Supramolecular assembled of hexameric water clusters into a 1D chain containing \((\text{H}_2\text{O})_6\) and \([\text{H}_2\text{O}]_4\text{O}_2\) 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:** \([\text{Cu(pydc)}(\text{amp})].3\text{H}_2\text{O}]_n\) 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 \([\text{Cu(pydc)}(\text{amp})].3\text{H}_2\text{O}]_n\), 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 \((\text{H}_2\text{O})_6\) and \([\text{H}_2\text{O}]_4\text{O}_2\) rings. \([\text{H}_2\text{O}]_4\text{O}_2\) 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 \((\text{H}_2\text{O})_n\) \((n = 2-100)\) 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 Ih [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,
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$_3$)$_2$ ·3H$_2$O with Pyridine-2,6-dicarboxylic acid and 2-aminopyrimidine was investigated. Crystal structure of complex moiety of the copper complex, [{Cu(pydc)(amp)].3H$_2$O}, (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$_2$O}$_n$ were obtained from the reaction of pyridine-2,6-dicarboxylic acid, 2-aminopyrimidine and Cu(NO$_3$)$_2$ ·3H$_2$O 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$_2$O)$_6$ and [(H$_2$O)$_4$O$_2$] rings (O-H...O hydrogen bonds range from 2.79-2.85 Å). Six-membered rings of [(H$_2$O)$_4$O$_2$] 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
H$_2$O (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$_2$O and 0.095 g (1 mmol) of 2-amino-pyrimidine 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)

| D-H...A  | 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                  |
| O1W-H1WA...O4 | 0.85    | 2.02    | 2.851(4) | 165                  |
| O1W-H1WB...O3W | 0.85   | 1.97    | 2.790(4) | 163                  |
| O2W-H2WA...O1W | 0.85   | 1.96    | 2.771(4) | 164                  |
| O2W-H2WB...O2 | 0.85    | 2.04    | 2.866(4) | 163                  |
| O3W-H3WB...O2W | 0.85   | 1.90    | 2.744(4) | 176                  |
| O3W-H3WA...O4 | 0.85    | 2.05    | 2.827(4) | 152                  |
| O3W-H3WB...O2 | 0.85    | 2.29    | 3.226(6) | 167                  |
| C11- H11A...O1 | 0.95    | 2.31    | 2.963(5) | 126                  |
| C11- H11A...O3W | 0.95   | 2.41    | 3.122(5) | 131                  |
Figure 3 General view of [[Cu(pydc)(amp)].3H$_2$O]$_n$. 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 (H₂O)₆ and [(H₂O)₄O₂] rings.

Figure 6 Chair conformation six-membered rings of [(H₂O)₄O₂].

Figure 7 The FTIR spectra of [Cu(pydc)(amp)].3H₂Oₙ.
Figure 8 The thermal analyses curves of ([Cu(pydc)(amp)].3H$_2$O)$_n$.
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, \([\text{[Cu(pydc)(amp)] \cdot 3H_2O}]_{\text{aq}}\), 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 \((\text{H}_2\text{O})_\text{aq}\) and \([\text{H}_2\text{O})_\text{aq}\)] 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: deposit@ccdc.cam.ac.uk]. Structure factor table is available from the authors.

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

| Formula          | \(\text{C}_{11}\text{H}_{14}\text{CuN}_{4}\text{O}_{7}\) |
|------------------|-------------------------------------------------|
| \(M_r\)          | 377.80                                          |
| Color and habit  | dark blue, prismatic                            |
| Crystal system, space group | Triclinic, \(T\)                           |
| Crystal dimensions/mm\(^3\) | 0.12 \(\times\) 0.08 \(\times\) 0.06 |
| \(a/\AA\)        | 7.4759(9)                                       |
| \(b/\AA\)        | 9.6901(12)                                      |
| \(c/\AA\)        | 11.2469(15)                                     |
| \(\alpha^\circ\) | 108.785(2)                                      |
| \(\beta^\circ\)  | 96.549(3)                                       |
| \(\gamma^\circ\) | 112.521(2)                                      |
| \(V/\AA^3\)      | 685.77(15)                                      |
| \(Z\)            | 2                                               |
| \(D_{\text{calc}}/\text{g/cm}^3\) | 1.830                                           |
| Temperature/K    | 120(2)                                          |
| \#range for data collection/\(\theta\) | 1.99-26.00                                      |
| No. measured reflections | 6016                                            |
| No. independent reflections \(R_{\text{red}}\) | 2668 (0.0371)                                   |
| No. observed reflections, \(I \geq 2\sigma(I)\) | 1714                                            |
| No. refined parameters | 208                                             |
| \(R^2\), \(wR^2\) \(I \geq 2\sigma(I)\) | 0.0394, 0.0626                                  |
| \(R\), \(wR\) [all data] | 0.0671, 0.0669                                 |
| Goodness of fit on \(R^2\), \(S\)          | 0.930                                           |
| Max. min. electron density/e \(\AA^{-3}\) | 1.382 - 0.510                                    |

*\(R = \Sigma|F_o| - |F_c|/\Sigma|F_o|\)
*\(wR = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^{1/2}\)
*\(S = \Sigma[w(F_o^2 - F_c^2)^2]/(N_{\text{obs}} - N_{\text{param}})^{1/2}\)

Acknowledgements
The author is grateful to Dr. Hopf for his valuable discussion. She also acknowledges Islamic Azad University, Yazd Branch, for the support of this work.

Competing interests
The authors declare that they have no competing interests.

References
1. Luna-García R, Darín-Muñillo BM, Barba V, Hopf H, Beltrán H, Zamudio-Rivera LS: Structural relationship between a host included chain of spirocyclic water hexamers and bulk water - the role of water clusters in self assembly and crystallization processes. Chem Commun 2005, 5527-5529.
2. Ma B-Q, Sun H-L, Gao S: Formation of Two-Dimensional Supramolecular Ice-like Layer Containing \([\text{H}_2\text{O})_{\text{aq}}\)] Rings. Angew Chem Int Ed 2004, 43:1374-1376.
3. Rodriguez-Cuamati P, Vargas-Diaz G, Hopf H: Modification of 2D Water That Contains Hexameric Units in Chair and Boat Conformations - A Contribution to the Structural Elucidation of Bulk Water. Angew Chem Int Ed 2004, 43:3041-3044.
4. Sreenivasulu B, Vitta JJ: Water Aggregates Hosted by the Metal Complexes of Reduced Schiff-base and Related Ligands. Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry 2008, 38:118-124.
5. Ghosh SK, Bhargavaj PK: Supramolecularly assembled pentameric and octameric water clusters stabilized by a mixed complex of N(III). Inorganica Chimica Acta 2006, 359:1685-1689.
6. Yang J, Ma J-F, Liu Y-Y, Ma J-C, Jia H-Q, Hu N-H: Two New Cu\(^{II}\) Coordination Polyoxometalates: Studies of Topological Networks and Water Clusters. Eur J Inorg Chem 2006, 1208-1215.
7. Moorthy JN, Natarajan R, Venugopalan P: Characterization of Planar Cyclic Ring Form of Water Hexamer in an Organic Supramolecular Complex. An Unusual Self-Assembly of Bimesityl-3,3'-Dicarbonylic Acid. Angew Chem Int Ed 2002, 41:3417-3420.
8. Doedens RJ, Yphannes E, Khan MI: Novel water clusters in the crystalline state: structures of a symmetrical, cyclic hexamer and an ‘opened-cube’ octamer. Chem Commun 2002, 62-63.
9. Mir MH, Wang L, Wong MW, Vittal JJ: Water helicate [\(\text{H}_2\text{O})_{\text{aq}}\)] hosted by a diamondoid metal-organic framework. Chem Commun 2009, 4539-4541.
10. Mir MH, Vittal JJ: Single-Crystal to Single-Crystal Transformation of Cyclic Water Hectamer to Another [\(\text{H}_2\text{O})_{\text{aq}}\)] Cluster Containing Cyclic Pentamer. Crystal Growth & Design 2008, 8:1478-1480.
11. Hedayatullah Mir M, Vittal JJ: Phase Transition Accompanied by Transformation of an Elusive Discrete Cyclic Water Hectamer to a Bicyclic [\(\text{H}_2\text{O})_{\text{aq}}\)] Cluster Angew. Chem Int Ed 2007, 46:5925-5928.
12. Atwood JL, Barbour LJ, Ness TJ, Raston CL, Raston PL: A Well-Resolved Ice-like \([\text{H}_2\text{O})_{\text{aq}}\)] Cluster in an Organic Supramolecular Complex. J Am Chem Soc 2001, 123:7192-7193.
13. Blanton WB, Gordon-Wylie SW, Clark GR, Jordan KD, Wood JT, Geiser U, Collins TJ: Synthesis and crystallographic characterization of an octameric water complex \([\text{H}_2\text{O})_{\text{aq}}\)]. J Am Chem Soc 1999, 121:3551-3552.
14. Jin Y, Che YX, Zheng JM: Supramolecularly assembled decameric water cluster stabilized by dichromate anions in complex of \(\text{Ni(II)}\). Inorg Chem Comm 2007, 10:514-516.
15. Barbour LJ, Orr GW, Atwood JL: Characterization of a well resolved supramolecular ice-like \([\text{H}_2\text{O})_{\text{aq}}\)] cluster in the solid state. Nature 1998, 393:671-673.
16. Barbour LJ, Orr GW, Atwood JL: An intermolecular \([\text{H}_2\text{O})_{\text{aq}}\)] cluster in a solid-state supramolecular complex. Chem Commun 2000, 859-860.
17. Sreenivasulu B, Vittal JJ: Encapsulation of Hydrogen-Bonded Water Molecules in a Staircase Coordination Polymer. Angew Chem Int Ed 2004, 43:5769-5772.
18. Leong WL, Vittal JJ: One-Dimensional Coordination Polymers: Complexity and Diversity in Structures, Properties, and Applications. Chem Reviews 2011, 111:688-764.

19. Sharif MA, Tabatabaee M, Adinehloo M, Aghabozorg H: 2-Amino-4-methylpyridinium 6-carboxypyridine-2-carboxylate sesquihydrate. Acta crystallogr 2010, E66:o3232.

20. Park K-M, Kuroda R, Iwamoto T: A Two-Dimensional Ice with the Topography of Edge-Sharing Hexagons Intercalated between CdNi(CN)4 Layers. Angew Chem Int Ed 1993, 32:884-886.

21. Lunelli B, Gave R, Destro R: Structure and stability of bis(dimethylamino)squaraine and its hydrates: A study using XRD, IR spectroscopy, and thermodynamic measurements. Phys Chem Chem Phys 1999, 1:1469-1477.

22. Ludwig R: Water: From Clusters to the Bulk. Angew Chem Int Ed 2001, 40:1808-1827.

23. Silverstein KAT, Haymet ADJ, Dill KA: A simple model of water and the hydrophobic effect. J Am Chem Soc 1998, 120:3166-3175.

24. Tabatabaee M, Kukovec B-M, Nasiriadieh M: Preparation and structural, spectroscopic, thermal, and electrochemical characterizations of iron(III) compounds containing dipicolinate and 2-aminopyrimidine or acridine. J Coor Chem 2011, 64:1718-1728.

25. Tabatabaee M: (2-Aminopyrimidine-κN1)diaqua-(pyridine-2,6-dicarboxylato-κ3-O2, N, O6)-nickel(II) monohydrate. Acta Crystallogr 2010, E66:m647-m648.

26. Altin E, Kirchmaier R, Lentz A: Crystal structure of (2-aminopyrimidine) (pyridine-2,6-dicarboxylato)-copper(II) trihydrate, Cu(C4H5N3)(C7H3NO4)·3H2O. Z Kristallogr NCS 2004, 219:35-36.

27. Aghabozorg H, Sadikhanlou E, Shokrollahi A, Ghaedi M, Shamsipur M: Synthesis, Characterization, Crystal Structures, and Solution Studies of Ni(II), Cu(II) and Zn(II) Complexes Obtained from Pyridine-2,6-dicarboxylic Acid and 2,9-Dimethyl-1,10-Phenanthroline. J Iran Chem Soc 2009, 6:55-70.

28. Sheldrick GM: A short history of SHELX. Acta Crystallogr A 2008, 64:112-122.