View Online / Journal Homepage / Table of Contents for this issue

Single-crystal to single-crystal transformations in discrete hydrated dimeric copper complexes†

Shaikh M. Mobin,[a,b] Ashwini K. Srivastava,*[b] Pradeep Mathur*[a] and Goutam Kumar Lahiri*[a]

Received 9th September 2009, Accepted 11th November 2009
First published as an Advance Article on the web 3rd December 2009
DOI: 10.1039/b918761h

The single crystals of *discrete* hydrated [(OAc)Cu(μ-hep)$_2$Cu(OAc)]·2H$_2$O (1·2H$_2$O) and [(OAc)Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H$_2$O (2·2H$_2$O) (the lattice H$_2$O molecules exist as a tetrameric water cluster, hep-H = 2-(2-hydroxyethyl)-pyridine), OAc$^-$ = acetate and O^{n}Pr$^-$ = n-propionate) undergo single-crystal to single-crystal (SCSC) transformations to the dehydrated 1 and 2, respectively, under the influence of heat. The reverse SCSC processes of 1/2→1·2H$_2$O/2·2H$_2$O involving the regeneration of the lattice water tetramers take place on exposure of 1/2 to water vapour. However, the *blue* single crystal of *discrete* hydrated [(O^{n}Pr)Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H$_2$O (3·2H$_2$O), incorporating the two bulkier O^{n}Pr$^-$ terminal bidentate ligands, irreversibly converts to the *green* single crystal of a unique *discrete* tetrameric [Cu$_4$(μ$_3$hep)$_2$(μ-hep)$_2$(μ-O^{n}Pr)$_2$(O^{n}Pr)$_2$] (4) with *double open cubane* core either by heating or by a simple vapour diffusion technique *via* the breaking and forming of multiple covalent bonds.

Facile single-crystal to single-crystal (SCSC) transformation of discrete or polymeric molecular frameworks without loss in crystallinity has been a contemporary area of research in material sciences.[1,2] Transformations involving the breaking and formation of new bonds often destroy the crystalline state of molecules,[3] and therefore, to develop systems which can retain the crystallinity on SCSC transformation poses a formidable challenge.[4-7]

The reversible or irreversible dehydration of lattice water molecules by heating or vapour diffusion at the SCSC level is primarily centred around the porous polymeric structures.[8] The present report describes an unprecedented dehydration of the lattice water molecules,[9] which exist as water tetramers (*vide infra*), of the *discrete* [(OR)Cu(μ-hep)$_2$Cu(OR′)]·2H$_2$O [OR=OR′ = bidentate OAc (**1**·2H$_2$O), O^{n}Pr (**3**·2H$_2$O) and the bidentate mixed OR = OAc/OR′ = O^{n}Pr (**2**·2H$_2$O)], either by heating or even by a simple vapour diffusion technique at the SCSC level. Remarkably, the dehydration of the *lattice* water tetramers at the SCSC level in **1**·2H$_2$O–**3**·2H$_2$O is sensitive to the R/R′ groups associated with the terminal ligands (OR/OR′). This leads to either a reversible dehydration–rehydration of water tetramers, **1**·2H$_2$O/**2**·2H$_2$O ⇌ **1**/**2** or an irreversible molecular transformation with a distinct change in colour from dimeric *blue*-**3**·2H$_2$O to unique anhydrous *double open cubane* tetrameric structure of *green*-[Cu$_4$(μ$_3$hep)$_2$(μ-hep)$_2$(μ-O^{n}Pr)$_2$(O^{n}Pr)$_2$] (**4**) by heating as well as by simple vapour diffusion techniques.

The reaction of dihydrated copper acetate with hep-H in MeOH yields the dimeric [(OAc)Cu(μ-hep)$_2$Cu(OAc)]·2H$_2$O (**1**·2H$_2$O). Furthermore, the addition of propionic acid to a methanolic solution of **1**·2H$_2$O in 1 : 2 and 2 : 1 ratios, respectively, leads to the formation of [(OAc)Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H$_2$O (**2**·2H$_2$O) having mixed OR/OR′ terminal ligands and [(O^{n}Pr)Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H$_2$O (**3**·2H$_2$O) (see ESI†). Molecular structures of **1**·2H$_2$O–**3**·2H$_2$O have been authenticated by single crystal X-ray structural analysis (Fig. 1 and 2, Tables S1–S3†).

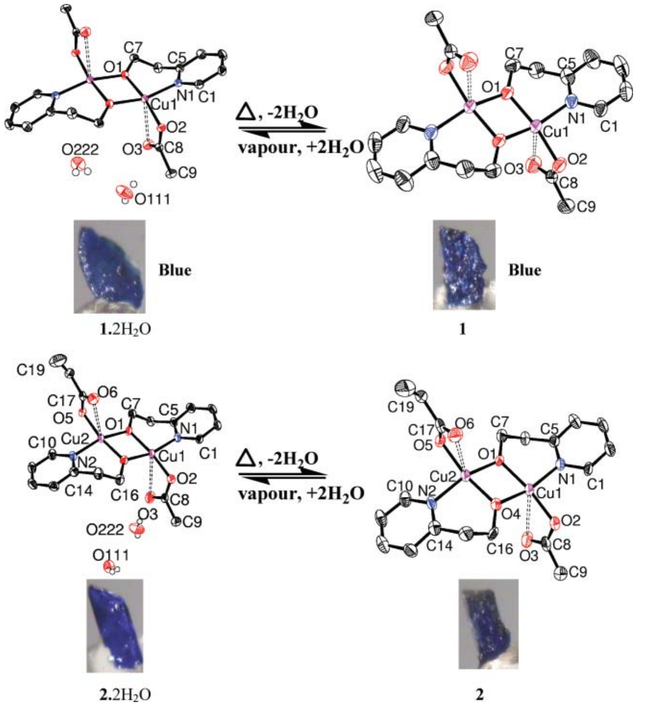

Fig. 1 Perspective view showing reversible dehydration and rehydration at the SCSC level.

1·2H$_2$O–**3**·2H$_2$O crystallise in the same triclinic $P\bar{1}$ space group with a crystallographically imposed inversion centre in **1**·2H$_2$O (ESI†). Each Cu(II) ion in **1**·2H$_2$O–**3**·2H$_2$O is in a penta-coordinated square pyramidal N1O4 environment (Fig. 1 and 2, Table S4†).

---

[a]*National Single Crystal X-ray Diffraction Facility and Department of Chemistry, IIT Bombay, Powai, Mumbai, -400076, India. E-mail: mathur@iitb.ac.in, lahiri@chem.iitb.ac.in*
[b]*Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai, 400098, India. E-mail: aksrivastava@chem.mu.ac.in*

† Electronic supplementary information (ESI) available: Experimental procedures, crystallographic data, IR spectral details and thermal analysis of complexes. CCDC reference numbers 652141, 737391–737396, 747411 and 747412. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b918761h

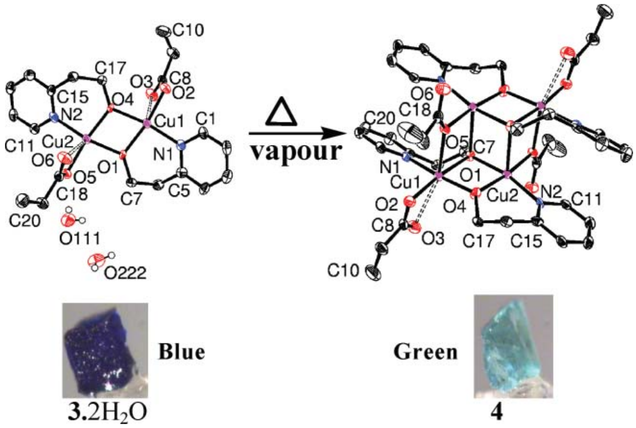

Fig. 2 Perspective view showing irreversible SCSC transformation of the *blue* single crystal of $\mathbf{3}\cdot2H_2O$ to the *green*-single crystal of **4**.

In each case the packing diagram shows four lattice water molecules from two neighbouring dimeric units to form a water tetramer (Fig. 3 and Fig. S1†) with two different O···O distances of 2.781/2.811 ($\mathbf{1}\cdot2H_2O$), 2.786/2.815 ($\mathbf{2}\cdot2H_2O$) and 2.745/2.810 ($\mathbf{3}\cdot2H_2O$) Å.[10] Packing diagrams also reveal the presence of a hydrogen bonded 2D polymeric chain (Fig. S2, Table S5†).

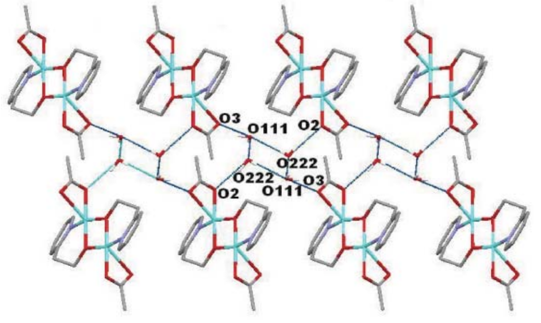

Fig. 3 Packing of $\mathbf{1}\cdot2H_2O$ along the *a*-axis showing the formation of water tetramer.

On heating, at 110 °C in air for 3 h, the single crystals of $\mathbf{1}\cdot2H_2O$ and $\mathbf{2}\cdot2H_2O$ undergo selective dehydration of the lattice water tetramers, while retaining their crystallinity, resulting in **1** and **2**, respectively, without any change in their core structural motif or the *blue* colour (Fig. 1, SI†). The single crystal of **1** possesses the same $P\bar{1}$ space group with a crystallographically imposed inversion centre (Table S1†). A 16% decrease in the unit cell volume, from 593 Å^3 in $\mathbf{1}\cdot2H_2O$ to 496 Å^3 in **1** is consistent with the loss of two lattice water molecules per dimeric unit. A similar decrease in the unit cell volume from 1143 Å^3 in $\mathbf{2}\cdot2H_2O$ to 1017 Å^3 in **2** is also observed. The packing diagrams establish the presence of C–H···O hydrogen bonding in **1** and **2** and π···π stacking interactions in **2** (Fig. S2, Table S5†). If the weak interactions are ignored, then $\mathbf{1}\cdot2H_2O\rightarrow\mathbf{1}$ or $\mathbf{2}\cdot2H_2O\rightarrow\mathbf{2}$ can be considered as 1D to 0D transformations (Fig. S3†).

On subsequent exposure of the dehydrated single crystals, **1** and **2** to water vapour for 24 h, the starting hydrated single crystals of $\mathbf{1}\cdot2H_2O$ and $\mathbf{2}\cdot2H_2O$ are regenerated. Importantly, the lattice water molecules in the regenerated crystals also exist as a tetrameric water cluster as has been observed initially (Tables S1 and S2†).

On the other hand, increasing the bulk of the terminal ligands, as in $[(O^nPr)Cu(\mu\text{-hep})_2Cu(O^nPr)]\cdot2H_2O$ ($\mathbf{3}\cdot2H_2O$), introduces an interesting contrast. Heating single crystals of $\mathbf{3}\cdot2H_2O$ at 110 °C in air for 3 h causes a distinct change in colour of the crystals from *blue* (**3**) to *green* (**4**) with retention of crystallinity. Structural analysis of **4** reveals its identity as a new *double open cubane*[11] tetrameric copper complex $[Cu_4(\mu_3\text{hep})_2(\mu\text{-hep})_2(\mu\text{-}O^nPr)_2(O^nPr)_2]$ (Fig. 2).

Thus, unlike $\mathbf{1}\cdot2H_2O$ and $\mathbf{2}\cdot2H_2O$, the dehydration of the lattice water tetramer in the crystal of $\mathbf{3}\cdot2H_2O$ results in a unique complex molecular level transformation from a dinuclear $\mathbf{3}\cdot2H_2O$ to a tetranuclear **4**. It possesses a monoclinic $P2_1/c$ space group with a crystallographically imposed inversion centre (see ESI†). The four Cu(II) ions in **4** are interconnected by two μ-hep$^-$, two μ_3-hep$^-$, and two μ-O^{n}Pr$^-$ ligands. The central Cu_4O_4 unit in **4** is arranged in a *double open cubane* conformation (Fig. 4).

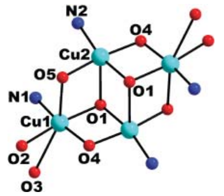

Fig. 4 Ball and stick representation of the central Cu_4 core structure of **4** showing the *double open cubane* form.

The Cu(II) ions in **4** hold two different configurations. The Cu1 atom exhibits octahedral geometry with basal positions occupied by one nitrogen atom of hep$^-$, three oxygen atoms each from μ_3-hep$^-$, μ-hep$^-$ and O^{n}Pr$^-$, and the two apical sites are composed of oxygen atoms of μ-O^{n}Pr$^-$ and the terminal O^{n}Pr$^-$. Unlike Cu1, the Cu2 in **4** exhibits square pyramidal geometry (4 + 1) where basal plane is constituted by one nitrogen atom of μ-hep$^-$, three oxygen atoms each from μ-hep$^-$, μ_3-hep$^-$, μ-O^{n}Pr$^-$ and the axial position is linked with one oxygen atom of μ_3-hep$^-$. The Cu–N distances in **4** vary slightly: Cu(1)–N(1), 1.979(3) Å and Cu(2)–N(2), 2.062(3) Å. However, appreciable variation in Cu–O distances, 1.902–2.675 Å, exists depending on their connectivities. The packing diagram reveals the presence of intermolecular C–H···O hydrogen bonding such that each tetramer is surrounded by six neighbouring tetramers yielding a 3D polymeric chain (Fig. S4, Table S5†).

In contrast to the selective formation of the *double open cubane* tetrameric copper complex (**4**) *via* the dehydration of the *lattice* water molecules in $\mathbf{3}\cdot2H_2O$, the dehydration of the *coordinated* water molecules associated with the analogous discrete dimeric complex $[Cu(\mu_2\text{-hep})(TFA)(H_2O)]_2$ (TFA = monodentate trifluoroacetate) at the SCSC level was reported[12] to yield a tetrameric copper complex, $[Cu_4(\mu_3\text{hep})_2(\mu\text{-hep})_2(\mu\text{-TFA})_2(TFA)_2]$ (**A**) having the preferential *chair* configuration (**B**) under the influence of vapour only. In **A** the terminal TFA is monodentate and oxygen atoms of μ-TFA bind separately with the two Cu ions of two parent dimeric units (Chart 1) but in **4** the terminal O^{n}Pr is bidentate and only one oxygen atom of μ-O^{n}Pr links with the two Cu ions of two parent dimeric units leaving the second oxygen atom of O^{n}Pr free (Fig. 2).

Single crystals of $\mathbf{1}\cdot2H_2O$–$\mathbf{3}\cdot2H_2O$ were also subjected to solvent vapour to explore the feasibility of gas–solid mediated SCSC

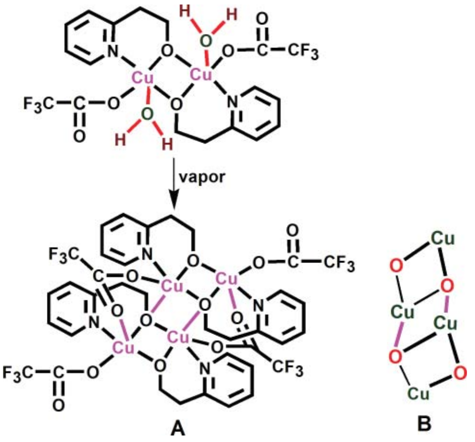

Chart 1 Schematic representation of **A** and its chair form **B**.

transformations. While the single crystals of **1**·$2H_2O$ and **2**·$2H_2O$ failed altogether to show any transformation on exposure to vapours of ROH (R = Me, Et or ^{i}Pr), CH_3CN, CH_2Cl_2 or DMF, a facile selective transformation of the single crystal of **3**·$2H_2O$ (*blue*) to **4** (*green*) was observed by the vapour diffusion technique. Though **3**·$2H_2O$→**4** in MeOH occurs spontaneously within 5 min, in EtOH, ^{i}PrOH, or CH_3CN the transformation proceeds at a much slower rate of 2 h, 24 h and 8 d, respectively. This solvent dependent varying rates of transformation implies that the initial dehydration of the lattice water tetramers of **3**·$2H_2O$ is the key step towards the subsequent spontaneous intermolecular coupling process between the adjacent two dehydrated molecules of **3** to the tetrameric **4** which indeed precluded to trap the crystal of the intermediate **3**.

The facile SCSC transformation of **3**·$2H_2O$ to **4** either by heat or vapour is accompanied by the conversion of one terminal bidentate $O^{n}Pr^{-}$ and μ-hep^{-} of each dimeric unit to μ-$O^{n}Pr^{-}$ and μ_3-hep^{-}, respectively (Fig. 2). The involvement of multiple bond breaking and formation of new covalent bonds in the transformation of **3**·$2H_2O$ to **4** indeed makes it an irreversible process such that the backward SCSC reaction of **4**→**3** or **3**·$2H_2O$ does not occur at all on exposure of the crystals of **4** to the water vapour.

The ν_{OH} vibration of the lattice water molecules in the single crystals of **1**·$2H_2O$–**3**·$2H_2O$ near 3400 cm^{-1} is expectedly absent in **1**, **2** and **4** (Figs. S5–S7†). The TGA of **1**·$2H_2O$–**3**·$2H_2O$ reveals a weight loss of 5–7% in the temperature range of 25–180 °C corresponding to the weight loss of two lattice water molecules per dimeric unit (Figs. S8–S10†). The powder XRD of **4** in different solvents are shown in Fig. S11. †At 298 K, **1**·$2H_2O$ and **1** exhibit μ = 1.308 and 1.132 B.M., respectively, however, the Cu(II) centres in **2**·$2H_2O$, **2**, **3**·$2H_2O$ and **4**, are strongly antiferromagnetically coupled leading to a diamagnetic state.

The present communication thus demonstrates an unprecedented reversible dehydration–rehydration of the *lattice* water tetramers in discrete molecular frameworks at the SCSC level and also shows remarkable influence of the terminal bidentate carboxylate ligands towards the mode of SCSC transformations, either reversible **1**·$2H_2O$/**2**·$2H_2O$⇌**1/2** or dehydration of **3**·$2H_2O$ to the transient anhydrous **3** followed by selective spontaneous intermolecular coupling of two units of **3** to generate **4** with the unique *double open cubane structure* which otherwise does not take place *via* the conventional synthetic routes.

Notes and references

1 (*a*) M. C. Das and P. K. Bharadwaj, *J. Am. Chem. Soc.*, 2009, **131**, 10942; (*b*) J. J. Vittal, *Coord. Chem. Rev.*, 2007, **251**, 1781; (*c*) K. Hanson, N. Calin, D. Bugaris, M. Scancella and S. C. Sevov, *J. Am. Chem. Soc.*, 2004, **126**, 10502; (*d*) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109; (*e*) E. Y. Lee, S. Y. Jang and M. P. Suh, *J. Am. Chem. Soc.*, 2005, **127**, 6374; (*f*) K. Takaoka, M. Kawano, M. Tominaga and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 2151; (*g*) D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033; (*h*) M.-H. Zeng, X.-L. Feng and X.-M. Chen, *Dalton Trans.*, 2004, 2217; (*i*) D. Armentano, G. D. Munno, T. F. Mastropietro, M. Julve and F. Lloret, *J. Am. Chem. Soc.*, 2005, **127**, 10778.

2 (*a*) O. Sato, J. Tao and Y.-Z. Zhang, *Angew. Chem., Int. Ed.*, 2007, **46**, 2152; (*b*) D.-F. Li, R. Clérac, O. Roubeau, E. Harté, C. Mathoniére, R. L. Bris and S. M. Holmes, *J. Am. Chem. Soc.*, 2008, **130**, 252; (*c*) M. B. Duriska, S. M. Neville, B. Moubaraki, J. D. Cashion, G. J. Halder, K. W. Chapman, C. Balde, J.-F. Létard, K. S. Murray, C. J. Kepert and S. R. Batten, *Angew. Chem., Int. Ed.*, 2009, **48**, 2549.

3 (*a*) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190; (*b*) W. Ouellette, A. V. Prosvirin, K. Whitenack, K. R. Dunbar and J. Zubieta, *Angew. Chem., Int. Ed.*, 2009, **48**, 2140; (*c*) M. Nagarathinam and J. J. Vittal, *Chem. Commun.*, 2008, 438; (*d*) M. Nagarathinam, A. M. Puthan and J. J. Vittal, *Chem. Commun.*, 2008, 5277.

4 (*a*) J. D. Ranford, J. J. Vittal, D.-Q. Wu and X.-D. Yang, *Angew. Chem., Int. Ed.*, 1999, **38**, 3498; (*b*) L. Iordanidis and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2000, **122**, 8319; (*c*) J. J. Vittal and X.-D. Yang, *Cryst. Growth Des.*, 2002, **2**, 259; (*d*) C. Hu and U. Englert, *Angew. Chem., Int. Ed.*, 2005, **44**, 2281; (*e*) S. Kitagwa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2234.

5 (*a*) H. Li, M. Eddaoudi, M. O'Keefe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (*b*) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; (*c*) E. Y. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 2004, **43**, 2798; (*d*) J. H. Kim, S. M. Hubig, S. V. Lindeman and J. K. Kochi, *J. Am. Chem. Soc.*, 2001, **123**, 87.

6 (*a*) N. L. Toh, M. Nagarathinam and J. J. Vittal, *Angew. Chem., Int. Ed.*, 2005, **44**, 2237; (*b*) X. Ouyang, F. W. Fowler and J. W. J. Lauher, *J. Am. Chem. Soc.*, 2003, **125**, 12400; (*c*) G. S. Papaefstathiou, Z. Zhong, L. Geng and L. R. MacGillivray, *J. Am. Chem. Soc.*, 2004, **126**, 9158.

7 C.-L. Chen, A. M. Goforth, M. D. Smith, C.-Y. Su and H.-C. zur Loye, *Angew. Chem., Int. Ed.*, 2005, **44**, 6673.

8 (*a*) B. Rather and M. J. Zaworotko, *Chem. Commun.*, 2003, 830; (*b*) W. Kaneko, M. Ohba and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 13706; (*c*) J.-P. Zhang, Y.-Y. Lin, W.-X. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 14162; (*d*) T. K. Maji, G. Mostafa, R. Matsuda and S. Kitagawa, *J. Am. Chem. Soc.*, 2005, **127**, 17152; (*e*) M. P. Suh, J. W. Ko and H. J. Choi, *J. Am. Chem. Soc.*, 2002, **124**, 10976.

9 X. -N. Cheng, W. -X. Zhang and X. -M. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 15738.

10 B. K. Saha and A. Nangia, *Chem. Commun.*, 2006, 1825.

11 S.-T. Zheng, M.-H. Wang and G.-Y. Yang, *Chem.–Asian J.*, 2007, **2**, 1380.

12 M. M. Shaikh, A. K. Srivastava, P. Mathur and G. K. Lahiri, *Inorg. Chem.*, 2009, **48**, 4652.