

The coordination polymers poly[μ -4,4'-bipyridyl-di- μ -formato-copper(II)] and *catena*-poly[[[diaqua(1-benzofuran-2,3-dicarboxylato)copper(II)]- μ -1,2-di-4-pyridylethane] dihydrate]

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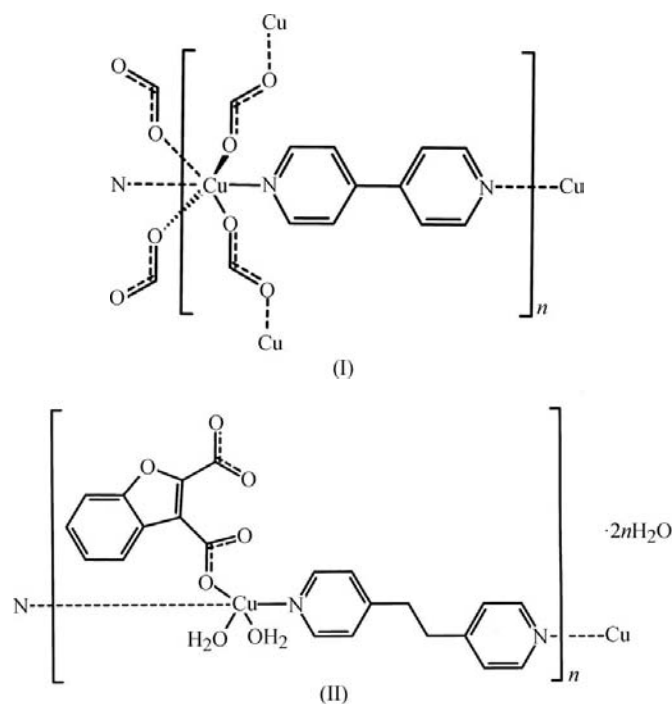
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The title compounds, $[\text{Cu}(\text{CHO}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)]_n$, (I), and $\{[\text{Cu}(\text{C}_{10}\text{H}_4\text{O}_5)(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$, (II), are composed of one-dimensional linear coordination polymers involving copper(II) ions and bidentate bipyridyl species. In (I), the polymeric chains are located on twofold rotation axes at $(x, x, 0)$ and are arranged in layered zones centered at $z = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$ parallel to the ab plane of the tetragonal crystal. Weak coordination of the formate anions of one layer to the copper centers of neighboring layers imparts a three-dimensional connectivity to this structure. In (II), the polymeric chains propagate parallel to the a axis of the crystal. Noncoordinated water molecules link the chains through $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonding in directions perpendicular to c , imparting to the entire structure three-dimensional connectivity. The metal ions adopt distorted octahedral and square-based pyramidal environments in (I) and (II), respectively. This study indicates that, under the given conditions, extended coordination involves Cu^{II} centers associating with the bipyridyl ligands rather than with the competing benzofurandicarboxylate entities.

Comment

This study is part of our exploratory search for multidentate polycarboxylic acid ligands that can be utilized, in combination with metal ions, in the construction of framework solids (Goldberg, 2005). In earlier reports, we investigated the supramolecular reactivity of the novel previously unexplored ligand 1-benzofuran-2,3-dicarboxylic acid (BFDC) (Koner & Goldberg, 2009*a,b*). It was shown that in reactions of BFDC with various metal ions, carried out under mild conditions, this ligand converts readily into a monoanionic species (BFDC^-) by deprotonation of one carboxyl group. The H atom in the second carboxyl group is then involved in an intramolecular

hydrogen bond to the carboxylate function. BFDC^- was found to act as a good coordinating ligand, as well as a singly charged noncoordinated counter-anion to 2+ and 3+ transition metal cations (Koner & Goldberg, 2009*a,b*). It has also been shown that in more forcing (strongly basic) reaction environments it is possible to doubly deprotonate this ligand to a dianion, BFDC^{2-} , which can then function as a bridging ligand in the construction of extended coordination networks with an oxophilic metal ion such as La^{III} (Koner & Goldberg, 2009*c*). In subsequent investigations, we have examined the reactivity of BFDC^{2-} towards Cu^{II} ions in the presence of bipyridyl ligands. As no coordination polymers have been obtained thus far by direct reaction between benzofurandicarboxylic acid and copper ion moieties, we introduced (in addition to the BFDC) different bipyridine reagents into the reaction mixtures, anticipating that the latter might provide additional connectivity features and assist in the formation of polymeric aggregates (see *Experimental*). We report here the structural features of two compounds synthesized in the above context, namely, poly[μ -4,4'-bipyridyl-di- μ -formato-copper(II)], (I), and *catena*-poly[[[diaqua(1-benzofuran-2,3-dicarboxylato)-copper(II)]- μ -1,2-di-4-pyridylethane] dihydrate], (II).



Displacement ellipsoid plots of the structures of (I) and (II) are depicted in Figs. 1 and 2, respectively. Disappointingly, in neither case was the BFDC^{2-} ligand involved in the formation of the polymer. It has not been incorporated into (I) at all, while in (II) it plays the role of a counter-ion coordinated to only one metal site. Instead, the two structures contain linear coordination polymers composed of alternating Cu^{II} ions and the respective bipyridyl ligands. Structure (I) resulted from the reaction of copper nitrate with 4,4'-bipyridine, BFDC and sodium hydroxide in an *N,N*-dimethylformamide (DMF)–

metal-organic compounds

water solvent environment. It turned out that under these experimental conditions, the DMF was hydrolysed to dimethylamine with the release of the formate (HCO_2^-) anion (Burrows *et al.*, 2005; Muniappan *et al.*, 2007), and the latter was incorporated into the crystal structure along with the copper ions. The FT-IR spectrum of the solid product (see *Experimental*) was difficult to analyse due to partial overlap between absorption bands of the 4,4'-bipyridyl ligand (Litvinov *et al.*, 2005; Popov *et al.*, 1961) and the formate anion (Ito & Bernstein, 1956). It revealed typical signals for symmetric and asymmetric vibrations of the COO^- group and ring vibrations of the coordinated 4,4'-bipyridyl ligand, as well as C–O and C–N stretching vibrations in the 1200–1300 cm^{-1} region which could not be assigned to a specific group. The $[\text{Cu}(\text{CHO}_2)_2(4,4'\text{-bipyridyl})]_n$ linear coordination polymer which formed is shown in Fig. 3. The polymer is located on a twofold rotation axis at $(x, x, 0)$, with the metal ion and the N··N axis of the bipyridyl ligand positioned on it. The two formate anions are directed sideways. The polymers are aligned side by side in layers parallel to the ab plane of the

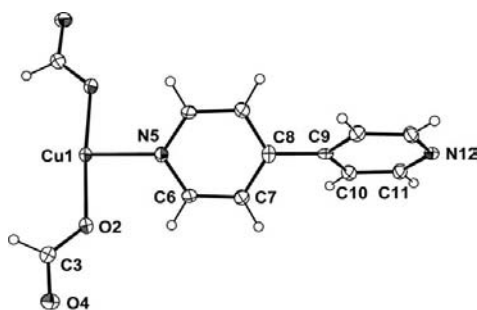


Figure 1

The molecular structure of compound (I). It is located on a twofold rotation axis at $(x, x, 0)$, and only atoms of the asymmetric unit are labeled. Atoms Cu1, N5, C8, C9 and N12 are located on this symmetry axis. The ellipsoids represent displacement parameters at the 50% probability level at 110 (2) K. Cu1 is further coordinated to a translation-related bipyridyl species. It is also approached by two symmetry-related formate anions at somewhat longer distances (Table 1), generating a distorted octahedral coordination.

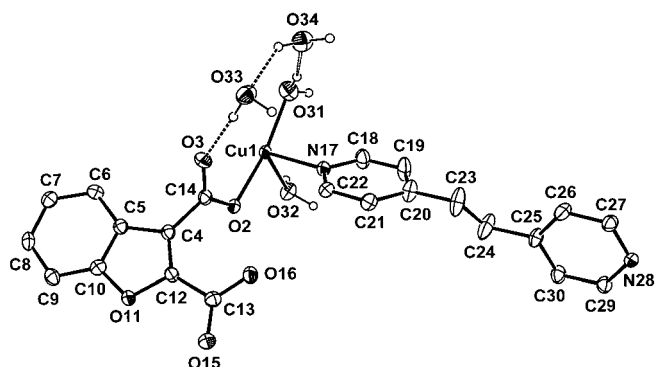


Figure 2

Displacement ellipsoid plot of the asymmetric unit of compound (II), showing the atom-labeling scheme. The ellipsoids represent the 50% probability level at 110 (2) K. H atoms, except for those of the water molecules, have been omitted. Hydrogen bonds (Table 3) are denoted by dashed lines. Cu1 is further coordinated to a translation-related bipyridyl species (Table 2), generating a square-based pyramidal coordination.

tetragonal crystal (Fig. 3). The layers are centered at the $z = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$ levels of the unit cell. Polymeric arrays located at $z = 0$ and $\frac{1}{2}$ propagate along the $[110]$ axis, while those at the

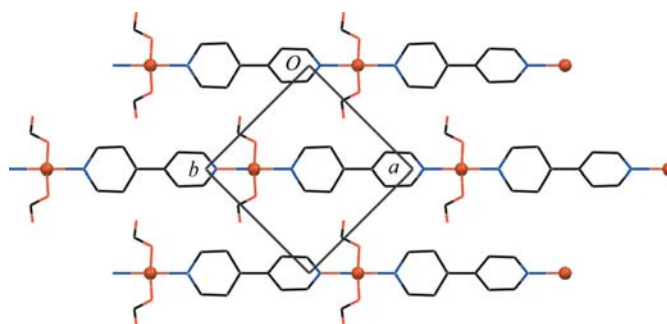


Figure 3

Coordination polymers in (I), located at $z = \frac{1}{4}$ in the unit cell (see *Comment*). This wireframe representation, with only the Cu^{II} ions depicted as small spheres, is a projection down the c axis. H atoms have been omitted for clarity.

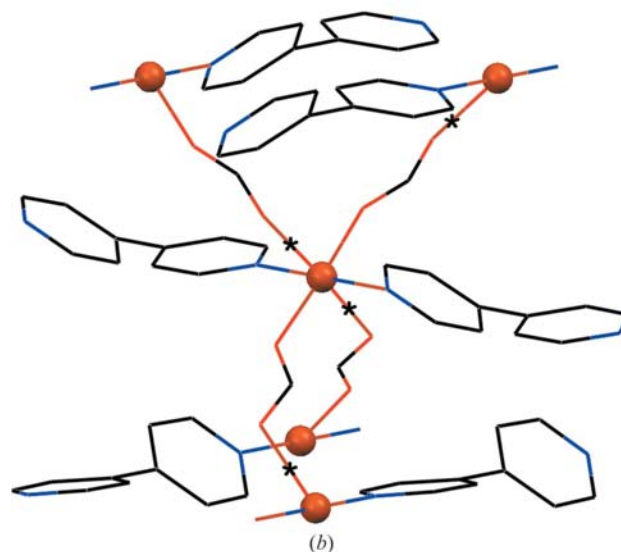
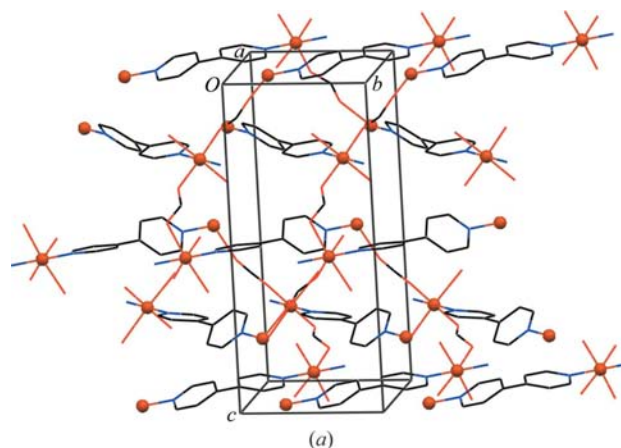


Figure 4

(a) The Cu^{II} ions in (I) depicted as small spheres. Note that the polymeric chains at the consecutive z levels ($0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$) of the unit cell propagate in perpendicular directions. Note also the crosslinking between the different polymers by the formate anions. (b) An expanded view of the octahedral environment of the copper(II) ion. The long *trans*-axial Cu–O bonds in the distorted octahedron are indicated by asterisks.

$z = \frac{1}{4}$ and $\frac{3}{4}$ levels extend along the $[1\bar{1}0]$ axis (Fig. 4). Coordination of the pyridyl ligands and the two formate anions to the Cu^{II} ions defines a square-based planar geometry with the corresponding Cu–N and Cu–O bond distances being around 2.0 Å (Table 1). A distorted octahedral environment around the metal ions is completed by two mutually *trans*-axial Cu–O4 [2.468 (3) Å] bonds from adjacent polymeric arrays (Fig. 4). Thus, the O2 donor of every formate anion binds to the copper ion of a given polymeric chain, while the O4 donor is more weakly coordinated to a neighboring array. This corresponds to a strong Jahn–Teller effect, associated with a considerable axial distortion of the octahedral environment around the copper ions. The resulting inter-coordinated structure thus represents a single-framework coordination polymer, with an unexpected connectivity scheme. There are no apparent voids in this architecture. The $[(\mu_2\text{-}4,4'\text{-bipyridyl-}N,N')\text{copper}]_n$ and $[(\mu_2\text{-formate-}O,O')\text{copper}]_n$ coordination polymers are abundant in the literature; a search of the Cambridge Structural Database (CSD; Allen, 2002; Version 5.30, November 2008) revealed 438 and 57 hits, respectively, for these motifs. However, the simultaneous inter-coordination of copper ions *via* the two ligands into polymeric architectures has not been observed before.

The use of copper chloride instead of the copper nitrate in the second experiment with the 1,2-di-4-pyridylethane is associated with the replacement of the CHO_2^- anions by BFDC^{2-} . The polymeric arrangement of the constituent species in (II) is illustrated in Fig. 5. The copper(II) ion in this compound occupies a general position and is five-coordinate with a square-based pyramidal geometry. The two mutually linked pyridyl N-atom donors, the monocoordinated carboxylate donor, and the O31 water molecule define the base of the pyramid, with Cu–O and Cu–N bonds of around 2.0 Å (Table 2). The O32 molecule of water coordinated at the apical site is more distant, as expected (Table 2). The metal ion deviates by 0.140 (1) Å from the mean plane through the four basal atoms towards atom O32. The polymeric arrays propagate along the *a* axis of the crystal and are aligned parallel to the *ab* plane. The side-coordinated bulky BFDC^{2-} ligands impart an irregular shape to the polymeric arrays, apparently preventing close packing next to one another and inducing the incorporation of noncoordinated molecules of water as crys-

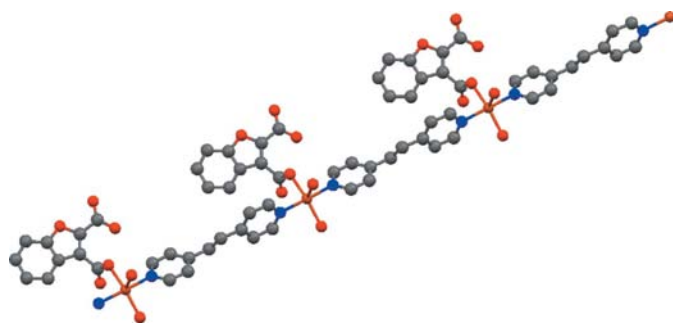


Figure 5

Ball-and-stick illustration of the fully extended coordination polymer in (II). Note the square-based pyramidal coordination environment around the copper(II) ions.

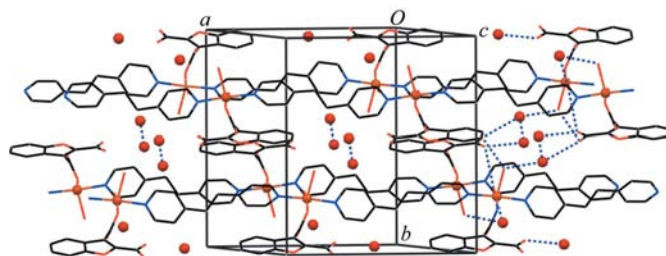


Figure 6

The copper(II) ions in (II), with the noncoordinated water molecules depicted as small spheres. The hydrogen bonding is marked by dotted lines. On the right-hand side of the figure, hydrogen bonds between the solvent water molecules and the polymeric arrays are also marked.

tallization solvent in order to fill the interchain space. The latter are involved in hydrogen bonds with the surrounding polymers, interacting with the free carboxylate site of BFDC^{2-} and the Cu-bound water ligands (Table 3). The hydrogen bonding extends in flat zones perpendicular to the $[100]$ direction, which are centered at $x = \frac{1}{2}$. The resulting structure thus combines coordination polymerization and hydrogen bonding between the constituent moieties (Fig. 6), imparting to it supramolecular connectivity in three dimensions. Coordination polymers involving copper ions and the 1,2-di-4-pyridylethane ligand are also known, although to a much lesser extent than those with 4,4'-bipyridine; the CSD (Allen, 2002) lists a few tens of structures with the former *versus* hundreds with the latter (see above). However, in most of the reported examples, the polymeric arrays are not in a fully extended form due to the flexibility of this ligand about the central $\text{CH}_2\text{—CH}_2$ bond (*e.g.* Power *et al.*, 1998; Carlucci *et al.*, 2000; Noro *et al.*, 2006). Coordination complexes and polymers of copper with the divalent BFDC^{2-} ligand as counter-ion have not been reported before.

With a single exceptional example (Koner & Goldberg, 2009c), it is tentatively evident from our studies that benzo-furandicarboxylic acid has a low capacity to act as a bridging ligand and induce the formation of coordination polymers with transition metal ions. Copper(II) ions reveal a preference for *N*-donor over *O*-donor ligands, and thus more readily form coordination polymers with the bipyridyl moieties. The *trans*-disposition of the *N*-atom sites in the bipyridine ligand, as opposed to the *cis* disposition of the carboxyl functions in BFDC , may also favor coordination polymerization with the former. With Cu^{II} , both BFDC^- (Koner & Goldberg, 2009a) and BFDC^{2-} (this study) play the role of coordinating counter-ions only. A somewhat more favorable situation has been experienced with La^{III} ions, which are characterized by a considerably higher affinity for oxo ligands, as is reflected in a recent report of a two-dimensional coordination network composed of $\text{La}_2(\text{BFDC}^{2-})_3$ building blocks (Koner & Goldberg, 2009c).

Experimental

All the reactants and solvents (see below) were obtained commercially. For (I), an aqueous solution (4 ml) of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$

(0.058 g, 0.25 mmol) was added dropwise with stirring to a solution containing benzofuran-2,3-dicarboxylic acid (0.052 g, 0.25 mmol) and NaOH (0.02 g, 0.5 mmol) in 1:1 DMF/H₂O (10 ml). The color of the solution changed from deep blue to blue–green. To this solution, 4,4'-bipyridine (0.078 g, 0.5 mmol) dissolved in DMF (5 ml) was added dropwise with stirring. The reaction mixture was then stirred for a further 1 h, filtered, and the filtrate left undisturbed to allow slow evaporation. After a few days, green crystals were deposited, filtered off, washed with DMF and air-dried. IR (KBr, cm⁻¹): (A) 1598 (*s*, ν_{as} of OCO⁻), 1380 (*m*, ν_{s} of OCO⁻); (B) 1491 (*m*), 1402 (*m*), 1323 (*s*) (ring stretching of the coordinated 4,4'-bipyridyl ligand); (C) 1308, 1298, 1270, 1224 and 1205, a series of bands associated with C–O and C–N stretching in the two ligands. For (II), CuCl₂·2H₂O (0.043 g, 0.25 mmol) was initially mixed with NaOH (0.02 g, 0.5 mmol) in water (10 ml), yielding Cu(OH)₂. Cu(OH)₂ (0.25 mmol), benzofuran-2,3-dicarboxylic acid (0.052 g, 0.25 mmol) and 1,2-di-4-pyridylethane (0.092 g, 0.5 mmol) were then dissolved in ammonia (25% *v/v*, 3 ml). Slow evaporation of the resulting solution at ambient temperature yielded blue single crystals of the final product. IR (KBr, cm⁻¹): 3383 (broad band of water O–H stretching modes), 1635 (*s*) and 1609 (*m*, ν_{as} OCO), 1556 (*s*) and 1487 (*m*, ν_{s} OCO).

Compound (I)

Crystal data

[Cu(CHO ₂) ₂ (C ₁₀ H ₈ N ₂)]	<i>Z</i> = 4
<i>M_r</i> = 309.76	Mo <i>K</i> α radiation
Tetragonal, <i>P</i> 4 ₁ 2 ₁ 2	μ = 1.96 mm ⁻¹
<i>a</i> = 7.8505 (1) Å	<i>T</i> = 110 K
<i>c</i> = 18.1513 (5) Å	0.30 × 0.20 × 0.15 mm
<i>V</i> = 1118.67 (4) Å ³	

Data collection

Nonius KappaCCD diffractometer	6143 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	1331 independent reflections
<i>T</i> _{min} = 0.590, <i>T</i> _{max} = 0.757	1248 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.096$	$\Delta\rho_{\text{max}} = 1.04 \text{ e } \text{Å}^{-3}$
<i>S</i> = 1.05	$\Delta\rho_{\text{min}} = -0.65 \text{ e } \text{Å}^{-3}$
1331 reflections	Absolute structure: Flack (1983)
89 parameters	Flack parameter: -0.04 (3)

Compound (II)

Crystal data

[Cu(C ₁₀ H ₄ O ₅)(C ₁₂ H ₁₂ N ₂)(H ₂ O) ₂ ·2H ₂ O]	β = 110.9824 (7)°
<i>M_r</i> = 523.97	<i>V</i> = 2242.73 (8) Å ³
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	<i>Z</i> = 4
<i>a</i> = 13.3333 (3) Å	Mo <i>K</i> α radiation
<i>b</i> = 15.1250 (3) Å	μ = 1.03 mm ⁻¹
<i>c</i> = 11.9108 (2) Å	<i>T</i> = 110 K
	0.40 × 0.25 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer	18429 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	5329 independent reflections
<i>T</i> _{min} = 0.683, <i>T</i> _{max} = 0.820	3899 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	307 parameters
$wR(F^2) = 0.141$	H-atom parameters constrained
<i>S</i> = 1.05	$\Delta\rho_{\text{max}} = 0.80 \text{ e } \text{Å}^{-3}$
5329 reflections	$\Delta\rho_{\text{min}} = -0.83 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

Cu1–O2	1.988 (2)	Cu1–N5	1.9903 (5)
Cu1–O4 ⁱ	2.468 (3)	Cu1–N12 ⁱⁱ	2.015 (3)
O2–Cu1–O2 ⁱⁱⁱ	175.39 (13)	O2–Cu1–N12 ⁱⁱ	92.30 (6)
O2–Cu1–N5	87.70 (6)		

Symmetry codes: (i) $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{4}$; (ii) $x + 1, y + 1, z$; (iii) $y + 1, x - 1, -z$.

Table 2

Selected geometric parameters (Å, °) for (II).

Cu1–O2	1.9887 (18)	Cu1–N17	2.014 (2)
Cu1–O31	2.019 (2)	Cu1–N28 ⁱ	2.011 (2)
Cu1–O32	2.301 (2)		
O2–Cu1–O31	167.04 (9)	O31–Cu1–N17	90.78 (10)
O2–Cu1–O32	88.43 (7)	O31–Cu1–N28 ⁱ	89.79 (10)
O2–Cu1–N17	92.08 (9)	O32–Cu1–N17	87.94 (9)
O2–Cu1–N28 ⁱ	86.58 (9)	O32–Cu1–N28 ⁱ	95.38 (8)
O31–Cu1–O32	104.30 (9)	N17–Cu1–N28 ⁱ	176.38 (10)

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

Table 3

Hydrogen-bond geometry (Å, °) for (II).

<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>
O31–H31B...O16 ⁱⁱ	0.90	2.29	2.971 (3)	133
O31–H31A...O34	0.90	2.09	2.981 (3)	168
O32–H32A...O15 ⁱⁱ	0.90	1.83	2.728 (3)	172
O32–H32B...O34 ⁱⁱⁱ	0.90	1.95	2.836 (3)	166
O33–H33A...O3	0.90	1.87	2.772 (3)	176
O33–H33B...O16 ^{iv}	0.90	1.83	2.707 (3)	165
O34–H34A...O15 ^{iv}	0.90	2.20	2.963 (3)	143
O34–H34B...O33	0.90	1.95	2.739 (3)	145

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

The 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 and 0.99 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bound to O atoms in (II) were either located in difference Fourier maps, or positioned to optimize intermolecular hydrogen bonding. All the O–H bond lengths were first restrained to 0.90 (2) Å, but then kept fixed in the final least-squares cycles, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

For both compounds, 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); 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: BM3078). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Burrows, A. D., Cassar, K., Friend, R. M. W., Mahon, M. F., Rigby, S. P. & Warren, J. E. (2005). *CrystEngComm*, **7**, 548–550.
- Carlucci, L., Ciani, G., Proserpio, D. M. & Rizzato, S. (2000). *Dalton Trans.* pp. 3821–3827.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Goldberg, I. (2005). *Chem. Commun.* pp. 1243–1254.
- Ito, K. & Bernstein, H. J. (1956). *Can. J. Chem.* **34**, 170–178.
- Koner, R. & Goldberg, I. (2009a). *Acta Cryst.* **C65**, m37–m41.
- Koner, R. & Goldberg, I. (2009b). *Acta Cryst.* **C65**, m62–m65.
- Koner, R. & Goldberg, I. (2009c). *Acta Cryst.* **C65**, m149–m151.
- Litvinov, A. L., Konarev, D. V., Kovalevsky, A. Yu., Neretin, I. S., Coppens, P. & Lyubovskaya, R. N. (2005). *Cryst. Growth Des.* **5**, 1807–1819.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Muniappan, S., Lipstman, S., George, S. & Goldberg, I. (2007). *Inorg. Chem.* **46**, 5544–5554.
- Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Noro, S., Horike, S., Tanaka, D., Kitagawa, S., Akutagawa, T. & Nakamura, T. (2006). *Inorg. Chem.* **45**, 9290–9300.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Popov, A. I., Marshall, J. C., Stute, F. B. & Person, W. B. (1961). *J. Am. Chem. Soc.* **83**, 3586–3590.
- Power, K. N., Hennigar, T. L. & Zaworotko, M. J. (1998). *Chem. Commun.* pp. 595–596.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.