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First crystallographic report on a novel 2D layer of water pentagons: L5(7) water motif enclathrating [Co(cyclam)Cl_2]

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ABSTRACT

X-ray crystallographic study on [Co^{II}(cyclam)Cl_2]·$3H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) reveals that the three water molecules form water pentamers, four of such adjacent water pentamers are fused together to form boat-shaped dodecamers $(H_2O)_{12}$ which are further H-bonded to form 2D water layers. Between the successive water layers, H-bonded 1D chains of [Co(cyclam)Cl_2] monomers are sandwiched and stacked along the crystallographic *c*-direction. Thermal studies reveal that the coordinated water molecules are strongly bound to the polymeric framework which can be thermally dehydrated and readsorbed, as evidenced by the PXRD studies of the parent, dehydrated and rehydrated forms of the complex.

Though water plays a crucial role in countless biological and chemical processes and is extremely important in living organisms, its structure and chemistry are not fully understood. Liquid water molecules are associated through a hydrogen bonding network that arises due to internal polarization of the covalent bonds. The exploration of the structural and binding properties of water clusters is the first step to understanding the properties of bulk water and have been the subject of numerous experimental [1–9] and theoretical [10–14] investigations. On the other hand, information regarding the structural aspects of higher dimensional water networks is gathered mainly through X-ray crystallographic studies of organic and metallorganic hydrated crystalline materials. Larger water clusters may have 1D, 2D or 3D structures [3,5–7,15,16], whereas, the smaller water clusters $(H_2O)_n$ (n = 2, 3, 4, 5) adopt mostly planar conformations [2]. The structural relationship between the polymeric water structure and the metal ligand assembly is gradually being revealed, which has even opened up the possibilities of engineering the water clusters [17,18]. This interest is mainly a consequence of the fact that the investigations on small water clusters are perfect means to characterize structural changes and bonding mechanisms in passing from isolated molecules to bulk state.

The water pentagon appears to be ubiquitous in nature, as for example, it is observed in clathrate hydrates and in the solvation of hydrophobic groups of small molecules as well as proteins and DNA molecules. *Ab initio* calculations [19] predicted that the most stable structure for the water pentamer follows from the cyclic, puckered and quasi-planar chiral ring structures [20]. Wales [21] pointed out the existence of different ring structures that can be interconverted through low energy barrier pathways simply by flipping of hydrogen atoms and bifurcation mechanisms. Curiously, in contrast to the most frequently observed even-membered water ring morphologies such as $(H_2O)_n$ (n ~ 4, 6, 8, 10, 12 and 18) in solid state complexes, the odd-membered water rings, particularly 5-membered rings, are seldom reported [22] which prevails only tape like architecture with water-pentamers as the building blocks. There are few reports [23,24] on 2D sheet of water pentagons in combination with other water polygons like tetra-, hexa-, dodecamers, etc. In the present communication, we are going to disclose, for the first time, a 2D sheet constructed only by water pentamers as the building blocks which again enclathrates H-bonded 1D chain of [Co(Cyclam)Cl_2] (cyclam = 1,4,8,11-tetraazacyclotetradecane). So far, there are only two reports of Co-cyclam complexes [25]; in all cases central cobalt atom is in +3 oxidation state, except in one, where [Co^{II}(cyclam)Cl_2] was claimed to be isolated, though it was not structurally characterized separately [26]. Here, we have been successful in isolating and structurally characterizing [Co^{II}(cyclam)Cl_2]·$3H_2O$ with the central cobalt in +2 oxidation state.

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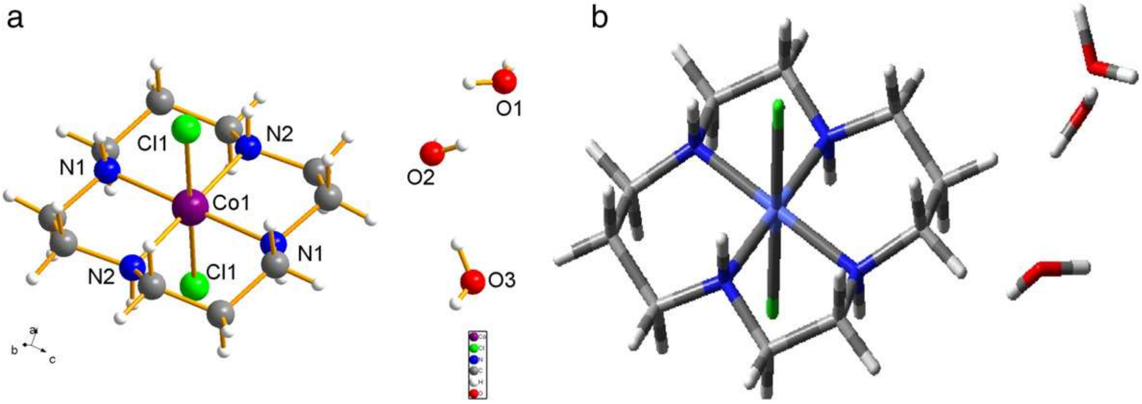

Fig. 1. (a) Molecular view of $[Co^{II}(cyclam)Cl_2]\cdot 3H_2O$ with atom numbering scheme [* = −x,−y,−z]; (b) DFT optimized structure.

Complex 1 was prepared[1] as hexagonal crystals by the reaction of $CoCl_2\cdot 4H_2O$ dissolved in water with cyclam under ordinary conditions.

The single crystal[§] X-ray study reveals a mono-nuclear complex (Fig. 1) having formula $[Co^{II}(cyclam)Cl_2]\cdot 3H_2O$. The Co atom occupies the center of inversion with octahedral coordination environment where four N atoms (N1, N2 and their inversion symmetry related counterparts N1* and N2*; * = −x,−y,−z) form the equatorial plane and two Cl atoms (Cl1 and its symmetry related counterparts Cl1*) occupy the *trans*-axial positions. Co–N1 and Co–N2 bond distances are 1.973 Å and 1.977 Å, respectively, while Co–Cl1 distance is 2.249 Å. The geometric parameters of the pentamer are summarized in Table S1 (see ESI[§]). The bond distances and bond angles are in the usual range as shown by similar Co(II) complexes [26]. Successive $[Co(cyclam)Cl_2]$ units form a hydrogen bonded one dimensional chain between axial Cl atoms and NH protons belonging to two adjacent complex moieties along the crystallograhphic *a*-axis (Fig. 2 and Table S2).

The lattice water molecules (O1W, O2W and O3W) present in the asymmetric unit form an interesting hydrogen bonded network through cooperative interactions among themselves and give rise to a 2D water layer of cyclic water pentamers (Fig. 3a). The O–O distances in the pentamer vary in the range 2.772 Å–3.053 Å and the O–O–O angle range is 89.88°–120.92° [Table S3].

In the water layer, the fused pentameric water tapes, that have been observed in two earlier cases [25], here run along the crystallographic *b*-direction. These tapes are aligned side by side along the crystallographic *a*-axis and form the 2D water layer. As it is known that a plane cannot be filled completely by a pentagon (Fig. 3a), the four adjacent pentamers in the water layer are not co-planar; instead they form a boat-like unit in three dimensions comprising 12 water molecules of four fused water pentamers. Though there are two types of water-pentamers in this boat-like structure with (i) two O1W, two O2W, and one O3W and (ii) two O1W, two O3W, and one O2W, all the pentamers differ slightly from each other with respect to bond lengths and bond angles which may be due to the non-planar nature of the pentagon. This super assembly of four water-pentamers can be taken as the basic building blocks of the pentameric 2D water layer. These units flip up and down and give rise to a corrugated 2D water layer.

The successive water layers sandwich a H-bonded 1D layer of $[Co(cyclam)Cl_2]$ monomers (Fig. 4) and these are stacked along the crystallographic *c*-direction. The DFT optimized structure of $[Co^{II}(cyclam)Cl_2]\cdot 3H_2O$ starting from crystallographic geometry resembles closely the crystallographic data.

In order to get an idea of how a part of bare water cluster looks and also in the presence of Co(II) complex, we have performed DFT calculations using Gaussian 03 program [27]. Starting from the X-ray coordinates we have fully optimized the geometries of the $[Co^{II}(cyclam)Cl_2]\cdot 3H_2O$ (Fig. 1), H_2O, $(H_2O)_5$ and $(H_2O)_{12}$ (Fig. 3b and c) that were constituted from four fused water pentamers to form a tray or boat-shaped architecture. The PW91PW91 [28] functional has been adopted along with 6-311+G(d,p) basis set for H, O, C, Cl atoms and LANL2DZ effective core potentials and basis set [29] for the Co atom. The global minima of all these species were confirmed by the positive harmonic vibrational frequencies.

In the water pentamer, five bridging hydrogen atoms (H_b) are hydrogen-bonded to oxygen atoms in a cyclic ring in the chair form. Three of the five free hydrogen atoms (H_f) lie above the ring, while the other two lie below. In the DFT optimized structure, O-H_b bond length is about 1.003 Å while O-H_f is around 0.968 Å. The H…O bond distances in the ring structure fall in the range 1.667–1.669 Å. The calculations at the PW91PW91/6-311+G(d,p) level with zero-point corrections predict 7.41 $kcal\ mol^{-1}$ as the interaction energy per H-bond in the water pentamer. At the same level of calculations the optimized four fused water pentamers look nearly boat-shaped with 15 H-bonds in total. For the two water molecules at the bottom of the bowl, all four H-atoms are involved in bridging comprising as many as 5 H-bonds with bond distances in the range 1.722–1.946 Å. Of the remaining 10 water molecules in the superstructure, one is involved in the H-bonding using both its H-atoms, while for the

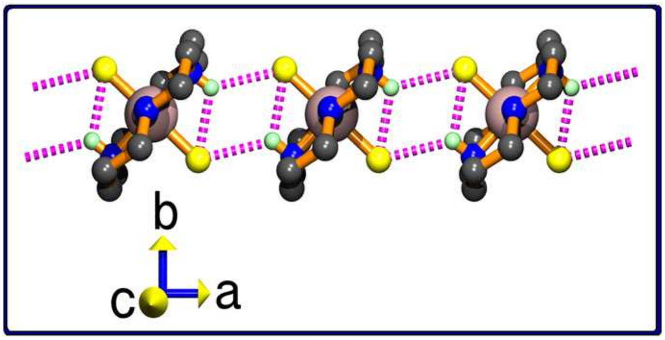

Fig. 2. 1D chain of hydrogen bonded (NH…Cl) hydrogen bonded cyclam units along the crystallographic *a*-axis.

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[1] Synthesis of $[Co(cyclam)Cl_2]\cdot 3H_2O$: To an aqueous solution (10 ml) of $CoCl_2\cdot 4H_2O$ (0.245 g, 1.0 mmol) cyclam (0.200 g, 1.0 mmol) dissolved in 5 ml water was added dropwise with constant stirring for 3 h. The pale pinkish precipitate that appeared was filtered off and the deep brown filtrate was kept in refrigerator at 4 °C for several weeks, during which time green block shape crystals suitable for X-ray study are formed. It was filtered and washed with cold water and dried in air at room temperature. Yield: 52% based on $CoCl_2\cdot 4H_2O$. Yield 50%, based on $CoCl_2\cdot 4H_2O$. Anal. found (calcd.) for $C_{10}H_{30}N_4O_3Cl_2Co$: C, 31.50 (31.33); H, 7.97 (7.83); N, 14.56 (14.62) %. IR in cm-1 (KBr): 3209(s), 3110 (s) for NH protons, 3400 (br) for water molecules, 1020–1150(s), for C-N. X-ray data collected on a Siemens P4 diffractometer; MoK_α radiation ($\lambda = 0.71073$ Å) and the ω–2θ scan mode in the range $1.90 \le \theta \le 27.5$. Crystal data: $M = 426.16$, $T = 273(2)$ K, Monoclinic, $P2_1/n$ (No. 14), $a \sim 6.3971(5)$, $b \sim 7.4148(6)$, $c = 21.0404(18)$; $V = 997.90(14)$ Å^3, $Z = 2$, independent 2064 reflections (2296 measured), all data $wR_2 \sim 0.0686$, $R_1 \sim 0.0648$.

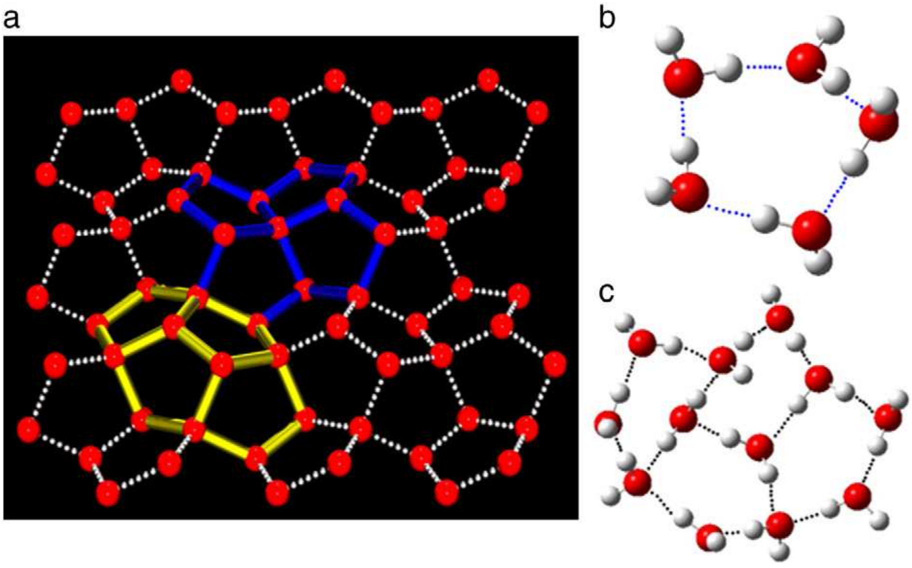

Fig. 3. (a) 2D layer of L5(7) water pentamer. DFT optimized structures of (b) water-pentamer, (c) water dodecamer formed from 4-fused water-pentamer.

remaining 9 water molecules there is one H-bond per water molecule leaving other as H_f with O–H_f bond distances in the range 0.968–0.970 Å. The present DFT calculations suggest an average stabilization energy per H-bond in $(H_2O)_{12}$ cluster of 6.68 kcal mol^{-1}. So these stable $(H_2O)_{12}$ clusters combine to form 2D water layers in between which the [Co(cyclam)Cl_2] complexes are sandwiched. A slightly lower value for each H-bond compared to the isolated pentamers may be rationalized by the fact that due to formation of this super structure from the four fused pentamers, the H···O bond distances increase slightly due to the non-planarity of $(H_2O)_{12}$ moiety.

Thermal decomposition of the complex starts at ~27 °C and continues up to ~74 °C and during this process it loses almost three (3.3) uncoordinated water molecules in the first step (found/calcd.: 15.57%/14.08% with respect to loss of weight %) which is accompanied by a small endo-effect on the DTA curve at *ca.* 73.22 °C (SUP Fig. 2). After this initial loss the complex maintains its thermal stability up to *ca.* 257 °C which on further heating loses two chlorine atoms (found/calcd.: 18.87%/18.49%) in the temperature range 257–353 °C with two small exo-peaks at *ca.* 259 °C and 350 °C in the DTA curve. After this the complex decomposes completely. It should be mentioned here that on losing three water molecules of crystallization the crystalline mass turns into powder. Thermal stability of the partly dehydrated complex in the temperature range 74–250 °C indicates that the three water molecules may be re-adsorbed. To verify this proposition, a sample was heated at 80 °C in the TGA run under N_2 atm, where all the three water molecules are eliminated. It was cooled to room temperature and then exposed to moisture in an open atmosphere for 3 days. We studied PXRD patterns on the parent, dehydrated and rehydrated complexes. The PXRD patterns of the parent and rehydrated complexes remain almost identical (Fig. 5), while the dehydrated complex has a very different pattern. All these observations clearly indicate that the present material exhibits reversible water adsorption.

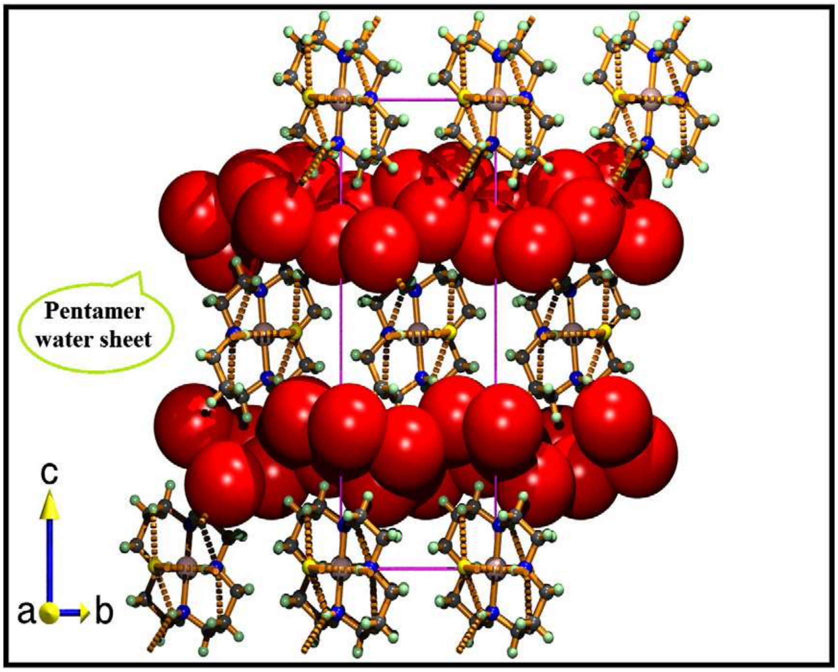

Fig. 4. Packing of successive Co and water layers.

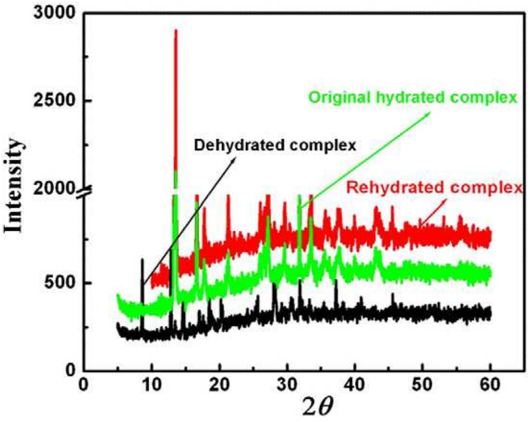

Fig. 5. PXRD patterns of parent, dehydrated and rehydrated complex after dehydration.

In summary,we have prepared $[Co^{II}(cyclam)Cl_2]\cdot 3H_2O$, in which the three water molecules form water pentamers, four of which are fused together to form a dodecamer $(H_2O)_{12}$ which is further H-bonded to form 2D water layers. Between successive water layers, $[Co(cyclam)Cl_2]$ monomers are sandwiched and stacked along the crystallographic *c*-direction. Thermal studies establish the unusually high thermal stability of the coordinated water molecules strongly bound to the polymeric framework. Also the dehydrated compound shows reversible adsorption of the lost water molecules. This has been supported by the PXRD study on both the parent and rehydrated complex after dehydration.

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Appendix A. Supplementary material

[ξ]The intensities were corrected for Lorentz and polarization effects and for absorption with ω-scans. The structures were solved by direct methods. All the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using the PLUS-PC version of SHELXTL [30]. H atoms attached to C and N atoms were positioned geometrically, while H-atoms of water molecules were found from difference Fourier Map, and refined using a riding model with $U_{iso}(H)$ values of $1.2U_{eq}(C,N,O)$. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC reference number 278583. See http://www.rsc.org/suppdata/ce/……for crystallographic data in CIF format.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.06.011.

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