A cyclic $(H_2O)_4$ cluster characterized in the solid state disappears on heating and regenerates from water vapor: A supramolecular reversible gas–solid reaction†

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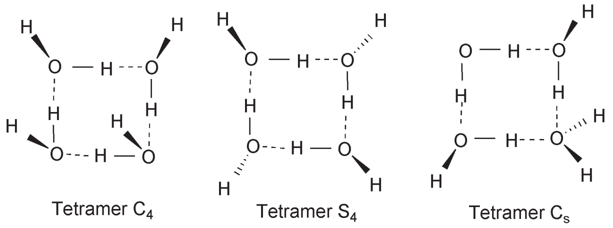
An unusual trinuclear iron(III) cluster described herein, $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]$ $ClO_4{\cdot}4H_2O$ (**1**) (C_5H_5NO = 2-pyridone), features a cyclic hydrogen bonded supramolecular water tetramer at one of the iron centres, as characterized by X-ray crystallography and thermogravimetry. The water cluster is formed by one iron-coordinated water and three lattice/solvent water molecules. The molecular environment of the water tetramer in the crystal structure consists of a Fe^{3+} ion (which is covalently bonded to one water of the $(H_2O)_4$ cluster), a perchlorate anion and the fourth lattice water. The facile removal of the lattice water molecules was anticipated from the knowledge of the type of interaction of these water molecules with their surroundings. Indeed, this hydrogen bonded water tetramer disappears with the formation of dehydrated solid $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]$ ClO_4 (**2**), when the compound **1** is heated at ~135 °C. Interestingly, when the dehydrated solid **2** is exposed to water vapor, it regenerates to **1** in a gas–solid reaction. The exposure of **2** to D_2O vapor yields partially deuterated complex $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2\text{-}(H_2O)]$ $ClO_4{\cdot}4D_2O$ (**3**). As expected, the material **3** changes to **2** on heating at ~135 °C, which again, on exposure to water vapor, returns to **1**. The reversible loss/formation of $(H_2O)_4$ cluster in a gas–solid reaction has been established by elemental analyses, IR and X-ray powder diffraction studies including the single crystal X-ray structural analysis of **1**.

Introduction

Small water clusters have been extensively studied both theoretically[1] and experimentally,[2] and include reported $(H_2O)_2$,[3] $(H_2O)_4$,[4] $(H_2O)_6$,[5] $(H_2O)_8$[5c,6] and $(H_2O)_{10}$[7] clusters in the solid state in crystal hosts. A detailed understanding of the numerous possible structures and stabilities of water aggregates is important for obtaining insight into the nature of water–water interactions in bulk water or ice.[8] Among the water clusters, the cyclic water tetramer is of particular interest. According to a simple two-structure model for liquid water, cubic-shaped water octamers can dissociate into two cyclic water tetramers, which appear to be the principal species present in liquid water. The model can explain many physical properties, including the anomalous heat capacity of liquid water.[8a,9] The cyclic $(H_2O)_4$ clusters of C_4, S_4 and C_s symmetry (Scheme 1) have been theoretically predicted on the basis of *ab initio* electronic structure calculations.[10] Far-infrared vibration–rotation tunneling (FIR-VRT) spectroscopy[11] of $(D_2O)_4$ cluster (from liquid D_2O) has been described to predict a cyclic quasi-planar minimum energy structure of S_4 symmetry (Scheme 1). Characterization of hydrogen bonded water tetramers in different crystal hosts is well documented in the literature.[4]

We describe here the formation of a cyclic quasi-planar water tetramer in an unusual Fe_3 cluster (Scheme 2) containing compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]$ $ClO_4{\cdot}4H_2O$ **1** (C_5H_5NO = 2-pyridone). A preliminary report on its crystal structure has already appeared.[12] In this regard, we wish to establish here an intriguing observation, that the supramolecular water tetramer disappears on moderate heating and regenerates from water vapor under ambient conditions. To our knowledge, until the present work, the reversible loss/formation of any such small water cluster (including $(H_2O)_2$, $(H_2O)_4$, $(H_2O)_6$, $(H_2O)_8$ and $(H_2O)_{10}$ clusters) has not been possible.



Scheme 1 The C_4 tetramer is a quasiplanar cyclic form with each water monomer acting as both single hydrogen bond donor and acceptor, and with all the free four hydrogens oriented in the same direction above or below the ring. The hydrogen bonding connectivity and planarity of the S_4 cluster are same as those in C_4, but in S_4 the free hydrogens orient alternately above and below the ring. In the C_s tetramer (which is cyclic and quasi planar too), one monomer acts as double donor and another monomer as double acceptor with the other two water molecules each acting as both single donor and single acceptor.

Experimental

General procedures and instrumentation

Powder X-ray diffraction data were collected on a Phillips PW 3710 diffractometer. TGA analysis of compound **1** was

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† Electronic supplementary information (ESI) available: magnetic data, TGA plot and unit cell packing diagram of 1. See http://www.rsc.org/suppdata/nj/b3/b303539p/

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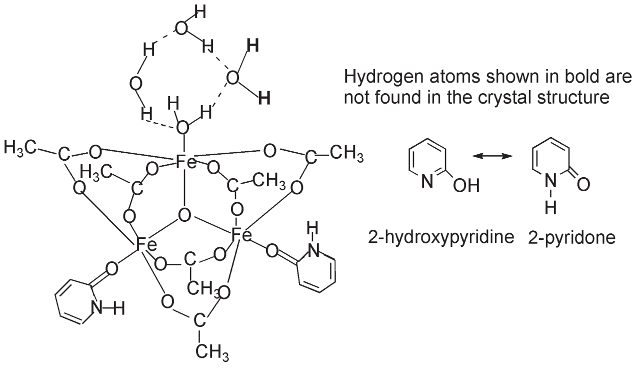


Scheme 2

performed on a Mettler Toledo Star System thermal analyzer under nitrogen atmosphere at a scan rate of 10 °C min^{-1}. The DSC curve was obtained from a DSC-4 Perkin-Elmer Differential Scanning Calorimeter. Microanalytical (C, H, N) data were obtained with a Perkin-Elmer model 240C elemental analyzer. The infra red spectrum was recorded by using a KBr pellet on a Jasco-5300 FT-IR spectrophotometer. The variable temperature (15–298 K) magnetic susceptibility measurements were performed using the Faraday technique with a setup comprising a George Associates Lewis Coil force magnetometer, a CAHN microbalance, and an Air Products cryostat. $Hg[Co(NCS)_4]$ was used as the standard. Diamagnetic correction (-411×10^{-6} cgsu) for $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4{\cdot}4H_2O$ **1** calculated from Pascal's constants were used to obtain the molar paramagnetic susceptibilities. All chemicals were used as purchased without further purification.

Synthesis of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4\cdot 4H_2O$ (1)

To a stirred solution containing 2.0 g (12.33 mmol) of $FeCl_3$ in 25 mL of water were added 10 mL of CH_3COOH (100%) and, 0.9 g (9.46 mmol) of 2-hydroxypyridine. 4.5 g (36.75 mmol) of $NaClO_4$ was subsequently dissolved in this solution, followed by the dropwise addition of aqueous NaOH (29 mL, 1M). From the final red-brown solution, which was filtered and kept in an open flask at room temperature for seven days, block-shaped brown crystals of **1** were obtained. Yield: 2.5 g (66% based on Fe). X-ray quality crystals were obtained from a relatively dilute solution. IR (KBr, cm^{-1}) 3510s, 3260s, 3108s, 2940s, 2528w, 2467w, 2382w, 1576s, 1445s, 1267m, 1222m, 1161m, 1088s, 999m, 902m, 860m, 825w, 796m, 773m, 731m, 661m, 590s, 525m, 498m, 464w. Elemental analysis calcd for $C_{22}H_{38}ClFe_3N_2O_{24}$ (M 917.54): C 28.79% H 4.17% N 3.05%. Found: C 29.03% H 4.01% N 3.11%.

Dehydration (water-loss) experiment

A freshly prepared sample of **1** (0.313 g, 0.341 mmol) was heated at 135–140 °C in a conventional oven for 5 hours. The measured weight loss (0.024 g) was equivalent to the loss of four water molecules per formula unit of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4{\cdot}4\ H_2O$ **1** (calcd 0.0246 g). This supports the formulation of the desolvated compound as $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2\ (H_2O)]\ ClO_4$ **2**. This is in agreement with the elemental analysis. Anal. found C 31.35% H 3.49% N 3.28%. Calcd: C 31.24% H 3.58% N 3.31%. The X-ray powder diffraction pattern of dehydrated material **2** reveals a new phase compared to that of **1**.

Regeneration experiment

Desolvated material **2** (0.289 g) was exposed to water vapour (by keeping the sample in a dessicator which contained water in a separate beaker) for 24 hours. During this time **1** regenerates from desolvated solid **2** by absorbing water vapor. The solid was dried at room temperature until a constant weight (0.311 g) was obtained. The increase in the weight (0.022 g) was equivalent to the gain of four water molecules per formula $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4$ **2** (calcd 0.024 g). The regenerated material showed identical XRD pattern, IR spectrum, TGA and DSC curves with those of the original **1**. Elemental analyses of the regenerated material, calcd for $C_{22}H_{38}ClFe_3N_2O_{24}$ (M 917.54): C 28.79% H 4.17% N 3.05%. Found: C 28.98% H 4.09% N 3.10%.

X-ray crystallography

Data for **1**, were collected on a Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-Kα radiation. The structure was solved (SHELXS-97)[13] and refined over F^2 by using the SHELXL-97 program.[14] All non-hydrogen atoms were refined anisotropically. The ring hydrogens of 2-pyridone ligands and acetate hydrogens were allowed to ride upon the respective carbon and nitrogen atoms. Among the four lattice water molecules, the hydrogens of two waters (O(22) and O(24)) could not be located. The hydrogen atoms of the two other crystal water molecules (O(21) and O(23)) and the iron-coordinated water molecule (O(2)) were located from different Fourier maps, and their positions were refined. Relevant crystallographic data and selected bond lengths and angles are presented in Tables 1 and 2, respectively.

CCDC reference number 178947. See http://www.rsc.org/suppdata/nj/b3/b303539p/ for crystallographic files in .cif or other electronic format.

Results and discussion

Synthesis of compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2\text{-}(H_2O)]\ ClO_4\cdot 4H_2O$ 1

Compound **1** was synthesized in a one-pot reaction involving ferric chloride, acetic acid, sodium hydroxide, sodium perchlorate and the ligand 2-hydroxy pyridine. In the resulting compound, the tautomeric form of the ligand 2-pyridone coordinates to the iron centers (Scheme 2) as confirmed by the X-ray crystal structure (*vide infra*). This preparation is unique, in the sense that the trinuclear Fe_3 cluster always coordinates to two monodentate 2-pyridone ligands irrespective of the amounts of 2-hydroxypyridine ligand used in the synthesis. The Fe_3 complex crystallizes from aqueous solution as perchlorate salt with five water molecules (one coordinated and four crystal water molecules) per formula unit as revealed by X-ray crystallography and thermogravimetric analysis.

Table 1 Crystallographic data for $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4{\cdot}4H_2O$ **1**

Formula	$C_{22}H_{38}ClFe_3N_2O_{24}$
FW	917.54
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	16.810 (3)
b/Å	17.682(3)
c/Å	24.199(4)
U/Å^3	7193 (2)
Z	8
ρ_{cal}/g cm^{-3}	1.695
μ/mm^{-1}	1.362
$R_1(F^2{}_0)$ [$I > 2\ \sigma(I)$]	0.0550
wR_2 $(F^2{}_0)$ [$I > 2\ \sigma(I)$]	0.1306
$R_1(F^2{}_0)$ (all data)	0.1125
wR_2 $(F^2{}_0)$ (all data)	0.1756

Table 2 Selected bond lengths and angles for **1**

Bond	Length/Å	Bond	Length/Å
Fe(1)–O(1)	1.901(5)	O(4)–C(1)	1.250(10)
Fe(1)–O(3)	1.989(6)	O(6)–C(3)	1.254(9)
Fe(1)–O(2)	2.049(6)	O(9)–C(7)	1.256(10)
Fe(1)–O(5)	2.052(6)	O(7)–C(5)	1.263(10)
Fe(2)–O(1)	1.907(5)	O(13)–C(11)	1.251(10)
Fe(2)–O(10)	1.996(6)	O(11)–C(9)	1.250(9)
Fe(2)–O(8)	2.003(6)	O(15)–C(13)	1.271(9)
Fe(2)–O(16)	2.081(5)	O(16)–C(18)	1.282(9)
Fe(3)–O(1)	1.913(5)	O(12)–C(9)	1.254(10)
Fe(3)–O(12)	2.007(6)	N(1)–C(13)	1.367(9)
Fe(3)–O(14)	2.019(6)	N(2)–C(18)	1.352(10)
Fe(3)–O(15)	2.046(5)	C(9)–C(10)	1.507(12)

Bond	Angle/°	Bond	Angle/°
O(1)–Fe(1)–O(3)	95.2(2)	Fe(1)–O(1)–Fe(2)	119.5(2)
O(1)–Fe(1)–O(7)	98.6(2)	Fe(1)–O(1)–Fe(3)	119.8(3)
O(1)–Fe(1)–O(2)	177.1(2)	Fe(2)–O(1)–Fe(3)	120.7(3)
O(3)–Fe(1)–O(7)	166.1(2)	C(1)–O(3)–Fe(1)	135.4(6)
O(9)–Fe(1)–O(5)	171.9(2)	C(3)–O(5)–Fe(1)	128.2(5)
O(2)–Fe(1)–O(5)	87.6(3)	C(5)–O(8)–Fe(2)	135.7(6)
O(7)–Fe(1)–O(2)	84.3(2)	C(7)–O(10)–Fe(2)	132.7(6)
O(1)–Fe(2)–O(10)	93.9(2)	C(9)–O(12)–Fe(3)	131.7(5)
O(1)–Fe(2)–O(8)	96.3(2)	C(3)–O(6)–Fe(3)	132.9(5)
O(1)–Fe(2)–O(16)	178.5(2)	C(13)–O(15)–Fe(3)	132.8(5)
O(10)–Fe(2)–O(13)	171.1(2)	C(18)–O(16)–Fe(2)	121.9(5)
O(8)–Fe(2)–O(11)	168.2(2)	C(17)–N(1)–C(13)	123.9(8)
O(13)–Fe(2)–O(16)	85.2(2)	C(18)–N(1)–C(22)	123.4(8)
O(11)–Fe(2)–O(16)	85.9(2)	O(4)–C(1)–O(3)	124.6(8)
O(1)–Fe(3)–O(12)	96.5(2)	O(4)–C(1)–C(2)	119.6(8)
O(1)–Fe(3)–O(14)	90.2(2)	O(3)–C(1)–C(2)	115.8(8)
O(1)–Fe(3)–O(15)	175.4(2)	O(8)–C(5)–O(7)	124.1(7)
O(14)–Fe(3)–O(4)	174.5(2)	O(7)–C(5)–C(6)	117.7(8)
O(12)–Fe(3)–O(6)	167.0(2)	O(8)–C(5)–C(6)	118.2(8)
O(4)–Fe(3)–O(15)	88.8(2)	O(15)–C(13)–N(1)	117.5(7)
O(6)–Fe(3)–O(15)	86.8(2)	O(16)–C(18)–N(2)	118.5(8)

Crystal structure of 1

The Fe_3 complex is trinuclear (overall "basic carboxylate" structure) with the central oxygen atom O(1) lying approximately on the plane (deviation 0.003 Å) of the three irons; but unlike the symmetric μ_3-oxo triiron(III) cluster in the basic iron carboxylates, it has unusual water coordination at one of three iron centers with other two iron atoms coordinating two 2-pyridone ligands respectively (Fig. 1a). Examples of such unusual Fe_3 clusters with mixed-monodentate ligands are well-known in the literature.[15] Numerous CHN analyses support the presence of two 2-pyridone ligands in **1**. Bond lengths and angles (Table 2) within the trinuclear cluster are consistent with values found for other iron basic carboxylate structures.[16]

The Fe_3 cluster features an interesting water tetramer comprising the iron-coordinated water (O(2)) and three solvent water molecules (O(21), O(22) and O(23)) as shown in Fig. 1. The fourth crystal water molecule (O(24)) keeps hydrogen-bonding distance with the perchlorate anion and also with one water (O(22)) of the $(H_2O)_4$ cluster (Fig. 2). The average O···O distance in this tetramer is 2.768 Å. For comparison, the corresponding value in $(D_2O)_4$ cluster (from liquid D_2O) as deduced from its VRT spectrum is 2.78 Å.[11] Among reported cyclic water tetramers in crystalline hydrates, the inclusion of $(H_2O)_4$ cluster by α-cyclodextrin, in its cavity, is worth mentioning.[4a] In α-cyclodextrin·7.57 H_2O, five water molecules were located outside the cavity and 2.57 disordered water molecules (split into four positions with 0.64 occupancy) were found inside the annular cavity. These four disordered water oxygens were hydrogen bonded to each other forming a cyclic water tetramer with hydrogen-bond distances in the range of 2.38 to 2.52 Å.[4a] In terms of connectivity of hydrogen bonds in the present ring system of $(H_2O)_4$ cluster (Fig. 1b), it has C_s symmetry with quasi planar ring structure (when the water tetramer is considered separately from the Fe_3 complex).

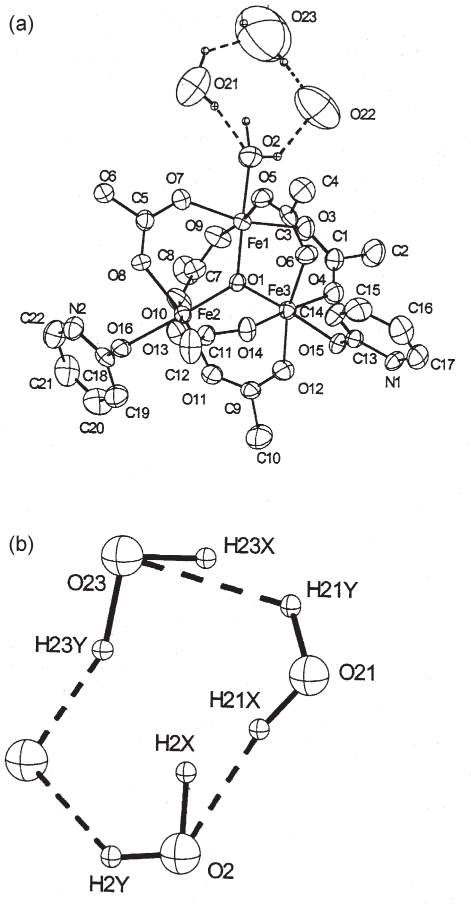


Fig. 1 (a) Unusual Fe_3 complex (thermal ellipsoid plot at 50% probability) featuring a hydrogen bonded cyclic water tetramer in the solid state. (b) $(H_2O)_4$ cluster is shown separately. The hydrogen atoms of O(22) water could not be located in the crystal structure. Covalent chemical bonds are shown as solid lines and H-bonds as dashed lines.

In the crystal, each Fe_3 cluster is linked by four N–H···O hydrogen bonds forming chains that run along the crystallographic *b* axis (Fig. 3). The linking region involves two 2-pyridone rings from two different Fe_3 clusters, whereby these two rings are connected by two N–H···O hydrogen bonds (Fig. 3c). The chain is zigzag type with respect to the positions of water tetramers. The relevant hydrogen bonding distances are N(1)···O(16), 2.851 (19) Å and N(2)···O(15), 3.088 (18) Å.

Magnetic studies

Magnetic susceptibility measurements with a powdered sample of **1** were performed in the temperature range 15–298 K at a constant magnetic field of 5 kG. A diamagnetic correction ($-\ 411 \times 10^{-6}$ cgsu) calculated from Pascal's constants[17] was applied to obtain the molar para magnetic susceptibilities. At 298 K the value of the effective magnetic moment (5.84 μ_B) is considerably smaller than the spin only value (10.25 μ_B) for a trinuclear cluster containing three high spin Fe(III) ions (s = 5/2). The magnetic moment gradually decreases to 3.635 μ_B at 15 K indicating an antiferromagnetic interaction between the three Fe(III) centers situated at the equilateral position of an approximate triangle (Fig. 4). The data were fitted[18] using an expression for χ_m *vs.* T for a trinuclear Fe(III) complex in which metal ions are equivalent (as far as immediate coordination of iron ion is concerned) and have the spin

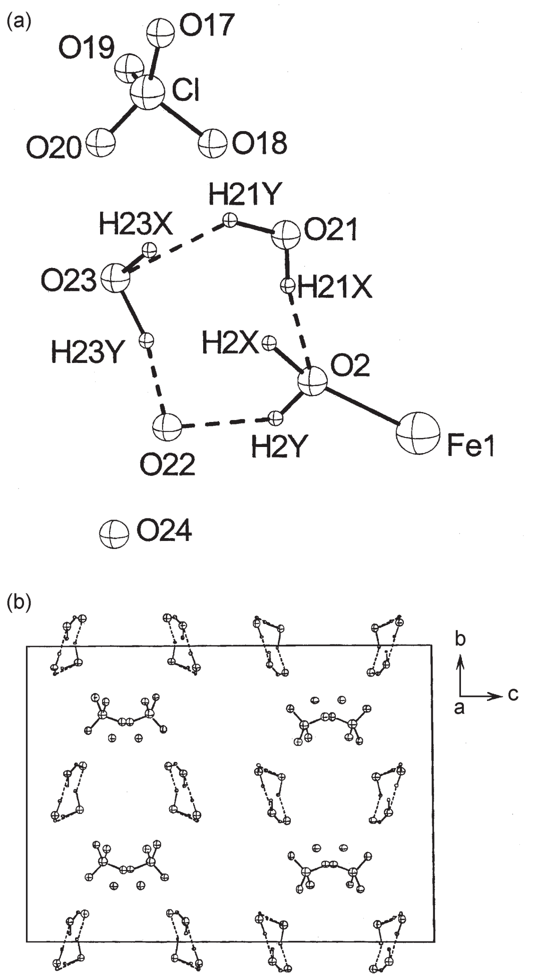


Fig. 2 (a) The molecular environment of an $(H_2O)_4$ cluster. Covalent chemical bonds are shown as solid lines and H-bonds as dashed lines. (b) The unit cell packing of water clusters, perchlorate anions and other crystal waters (excluding Fe_3 complexes).

state 5/2. The Hamiltonian associated with the interaction is taken as, $H = -2$ J (S1 . S2 + S2.S3 + S3.S1), where S1 = S2 = S3 = 5/2.[17] The best least-squares fit was obtained with $J = -22.41$ cm^{-1} and $g = 1.90$, where J is the antiferromagnetic coupling constant. Antiferromagnetic interactions are reported for the $[Fe_3(\mu_3\text{-}O)(O_2CR)L_3]^{1+}$ (R = alkyl groups, L = monodentate ligands) complexes;[19] the $-J$ values are in the range of 15–30 cm^{-1}. In these complexes, each of the metal ion is in a distorted octahedral co-ordination sphere. The oxygen atoms of the bridging carboxylates form an approximate O_4 square plane. The μ_3-oxo group and the monodentate ligand L occupy the remaining two *trans* sites. The magnetic interactions are considered to be propagated mainly *via* the μ_3-oxo bridge.[20] Similar antiferromagnetic interactions appear to be operated in the present system **1**. The systematic deviation of the observed data from the fitted curve (Fig. 4) is probably due the presence of trace amounts of a paramagnetic Curie-type impurity.

Reversible loss/formation of water tetramer

The packing diagram of the water tetramers, other crystal waters (O(24) type) and perchlorate anions is shown in Fig. 2b (excluding Fe_3 clusters). The molecular environment of an $(H_2O)_4$ cluster is presented in Fig. 2a. O(2) water is covalently bonded to Fe(III) iron. The O(22)···O(24) distance of 2.422 Å suggests strong hydrogen bonding between these oxygen atoms. However, the hydrogen atoms of both these water molecules (O(22) and O(24) waters) could not be located in

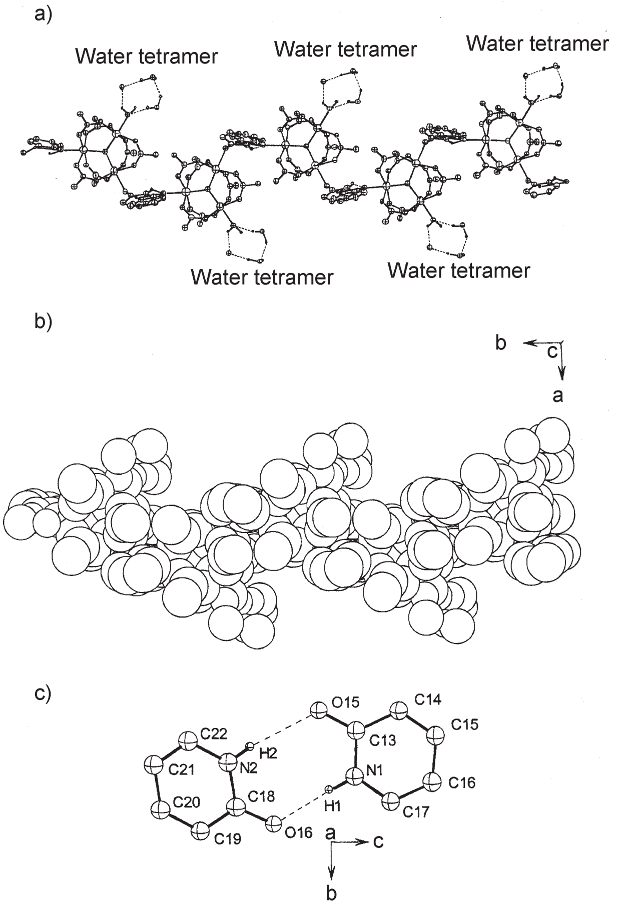


Fig. 3 (a) The ball and stick representation and (b) the space filling plot of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]^{1+}$ cation showing chain formation along crystallographic *b* axis. (c) The linking region, which involves two 2-pyridone rings from two different Fe_3 clusters, is highlighted and it is shown that rings are linked by two N–H···O hydrogen bonds.

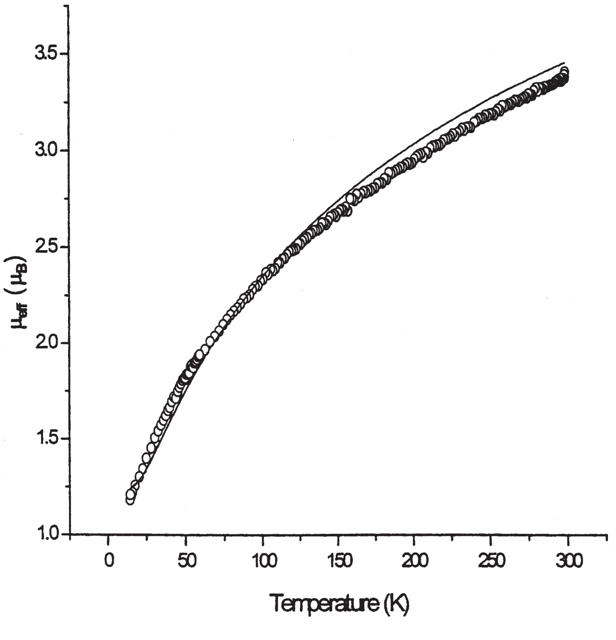


Fig. 4 Effective magnetic moment (○) of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6\text{-}(C_5H_5NO)_2(H_2O)]\ ClO_4{\cdot}4H_2O$ (**1**) as a function of temperature. The solid line was generated from best least squares fit parameters given in the text.

the crystal structure. Although the O(18)···O(21) distance of 2.99 Å and O(20)···O(23) distance of 3.00 Å suggest hydrogen bonding interactions between perchlorate anion and water tetramer, the positions of hydrogen atoms on O(21) and O(23) oxygens do not allow such interactions. The O(24) lattice water is in the hydrogen bonding distance range of water tetramer and perchlorate anion. Thus, the facile removal of water molecules (except the iron-coordinated O(2) water) in **1** is anticipated. Thermogravimetric analysis (TGA) in a nitrogen atmosphere showed a first weight loss of *ca.* 4% at 100 °C due to removal of two molecules of lattice water. At ~ 200 °C the other two crystal water molecules are removed with the loss of *ca.* 8% in the TGA curve. The fifth water molecule, which is directly coordinated to one of the Fe^{3+} ions, is lost along with six acetate ligands at ~ 220 °C with the decomposition of the trinuclear cluster as shown in the TGA plot. Some crystal waters are also released at room temperature, as indicated by a TGA taken on an eight-month-old sample. It appears that there is a phase change after release of four lattice waters at 135 °C, as demonstrated by powder X-ray diffraction study, which shows different patterns for the initial **1** and 135 °C heated dehydrated compound **2** (*vide infra*). CHN analysis supports the formulation of the dehydrated solid (obtained by heating **1** at 135 °C for 5 h) as $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4$ **2** (see Experimental section). At this stage, we wanted to check whether the loss/formation of water tetramer is reversible and we performed following experiments. First, we attempted to assign the O–H stretching vibrations of the water molecules (one coordinated and four crystal waters) on the basis of the difference between the FT-IR spectrum of the initial complex **1** and that of the solid **2** obtained after removing the crystal waters by heating **1** at 135 °C for 5 h (**1** is a perchlorate salt! Heating was carried out with precaution).[21] As illustrated in Fig. 5a, the bands (solid line, compound **1**) centered around 2528 and 2470 cm^{-1} disappear (dotted line, compound **2**) and the intensity of the band at 3500 cm^{-1} (solid line, compound **1**) decreases drastically (dotted line, compound **2**) upon heating. We therefore assign these bands to the O–H bonds of total water molecules (one coordinated and four crystal waters) in **1**. We assume that sharp bands which appear at 2528 and 2470 cm^{-1} respectively (solid line, Fig. 5a) in the IR spectrum of **1** are due to hydrogen bonding and caused by Fermi resonance of ν_{OH} with the in-plane, δ_{OH}, and out-of-plane, γ_{OH}, bending modes.[22] Surprisingly, these peaks (at 2528 and 2470 cm^{-1}) along with the 3500 cm^{-1} peak do reappear in the IR spectrum (dotted line, Fig. 5b) of the material, obtained by exposing the dehydrated solid **2** to water vapor. This IR spectrum (dotted line, Fig. 5b) is practically identical to that (solid line, Fig. 5a) of initial **1**. This strongly suggests that the regeneration of **1** is reversible in the solid state with the incorporation of lost water molecules. When the dehydrated solid **2** is exposed to D_2O vapor, the resulting partially deuterated complex, $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4{\cdot}4D_2O$ **3** shows the IR spectrum as shown in Fig. 5b (solid line). The 3500 cm^{-1} peak (for the initial complex **1**, solid line in Fig. 5a) shifts to 2390 cm^{-1} in **3** (solid line, Fig. 5b).[23] The shift of other two bands (2528 and 2470 cm^{-1}) of **1** could not be observed in the IR spectrum of **3**, because the acetate bands are predominant in the expected region of shifted bands. The deuterated complex **3** on heating at 135 °C for 5 h shows the same feature in the IR spectrum (dotted line, Fig. 5a) as **1** shows after heating. When this solid, obtained on heating **3**, is exposed to H_2O vapor, it gives identical IR spectrum (dotted line, Fig. 5b) to that of the initial **1**. The reversible formation of $(H_2O)_4$ cluster, which is schematically shown in Scheme 3, is further supported by X-ray powder diffraction (XRPD) studies (Fig. 6). The XRPD pattern of initial **1** is shown in Fig. 6a. The XRPD pattern of the dehydrated solid **2** reveals a new phase (Fig. 6b). This is consistent with the fact that compound **1** on heating shows an endothermic phase transition (peak 90 °C) in the DSC curve. The resolvated material, obtained by the exposure of dehydrated solid **2** to water vapor, exhibits an almost identical XRPD pattern (Fig. 6c) with that of the original **1** (they are *almost* identical in the sense that the *intensities* of some peaks are not identical).

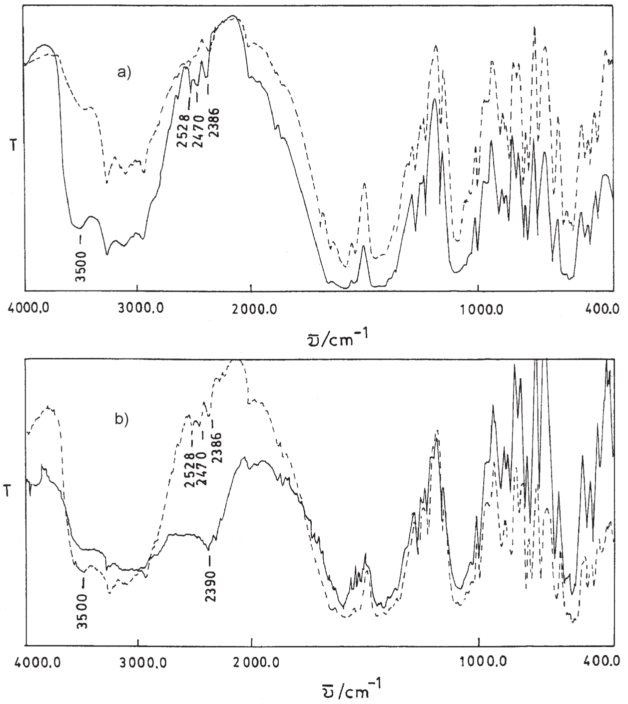
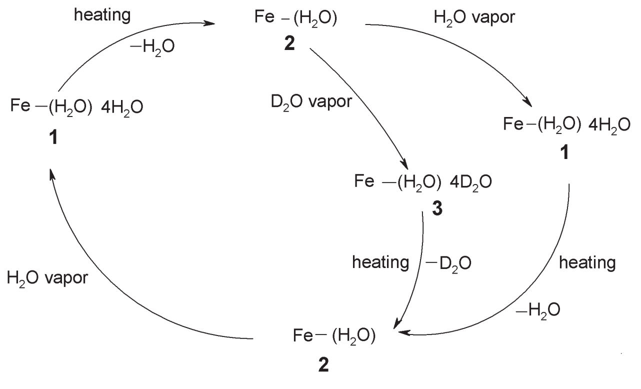


Fig. 5 (a) FT-IR spectra of the initial **1** (solid line) and the dehydrated solid **2** (dotted line), obtained on heating at 135 °C for 5 h. (b) FT-IR spectra of the material **3** (solid line), obtained when the dehydrated solid **2** was exposed to D_2O vapor, and the regenerated solid (dotted line), achieved by resolvation of dehydrated solid **2**. The IR spectrum of the regenerated solid (dotted line, Fig. 5b) is essentially identical to that (solid line, Fig. 5a) of initial **1**.

The computer simulated[24] XRPD pattern, obtained from the single crystal data of **1**, established the identity of the regenerated material as **1**. This confirms the reversible formation of $(H_2O)_4$ clusters from water vapor in the solid state. The regenerated material showed similar TGA and DSC curves as those shown by initial **1**. Elemental analysis supports the formulation of the regenerated solid as $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4{\cdot}4H_2O$ **1** (see regeneration experiment in Experimental section).



Scheme 3 The reversible loss/formation of $(H_2O)_4$ cluster in a solid–gas reaction. **1**: $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4{\cdot}4H_2O$; **2**: $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4$; **3**: $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]\ ClO_4{\cdot}4D_2O$.

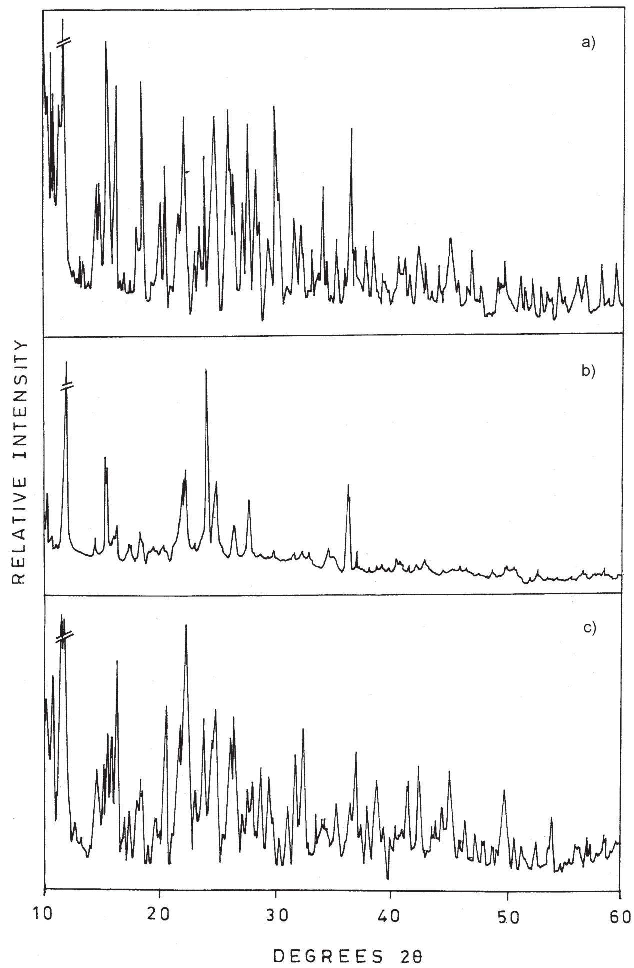


Fig. 6 (a) The X-ray powder diffraction pattern of initial **1**. (b) The X-ray powder diffraction pattern of the dehydrated solid **2**, obtained on heating at 135 °C for 5 h. c) The X-ray powder diffraction pattern of the regenerated solid, obtained by exposing the dehydrated solid **2** to water vapor.

Thermogravimetric analysis

The TGA curve shows the loss of water molecules in several steps. A mass loss was observed at ~100 °C corresponding to the loss of two water molecules (3.92% calcd, 4.09% obsd). Heating beyond 180 °C, a more gradual mass loss occurs to ~210 °C corresponding to the loss of two more water molecules (7.84% calcd, 7.5% obsd). The sample is unstable beyond 220 °C losing iron coordinated water and acetates including the (μ_3–O) group with the decomposition of the trinuclear cluster (50.13% calcd, 50.09% obsd).

Conclusion

We have reported a cyclic supramolecular $(H_2O)_4$ cluster in the solid state in a crystal host. For the first time, we have succeeded in demonstrating the reversible loss/formation of a small water cluster in the solid state in a gas–solid reaction. This is an unprecedented and unique example in water chemistry. The fact that, despite employing weaker perchlorate–water tetramer interaction, the dehydrated solid is able to sustain the reversible formation of $(H_2O)_4$ clusters is very significant. In a broad sense, these results serve in the understanding of the basic principles of supramolecular chemistry.

Compound **1** can be described as a water storage/drainage system which works in a supramolecular reversible gas–solid reaction with the disruption of O–H···O bonds, while covalent bonds are not affected.

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21 We have chosen "135 °C temperature for 5 hours" as the necessary condition for reversible water-loss experiments because of the following reasons. There are a total five water molecules (one coordinated and 4 lattice waters) in **1**. Three lattice waters and the iron-coordinated water are involved in forming the water tetramer. Numerous water-loss experiments settle the fact that **1** can be dehydrated to **2** with the loss of four crystal waters and **1** regenerates from **2** on the exposure of **1** to water vapor. However, **1** does not regenerate when it loses the iron-coordinated water. This is because, when the iron-coordinated water is (thermally) lost, the system becomes unstable with the loss of bridging bidentate acetate ligands and the μ_3-O group, as shown in the TGA curve, and the system collapses. The TGA plot shows the loss of four lattice water molecules at ~ 210 °C and a more gradual mass loss occurs (immediately after this) to ~ 220 °C corresponding to the loss of coordinated water, all acetates and the μ_3-O group. For this reason, we decided to perform the reversible water loss experiment at 135–140 °C, so that the iron-coordinated water is retained. In this temperature range complete loss of four lattice waters takes 5 hours because this process is kinetically slow at relatively lower temperature, as evidenced by the TGA plot of **1** taken after eight months from its preparation which shows gradual water loss even under ambient conditions.

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23 The shift of the 3500 cm^{-1} peak in the IR spectrum of the deuterated compound **3** was not complete. This is because the iron-coordinated water is retained in the dehydrated material **2**, obtained by heating **1** at 135 °C. The deuteration experiment was performed in a vacuum desiccator by exposing **2** to D_2O vapor with the formation of **3**. The possibility of absorbing H_2O vapor (as impurity) with D_2O vapor is not ruled out.

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