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Reversible dehydration polymerization of terephthalate bridged $[\{Cu_2(2,2'\text{-bpy})_2(tp)(H_2O)_3(NO_3)\}\cdot H_2O\cdot NO_3]_2$

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The title compound is the first example of a molecular magnet sponge, which exhibits a carboxylate-assisted unique reversible dehydrative polymerization–rehydrative monomerization phenomenon.

Terephthalate (tp) as a ligand has attracted considerable attention due to its extended conjugation, exodentate nature and versatility of bonding modes.[1] The ligand has been systematically explored as a spin carrier between paramagnetic metal ions to understand structural magnetic correlations.[2–11] It is increasingly being employed to generate supramolecular arrays of different structural motifs such as chains, sheets and grids.[12–33] Variable sized open cavities and channels (neutral or anionic) have especially been synthesised.[34–36]

The polymerization approach associated with the dehydration of spin bearing monomers has recently been developed. The enhanced dimensionality of the resulting polymer is of particular interest in terms of magnetic properties.[37,38] Because of the versatility of bonding modes and extended conjugation, terephthalate is a suitable candidate to assist such transformations. It has a potential to generate 1, 2 or 3D complexes with a variety of architectures and unusual magnetic properties while expanding its coordinating mode from monodentate (uni or bis) to tri or tetrakis monodentate modes to compensate for the loss of coordinated water during such transformations. The dinuclear monomeric $[Mn_2(phen)_4(H_2O)_2(tp)][ClO_4]_2$ ($J = -0.65$ cm^{-1}) is converted into 1D $[Mn_2(phen)_4(tp)][ClO_4]_2$ ($J = -1.6$ cm^{-1}) after the removal of water molecules.[8] Dehydration is accomplished with the change of the bis monodentate mode of coordination to the tetrakis monodentate mode.

Here, we report the dehydration–rehydration and magnetic properties of $[\{Cu_2(2,2'\text{-bpy})_2(tp)(H_2O)_3(NO_3)\}\cdot H_2O\cdot NO_3]_2$.

The test crystals were obtained by layering an acetonitrile solution of $[Cu(2,2'\text{-bpy})(NO_3)_2]$ (0.34 g, 1.0 mmol) over a methanolic solution of piperidinium terephthalate (0.17 g, 0.5 mmol). Deep blue crystals were separated after two days in 60% yield; they were collected by filtration and air dried.[†]

The asymmetric unit is dimeric, formed from two equivalent dinuclear monomers. Further each dinuclear is generated from two non-equivalent Cu^{II} ions held together by terephthalate and corresponds to the formula $Cu_2(2,2'\text{-bpy})_2(tp)(H_2O)_4(NO_3)_2$. Three water molecules are directly coordinated to each copper centre while the remaining molecule is present as solvate. One nitrate is coordinated through oxygen to one of the copper atoms in a monodentate mode while the other one is uncoordinated. Both the copper atoms are nearly square pyramidal in nature; however, the two differ in the nature of the apical ligand attached

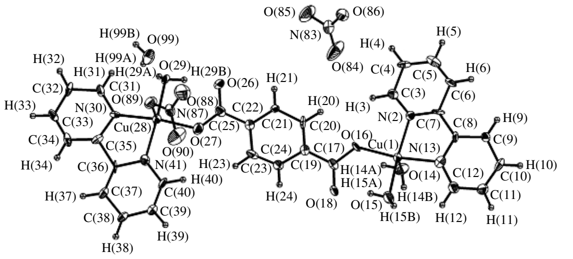

Figure 1 The asymmetric unit of **1** and the numbering scheme.

to them. The square of both Cu atoms is formed from Cu···2N (2,2′-bpy, ≈1.994 Å), Cu···O (H_2O, 1.957 Å) and Cu···O (tp, 1.954 Å) where terephthalate coordinates in an anti bis monodentate manner. In Cu(1) the square pyramid is completed by fifth water ligand on the apical direction with a slightly longer Cu–O bond (2.234 Å due to the Jahn–Teller distortion). In Cu(28), on the other hand, O from the NO_3 group takes up the apical position forming a slightly weaker bond (2.325 Å). Apical Cu(1)–H_2O and Cu(28)–NO_3 are in *trans* positions to each other. The two Cu atoms are 11.2 Å apart. The complex exists in a chair conformation, the displacement of one copper atom from the plane formed by the coordination plane of another copper is 0.82 Å. The equatorial water molecule of Cu(1) is not involved in hydrogen bonding. Coordinated H_2O molecule of Cu(28) is hydrogen bonded to solvate water molecule.[‡] However, in the dimer the monomers are placed in a tail-to-head manner and are held together by π–π interaction and weak hydrogen bonds between the layers. The distance of the planes of the rings is approximately 3.50 Å, which is within the range of π–π interaction. The terephthalate ring and one of the bipyridine rings are roughly in edge-to-edge overlapping positions (Figure 2) with disposition of two monomers of approximately 9.7 Å.

The distance between two molecules within a layer is 16.8 Å.

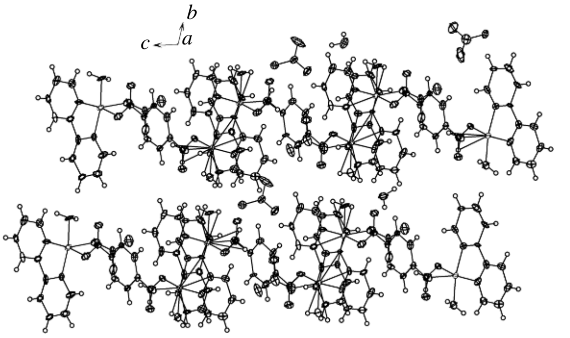

Figure 2 The packing view of **1** along the *a* axis showing π-π interactions between the molecules.

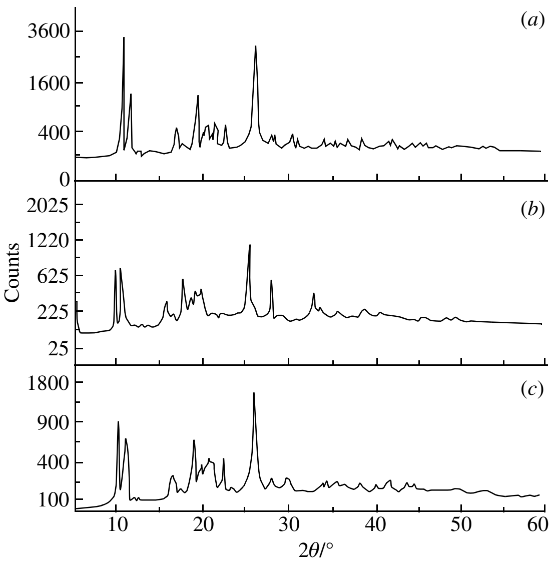

Figure 3 The XRPD pattern of (*a*) synthesised material, (*b*) evacuated solid and (*c*) regenerated solid resulting from the reintroduction of water.

The terminal hydrogen of the second molecule is on top of the middle of the bond between the first carbonyl carbon of terephthalate [C(17)] and the first ring carbon of terephathalate [C(19)]. In this way, one molecule of the upper layer π-interacts with two molecules below and above it in the adjacent layers and keeps the molecules within a layer.

The TGA and DTA of the complex show that the loss of uncoordinated water molecules occurs at 86–101 °C [Found 2.5%. Calc. 2.2%]. The second loss of apically coordinated water molecules is reported between 137–162 °C. The framework is stable up to 268 °C, which is followed by continuous degradation up to 283 °C corresponding to the loss of two equatorially coordinated H_2O molecules, the NO_3 anion and one 2,2′-bpy molecule [Found 32%; Calc. 31.7%]. The loss of second 2,2′-bpy molecule and coordinated NO_3 [Found 28.3%; Calc. 27.2%] is completed at 362 °C. The final skeleton composed of Cu and terephthalate is stable up to 490 °C.

Hydrative–dehydrative and heating–cooling experiments were carried out according to TGA results and were monitored by XRPD. The complex was heated at 200 °C for 3 h. The resulting complex $[Cu_2(2,2'\text{-bpy})_2(tp)(H_2O)_2(NO_3)]\cdot NO_3$ **2** was rehydrated by exposure to water vapour for 12 h. The XRPD pattern of dehydrated complex **2** exhibits certain prominent changes. New peaks appeared at $2\theta = 26.455$, 29.635, 35.340, 36.120 and 36.845°, whereas a peak at $2\theta = 21.880°$ due to complex **1** was absent. The intensities of various peaks also changed (Figure 2). On the rehydration of complex **2**, the XPRD of the resulting complex superimposes with the original complex **1** in terms of their positions and intensities. The IR spectrum of this complex exhibits three absorption bands at 1655, 1615 and 1325 cm^{-1} strongly suggesting the μ^3-η^1 mode of coordination[39] converting monomeric complex **1** into a 1D chain. Temperature dependent magnetic susceptibility measurements for complexes **1** and **2** were performed on polycrystalline samples in the ranges 4.5–180 and 4.5–100 K, respectively.[§] For both the complexes,

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[†] Found (%): C, 41.5; H, 3.8; N, 10.9. Calc. for $C_{14}H_{14}CuN_3O_7$ (%): C, 42.0; H, 3.5; N, 10.5. The IR spectrum of the complex (KBr pellet) shows strong peaks due to ν_{asym} and ν_{sym} at 1580 and 1380 cm^{-1}, respectively. Δν of 200 cm^{-1} suggests the monodentate mode of terephthalate coordination to the metal ion. A broad peak at ~3400 cm^{-1} indicates the presence of water in the complex, while peaks at 1490 (s), 1245 (b) and 810 cm^{-1} (w) are attributed to the NO_3 anion.[39]

X-ray data. $C_{14}H_{14}CuN_3O_7$; $M = 399.07$; crystal size, 0.3×0.15×0.08 mm; triclinic; space group, $P\bar{1}$, No. 1; $a = 10.0369(2)$, $b = 10.2079(2)$ and $c = 17.4582(4)$ Å, $\alpha = 103.4492°$, $\beta = 90.5715(10)°$, $\gamma = 116.4515°$, $V = 1544.2(12)$ Å^3, $Z = 2$, $U = 1.720$ mg m^{-3}, $\mu = 1.460$ mm^{-1}, $F(000) = 816$, reflection collected/reflection unique, 9644/9644 ($R_{int} = 0.000$). Final indices [$I > 2\sigma(I)$], $R_1 = 0.0304$, $wR_2 = 0.0734$. R indices (all data) $R_1 = 0.0421$, $wR_2 = 0.0818$.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 210591. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

[‡] Hydrogen bonding pattern is as follows: from the water molecule coordinated to Cu(69) there is a hydrogen bond O(70)–H(70B)···O(100) (D–H···A, 1.825 Å). To this water molecule there is a weak hydrogen bond from the hydrogen H(39) of C(39) (D–H···A, 2.657 Å). On the opposite side of the molecule there is a similar pattern with following atoms and bond lengths involved: Cu(29)–O(29)–H(29B)···O(99) (D–H···A, 1.851 Å) and C(80)–H(80)···O(99) (D–H···A, 2.664 Å). The molecules are packed as tiles forming walls. There are weak hydrogen bonds between the terminal ends of the molecules, for example, from H(75) to O(89) (2.531 Å), H(9)···O(55) (2.480 Å) and π–π interactions between the aromatic rings of the molecules. The uncoordinated nitrate anions, as well as water molecules, between the molecules create hydrogen bonds, which allow packing of molecules in the layer.

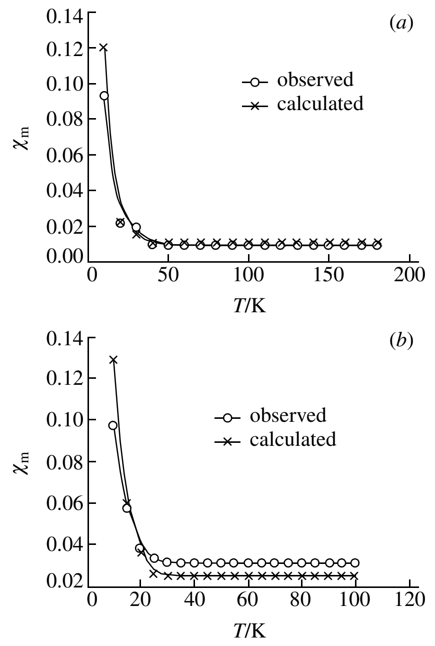

Figure 4 Plots of variable temperature magnetic moment susceptibility per Cu^{II} ion χ_M *vs.* *T* (data obtained as powder solid) of (*a*) complex **1** and (*b*) complex **2**.

the plots of χ_M *vs T* (Figure 4) indicate that χ_M values increased first only slowly and then abruptly as the temperature was lowered, suggesting the existence of ferromagnetic interactions between the metal centres. The goodness of fit for **1** and **2** is 5.0×10^{-3} and 4.43×10^{-3}, respectively. Good quality fits are obtained keeping $g = 2.1$ and 2.2 and $J = 0.1$ and 1.25 cm^{-1}, respectively, for compounds **1** and **2**. The J value of 0.1 cm^{-1} for complex **1** suggests lack of any practical interaction between metal centres due to a large Cu–Cu intramolecular distance. The enhanced magnitude of J in complex **2** can be attributed to a trikis mode of terephthalate coordination, which results in a short bridge induced by the carboxylate assisted loss of the apical water molecule. The bis bidentate mode of coordination is ruled out because this mode results in lower magnetic moments as compared to the monodentate mode for any kind of geometry.[5] The trikis mode of coordination has also been supported by IR studies. A similar transformation has been reported by Cano *et al.*[8] for the related $[Mn_2(phen)_4(tp)][ClO_4]_2$ complex, where tp binds in a tetrakis-monodentate mode after the loss of water from $[Mn_2(phen)_4(H_2O)_2(tp)][ClO_4]_2$. To determine whether these complexes undergo metameric transitions, magnetization verses applied field experiments were carried out. As shown in Figure 5, the complexes do not show any magnetic transition up to 10000 Oe.

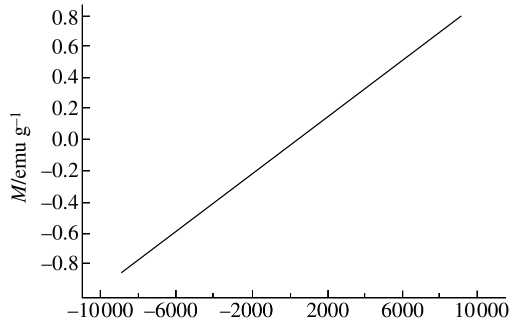

Figure 5 Magnetization *versus* applied field for complex **1** at $T = 4.5$ K.

The reported Cu^{II}–tp compound is the first example of a molecular sponge in the category of tp-bridged complexes. It reversibly releases and reabsorbs water, both coordinated and uncoordinated, possibly through a rare phenomenon of monomerization–polymerization isomerism. This structural transformation is associated with a change in magnetic properties. When the sponge is hydrated, it exists as a monomer which when looses apically coordinated water molecule is converted into chain polymer, the vacant coordination position being taken by terephthalate by converting its bis monodentate mode to trikis μ_3-$\tilde{\eta}^1$. This phenomenon is completely reversible. Hydration-dehydration studies are lacking for the related $[Mn_2(phen)_4(H_2O)_2(tp)][ClO_4]_2$ complex.[8]

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§ Baker's equation was used to calculate magnetic moments.

$$\chi_M = \frac{Ng^2\beta^2}{4kT} - \left[\frac{N}{D}\right]^{2/3},$$

where

$$N = 1 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5,$$

$$D = 1 + 2.7979916y + 7.0086780y^2 + 8.653644y^3 + 4.5743114y^4,$$

$$y = J/kT.$$

The parameters N, β and k have their usual meanings.

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