metal-organic papers

catena-Poly[[[aqua(di-2-pyridylamine-$\kappa^2 N^2,N^{2'}$)-copper(II)]-μ-thiophene-2,5-dicarboxylato-$\kappa^2 O^2{:}O^5$] N,N-dimethylformamide monohydrate]

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.031
wR factor = 0.075
Data-to-parameter ratio = 14.7

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

In the title cooordination polymer, $\{[Cu(C_6H_2O_4S)(C_{10}H_9N_3)(H_2O)]{\cdot}C_3H_7NO{\cdot}H_2O\}_n$, the Cu^{II} atom is in a square-pyramidal environment defined by an apically coordinated water molecule, carboxyl O atoms from two different thiophene-2,5-dicarboxylate dianions and the two N atoms of a chelating di-2-pyridylamine ligand. The thiophene-2,5-dicarboxylate dianion functions as a μ_2-bridging ligand to form a zigzag polymeric chain. In addition, N—H$\cdots$O and O—H$\cdots$O intermolecular hydrogen bonds link the chains into a three-dimensional network structure.

Comment

Like other dicarboxylic acids, such as pyridine-2,6-dicarboxylic acid (Ghosh & Bharadwaj, 2005; Lu *et al.*, 2005) and benzene-1,4-dicarboxylic acid (Thirumurugan & Natarajan, 2004; Xiao & Zhu, 2003), which show diverse coordination modes, thiophene-2,5-dicarboxylic acid (H$_2$tda) is also a versatile ligand and can function variously as a monodentate, bidentate or tridentate ligand; it can also bridge or chelate (Chen *et al.*, 1998, 1999; Sun *et al.*, 2003). In the title complex, $\{[Cu(C_{10}H_9N_3)(C_6H_2SO_4)(H_2O)]{\cdot}C_3H_7NO{\cdot}H_2O\}_n$, (I), the tda dianion functions as a bridge between adjacent Cu^{II} centres.
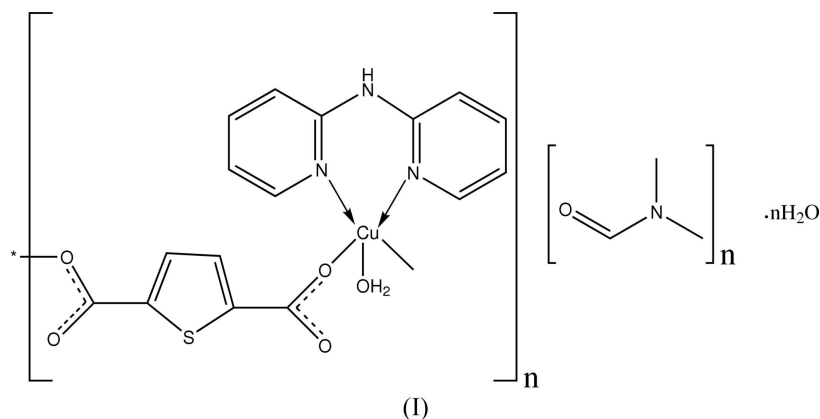
(I)

The Cu^{II} atom is in a square-pyramidal environment defined by an apically coordinated water molecule, two carboxylate O atoms from two different thiophene-2,5-dicarboxylate dianions and the two N atoms of the chelating 2,2′-dipyridylamine (dpa) ligand (Fig. 1). The basal plane [O1/O4^i/N1/N3; symmetry code: (i) $-x, -y + 1, z + \frac{1}{2}$], with a mean deviation of 0.013 (1) Å, comprises the two N atoms of dpa and carboxylate O atoms from two different tda dianions. The Cu1—O5 apical distance is significantly longer than those in the basal plane (Cu1—O1 and Cu1—O4^i; Table 1). The thiophene-2,5-dicarboxylate dianions function as μ_2-bridging
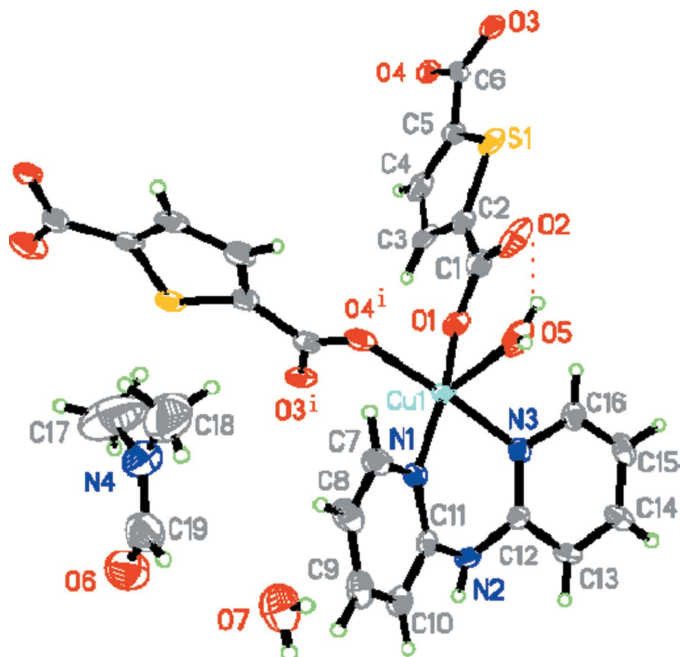
Figure 1
The coordination environment of Cu in (I), with the atom numbering, showing displacement ellipsoids at the 30% probability level. [Symmetry code (i) $-x$, $1 - y$, $z + \frac{1}{2}$]. The intramolecular O5—H5···O2 hydrogen bond is shown as a dashed line.

ligands forming an undulating zigzag chain with the 2,2′-dipyridylamine molecules protruding alternately from the upper and lower surfaces of the chain (Fig. 2).
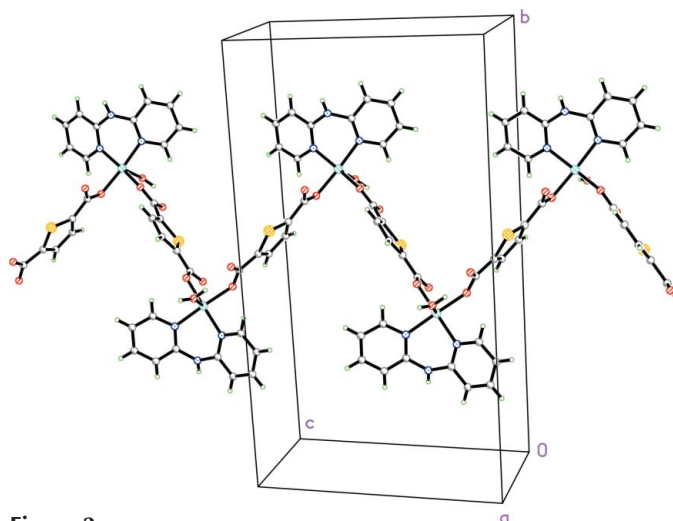
The stability of the solid-state structure of (I) is enhanced significantly by hydrogen-bonding interactions (Table 2). An intramolecular hydrogen bond forms between the O5 atom of the coordinated water and the uncoordinated carboxylate O2 atom [O5—H2B···O2]. Additional N2—H2···O3 and O5—H5A···O3 intermolecular hydrogen bonds link neighbouring zigzag chains into a three-dimensional network structure and form large voids. These are filled by dimethylformamide and water solvent molecules, which in turn are linked by O7—H7A···O6 and O7—H7B···O6 hydrogen bonds (Fig. 3).
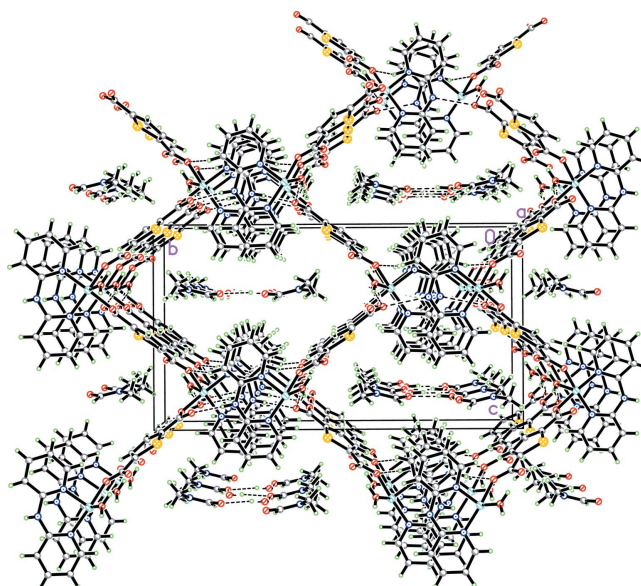
Experimental

An aqueous solution (10 ml) of Cu(NO$_3$)$_2$·3H$_2$O (0.30 mmol, 0.072 g) was added slowly to a solution (10 ml) of *N,N*-dimethylformamide containing 2,2′-dipyridylamine (0.30 mmol, 0.051 g) and thiophene-2,5-dicarboxylic acid (0.30 mmol, 0.052 g). Blue crystals suitable for X-ray analysis were obtained on allowing the solution to stand at room temperature for about a month.

Figure 2
The polymeric zigzag chain structure of (I).

Figure 3
The crystal packing of (I), showing the three-dimensional network structure formed by hydrogen-bonding interactions (shown as dashed lines).

Crystal data

[Cu(C$_6$H$_2$O$_4$S)(C$_{10}$H$_9$N$_3$)(H$_2$O)]·C$_3$H$_7$NO·H$_2$O	$D_x = 1.497$ Mg m^{-3}
$M_r = 514.01$	Mo $K\alpha$ radiation
Orthorhombic, $Pna2_1$	Cell parameters from 6159
$a = 7.067$ (1) Å	reflections
$b = 24.123$ (2) Å	$\theta = 2.9–25.7°$
$c = 13.379$ (1) Å	$\mu = 1.10$ mm^{-1}
$V = 2280.8$ (4) Å^3	$T = 298$ (2) K
$Z = 4$	Block, blue
	$0.46 \times 0.41 \times 0.17$ mm

Data collection

Bruker SMART APEX area-detector diffractometer	4485 independent reflections
	4174 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.028$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SADABS*; Bruker, 2002)	$h = -9 \rightarrow 9$
$T_{min} = 0.633$, $T_{max} = 0.836$	$k = -30 \rightarrow 28$
13430 measured reflections	$l = -17 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0436P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.075$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
4485 reflections	$\Delta\rho_{min} = -0.35$ e Å^{-3}
306 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	5538 Friedel pairs
	Flack parameter: 0.012 (11)

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Table 1
Selected geometric parameters (Å, °).

Cu1—O4^i	1.958 (2)	Cu1—N1	2.002 (2)
Cu1—O1	1.963 (2)	Cu1—O5	2.220 (2)
Cu1—N3	1.996 (2)		
O4^i—Cu1—O1	87.90 (8)	O4^i—Cu1—O5	94.65 (10)
O4^i—Cu1—N3	172.76 (8)	O1—Cu1—O5	94.73 (8)
O1—Cu1—N3	91.30 (8)	N3—Cu1—O5	92.59 (10)
O4^i—Cu1—N1	90.23 (9)	N1—Cu1—O5	97.37 (9)
O1—Cu1—N1	167.87 (8)	C1—O1—Cu1	128.24 (18)
N3—Cu1—N1	89.05 (9)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$B\cdots$O2	0.84 (1)	1.99 (3)	2.671 (3)	138 (4)
O7—H7$B\cdots$O6^{ii}	0.85 (1)	2.05 (2)	2.879 (5)	168 (4)
O7—H7$A\cdots$O6^{iii}	0.85 (1)	2.02 (1)	2.861 (5)	170 (5)
N2—H2$\cdots$O3^{iv}	0.86	2.24	2.910 (3)	134
O5—H5$A\cdots$O3^{v}	0.84 (1)	1.98 (2)	2.773 (3)	158 (4)

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

H atoms of the water molecules were located in a difference map and were refined isotropically, with O–H distances restrained to 0.85 (1) Å. All H atoms of the DMF molecules were placed in calculated positions using a riding-model approximation, with C—H distances of 0.93 Å for OC—H and 0.96 Å for methyl H atoms [U_{iso}(H) values of 1.2(CH) or 1.5(CH$_3$) times U_{eq}(parent atom)]. The remaining H atoms were positioned geometrically (C—H = 0.93 Å and N—H = 0.86 Å) and allowed to ride on their parent atoms, with U_{iso}(H) values equal to 1.2U_{eq}(C,N).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); 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, 2002); software used to prepare material for publication: *SHELXL97*.

References

Bruker (2002). *SADABS* (Version 2.03), *SAINT* (Version 6.02), *SMART* (Version 5.62) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, B. L., Mok, K. F., Ng, S. C. & Drew, M. G. B. (1999). *Polyhedron*, **18**, 1211–1220.

Chen, B. L., Mok, K. F., Ng, S. C., Feng, Y. L. & Liu, S. X. (1998). *Polyhedron*, **17**, 4237–4247.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Ghosh, S. K. & Bharadwaj, P. K. (2005). *Inorg. Chem.* **44**, 3156–3161.

Lu, J., Shen, E., Li, Y., Xiao, H., Wang, E. & Xu, L. (2005). *Cryst. Growth Des.* **5**, 65–67.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sun, X. Z., Sun, Y. F., Ye, B. H. & Chen, X. M. (2003). *Inorg. Chem. Commun.* **6**, 1412–1414.

Thirumurugan, T. & Natarajan, S. (2004). *Inorg. Chem. Commun.* **7**, 395–399.

Xiao, H. P. & Zhu, L. G. (2003). *Chin. J. Inorg. Chem.* **19**, 1179–1183.