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Supramolecular assembled of hexameric water clusters into a 1D chain containing $(H_2O)_6$ and $[(H_2O)_4O_2]$ stabilized by hydrogen bonding in a copper complex

Masoumeh Tabatabaee

Abstract

Background: Various water clusters including hexamers, heptamers, octamers, decamers and 1D or 2D infinite water chains in a number of organic and inorganic-organic hybrid hosts, have been reported.

Results: $\{[Cu(pydc)(amp)].3H_2O\}_n$ has been hydrothermally synthesized and characterized by elemental analysis and by IR spectroscopy. A wide range of hydrogen bonds (of the O-H...O, N-H...O and N-H...N type) are present in the crystal structure. Hydrogen bond interactions between the co-crystallized water molecules led to formation of six-membered rings with chair conformation.

Conclusion: In $\{[Cu(pydc)(amp)].3H_2O\}_n$, there are three uncoordinated water molecules. Thermal methods confirm number of co-crystallized water molecules in polymer. Hydrogen bond interactions between the co-crystallized water molecules led to the formation of a six-membered ring with the chair conformation. These rings are part of a 1D chain containing six-membered O6 rings, which are alternately made from $(H_2O)_6$ and $[(H_2O)_4O_2]$ rings. $[(H_2O)_4O_2]$ rings are also in chair conformation.

Background

Water is nature's solvent and plays a fundamental role in biological and chemical processes. It is the most abundant and cheapest solvent available for the development of new reagents and the study of chemical processes [1]. Understanding of the behavior of water clusters are important and structural information of small water clusters is the first step towards the understanding of the behavior of bulk water [2]. An extensive investigation of small and medium sized water cluster $(H_2O)_n$ (n = 2-100) structures have been reported in recent years [3,4]. Various water clusters including pentamers [5,6], hexamers [6-8], heptamers [9-11], octamers [6,8,12,13], decamers [6,14-16] and 1D or 2D infinite water chains [2,17,18] in a number of organic and inorganic-organic hybrid hosts, have been structurally characterized. Recently, we also reported a tetrameric water cluster rings in the crystal structure of a new proton transfer system derived from pyridine-2,6-dicarboxylic acid and 2-amino-4-methylpyridine [19]. Several different conformations for the water hexamer, such as all-boat [20], all chairs or an intermediate between chair and boat [3,21] have been characterized by x-ray crystallography. The search for an understanding of small water cluster structures is important for an improvement of our knowledge about structures of liquid water or ice. The water hexamer is the building block of ice I_h [6] and it is known that cyclic hexameric water clusters are present in liquid water [22,23].

Recently, Synthesis of supramolecular compounds has attached great interest due to their interesting topologies and potential applications as functional materials. The reasonable design of supramolecular structure necessarily depends on the concepts of self-assembly and utilizes non-covalent forces as varied as follows: (1) coordination bonds, (2) hydrogen bonding, including both strong hydrogen bonding (e.g., O-H···O) and weak hydrogen bonding (e.g., C-H···O and C-H···N), (3) electrostatic and charge-transfer attractions,

Correspondence: tabatabaee45m@yahoo.com
Department of chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran

and (4) aromatic π stacking interactions [24]. Hydrothermal synthesis has been successful for the preparation of some supramolecular compounds. In continuation of our earlier work on the synthesis of metal complexes with polycarboxylate ligands in the presence of 2-aminopyrimidine and under hydrothermal condition [25,26], the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ with Pyridine-2,6-dicarboxylic acid and 2-aminopyrimidine was investigated. Crystal structure of complex moiety of the copper complex, $\{[Cu(pydc)(amp)].3H_2O\}_n$, (pydc = pyridine-2,6-dicarboxylate ion, amp = 2-aminopyrimidine), was reported by Altin et al. in 2004 [27]. Here we report the formation of hexameric water clusters with chair configuration in the crystal structure of above mentioned compound. Crystals of $\{[Cu(pydc)(amp)].3H_2O\}_n$ were obtained from the reaction of pyridine-2,6-dicarboxylic acid, 2-aminopyrimidine and $Cu(NO_3)_2 \cdot 3H_2O$ under hydrothermal condition.

Results and discussion

Crystal structure

The crystal is built up of a complex Cu(pydc)(amp) and three co-crystallized water molecules (Scheme 1). The one-dimentional polymeric chains showing the connectivity and extending along the [010] direction are shown in Figure 1. Each Cu^{II} atom is coordinated by O,N,O-tridentate dipicolinate ligand (bound via pyridine N and two carboxylate O atoms) and one heterocyclic nitrogen atom of 2-aminopyrimidine ligand. Each metal ion is weakly connected to two neighboring ones, through two carboxylate bridging groups of dipicolinate and amino-nitrogen of NH_2 group of 2-aminopyrimidine to form an infinite polymeric chain along the [010] direction. The crystal packing of complex is dominated by numerous hydrogen bonds of the O-H...O, N-H...O and N-H... N types (Figure 2).

The hydrogen bonding parameters are outlined in Table 1. As it was shown in Figure 3, uncoordinated water molecules are linked together and to carboxylate group of complex via hydrogen bonds. Hydrogen bond interactions between the co-crystallized water molecules (O-H···O hydrogen bonds, range from 2.74 - 2.79 Å) led to formation of a six-membered ring water cluster with chair conformation (Figure 4). These rings are part of a 1D chain (Figure 5) containing six-membered O6 rings, which are alternately made from $(H_2O)_6$ and $[(H_2O)_4O_2]$ rings (O-H···O hydrogen bonds range from 2.79-2.85 Å). Six- membered rings of $[(H_2O)_4O_2]$ are also in chair conformation (Figure 6) and the rings are linked as in cis-decalin. Hexameric water clusters with all-boat conformation are similar to ice I_h [20] and structures with all-chair conformation (all-cis) are different from ice I_h (all- trans) [3].

In addition, the crystal structure of complex is stabilized by some intermolecular C-H...O hydrogen bond interactions (C3-H3A...O2; D...A = 3.226(6) Å, < DHA = 167° and C11- H11A...O3W; D...A = 3.122(5) Å, < DHA = 131°).

IR Spectra

The FTIR spectrum of the compound (Figure 7) shows broad strong bands at the region 3275-3520 cm^{-1}, which could be related to the existence of O-H···O hydrogen bonds between water molecules. It must have been coupled by other indicative peaks such as N-H and O-H stretching frequencies and the stretching frequencies due to the aromatic rings, which originally fall within this region [28-30].

Thermal Analyses

The thermogravimetric analysis curve (Figure 8) for compound shows that the weight loss from 200°C to 250°C, corresponds to the loss of three molecules of

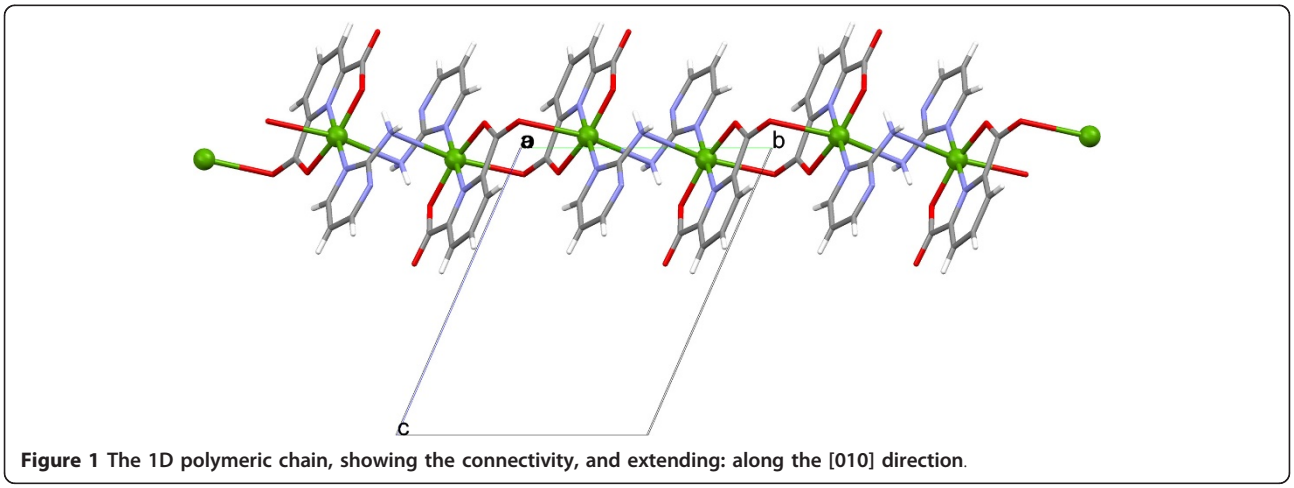


Figure 1 The 1D polymeric chain, showing the connectivity, and extending: along the [010] direction.

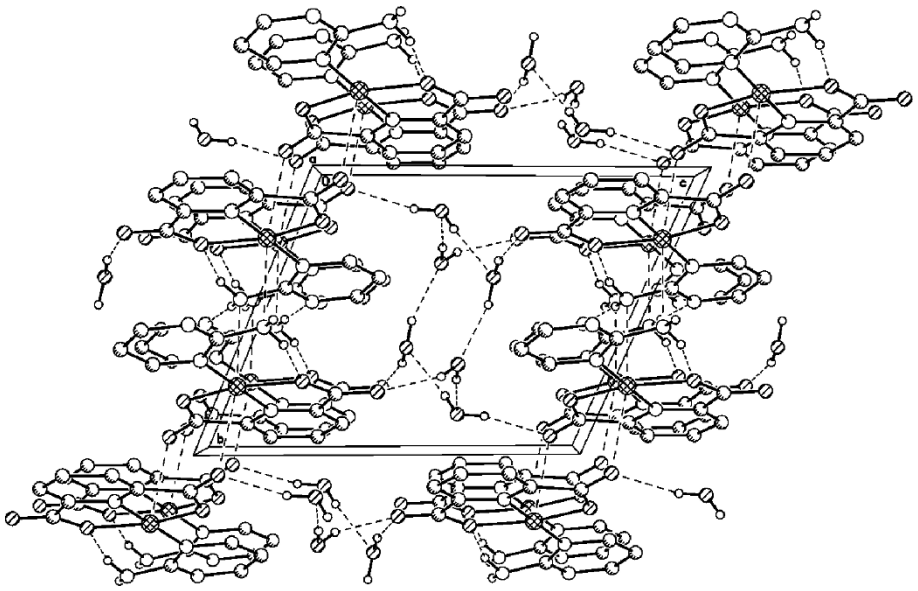


Figure 2 Crystal packing of {[Cu(pydc)(amp)].3H_2O}$_n$.

H_2O (experimental value 15.20% and calculated value 14.30%).

The further exothermic decomposition began at 400°C and finished at 500°C indicating the complete removal of the organic part of the complex. The main product was CuO with a residual value of 20.0% (theoretical residual value, 21.1%).

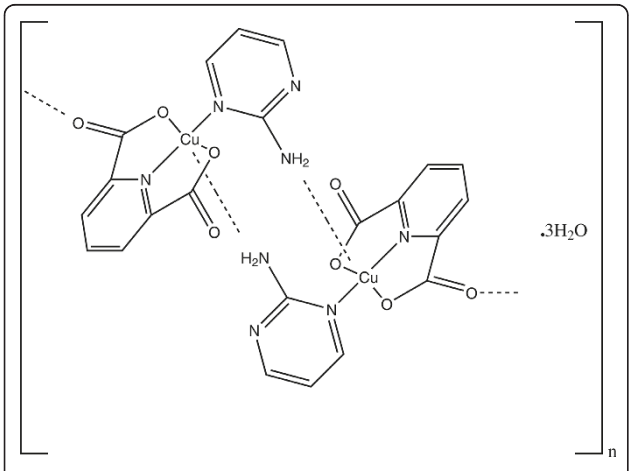
Experimental

Materials and physical measurements

All purchased chemicals were of reagent grade and used without further purification. IR spectra were recorded using FTIR Spectra Bruker Tensor 27 spectrometer (KBr pellets, 4000-400 cm^{-1}). TGA/DTA measurements were performed at heating rate of 10°C min^{-1} in the temperature range of 25-800°C, under nitrogen flow of 20 mL min^{-1} on instrument Shimadzu DTG-50H. Elemental analyses were performed using a Costech ECS 4010 CHNS analyzer.

Synthesis of complex

Pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) was dissolved in 10 ml deionized water containing 0.08 g (2 mmol) of NaOH and stirred for 30 min at room temperature. An aqueous solution of 0.241 g (1 mmol) of $Cu(NO_3)_2.3H_2O$ and 0.095 g (1 mmol) of 2-aminopyrimidine was added to pyridine-2,6-dicarboxylate acid solution. Reaction mixture was placed in a Parr-Teflon lined stainless steel vessel. It was sealed and heated at 130°C for 4 h. Blue crystals of the complex were obtained upon slow cooling (Yield 91%). IR (KBr)



Scheme 1 The scheme diagram of {[Cu(pydc)(amp)].3H_2O}$_n$.

Table 1 Hydrogen bond geometry for {[Cu(pydc)(amp)].3H_2O}n

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)	Symmetry operations
N4-H4NA...O3	0.90	1.89	2.744(4)	157	
N4-H4NB...N3	0.90	2.14	3.036(5)	175	1-x, 1-y, -z
O1W-H1WA...O4	0.85	2.02	2.851(4)	165	
O(1W)-(1WB)...O3W	0.85	1.97	2.790(4)	163	1-x, 1-y, 1-z
O2W-H2WA...O1W	0.85	1.96	2.771(4)	164	
O2W-H2WB...O2	0.85	2.04	2.866(4)	163	1+x, y, 1+z
O3W-H3WB...O2W	0.85	1.90	2.744(4)	176	
O3W-H3WA...O4	0.85	2.05	2.827(4)	152	1+x, y, z
C3-H3A...O2	0.95	2.29	3.226(6)	167	-1-x, 2-y, -z
C11- H11A...O1	0.95	2.31	2.96395)	126	
C11- H11A...O3W	0.95	2.41	3.122(5)	131	-1+x, y, -1+z

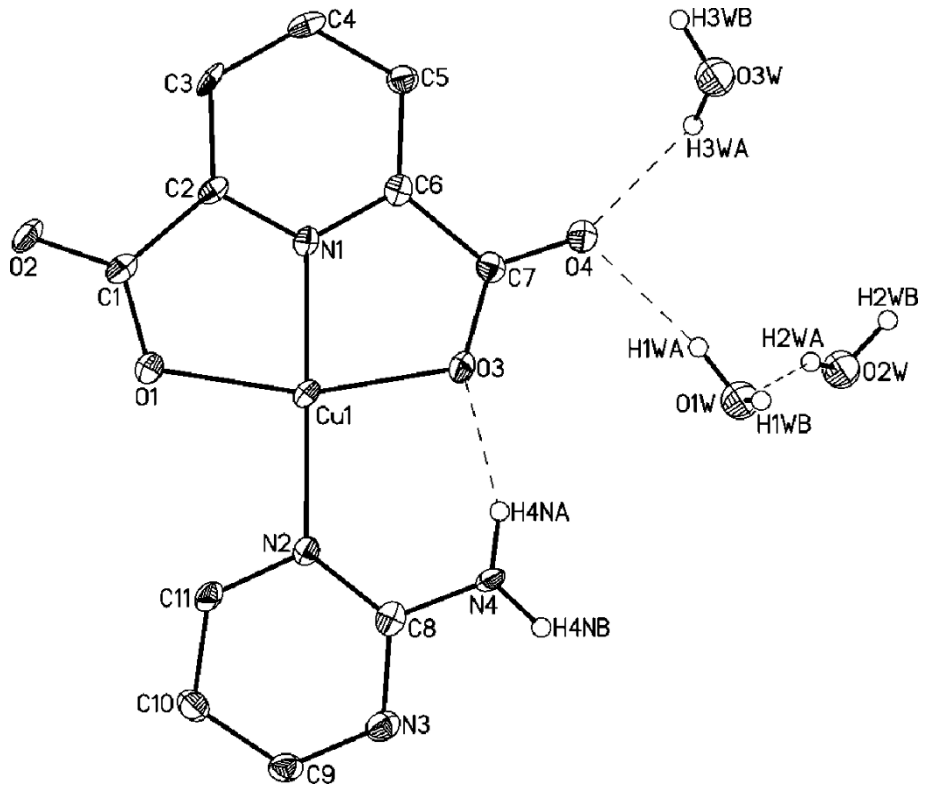


Figure 3 General view of {[Cu(pydc)(amp)].3H_2O}$_n$. Thermal ellipsoids are drawn at the 50% probability level.

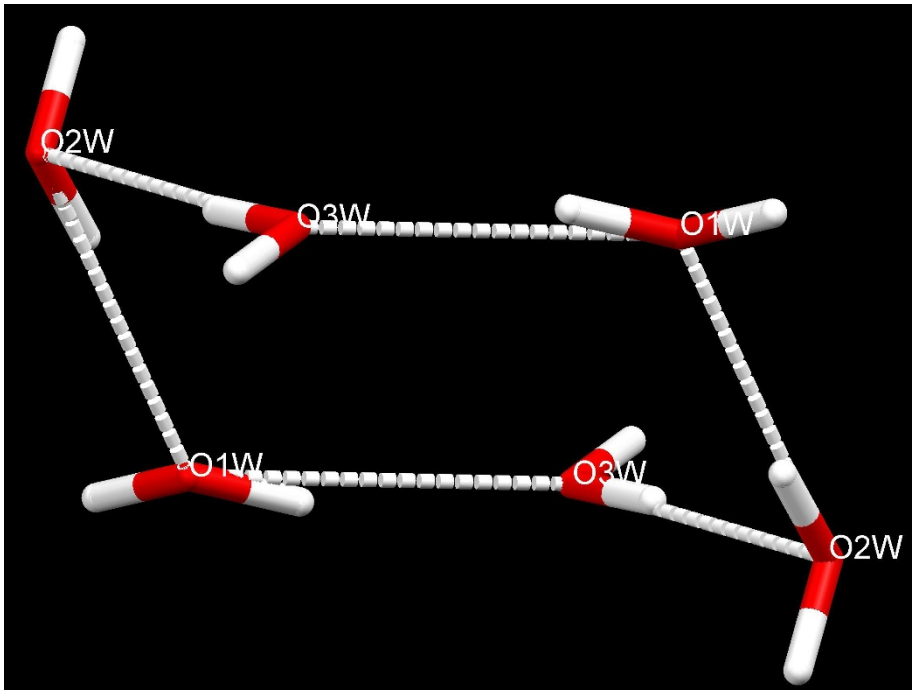


Figure 4 Chair conformation of six-membered ring water molecules.

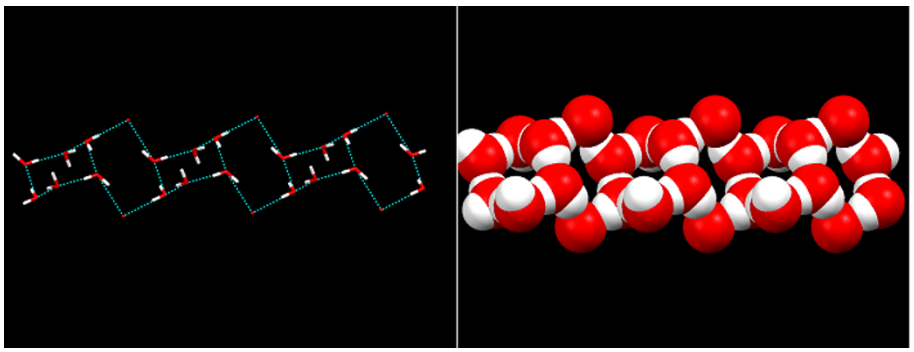


Figure 5 1D chain containing six-membered O6 rings, which are alternately made from $(H_2O)_6$ and $[(H_2O)_4O_2]$ rings.

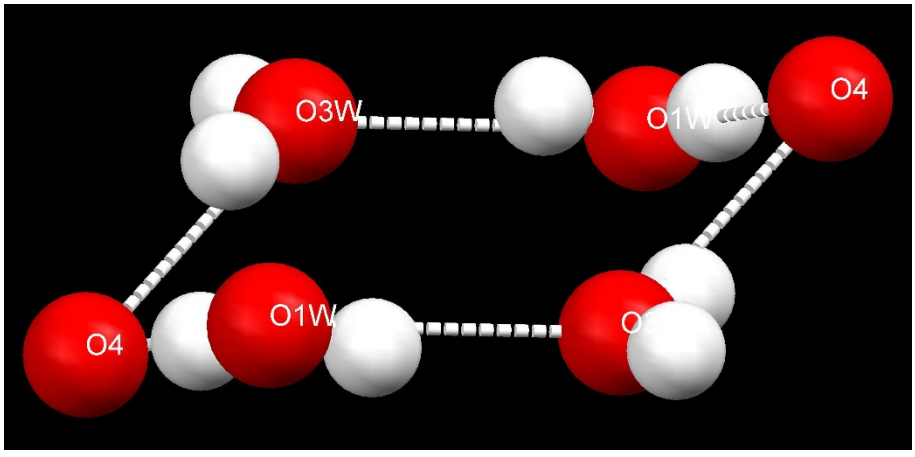


Figure 6 Chair conformation six- membered rings of $[(H_2O)_4O_2]$.

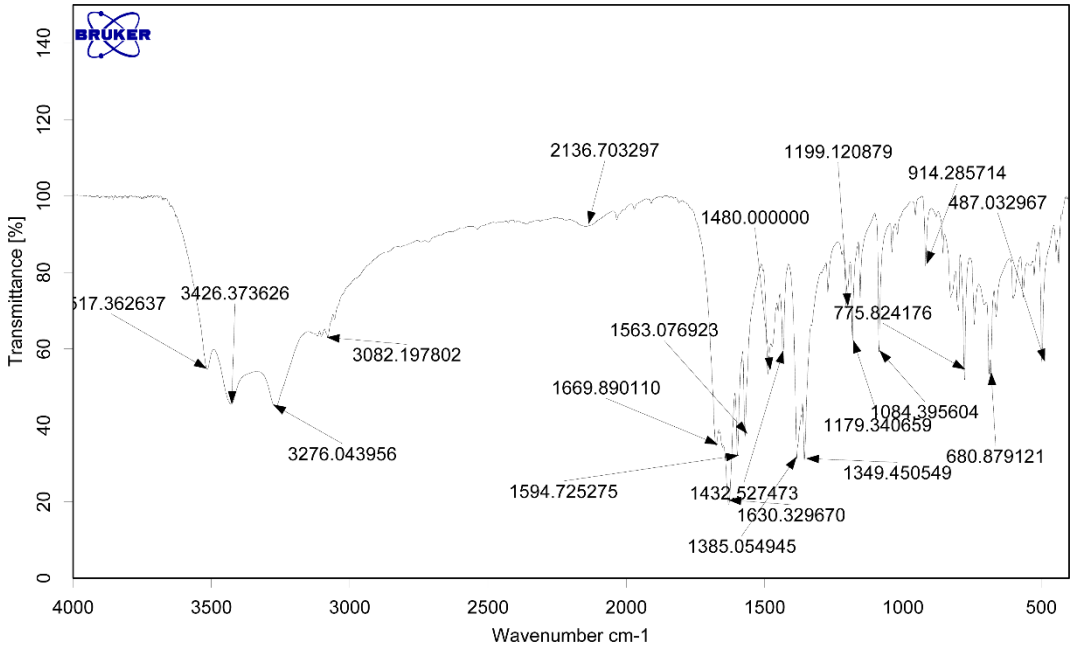


Figure 7 The FTIR spectra of $\{[Cu(pydc)(amp)].3H_2O\}_n$.

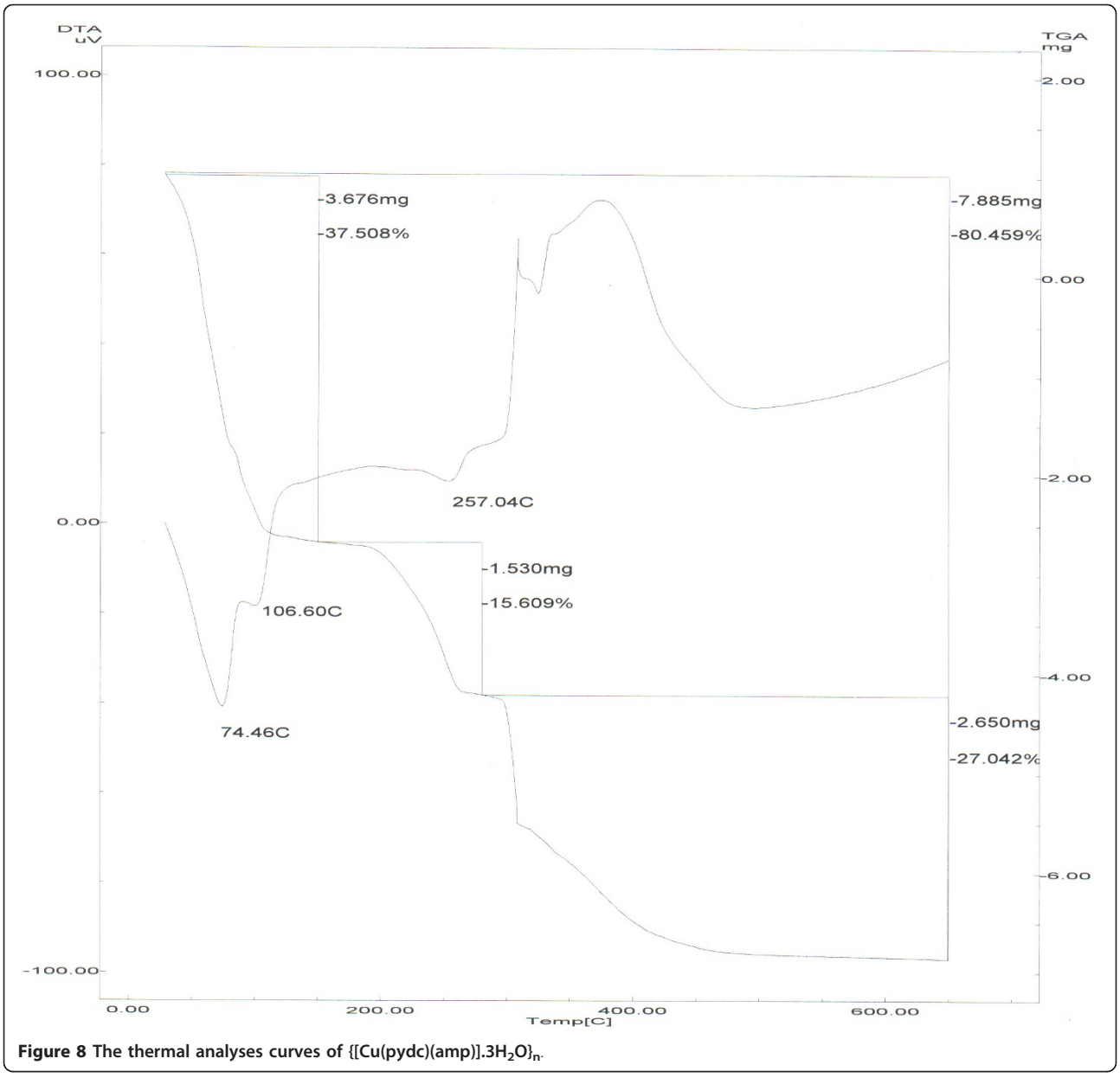


Figure 8 The thermal analyses curves of $\{[Cu(pydc)(amp)].3H_2O\}_n$.

($\tilde{\upsilon}$, cm^{-1}): 3275-3520 (b), 1669 (s), 1630 (s), 1594 (s), 1563(s), 1432 (s), 1385 (s), 1349 (s), 1199 (m), 1179 (m), 1084 (s), 914 (w), 775 (m), 680 (m), 487 (w). Anal. Calc. for $C_{11}H_{14}CuN_4O_7$ (M = 377.8): C, 49.93, H, 3.70, N, 14.82%. Found: C, 46.19, H, 3.58, N, 14.08%.

Crystallography

X-ray structure analysis was carried out on a Smart 1000 CCD area detector (Mo-Ka radiation, graphite monochromator, λ = 0.71073 Å, at 120(2) K). The crystal structure was solved by direct methods and refined by full-matrix least squares methods based on F^2 values against all reflections including anisotropic displacement parameters for all non-H atoms. All hydrogen atoms were located from difference Fouier maps with exception of H3A, H4A, H5A, H9A, H10A and H11A, which were calculated from geometrical point of view. The H atoms were refined in isotropic approximation in riding model with the Uiso(H) parameters equal to 1.2 Ueq(C, N) and 1.5 Ueq(O), where U(C, N, O) are respectively the equivalent thermal parameters of the carbon, nitrogen and oxygen atoms to which corresponding H atoms are attached. Data collection, cell refinement and data reduction were performed with SMART (Bruker, 1998), SAINT Plus (Bruker, 1998) [31] respectively. Program used to solve structure: SHELXTL (Sheldrick, 2008) and program(s) used to refine structure: SHELXTL [32]. The

molecular graphics were done with MERCURY (Version 2.3) [33]. The crystal parameters and data collection for compound are summarized in table 2.

Conclusion

In this paper, hydrothermally preparation, spectroscopic characterization, thermal properties and crystal structure of a copper complex, $\{[Cu(pydc)(amp)].3H_2O\}_n$, were presented. There are a wide range of intermolecular and intramolecular hydrogen bonds in this crystal structure which play important role in its stabilization. 1D chains containing six-membered O6 rings, which are alternately made from $(H_2O)_6$ and $[(H_2O)_4O_2]$ rings, are formed by hydrogen bond interactions.

Supplementary material

CCDC 772299 for complex contains the supplementary crystallographic data for this paper. 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 (CCDC), 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; email: http://deposit@ccdc.cam.ac.uk]. Structure factor table is available from the authors.

Table 2 Crystal data and details of the structure determination for $\{[Cu(pydc)(amp)].3H_2O\}_n$.

Formula	$C_{11}H_{14}CuN_4O_7$
M_r	377.80
Color and habit	dark blue, prism
Crystal system, space group	Triclinic, $P\overline{1}$
Crystal dimensions/mm^3	0.12 × 0.08 × 0.06
a/Å	7.4759(9)
b/Å	9.6901(12)
c/Å	11.2469(15)
α/°	108.785(2)
β/°	96.549(3)
γ/°	112.521(2)
V/Å^3	685.77(15)
Z	2
D_{calc}/g cm^{-3}	1.830
Temperature/K	120(2)
θrange for data collection/°	1.99-26.00
No. measured reflections	6016
No. independent reflections (R_{int})	2668 (0.0371)
No. observed reflections, $I \geq 2\sigma(I)$	1714
No. refined parameters	208
R^a, wR^b[$I \geq 2\sigma(I)$]	0.0394, 0.0626
R, wR [all data]	0.0671, 0.0669
Goodness of fit on F^2, S^c	0.930
Max., min. electron density/e Å^{-3}	1.382, -0.510

[a] $R = \Sigma||F_o|- |F_c||/\Sigma|F_o|$

[b] w$R = [\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

[c] $S = \Sigma[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$

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Competing interests

The authors declare that they have no competing interests.

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