A supramolecular assembly of {Fe10} molecular wheels with tubular structures†

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A 3-D supramolecular assembly of {Fe_{10}} molecular wheels, [$Fe(CH_3O)_2(O_2CCH_2O{-}Ph)]_{10}\cdot 6H_2O$ (1) with tubular structure was successfully prepared by a novel approach of simple modification of the building blocks for making symmetric clusters, Fe_{10}. The diameter of the tubes is approximately 8.9 Å. Meanwhile, this tubular structure as the host traps hexameric clusters of water and the magnetic property of complex 1 shows that antiferromagnetic interactions exist between the high–spin iron(III) ions (S = 5/2) with J = 5.36 cm^{-1} and g = 2.03.

Recent years have witnessed the rapid development of open frameworks due to their intrinsic beauty and potential application in catalysis, separation techniques, gas storage, *etc.*[1] Meanwhile, metal–oxo clusters have been intensively investigated due to their interesting magnetic properties, such as single molecular magnets (SMMs).[2] However, molecular solids with open frameworks based on metal–oxo clusters, even metal–oxo nanoclusters through weak interactions are rare and their design and synthesis are still a challenge for crystal engineering.[3]

We are interested in the construction of supramolecular solids based on highly symmetric building blocks.[4] Is it possible to simply modify the building blocks towards making such clusters[3a,3c] through weak interactions to produce 3-D supramolecular frameworks, even open frameworks? Therefore we focused our attention on the ligand, phenoxyacetate acid. Firstly, it combines the characteristics of both flexibility and rigidity and contains the phenyl group for π–π stacking. Secondly, the group, OCH_2, is introduced to induce the formation of intermolecular C–H···O or C–H···π interactions. Furthermore, it can stabilize many highly symmetric clusters which might be novel building blocks for complicated supramolecular networks.[5] Herein, we make use of this to prepare successfully an unprecedented 3-D supramolecular network with tubular structures constructed by {Fe_{10}} molecular wheels, [$Fe(CH_3O)_2(O_2\ CCH_2OPh)]_{10}\cdot 6H_2O$ (**1**) .

Complex **1** was prepared by the reaction of $Fe(NO_3)_3\cdot 9H_2O$ in MeOH and $PhOCH_2COOH$.‡ Single crystal structure analysis§ at 173 K reveals that the structure of this molecular wheel is like those reported.[6] A centrosymmetric ring of ten Fe(III) ions is held together by twenty μ_2-methoxide ligands and ten bidentate phenoxyacetate ligands. Each iron(III) ion in complex **1** has a slightly distorted octahedral environment with six oxygen donors, four from methoxide and two from phenoxyacetate ligands (Fig. 1). The distances between adjacent Fe(III) ions, ranging from 3.0191(9) to 3.0315(9) Å, are almost identical. The Fe–O bond lengths are in the range of 1.923 (2) Å–2.074 (2) Å, while Fe–O–Fe bond angles vary from 99.17(9) to 102.54 (11)°. The ten iron ions are nearly coplanar and the mean deviation is only 0.0391 Å.

However, quite interestingly, these molecular wheels {Fe10} further link each other into a framework with tubular structures by π–π stacking of the phenyl groups and hydrogen-bond interactions from the sidearms of the ferric wheel (Fig. 2a), which is also found in six-membered ferric wheels.[3a,b] In each tubular structure, a series of six {Fe10} units possess three orientations and the orientations of each couple of wheels seated in the opposite positions are same. The plane of the {Fe10} wheel is tipped *ca.* 53.91(1)° from the adjacent wheels. Edge-to-face π–π stacking interactions [C(14)–H(14)···Cg(1): C(14)···Cg(1) 3.468 Å, H(14)···Cg(1) 2.643 Å, C(14)–H(14)···Cg(1) 148.20°, symmetry code C(14): *x*, *y*, −1 + *z*; Cg(1); *x*, *y*, *z*] that cause stacking along the *c* axis (Fig. 3a) occur between two the phenyl groups of the nearest-neighboring ferric wheels.[7,8] Moreover, tricentered hydrogen[8] bonds which exist in

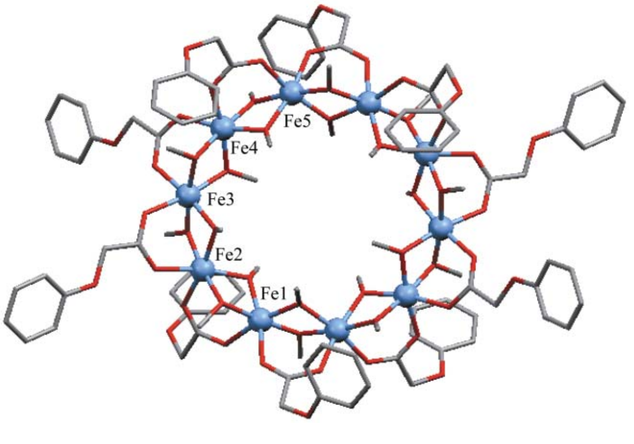

Fig. 1 The structure of the molecular wheel,{Fe_{10}}. Color code: Fe blue; O red; C gray.

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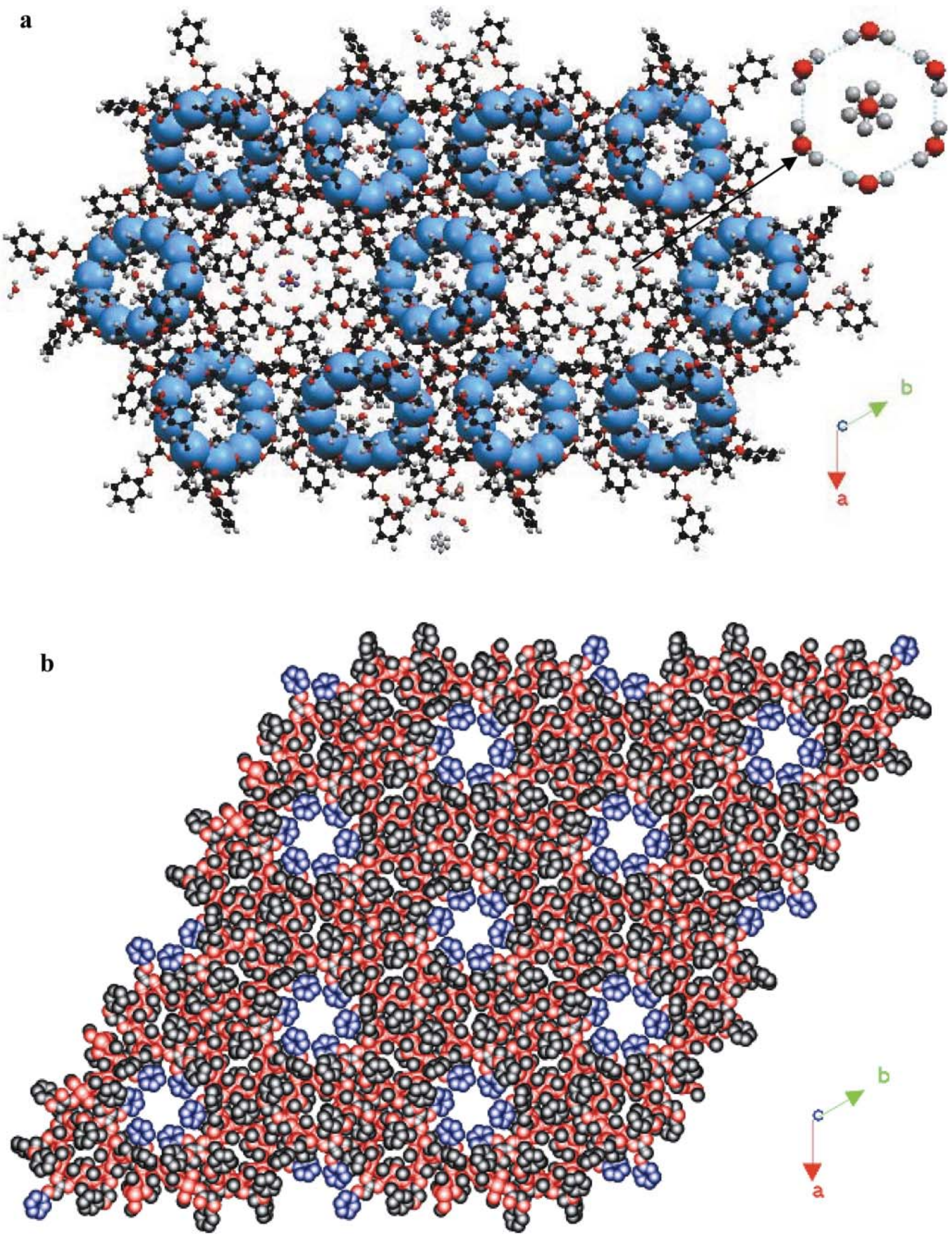

Fig. 2 (a) Packing diagram of complex **1** along [001]. For clarity, hexameric $(H_2O)_6$ and water molecules of the center of the $(H_2O)_6$ cluster from the channel are shown in the top-right corner. (b) The space filling diagram of complex **1**. All solvate molecules have been omitted for clarity.

the interpenetrating sidearms of the ferric wheels [C(39)–H(39A)···O(6): C(39)···O(6) 3.310 Å, H(39A)···O(6): 2.708 Å, C(39)–H(39A)···O(6) 120.67°; C(39)–H(39A)···O(3): C(39)···O(3) 3.282 Å, H(39A)···O(3): 2.428 Å, C(39)–H(39A)···O(3) 146.63°; symmetry code C(39): x, y, z; O(6) and O(3): $1/3 + y$, $2/3 - x + y$, $5/3 - z$, respectively] are formed between hydrogen atoms from the methylene group (OCH_2) and oxygen atoms of adjacent carboxylate ligands(Fig. 3b). Furthermore, the columns pack in a hexagonal array to give tubular structures centered on the c-axis and the resulting tubes are approximately 8.9 Å in diameter (Fig. 2b). The uncoordinated water molecules are trapped in the tubular structures which constitute 18.1% of the unit cell volume.

Interestingly, hexameric clusters of water are formed in the tubular structures, and other disordered H_2O molecules almost symmetrically occupy the center of the $(H_2O)_6$ cluster, and the periphery and center of the Fe_{10} molecule viewed down the c-axis (Fig. 2a). The coordination environment of the water hexamers and the geometric parameters are shown in Fig. 4. Within the cluster, the six water molecules adopt chair conformation, which is also found in hexagonal ice (ice I_h) as well as in the metastable cubic I_c.[9] All the O–O distance and the O–O–O angles are same with values of 2.914 Å and 118.52°, respectively. However, the torsion angle of the chair in the present case (20.9°) is considerably smaller than the corresponding value of 60.2° in ice and

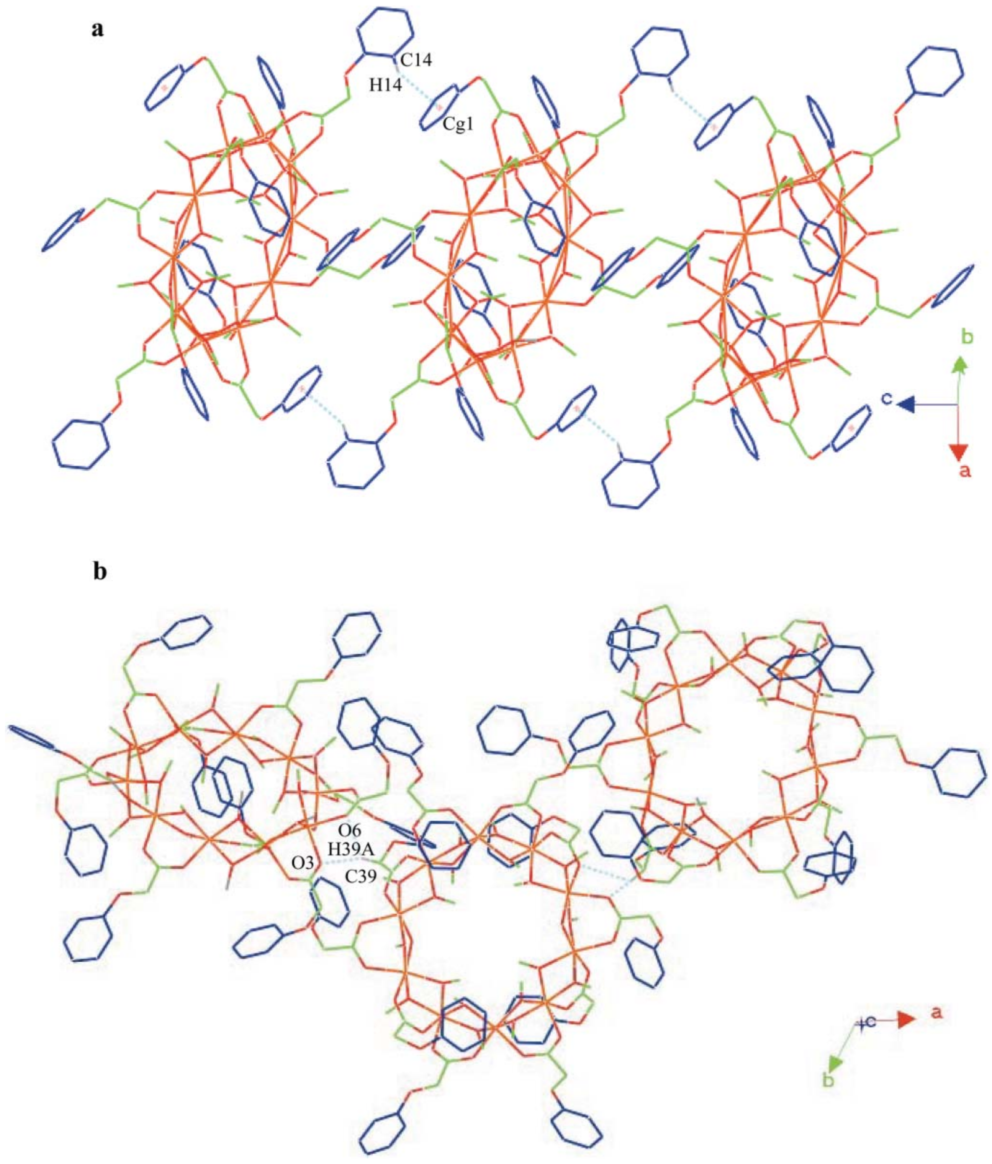

Fig. 3 Columns of **1** shown from two perspectives: (a) viewed perpendicular to the *c*-axis and (b) viewed along the *c*-axis (the steroid molecules are shown in blue, green and red, and edge-to-face π–π interactions and hydrogen bonds interactions in dashed lines).

other hexameric clusters of water reported previously.[10] The intra-ring O–O (2.914 Å) distance is significantly longer than 2.759 Å in deuterated ice I_h[11] and O–O–O angles (118.52°) deviates considerably from the corresponding value of 109.3° in hexagonal ice.

The magnetic susceptibility of complex **1** was determined in the 1.8–300 K range at 2 KOe field. On lowering the temperature, the magnetic susceptibility increases gradually and reaches the maximum at 65K, and then decreases rapidly at low temperatures. This behavior is characteristic of antiferromagnetic interactions between the high–spin iron(III) ions (S = 5/2) with $J = -5.36\ \mathrm{cm}^{-1}$ and g = 2.03.

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In conclusion, the first supramolecular assembly of {Fe10} molecular wheels with tubular structure was successfully prepared. Its structure and magnetic properties were further investigated. This work demonstrates a novel approach to construct molecular solids with open frameworks through simply modifying the building blocks for making such clusters and one new application of metal–oxo clusters. Further construction of chiral and more stable porous supramolecular solids based on clusters is underway.

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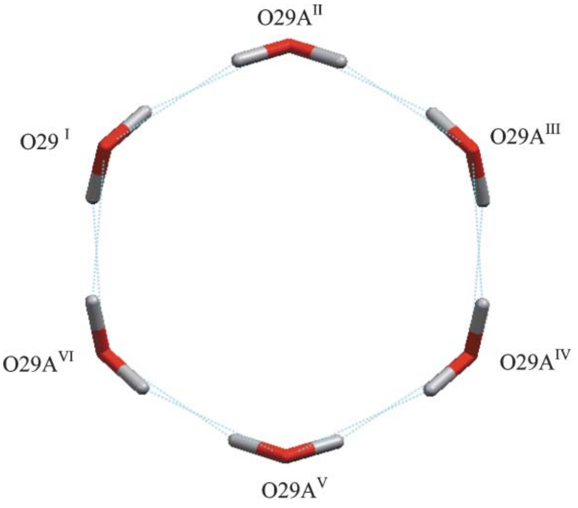

Fig. 4 The water hexamer linked through O···H···O hydrogen bonds. Hydrogen-bond lengths [Å] and angles [°] O29–H29B···O29: O···O 2.914(6), H···O: 2.189, 143.2; O29–H29C···O29: O···O 2.914(6), H···O: 2.187, 143.4. Symmetry code: (i) x, y, z (ii) $1/3 + y, 2/3 - x + y, 2/3 - z$; (III) $1 - x + y, 1 - x, z$; (iv) $1.33333 - x, 2/3 - y, 2/3 - z$; (v) $1 - y, x - y, z$; (vi) $1/3 + x - y, -1/3 + x, 2/3 - z$.

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‡ $[Fe(CH_3O)_2(O_2CCH_2OPh)]_{10}\cdot 6H_2O$ (**1**). $PhOCH_2COOH$ (0.152 g, 1.0 mmol) was added to a stirred solution of $Fe(NO_3)_3\cdot 9H_2O$ (0.2 g, 0.5 mmol) in MeOH (20 ml) to give an orange–red solution. The reaction mixture was refluxed for 10 min and then the pH value was adjusted to 4 with a solution of LiOH in MeOH. The solution was further refluxed for 1 h, during which time a yellow precipitate was formed (complex **1**). The solid was collected by filtration, washed with MeOH and Et_2O and then dried in vacuum, yield ~50%. Yellow solid was dissolved in CH_2Cl_2, ethyl ether and hexanes (v/v = 1 : 1) vapors were diffused slowly into the clear solution, from which orange yellow crystals along with yellow microcrystalline solids formed in several weeks. The single crystals were maintained in the mother liquor for X-ray crystallography and magnetic analysis, or collected by filtration for other use. Elemental analysis: calcd (%) for $Fe_{10}C_{100}H_{142}O_{56}$ C, 42.92; H, 5.11. found: C, 42.67; H, 5.08.

§ Crystal data for $0.18 \times 0.13 \times 0.10$ mm, hexagonal, space group $R\bar{3}$, $a = 51.227(3)$ Å, $c = 12.8243(8)$ Å, $\alpha = 90°$, $\gamma = 120°$, $V = 29145(3)$ Å^3, $Z = 3$, $\rho = 1.435$ g cm^{-3}, $M = 8395.91$, μ(Mo Kα) = 1.172 mm^{-1}. Of the 12715 symmetry independent reflections ($1.59 < \theta < 26.00°$), 8639 reflections are observed ($I > 2\sigma(I)$). On the basis of all these data and 782 refined parameters, $R1 = 0.0598$, $wR2 = 0.1222$, and GOF on F^2 of 1.064 were obtained.

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