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The first crystallographic observation of up to the third hydration layer of Cu(II) ion in an unusual 'water-cation layer' templated by an Anderson polyoxometallate†

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This constitutes the first crystallographic observation of hydrated Cu(II) ion retaining up to its third hydration layer which, along with the chair form water hexamer, builds up a unique water-cation layer. Moreover, an unprecedented supramolecular honeycomb network of $[Cu(phen)_3]^{2+}$ units templated by Anderson polyoxometallate units occupy the intervening spaces between successive water layers. Complex 1 is a rare example of parallel interpenetration of a 2D π–π network and a 3D pillar-layered hydrogen bonded network.

The knowledge regarding the structure of solvation shells around the metal cations is important from a basic scientific as well as technological point of view. With the rapid progress in the field of nanoscience and technology the knowledge of solvation shells around a metal cation is becoming much more relevant as the control over the molecular and atomic arrangements at the nano-scale level surely depends on the nature of mutual interactions between metal ions and organic ligands and also with solvent water molecules.[1] Metal cations, especially transition metal cations play an important role in various technological applications and in many biochemical processes. The geometry of the first hydration shell around various transition metal ions is well known from X-ray crystal structures, but the information beyond the first coordination shell is accessible only through computational and X-ray scattering experiments such as X-ray absorption fine structure (EXAFS) studies in solution.[2] A CSD search (version 5.30, November, 2008) for $[M(H_2O)_x]^{n+}$ motif [M stands for transition and lanthanide metal ions] resulted 671 hits. A careful inspection of these structures revealed no hydrated metal ions exhibiting hydration shell beyond the first coordination sphere. In this report, we present the single crystal X-ray structure of an interesting hybrid inorganic–metalloorganic complex which entraps a unique water-cation layer where the copper(II) cations are surrounded by three successive layers of solvent water molecules. Moreover, the structure also hosts a unique supramolecular honeycomb network of $[Cu(phen)_3]^{2+}$ units templated by Anderson type polyoxometallate units.

The ORTEP diagram of the molecular units present in 1‡ has been depicted in Fig. 1. Cu1 atom is situated on a three fold axis and thus the asymmetric unit contains one-third of the tris-chelated $[Cu(phen)_3]^{2+}$ unit (phen = 1,10 phenanthroline). The copper (Cu2) atom of the $[Cu(H_2O)_6]^{2+}$ unit lies at a site having a 3_2 symmetry. The tellurium atom (Te) of the Anderson type polyoxometallate (POM) unit, $[TeMo_6O_{24}]^{6-}$ lies at a site with $\bar{3}$ symmetry. Besides, the complex also contains 27 solvent water molecules per formula unit.§ The hydrogen bonded superstructural assembly of the $[Cu(H_2O)_6]^{2+}$ units, Anderson POM units and the solvent water molecules can be viewed as a 3D hydrogen bonded network having pillared layer architecture (Fig. 2, Fig. S1‡). In this architecture the self-assembled layers of the solvent water molecules and $[Cu(H_2O)_6]^{2+}$ cationic units are pillared by disk shaped Anderson POM units. These Anderson POM units supporting the water-$[Cu(H_2O)_6]^{2+}$ layers (Fig. 3) simultaneously act as templates for a unique honeycomb network (Fig. 4) of $[Cu(phen)_3]^{2+}$ units formed thrgouh π–π interaction. The honeycomb layers of tris-chelated $[Cu(phen)_3]^{2+}$ units occupy the vacant space between successive water layers leading to interpenetrtion of a 3D hydrogen bonded network and a 2D π–π layer (Fig. 2).

The water-cation layers (*ab* plane) consist of two distinct structural entities: (i) the chair form water hexamer (Fig. 5a) and (ii) the

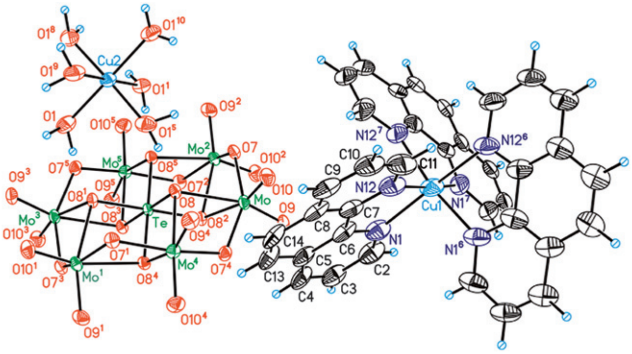

Fig. 1 The ORTEP diagram [generated by SHELXTL(Sheldrick, 1998)][3] of the complex drawn at 30% ellipsoidal probability. Solvent water molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: #1 $-y, x-y, z$; #2 $y, -x+y, -z+1$; #3 $-x, -y, -z+1$; #4 $x-y, x, -z+1$; #5 $-x+y, -x, z$; #6 $-x+y, -x+1, z$; #7 $-y+1, x-y+1, z$; #8 $-x+y, y, -z+1/2$; #9 $x, x-y, -z+1/2$; #10 $-y, -x, -z+1/2$.

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† Electronic supplementary information (ESI) available: Details of hydrogen bonding parameter of the complex (Table S1); overall supramolecular assembly in complex **1** (Fig. S1); ORTEP diagram of the hydration layers around $[Cu(H_2O)_6]^{2+}$ unit (Fig. S2); hydrogen bonded network of three water hexamer with the central hydrated Cu(II) cation (Fig. S3); the pillar formed through the hydrogen bonding water molecules with the POM units (Fig. S4). CCDC reference number 706251. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b910732k

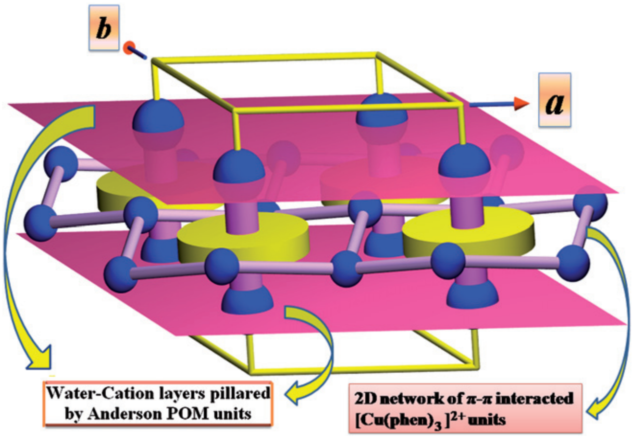

Fig. 2 Schematic representation of the interpenetrated architecture of the complex. 2D honeycomb layer of tris-chelated $[Cu(phen)_3]^{2+}$ units (blue spheres) assembled through π–π interaction that penetrates the 3D hydrogen bonded network of water–Cu(II) cation layer pillared by POM [Cu(II) cations represented by large blue spheres and POM by yellow plates].

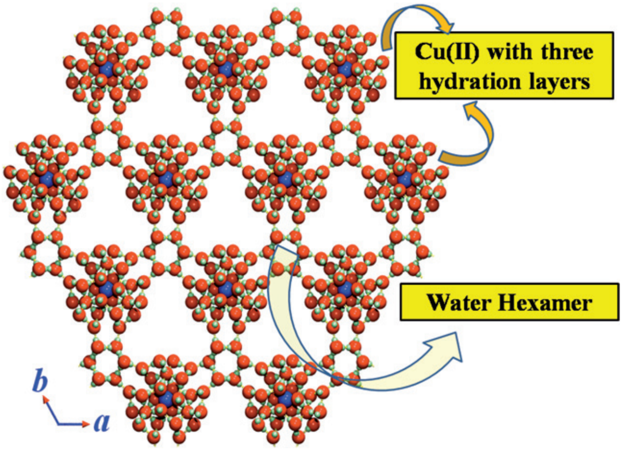

Fig. 3 The water-cation layer having honeycomb network topology with chair shaped hexagonal water cluster and hexa-aquo copper(II) as its building units.

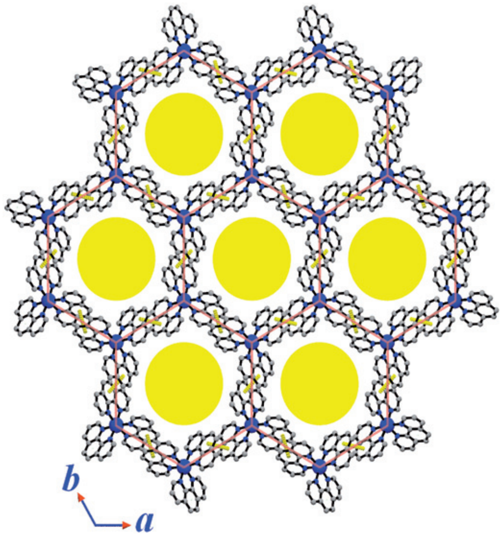

Fig. 4 Anderson POM templated π–π network of $[Cu(phen)_3]^{2+}$ units with honeycomb network architecture.

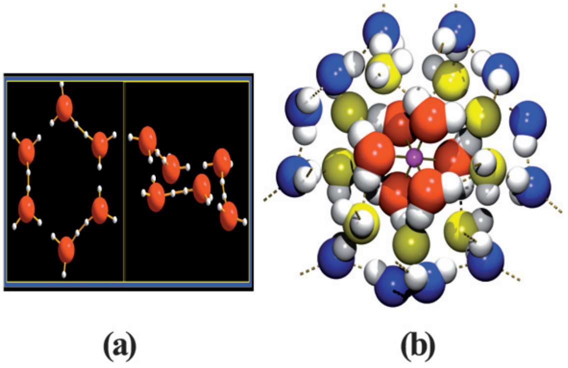

Fig. 5 Two building blocks of the water layer shown in Fig. 3. (a) The chair form water hexamer. (b) The hydrated Cu(II) with three hydration layers depicted in red, yellow and blue.

hydrated copper(II) cation retaining up to its third hydration layer (Fig. 5b). The solvent water molecule (O3) forms the chair form water hexamer through symmetry expansion that acts as a tri-topic node of the extended water-cationic layers (Fig. 3). Other uncoordinated water molecules (O2,O4, O5 and O6) surround the $[Cu(H_2O)_6]^{2+}$ units and act as a bridge between two such units. The hexa-aquo copper(II) unit is interesting because it is surrounded not only by the first hydration shell of coordinated water molecules but also by the second and third hydration layers (Fig. 5b, Fig. S2‡). This provides very important structural information on the higher hydration layers of solvated copper(II) ion. The first hydration layer is constituted by coordinated water molecules (O1 and its symmetry related counterparts) (red in Fig. 5b) being at a distance of 2.0324 Å from the central copper(II) ion in an usual octahedral coordination environment.

The yellow O atoms (O4 and O6 water molecules) in Fig. 5b constitute the second hydration layer of the Cu(II) cation which contains a total of nine water molecules. The O4 water molecules are relatively closer (Cu–O4 = 3.524 Å) than the O6 water molecules (Cu–O6 = 3.790 Å) with an average of 3.657 Å from the central ion. The observed distance here is shorter than that obtained by the EXAFS studies in solution with a mean $Cu\cdots O_{II}$ distance (O_{II} signifies the water molecules in the second hydration shell) of 4.17(3) Å.[4] This may be due to the sandwiching effect of the POM units on both sides. The O2 and O5 water molecules comprise the outermost third hydration layer bearing twelve water molecules (blue O atoms in Fig. 5b). O2 is relatively closer to the central ion (Cu–O2 = 5.465 Å) than O5 (Cu–O5 = 5.515 Å) with an average distance of 5.490 Å from the central copper(II) ion. So the distance between the first and the second hydration layers is 1.625 Å and that between the second and third hydration layers is 1.833 Å. It is important to note that our result provides the first crystallographically characterized structural information about the second and third hydration layers of copper(II). To date there is no report giving unambiguous structural information beyond the first hydration layer of metal cations in the solid state. In the outermost third hydration layer water molecules are rather arranged in the form of rings instead of a shell. This facilitates its smooth integration with the chair form water hexameric nodes in the water layer. The water molecules on the second and third layers establish a hydrogen bonding contact with three water hexamers [Fig. S3‡] nodes as well as with the two POM units above and below which act as pillars [Fig. S4, Table S1‡] for successive water-$[Cu(H_2O)_6]^{2+}$ layers. The chair shaped hexagon (Fig. 5a) is generated by a solvent water molecule [O3] which is disordered in its hydrogen atom positions (H3v, H3w, H3x) and generates the hexamer through symmetry expansion.

This kind of disordered water hexamers have been observed previously.[5] There are two sets of O⋯O distances within the hexamer (O3⋯O3* = 2.610(2) Å [* = $1 - y, 1 - x, 3/2 - z$] and O3⋯O3** = 2.898(2) Å, [** = $-x + y, y, 3/2 - z$]. All O⋯O⋯O angles are identical (105.11°). Two dihedral angles between the planes of the chairs are 64.14° each. The shortest hydrogen bonded O⋯O distance between O4 and O2 located in the second and third hydration layers, respectively, was found to be 2.393 Å and conforms to the previous observation.[6]

Anderson type POMs are inherently planar and promising candidates as templates for the self-organization of molecular building blocks[7]—especially one can expect a layered assembly in the presence of these units. Disc shaped Anderson POM units besides supporting the $[Cu(H_2O)_6]^{2+}$ layers through axial hydrogen bonding with the water molecules also act as templates (red circles in Fig. 4) for the 2D honeycomb layer of $[Cu(phen)_3]^{2+}$ units which is assembled by π–π interaction (Fig. 4).[8] It is important to mention, at this point, that tris-chelated $[Cu(phen)_3]^{2+}$ units generally yield completely different supramolecular assemblies involving a multi-fold embrace motif[9] and the 2D honeycomb architecture observed here for these units is a unique one. This π–π honeycomb network is the result of the π–π interaction of a tris-chelated $[Cu(phen)_3]^{2+}$ unit with three other $[Cu(phen)_3]^{2+}$ units. Thus any of the units acts as a tri-topic node propagating the honeycomb network. The π–π contact is established through the central phenyl ring of each phen unit. The centroid–centroid separation is 3.520(6) Å, the dihedral angle is 0° and the slip angle is 23.01° indicating that the π–π interaction is quite strong. Successive Cu⋯Cu separation in this network is 10.13 Å.

In summary, for the fist time we have been able to characterize crystallographically the geometric parameters of the hydrated copper(II) cation which retains up to its third hydration layer. These hydrated copper(II) cations are the building blocks of a unique extended 2D water-cation layers exhibiting a chair form water hexamer as one of its constituents. The water layers are sandwiched between the hydrophobic layers of $[Cu(phen)_3]^{2+}$ units, which also form a unique supramolecular honeycomb network by π–π forces.

Acknowledgements

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Notes and references

‡ *Synthesis of* $\{[Cu(H_2O)_6][Cu(Phen)_3]_2\}\{[TeMo_6O_{24}]\}\cdot 27H_20$ - 0.004 M (0.92 g) of $H_2TeO_4.2H_2O$, 0.0042 M (1.016 g) of $Na_2MoO_4\cdot 2H_2O$, 4 M (8 ml) HCl, 3 mM (0.595 g) 1,10-phenanthroline and 1 mM (0.242 g) $Cu(NO_3)_2\cdot 3H_2O$ were added to 40 ml H_2O and stirred for 2.5 h. Then the mixture was transferred to a Teflon bomb and kept in an oven at 160 °C for 6 d. The green solution obtained on cooling down to room temperature in steps of 5 °C was filtered and allowed to undergo slow evaporation at ambient temperature. Green hexagonal crystals suitable for X-ray diffraction were obtained in 15 d.

§ Crystal data: Compound **1**: $2(C_{36}H_{24}CuN_6)$, $Mo_6O_{24}Te,H_{12}O_6Cu$,27 (H_2O), M_r =2953.64, trigonal, $P\bar{3}1c$(No.163), a = 17.2848(6), b = 17.2848(6) c = 19.2560(11) Å; $\alpha = \beta = 90$, $\gamma = 120°$; V = 4982.2 (4) $Å^3$, Z = 2, D(calc) [g cm^{-3}] 1.960, crystal size [mm] = 0.20 × 0.30 × 0.30; μ(Mo Kα) [mm^{-1}] 1.754 $F(000)$ = 2954. A total of 37123 reflections were collected and 2951 unique used during refinement. Observed data [$I > 2.0\sigma(I)$] = 2580. Data were collected with a four-circle kappa-axis diffractometer Kuma KM-4 equipped with a CCD detector using monochromated (monochromator Enhance, Oxford Diffraction) MoKα (λ = 0.71073) at 120(2) K. The data reductions were carried out using the CrysAlis RED (Oxford Diffraction) program, a multi-scan absorption correction integrated in the CRYSALIS software was applied on the data. Final R-vales for observed data: R = 0.056, $wR2$ = 0.1353. CheckCIF/PLATON test generates 5 level B PLAT417 alerts during test for short non-bonding inter D-H⋯H-D contacts with the refined structure, wherefore some of water H-atoms should not be placed on the reported locations.

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8 Cg6-cg6* = 3.520(6)Ådihedral angle = 0.0° slip angle = 23.01°Ring6 = C5–C6–C7–C8–C14–C13* = −X, 1 − Y, 1 − Z.

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