metal-organic papers

Poly[di-μ_2-aqua-μ-pyrazole-3,5-dicarboxylato-copper(II)]

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The copper(II) coordination polymer $[Cu(pydc)(H_2O)_2]_n$ (pydc = 3,5-pyrazoledicarboxylate, $C_5H_2N_2O_4$), was synthesized by treating Cu(II) nitrate with 3,5-pyrazoledicarboxylic acid under hydrothermal conditions. Single-crystal X-ray diffraction indicates that the copper coordination polymer has a pydc-bridged ladder-like chain structure.

Comment

The design and construction of coordination polymers has attracted much attention owing to their intriguing topologies and potential applications as functional materials (Inoue *et al.*, 2001). Many networks with various structural motifs have been documented in the past decade (Amabilino & Stoddart, 1995). Recently, a new type of stable three-dimensional metal–organic framework has been reported (Lu *et al.*, 2006). Unlike pyridine 2,4-, 3,4- 2,5- and 2,6-dicarboxylic acids, which have been widely reported as bridging ligands for the assembly of various coordination polymers, complexes with 3,5-pyrazole-dicarboxylic acid (H_2pydc) have been reported only rarely (Pan *et al.*, 2000). We report here the synthesis and structure of a copper(II) coordination polymer with 3,5-pyrazole-dicarboxylic acid, (I).

(I)
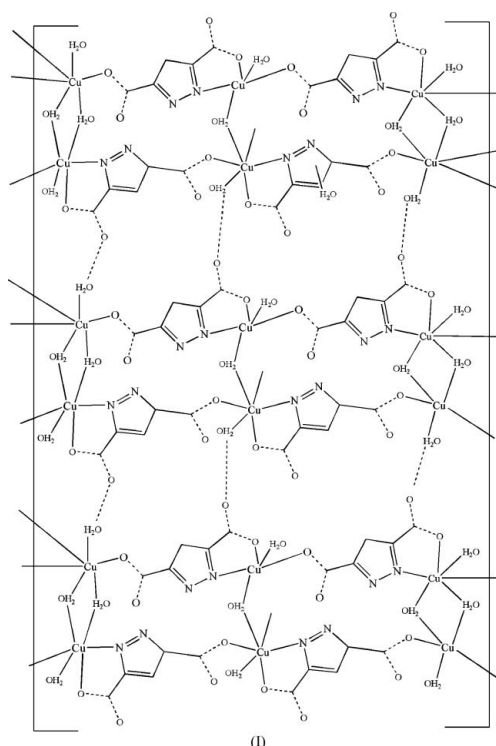
In (I), the Cu atom adopts a distorted octahedral CuO$_5$N coordination geometry (Fig. 1 and Table 1). Pairs of Cu atoms are bridged by molecules of the 3,5-pyrazoledicarboxylate ligand *via* its *N*– and *O*-donor atoms. and one *O*-donor atom of the second carboxyl group. The copper centers are further bridged by two μ_2-aqua ligands, generating a ladder-like chain (Fig. 2), with a Cu···Cu distance of 3.269 (3) Å. These chains are further linked *via* N—H···O hydrogen bonding between pyridyl N atoms, carboxylate O atoms and aqua ligands (Table 2), forming a three-dimensional network.

Experimental

A mixture of Cu(NO$_3$)$_2$·2H$_2$O (0.5 mmol, 0.120 g), 3,5-pyrazole-dicarboxylic acid (0.5 mmol, 0.087 g), NaOH (1 mmol, 0.04 g), and water (10 ml) was mixed in a 23 ml Teflon reactor which was heated at 453 K for 6 d and then cooled to room temperature at a rate of 5 K h^{-1} (yield: 42%). Analysis for C$_5$H$_6$CuN$_2$O$_6$ (found/calc %): C 23.48 (23.68), H 2.34 (2.38), N 11.23 (11.04).

Crystal data

[Cu(C$_5$H$_2$N$_2$O$_4$)(H$_2$O)$_2$]	V = 383.55 (7) Å^3
M_r = 253.66	Z = 2
Triclinic, $P\bar{1}$	D_x = 2.196 Mg m^{-3}
a = 6.8178 (7) Å	Mo $K\alpha$ radiation
b = 7.4015 (8) Å	μ = 2.86 mm^{-1}
c = 8.5079 (9) Å	T = 293 (2) K
α = 104.775 (2)°	Block, green
β = 90.733 (2)°	0.37 × 0.25 × 0.21 mm
γ = 111.497 (2)°	

Data collection

Bruker APEX area-detector diffractometer	3017 measured reflections
φ and ω scans	1494 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1434 reflections with $I > 2\sigma(I)$
T_{min} = 0.419, T_{max} = 0.582 (expected range = 0.396–0.549)	R_{int} = 0.013
	θ_{max} = 26.0°

Refinement

Refinement on F^2	w = 1/[$\sigma^2(F_o^2)$ + (0.029P)^2 + 1.0214P]
$R[F^2 > 2\sigma(F^2)]$ = 0.030	where P = (F_o^2 + 2F_c^2)/3
$wR(F^2)$ = 0.078	($\Delta/\sigma)_{max}$ < 0.001
S = 1.13	$\Delta\rho_{max}$ = 0.46 e Å^{-3}
1494 reflections	$\Delta\rho_{min}$ = −0.40 e Å^{-3}
143 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O2^i	1.990 (2)	Cu1—N2	2.056 (2)
Cu1—O4	2.032 (2)	Cu1—O1W^{ii}	2.075 (2)
Cu1—O2W	2.038 (2)	Cu1—O1W	2.152 (2)
O2^i—Cu1—O4	89.38 (9)	O2W—Cu1—N2	91.44 (10)
O2^i—Cu1—O2W	89.72 (10)	O4—Cu1—O1W	90.52 (9)
O4—Cu1—O2W	96.53 (10)	O2W—Cu1—O1W	172.86 (9)
O2^i—Cu1—N2	169.15 (9)	N2—Cu1—O1W	90.91 (9)
O4—Cu1—N2	79.76 (9)	O1W^{ii}—Cu1—O1W	78.74 (9)

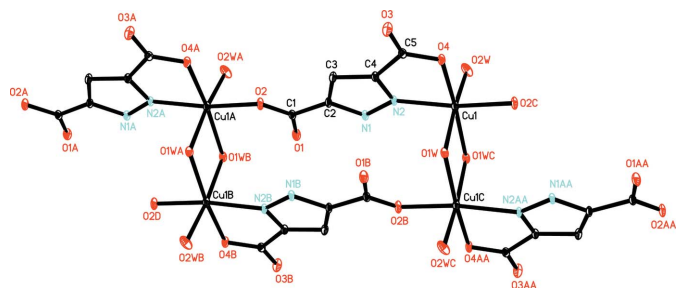Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, -y, -z - 3$.

Figure 1
View of the structure of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $x, y, z + 1$; (ii) $-x, -y, -z - 2$; (iii) $-x, -y, -z - 1$; (iv) $x, y, z - 1$.]
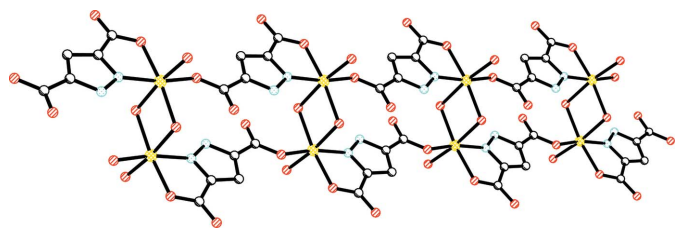

Figure 2
A fragment of the ladder-like chain in (I).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{iii}	0.86	2.09	2.831 (3)	144
O1W—H1WB···O3^{iv}	0.843 (10)	1.823 (12)	2.650 (3)	167 (3)
O1W—H1WB···O4^{iv}	0.843 (10)	2.50 (3)	3.145 (3)	134 (3)
O2W—H2WA···O1^v	0.840 (10)	1.959 (15)	2.782 (3)	166 (3)
O2W—H2WB···O4^{vi}	0.839 (10)	1.954 (11)	2.791 (3)	176 (4)
O1W—H1WA···O1^{vii}	0.842 (10)	1.903 (19)	2.684 (3)	154 (4)

Symmetry codes: (iii) $x - 1, y, z$; (iv) $-x + 1, -y, -z - 3$; (v) $-x, -y + 1, -z - 2$; (vi) $-x + 1, -y + 1, -z - 3$; (vii) $-x, -y, -z - 2$.

The water H atoms were located in a difference Fourier map and refined with distance restraints O—H = 0.85 (1) Å and H···H = 1.39 (1) Å. Other H atoms were placed at calculated positions (C—H = 0.93 Å and N—H = 0.86 Å) and refined using the riding-model approximation with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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