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A one-dimensional copper coordination polymer containing both dicyanamide and 1,10-phenanthroline ligands

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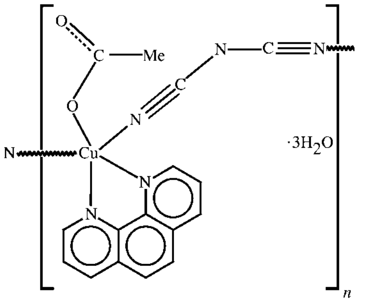
The crystal structure of *catena*-poly[[[acetato(1,10-phenanthroline-κ^2N,N')copper(II)]-μ-dicyanamido-$\kappa^2N^1:N^5$] trihydrate], $\{[Cu(C_2H_3O_2)(C_2N_3)(C_{12}H_8N_2)]\cdot 3H_2O\}_n$, consists of a zigzag chain formed by the polymer $[Cu(CH_3COO)(dca)(phen)]_n$ (phen is 1,10-phenanthroline and dca is dicyanamide), with three water molecules per repeat unit of the polymer. The Cu^{II} atom has a slightly distorted square-pyramidal coordination environment consisting of two N atoms of the phen ligand, two nitrile N atoms of different dca ligands, one of them axial, and one O atom of the acetate anion. The compound forms a one-dimensional chain using dca as an end-to-end bridging ligand. Non-covalent interactions, π–π stacking and hydrogen bonding mediate the bundling of the polymer chains into a three-dimensional structure, with the water molecules playing an important role in the hydrogen bonding.

Comment

The construction of supramolecular aggregates has received much attention due to their intriguing network topologies and potential functions as new classes of materials (Eddaoudi *et al.*, 2002; Li *et al.*, 1999). Hydrogen-bonding and π–π stacking interactions have been commonly used as supramolecular 'cement' due to their directionality, specificity and biological relevance (Fyfe & Stoddart, 1999; Roesky & Andruh, 2003). Combinations of hydrogen-bonding patterns can generate a variety of supramolecular synthons, which have been summarized in a review by Fyfe & Stoddart (1999). It is known that π–π stacking interactions can influence the stereochemistry of organic reactions, binding affinities in host–guest chemistry and protein stability (Hunter, 1994; Jorgensen & Severance, 1990).

In a separate area, metal dicyanamide {dca, $[N(CN)_2]^-$} coordination chemistry is a fast-growing research field because of the interesting possibilities for coordination and physical properties that these complexes possess (Miller & Manson, 2001). Dicyanamide is a versatile ligand for coordinating to metal ions in various modes, such as monodentate bonding through a nitrile N atom (Marshall *et al.*, 2000), end-to-end bridging through the two nitrile N atoms (Manson, Arif & Miller, 1999; Jensen *et al.*, 1999) and triply coordinating through its three N atoms, bridging three metal atoms (Jensen *et al.*, 2000; Kurmco & Kepert, 1998). The coordination properties thus allow for the preparation of compounds with a large variety of architectures, both mononuclear and dinuclear, as well as one-, two- and three-dimensional networks. Compounds formulated as $[M(dca)_2]_n$ (M is Mn, Fe, Co, Ni, Cu, Zn *etc.*), containing only dca ligands, have been synthesized (Jensen *et al.*, 1999; Batten *et al.*, 1998). Many ternary compounds have been synthesized by the introduction of monodentate or bidentate co-ligands such as pyridine, bipyridine, 1,10-phenanthroline and 2,2′-biimidazole, resulting in various interesting structures (Marshall *et al.*, 2000; Manson, Arif, Incarvito *et al.*, 1999; Potočňák *et al.*, 1995). As an extension of this research, we have synthesized the novel title one-dimensional compound, $\{[Cu(CH_3COO)(dca)(1,10\text{-}phen)]\cdot 3H_2O\}_n$, (I), and we report here its synthesis and crystal structure, the network of which is sustained by π–π stacking and hydrogen-bonding interactions.



(I)

The Cu atom in (I) is in a distorted square-pyramidal environment, with the equatorial positions occupied by two phen N atoms [Cu1—N1 = 2.0246 (16) and Cu1—N2 = 2.0195 (16) Å], one nitrile N atom of the bridging dca [Cu1—N5^i = 1.9958 (16) Å; symmetry code: (i) $x, y-1, z$] and one carboxyl O atom of the acetate anion [Cu1—O1 = 1.9333 (13) Å], which are coplanar with a mean deviation of 0.159 (2) Å. The apical position is occupied by a nitrile N atom of another bridging dca, with a Cu1—N3 distance of 2.1777 (18) Å, which is about 0.164 (2) Å longer than the mean Cu—N(eq) bond distance. The Cu atom is displaced by 0.246 (2) Å from the equatorial plane in the direction of the apical atom.

The $[N(CN)_2]^-$ ligands form end-to-end bridges between Cu^{II} atoms to give an infinite zigzag chain extended along the b axis, while the phen ligands chelated to the Cu atoms are located on the same side of the chain, as shown in Fig. 1. The –Cu–dca–Cu–dca– backbone chain in (I) is similar to those

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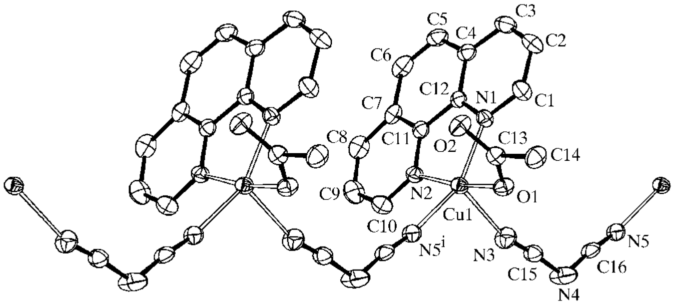

Figure 1
The chain structure of (I) with displacement ellipsoids at the 30% probability level; H atoms have been omitted for clarity. [Symmetry code: (i) $x, y-1, z$.]

found in other dca-bridged Cu chain compounds (Wang *et al.*, 2000; Wu *et al.*, 2003; Luo *et al.*, 2002). However, the Cu1···N4···Cu1 and N4···Cu1···N4 angles in (I) are both 113.46 (4)°, which is notably different from the corresponding values for the four-coordinate Cu compound (132.82 and 95.98°, respectively; Wu *et al.*, 2003), as a result of the different coordination modes of copper in the two cases. A similar result was found for the five-coordinate Cu analogues (Luo *et al.*, 2002), in which the corresponding angles are 120.82 and 114.31°, respectively.

The intrachain Cu···Cu distance of 7.485 (1) Å and the shortest interchain Cu···Cu distance of 6.353 (1) Å in (I) are shorter than those found in the analogues mentioned above {7.708 and 6.452 Å, respectively, in [Cu(phen)(dca)$_2$] (Wang *et al.*, 2000), 8.007 and 6.703 Å in [Cu(phen)(dca)] (Wu *et al.*, 2003), and 7.710 and 6.546 Å in [Cu(phen)(dca)$_2$] (Luo *et al.*, 2002)}.

The dca ligands in (I) have approximate C_{2v} symmetry, with average single C—N and triple N—C bond lengths of 1.296 (3) and 1.136 (3) Å, respectively, which are consistent with typical values for the $[N(CN)_2]^-$ anion (Potočňák *et al.*, 1996). The bond distances and angles in the phen ligands of (I) are in accord with those reported by Anderson (1973).

In comparison with the Cu analogues mentioned above (Wang *et al.*, 2000; Wu *et al.*, 2003; Luo *et al.*, 2002), it is noteworthy that adjacent chains in (I) are organized into pairs through face-to-face π–π stacking interactions between adjacent phen ligands to form a double chain, as shown in Fig. 2. The π–π stacking interactions in (I) can be classified as two types, firstly, ring $R1$ (atoms C4, C5, C6, C7, C11 and C12) to ring $R1$ of a neighbouring phen ligand, denoted $R1\cdots R1$, and secondly, ring $R1$ to ring $R2$ (atoms C7, C8, C9, C10, N2 and C11) of two adjacent phen ligands, denoted $R1\cdots R2$. The two rings involved in a π–π stacking interaction are nearly parallel, with a dihedral angle of 2.28 (9)° and a centroid-to-centroid distance of 3.6161 (16) Å. Two $R1\cdots R2$ and one $R1\cdots R1$ π–π stacking interactions alternately link two adjacent backbones to form a double chain propagated along the b axis. The water molecules are located between the double chains and form hydrogen bonds to each other and to the unbonded O atom of the acetate ligand, thus bridging the double-chain units to form a three-dimensional framework along the a and c directions, as shown in Fig. 3. The π–π stacking and hydrogen-bonding interactions lead to stabilization of the crystal structure of (I).

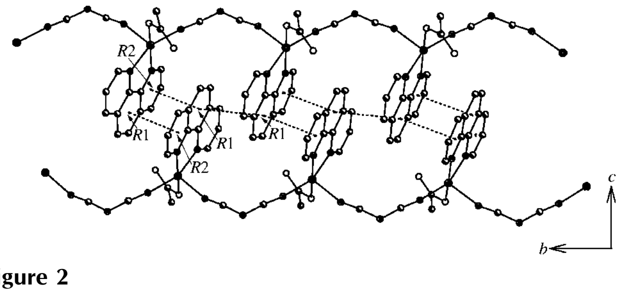

Figure 2
The π–π stacking interactions (dotted lines) between two adjacent chains in (I), extending along the b direction.

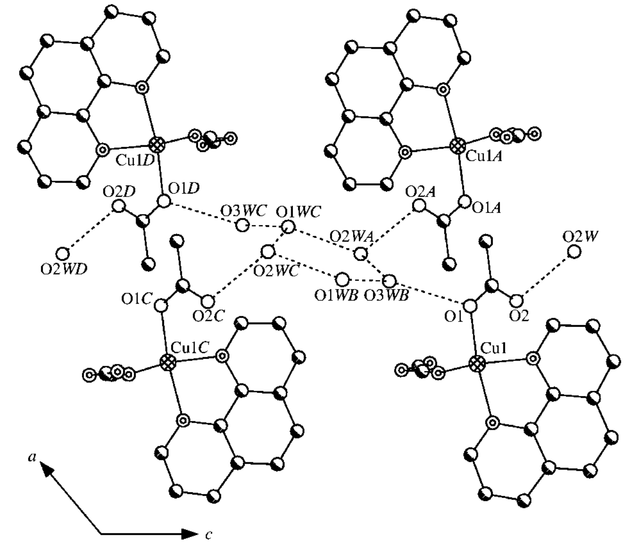

Figure 3
The hydrogen bonding involving acetate O atoms and unligated water molecules in the hydrophilic region of the structure of (I). [Suffix *A* denotes atoms at the symmetry position ($\frac{1}{2}-x, \frac{1}{2}-y, 1-z$), *B* ($\frac{1}{2}-x, \frac{3}{2}-y, 1-z$), *C* ($x, 1-y, z-\frac{1}{2}$) and *D* ($\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$)].

Experimental

Aqueous solutions of $Cu(CH_3COO)_2$ (101 mg, 0.51 mmol) and Na(dca) (91 mg, 1.0 mmol, 4 ml) were mixed thoroughly and an ethanol solution of 1,10-phen (100 mg, 0.51 mg, 10 ml) was added dropwise with stirring. The resulting mixture was filtered and the filtrate was left undisturbed at room temperature. A small quantity of transparent blue crystals of (I) was obtained after a few days.

Crystal data

$[Cu(C_2H_3O_2)(C_2N_3)(C_{12}H_8N_2)]\cdot 3H_2O$
$M_r = 422.89$
Monoclinic, $C2/c$
$a = 26.717\ (4)$ Å
$b = 7.4853\ (10)$ Å
$c = 20.601\ (3)$ Å
$\beta = 117.906\ (9)°$
$V = 3640.8\ (10)$ Å^3
$Z = 8$

$D_x = 1.543$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5119 reflections
$\theta = 3.1$–$27.5°$
$\mu = 1.24$ mm^{-1}
$T = 293\ (2)$ K
Block, blue
$0.45 \times 0.30 \times 0.25$ mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
$T_{\min} = 0.590$, $T_{\max} = 0.734$
11 803 measured reflections
3212 independent reflections
2583 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 25.0°$
$h = -31 \rightarrow 28$
$k = -8 \rightarrow 8$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.138$
$S = 1.07$
3212 reflections
262 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9333 (13)	N3—C15	1.136 (3)
Cu1—N5$^{\rm i}$	1.9958 (16)	N4—C16	1.285 (3)
Cu1—N2	2.0195 (16)	N4—C15	1.300 (3)
Cu1—N1	2.0246 (16)	N5—C16	1.143 (2)
Cu1—N3	2.1777 (18)		
O1—Cu1—N5$^{\rm i}$	91.85 (6)	N2—Cu1—N1	80.51 (6)
O1—Cu1—N2	172.41 (6)	O1—Cu1—N3	92.79 (6)
N5$^{\rm i}$—Cu1—N2	92.67 (7)	N5$^{\rm i}$—Cu1—N3	99.38 (7)
O1—Cu1—N1	92.93 (6)	N2—Cu1—N3	92.48 (7)
N5$^{\rm i}$—Cu1—N1	156.03 (7)	N1—Cu1—N3	103.83 (7)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3W—H31$A\cdots$O1$^{\rm ii}$	0.957 (7)	1.867 (7)	2.810 (2)	167.8 (6)
O3W—H31$B\cdots$O2$W^{\rm iii}$	0.953 (7)	1.971 (12)	2.821 (2)	147.4 (15)
O2W—H21$A\cdots$O2	0.954 (6)	1.859 (10)	2.7506 (18)	154.4 (16)
O2W—H21$B\cdots$O1W	0.955 (6)	1.964 (8)	2.910 (2)	170.6 (15)
O1W—H11$B\cdots$O2$W^{\rm iv}$	0.950 (7)	2.010 (13)	2.808 (3)	140.4 (16)
O1W—H11$A\cdots$O3W	0.952 (7)	1.804 (8)	2.752 (2)	173.8 (15)

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

The H atoms of the water molecules were located in difference Fourier syntheses and refined with O—H distances restrained to a target value of 0.96 (1) Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm O})$. The remaining H atoms were added according to theoretical models, assigned isotropic displacement parameters and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); 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: FA1028). Services for accessing these data are described at the back of the journal.

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