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# The Cation as a Tool to Get Spin-Canted Three-Dimensional Iron(III) Networks

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Alkyl-substituted ammonium cations (X) allow the preparation of a series of spin-canted oxo- and oxalato-bridged three-dimensional iron(III) networks, exhibiting magnetic ordering at $T_c$ values ranging from 40 to 56 K. The value of $T_c$ varies with the cation despite the lack of significant structural modifications.

The use of molecular complexes to construct lattices exhibiting long-range magnetic ordering has been a strong growth point for preparative chemists over recent years.[1] This success is due to the versatility of inorganic synthetic methods. There are a variety of factors which can play a role in modulating structural parameters and the associated magnetic behavior which can be opportunely adjusted to engineer materials that possess a predictable order and useful solid-state properties.[2,3]

In this context, the use of the oxalate ligand in designing molecule-based magnets has been of considerable interest in the past decade.[4] Three main features are at the origin of this interest: (i) the remarkable ability of the oxalate group to transmit magnetic interactions between the paramagnetic centers it bridges, (ii) the relatively easy achievement of anionic two- and three-dimensional (*n*D) oxalato-bridged bimetallic networks whose dimensionalty is governed by the nature of the cation, and (iii) the fact that some of them exhibit ferro-,[5] ferri-,[6] or antiferromagnetic[7,8] long-range ordering with $T_c$ values ranging from 5 up to 48 K. Recently, the enantioselective control of these high dimensional compounds by using chiral building blocks as starting chemicals has provided optically active *n*D molecule-based magnets (bifunctional materials).[9]

In a recent work,[10] we have shown how the coexistence of the oxo and oxalato bridges in the three-dimensional iron(III) complex of formula $\{(NH_4)_2[Fe_2(ox)_2Cl_2(\mu\text{-O})]\cdot 2H_2O\}_n$ (**1**) leads to a spin-canted structure with magnetic ordering ($T_c = 40$ K) through antisymmetric exchange. Aiming at monitoring the value of $T_c$ of the anionic iron(III) network by playing on the shape and nature of the univalent counterion, we have started a systematic study with different alkyl-substituted ammonium derivatives (X) as cations.

The use of X = $MeNH_3^+$ (**2**), $Me_2NH_2^+$ (**3**), and $EtNH_3^+$ (**4**) afforded the compounds of general formula $\{(X)_2[Fe_2(ox)_2Cl_2(\mu\text{-O})]\cdot 2H_2O\}_n$. These compounds present a three-dimensional network isostructural to that of **1**, without significant structural modifications. Surprisingly, the study of the magnetic properties reveals that the nature of the cation modifies the value of $T_c$, with a significant increase from 40

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to 56 K, the higher value being observed for the ethylammonium-containing iron(III) compound.

We present here the synthesis,[11] crystal structures,[12] and magnetic characterization[13] of compounds **2**−**4**.

All the compounds were obtained as red rhomboids from an aqueous solution (total volume 10 mL) containing 2 mmol of oxalic acid, $FeCl_3$, and XCl salts (pH = 2) by slow evaporation at room temperature in the darkness, the only difference being the evaporation rate.

In fact, while compound **2** was obtained in a week, longer reaction times are needed in the case of compounds **3** (10 days) and **4** (two weeks). At this goal, the time required for evaporation has been increased by partially covering the crystal growing vessel.

On the contrary, the faster evaporation (a week) of the solution containing dimethylammonium cation affords a compound of formula $\{(Me_2NH_2)_2[Fe_2(ox)_2Cl_4]\cdot H_2O\}_n$, this latter being an oxalato-bridged iron(III) chain in which no hydrolysis occurs. On the other hand, after 10 days only a partial hydrolysis can be noticed in the case of ethylammonium, affording a 3D compound of formula $\{[EtNH_3][Fe^{III}(H_2O)_6]Fe^{III}[Fe^{III}_2O(ox)_3Cl_2][Fe^{III}(ox)_2Cl_2]\}_n\cdot 6nH_2O$.[14]

It is noteworthy that **2** is the only product isolated with $MeNH_3^+$ as a cation, even after changing the evaporation rate. The use of bulkier cations such as $Me_3NH^+$ and $Me_4N^+$ affords only oxalato-bridged iron(III) chain compounds. These results clearly suggest the templating role of the counterion in the formation of the three-dimensional iron(III) hydrolysis products. Attempts with other non-amine cations are in progress.

X-ray analysis on compounds **2**−**4** revealed that they are isostructural to **1**, their structure consisting of the anionic 3D $[Fe_2O(ox)_2Cl_2]_n^{2n-}$ framework with large channels (ca. 43% of the unit cell) (Figure 1) filled with disordered cations.

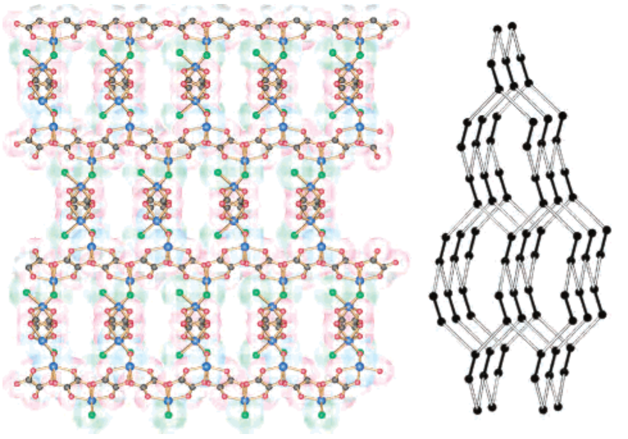

**Figure 1.** View of the 3D channels along [101] and the resulting 3-connected 10-gon net (102.104.104) observed connecting the iron atoms only in compound **3**.

**Table 1.** Selected Structural and Magnetic Parameters for the Series $\{X_2[Fe_2(ox)_2Cl_2(\mu\text{-}O)]\cdot 2H_2O\}_n$

| $X^+$ | Fe−O (oxo) (Å) | Fe−O−Fe (deg) | Fe···Fe (oxo) (Å) | Fe···Fe (ox) (Å) | $T_c$ (K) |
|---|---|---|---|---|---|
| $NH_4$ (**1**) | 1.825(2) | 135.9(4) | 3.384(2) | 5.496(2) | 40 |
| $MeNH_3$ (**2**) | 1.872(3) | 136.0(5) | 3.472(2) | 5.462(2) | 40 |
| $Me_2NH_2$ (**3**) | 1.817(5) | 136.6(8) | 3.377(2) | 5.475(3) | 52 |
| $EtNH_3$ (**4**) | 1.809(1) | 137.1(2) | 3.367(1) | 5.496(1) | 56 |

Each iron atom is in a distorted octahedral environment, being bonded to four oxygen atoms of two *cis* oxalate ligands, one oxygen atom of the oxo group, which lies on a 2-fold screw axis, and one chlorine atom. The Fe−O(ox) [1.989(10)−2.201(2) Å] and Fe−Cl bond lengths [average value 2.303(4) Å] are in agreement with those reported in the literature for other similar complexes.[15] No significant variations have been observed in the Fe−O($\mu$-ox) and Fe−O($\mu$-oxo) bond lengths for all the titled compounds [see Table 1]. The values of the Fe−O−Fe angles are the shortest ones reported so far for this type of bridge [previous values ranging from 139° to 180°].[16] Taking into account the connectivity of the iron atoms only, the overall structure can be described as a three-connected 10-gon net ($10_2.10_4.10_4$) (Figures 1 and 2), and accordingly, it may be considered as the three-connected analogue of the $ThSi_2$ net.[17]

The thermal variation of the $\chi_M T$ product for **2** [$\chi_M$ is the magnetic susceptibility per two iron(III) ions] is shown in Figure 3. At room temperature, $\chi_M T$ is equal to 2.26 $cm^3$ $mol^{-1}$ K, a value much smaller than that expected for two magnetically isolated spin sextets [8.75 $cm^3$ $mol^{-1}$ K for *S*

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[11] Analytical data for compound **2**: yield ∼65%. Anal. Calcd for $C_6H_{16}Cl_2Fe_2N_2O_{11}$: C 15.18, H 3.40, N 5.90. Found: C 14.82, H 3.95, N 6.25. Analytical data for compound **3**: yield ∼60%. Anal. Calcd for $C_8H_{20}Cl_2Fe_2N_2O_{11}$: C 19.11, H 4.01, N 5.57. Found: C 20.40, H 3.75, N 6.40. Analytical data for compound **4**: yield ∼20%. Anal. Calcd for $C_8H_{20}Cl_2Fe_2N_2O_{11}$: C 19.11, H 4.01, N 5.57. Found: C 18.20, H 3.60, N 6.10. The amount of water was confirmed by thermogravimetric analysis (TGA).

[12] Crystal data for compound **2**: $C_6H_{16}Cl_2Fe_2N_2O_{11}$, orthorhombic, $a$ = 14.956(7) Å, $b$ = 23.671(9) Å, $c$ = 9.026(4) Å, $U$ = 3195 (2) $Å^3$, space group *Fdd*2 (No. 43), $Z$ = 8. Least-squares refinement based on 1427 reflections with $I > 2\sigma(I)$ and 78 parameters led to convergence with final R1 = 0.0611, wR2 = 0.1582. **3**: $C_8H_{20}Cl_2Fe_2N_2O_{11}$, orthorhombic, $a$ = 14.963(5) Å, $b$ = 23.345(8) Å, $c$ = 9.317(3) Å, $U$ = 3254.5(18) $Å^3$, space group *Fdd*2 (No. 43), $Z$ = 8. Least-squares refinement based on 1284 reflections with $I > 2\sigma(I)$ and 76 parameters led to convergence using SQUEEZE (see ESI), with final R1 = 0.0767, wR2 = 0.1750. **4**: $C_8H_{20}Cl_2Fe_2N_2O_{11}$, orthorhombic, $a$ = 14.779(1) Å, $b$ = 23.754(1) Å, $c$ = 9.175(1) Å, $U$ = 3220.9 (3) $Å^3$, space group *Fdd*2 (No. 43), $Z$ = 8. Least-squares refinement based on 1733 reflections with $I > 2\sigma(I)$ and 97 parameters led to convergence with final R1 = 0.0297, wR2 = 0.0844.

[13] Variable-temperature (1.9−300 K) magnetic susceptibility and magnetization measurements on crushed single crystals of complexes **2**, **3**, and **4** (amounting to ca. 10 mg) were carried out with a Quantum Design SQUID device in the temperature range 1.9−300 K using an applied magnetic field ranging from 100 G to 5 T. The data were corrected for the diamagnetic contributions of the constituent atoms through Pascal's constants.

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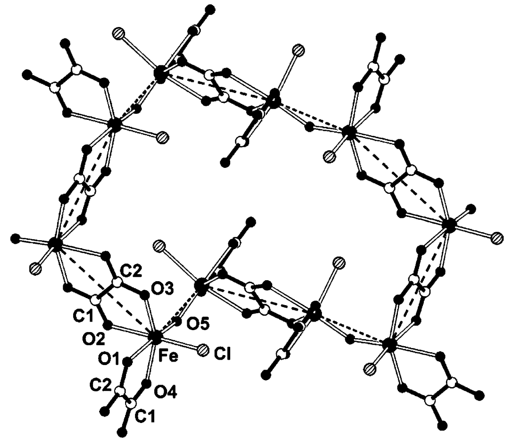

**Figure 2.** View showing one 10-gon ring in compound **3**. The values of the iron−iron separation through the single oxo- and oxalato-bridges are reported in Table 1.

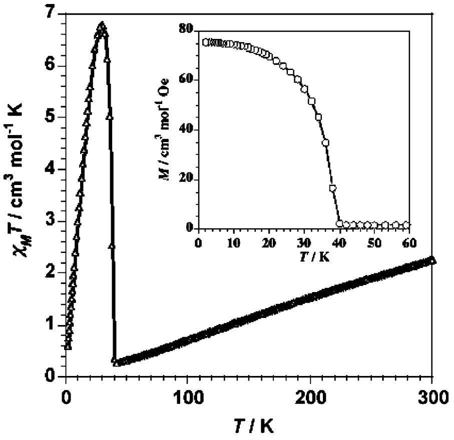

**Figure 3.** Thermal variation of the $\chi_M T$ product for **2** at $H = 250$ Oe. The inset shows the field-cooled magnetization of **2** at $H = 250$ Oe.

$= {}^5/_2$ with $g = 2.0$]. Upon cooling, $\chi_M T$ decreases, and it attains a mimimum at 42 K. Below this temperature, $\chi_M T$ increases abruptly to reach a maximum at 28.5 K ($\chi_M T = 6.80$ cm$^3$ mol$^{-1}$ K), and in the very low-temperature range, $\chi_M T$ varies linearly with $T$, and it vanishes. The $M$ versus $T$ plot for **3** exhibits a rapid increase below 40 K (see inset of Figure 3). These features can be attributed to a spin canting.

The magnetization versus $H$ plot at 2.0 K (Figure 4) exhibits a *quasi* plateau at low magnetic fields ($M$ ca. 0.02 $\mu_B$) and then increases linearly to reach a maximum value of ca. 0.07 $\mu_B$ at 5 T. The hysteresis loop of **2** at 2.0 K (see inset of Figure 4) shows values of the coercive field ($H_c$) and remnant magnetization ($M_r$) of 400 Oe and 0.016 $\mu_B$, respectively. From the saturation value of the magnetization of the canting (ca. 0.020 $\mu_B$) and that expected for a spin $S = {}^5/_2$ (5 $\mu_B$), a value of the canting angle of ca. 0.1° is calculated. Similar behavior is observed for complexes **3** and **4** (Figures S1−S4), the most striking difference being the significant shift toward higher temperatures [$T_c = 52$ (**3**) and 56 K (**4**)].

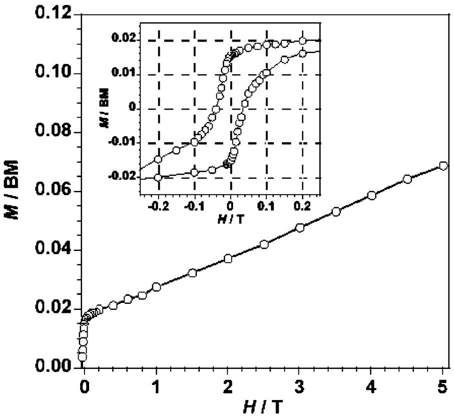

**Figure 4.** Magnetization versus $H$ plot for **2** at 2.0 K. The inset shows the hysteresis loop at 2.0 K.

The well-known ability of the oxo and oxalato bridges to mediate strong antiferromagnetic interactions between iron(III) ions accounts for the reduced values of $\chi_M T$ of **2**−**4** in the high temperature range. The spin canted phenomenon at low temperatures for these compounds is unambiguously attributed to the antisymmetric exchange which is compatible with the lack of inversion center in their structure [the isotropic character of the high-spin iron(III) ruling out the magnetic anisotropy as source of spin canting]. In light of the data listed in Table 1, there is no clear correlation between the shift of $T_c$ and the structural parameters in **1**−**4**.

However, this work demonstrates clearly that the insertion of alkyl groups in the ammonium cation from **1** appears as a suitable tool to tune the value of $T_c$ of these 3D compounds. Of course, much remains to be done in order to understand the detailed relation of the canting with the crystal structure as a function of X. Our first attempts using alkaline cations afforded the 3D network with $T_c$ values close to that of the alkylammonium substituted derivatives. Finally, coupled magneto-structural studies on single crystals (X-ray and neutron diffraction experiments) will be performed in the future in order to get a deeper knowledge of the spin canting observed in this family.

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**Supporting Information Available:** X-ray crystallographic files in CIF format; details of the crystallography for **3**; thermal variation of the $\chi_M T$ product for **3** and **4** (Figures S1 and S2); magnetization versus $H$ plot at 2 K for **3** and **4** (Figures S3 and S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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