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Synthesis and Characterization of a Soluble Bimetallic Oxalate-Based Bidimensional Magnet: $[K(18\text{-crown-6})]_3[Mn_3(H_2O)_4\{Cr(ox)_3\}_3]$

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The “templating” K crown ether cation allows for the preparation of soluble layered oxalate-based bimetallic magnets, as in $[K(18\text{-crown-6})]_3\{Mn_3(H_2O)_4[Cr(ox)_3]_3\}$, with an unprecedented bidimensional polymeric anionic network that involves both oxalato bridges and H bonds. As in other 2D oxalate-bridged compounds, the compound behaves as a soft ferromagnet, with the onset of magnetic ordering occurring at 3.3 K.

Oxalate bimetallic complexes have been used extensively for the construction of molecule-based magnets since the discovery, more than 10 years ago, that the bimetallic layered oxalate-bridged compounds of the general formula $A[M^{II}M^{III}(ox)_3]$[1,2] (A = alkylammonium or alkylphosphonium; M^{II} = Mn, Fe, Co, Ni, Cu; M^{III} = Cr, Fe, Ru) behave as ferro- and ferrimagnets with critical temperatures up to 45 K.[3–5] When electroactive cations have been combined with these oxalate-based 2D anionic magnets, hybrid multifunctional materials have been obtained, such as magnetic multilayers,[6] photoactive magnets,[7] and the first family of molecular ferromagnetic metals.[8,9] The “templating” effects of other cation types have been investigated, giving rise to different oxalate-based bimetallic architectures. Tris(bipyridyl) complexes, for example, favor the formation of chiral 3D bimetallic networks of the general formula $[Z^{II}(bpy)_3][ClO_4][M^{II}M^{III}(ox)_3]$ (Z^{II} = Fe, Co, Ni, Ru).[10,11] These 3D derivatives behave also as ferro- and ferrimagnets but with lower ordering temperatures than their 2D analogues. Monocationic organic radicals of the nitronyl−nitroxide type can also stabilize more complex 3D structures, where the oxalate anions act as a chelating bridge and also as monodentate ligands, where competition between ferro- and antiferromagnetic interactions gives rise to the overall antiferromagnetic ordering.[12]

A common characteristic for all of these materials is its polymeric nature and insolubility in common solvents. Particularly, the 2D phases are usually obtained as rapidly precipitated polycrystalline powders that often show structural defects, such as stacking faults.[13] Single crystals of good quality and size are rarely available. Because the shape, size, geometry, and charge of the cations are key elements for the preparation of different oxalate-based bimetallic architectures, we tested the possibilities of the planar $[K(18\text{-crown-6 ether})]^+$ cation. As a result, here we report on the synthesis, structure, and magnetic properties of the coordination bidimensional polymer $[K(18\text{-crown-6})]_3\{Mn_3(H_2O)_4[Cr(ox)_3]_3\}$ (**1**), which represents the first soluble magnet based on bimetallic oxalate complexes.

Compound **1** is formed, as a polycrystalline powder, by the reaction in methanol of $[K(18\text{-crown-6})]_3[Cr(ox)_3]$ and a Mn^{II} salt.[14] It is soluble in water and other polar solvents but insoluble in organic solvents. This allows for the preparation of large crystals by layering a water solution of **1** with alcohols or by layering a water solution of a Mn^{II}

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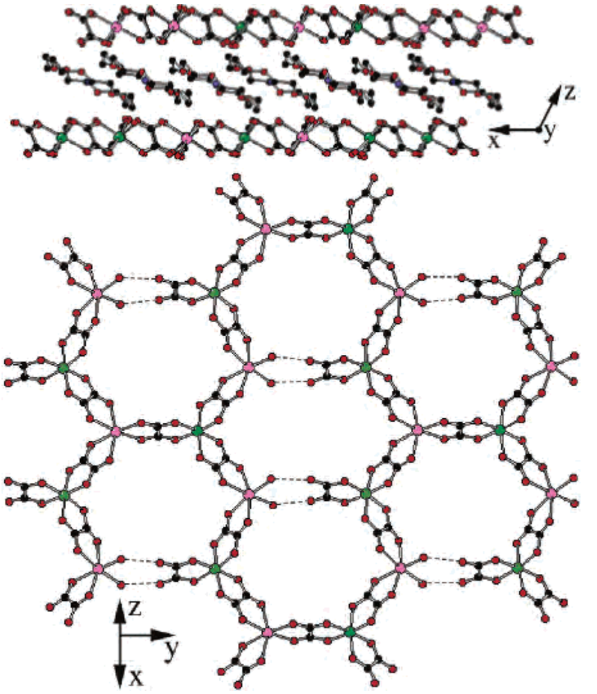

Figure 1. View of the multilayered structure of **1** (top) and of the structure of the anionic layers on the *ab* plane: Cr, green; Mn, pink; O, red; C, black; H bonding, dashed lines.

salt with a methanolic solution of $[K(18\text{-crown-}6)]_3[Cr(ox)_3]$. Single rhombic crystals of over 3 mm have been obtained this way.

1 crystallizes in the $C2/c$ monoclinic space group,[15] and it is formed by alternating cationic and anionic layers (Figure 1). The stoichiometry of the latter corresponds to the formula $\{Mn_3(H_2O)_4[Cr(ox)_3]_3\}^{3-}$. It is a polymeric network reminiscent of the hexagonal honeycomb $\{Mn[Cr(ox)_3]\}^-$ structure,[2] but in this case, the connectivity is broken by the presence of water molecules binding part of the Mn^{II} metal ions, forcing part of the oxalate anions to act as terminal ligands. There are two different types of Mn centers, Mn1 and Mn2, in a 2:1 ratio. Mn1 is coordinated by two chelating oxalate ligands and two water molecules in a cis fashion, and Mn2 is coordinated by three chelating oxalate ligands in an octahedral fashion. Thus, there are also two different $[Cr(ox)_3]^{3-}$ units: one bound to three Mn^{II} ions and the other one bound to only two Mn^{II} ions. The terminal oxalate units are H-bonded to the two water molecules coordinated to the Mn centers, in a pseudochelating fashion, and the metal-to-metal distances are elongated from the 5.43−5.45-Å range in the bis-chelating oxalate bridge up to 7.77 Å.

In each layer, all Cr ions are homochiral and have chirality opposite to that of the Mn centers. The layers show an eclipsed packing, where adjacent layers possess opposite chirality and orientation, because they are related by a center of symmetry. This structure is formed by 14-membered rings, with alternating Mn and Cr centers of opposite chirality, taking into account only coordination bonds. If the H bonding is also considered, the structure presents six-membered rings of two types: one type with five oxalate and one H-bonded oxalate bridges and the other one with two H-bonded interactions. This causes an elongation of the diagonal of the hexagon, from ∼10.8 Å in a perfect honeycomb to 12.29 and 14.60 Å, respectively.

Overall, the oxalate-bridged layer resembles a precursor of the 2D hexagonal network. If the coordinated water molecules are eliminated, with the corresponding H-bonded oxalate ligands taking its place as chelating moieties, the result would be the formation of a typical honeycomb structure.

Locally, there are no significant differences between the two types of Cr centers, with all of them showing typical and regular Cr−O distances [between 1.945(3) and 1.992(3) Å] and angles close to octahedral, with small deviations for the bite angle of the oxalate (between 82 and 83°). Mn2 also shows little deviation in its Mn−O distances [between 2.186(3) and 2.203(3) Å] and more acute angles for the bite of the oxalate ligands (76°). Mn1 shows a slightly more distorted octahedral environment regarding the bonding distances, with shorter $Mn-O_w$ distances [2.107(4) and 2.112(4) Å] when compared to the $Mn-O_{ox}$ ones [2.201(3) and 2.203(3) Å].

In the cationic layers, the $[K(18\text{-crown-}6)]^+$ units adopt a pseudohexagonal packing, with the mean plane for the crown ether molecules essentially perpendicular to the *c* axis and therefore forming an angle of approximately 26° with the *ab* plane. This particular orientation creates an interlayer separation of 8.18 Å, as the distance between the mean plane of the adjacent anionic layers. The K atoms occupy the center of the crown ether rings, with very small deviations from the corresponding mean plane.

The dc magnetic susceptibility of **1** was studied under an applied field of 100 G. The $\chi_m T$ product at room temperature ($17.8\ emu{\cdot}K{\cdot}mol^{-1}$) is in good agreement with the expected value for a magnetically diluted sample containing three Cr^{III} ($S = 3/2$) and three Mn^{II} ($S = 5/2$). $\chi_m T$ remains constant down to 50 K, when it starts to increase because of the presence of ferromagnetic interactions between the paramagnetic centers. Below 10 K, a rapid increase in $\chi_m T$ occurs, reaching a maximum at 3.2 K ($431\ emu{\cdot}K{\cdot}mol^{-1}$). In the χ_m vs T plot, a sharp increase is seen below 4 K that tends to saturate at lower temperatures (Figure 2, inset). These features suggest the presence of long-range magnetic ordering. To confirm this point, ac magnetic susceptibility measurements were

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(14) Single crystals were prepared by the layering of a water (10 mL) and $MnCl_2{\cdot}4H_2O$ (0.198 g, 1 mmol) solution with a methanol (15 mL) and $[K(18\text{-crown-}6)]_3[Cr(ox)_3]$ (0.751 g, 1 mmol) solution. After 1 day, the rhombohedral crystals that grow in the interphase are filtered, washed with methanol, and dried in air. Anal. Calcd (found) for **1**: C, 30.95 (30.97); H, 3.85 (3.85).

(15) Crystal data for **1**. Data were collected with a Nonius-Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ nm) at 293 K. The structure was solved by direct methods (SIR97), followed by Fourier synthesis, and refined on F^2 (*SHELXL-97*). The non-H atoms were refined anisotropically. $C_{54}H_{80}Cr_3K_3Mn_3O_{58}$, $M_w = 2095.30$, monoclinic, $C2/c$, $a = 26.7760(6)$ Å, $b = 20.0490(5)$ Å, $c = 18.1900(5)$ Å, $\beta = 115.9321(9)°$, $V = 8781.8(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\rho_{calcd} = 1.585\ g{\cdot}cm^{-3}$, $F(000) = 4288$, $\mu = 1.025\ mm^{-1}$, 15 488 reflections, 8769 unique ($R_{int} = 0.0546$), $2\theta_{max} = 52.98°$, $R(F) = 0.0538$ and $R_w(F^2) = 0.1233$ for 3825 reflections [$I > 2\sigma(I)$]. CCDC 280068 contains the supplementary crystallographic data for this paper. It can be obtained free of charge via www.ccdc.cam.ac.uk/retrieving.html (or from Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K., deposit@ccdc.cam.ac.uk).

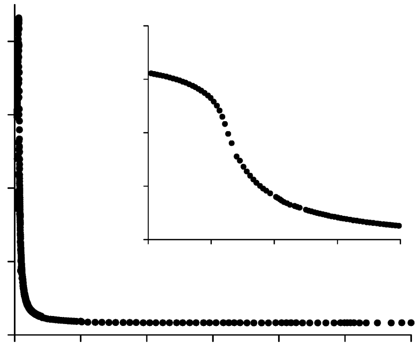

Figure 2. Magnetic behavior of **1**: $\chi_m T$ vs T and χ_m vs T (inset).

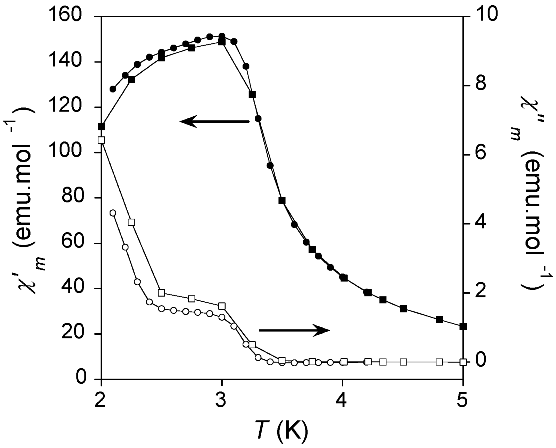

Figure 3. Temperature dependence of the ac magnetic susceptibility for **1** at 1 Hz (circles) and 110 Hz (squares).

performed (Figure 3). The in-phase signal (χ_m') shows a broad maximum, with the out-of-phase signal (χ_m'') becoming nonzero at 3.3 K, which defines T_c for this material. This is in very good agreement with the zero-field-cooled and field-cooled dc susceptibility measurements that deviate from each other below 3.3 K (Figure S1 in the Supporting Information). After a small plateau, χ_m'' shows a second abrupt jump below 2.5 K, which seems to correspond to a second peak that occurs below 2 K. While the temperature at which χ_m'' becomes nonzero is frequency-independent, a small frequency dependence is found for this second feature, suggesting that it is related to dynamic effects, such as domain wall movement, in the ferromagnetically ordered state. Similar features have already been observed in other low-dimensional molecular magnets.[16]

The ferromagnetic nature of this ordering is confirmed by the field dependence of the magnetization (Figure 4), which at 2 K shows a rapid increase, and an almost complete saturation above 1 T, reaching a value of 23.8 μ_B at 5 T. This value is close to the one expected for parallel alignment of all spins (24 μ_B). No hysteresis is present, even at 2 K, which classifies this material as a soft ferromagnet.

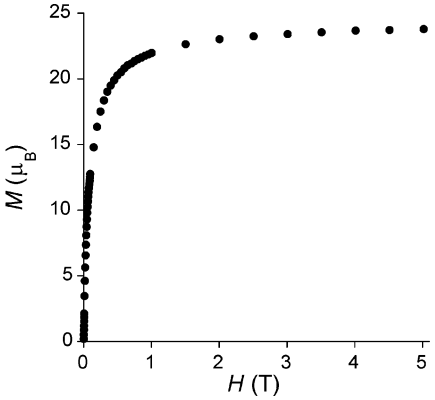

Figure 4. Field dependence of the magnetization for **1** at 2 K.

Compared to the honeycomb 2D analogue, T_c for **1** occurs at lower temperature (3.3 K compared to 5.5 K). This difference is a consequence of the fact that in the present case two-thirds of the oxalate bridges have been substituted by H bonds, resulting in longer metal−metal distances and weaker magnetic superexchange through the Cr−ox−H_2O−Mn bridge.

This novel structural motif can now be extended to other metal ions. Preliminary results indicate that all $[K(18\text{-crown-}6)]_3\{M_3(H_2O)_4[Cr(ox)_3]_3\}$ (M^{II} = Fe, Co, Ni, Cu) series behave as ferromagnets with higher critical temperatures. Substitution of Cr^{III} by Fe^{III} should also yield ferrimagnets or weak ferromagnets with higher critical temperatures. This work is in progress. It is important to note that the solubility of this family of magnets allows for the convenient preparation of large single crystals for future single-crystal studies of their physical properties. This solubility can also be an advantage to processing these magnets as thin films or for the preparation of crystals of multifunctional hybrid materials.

Notice that other intermediate phases of lower dimensionalities can also be obtained using this type of template. Thus, if the crystallization process is slow enough and carried out in the presence of excess crown ether, a kinetic product, $[K(18\text{-crown-}6)]\{M(H_2O)_2[Cr(ox)_3]\}\cdot 0.5(18\text{-crown-}6)$, is obtained, although it can only be isolated as the Mn^{II} derivative. This compound is formed by H-bonded oxalate-bridged bimetallic chains.[17]

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Supporting Information Available: CIF data for compound **1** and additional magnetic measurements (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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