

Square-grid coordination networks of diaquabis(4,4'-bipyridyl)copper(II) crosslinked by hydrogen bonds through two monoanions of 1-benzofuran-2,3-dicarboxylic acid and five molecules of water

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The title compound, poly[[[diaquacopper(II)]-di- μ -4,4'-bipyridyl] bis(3-carboxy-1-benzofuran-2-carboxylate) pentahydrate], $\{[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_{10}\text{H}_5\text{O}_5)_2 \cdot 5\text{H}_2\text{O}\}_n$, crystallizes in a single-framework architecture. It is composed of two-dimensional square-grid coordination networks of 1:2:2

copper–4,4'-bipyridine–water units, wherein each copper ion coordinates equatorially to four bipyridyl units and axially to two water ligands. The polymeric nets are intercalated by layers of the benzofurandicarboxylic acid monoanions and additional water species. An extensive array of hydrogen bonds interlinks the various components of the structure. The Cu atom and the bipyridyl entities are located on axes of twofold rotation. This study confirms the preferred monoanionic nature of the benzofurandicarboxylic acid molecule. It reveals a rarely observed extended coordination polymer composed only of copper ions and bipyridyl linkers, and an interesting hydrogen-bonding connectivity between the polymeric layers aided by the benzofurandicarboxylic acid and water components intercalated in the structure.

Comment

This study is part of our investigation of the supramolecular reactivity of 1-benzofuran-2,3-dicarboxylic acid. It was shown in a preceding report (Koner & Goldberg, 2009) that one carboxyl group can be readily deprotonated to convert this ligand into a monoanionic species (BFDC^-), while the H atom of the second carboxyl group is involved in an intramolecular hydrogen bond and is more difficult to ionize. It has also been shown that BFDC^- can act as a good coordinating ligand, as well as a 1- counter-ion, to 2+ and 3+ transition metal cations. This includes the formation of an octahedral complex, *viz.* $[\text{Cu}(\text{BFDC}^-)_2(\text{imidazole})_4]$ (Koner & Goldberg, 2009). In an additional experiment, the imidazole component was replaced

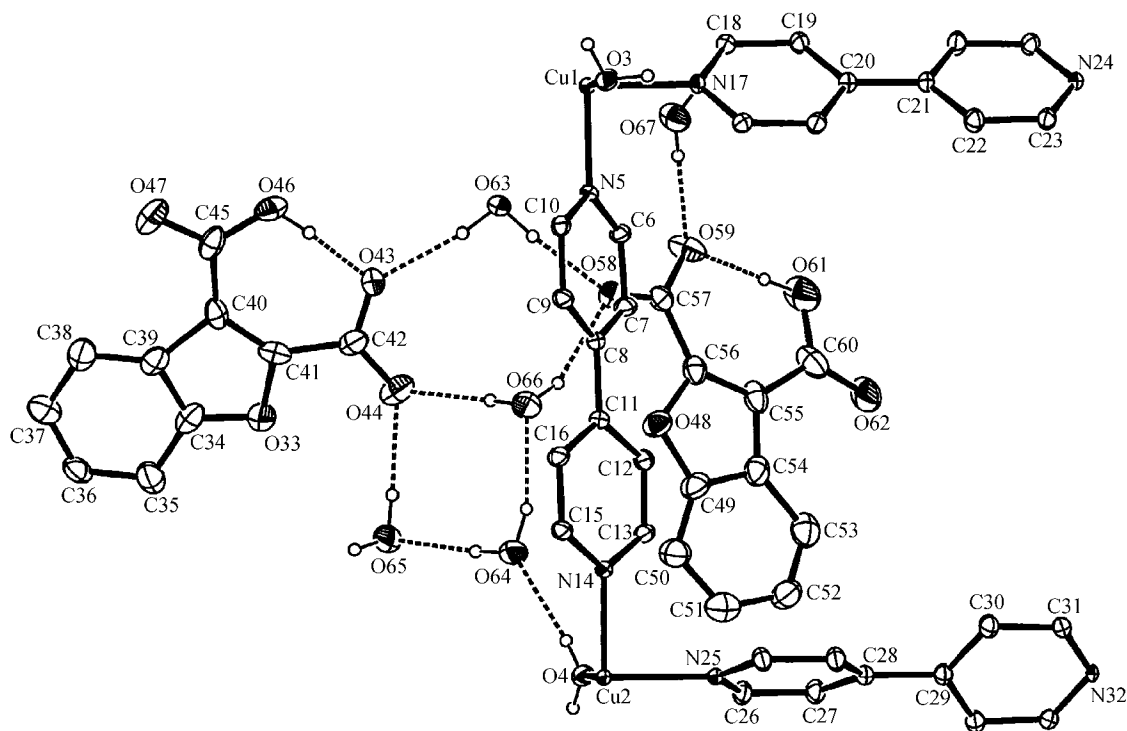
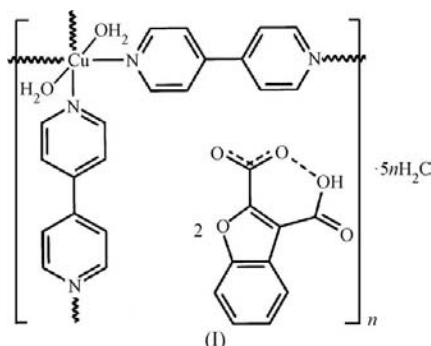


Figure 1

The molecular structure of (I), showing the atom-labeling scheme. Ellipsoids represent displacement parameters at the 40% probability level at *ca* 110 K. The Cu–bipyridine units reside on axes of twofold rotation at $(\frac{1}{4}, \frac{1}{4}, z)$ (atoms Cu1, N17, C20, C21 and N24) and at $(\frac{1}{4}, -\frac{1}{4}, z)$ (atoms Cu2, N25, C28, C29 and N32), and only the asymmetric unit is labeled. Hydrogen bonds are indicated by dashed lines. H atoms of the benzene and pyridyl rings have been omitted.

in the reaction mixture by 4,4'-bipyridine, anticipating that the latter may provide extended connectivity features in order to afford the formation of two- or three-dimensional coordination frameworks instead of discrete complexes. Coordination of BFDC⁻ to the copper ions was also envisioned (as in the earlier example), to account for charge balance. The asymmetric unit of the resulting multicomponent product, (I), is shown in Fig. 1.



The crystal structure can be best described as composed of alternating layered zones of extended coordination and hydrogen-bonded assemblies. The former features a square-grid network in which the bipyridine units line the sides of the grids, while the copper ions serve as connecting nodes (Fig. 2). Each ion has an octahedral coordination environment (Table 1), where the equatorial positions are occupied by the N atoms of four adjacent bipyridine ligands. The *trans*-axial positions at every site are occupied by coordinated water ligands. In accordance with the Jahn–Teller effect, the octahedra are axially distorted with longer Cu–O bonds compared with Cu–N (Table 1). Correspondingly, each of the

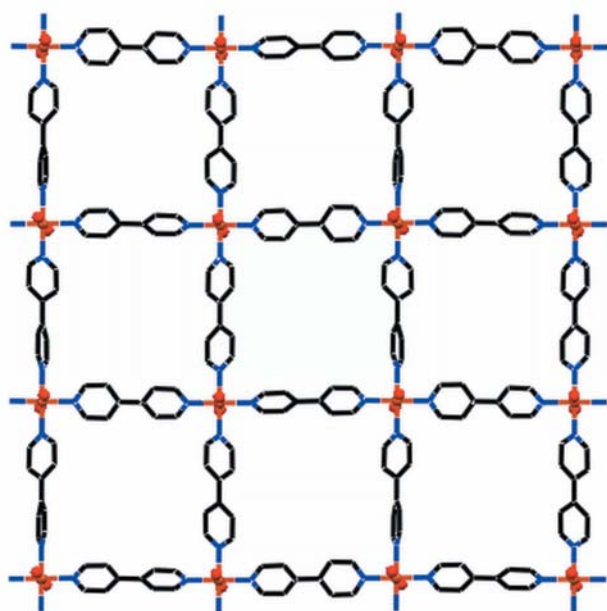


Figure 2

A wireframe illustration of the square-grid coordination network, which is aligned parallel to the *bc* plane of the crystal structure. The Cu and water O atoms are depicted by small spheres.

bipyridine spacers binds to two adjacent six-coordinated copper ions. The Cu1/N17/C18–C23/N24 entities are located on axes of twofold rotation at $(\frac{1}{4}, \frac{1}{4}, z)$, while the Cu2/N25/C26–C31/N32 units are positioned on twofold axes at $(\frac{1}{4}, -\frac{1}{4}, z)$.

The coordination networks are aligned parallel to the *bc* plane of the crystal structure, being centered at $x = \frac{1}{4}$ and $x = \frac{3}{4}$. The size of the grid is characterized by Cu···Cu distances of 11.144 (2) and 11.275 (2) Å between the consecutive copper ions along the *b* and *c* axes, respectively. While many coordination polymers and complexes involving transition metal ions and 4,4'-bipyridine are known, those involving a square-shaped arrangement of this ligand with copper ions have been reported only recently. They involve, for example, the discrete *cyclo*-tetrakis(μ_2 -4,4'-bipyridine)tetracopper(II) molecule (Dey *et al.*, 2004) and square-grid-like copper–4,4'-bipyridine coordination layers with connectivity and coordination distances similar to those observed in this study (Wang *et al.*, 2007).

In the crystal structure, the polymeric layers shown in Fig. 2 are intercalated by parallel hydrogen-bonded layers centered at $x = 0$ and $x = \frac{1}{2}$. These are composed of water molecules and the planar monoanionic benzofurandicarboxylic acid entities (see below). The latter are grouped in pairs in a partly overlapping manner across centers of inversion. The mean interplanar distances between the overlaid units are 3.56 (3) and 3.23 (3) Å for the more overlapping [across inversion at $(\frac{1}{2}, 0, 0)$] O33/C34–C41 and the less overlapping [across inversion at $(\frac{1}{2}, 0, \frac{1}{2})$] O48/C49–C56 aromatic fragments, respectively (Fig. 3). The hydrogen-bonded layers interact further with the coordination networks from above and below by additional hydrogen bonding of the O63, O64 and O67 water molecules to the Cu(H₂O)₂ nodes, through the coordinated O3 and O4 water ligands (Table 2). Correspondingly, the BFDC⁻ units approach from above and below, and partly protrude into, the void segments of the adjacent coordination networks. This in turn allows the preservation of a nearly ideal square geometry of the grid, while rhombus distortion of the network to minimize the void space has frequently been

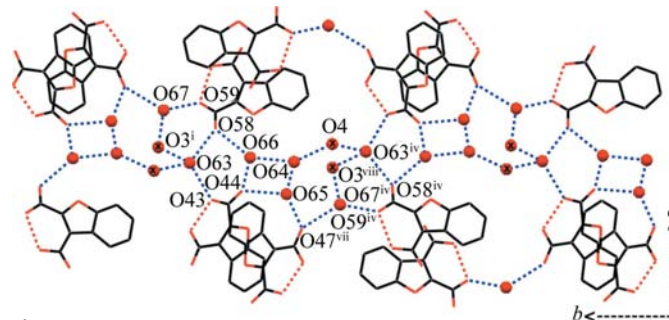


Figure 3

A face-on view of the hydrogen-bonded layer containing BFDC⁻ anions and water molecules centered around $x = \frac{1}{2}$. This and the symmetry-related layer at $x = 0$ are aligned parallel to the *bc* plane of the crystal structure. Hydrogen bonds are denoted by dashed lines. The O atoms of the water molecules are denoted by small spheres; those coordinated to copper (O3 and O4) are marked with an 'x'. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x + 1, -y, -z$; (viii) $x + \frac{1}{2}, -y, -z + \frac{1}{2}$.]

observed in other framework solids (Wang *et al.*, 2007; George *et al.*, 2006).

A rigorous graph-set analysis (Bernstein *et al.*, 1995) of the hydrogen-bonded networks in this structure is quite complex, as the latter involve different types of hydrogen bonds within and between the different component species. Therefore, the current discussion is limited to the type-specification of the basic localized ring patterns. The intramolecular hydrogen bonding in the BFDC⁻ ligands is characterized by the *S*(7) descriptor. The association of the two anions of the asymmetric unit through the O63 and O66 water molecules, involving also atoms O43, O44 and O58, forms a ten-membered *R*₄³(10) ring with four H-atom donors and three H-atom acceptors. An adjacent ring involves the carboxylate O44 atom and the O64, O65 and O66 water molecules, and is specified as *R*₄⁴(8). Two further rings represent association of the anionic layers to the copper-coordinated water ligands. As shown in Fig. 3, one involves atoms O58, O59, O63, O67 and O3(-*x* + ½, -*y* + ½, *z*) and is defined as *R*₄⁴(10); the other ring is composed of atoms O4, O64, O65, O47(-*x* + 1, -*y*, -*z*), O3(*x* + ½, -*y*, -*z* + ½), O63(-*x* + 1, *y* - ½, -*z* + ½) and O67(-*x* + 1, *y* - ½, -*z* + ½) assembled into an *R*₇⁵(14) pattern. These four types of ring patterns are fused into a continuous hydrogen-bonding array, which propagates parallel to the *b* axis of the crystal structure. Similar arrays occur in a periodic manner along the ±*c* directions, at the interfaces between adjacent rows of the BFDC⁻ anions.

The intercalated crystal structure of (I) is illustrated in Fig. 4.

In summary, compound (I) exhibits a framework architecture formed by an interesting combination of coordination and hydrogen-bonding networking. It is composed of alternating layers of square-grid coordination polymers of the Cu(H₂O)₂ and bipyridine species and hydrogen-bonded assemblies of BFDC⁻ and water molecules. These layered fragments are further interconnected to one another by

hydrogen bonds from the axial copper-coordinated water ligands to water molecules of the hydrophilic zones.

Experimental

Copper nitrate, 1-benzofuran-2,3-dicarboxylic acid, 4,4'-bipyridine and all other solvents (see below) were obtained commercially. Cu(NO₃)₂·2.5H₂O (0.058 g, 0.25 mmol) and 1-benzofuran-2,3-dicarboxylic acid (0.52 g, 0.25 mmol) were added in a glass tube to a 1:1 mixture (10 ml) of *N,N*-dimethylformamide and water. A solution of 4,4'-bipyridine (0.078 g, 0.5 mmol) in ethanol (4 ml) was then layered carefully on top of the mixture. Green blocks of the title compound deposited after about one week. IR (KBr, cm⁻¹): 3447 (water stretching vibration), 1718 (COOH), 1630 and 1590 (COO⁻ asymmetric stretching), 1402 and 1323 (COO⁻ symmetric stretching), 1224 (*m*), 1093 (*m*), 1018 (*w*), 869 (*m*), 831 (*m*), 745 (*w*), 635 (*w*). The asymmetric and symmetric O—H stretching vibrations of the water of hydration appear as a broad band centered at 3447 cm⁻¹. The IR spectrum clearly indicates the presence of both protonated carboxyl and deprotonated carboxylate groups, as is also confirmed by the crystallographic analysis. The series of medium or weak intensity bands within 1224–645 cm⁻¹ is associated with the 4,4'-bipyridyl and benzofuran units.

Crystal data

[Cu(C ₁₀ H ₈ N ₂) ₂ (H ₂ O) ₂]- (C ₁₀ H ₅ O ₅) ₂ ·5H ₂ O	<i>V</i> = 7962.49 (18) Å ³
<i>M_r</i> = 912.30	<i>Z</i> = 8
Orthorhombic, <i>Pccn</i>	Mo <i>K</i> α radiation
<i>a</i> = 15.8470 (2) Å	<i>μ</i> = 0.63 mm ⁻¹
<i>b</i> = 22.2874 (3) Å	<i>T</i> = 110 (2) K
<i>c</i> = 22.5446 (3) Å	0.40 × 0.40 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer	6077 reflections with <i>I</i> > 2σ(<i>I</i>)
58792 measured reflections	<i>R</i> _{int} = 0.057
9629 independent reflections	

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.065	6 restraints
<i>wR</i> (<i>F</i> ²) = 0.210	H-atom parameters constrained
<i>S</i> = 1.09	Δ <i>ρ</i> _{max} = 1.97 e Å ⁻³
9628 reflections	Δ <i>ρ</i> _{min} = -0.88 e Å ⁻³
564 parameters	

Table 1 Selected geometric parameters (Å, °).

Cu1—N5	2.024 (3)	Cu2—N14	2.030 (3)
Cu1—N17	2.070 (3)	Cu2—N25	2.094 (3)
Cu1—O3	2.351 (2)	Cu2—O4	2.380 (2)
N5 ⁱ —Cu1—N5	179.76 (13)	N14 ⁱⁱⁱ —Cu2—N14	179.08 (13)
N5—Cu1—N17	90.12 (7)	N14—Cu2—N32 ⁱⁱ	90.46 (7)
N5—Cu1—N24 ⁱⁱ	89.88 (7)	N14—Cu2—N25	89.54 (7)
N17—Cu1—N24 ⁱⁱ	180	N32 ⁱⁱ —Cu2—N25	180
N5 ⁱ —Cu1—O3 ⁱ	88.10 (9)	N14—Cu2—O4 ⁱⁱⁱ	91.68 (9)
N5—Cu1—O3 ⁱ	91.90 (9)	N14—Cu2—O4	88.32 (9)
N17—Cu1—O3 ⁱ	90.77 (5)	N25—Cu2—O4	89.77 (5)
N24 ⁱⁱ —Cu1—O3 ⁱ	89.23 (5)	O4 ⁱⁱⁱ —Cu2—O4	179.54 (10)
O3 ⁱ —Cu1—O3	178.46 (11)		

Symmetry codes: (i) -*x* + ½, -*y* + ½, *z*; (ii) -*x* + ½, *y*, *z* - ½; (iii) -*x* + ½, -*y* - ½, *z*.

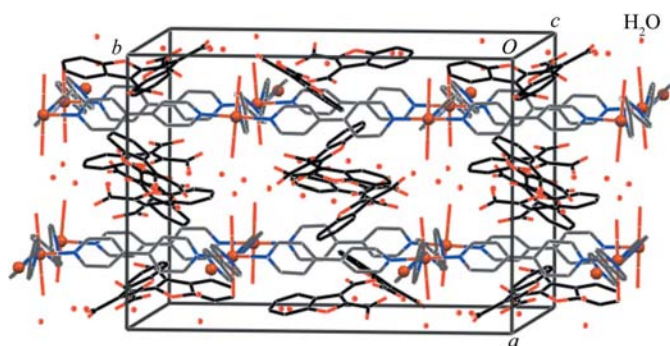


Figure 4 The crystal packing of (I), showing edge-on the alternating zones of the coordination networks and the hydrogen-bonded layers. The Cu atoms are denoted by small spheres; the uncoordinated water molecules are indicated as thick isolated dots. Pale wireframe and dark wireframe denote the bipyridine and BFDC⁻ fragments, respectively. Note that the latter are located above and below the void spaces of the Cu–bipyridine coordination networks.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3A...O63 ⁱ	0.85	1.89	2.730 (3)	168
O3—H3B...O67 ⁱ	0.85	1.90	2.738 (3)	167
O4—H4A...O64	0.85	1.96	2.764 (3)	159
O4—H4B...O63 ^{iv}	0.85	1.99	2.817 (3)	164
O46—H46...O43	0.85	1.56	2.410 (4)	172
O61—H61...O59	0.85	1.74	2.594 (4)	179
O63—H63A...O43	0.85	1.90	2.740 (3)	172
O63—H63B...O58	0.85	1.86	2.702 (3)	173
O64—H64A...O65	0.85	1.93	2.779 (4)	174
O64—H64B...O66	0.85	1.97	2.790 (4)	163
O65—H65A...O47 ^v	0.85	1.86	2.711 (4)	174
O65—H65B...O44	0.85	1.98	2.809 (4)	164
O66—H66A...O44	0.85	1.95	2.791 (5)	170
O66—H66B...O58	0.85	2.15	2.950 (4)	158
O67—H67A...O59	0.85	2.00	2.853 (4)	177
O67—H67B...O47 ^{vi}	0.85	2.06	2.896 (4)	167

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

Reflection (012) was partially hidden by the beam stop, could not be measured reliably, and was thus omitted in the refinement. H atoms bound to C atoms were located in calculated positions and were constrained to ride on their parent atoms, with C—H distances of 0.95 Å and with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{C})$. Most of the H atoms bound to O atoms could be located in difference Fourier maps. The remaining H atoms, which could not be located reliably, were placed in calculated positions to optimize intermolecular hydrogen bonding. The corresponding O—H distances were then constrained to 0.85 Å, and assigned $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{O})$. Their parameters were not refined in the final least-squares calculations. The residual electron-density Fourier maps contained four peaks within $1\text{--}2 \text{ e \AA}^{-3}$, reflecting possible partial rotational disorder of the uncoordinated benzofurandicarboxylic acid molecules. This disorder could not be reliably modeled by discrete atoms. Six SIMU-type restraints were applied to the displacement parameters of atoms C39 and C40.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3104). Services for accessing these data are described at the back of the journal.

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