$a = 10.718$ (5) Å
$b = 14.292$ (7) Å
$c = 12.192$ (6) Å
$\beta = 101.119$ (7)°
$V = 1832.5$ (16) Å^3
$Z = 4$
$D_x = 1.797$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 596 reflections
$\theta = 2.6$–21.4°
$\mu = 1.25$ mm^{-1}
$T = 298$ (2) K
Prism, blue
0.37 × 0.18 × 0.12 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.763$, $T_{max} = 0.860$
5730 measured reflections
2129 independent reflections
1567 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.9°$
$h = -14 \rightarrow 11$
$k = -16 \rightarrow 18$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.100$
$S = 0.96$
2129 reflections
155 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL*97 in *SHELXTL* (Bruker, 2000)
Extinction coefficient: 0.67 (3)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9363 (19)	Cu1—N1	2.006 (2)
$O1^i$—Cu1—O1	88.55 (12)	O1—Cu1—N1	168.32 (9)
O1—Cu1—$N1^i$	95.93 (9)	$N1^i$—Cu1—N1	81.78 (13)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···$O2^{ii}$	0.85 (3)	1.74 (3)	2.577 (3)	165 (4)

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

The O—H distances were refined subject to O—H = 0.85 (1) Å. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at C—H distances of 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1146). Services for accessing these data are described at the back of the journal.

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