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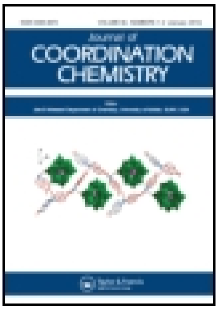

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A cyclic water octamer in a binuclear copper(II) complex: synthesis, crystal structure, and properties

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A cyclic water octamer in a binuclear copper(II) complex: synthesis, crystal structure, and properties

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A cyclic octameric water cluster is trapped in a 3-D supramolecular architecture $[Cu_2(H_2O)_2(bpca)_2L]\cdot 8H_2O$, where bpca = bis(2-pyridylcarbonyl)amide and L = sebacic acid. The striking feature of the octameric cluster is that each water donates one hydrogen to adjacent waters to form a circular water ring in a $(O–H\cdots O–H\cdots)_4$ connecting fashion, with the same orientations of OH bonds in the ring. Thermogravimetric and magnetic properties are also reported.

Keywords: Cu(II) complex; Water cluster; Crystal structure; Magnetic property

1. Introduction

Water clusters, groups of lattice water molecules held together by hydrogen bonds, have been studied both experimentally and theoretically because of fundamental importance in biological and chemical processes and the clusters are believed to be models connecting isolated molecules to bulk water [1, 2]. However, very little is known about how these clusters, such as isolated water clusters, chains, and sheets, link themselves to form larger networks of water molecules. Therefore, precise structural data of water clusters in confined environments such as organic and inorganic host matrices provide understanding of water morphology assembly from low to high nuclearity clusters and from clusters to multidimensional systems [3, 4].

Although many discrete water clusters, with numbers of water molecules varying from three to more than 12, have been structurally characterized in a variety of inorganic and organic crystal hosts [5–16], our particular interest is the structure of the $(H_2O)_8$ cluster. Octameric clusters observed in organic or inorganic–organic host structures exhibit conformations of cubane [17–19], opened cube [20], cyclic ring [21], book-shaped [22], crowned chair [23–25], bicycle[2,2,2]octane [26], and cyclic quasi-planar tetramer [27, 28] due to different environments imposed by the host. Theoretical calculations predict that the most stable conformation for $(H_2O)_8$ is the cubic structure. Large ring structures which are not favorable through enthalpy usually will have more entropy content than denser, cubic-like structures [29]. The only discrete cyclic $(H_2O)_8$ cluster that closely resembles a portion of

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the ice Ic structure has been found in an organic supramolecular complex reported by Atwood and co-workers [21].

2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz), which functions simultaneously as a tridentate and a bidentate ligand, is used as a spacer for designing supramolecular complexes [30, 31]. The compounds of 2,4,6-triaryltriazines are usually stable toward hydrolysis and concentrated mineral acid, with 150 °C required for hydrolytic reaction [32]. However, Lerner and Lippard found that Cu(II) in aqueous media promoted the hydrolysis of tptz to bis(2-pyridylcarbonyl)amide (bpca) anions [33, 34]. The crystallographic characterizations of Cu(II) complexes with hydrolyzed tptz were reported [35, 36]. In this paper, we describe the synthesis, structure, and magnetic properties of a new binuclear copper(II) complex, $[Cu_2(H_2O)_2(bpca)_2L]\cdot 8H_2O$ (**1**) (bpca = bis(2-pyridylcarbonyl)amide and L = sebacato), including an isolated octameric water cluster. The centrosymmetric cluster is formed by hydrogen bonding of four waters to an extended octamer in a chair conformation.

2. Experimental

2.1. *Materials and physical methods*

All chemicals of reagent grade were commercially available and used without purification. Powder X-ray diffraction measurements were carried out with a Bruker D8 Focus X-ray diffractometer to check the phase purity. C, H, N, and S microanalyses were performed with a Perkin Elmer 2400II CHNO/S elemental analyzer. The FT–IR spectra were recorded as KBr pellets from 4000–400 cm^{-1} on a Shimadzu FTIR–8900 spectrometer. Thermogravimetric measurement was carried out from R.T. to 700 °C on preweighed samples using a Seiko Exstar 6000 TG/DTA 6300 apparatus with a heating rate of 10 °C min^{-1}. Single-crystal X-ray diffraction data were collected by a Rigaku *R*–Axis Rapid X-ray diffractometer. The temperature-dependent magnetic susceptibility was determined with a Quantum Design SQUID magnetomer (Quantum Design Model MPMS-7) from 2 to 300 K with an applied field of 5 kOe.

2.2. *Synthesis of $[Cu_2(H_2O)_2(bpca)_2(L)]\cdot 8H_2O$ (1)*

A 2.0 mL (1 M) NaOH solution was dropwise added to an aqueous solution of 0.172 g (1.0 mmol) $CuCl_2\cdot 2H_2O$ to obtain blue precipitate, which was then centrifuged and washed with doubly distilled water until no Cl^- was detectable. The fresh precipitate was subsequently added to a stirred solution of 0.312 g (1.0 mmol) tptz and 0.202 g (1.0 mmol) sebacic acid in 20 mL CH_3OH/H_2O (1 : 1 v/v). The mixture was further stirred for half an hour and filtered, the green filtrate (pH 5.16) was maintained at room temperature and blue plate crystals were formed five days later (yield: 61% based on the initial $CuCl_2\cdot 2H_2O$). The phase purity of the crystalline product was confirmed by comparing an experimental powder X-ray diffraction pattern with the corresponding one simulated on the basis of single-crystal data (figure S1). Anal. Calcd. for $C_{34}H_{52}Cu_2N_6O_{18}$ (%): C, 42.54; H, 5.46; N, 8.76. Found: C, 42.48; H, 5.54; N, 8.72. IR spectrum (cm^{-1}, KBr): 3445m, 3094w, 2926m, 2852w, 1717vs, 1637m, 1603m, 1562vs, 1454w, 1416m, 1360vs, 1288m, 1192w, 1157w, 1101m, 1024m, 912w, 760s, 702s, 631m.

Table 1. Summary of crystal data, data collection, structure and refinement details for **1** ($T = 295(2)$ K).

Compound	**1**
Empirical formula	$C_{34}H_{52}Cu_2N_6O_{18}$
Formula mass	959.90
Crystal system	Triclinic
Space group	*P*–1 (No. 2)
Description	Blue block
Crystal size (mm)	0.42 × 0.34 × 0.29
a (Å)	9.884(2)
b (Å)	10.852(2)
c (Å)	11.159(2)
α (°)	61.58(3)
β (°)	78.94(3)
γ (°)	88.40(3)
Volume (Å^3)	1030.4(4)
Z	1
D_{calc} (g cm^{-3})	1.547
$F(0\,0\,0)$	500
μ (mm^{-1})	1.115
Refinement method	Full-matrix least-squares on F^2
θ range (°)	3.11–24.99
Reflections collected	8093
Unique reflections (R_{int})	3428 (0.0167)
Data, restraints, parameters	3617, 0, 271
Goodness of fit on F^2	1.089
R_1,wR_2 [$I \geq 2\sigma(I)$][a]	0.0406, 0.1094
R_1,wR_2 (all data)[a]	0.0424, 0.1107
A, B values in weighting scheme[b]	0.0580, 2.0321
$\delta\rho_{\max}$, $\delta\rho_{\min}$ (e Å^{-3})	0.967, −0.969

[a] $R_1 = \sum(|F_o - F_c|)/\sum|F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

[b] $w = [(\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

2.3. *X-ray crystallography*

A suitable single crystal was selected under a polarizing microscope and fixed with epoxy cement on a fine glass fiber, which was then mounted on a Rigaku *R*-Axis Rapid IP X-ray diffractometer with graphite-monochromated Mo*Kα* radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection. The data were corrected for *Lp* and absorption effects. SHELXS-97 and SHELXL-97 were used for structure solution and refinement [37]. The structure was solved by direct methods and all non-hydrogen atoms were located in the subsequent difference-Fourier syntheses. After several cycles of refinement, hydrogens associated with carbons were geometrically generated and the rest of the hydrogens were located from successive difference-Fourier syntheses. Finally, all non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares and hydrogens with isotropic displacement parameters set to 1.2 times the values for the associated heavier atoms. Detailed information about the crystal data and structure determination is summarized in table 1. Selected interatomic distances and bond angles are tabulated in table 2.

3. Results and discussion

3.1. *Description of the crystal structure*

Single-crystal X-ray diffraction analysis reveals that **1** consists of dinuclear Cu$^{\mathrm{II}}$ complex and lattice waters. As shown in figure 1, the complex molecule displays a centrosymmetric-

Table 2. Selected bond lengths (Å) and angles (°) for **1**[a].

Cu1–O3	1.947(2)	Cu1–N1	2.011(3)	Cu1–N3	2.020(2)
Cu1–O5	2.368(2)	Cu1–N2	1.940(2)		
O3–Cu1–O5	88.9(1)	O5–Cu1–N1	96.4(1)	N1–Cu1–N3	160.3(1)
O3–Cu1–N1	98.8(1)	O5–Cu1–N2	92.3(1)	N2–Cu1–N3	81.5(1)
O3–Cu1–N2	178.5(1)	O5–Cu1–N3	94.7(1)		
O3–Cu1–N3	97.5(1)	N1–Cu1–N2	81.9(1)		

Hydrogen bonding contacts

D–H···A	d(D–H)	d(H···A)	<DHA	d(D···A)
O5–H5A···O3$^{\#1}$	0.82	2.01	157	2.791(7)
O5–H5B···O1$^{\#2}$	0.84	2.17	140	2.876(6)
O5–H5B···O2$^{\#2}$	0.84	2.34	141	3.041(7)
O6–H6A···O4	0.83	1.92	166	2.731(7)
O6–H6B···O9	0.81	1.97	168	2.772(8)
O7–H7A···O6$^{\#4}$	0.85	1.97	173	2.813(7)
O7–H7B···O2$^{\#5}$	0.88	2.10	170	2.969(8)
O8–H8A···O5	0.89	2.13	140	2.872(6)
O8–H8B···O7	0.88	1.83	168	2.701(7)
O9–H9B···O1$^{\#2}$	0.81	2.05	147	2.772(6)
O9–H9C···O8	0.76	1.79	142	2.434(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 = $-x+1$, $-y+1$, $-z+1$; #2 = $-x+2$, $-y+1$, $-z+1$; #3 = x, $y-1$, z; #4 = $-x+1$, $-y+1$, $-z$; #5 = $x-1$, y, z.

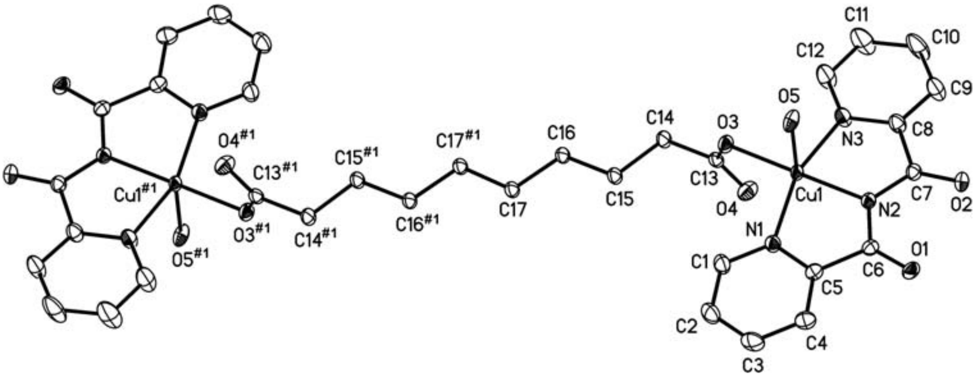

Figure 1. The molecular structure of **1** showing the coordination environment of Cu(II). Displacement ellipsoids are drawn at 45% probability level; waters and hydrogens are omitted for clarity.

dumbbell structure, in which two [Cu(H_2O)(bpca)] moieties are bridged by a sebacate. Each Cu is square-pyramidally coordinated by two oxygens and three nitrogens. The water ligand is situated at the apical position and the basal plane is defined by three nitrogens of tridentate bpca and one carboxyl oxygen of the bridging sebacate. Cu is shifted by 0.103(1) from the basal plane towards the apical water. The Addison's τ value of 0.30 ($\tau = 0$ for an ideal square pyramid and $\tau = 1$ for an ideal trigonal bipyramid) indicates more square-pyramid character with "4 + 1" coordination type. The Cu–N bond lengths vary from 1.940(2) to 2.020(2) Å, the basal Cu1–O3 bond distance is 1.947(2) Å while the axial Cu1–O5 bond length is 2.368 (2) Å – comparable with those in known copper(II) bpca complexes [38]. The *trans* and *cis* O–Cu–O angles fall in the regions 81.5(1)–98.8(1)° and 160.3(1)–178.5(1)°, respectively (table 2), exhibiting considerable deviation from the corresponding values for a regular geometry. The pyridyl rings of bpca are planar and the dihedral angle between them is 9.2 (1)°. In bpca, C(sp^2)–C(sp^2) distances within the ring are normal (average 1.384(3) Å), and the exterior bonds C5–C6 and C7–C8 average to 1.513(4) Å. The value of the bond angles at the carbonyl-carbons (111.4(2)° and 115.7(3)° for C5–C6–N2 and C8–C7–N2) exhibits significant deviation from the expected value of 120° for sp^2-hybridization. The coordinated water O5 functions as connector through intermolecular hydrogen bonds to the carboxylate of sebacate ($O3^{\#1}$; $\#1 = -x+1, -y+1$, and $-z+1$) and the $O1^{\#2}$, $O2^{\#2}$ ($\#2 = -x+2, -y+1$, and $-z+1$) of bpca forming two-dimensional layers parallel to (001) as illustrated in figure 2(a) ($d(O5\cdots O3^{\#1}) = 2.791(7)$ Å, $d(O5\cdots O1^{\#2}) = 2.876(6)$ Å, and $d(O5\cdots O2^{\#2}) = 3.041(7)$ Å).

Four crystallographically unique-free waters are in the asymmetric unit of **1** in an octameric water cluster $(H_2O)_8$ associated by O–H···O hydrogen bonds. The geometric parameters of the cluster are summarized in table 2. A wide variation in O···O non-bonding distances is found, 2.434(6)–2.813(7), compared to 2.76 Å in ice I_h at –90 °C or 2.85 Å in liquid water [39]. The O···O···O angles also vary widely (range 110–152°) with an average of 130° deviating considerably from the corresponding value of 109.3° in hexagonal ice. As shown in figure 2(b), eight waters form a circular water ring in a $(O–H\cdots O–H\cdots)_4$ connecting fashion, with the same orientations of OH bonds in the ring. This cyclic water octamer ring has a chair conformation. The overall $(H_2O)_8$ cluster can be represented by $R_8^8(16)$ in the graph set notation, and R8 by water cluster notation. A good comparison can be made with the cyclic $(H_2O)_8$ cluster reported by Atwood *et al.* [21], in which four waters serve as double hydrogen-bond donors and the remaining four as double acceptors within the ring. To the best of our knowledge, such an arrangement has not been experimentally observed so far, and it is stabilized by the environment.

A large variety of water-cluster motifs are present in previous works containing polynuclear Cu(II) complexes, which involve the cation, coordinated, and non-coordinated waters, hydroxyl, and counteranions. The variability of motifs (such as tetramer [40], heptamer [11], crowned chair octamer [41, 42], nonamer [43], chair-like decamer [44], dodecamer [45], $(H_2O)_{20}$ [16], *etc.*) is extensive, yet we have not been able to identify the cyclic water octamer ring reported here.

The octameric water clusters $(H_2O)_8$ are sandwiched between the 2D layers through hydrogen-bonding interactions to give an overall complicated 3D supramolecular configuration [figure 2(c)]. Carboxyl O1, O2, the uncoordinated O4 and water O5 are hydrogen-bond acceptors from water of the $(H_2O)_8$ cluster with O···O distances of 2.731(7)–2.969 (8) Å. Extensive hydrogen bonding between the coordinated waters and carboxylate assembles the 2-D layers and lattice waters to complete the crystal structure.

3.2. *Infrared spectrum*

As illustrated in figure S1, the IR spectrum shows a broad band centered at 3445 cm^{-1}, diagnostic of the presence of water in agreement with the X-ray crystallographic analysis. The sharp and strong intensity peak at 1717 cm^{-1} [$\nu_{asy}(CO)$ vibration of the imide group] is the signature of the presence of the bpca in the complex. The asymmetric stretching vibration of –COO group results in strong absorptions at 1603 cm^{-1}, while the symmetric stretching vibration of –COO groups causes absorptions at 1360 cm^{-1}. The differences $\Delta\nu_{as-s} = (\nu(CO_2)_{asym} - \nu(CO_2)_{sym})$ is 243 cm^{-1}, corresponding to monodentate carboxylate [46]. The pyridyl C–H stretch and dicarboxylic $-CH_2-$ stretch cause weak absorptions at 3094, 2926, and 2852 cm^{-1}.

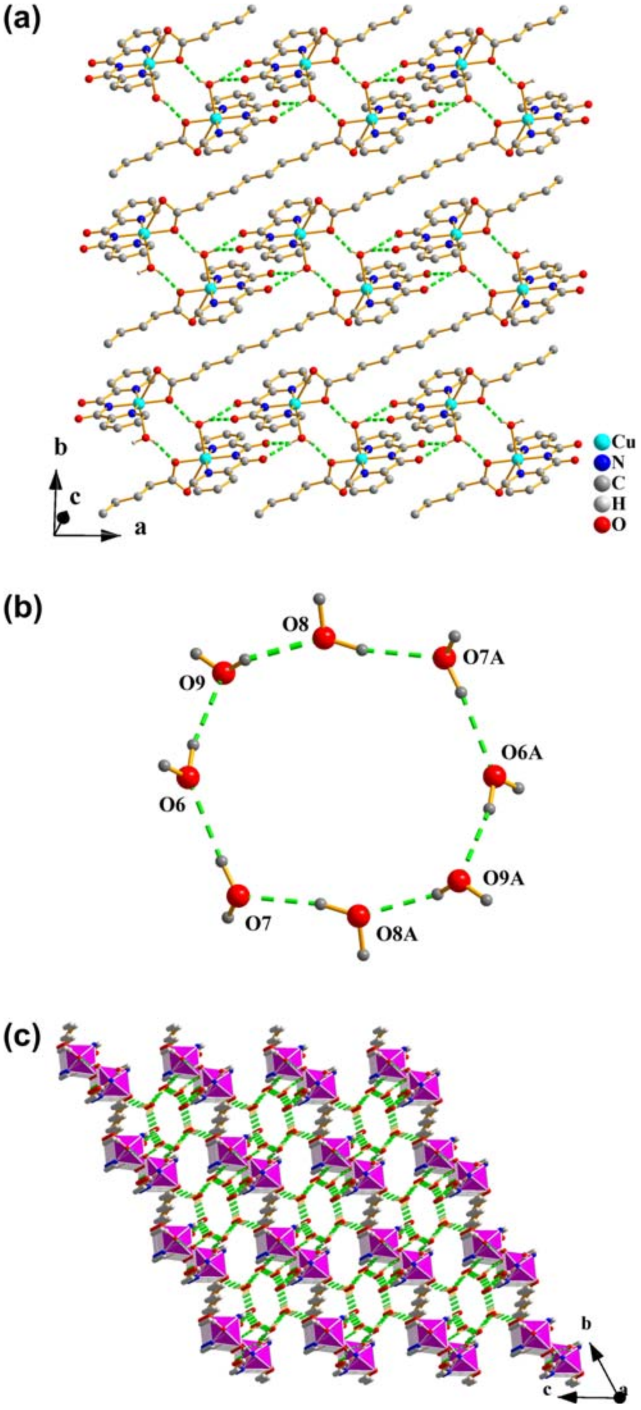

Figure 2. (a) View showing the 2D layer of **1** in which hydrogen bonds are indicated by dashed lines. (b) A perspective view of the water cluster $(H_2O)_8$. (c) The 3D supramolecular network of **1** (dashed line represents hydrogen bonding, omitting the C–C bonds of the pyridine rings).

3.3. *Thermal analysis*

The TG curve (figure S1) demonstrates dehydration of **1** upon heating in air and weight loss of 16.6% from 30–110 °C (calculated 16.9%) for the release of eight lattice waters and one coordinated water per formula unit, yielding $[Cu_2(H_2O)(bpca)_2(C_{10}H_{16}O_4)]$. Upon heating, the resulting intermediate is stable at 110–270 °C. When further heating, the intermediate exhibits gradual weight loss followed by sharp weight loss; the weight loss from 270–410 °C is 66.9%, close to the value of 66.5% calculated for the complete combustion of bpca and sebacate and the release of one water. At 410 °C, the black residual weight of 16.6% is close to the calculated value of 16.5% for two CuO molecules.

3.4. *Magnetic property*

The magnetic behavior of **1** in the form of $\chi_m T$ and χ_m vs. T plots is depicted in figure 3 (χ_m being the magnetic susceptibility per two Cu(II) ions). At 300 K, the $\chi_m T$ value is $0.63\,\mathrm{cm^3\,mol^{-1}\,K}$, smaller than the spin-only value of $0.83\,\mathrm{cm^3\,mol^{-1}\,K}$ for two magnetically isolated spin doublets. The $\chi_m T$ value increases smoothly from 300 K on cooling, where it can be seen that this complex exhibits a weak ferromagnetic interaction. The $\chi_m T$ gives a maximal value of $0.85\,\mathrm{cm^3\,mol^{-1}\,K}$ at 15 K and decreases further to $0.82\,\mathrm{cm^3\,mol^{-1}\,K}$ at 2 K. The decrease of $\chi_\mathrm{m} T$ after maximum in the curve of **1** is most likely due to zero-field splitting (D) and/or intermolecular interactions. The variable-temperature magnetic susceptibility of **1** was studied to examine the possibility of magnetic superexchange across the supramolecular $\{Cu_2(OHO)_2\}$ kernels and was least-squares fit to the Bleaney–Bowers equation (equation (1)) [47]. Because only a weak magnetic interaction was expected in the molecular-field approximation as zJ', the measured magnetic susceptibility data were fitted to (equation (2)).

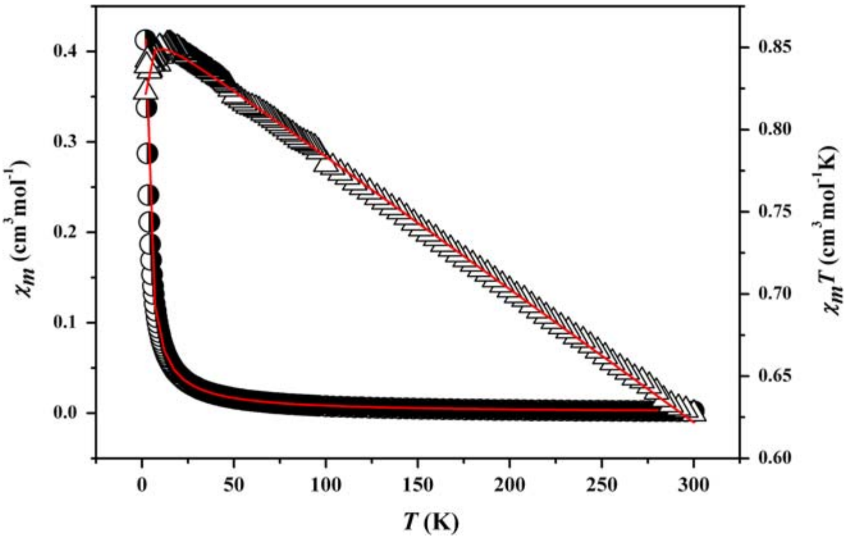

Figure 3. χ_m and $\chi_m T$ vs. T plots for **1**. Solid lines represent the best fits.

$$\chi_m = \frac{N\beta^2 g^2}{kT}\left[\frac{2\exp(-D/kT)}{1+2\exp(-D/kT)+\exp(-2J/kT)}\right] + N\alpha \qquad (1)$$

$$\chi'_m = \frac{\chi_m}{1-\chi_m(2zJ'/N\beta^2 g^2)} \qquad (2)$$

A very satisfactory fit was reached for the data from 2 to 300 K. The results are $g = 2.148$ (5), $J = 0.21(5)\,\mathrm{cm}^{-1}$, $zJ' = –0.07(4)\,\mathrm{cm}^{-1}$ and $D = 0.18(2)\,\mathrm{cm}^{-1}$, with the agreement factor $R = 8.00 \times 10^{-6}$ $(\Sigma[(\chi_m)^{\mathrm{obs}} - (\chi_m)^{\mathrm{calc}}]^2/[(\chi_m)^{\mathrm{obs}}]^2)$. The positive J corroborates intermolecular-ferromagnetic superexchange mechanism across hydrogen-bonded $\{Cu_2(OHO)_2\}$ and the negative zJ' clearly indicates the existence of very weak antiferromagnetic coupling between adjacent Cu(II) ions, which is consistent with the magnetic behavior.

4. Conclusion

We describe an unusual water octamer in $[Cu_2(H_2O)_2(bpca)_2L]\cdot 8H_2O$ (bpca = bis(2-pyridylcarbonyl)amide and L = sebacic acid), which was characterized by elemental analysis, FT-IR spectroscopy, TG-DTA analysis, magnetic measurement, and single-crystal X-ray diffraction. The unusual cyclic water octamer demonstrated herein enriches the water cluster family, helpful in modeling some of the unexplained properties of water.

Supplementary material

CCDC-817413 contains the supplementary crystallographic data for the title complex. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, United Kingdom [Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk]).

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