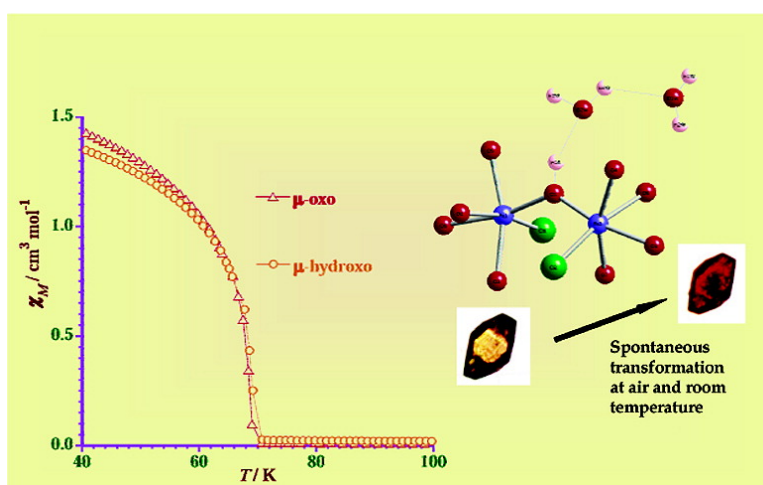## Communication

Intermolecular Proton Transfer in Solid Phase: A Rare Example of Crystal-to-Crystal Transformation from Hydroxo- to Oxo-Bridged Iron(III) Molecule-Based Magnet

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Intermolecular Proton Transfer in Solid Phase: A Rare Example of Crystal-to-Crystal Transformation from Hydroxo- to Oxo-Bridged Iron(III) Molecule-Based Magnet

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The recent upsurge in the crystal engineering of coordination nets is caused by their several useful functional properties such as porosity and use in separation,[1] catalysis,[2] and magnetism.[3] In magnetism, molecular chemistry is well suited to design new magnetic systems whose structure and properties can be tuned.[4,5]

Here we report a three-dimensional (3D) metal−organic open framework of formula $\{EtNH_3[Fe_2(ox)_2Cl_2(\mu\text{-}OH)]\cdot 2H_2O\}_n$ (**1**) which retains its framework and the single crystallinity upon proton-transfer reaction that occurs within the net, leading to a new species of formula $\{(H_3O)(EtNH_3)[Fe_2(ox)_2Cl_2(\mu\text{-}O)]\cdot H_2O\}_n$ (**2**). To the best of our knowledge, **1** is one of the few examples of iron(III) complexes with a single hydroxo bridge unsupported by ancillary ligands and the first one in which the hydroxo bridge occurs in a polymeric 3D net.[6] **1** and **2** behave as magnets through spin canting, and our study provides evidence that the transformation is a suitable tool to tune the magnetic properties. Slow evaporation at room temperature of an aqueous solution containing a mixture of oxalic acid dihydrate (0.2 mmol), $FeCl_3$ (0.2 mmol), and $EtNH_3Cl$ (0.1 mmol), which was heated at 60 °C for 10 min, afforded single crystals of **1**.

Crystals of **1** allowed to stand in air at ambient temperature for 3 days undergo an irreversible transformation to yield **2**, this process being accompanied by a color change from yellow to deep red (Figure 1a). It was possible to obtain directly **2** from a solution at pH ca. 3 by addition of $NaHCO_3$. It was possible to perform X-ray analysis on a single crystal before and after the transformation. While the yellow phase crystallizes in the monoclinic *Cc* space group, an orthorhombic *Fdd*2 cell is found for the red phase, providing us with one of the few examples of crystal-to-crystal reaction.[7] The anionic network in **1** and **2** forms, basically, the 3D pattern analogous to those of the previous compounds $\{X_2[Fe_2(ox)_2Cl_2(\mu\text{-}O)]\cdot 2H_2O\}_n$ (X = NH_4^+, $MeNH_3^+$, $Me_2NH_2^+$ and $EtNH_3^+$) reported by us,[8] with the cationic moieties located in the anionic cages having, as the only difference for **1**, the presence of a hydroxo bridge instead of the oxo one that merely causes slight modifications in the 3D framework. Unlike the oxo-bridged compounds, it was possible to determine the positions of the cations and water molecules in **1**. The larger structural modifications when comparing **1** and **2** concern the values of the Fe−O−Fe angle, which is more bent in the former compound [132.4(2) (**1**) and 136.0(5)° (**2**)] and the Fe−O(bridge), which is shorter in the latter [1.984(3) and 1.882-(3) (**1**) and 1.825(3) Å (**2**)]. While the values of the Fe−O bond lengths in **1** agree with those reported in the literature for hydroxo compounds,[6] they are longer in **2** than those usually observed for oxo compounds.[8,9] However, spectroscopic analysis performed on both compounds removes any doubt on the formation of a μ-oxo
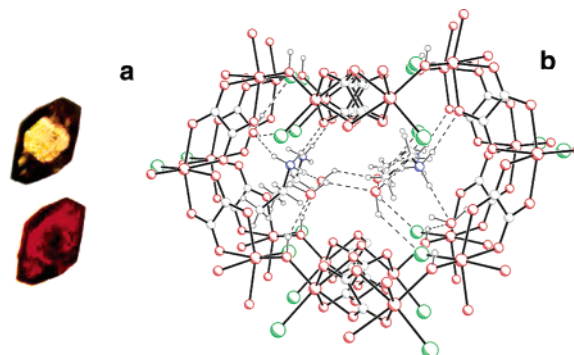

Figure 1. (a) Crystal appearance before and after transformation; (b) view of the 3D channels in compound **1**.

bridge. In particular the M−OH bending mode[10] in the IR spectrum of **1** appears at 1135 cm^{-1} and disappears in the IR spectrum of **2**.

We postulate a general mechanism of this solid−solid transformation, foreseeing a proton transfer from the hydroxo bridge to a water molecule with a concomitant opening of the Fe−O−Fe angle but without collapsing the channel framework. This assumption is supported by the occurrence, in **1**, of an intermolecular hydrogen bond involving a water molecule behaving as an acceptor toward a hydroxo group [O(1)−H···O(2w), O(1)···O(2w) = 2.82 Å] and as donor toward a second water molecule [O(2w)−H(4w)···O(1w), O(2w)···O(1w) = 2.76 Å]. Furthermore, the water molecules act as acceptors toward ethylammonium cations [N(1)−H(1c)···O(1w), N(1)···O(1w) = 2.96 Å and N(1)−H(1d)···O(2w), N(1)···O(2w) = 2.79 Å] and are attached to the net through interactions with chlorine atoms [O(1w)−H(1w)···Cl(1) and O(1w)−H(2w)···Cl(2) with O(1w)···Cl(1) and O(1w)···Cl(2) = 3.51 Å]. Moreover, we have noted that dehydration inhibits crystal-to-crystal transformation. If the yellow compound is completely dehydrated, the transformation occurs more slowly, probably after a rehydration process, demonstrating the fundamental role which is played by crystallization water molecules. The proton transfer is followed by a disordered rearrangement of cations and water molecules, probably induced by the repulsive interactions between the H_3O^+ and $EtNH_3^+$ cations. In the red phase oxygen atoms of water molecules/cations are no longer close to the oxo bridge (as occurs in **1** for the hydroxo group) being substituted by the −NH_3^+ group of the ethylammonium cation. It deserves to be pointed out that the space group of the resulting red phase (**2**) is identical to that of the related family $\{X_2[Fe_2(ox)_2Cl_2(\mu\text{-}O)]\cdot 2H_2O\}_n$[8] where two cations are present. Preliminary results show that an analogous behavior is obtained when the $PrNH_3^+$ cation is used. Although it shows a similar network of hydrogen bonds, the yellow phase is more stable, probably due to a minor flexibility in rearranging a bigger cation.

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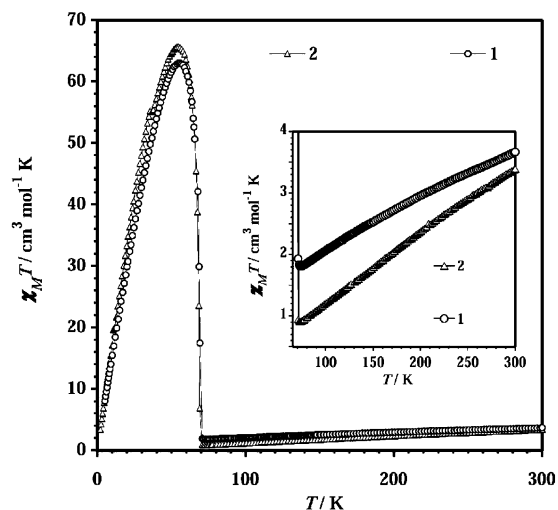[‡] Universitat de València.

Figure 2. Thermal variation of the $\chi_M T$ product for **1** ($\bigcirc$) and **2** ($\triangle$) at H = 100 G. (Inset) Detail of the high-temperature region.
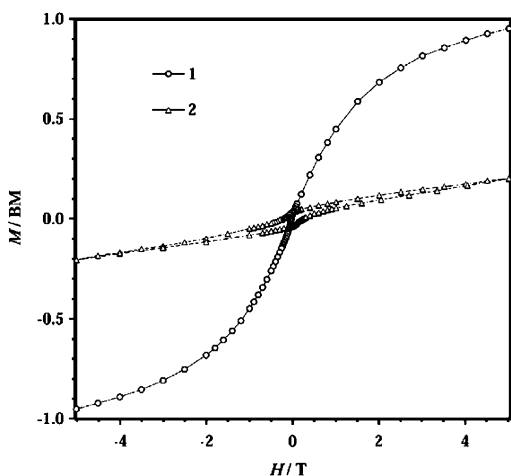

Figure 3. Hysteresis loops of **1** ($\bigcirc$) and **2** ($\triangle$) at 2.0 K.

The magnetic properties of **1** and **2** are typical of spin-canted systems (Figure 2). The values of $\chi_M T$ (χ_M is the magnetic susceptibility per two iron(III) ions) at room temperature are 3.67 (**1**) and 3.40 cm^3 mol^{-1} K (**2**), below that calculated for two magnetically isolated spin sextets (8.75 cm^3 mol^{-1} K for $S = \frac{5}{2}$ and $g = 2.0$), indicating that a strong antiferromagnetic interaction occurs in both compounds. This is in agreement with the known ability of the oxo, hydroxo, and oxalato groups to mediate antiferromagnetic interactions in the corresponding oxo- ($-J$ values falling into the 45–240 cm^{-1} range) (**2**),[8,9] hydroxo- ($-J$ values in the range 7–17 cm^{-1} range)[11] (**2**) and oxalato-bridged ($-J$ values about -7 cm^{-1}) (**1** and **2**)[12] iron(III) complexes. Upon cooling in a magnetic field of 100 G, $\chi_M T$ of **1** and **2** decreases, it attains a minimum at ca. 70 K [$\chi_M T = 1.81$ (**1**) and 0.91 cm^3 mol^{-1} K (**2**)], and then it exhibits an abrupt increase to achieve a maximum at ca. 55 K [$\chi_M T = 63$ (**1**) and 66 cm^3 mol^{-1} K (**2**)] and further decreases sharply at lower temperatures. At $T < 70$ K, the magnetization of **1** and **2** is strongly field dependent, and the field-cooled magnetization (Figure S1) reveals the occurrence of magnetic ordering below 70 K. Frequency independent ac signals are observed below this temperature for **1** and **2**, confirming the magnetic ordering. The magnetic hysteresis loops of **1** and **2** (Figure 3) show values of the coercive field (H_c) of 250 G (**1**) and 2500 G (**2**) and remnant magnetization (M_r) of 0.025 μ_B (**1**) and 0.036 μ_B (**2**). Because of the plateau of the magnetization due to the saturation of the spin canting is not observed, we estimated the lower limit

of the angle of the spin canting [0.14° (**1**) and 0.21° (**2**)] from the values of the remnant magnetization. Given the isotropic character of the high-spin iron(III) ion, the origin of the spin canting in **1** and **2** must be due to the antisymmetric exchange, a fact which is compatible with the acentric character of their spatial groups.[8,9,11,13]

The relatively high value of T_c for **1** and **2** and the observed shift of ca. 30 K of T_c toward higher temperatures in **2** when compared to the related oxo- and oxalato-bridged 3D iron(III) networks[8] are very appealing. In particular, the comparison between **2** ($T_c = 70$ K) and $\{(EtNH_3)_2[Fe_2(ox)Cl_2(\mu\text{-}O)]\cdot H_2O\}_n$ (**3**) ($T_c = 56$ K)[8b] is striking. **2** and **3** crystallize in the orthorhombic system, spatial group *Fdd*2, the main difference being the occurrence of two different univalent cations in the former (hydronium and ethylammonium cations in **2** vs two ethylammonium cations in **3**). The cations and the water molecule are located in the pseudohexagonal tunnels defined by oxo- and oxalato-bridged iron(III) network. This lowering of the symmetry of the cavities seems to be at the origin of the increase of the T_c value in **2**, suggesting a new strategy to prepare high T_c iron(III) compounds through the use of different cations to neutralize the charge of the anionic oxo- and oxalato-bridged iron(III) 3D network. Magneto–structural studies on additional examples containing pairs of univalent cations are in route to illustrate and clarify this strategy.

Supporting Information Available: X-ray crystallographic files in CIF format; details of the crystallography for **1** and **2**; plot of the thermal dependence of χ_M of **1** and **2** at $T \leq 100$ K and $H = 100$ G (Figure S1), TGA curve of **2** (Figure S2), and UV–visible and IR spectra of **1** and **2** (Figures S3–S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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