Reversible ferromagnetic–antiferromagnetic transformation upon dehydration–hydration of the nanoporous coordination framework, $[Co_3(OH)_2(C_4O_4)_2]\cdot 3H_2O$†

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Reversible crystal-to-crystal transformation accompanied by change from ferromagnetic to antiferromagnetic ground states at 8 K upon dehydration–rehydration of the nanoporous coordination framework $[Co^{II}_3(OH)_2(C_4O_4)_2]\cdot 3H_2O$.

One of the challenges in the field of molecule-based magnetism is the realisation of compounds that display dual phenomena, combining magnetic ordering with, for example, superconductivity,[1] optical properties (*e.g.*, transparency, nonlinearity),[2] spin crossover,[3] and, most recently, nanoporosity.[4] In the latter challenge, the achievement of porosity commonly requires the use of relatively long molecular connecting units, whereas long-range magnetic ordering requires relatively short exchange pathways between nearest neighbour (NN) metal sites. Our efforts to combine these inimical properties within the one material have focused on 1D, 2D and 3D framework compounds having one-atom bridges (*e.g.*, hydroxide, carboxylate). Such an approach has generated a number of porous magnetic phases, including a novel pillared-layer compound that orders as a ferrimagnet at 60 K independent of the sorption/desorption of guest water[5] and a series of porous framework magnets with solvent-sensitive Curie temperatures.[6] Here we explore the nanoporosity of the coordination framework $[Co^{II}_3(OH)_2(C_4O_4)_2]\cdot 3H_2O$ (**A**$\cdot 3H_2O$) and show that this phase transforms between markedly different types of magnetic behaviour upon reversible dehydration–rehydration despite there being only very minor changes to the framework geometry.

The 3D framework structure of **A**$\cdot 3H_2O$ was first reported by Wood *et al.*[7] The rapid sorption of water following dehydration of this phase was noted, but the dehydrated phase was otherwise uncharacterised. No magnetic properties were reported. We have consequently prepared this phase by a different route‡ and investigated the dehydration and rehydration processes and their influence on the magnetic behaviour of this material.

The structure of **A**$\cdot 3H_2O$§ consists of brucite-like ribbons of formula $[Co^{II}_3(\mu_3\text{-}OH)_2]^{4+}$ which are bridged by μ_4-squarate dianions to form a 3D framework lattice (Fig. 1). Unbound water molecules occupying 1D channels in the *c*-direction participate in numerous hydrogen-bonding interactions with the host framework.† The material undergoes two dehydration steps with heating in air: two formula water molecules are lost continuously from 20 to 100 °C and the third is lost with heating to *ca.* 200 °C, close to the decomposition temperature. The complete dehydration of this phase is fully reversible, as determined by repeated thermal cycles in this temperature range (Fig. S1†).

The magnetic properties of the hydrated and dehydrated phases were determined by measurement of the ac- and dc-magnetization as a function of both temperature and field on a SQUID magnetometer (Fig. 2). The magnetization of the virgin sample,

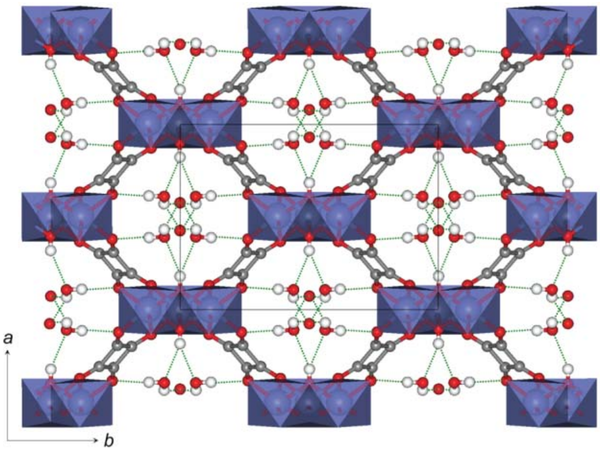

Fig. 1 The 3D framework structure of **A**$\cdot 3H_2O$ viewed down the *c*-axis, showing the 1D cobalt(II)–hydroxide ribbons (viewed end-on) connected by squarate dianions. Hydrogen-bonding interactions between unbound guest water molecules and the host framework are shown as dashed lines.

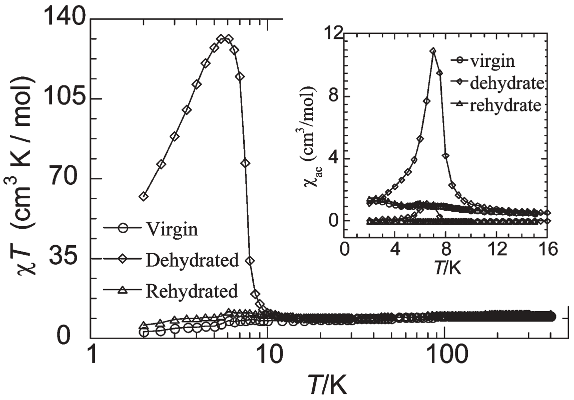

Fig. 2 Temperature dependence of χT measured in a field of 100 Oe for **A**$\cdot 3H_2O$ (○), **A** (◇) and **A**$\cdot 3H_2O$(rehyd) (△). The insert shows the corresponding ac-susceptibilities (1 Oe, 17 Hz).

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† Electronic supplementary information (ESI) available: thermogravimetry and single crystal X-ray diffraction (variable temperature unit cell and structural refinement data). See http://www.rsc.org/suppdata/cc/b5/b500614g/

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A·$3H_2O$, was first measured and then dehydrated to **A** *in situ* under a helium flow at 400 K for 2 h, followed by remeasurement. The sample was subsequently allowed to rehydrate in air for two weeks before further measurement. The susceptibility data suggest a paramagnetic state above 10 K for all three phases, with C = 9.91(2) for **A**·$3H_2O$, 9.89(2) for **A** and 9.95(2) cm^3 K mol^{-1} for **A**·$3H_2O$(rehyd). These values are as expected for octahedral divalent cobalt. The Weiss constants of 0.2(3), 2.7(4) and 0.0(2) K, respectively, suggest ferromagnetic coupling between NN moments, a feature that is enhanced in **A**. **A**·$3H_2O$ shows complex magnetic behaviour below 10 K, where it undergoes an antiferromagnetic (AF) transition at 8 K followed by another transition to a canted AF state below 6 K (Fig. S2†). The latter is characterised by a bifurcation point at 6 K for the zero-field and field cooled measurements in 1 Oe and by a non-zero imaginary component of the ac-susceptibility. Field dependent magnetization data at different temperatures suggest a metamagnetic ground state for **A**·$3H_2O$ with a critical field of *ca.* 1200 Oe and no observable hysteresis. In contrast, **A** orders as a ferromagnet at 8 K (Fig. 2), as evidenced by a sharp increase in the dc-magnetization in 1 Oe and by peaks in both the real and imaginary ac-susceptibilities (inset of Fig. 2 and Fig. S2†). The saturation magnetization in 50 kOe amounts to 6 μ_B, slightly less than expected. There is no dependence of the ac-susceptibilities as a function of frequency of the oscillating field, eliminating the possibility of disorder or a spin-glass ground state. Upon rehydration to **A**·$3H_2O$(rehyd), the magnetic behaviour is similar to that of **A**·$3H_2O$; this experiment was found to be reproducible.

The key structural feature with respect to the magnetic properties is the single-atom bridged Co–O–Co connections within the moment-carrying brucite-like ribbons (Fig. 3). The binding constraints of the squarate units and the preferred tetrahedral (rather than right-angle) geometry of the μ_3-hydroxyl units distort the Co octahedra and cause a buckling of the ribbons; Co(1) is within a flattened octahedron with Co(1)–O distances of 2.028 and 2.106 Å and the Co(2) octahedron is elongated with Co(2)–O distances of 2.173, 2.054 and 2.051 Å; O–Co–O angles range from 85.8 to 97.3° for Co(1) and 80.5 to 96.4° for Co(2); the Co–O–Co angles are 94.7° (squarate bridge) and 97.6, 101.4° (hydroxyl). These structural parameters define ferromagnetic exchange pathways between NN cobalt ions, as has also been seen in $Co(OH)_2$,[8] $Co_2(OH)_3NO_3$[9] and $Co_5(OH)_6(SO_4)_2(H_2O)_4$.[10] The second structural feature of note is the connection of the ribbons *via* four-atom bridges, M–O–C–C–O–M; these linkages are expected to facilitate weak exchange coupling between the ferromagnetic ribbons.

In situ single crystal X-ray diffraction was used to follow the temperature- and guest-dependent unit cell dimensions and crystal structure of the host lattice.† No increase in crystal mosaicity was observed, making this one of the few molecular frameworks known which remain monocrystalline upon guest desorption.[11] Measurement of the unit cell parameters during dehydration† revealed a hinging of the framework in the *ab*-plane, with contraction along *b* and expansion along *a* (Fig. 4). A similar scissoring action has been observed in other frameworks,[12] although it is noteworthy here that the channels become more open following water desorption; the pore dimensions change from 3.94 × 6.76 to 4.18 × 6.67 Å^2 and the pore volume increases from 176.8 to 183.0 Å^3 per unit cell.[13] Similar behaviour has been observed in $Mn_3(HCO_2)_6$·solvent[6] and we similarly attribute this to the removal of the hydrogen-bonding between the guest and the framework host. The *c*-direction, corresponding to the ribbon axis, remains relatively unchanged with water desorption, as does the β angle. Overall, the framework hinging action causes, unusually, an increase in crystal volume of *ca.* 0.5% (Fig. S3†).

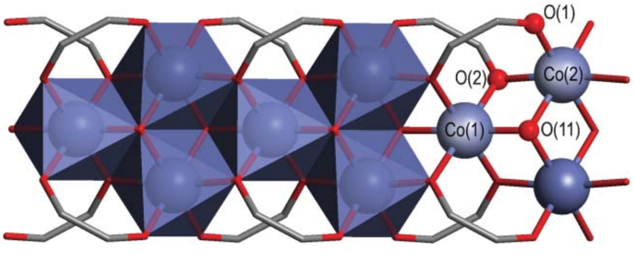

Fig. 3 View of the edge-shared octahedral ribbon of **A**·$3H_2O$, showing the coordinated squarate and hydroxyl bridges.

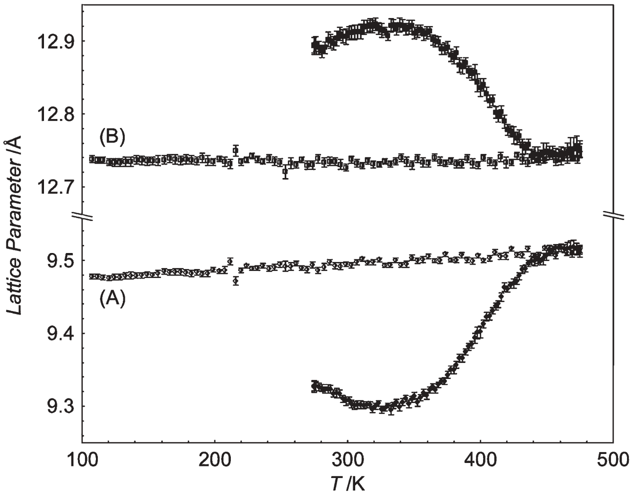

Fig. 4 Evolution of the unit cell *a* (A) and *b* (B) parameters with heating (●: dehydration of **A**·$3H_2O$ to **A**) and cooling (○: **A**). Error bars are ±1 e.s.d.

Solution and refinement of **A**§ confirmed that the framework connectivity is retained on dehydration and that there are only very minor changes in structural geometry. Importantly, the space group and therefore symmetry of the magnetic lattice remains unchanged. The removal of hydrogen-bonding interactions of the guest water molecules with the host framework has some subtle consequences. The largest percentage change in bond length is a 1.5% decrease in the Co(2)–O(1) distance with removal of the channel water, consistent with O(1) acting as a hydrogen-bond acceptor in **A**·$3H_2O$. In contrast, the Co(2)–O(11) bond is elongated by 0.9%, O(11) acting as a hydrogen-bond donor. Overall, dehydration causes a decreased deviation of coordination bond angles from octahedral geometry, with greater changes evident in the Co(2) environment compared to Co(1) due to the comparatively greater influence of guest water hydrogen-bonding on O(1) than O(11). These changes occur concomitantly with an increased tilt of the squarate ligand from 46.4 to 47.3° with respect to the plane of the ribbons and an opening of the 1D channels; it is not clear whether this tilting is driven principally by the bond length changes mentioned above, or whether it arises due to the loss of bridging framework–water hydrogen-bonds that may serve to compress the channels in **A**·$3H_2O$. Given the very subtle nature of the structural perturbation with dehydration, we propose that the transformation between antiferromagnetic and ferromagnetic ground states is caused by the presence of very weak AF coupling between the ferromagnetic ribbons *via* the hydrogen-bonded water molecules in **A**·$3H_2O$, rather than from a significant change in exchange coupling within the framework lattice.[14] To explore the relative importance of bond-mediated and through-space magnetic exchange in this phase, and therefore verify the mechanism for the magnetic transformation, the sorption of a range of other guests (including paramagnetic species) is planned.

In conclusion, **A** is one of only very few molecular frameworks known to support void volume without structural collapse and is novel in transforming between different magnetic ground states following water sorption–desorption. Single crystal X-ray diffraction data show that the void channels remain intact on removal of the guest water and that only minor structural relaxation occurs. We attribute the dramatic change in magnetic properties principally to the loss of host–guest hydrogen-bonding interactions, although note also that subtle changes to the framework geometry may directly influence the exchange coupling within and/or between the 1D brucite ribbons.

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Notes and references

‡ $Co(OH)_2$ (0.26 g) and $H_2C_4O_4$ (0.11 g) were suspended in H_2O (*ca.* 50 ml) and refluxed for 2 h. The mixture was then placed in a Teflon lined autoclave, sealed and heated to 200 °C for 3 days followed by cooling to 25 °C in a water bath. The brown-red crystals and few small yellow crystalline crystals were filtered, washed with water and dried in air. The crystals were separated under a microscope for characterisations. Anal. calcd. for $Co_3O_{13}C_8H_8$: C, 19.65; H, 1.65%. Found: C, 19.82, H, 1.57%.

§ Crystal data for $[Co^{II}_3(OH)_2(C_4O_4)_2]\cdot 3H_2O$ (**A**·$3H_2O$), M = 488.94 g mol^{-1}, monoclinic, space group $C2/m$, a = 9.2966(10), b = 12.8636(13), c = 5.4998(6) Å, β = 90.533(2)°, V = 657.68(12) Å^3, Z = 2, D_c = 2.469 Mg m^{-3}, T = 150 K, μ(Mo Kα) = 3.816 mm^{-1}, $wR2$ = 0.0655 (for 810 independent reflections [R_{int} = 0.0231]), $R1$ = 0.0270 [$I > 2\sigma(I)$]. Crystal data for $[Co^{II}_3(OH)_2(C_4O_4)_2]$ (**A**), M = 434.89 g mol^{-1}, monoclinic, space group $C2/m$, a = 9.4684(11), b = 12.7225(15), c = 5.4873(7) Å, β = 90.314(2)°, V = 661.00(14) Å^3, Z = 2, D_c = 2.185 Mg m^{-3}, T = 100 K, μ(Mo Kα) = 3.766 mm^{-1}, $wR2$ = 0.0598 (for 813 independent reflections [R_{int} = 0.0238]), $R1$ = 0.0249 [$I > 2\sigma(I)$]. CCDC 261656 and 261657. See http://www.rsc.org/suppdata/cc/b5/b500614g/ for crystallographic data in CIF or other electronic format.

1 M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse and P. Guionneau, *J. Am. Chem. Soc.*, 1995, **117**, 12209; E. Coronado and P. Day, *Chem. Rev.*, 2004, **104**, 5419.
2 O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **271**, 49; P. G. Lacroix, R. Clement, K. Nakatani, J. Zyss and I. Ledoux, *Science*, 1994, **263**, 658.
3 K. S. Murray and C. J. Kepert, *Top. Curr. Chem.*, 2004, **233**, 195.
4 P. M. Forster, M. M. Tafoya and A. K. Cheetham, *J. Phys. Chem. Solids*, 2004, **65**, 11; 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; C. Serre, F. Millange, S. Surble, J. M. Greneche and G. Ferey, *Chem. Mater.*, 2004, **16**, 2706; A. Rujiwatra, C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 2307; A. Rujiwatra, C. J. Kepert, J. B. Claridge, M. J. Rosseinsky, H. Kumagai and M. Kurmoo, *J. Am. Chem. Soc.*, 2001, **123**, 10584; S. A. Chavan, J. Larionova, O. Kahn and J. V. Yakhmi, *Philos. Mag. B*, 1998, **77**, 1657; O. Kahn, J. Larinovia and J. V. Yakhmi, *Chem. Eur. J.*, 1999, **5**, 3443; S. Ohkoshi, K. Arai, Y. Sato and K. Hashimoto, *Nat. Mater.*, 2004, **3**, 857; L. G. Beauvais and J. R. Long, *J. Am. Chem. Soc.*, 2002, **124**, 2110.
5 M. Kurmoo, H. Kumagai, S. M. Hughes and C. J. Kepert, *Inorg. Chem.*, 2003, **42**, 6709.
6 Z. Wang, B. Zhang, H. Fujiwara, H. Kobayashi and M. Kurmoo, *Chem. Commun.*, 2004, 416; Z.-M. Wang, B. Zhang, M. Kurmoo, M. A. Green, H. Fujiwara, T. Otsuka and H. Kobayashi, *Inorg. Chem.*, 2005, **44**, 1230.
7 S. O. H. Gutschke, M. Molinier, A. K. Powell and P. T. Wood, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 991.
8 T. Takada, Y. Bando, M. Kiyama and H. Mitamoto, *J. Phys. Soc. Jpn.*, 1966, **21**, 2726.
9 M. Kurmoo, *Philos. Trans. R. Soc. London, Ser. A*, 1999, **357**, 3041–3061.
10 M. Ben Salah, S. Vilminot, M. Richard-Plouet, G. André, T. Mhiri and M. Kurmoo, *Chem. Commun.*, 2004, 2548–2549.
11 See, for example: K. Biradha and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3392; B. F. Abrahams, P. A. Jackson and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 2656; K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3395; K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem., Int. Ed.*, 2002, **41**, 281; C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 375; C. J. Kepert, D. Hesek, P. D. Beer and M. J. Rosseinsky, *Angew. Chem. Int. Ed.*, 1998, **37**, 3158.
12 G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762.
13 A. L. Spek, *PLATON for Windows*, The Netherlands, 2000.
14 M. A. Hayward, E. J. Cussen, J. B. Claridge, M. Bieringer, M. J. Rosseinsky, C. J. Kiely, S. J. Blundell, I. M. Marshall and F. L. Pratt, *Science*, 2002, **295**, 1882.