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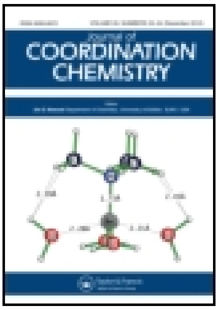

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1-D Hydrogen bonded water in Cu(II)-picolinate coordination polymer: synthesis, crystal structure, and thermogravimetric analysis

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1-D Hydrogen bonded water in Cu(II)-picolinate coordination polymer: synthesis, crystal structure, and thermogravimetric analysis

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A new Cu(II)-picolinate complex was synthesized and characterized by single crystal X-ray crystallography. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (no. 2). Picolinate in the complex extends the neutral unit into a 1-D chain through μ_2-bridging carboxylate. The complex has a hydrogen bonding acceptor in the second coordination sphere allowing lattice water to assemble neighboring chains. Water self-assembles to form a zig-zag 1-D chain. The adjacent chains are assembled by C–H···O interactions result in the formation 2-D hydrogen bonded network. The overall hydrogen bonding between water chain and Cu-picolinate network yields a 3-D hydrogen bonded coordination network. X-ray structural analysis, FTIR and thermal analysis have been used to characterize the reported compound in the solid state.

Keywords: Crystal engineering; Copper complex; Hydrogen bonding; Water chain; Metallo-supramolecular chemistry

1. Introduction

Crystal engineering is construction of crystal structures of organic and metal organic species using design principles that are derived from an understanding of the intermolecular interactions in molecular solids [1, 2]. Ideally, the designed crystal has a specific function whether it is chemical reactivity of a desired kind, an optical, magnetic or electronic property, or the ability to absorb within the crystal other than small molecules like water. Inspired by fascinating structural features of cooperative self-assembly and recognition, as well as remarkable functions such as chemical transport and screening by membrane channels in biological systems, helicity has been introduced into artificial systems by metallo-supramolecular chemists [3–6].

1-D Polymers are among the most explored and best investigated supramolecular architectures [7–9]. As hydrogen bonds and other non-covalent interactions are the main driving forces, supramolecular chemistry is characterizing and understanding various hydrogen-bonded water clusters in metal-organic hosts in the form of tetramers

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[10], hexamers [11], octamers [12], decamers [13], and 1-D infinite water chains [14, 15] in various organic and metal-organic crystal hosts. Zeolite-like 3-D network structures with chiral channels filled with highly ordered water molecules are well known [16].

1-D Water chains attract attention because of their vital role in biological transport of water, protons, and ions [17]. Transport of water or protons across the cell involves assembly of highly mobile hydrogen-bonded water molecules into a single chain at the positively charged constricted pore of the membrane-channel protein aquaporin-1 [18]. While 1-D water chains play crucial roles in stabilizing the native conformation of biopolymers, helical water chains are extremely rare in synthetic crystal hosts [14, 15]. Here, we report an interesting 1-D coordination polymeric architecture of a neutral Cu(II)-picolinate complex that hosts a 1-D zig-zag chain of lattice water molecules through hydrogen bonding.

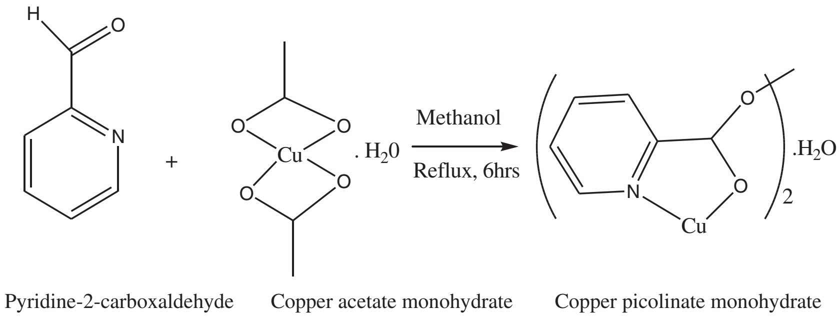
As a part of our ongoing research on molecular self-assembly through in-built peripheral hydrogen bonding group into higher dimensionality [19, 20] and trapping of water in host lattices [10, 11], in this manuscript crystal engineering of copper picolinate complex formed by *in situ* oxidation of pyridine-2-carboxaldehyde with copper(II) acetate monohydrate is discussed. The carboxylates ions not only take part in coordination to metal but also provide hydrogen bond acceptor sites for lattice water.

The synthesis, single-crystal X-ray structure, FTIR, and thermal studies of a new Cu(II)-picolinate coordination complex are reported. The title compound was synthesized by reaction of pyridine-2-carboxaldehyde and $Cu(Ac)_2 \cdot H_2O$ in dry methanol on refluxing for 6 h. Copper acetate acts as self oxidant for oxidation of pyridine-2-carboxaldehyde into 2-picolinic acid (scheme 1). Lattice water molecules from the metal salt are trapped in the Cu-picolinate network lattice forming a 1-D water chain and playing a major role in formation of the H-bonded coordination network.

2. Experimental

2.1. *Materials and methods*

$Cu(Ac)_2 \cdot H_2O$ was purchased from Finar Chemicals. Pyridene-2-carboxaldehyde was purchased from Sigma Aldrich. All reagents and solvents were of commercial grade and used without purification.



Scheme 1. Schematic representation of the reaction.

2.2. *X-ray crystallography*

Single-crystal of **1** with a dimension $0.45 \times 0.34 \times 0.24\,mm^3$ was mounted on a Rigaku Mercury375R/M CCD (XtaLAB mini) diffractometer using graphite monochromated Mo-Kα radiation equipped with a Rigaku low temperature gas spray cooler. Data were processed with Rigaku Crystal Clear software [21, 22]. Structure solution and refinements were performed using SHELX97 [23] with the WINGX suite [24]. The crystal structure and refinement data are tabulated in table 1.

2.3. *Synthesis of [Cu(2-picolinate)$_2 \cdot H_2O$] (1)*

Dry methanolic solution (10 mL) of $Cu(Ac)_2 \cdot H_2O$ (1 mmol) was added dropwise to hot stirred dry methanolic solution (10 mL) of pyridine-2-carboxaldehyde (1 mmol). The resulting reaction mixture was refluxed for 6 h. The red solution was filtered and left for crystallization at room temperature. After 15 days, fine crystals suitable for X-ray single crystallography were collected.

3. Results and discussion

3.1. *Description of the crystal structure of [Cu(2-picolinate)$_2 \bullet H_2O$] (1)*

Complex **1** crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ (no. 2). The asymmetric unit consists of crystallographically independent water and neutral Cu-picolinate complex. The copper sites exhibit "4 + 2" distorted octahedral geometry with the basal plane defined by four carboxylate oxygen atoms; the apical sites are occupied by two picolinate nitrogen atoms. The crystallographically independent Cu^{II} has two 2-picolinate ions coordinated axially through two nitrogen atoms. Two oxygen atoms of the same picolinate and two of a nearby unit complete the octahedral coordination sphere. Nitrogen atoms of each picolinate result in formation of one symmetrical axis N5···Cu···N5A. Four oxygen atoms of bridging carboxylate, two from the same unit and two from nearby complex, describe the second O1···Cu···O1A and third axes O96···Cu···O96A (figure 1). The Cu···N distance for both picolinates (Cu···N1 1.965 Å) is slightly longer than the Cu···O distance of bridging carboxylate (Cu···O1 1.945 Å).

Intermolecular connectivity *via* the second carboxylate oxygen generates a 1-D chain (figure 2a). Bridging carboxylates result in formation of an eight-membered macrocyclic unit, which is a repeating unit throughout the network and provides robustness of the framework (figure 2b). Neighboring chains are further assembled by neutral complimentary weak C–H(1)···O(1) hydrogen bonds involving a $R_2^2(10)$ supramolecular synthon as nodes that result in formation of a 2-D hydrogen bonded coordination network (figure 2c). The H(1)···O(1) bond distance is 2.49(9) Å and C–H(1)···O(1) bond angle is 145(9)°.

Lattice water molecules originating from the metal salt monohydrate play a role in hydrogen bonding. Two lattice water molecules assemble to form wO(3)–H···O(6)w dimer, [H···O(6)w distance is 2.0532 Å and wO(3)–H···O(6)w bond angle is 163.29°] and further aggregates in zig-zag manner through O···O contact between the 2-D H-

Table 1. Crystal data and structure refinement of [Cu(2-picoliniate)$_2 \cdot H_2O$].

Empirical formula	$C_{12}H_{12}CuN_2O_6$
Formula weight	343.7826
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions (Å, °)	
a	5.110(3)
b	7.571(3)
c	9.134(4)
α	75.53(3)
β	84.80(4)
γ	71.87(3)
Volume (Å^3), Z	325.2(4), 1
Calculated density (Mg m^{-3})	1.756
Absorption coefficient (mm^{-1})	1.670
F(000)	155
Crystal size (mm^3)	0.45 × 0.34 × 0.24
θ range for data collection (°)	2.1–27.50
Index ranges	$-6 \le h \le 6$; $-9 \le k \le 9$; $-11 \le l \le 11$
Reflections collected	3385
Independent reflections	1473 [$R_{\text{int}} = 0.0902$]
Completeness to $\theta = 25.00$ (%)	99.1
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.747
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1473/4/105
Goodness-of-fit on F^2	1.096
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0353$, $wR_2 = 0.0936$
R indices (all data)	$R_1 = 0.0355$, $wR_2 = 0.0934$
Largest difference peak and hole (e Å^{-3})	0.553 and −0.705

bonded [Cu-(2-picolinate)$_2$]$_n$ coordination polymer (figure 3a). The distance between the water chain and coordination layer is 2.826 Å (based on distance between water oxygen and carboxylate oxygen).

The water molecules are at two crystallographic general positions (figure 3b). Two water molecules are connected by hydrogen bonding and the inversion center is between discrete water molecules. These dimers are further connected by O···O contact and the inversion center is between the dimers. Because of this crystallographic inversion center lattice water adopts a 1-D zig-zag topology in the host framework (figure 3a). Neighboring 2-D hydrogen bonded coordination networks are further connected by zig-zag chains of water resulting in formation of the 3-D H-bonded metal-organic framework (figure 3c). Lattice water has an important role in the extensive hydrogen bonding of the Cu-picolinate coordination network. The lattice water chain also stabilizes the crystal structure by acting as glue between the coordination network.

3.2. *Thermogravimetric analysis*

The 3-D structure is a consequence of hydrogen bonding interactions among water molecules and the coordination network. This association is quite strong as thermal

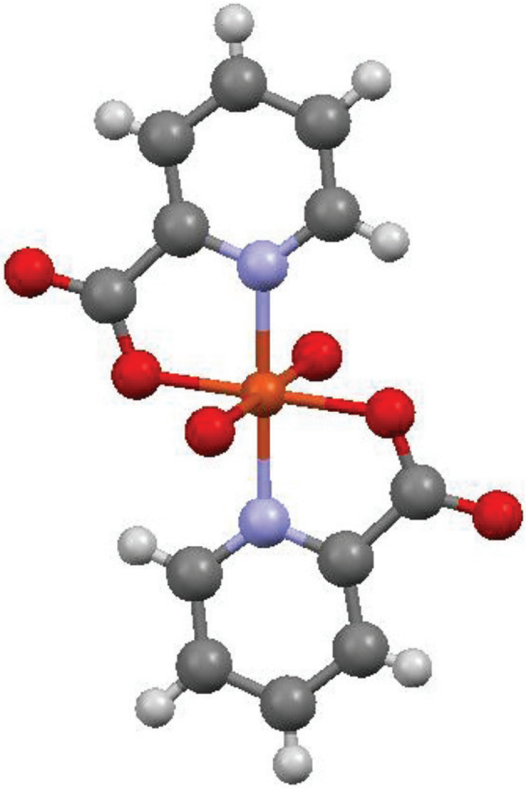


Figure 1. Local coordination environment around the copper(II) in **1**.

gravimetric analysis (figure S1) of **1** with a 5.62 mg sample in N_2 shows that the compound begins to lose weight above 60°C. Water removal begins at 80°C and loss of all water molecules takes place at 115°C. Complete decomposition of complex takes place in steps between 151 and 255°C. DTA analysis shows three endothermic peaks at 115°C, 151°C, and 255°C, attributed to release of coordinated water, carboxylate and the ring moiety from copper.

3.3. *FTIR spectroscopy*

The FTIR spectrum (figure S2) of the complex shows a broad band at 3376 cm^{-1} which vanishes on heating the compound under vacuum (0.1 mm) at 120°C for 2 h due to escape of water from the lattice. Deliberate exposure to water vapor for 2 days does not lead to re-absorption of water into the lattice as monitored by FTIR spectroscopy. The O–H stretching vibration of small water clusters $(H_2O)_n$ ($n = 2$–10) in the gaseous state have been investigated using infrared depletion fragment spectroscopy. The stretching vibrations are size specific spreading over a wide range from 3720 to 2935 cm^{-1} with the vibration below 3400 cm^{-1}. In comparison, the O–H stretch in ice is at 3220 cm^{-1} while in liquid it shifts to 3280–3490 cm^{-1} [25]. Therefore, the O–H stretching frequency of

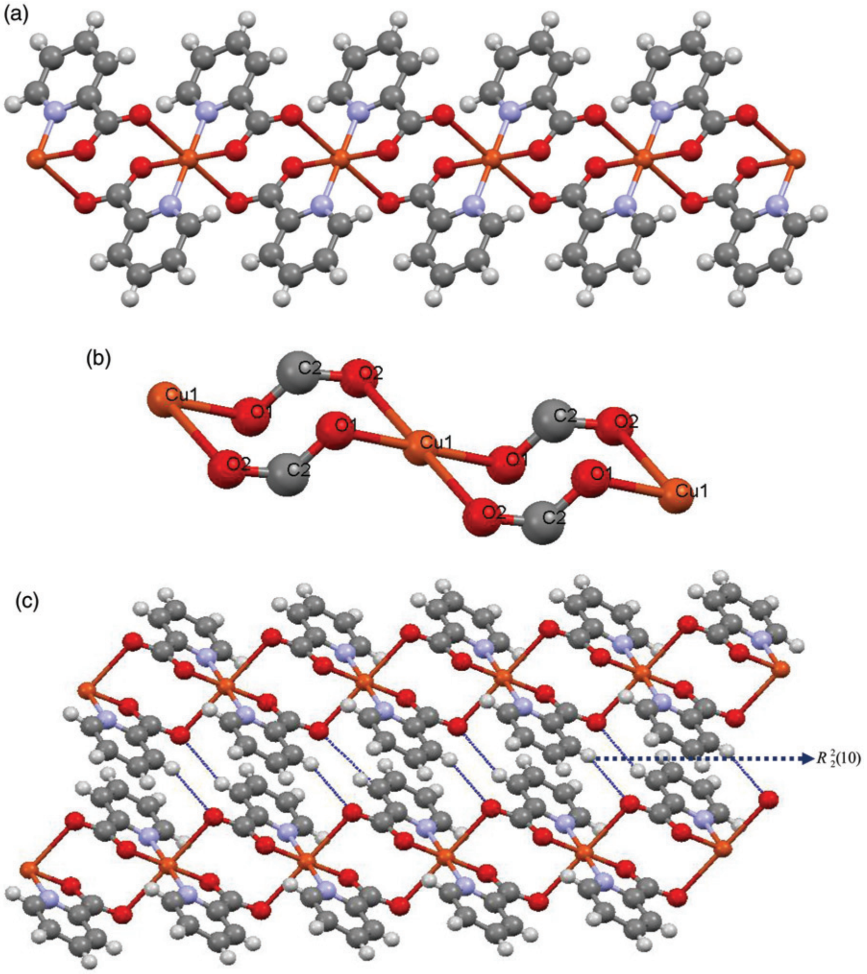


Figure 2. View of the crystal lattice showing: (a) 1-D layered polymeric architecture along the "*c*" axis; (b) eight-membered macrocyclic units; and (c) 2-D H-bonded coordination polymer forms $R_2^2(10)$ supramolecular synthon.

the water cluster in **1** is more like liquid water with slight variation attributed to its surrounding. This result is expected, as the 1-D water chain assembles the supramolecular network leading to the 3-D structure (figure 3c).

3.4. *Literature status and importance of present study*

In this study, the metal complex is a result of *in situ* oxidation of pyridine-2-carboxaldehyde in reaction with copper acetate monohydrate metal salt while in other metal picolinate complexes [26] the synthesis involves picolinate as starting material. Although water clusters have been reported by different authors, this work is noteworthy owing to the following [27–30]: (i) The complex reported by Liu *et al*. [27] shows a chair-like cyclic water decamer which is composed of two pentamers and a

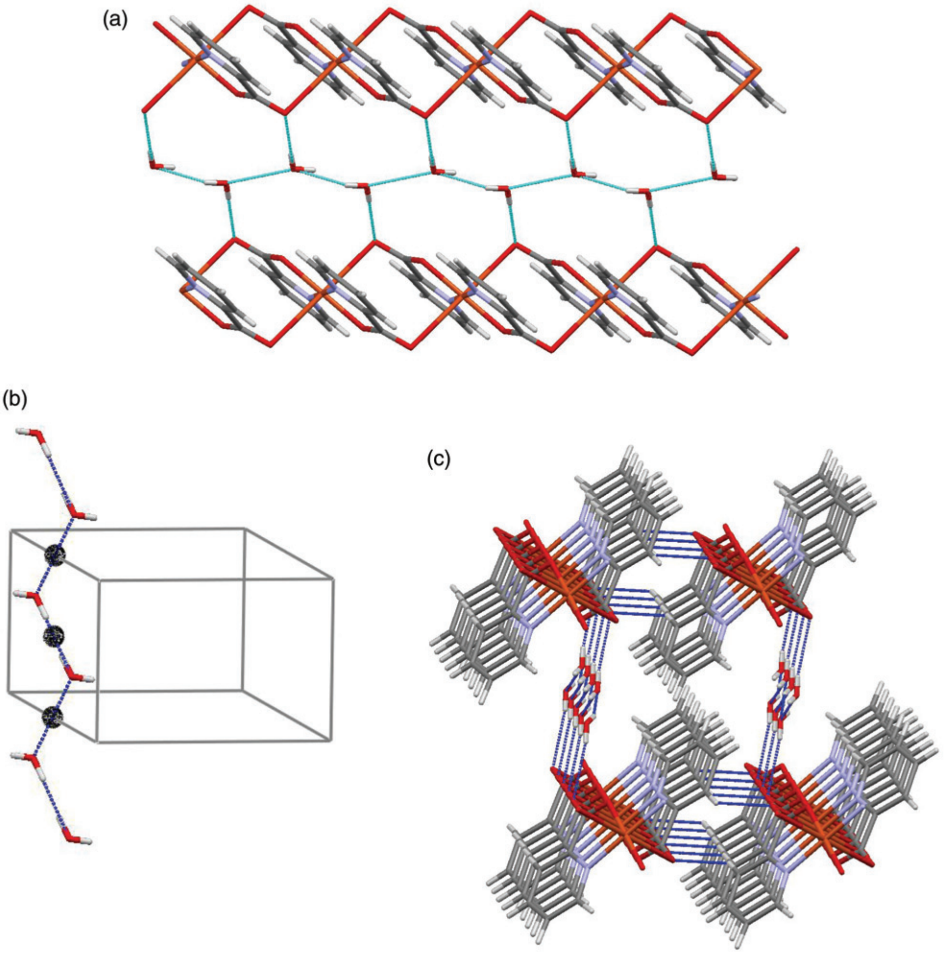


Figure 3. View of the crystal lattice showing: (a) 1-D zig-zag water chain between the host network; (b) water molecules are at the crystallographic general positions (hydrogen of water are disordered and could not be fixed); and (c) view of the 3-D H-bonded metal-organic framework along the "*a*" axis.

shared-edge tetramer while the complex reported in this study is an acyclic 1-D water cluster, i.e. no other water cluster unit is present. In complexes $\{(\mathrm{Hapy})_2[\mathrm{Cu}(\text{-pzdc})_2]\}_n$ and $[\mathrm{Cu}_2(\text{-pzdc})(\mathrm{phen})_4][\mathrm{N(CN)}_2]_2$ [27] the water cluster is assembled into a 1-D tape with discrete dicyanamide anions while the water cluster in $[\mathrm{Cu}(2\text{-picolinate})_2 \cdot \mathrm{H_2O}]$ (**1**) in this study is a 1-D chain and assembles the neutral 1-D metal organic chain, not the anion of the lattice. (ii) $\{[\mathrm{Cu(phen)(OH)}]_4 \cdot (\mathrm{H_2O})_2 \cdot (\mathrm{SO_4})_2 \cdot 8\mathrm{H_2O}\}$ [28] is a 3-D supramolecular network constituted by a 1-D metal water chain consisting of tetranuclear hydroxyl-bridged copper clusters and water octamers and also a 2-D water sulfate layer containing cyclic water octamers. In **1**, the water and metal organic chains are isolated, assembled by hydrogen bonding and devoid of counter anion. The dimensionality of water cluster reported by Gang *et al.* [28] is due to involvement of discrete metal complex and counter anion while in **1** the water molecules have 1-D topology without interaction with the counter ions. (iii) Li *et al.* [29] reported formation of a 1-D water tape consisting of $(H_2O)_{16}$ cluster units in $\{[Co(L)]\cdot 2NO_3\cdot 8H_2O\}$ $[L = N(CH_2CH_2OC_9H_6N)_3]$, in which the neighboring water tapes are connected by free nitrates *via* hydrogen bonding into a 2-D guest layer and weak C–H···N and C–H···O hydrogen bonds exist between the guest layer and host layer. In contrast in **1**, the 1-D water chain is acyclic and no other cyclic water clusters are in the system; also the water chain does not have any interaction with counter anion because the system does not have counter anion. This study also shows that the stability of the network is due to hydrogen bonding (both O–H···O and C–H···O) between the water cluster and neutral coordination network and is not a combination of hydrogen bonding among the water cluster, counter anion and metal complex. (iv) $[Cu_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(H_2O)_2(2,2'\text{-}bpy)_4]\cdot 2HFGA\cdot 4H_2O$ (H_2HFGA = hexafluoroglutaric acid and 2,2′-bpy = 2,2′-bipyridine) [30] is tetranuclear with four Cu^{2+} bridged by triple-bridging μ_3-OH and double-bridging μ_2-OH. The mononuclear and tetranuclear molecules are connected to construct different 3-D supramolecular architectures *via* noncovalent interactions. Particularly, the lone pair (lp)–π (F···π) interaction is observed. In the reported complex by Zhao *et al.* [30] there is weak hydrogen bonding with no water cluster while in the copper picolinate complex of the present study hydrogen bonding is conventional and between water cluster and the 2-D coordination network.

4. Conclusions

A new Cu-picolinate complex has been synthesized by *in situ* oxidation of pyridine-2-carboxaldehyde in the presence of copper acetate monohydrate. The μ_2-bridging carboxylate of picolinate in **1** extends the neutral molecular complex into a 1-D chain in which the in-built hydrogen bonding acceptor in the second coordination sphere makes room for lattice water to assemble the neighboring layers, resulting in formation of a hydrogen bonded 3-D network. The study enriches the role of water clusters toward coordination networks of higher dimensionality through hydrogen bonding without assistance of any other counter ions.

Supplementary material

X-ray crystallographic file in CIF format for the structure reported in this article have been deposited to the Cambridge Crystallographic Data Centre, CCDC Number 874633. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: C44 1223336033; E-mail: deposit@ccdc.cam.ac.uk; web: http://www.ccdc.cam.ac.uk/deposit].

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References

[1] G.R. Desiraju. *Crystal Engineering-The Design of Organic Solid*, Elsevier, Amsterderm (1989).
[2] G.R. Desiraju, J.J. Vittal, A. Ramanan. *Crystal Engineering-A Text Book*, IISc Press and World Scientific, Singapore (2011).
[3] J.M. Lehn. *Supramolecular Chemistry*, VCH, Weinhein (1995).
[4] M. Albrecht. *Chem. Rev.*, **101**, 3457 (2001).
[5] C. Piguet, G. Bernardinelli, G. Hopfgrartner. *Chem. Rev.*, **97**, 20052 (1997).
[6] M.J. Hannon, L.J. Childs. *Supramol. Chem.*, **16**, 7 (2004).
[7] O. Mamula, A. von Zelewsky, T. Bark, G. Bernardinelli. *Angew. Chem. Int. Ed.*, **38**, 2945 (1999).
[8] C. Kaes, M.W. Hosseini, C.E.F. Rickard, B.W. Skeleton, A.H. White. *Angew. Chem. Int. Ed.*, **37**, 920 (1998).
[9] D.A. McMorran, P.J. Steel. *Angew. Chem. Int. Ed.*, **37**, 3295 (1998).
[10] K.A. Siddiqui, G.K. Mehrotra, J. Mrozinski. *J. Coord. Chem.*, **64**, 2367 (2011).
[11] K.A. Siddiqui, G.K. Mehrotra, J. Mrozinski, R.J. Butcher. *Eur. J. Inorg. Chem.*, 4166 (2008).
[12] J.T. Atwood, L.J. Barbour, T.J. Ness, C.L. Ratson, P.L. Ratson. *J. Am. Chem. Soc.*, **123**, 7192 (2001).
[13] L.J. Barbour, W.G. Orr, J.L. Atwood. *Nature*, **393**, 671 (1998).
[14] L. Infantes, J. Chisholm, S. Motherwell. *CrystEngComm*, **5**, 480 (2003).
[15] S. Pal, N.B. Sankaran, A. Sumanta. *Angew. Chem. Int. Ed.*, **42**, 1741 (2003).
[16] Y.B. Dong, X. Zhao, B. Tang, H.Y. Wang, R.Q. Huang, M.D. Smith, H.C. zurLoye. *Chem. Commun.*, 220 (2004).
[17] R. Ludwig. *Angew. Chem. Int. Ed.*, **40**, 1808 (2001).
[18] K. Mitsuoka, K. Murata, T. Walz, T. Hirai, P. Agre, J.B. Heymann, A. Engel, Y. Fujiyoshi. *J. Struct. Biol.*, **128**, 34 (1999).
[19] K.A. Siddiqui, G.K. Mehrotra, R.L. LaDuca. *Polyhedron*, **28**, 4077 (2009).
[20] K.A. Siddiqui, G.K. Mehrotra, S.S. Narvi, R.J. Butcher. *Inorg. Chem. Commun.*, **14**, 814 (2011).
[21] Crystal clear 2.0; Rigaku Corporation: Tokyo, Japan.
[22] J.W. Pflugrath. *Acta Crystallogr., Sect. D*, **55**, 1718 (1999).
[23] G.M. Sheldrick. *SHELX97, Program for Crystal Structure Refinement*, University of Gottingen, Germany (1997).
[24] L.J. Farrugia. *J. Appl. Crystallogr.*, **32**, 837 (1999).
[25] D. Eisenberg, W. Kauzmann. *The Structure and Properties of Water*, Oxford University Press, Oxford (1969).
[26] S. Caglar, Z. Heren, O. Buyukgungor. *J. Coord. Chem.*, **64**, 2706 (2011).
[27] H.-Y. Liu, H.-Y. Wang, Y.-H. Shi. *J. Coord. Chem.*, **64**, 2859 (2011).
[28] Y.-N. Gong, C.-B. Liu, X.-H. Tang, A.-Q. Zhang. *J. Coord. Chem.*, **64**, 2761 (2011).
[29] Z. Li, L. Huang, P. Xi, H. Liu, Y. Shi, G. Xie, M. Xu, F. Chen, Z. Zeng. *J. Coord. Chem.*, **64**, 1885 (2011).
[30] K. Zhao, Y. Jiang, X. Qiu, J. Tian, X. Li. *J. Coord. Chem.*, **64**, 1375 (2011).