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$[Cu(C_8H_{16}N_4O_2)_{0.5}\{N(CN)_2\}]_n$, a novel ladder-like coordination polymer

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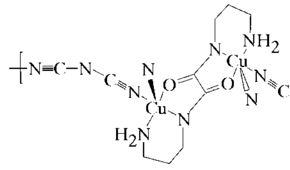
A new polymeric copper complex, *viz. catena*-poly-[[[μ-*N*,*N*′-bis(3-aminopropyl)oxamidato-$\kappa^6N,N',O:N'',N''',O'$]-dicopper(II)]-di-$\mu$-dicyanamido-1:1′$\kappa^2N^1:N^5$;2:2′$\kappa^2N^1:N^5$], $[Cu_2(C_8H_{16}N_4O_2)(C_2N_3)_2]_n$ or $[Cu(oxpn)_{0.5}\{N(CN)_2\}]_n$ [where H_2oxpn is *N*,*N*′-bis(3-aminopropyl)oxamide], has been synthesized by the reaction of Cu(oxpn), $[Cu(ClO_4)_2]\cdot6H_2O$ and NaN_3. In the crystal structure, the Cu atom is five-coordinate and has a square-pyrimidal (SP) configuration. In the polymer, dicyanamide (dca$^-$) groups link Cu^{II} cations in a μ-1,5-bridging mode, generating novel ladders in which each step is composed of dimeric $[Cu_2(oxpn)]^{2+}$ cations. Abundant hydrogen bonds connect the polymer ladders into a two-dimensional network structure.

Comment

In the area of crystal engineering, much attention has been paid to new supramolecular complexes with useful properties, because these compounds can potentially be applied to catalysis, molecular recognition and other fields (Batten, Hoskins *et al.*, 2000; Zhang *et al.*, 2001; Kou *et al.*, 2003). Of all the supramolecular complexes, coordination polymers with special bridging ligands have become very important building blocks of ligand-bridged complexes, which offer various dimensional structures and fascinating physical properties.

Over the past few years, dca$^-$ [dicyanamide, $N(CN)_2{}^-$] has been chosen as a ligand in the design and synthesis of a wide variety of coordination polymers (Vangdal *et al.*, 2002; Liang *et al.*, 2004). The dca$^-$ ion can coordinate to metal ions in versatile patterns, such as monodentate bonding, bidentate bridging, tris-monodentate bridging and four-coordination (Batten & Murray, 2003; Batten, Hoskins *et al.*, 2000; Batten, Jensen *et al.*, 2000; Manson *et al.*, 1998). In addition, *N*,*N*′-disubstituted oxamides with coordinating *N*-substituents are excellent ligands that can connect two metal ions (Ruiz *et al.*, 1999). Some dinuclear Cu^{II}–oxpn^{2-} [oxpn is *N*,*N*′-bis-(3-aminopropyl)oxamide(2−)] complexes have been synthesized, for example $[Cu_2(oxpn)(NCO)_2]$ (Lloret *et al.*, 1992), $[Cu_2(oxpn)(NCS)_2(H_2O)]$ and $[Cu_2(oxpn)(N_3)_2(H_2O)_2]$ (Chen *et al.*, 1994). However, all these substances are, surprisingly, not bridged by the quasi-halide ligands. Therefore, it is of interest to clarify whether dca$^-$ can further bridge $[Cu_2(oxpn)]^{2+}$ groups to give a coordination polymer. It is worth mentioning that $[Cu_2(oxen)(dca)_2]_n$ [oxen is *N*,*N*′-bis-(2-aminoethyl)oxamide(2−)] has a one-dimensional chain-like structure (Chu *et al.*, 2003) in which the dca$^-$ ion acts as a bridging ligand. In this study, we selected the oxpn^{2-} ion to synthesize a new polymeric complex, (I), the molecular structure of which is entirely different from that of $[Cu_2(oxen)(dca)_2]_n$.



(I)

The structure of $[Cu(oxpn)_{0.5}(dca)]_n$ is depicted in Fig. 1, and selected bond lengths and angles are listed in Table 1. The complex has a one-dimensional ladder-like molecular structure, with an oxpn-bridged dinuclear group. A centrosymmetric repeat unit is formed *via* the oxpn^{2-} ion connecting two Cu^{2+} cations. According to the principle of low energy, oxpn^{2-} adopts a *trans* conformation rather than a *cis* one. Therefore, the oxpn^{2-} group chelates two Cu^{II} ions, the coordination environments of which are identical (*i.e.* coordinated by two N atoms and one O atom of the oxpn group). The bond lengths and angles of the oxpn group are similar to those in the structure reported by Chen *et al.* (1994). The dicyanamide group binds to the Cu^{2+} cations in an end-to-end bridging mode through the two nitrile N atoms. The Cu^{2+} cation exhibits distorted square-pyramidal (SP) geometry; the basal plane is formed by one O atom and two N atoms from an oxpn^{2-} group, and one N atom from a dca$^-$ group. One N atom from another dca$^-$ ligand occupies the apical position. The equatorial Cu—N or Cu—O bond lengths [ranging from 1.950 (3) to 1.994 (2) Å] are shorter than the axial Cu—N bond length [2.583 (3) Å] as a result of the Jahn–Teller effect for the d^9 configuration of the Cu^{II} ion in an SP environment. The cell packing of the polymeric structure is shown in Fig. 2.

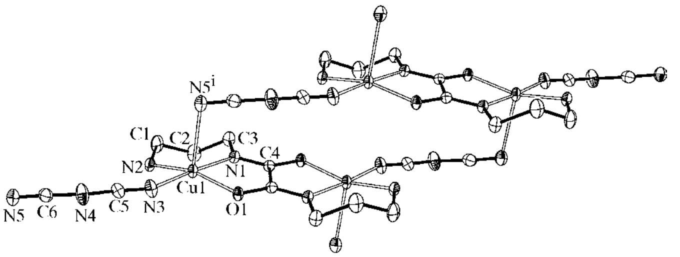


Figure 1
A fragment of the polymeric structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $1 + x, y, z$.]

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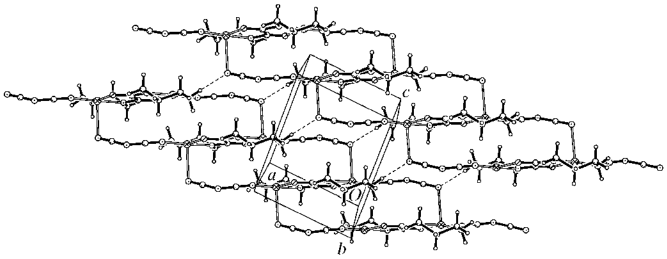

Figure 2
The packing of the two-dimensional hydrogen-bonding network of the title complex. Dashed lines represent hydrogen-bonding interactions.

It can be seen that the mutually parallel dinuclear units form a novel slanted one-dimensional and dca-bridging staircase configuration. Every step is composed of a bis-chelating oxpn bridge and two Cu^{2+} cations. The end-to-end-linking dca groups form the stair uprights. The Cu···Cu distances across the oxpn and dca bridges are 5.246 (1) and 6.745 (1) Å, respectively. Abundant hydrogen bonds (N—H···O and N—H···N) link the one-dimensional dca-bridged ladders to one another, forming a two-dimensional structure, as shown in Fig. 2.

Experimental

Cu(oxpn) was synthesized according to procedures described by Journaux *et al.* (1985). To a stirred purple aqueous solution (10 ml) of Cu(oxpn) (26.3 mg, 0.1 mmol) were slowly added $[Cu(ClO_4)_2]\cdot 6H_2O$ (27.1 mg, 0.1 mmol), and NaN_3 (13.0 mg, 0.2 mmol) in water. The resulting solution was filtered and the filtrate evaporated at room temperature until violet crystals formed.

Crystal data

$[Cu_2(C_8H_{16}N_4O_2)(C_2N_3)_2]$
$M_r = 459.42$
Triclinic, $P\bar{1}$
$a = 6.7451$ (6) Å
$b = 7.7744$ (7) Å
$c = 8.0605$ (7) Å
$\alpha = 88.794$ (2)°
$\beta = 84.323$ (2)°
$\gamma = 88.052$ (2)°
$V = 420.30$ (6) Å^3

$Z = 1$
$D_x = 1.815$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1430 reflections
$\theta = 5.1$–59.6°
$\mu = 2.56$ mm^{-1}
$T = 293$ (2) K
Platelet, purple
0.25 × 0.15 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.680$, $T_{max} = 0.815$
2347 measured reflections

1457 independent reflections
1268 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.0°$
$h = -5 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.092$
$S = 1.02$
1457 reflections
118 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.951 (3)	N3—C5	1.147 (5)
Cu1—N3	1.972 (3)	N4—C5	1.289 (5)
Cu1—N2	1.987 (3)	N4—C6	1.327 (6)
Cu1—O1	1.994 (3)	C6—N5	1.149 (5)
Cu1—N5^{i}	2.583 (3)		
N1—Cu1—N3	175.76 (13)	N2—Cu1—O1	162.46 (12)
N1—Cu1—N2	94.99 (12)	C5—N3—Cu1	157.0 (4)
N3—Cu1—N2	88.59 (14)	C5—N4—C6	120.8 (4)
N1—Cu1—O1	83.98 (11)	N3—C5—N4	172.6 (4)
N3—Cu1—O1	91.92 (13)	N5—C6—N4	174.2 (5)

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

H atoms bound to C and N atoms were placed using the HFIX command in *SHELXL*97 (Sheldrick, 1997). All H atoms were allowed for as riding atoms (C—H = 0.97 Å and N—H = 0.90 Å).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1157). Services for accessing these data are described at the back of the journal.

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