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

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Received (in Cambridge, UK) 10th February 2004, Accepted 30th March 2004
First published as an Advance Article on the web 21st April 2004

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. The interest in this class of compounds is enhanced when additional properties, such as spontaneous magnetization at high temperatures, are involved. 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. Very recently, we have described a three-dimensional homometallic compound of formula \([\text{NH}_4][\text{Fe}^3\text{O}(\text{ox})_3\text{Cl}_2\cdot 2\text{H}_2\text{O}], (1)\) which contains isotropic high-spin Fe(III) ions bridged by oxo and bisbidentate oxalate \( \text{O} \) groups 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). The use of ethylammonium cation gives rise to a very singular iron(III) compound of formula \([\text{EtNH}_3][\text{Fe}^{III}\text{O}(\text{H}_2\text{O})_6]\cdot \text{EtNH}_3\cdot \text{EtNH}_3\cdot \text{H}_2\text{O} \cdot (2)\), 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 \([\text{Fe}(\text{ox})_2\text{Cl}_3]^{3-}\) chains (I) and \([\text{Fe}(\text{ox})_2\text{Cl}_3]^{3-}\) monomeric units (II) self-assembled in an unprecedented supramolecular three-dimensional anionic network through Fe\(^{III}\) cations (III). The electroneutrality is achieved by means of \([\text{Fe}(\text{H}_2\text{O})_6]^{3+}\) (IV) and EtNH\(^+\) 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 the occurrence of four different iron(III) centers, depending on their relative environments. Among these, only the metal center of type 1 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\(_{\text{oxal}}\) and Fe–O\(_{\text{oxo}}\) bond lengths \([\text{range } 2.006(8) \text{ to } 2.109(8) \text{ Å and } 1.931(9) \text{ Å average value, respectively}] \) with respect to compound 1 \([2.049(4) \text{ to } 2.194(4) \text{ Å and } 1.825(2) \text{ Å average value, respectively} \). The value of the angle at the oxo bridge is 134.8(5)°, 

† Electronic supplementary information (ESI) available: Thermal dependence of \( \chi_M \) under an applied field of 50 Oe and of the in-phase and out-of-phase components of \( \chi_M \) 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

Fig. 1 View along \( \delta \) 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.
magnetically isolated $S_{\text{Fe(III)}} = 5/2$ (4.38 cm$^{-1}$ mol$^{-1}$ K with $g = 2.0$) indicating that a strong antiferromagnetic interaction occurs in agreement with the presence of $\langle-J\rangle$ values larger than 45 cm$^{-1}$, $H = -J S_A S_B$ and oxalate $\langle-J\rangle$ values about 7 cm$^{-1}$ bridges. Upon cooling under an applied magnetic field of 50 Oe [Fig. S1], $\chi_M$ 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) at 50 G reveals the occurrence of the coercive field ($H_c$) 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 $M_c$ (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. The relative high value of $T_N$ 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 $T_N$ in 2. In 1, each iron atom is six-coordinated and 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 $T_N$ value. This research was supported by the Italian Ministero dell’Università e della Ricerca Scientifica e Tecnologica, the Ministerio Español de Ciencia y Tecnología (Project BQU2001–2928) and the Agencia Valenciana de Ciencia y Tecnología (Grupos 03/197).

Notes and references

1 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$_2$Ox and EtNH$_3$Cl in the 1:1:1 molar ratio (2 mmol). Calcul. C$_{12}$H$_7$Cl$_2$FeO$_{13.5}$, C 12.65, H 2.83, Cl 12.45, N 1.25. Found: C 12.60, H 2.75, Cl 12.50, N 1.31%. IR data for 2 (cm$^{-1}$) on KBr pellets: 1675 vs $v_{\text{O}(O-C-O)}$; 1355m and 1305s $v_{\text{O}(O-C-O)}$; 850m $v_{\text{O}(O-C-O)}$; 725v $v_{\text{Fe(O-Fe)}}$; 3588s, br (H$_2$O).

$\xi$ Crystal data of compound 2: C$_{12}$H$_7$Cl$_2$FeO$_{13.5}$, $M_r = 1139.44$, orthorhombic, space group Fdd2 (refinement in Fddd was unsuccessful), $a = 27.328(6)$, $b = 32.125(6)$, $c = 18.424(4)$ Å, $V = 16175(6)$ Å$^3$, $Z = 16$, $\rho_{\text{calc}} = 1.872$ g cm$^{-3}$, $\lambda = 0.71073$ Å, $\mu_{\text{MoK}} = 21.18$ cm$^{-1}$, $F(000) = 9168$, GoF = 1.083. A total of 3787 reflections were collected and 3704 were unique. R$_1$ and wR$_2$ 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.

$\gamma$ 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.