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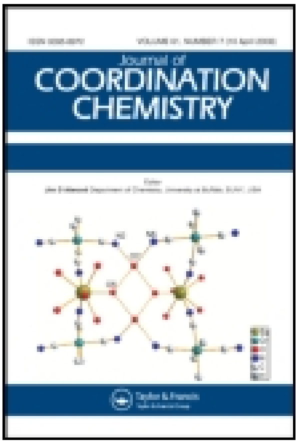

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Hui-Yan Liu [a b] , Hai-Ying Wang [a b] & Yan-Hui Shi [a b]
[a] School of Chemistry and Chemical Engineering, Xuzhou Normal University , Xuzhou 221116, China
[b] Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials , Xuzhou 221116, China

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Pyrazine-2,3-dicarboxylate-bridged polymeric and dinuclear complexes involving decameric water clusters

HUI-YAN LIU*†‡, HAI-YING WANG†‡ and YAN-HUI SHI†‡

†School of Chemistry and Chemical Engineering,
Xuzhou Normal University, Xuzhou 221116, China
‡Jiangsu Key Laboratory of Green Synthetic Chemistry for
Functional Materials, Xuzhou 221116, China

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Two copper(II) complexes of pyrazine-2,3-dicarboxylate (H_2pzdc) with 2-aminopyridine (apy), $\{(\mathrm{Hapy})_2[\mathrm{Cu}(\mu\text{-pzdc})_2]\}_n$ (**1**) and 1,10-phenanthroline (phen), $[\mathrm{Cu}_2(\mu\text{-pzdc})(\mathrm{phen})_4][\mathrm{N(CN)}_2]_2 \cdot 9\mathrm{H}_2\mathrm{O}$ (**2**) have been synthesized and structurally characterized. Complex **1** consists of a pyrazine-2,3-dicarboxylate bridging across a double chain, while **2** exists as a dinuclear complex in which two Cu(II) ions are bridged by pzdc *via* different coordination modes. One Cu(II) ion in the binuclear complex is a distorted octahedron, while the other Cu(II) is a distorted trigonal bipyramid. A chair-like decameric water cluster composed of two pentamers and a shared-edge tetramer is detected, which further associate into a 1-D tape with dicyanamide anions by hydrogen bonds.

Keywords: Pyrazine-2,3-dicarboxylate complexes; Water cluster; Coordination polymers; Copper(II) complexes

1. Introduction

Crystal engineering of metal-directed supramolecular architectures assembled by coordination as well as other interactions such as hydrogen bonding and aromatic stacking [1] have been a focus of research. The major aim for rational design of metal–organic coordination polymers with specific chemical and physical properties is achieved by choosing appropriate organic bridging ligands [1–3]. Pyrazine-2,3-dicarboxylic acid (H_2pzdc) is well-suited for designing new metal–organic supramolecular structures because of: (a) the presence of two carboxylates as substituents in the N-heterocyclic pyrazine ring allows multiple coordination modes and (b) steric hindrance between these groups leads to noncoplanarity of the carboxylates and the pyrazine ring nitrogen, which increases the dimensionality of the assembled covalent networks [1b]. The synthesis and characterization of metal coordination polymers based on pyrazine-2,3-dicarboxylate has evolved rapidly with various coordination modes for pzdc, such as monodentate [4], bidentate [5], bis(bidentate) bridging [6], tridentate

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*Corresponding author. Email: liuhuiyan72@163.com

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bridging [7], tetradentate bridging [1b, 8], and mixed chelating–bridging [9], have been reported.

Studies of water clusters attract increasing attention as they can provide new insight into the structure of bulk water and/or ice [10]. A variety of tetramer [11], pentamer [12], hexamer [13], octamer [14], and decamer [15] water clusters have been isolated in different solid crystalline hosts. Small water clusters $(H_2O)_n$ ($n = 4$–6) are crucial building units for extended water morphologies including tapes [16] and layers [17] whose physical properties are closely associated with those of bulk water.

We describe here a polymeric complex $\{(Hapy)_2[Cu(\mu\text{-pzdc})_2]\}_n$ (**1**) and a dinuclear complex $[Cu_2(\mu\text{-pzdc})(phen)_4][N(CN)_2]_2 \cdot 9H_2O$ (**2**) with pyrazine-2,3-dicarboxylic acid (H_2pzdc) as bridging ligand. In **2**, five lattice water molecules linked by 12 hydrogen bonds form a chair-like decameric water cluster composed of 2 pentamers and a shared-edge tetramer cluster, which further associates into a 1-D tape with dicyanamide anions by hydrogen bonds.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were of analytical grade and available commercially. Elemental analyses were carried out with a Varian EL elemental analyzer. IR spectra were recorded on a Bruker Tensor27 FT–IR spectrophotometer as KBr pellets.

2.2. *Synthesis*

2.2.1. $\{(Hapy)_2[Cu(\mu\text{-pzdc})_2]\}_n$ (1). An ethanol solution (5 cm^{-3}) of 2-aminopyridine (0.075 g, 0.8 mmol) was mixed with an aqueous solution (10 cm^{-3}) of pyrazine-2,3-dicarboxylic acid (0.067 g, 0.4 mmol). Then, an ethanol solution (8 cm^{-3}) of $Cu(O_2CCH_3)_2 \cdot H_2O$ (0.080 g, 0.4 mmol) was added gradually with stirring. A blue precipitate immediately formed. The mixture was stirred for 1 h, after which the solid was filtered and the filtrate was allowed to stand at room temperature for 1 month, giving crystals suitable for X-ray diffraction. Yield: 60%. Anal. Calcd for $C_{22}H_{18}CuN_8O_8$ (%): C, 45.05; N, 19.11; and H, 3.07. Found (%): C, 44.98; N, 19.05; and H, 3.12.

2.2.2. $[Cu_2(\mu\text{-pzdc})(phen)_4][N(CN)_2]_2 \cdot 9H_2O$ (2). An aqueous solution (10 cm^{-3}) of $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.5 mmol) was added gradually to a stirred aqueous solution (10 cm^{-3}) containing pyrazine-2,3-dicarboxylic acid (0.084 g, 0.5 mmol) and $NaN(CN)_2$ (0.089 g, 1 mmol). The solution immediately showed precipitate and was stirred for 4 h at 60°C. The addition of phen (0.16 g, 0.8 mmol) in ethanol (5 cm^{-3}) resulted in a clear solution. The mixture was stirred for 2 h at 60°C and then cooled to room temperature. Blue crystals separated after about 3 months and were collected. Yield: 30%. Anal. Calcd for $C_{58}H_{52}Cu_2N_{16}O_{13}$ (%): C, 53.21; N, 17.13; and H, 3.96. Found (%): C, 53.16; N, 17.08; and H, 4.02.

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{22}H_{18}CuN_8O_8$	$C_{58}H_{52}Cu_2N_{16}O_{13}$
Formula weight	585.98	1308.24
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	6.4690(7)	12.9850(13)
b	8.0071(8)	14.3819(15)
c	11.6101(12)	18.6101(19)
α	74.8020(10)	89.538(2)
β	86.198(2)	70.9890(10)
γ	84.880(2)	67.5720(10)
Volume (Å^3), Z	577.45(10), 1	3010.3(5), 2
Calculated density (g cm^{-3})	1.685	1.443
Absorption coefficient (mm^{-1})	1.015	0.784
F(000)	299	1348
θ range for data collection (°)	1.82–25.02	2.40–25.02
Reflections collected	2921	15,766
Independent reflections	1994 [R(int) = 0.0415]	10,407 [R(int) = 0.0491]
Observed reflections	1769 [$I > 2\sigma(I)$]	3000 [$I > 2\sigma(I)$]
Max. and min. transmission	0.8879/0.6694	0.8718/0.7293
Data/restraints/parameters	1994/0/178	10,407/0/884
Goodness-of-fit on F^2	1.098	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0542$, $wR_2 = 0.1463$	$R_1 = 0.1221$, $wR_2 = 0.3027$
R indices (all data)	$R_1 = 0.0592$, $wR_2 = 0.1513$	$R_1 = 0.2533$, $wR_2 = 0.3494$

2.3. *Crystal structure determination*

Diffraction data of **1** and **2** were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogens were located geometrically and refined isotropically. For **2**, N1, N2, O1–O3, C3–C6, H5, and C6 of pzdc were disordered over two positions, with site occupation factors of 0.633/0.367. Data collection and refinement details for **1** and **2** are summarized in table 1.

3. Results and discussion

3.1. *IR spectra*

The IR spectrum of **2** displays a broad band at 3383 cm^{-1} associated with stretching of crystal water molecules [7f]. Strong absorption bands in the ranges 1753–1690 and 1396–1357 cm^{-1} due to the asymmetric and symmetric ν(COO) vibrations of free pyrazine-2,3-dicarboxylic acid shift to lower wavenumbers in the IR spectra of the complexes, 1650–1581 and 1387–1327 cm^{-1} for **1** and 1604–1588 and 1373–1340 cm^{-1} for **2**. The differences between the asymmetric and symmetric stretches of carboxylates of **1** and **2**, $\Delta\nu = 259$ and 240 cm^{-1}, respectively, indicate monodentate pzdc [4, 5a].

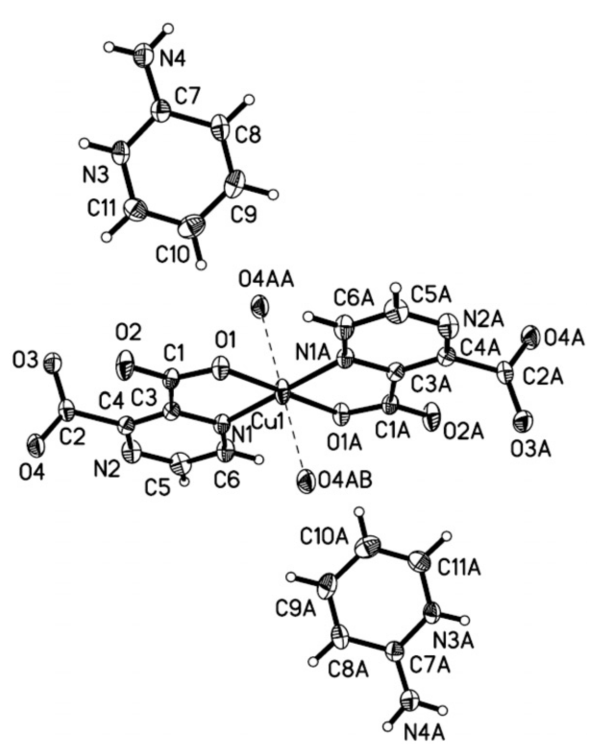

Figure 1. The coordination environment of Cu(II) in **1** with the atom labeling scheme.

3.2. *Crystal structure of 1*

The structure of **1** is comprised of $(\mathrm{Hapy})^+$ and $\{[\mathrm{Cu(pzdc)_2}]^{2-}\}_n$ chains. Figures 1 and 2 show the coordination sphere of Cu(II) and the polymeric structure propagating along the crystallographic *a*-axis. A selection of bond lengths and angles is reported in table 2.

The polymeric chain can be described as $[\mathrm{Cu(pzdc)_2}]^{2-}$ entities linked by O4 of a carboxylate belonging to a neighboring anion. Each Cu(II) is located at the center of an elongated octahedron as the result of a pronounced Jahn–Teller effect. The basal plane consists of two nitrogens [Cu1–N1 = 1.975(3) Å] and two oxygens [Cu1–O1 = 1.946(2) Å] belonging to two pzdc ligands related by the inversion center at the copper. The two apical positions are occupied by two oxygens [Cu1–O4 = 2.550(2) Å] of two symmetry-related ($-x+2$, $-y+1$, $-z+1$; $-1+x$, y, z) pzdc ligands belonging to two neighboring $[\mathrm{Cu(pzdc)_2}]^{2-}$ entities. The shortest Cu $\cdots$ Cu distance within the polymeric chain agrees with the value of the a crystallographic axis [6.469(7) Å]. The pzdc chelates Cu(II) *via* the nitrogen of pyrazine and oxygen of the adjacent carboxylate [bite angle = 82.88(10)°], while the remaining carboxylate is linked to another Cu(II) of a neighboring unit monodentate *via* one of its oxygens. The carboxylate involved in the chelation is almost coplanar to the pyrazine ring with dihedral angle of 2.12(9)°, while the other is almost perpendicular with dihedral angle of 83.08(2)°. This chain conformation has been previously observed in copper(II) complexes of pzdc [1b, 7c].

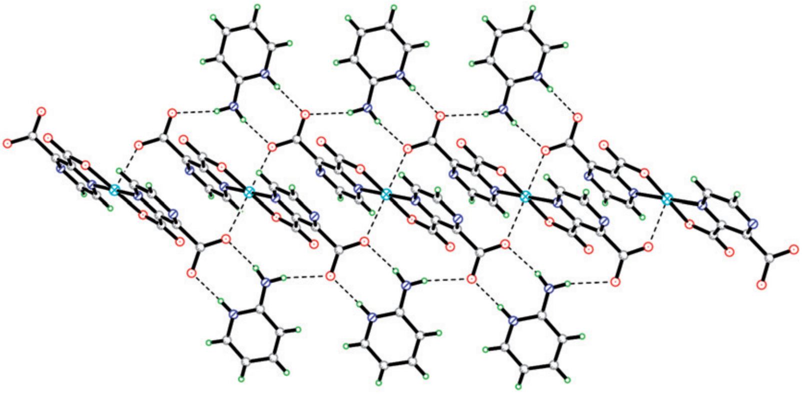

Figure 2. View of the 1-D chain observed in **1**.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Cu(1)–O(1)	1.946(2)	Cu(1)–N(1)	1.975(3)
Cu(1)–O(1)#1	1.946(2)	Cu(1)–N(1)#1	1.975(3)
Cu(1)–O(4)#2	2.550(2)	Cu(1)–O(4)#3	2.550(2)
O(1)–Cu(1)–O(1)#1	180.00(13)	O(1)–Cu(1)–N(1)#1	97.12(10)
O(1)#1–Cu(1)–N(1)#1	82.88(10)	O(1)–Cu(1)–N(1)	82.88(10)
O(1)#1–Cu(1)–N(1)	97.12(10)	N(1)#1–Cu(1)–N(1)	180.00(12)
O(1)–Cu(1)–O(4)#3	85.16(9)	O(1)–Cu(1)–O(4)#2	94.84(9)
O(4)–Cu(1)–N(1) #3	84.13(8)	O(4)–Cu(1)–N(1)#2	95.87(8)

Symmetry codes: #1 $-x+1$, $-y+1$, $-z+1$; #2 $-x+2$, $-y+1$, $-z+1$; #3 $-1+x$, y, z.

The supramolecular architecture of **1** is sustained by hydrogen bonds between cations and the anionic chains. The $\{[Cu(pzdc)_2]^{2-}\}_n$ chains run along the *a*-axis. The $(Hapy)^+$ cations distribute beside the anionic $\{[Cu(pzdc)_2]^{2-}\}_n$ chains and act as hydrogen-bond donors to the carboxylate oxygens with N3 ··· O3, N4 ··· O4, and N4 ··· O3 distances of 2.743, 2.913, and 2.994 Å, respectively.

3.3. *Crystal structure of 2*

The molecular structure of **2** with atom numbering scheme is illustrated in figure 3; selected bond parameters are listed in table 3.

The structure consists of crystallization water molecules, dicyanamide anions, and asymmetric $[Cu_2(\mu\text{-pzdc})(phen)_4]^{2+}$ binuclear units (figure 3) in which a tridentate pzdc bridges two Cu(II) ions with a Cu ··· Cu distance of 8.251(2) Å. The pzdc is chelate to one Cu(II) through nitrogen of pyrazine and oxygen of the adjacent carboxylate and binds monodentate to another Cu(II) through an oxygen of the remaining carboxylate, resulting in two different coordination environments around the Cu(II) ions. Cu1 is a distorted octahedral geometry defined by two phens, nitrogen of pyrazine, and oxygen of carboxylate. The Cu1–O1 and Cu1–N1 distances (2.09(10) and 2.40(10) Å) are comparable with that of $[Cu(pzdca)(phen)_2] \cdot 5.5H_2O$ (1.978(2) and 2.372(2) Å) [5a], but are significantly longer than those in a number of other Cu(II)

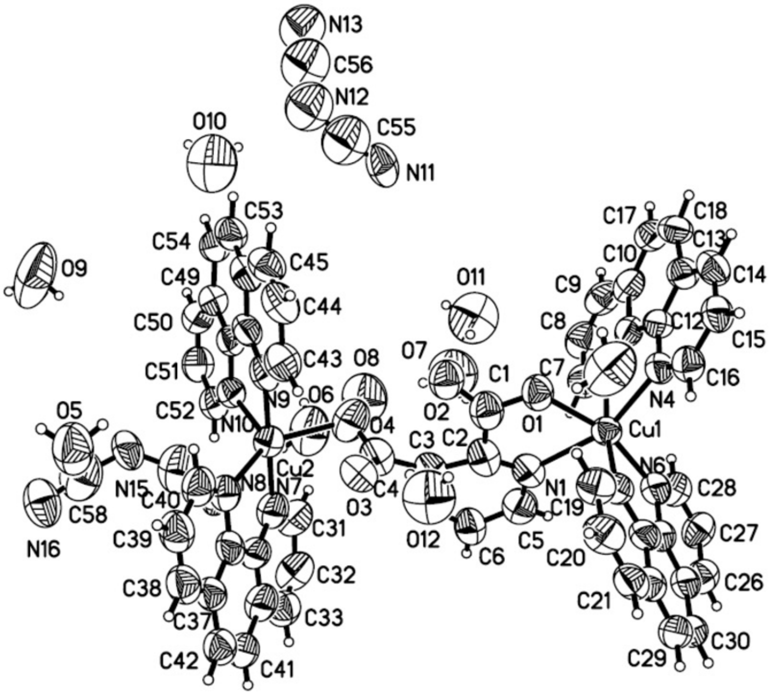

Figure 3. Structure of **2** with the atom labeling scheme. All disordered atoms are omitted for clarity.

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Cu(1)–N(3)	1.965(10)	Cu(2)–N(9)	1.954(11)
Cu(1)–N(5)	1.995(11)	Cu(2)–N(7)	1.988(13)
Cu(1)–O(1)	2.09(10)	Cu(2)–N(8)	2.074(11)
Cu(1)–N(6)	2.139(11)	Cu(2)–N(10)	2.108(10)
Cu(1)–N(4)	2.158(10)	Cu(2)–O(4)	2.219(11)
Cu(1)–N(1)	2.40(10)		
N(3)–Cu(1)–N(5)	173.5(4)	N(6)–Cu(1)–N(1)	88(3)
N(3)–Cu(1)–O(1)	90(2)	N(4)–Cu(1)–N(1)	159(3)
N(5)–Cu(1)–O(1)	95(2)	N(9)–Cu(2)–N(7)	178.0(6)
O(1)–Cu(1)–N(6)	161(3)	N(9)–Cu(2)–N(8)	98.3(5)
N(5)–Cu(1)–N(6)	80.3(5)	N(7)–Cu(2)–N(8)	79.9(6)
N(3)–Cu(1)–N(6)	96.2(5)	N(9)–Cu(2)–N(10)	81.3(5)
N(3)–Cu(1)–N(4)	78.9(4)	N(7)–Cu(2)–N(10)	100.4(5)
N(5)–Cu(1)–N(4)	97.0(4)	N(8)–Cu(2)–N(10)	123.1(4)
N(6)–Cu(1)–N(4)	109.4(4)	N(9)–Cu(2)–O(4)	91.6(5)
O(1)–Cu(1)–N(4)	89(3)	N(7)–Cu(2)–O(4)	89.4(5)
N(3)–Cu(1)–N(1)	89(3)	N(8)–Cu(2)–O(4)	143.8(4)
N(5)–Cu(1)–N(1)	97(3)	N(10)–Cu(2)–O(4)	92.7(4)
O(1)–Cu(1)–N(1)	74(4)		

complexes of pzdc [7], apparently because of steric hindrance of the terminal phen ligands. Steric hindrance of the two terminal phens is also responsible for the angle subtended at the Cu1 by pzdc (74.00(4)°), narrower than that found in many othercopper(II) complexes of pzdc [7], but comparable with that in $[Cu(pzdc)(phen)_2] \cdot 5.5H_2O$ (75.23(8)°) [5a]. The coordination of Cu2 are four nitrogens of two phen ligands

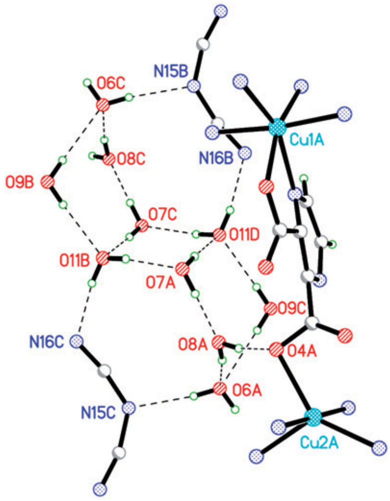

Figure 4. A perspective view of the chair-like decamer composed of two pentamers and a shared-edge tetramer, and its surrounding environment in **2**. The phens are omitted for clarity.

and oxygen of the remaining carboxylate. The coordination polyhedron around Cu2 could be best described as trigonal bipyramidal, which is reflected by the τ value of 0.57 defined by Addison *et al.* ($\tau = 0$ for an ideal square pyramid and 1 for an ideal trigonal bipyramid) [18]. The apical sites are occupied by N7 and N9, with O4, N8, and N10 making up the equatorial plane. The Cu2 is 0.070(1) Å out of the plane and the apical N7 and N9 are 1.872(6) and −1.991(5) Å on either side. The Cu2–O4 distance of 2.219 Å is slightly longer than Cu1–O1 but in the range (1.963–2.552 Å) reported for other structurally related copper(II) complexes of pzdc [7b–f].

Although there are many Cu(II) complexes of pzdc forming polymeric structures, dinuclear Cu(II) complexes of pzdc are relatively rare. As far as we are aware, the two other dinuclear Cu(II) complexes of pzdc are $[Cu_2(pzdca)(H_2O)_2(dmen)_2]\cdot 6H_2O$ [5a] and $[Cu_2(\mu\text{-}pzdc)_2(pen)_4]\cdot 2H_2O$ [7f]. However, the molecular pattern observed in **2** shows an unusual feature not encountered in $[Cu_2(pzdc)(H_2O)_2(dmen)_2]\cdot 6H_2O$ [5a] and $[Cu_2(\mu\text{-}pzdc)_2(pen)_4]\cdot 2H_2O$ [7f]: the occurrence of Cu(II) with different coordination modes and numbers caused by different coordinations of pzdc. The phens saturate the Cu(II) coordination sphere and preclude polymerization observed in other Cu(II) complexes of pzdc [1b, 1d, 7b–f, 8c, 9b].

The most striking feature is that **2** contains extensive hydrogen bonding between five water molecules [O6–O9, O11] to form a decameric water cluster composed of two pentamers and the shared-edges tetramer cluster (figure 4). The geometrical parameters of the hydrogen bonds are given in table 4. O(6), O(7), O(8), O(9), and O(11) form a pentameric water cluster and two pentamers join at [O(7)–O(11)] forming the tetrameric water clusters. The decamer adopts a chair conformation. Within the decamer the average O ··· O distance of 2.795 Å is very close to that found in a cyano-bridged copper(II) complex (2.79 Å) [15k], but is slightly longer than that in ice I_h at −90°C (2.759 Å) [15k].

Although adamantanoid [15a–c], opened-cube [15d], cubanoid [15h], and parallel cyclic pentamers [15e, 15f] of decameric water clusters were recently reported, the chair

Table 4. Hydrogen bonds for **2**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (°)
O6–H6C···N14	0.850	2.179	3.027	175.60
O6–H6D···N15[a]	0.850	2.064	2.910	173.66
O7–H7C···O8	0.850	1.643	2.493	177.90
O7–H7D···O11[b]	0.850	1.687	2.536	176.97
O8–H8C···O4	0.850	1.790	2.623	166.16
O8–H8D···O6	0.850	1.859	2.692	166.23
O9–H9C···O11[c]	0.850	2.112	2.961	175.79
O9–H9D···O6[a]	0.850	2.286	3.135	177.09
O11–H11C···O7	0.850	2.111	2.957	173.52
O11–H11D···N16[a]	0.850	1.876	2.718	170.10

Symmetry codes: [a] $-x, -y+1, -z+1$; [b] $-x, y+2, z+1$; [c] $-x, -y+1, -z+1$.

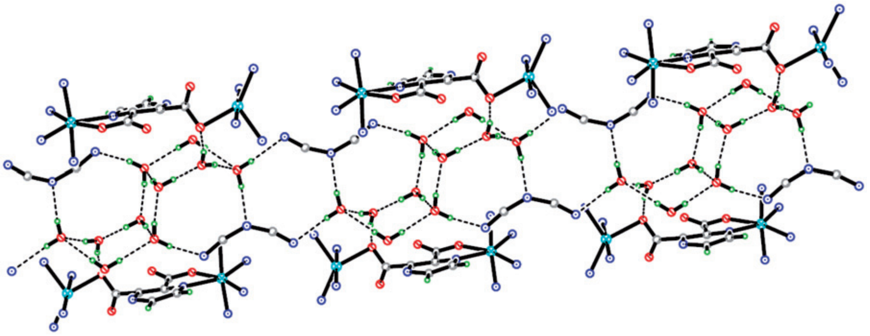

Figure 5. View of a 1-D chain linked by intermolecular hydrogen bonds between water tape and metal complexes in **2**. The phens are omitted for clarity.

decameric water cluster composed of two pentamers and the shared-edges tetramer cluster in **2** is unprecedented. Two comparable examples were recently found in $[H_6L][(PA)(HPA)]_2 \cdot (H_2O)_{10}$ [15j] and a cyano-bridged copper(II) complex [15k]; in both, only 10 hydrogen bonds are formed within the chair-like decamer. In **2**, five lattice water molecules are linked by 12 hydrogen bonds, indicating higher stability than the two known cases [15j, 15k]. Considering the hydrogen-bonded patterns of R_5^5 (10) for the pentameric and R_4^4 (8) for the tetrameric subunits in **2**, such a decameric water cluster is obviously different from the two known cases. Each decamer forms six hydrogen bonds with nitrogens of dicyanamide anions, resulting in a 1-D tape along *b*; O8–H8···O4 hydrogen bonds also anchor these 1-D water tapes to the host framework in **2** (figure 5).

4. Conclusions

Two pyrazine-2,3-dicarboxylate bridged polymeric and dinuclear copper(II) complexes, $\{(Hapy)_2[Cu(\mu\text{-pzdc})_2]\}_n$ (**1**) and $[Cu_2(\mu\text{-pzdc})(phen)_4][N(CN)_2]_2 \cdot 9H_2O$ (**2**), have been synthesized and structurally characterized. Complex **1** consists of a crossing double chain, where Cu(II) ions are linked by bridging carboxylates. The two Cu(II) ions in dinuclear **2** are bridged by a pzdc anion *via* different coordination modes, resulting in different coordination environments around Cu(II). Complex **2** also features a novel chair-like decameric water cluster composed of two pentamers and the shared-edges tetramer cluster, which further associate into a 1-D tape with dicyanamide anions by hydrogen bonds.

Supplementary material

CCDC 831388 and 831389 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223-336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgments

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