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catena-Poly[[[(4′-phenyl-2,2′:6′,2″-terpyridine-κ^3N)-copper(II)]-μ-terephthalato-κ^2O:O'] terephthalic acid]

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The title compound, $[Cu(C_8H_4O_4)(C_{21}H_{15}N_3)]\cdot C_8H_6O_4$, consists of polymeric chains in which the terpyridine heterocycle chelates to the Cu atom in an *N*,*N*′,*N*″-tridentate manner; the Cu atoms are also covalently bonded through the two singly-bonded carboxyl O atoms of the dicarboxylate dianions to give rise to a chain structure. An additional terephthalic acid molecule is hydrogen bonded to the chains. The asymmetric unit contains halves of two different half-molecule terephthalate ions; in each case, the complete ions are generated by inversion symmetry.

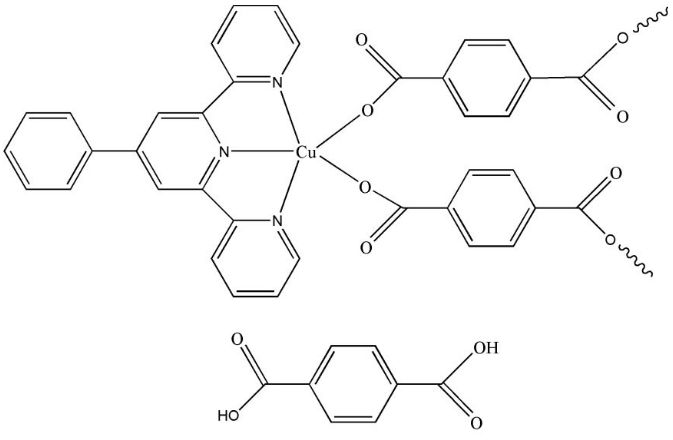
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.127
Data-to-parameter ratio = 15.6

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

Comment

The terephthalate (tp) ion, $C_8H_4O_4^{2-}$, has been widely used as a bridging ligand in the syntheses of coordination polymers (Xanthopoulos *et al.*, 1993; Bakalbassis *et al.*, 1986, 1988; Verdaguer *et al.*, 1984). In most cases, the dianion acts as a monodentate or bidentate ligand (Cano *et al.*, 1997, and references therein; Fun *et al.*, 1999). It has seldom been found as a neutral (protonated) filler in the crystal packing.



(I)

We describe here a zigzag polymeric complex, $[Cu(C_8H_4O_4)(C_{21}H_{15}N_3)]\cdot C_8H_6O_4$, (I), that was obtained by the hydrothermal reaction of copper(II) chloride with terpyridine and terephthalic acid (H_2tp), instead of a binuclear complex as reported by Sun *et al.* (2001). The Cu ions in (I) possess N_3O_2 coordination spheres (Table 1). If a very long bond to O2 [d = 2.801 (2) Å] was considered to be significant, a distorted CuN_3O_3 octahedron would result. According to the structural index τ (Atakol *et al.*., 1999), the coordination geometry about Cu approximates to distorted square-pyramidal, with atom O3 occupying the apex and atoms N1, N2, N3 and O1 forming the basal plane (Fig. 1). In the crystal packing,

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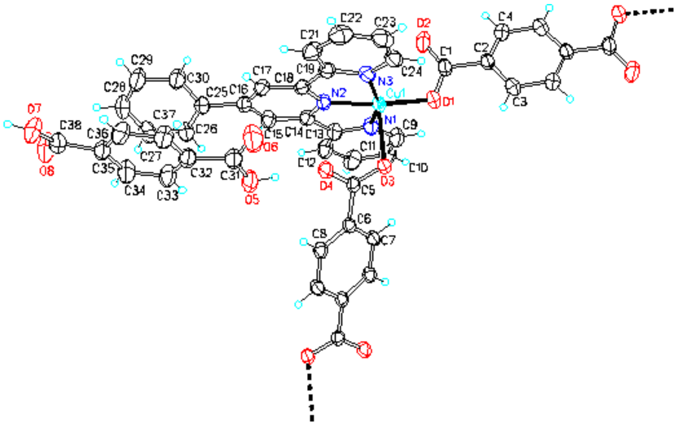

Figure 1
View of a fragment of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms drawn as spheres of arbitrary radii. The complete tp species containing O1 is generated by the symmetry code $(1 - x, 1 - y, 1 - z)$, and that containing O3 by $(1 - x, -y, -z)$.

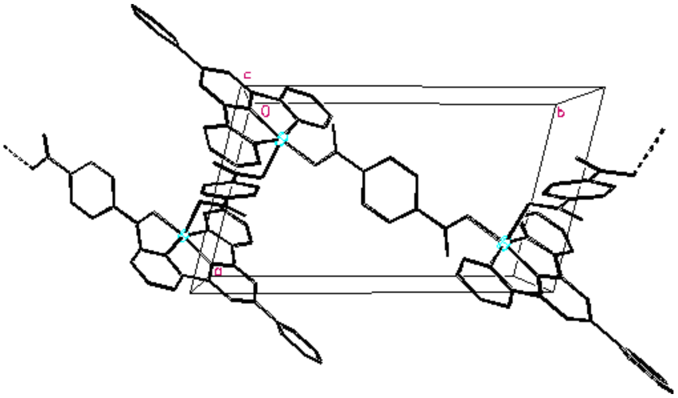

Figure 2
The polymeric chain in (I), with Cu atoms coloured light blue.

each tp ions acts as a doubly monodentate bridging ligand and binds with two copper ions to form a zigzag chain, $\cdots$Cu—tp—Cu—tp$\cdots$, with the O1 and O3 tp species alternating. Terpyridine acts as as a tridentate ligand to complete the coordination about each Cu atom (Fig. 2). Interestingly, a molecule of H2tp was also found in the structure of (I). It acts as a bridge to support the zigzag chains with hydrogen bonds (Table 2) to carbonyl O atoms of coordinated tp ions, which gives rise to a sheet-like network (Fig. 3).

Experimental

To an aqueous solution (15 ml) of copper(II) chloride dihydrate (0.10 g, 0.50 mmol) was added 4′-phenyl-2,2′:6′,2″-terpyridine [0.16 g, 0.50 mmol, synthesized according to a literature procedure (Constable *et al.*, 1990)], followed by terephthalic acid (0.04 g, 0.25 mmol) and piperidine (0.06 g, 0.5 mmol). The mixture was placed in a 25 ml Teflon-lined hydrothermal bomb and heated at 423 K for 40 h. The bomb was then cooled to room temperature at about 5 K h^{-1}. Green prismatic crystals of (I) were obtained from the cooled solution. Analysis calculated for $C_{37}H_{25}CuN_3O_8$: C 63.20, N 3.58, H 5.98%; found: C 63.21, H 3.32, N 6.01%. IR (KBr, cm^{-1}): 3432 (*br s*), 3060 (*w*), 2349 (*w*), 1699 (*w*), 1601 (*vs*), 1474 (s), 1417 (*s*), 1352 (*s*), 1247 (*w*), 1021 (*m*), 824 (*w*), 771 (*m*).

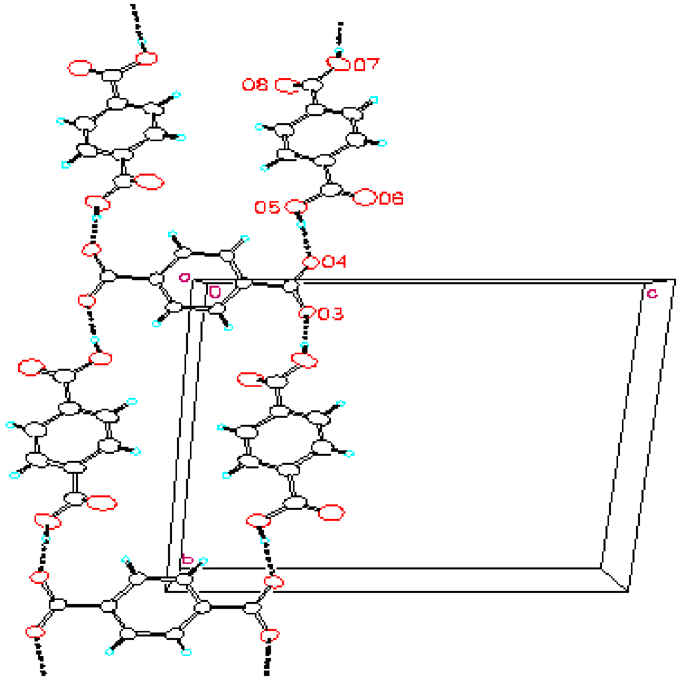

Figure 3
Detail of the hydrogen bonding between terephthalic acid and the terephthalate dianions in (I).

Crystal data

$[Cu(C_8H_4O_4)(C_{21}H_{15}N_3)]\cdot C_8H_6O_4$
$M_r = 703.14$
Triclinic, $P\overline{1}$
$a = 8.0952$ (5) Å
$b = 13.9570$ (8) Å
$c = 14.1416$ (8) Å
$\alpha = 93.925$ (1)°
$\beta = 91.488$ (1)°
$\gamma = 103.777$ (1)°
$V = 1546.70$ (16) Å^3
$Z = 2$
$D_x = 1.510$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4160 reflections
$\theta = 2.2$–26.0°
$\mu = 0.77$ mm^{-1}
$T = 295$ (2) K
Prism, green
0.26 × 0.18 × 0.11 mm

Data collection

Bruker APEX area-dectector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.707$, $T_{\max} = 0.920$
13 572 measured reflections
7024 independent reflections
5819 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 27.9$°
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 18$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.127$
$S = 1.08$
7024 reflections
450 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 0.1147P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.61$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.901 (2)	Cu1—N2	1.927 (2)
Cu1—O3	2.280 (2)	Cu1—N3	2.018 (2)
Cu1—N1	2.047 (2)		
O1—Cu1—O3	89.94 (6)	O3—Cu1—N2	97.43 (7)
O1—Cu1—N1	99.11 (8)	O3—Cu1—N3	101.00 (7)
O1—Cu1—N2	172.45 (7)	N1—Cu1—N2	79.65 (7)
O1—Cu1—N3	100.18 (8)	N1—Cu1—N3	158.81 (8)
O3—Cu1—N1	87.69 (7)	N2—Cu1—N3	80.07 (7)

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

	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5O$\cdots$O4	0.85 (1)	1.75 (1)	2.594 (2)	176 (4)
O7—H7O$\cdots$O3^{i}	0.84 (1)	1.82 (1)	2.666 (2)	177 (4)

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

Hydrogen atoms bonded to C atoms were placed in calculated positions (C–H = 0.93 Å) and were included in the refinement as riding [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$C)]. H atoms of the carboxylic acid (H5O and H7O) were located in a difference map and refined freely.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; 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.

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References

Atakol, O., Tatar, L., Akay, M. A. & Ülkü, D. (1999). *Anal. Sci.* **15**,199–200.

Bakalbassis, E. G., Bozopoulos, A. P. & Mrozinski, J. (1988). *Inorg. Chem.* **27**, 529–532.

Bakalbassis, E. G., Mrozinski, J. & Tsipis, C. A. (1986). *Inorg. Chem.* **25**, 3684–3690.

Bruker (2002). *SADABS*, *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cano, J., Munno, G. D., Sanz, J. L., Ruiz, R., Faus, J., Lloret, F., Julve, M. & Caneschi, A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1915–1923.

Constable, E. C., Lewis, J., Liptrot, M. C. & Raithby, P. R. (1990). *Inorg. Chim. Acta,* **178**, 47–54.

Fun, H.-K., Raj, S. S. S., Xiong, R. G., Zuo, J. L., Yu, Z. & You, X. Z. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1915–1916.

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

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

Sun, D., Cao, R. & Liang, Y. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2335–2340.

Verdaguer, M., Gouteron, J. & Jeannin, S. (1984). *Inorg. Chem.* **23**, 4291–4296.

Xanthopoulos, C. E., Sigalas, M. P. & Katsoulos, G. A. (1993). *Inorg. Chem.* **32**, 5433–5436.