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A novel supramolecular assembly in an iron(III) compound exhibiting magnetic ordering at 70 K†

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Ethyl-substituted ammonium cation allows the preparation of an unprecedented oxo- and oxalato-bridged supramolecular three-dimensional network. The compound exhibits magnetic ordering with T_c = 70 K due to a weak spin canting.

Coordination chemistry of paramagnetic metal ions exhibiting extended networks represents an important area of current research.[1,2] The interest in this class of compounds is enhanced when additional properties, such as spontaneous magnetization at high temperatures, are involved.[3] In this respect, over the last decade, considerable efforts have been devoted to the preparation of two- and three-dimensional oxalate-bridged bimetallic compounds, where ferro-, ferri- and antiferromagnetic long-range magnetic ordering with T_c ranging from 5 up to 44 K was observed.[4]

Very recently, we have described a three-dimensional homometallic compound of formula $\{[NH_4]_2[Fe_2O(ox)_2Cl_2]\cdot 2H_2O\}_n$ (**1**) which contains isotropic high-spin Fe(III) ions bridged by oxo and bisbidentate oxalate groups[5] and exhibits a ferromagnetic phase transition at T_c = 40 K. A weak spin canting, which has its origin in the antisymmetric exchange, accounts for this magnetic ordering. Aiming at investigating the role of the univalent cation on the spin canting and its influence on the T_c value, we have initiated a systematic study with a series of univalent ammonium derivatives. Our first attempts afforded the three-dimensional compound, analogous to **1**, exhibiting magnetic ordering at T_c = 56 K (dimethylammonium cation).[6] The use of ethylammonium cation gives rise to a very singular iron(III) compound of formula $\{[EtNH_3][Fe^{III}(H_2O)_6]Fe^{III}[Fe^{III}_2O(ox)_3Cl_2][Fe^{III}(ox)_2Cl_2]\}_n\cdot 6nH_2O$ (**2**), which shows a totally different three-dimensional framework from that of **1**. The T_c value in **2** has been shifted to 70 K through spin canting. Its preparation,‡ X-ray crystal structure§ and preliminary magnetic characterization¶ are reported herein.

Compound **2** consists of $[Fe_2O(ox)_3Cl_2]^{4-}$ chains (**I**) and $[Fe(ox)_2Cl_2]^{3-}$ monomeric units (**II**) self-assembled in an unprecedented supramolecular three-dimensional anionic network through Fe^{3+} cations (**III**). The electroneutrality is achieved by means of $[Fe(H_2O)_6]^{3+}$ (**IV**) and $EtNH_3^+$ cations that are linked to the network through hydrogen bonds, in which crystallization water molecules are involved. Keeping in mind the three-dimensional network of **1** where all iron(III) ions are equivalent, being bridged by oxalato and oxo groups, the substantial difference in **2** is due to the occurrence of four different iron(III) centers, depending on their relative environments. Among these, only the metal center of type **I** shows the same surrounding as in **1**, even if in **2** the overall motif is a chain containing iron(III) atoms with regular alternation of oxo and oxalate bridges. No significant variations have been observed in the Fe–O_{ox} and Fe–O_{oxo} bond lengths [range 2.006(8)–2.109(8) and 1.931(9) Å average value, respectively] with respect to compound **1** [2.049(4)–2.194(4) and 1.825(2) Å]. The value of the angle at the oxo bridge is 134.8(5)°, [135.9(4)° in **1**] the smallest one reported so far for oxo-bridged iron(III) compounds [the previous values ranging from 139° to 180°].[5] The values of the Fe···Fe distances through the oxo and oxalate bridges are 3.565(2) and 5.421(2) Å, respectively [3.384(2) and 5.496(2) Å in **1**]. The $[Fe(ox)_2Cl_2]^{3-}$ monomeric units **II** contain iron(III) ions in a distorted octahedral arrangement. The values of the Fe–O_{ox} and Fe–Cl bond lengths are in agreement with those reported in the literature for other similar iron(III) oxalate compounds containing coordinated chloride atoms.[5–7]

Fe(III) cations (**III**) are weakly coordinated to eight oxygen atoms of four oxalate groups, which interact with the chains **I** and the monomeric units **II** to form a supramolecular assembly. As far as we know, this is the third example of a compound containing an eight-coordinated iron(III) to be authenticated by X-ray studies.[8] The Fe···O_{ox} bond distances [ranging from 2.40(1) to 2.50(1) Å], are longer that those reported for the other two similar compounds [2.13(3) Å and 2.211(3)–2.325(3) Å]. This lengthening could suggest that the Fe(III) ions (**III**) in **2** are involved in weaker interactions with respect to the other octa-coordinated iron(III) complexes. The resulting supramolecular structure (Fig. 1) is noteworthy. A pair of $[Fe(ox)_2Cl_2]^{3-}$ monomeric units (**II**) is linked to two Fe^{III} ions (III) building a ring in the *ac* plane. The chains **I** are linked to the rings through supramolecular interactions with Fe^{III} ions (**III**). The $[Fe(H_2O)_6]^{3+}$ cations (**IV**) (Fig. 2) occupy the central part of the ring holes and are linked to the rings by means of hydrogen bonds. As far as we know, this is the second example of a crystal structure showing these $[Fe(H_2O)_6]^{3+}$ moieties,[9] and again their occurrence is observed in an oxo-bridged iron(III) complex.

The magnetic behaviour of **2** is typical of a spin canted system. $\chi_M T$ for **2** [χ_M is the magnetic susceptibility per one iron(III) ion] at room temperature is 1.83 $cm^3\ mol^{-1}$ K, below that calculated for a

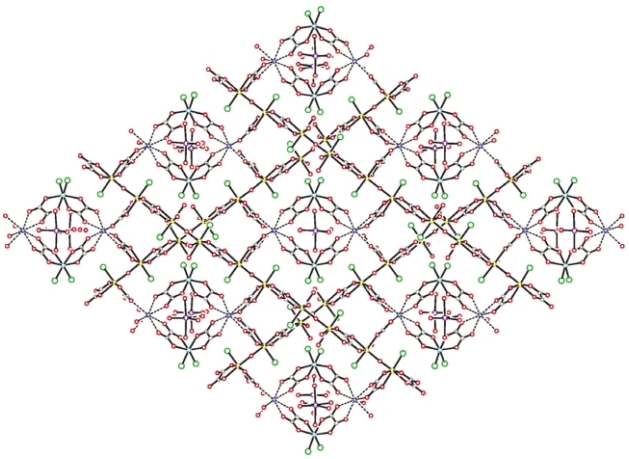

Fig. 1 View along *b* axis of the three-dimensional supramolecular network of **2** showing the different types of iron(III) ions. Eight-coordinated iron(III) interactions are represented by dashed lines.

† Electronic supplementary information (ESI) available: Thermal dependence of $\chi_M T$ under an applied field of 50 Oe and of the in-phase and out-phase components of the ac susceptibility of **2** at 100 Hz in zero applied static field and under an oscillating field of 1 Oe (Fig. S1 and S2); hysteresis loop at 2.0 K between ±5 T (Fig. S3). See http://www.rsc.org/suppdata/cc/b4/b402055c/

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magnetically isolated $S_{Fe(III)}$ = 5/2 (4.38 cm^3 mol^{-1} K with g = 2.0) indicating that a strong antiferromagnetic interaction occurs in agreement with the presence of oxo ($-J$ values larger than 45 cm^{-1}, $H = -J\,S_A \cdot S_B$) and oxalate ($-J$ values about 7 cm^{-1}) bridges.[6] Upon cooling under an applied magnetic field of 50 Oe [Fig. S1†], $\chi_M T$ decreases, attains a minimum at 73 K ($\chi_M T$ = 0.62 cm^3 mol^{-1} K), then exhibits an abrupt increase and further decreases in the very low temperature range. At T < 73 K, the magnetization of **2** is strongly field dependent and the field-cooled magnetization of **2** (Fig. 3) at 50 G reveals the occurrence of magnetic ordering below 70 K.

In-phase and out-of phase ac signals, which are frequency independent (frequency range 1000–10 Hz), are observed below 70 K [Fig. S2†], confirming the magnetic ordering. The magnetic hysteresis loop for **2** (see inset of Fig. 1 and Fig. S3†) shows values of the coercive field (H_c) and remnant magnetization (M_r) of 0.06 T and 0.020 BM. Although no saturation of the magnetization for the spin canting occurs, a lower limit of the value of the spin canting of 0.5° can be estimated from the expected saturation value of the magnetization for a spin S = 5/2 (5 BM) and considering the value of M_r (0.020 BM) as that of the saturation value of the magnetization of **2**. From the two mechanisms that lead to spin canting, namely the magnetic anisotropy and the antisymmetric exchange, the second one has to be responsible for the canting in **2**, because of the isotropic character of the high spin iron(III). The acentric character of the space group of **2** is compatible with the occurrence of the antisymmetric exchange.[10] The relative high value of T_c for **2** and its significant shift of 30 K towards higher temperatures when comparing **1** and **2** is very appealing.

The greater number of correlations paths (number of connections between the iron atoms) in **2** when compared to **1**, which is due to the presence of eight-coordinated iron(III), is most likely at the origin of the significant increase of T_c in **2**. In **1**, each iron atom is six-coordinated and it is linked to only three nearest-neighbours. Additional work is in progress on these spin canted three-dimensional systems in order to get further insights on the correlation between the network topology and the T_c value.

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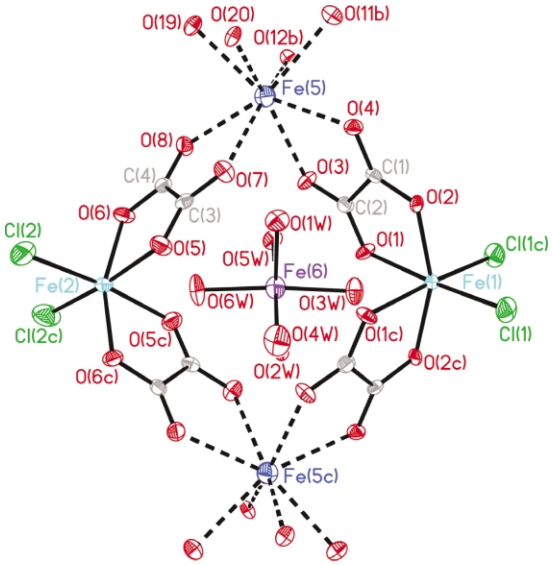

Fig. 2 View of the ring motif of **2** containing six- and eight-coordinated iron(III) atoms. Eight-coordinated iron(III) interactions are represented by dashed lines. Selected bond lengths [Å]: Fe(5)–O(3) 2.426(9), Fe(5)–O(4) 2.473(10), Fe(5)–O(7) 2.406(10), Fe(5)–O(8) 2.502(10), Fe(5)–O(11b) 2.443(10), Fe(5)–O(12b) 2.479(9), Fe(5)–O(19) 2.447(11), Fe(5)–O(20) 2.448(9). Symmetry code: (b) 0.5 − x, − y, 0.5 + z.

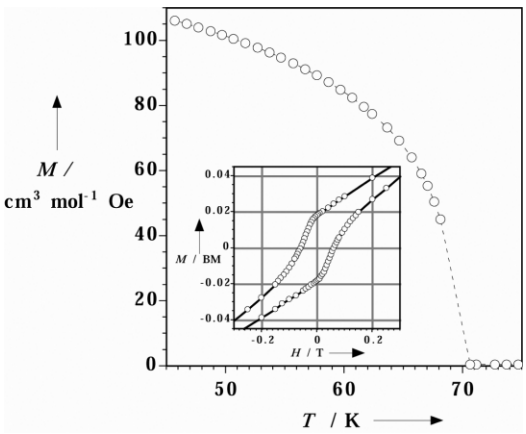

Fig. 3 Field-cooled magnetization (○) of **2** under an external field of 50 Oe. The inset shows the hysteresis loop of **2** at 2.0 K between ±0.30 T. The dashed line is an eye guide.

Notes and references

‡ Compound **2** was obtained (yield about 60%), as yellow rhomboid crystals, by slow evaporation of an aqueous solution (total volume 10 ml) containing $FeCl_3$, H_2ox and $EtNH_3Cl$ in the 1:1:1 molar ratio (2 mmol). Anal. Calcd for $C_{12}H_{32}Cl_4Fe_5NO_{33}$: C 12.65, H 2.83, Cl 12.45, N 1.23. Found: C 12.60, H 2.75, Cl 12.50, N 1.31%. IR data for **2** [ν/cm^{-1}] on KBr pellets: 1675 *vs* ν_{as}(O–C–O); 1355m and 1305s ν_s(O–C–O); 805m δ(O–C–O); 825m ν_{as}(Fe–O–Fe); 3588s,br (H_2O).

§ Crystal data of compound **2**: $C_{12}H_{32}Cl_4Fe_5NO_{33}$, M_r = 1139.44, orthorhombic, space group *Fdd*2 (refinement in *Fddd* was unsuccessful), a = 27.328(6), b = 32.125(6), c = 18.424(4) Å, V = 16175(6) $Å^3$, Z = 16, ρ_{calcd} = 1.872 g cm^{-3}, λ = 0.71073 Å, $\mu(Mo_{K\alpha})$ = 21.18 cm^{-1}, $F(000)$ = 9168, GoF = 1.083. A total of 3787 reflections were collected and 3704 were unique. $R1$ and $wR2$ were 0.0663 and 0.205 respectively, for 497 parameters and 3258 reflections [$I > 2\sigma(I)$]. The hydrogen atoms of the water molecules were not located. CCDC 221514. See http://www.rsc.org/suppdata/cc/b4/b402055c/ for crystallographic data in .cif or other electronic format.

¶ Magnetic measurements were carried out on a polycrystalline sample (10 mg) of **2** in the temperature range 1.9–295 K with a Quantum Design SQUID susceptometer and using applied magnetic field ranging from 50 G to 5 T. The susceptibility data of **2** were corrected for the diamagnetic contributions of the constituent atoms and sample holder.

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