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A “Cation-less” Oxalate-Based Ferromagnet Formed by Neutral Bimetallic Layers: $\{[Co(H_2O)_2]_3[Cr(ox)_3]_2(18\text{-crown-}6)_2\}_\infty$ (ox = Oxalate Dianion; 18-crown-6 = $C_{12}H_{24}O_6$)

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Neutral layers of the bimetallic oxalate complex $\{[Co(H_2O)_2]_3[Cr(ox)_3]_2\}_\infty$ are formed in the presence of a crown ether and stabilized by hydrogen bonding. The resulting soluble ferromagnet orders at $T_c = 7.4$ K.

The oxalate dianion (ox) has demonstrated to be one of the most versatile ligands used in the search for molecule-based magnets. As a bis-bidentate chelate linker, it affords incomparable possibilities for the tuning of the magnetic properties. Thus, in these systems, the topology, dimensionality, and sign of the magnetic exchange can be controlled at ease, allowing for the preparation of a large variety of novel magnetic materials (hybrid magnets,[1] chiral magnets,[2,3] conducting magnets,[4] or photoactive magnets).[5]

Such versatility is exemplified by the bimetallic oxalate complexes. These compounds are obtained by using a $[M^{III}(ox)_3]^{3-}$ octahedral complex as a ligand toward paramagnetic divalent ions. In a first step, this results in the formation of anionic oligomeric species in solution. In a second step, the presence of bulky cations in the media leads to the self-assembling of these molecular species and to the formation of nonsoluble coordination polymers. The first example of such a strategy was discovered in the early 1990s by Okawa et al. when they reported that the addition of a bulky monovalent cation, such as alkylammonium, yields layered 2D compounds of the general formula $[A][M^{II}M^{III}(C_2O_4)_3]$ (M^{II} = Mn, Fe, Co, Ni, Cu, Zn; M^{III} = Cr, Fe, V, Ru, Mn). Depending on the identity of the divalent and trivalent metallic ions, these compounds behave as ferromagnets, ferrimagnets, or weak ferromagnets with critical temperatures between 6 and 45 K.[6]

Substitution of the bulky monocation with tris(bipyridyl) metallic complexes $[Z^{II}(bpy)_3]^{2+}$ (Z = Fe, Co, Ni, Ru; bpy = $C_{10}H_8N_2$)[2] gives rise to the formation of 3D extended bimetallic oxalate-based networks: $[Z^{II}(bpy)_3][ClO_4][M^{II}M^{III}(C_2O_4)_3]$. These compounds show ferro- and ferrimagnetic behavior, with lower ordering temperatures than their 2D counterparts.

The flat [K(18-crown-6)]$^+$ cation induces, on the contrary, a reduction of the dimensionality, to yield other less connected 2D anionic layers and even 1D chains.[7,8] These systems also reach magnetic ordering at lower temperatures than their 2D counterparts.

Other cations, with the help of capping ligands, allow one to decrease the dimensionality even further, to yield discrete polynuclear compounds, such as dimers,[9] trimers,[10] or tetramers.[11]

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As described, the chemistry of bimetallic oxalate-based magnets has been controlled so far by the templating cation. Here we report the synthesis and structural and magnetic characterization of $\{[Co(H_2O)_2]_3[Cr(ox)_3]_2(18\text{-crown-6})_2\}_\infty$ (**1**). This is the first example of this family in which the extended oxalate-based bimetallic network is neutral and therefore does not require the presence of a countercation. In this case, hydrogen bonding with a neutral guest molecule, a crown ether, is the driving force for the isolation of this complex.

Compound **1** is obtained as single crystals by slow diffusion of a methanolic solution of $Ag_3[Cr(ox_3)]$ (prepared by metathesis of the corresponding potassium salt)[12] and $CoCl_2{\cdot}6H_2O$ into a methanolic solution of an excess of 18-crown-6.[13] As was previously reported,[7] the insertion of 18-crown-6 molecules into these types of compounds induces its solubility in water and other polar solvents, while they remain nonsoluble in a purely organic solvent, providing an easy route to obtain good-quality single crystals. $\{[Co(H_2O)_2]_3[Cr(ox)_3]_2(18\text{-crown-6})_2\}_\infty$ (**1**) crystallizes in the $Pc2_1n$ orthorhombic space group.[14] It is built up by neutral layers of formula $\{[Co(H_2O)_2]_3[Cr(ox)_3]_2\}_n$, leaving holes in the 2D structure for the 18-crown-6 guest molecules (see Figure 1). These layers run perpendicular to the *ac* plane, with adjacent layers related by an inversion center, with an interlayer distance of 7.825 (2) Å.

Each layer is formed by 12-membered rings, constituted of six $[Cr(ox)_3]^{3-}$ units and six Co^{II} atoms. Each Cr atom is shared between three rings, while each Co is shared between two adjacent rings. Within these rings, each Co^{II} ion is coordinated by two bridging oxalate ligands from $[Cr(ox)_3]^{3-}$ units and two water molecules. There exist two types of Co^{II} ions; while in Co1 the two water molecules appear in the cis conformation, in Co2 they are bonded in a trans fashion. Each $[Cr(ox)_3]^{3-}$ binds two Co2 centers and one Co1 center. In the 12-membered rings, the metallic centers exhibit alternating chirality with a repeating pattern ...Co2ΛΔΛΔΛCo2..., with nonchiral Co2 ions connecting two Cr atoms with opposite chirality.

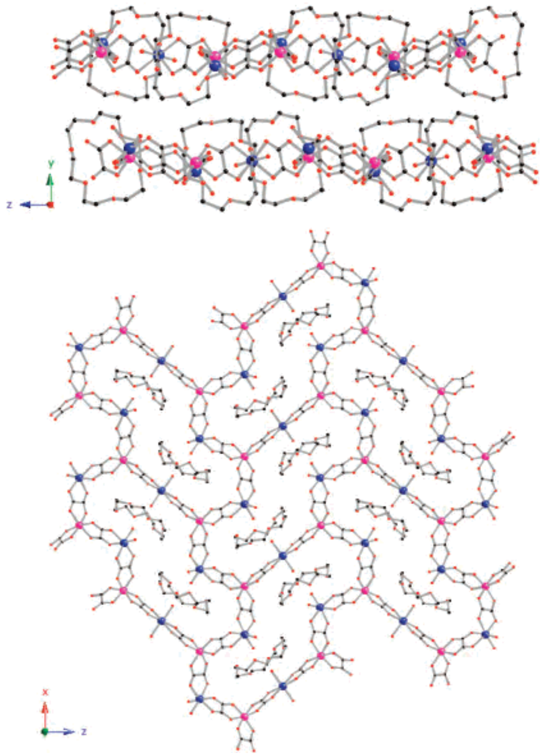

Figure 1. Perspective showing the structure of the neutral polymeric layers of **1** (down) and the packing of these layers along the *b* axis (up): Cr (pink), Co (blue), O (red), and C (black). For the sake of simplicity, H atoms have been omitted.

Both Co centers adopt regular octahedral coordination, with the Co−O_{ox} distances between 2.094(2) and 2.149(2) Å and the Co−O_w distances between 2.030 and 2.084(2) Å. The bonding angles slightly deviate from regular octahedral geometry because of the bite angle of the oxalate ligands (O_{ox}−Co−O_{ox}^0 between 78.097 and 79.879°). The local distortion observed in the Cr atoms coordination sphere is less intense than that for the Co atoms, with shorter Cr−O_{ox} distance values [between 1.957 and 2.017(2) Å] and less acute angles for the oxalate bridge (O_{ox}−Cr−O_{ox}^0 in the 81.227−82.730° range).

The hydrogen-bonding interactions play the key role for the formation of compound **1** (see Figure 2). The two crown ether molecules located in the middle of each 12-membered structural unit are interacting through their O atoms with the bonded water molecules. While the $O_w{\cdots}O_{crown}$ distances for the water molecules coordinated in a cis fashion are in the 2.701(2)−3.043(2) Å range, this parameter oscillates between 2.692(2) and 2.979(2) Å for the trans molecules. These distances are in good agreement with previously reported hydrogen-bonding interactions between coordinated water molecules and crown ether O atoms.[15]

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(13) $Ag_3[Cr(Ox_3)]{\cdot}3H_2O$ (1 mmol; 0.7 g) and $CoCl_2{\cdot}6H_2O$ (2 mmol; 0.48 g) were suspended in 5 mL of methanol. The solution was stirred for 15 min, and the AgCl precipitate was removed from the dark violet solution. This mixture was carefully poured into one H-tube leg, while 18-crown-6 (1 mmol; 0.264 g) was added in the other. The diffusion tube was filled with MeOH and left to stand. After 10 days, the dark blue prismatic crystals that grew in one of the tube legs were filtered, washed with MeOH, and dried in air. Anal. Calcd (Found) for (**1**): C, 29.91 (29.63); H, 4.18.

(14) Data were collected with a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$) at 293 K. The structure was solved by direct methods (SIR97), followed by Fourier synthesis, and refined on F^2 (SHELXL-97). The non-hydrogen atoms were refined anisotropically. $C_{36}H_{60}Co_3Cr_2O_{42}$, $M_w = 1445.63$, orthorhombic, $Pc2_1n$, $a = 14.3950(4)$ Å, $b = 15.6500(5)$ Å, $c = 26.6700(10)$ Å, $V = 6008.3(3)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\rho_{calcd} = 1.598$ g/cm^3, $F(000) = 2964$, $\mu = 1.265$ mm^{-1}, 27596 reflections, 7937 unique ($R_{int} = 0.1070$), $2\theta_{max} = 22.74°$, $R(F) = 0.0615$, and $R_w(F^2) - 0.1497$ for 5581 reflections [$I > 2\sigma(I)$]. CCDC 635244 contains supplementary crystallographic data for this paper. It can be obtained free of charge via www.ccdc.cam.ac.uk/retrieving.html.

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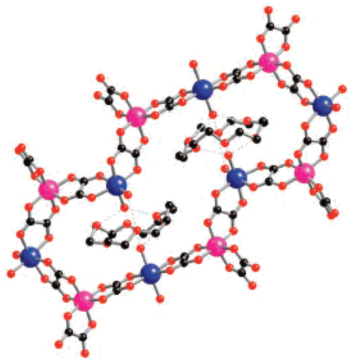

Figure 2. Picture showing the hydrogen-bonding interactions (dashed line) between the oxalate network and the neutral guest crown ether molecule.

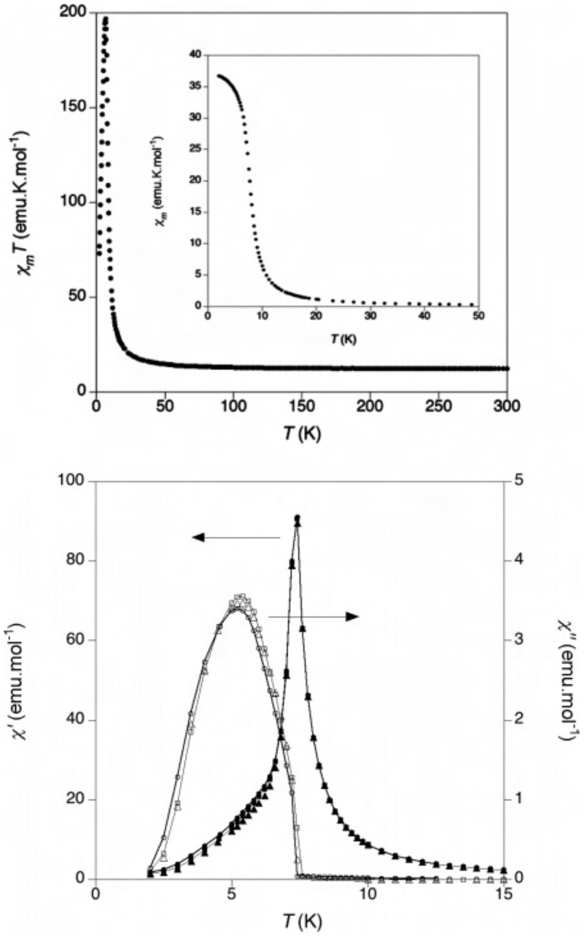

Figure 3. $\chi_m T$ product (top) under an applied field of 1000 G and χ_m values at 10 (circle), 110 (square), and 332 (triangle) Hz (bottom).

Magnetic dc measurements were performed on grained single crystals of **1** (see Figure 3). The $\chi_m T$ product at room temperature (12.040 emu K mol^{-1}) is higher than the expected spin-only value. This deviation is due to the typical anisotropy of the octahedral Co^{II} ions, explained because of the existence of a first-order orbital contribution to the magnetic moment. The $\chi_m T$ product remains essentially constant during cooling of the sample. At 50 K, $\chi_m T$ starts to increase, suggesting the presence of ferromagnetic interactions between the metallic ions through the bridging oxalate ligands, as expected for the interaction between Cr^{III} and Co^{II} through an oxalate bridge. This increase of the magnetic moment becomes more intense at around 20 K, reaching a maximum (196.985 emu K mol^{-1}) at 6.5 K and saturation below this temperature, indicating the presence of a magnetically ordered regime.

Susceptibility (ac) measurements under an applied oscillating field of 3.95 G (see Figure 3) show a frequency-independent sharp peak at 7.4 K in the in-phase signal. At the same temperature, the out-of-phase signal becomes nonzero (defining T_c), showing a broad maximum centered at about 5 K. The χ_m'' maximum presents a small frequency dependence. The ferromagnetic order is confirmed also by the field dependence of the magnetization at 2.5 K (see SI. 1 in the Supporting Information). It shows an abrupt jump at very low fields, typical for soft ferromagnetic systems, and tends to saturation above 2 T, reaching a maximum value of 12 μ_B at 5 T, close to that expected for parallel alignment of the spins. A small coercivity was found in the hysteresis loop (H_{Coer} = 11 G); thus, this material can be classified as a soft ferromagnet.

In conclusion, **1** represents the first neutral oxalate-based layered magnet. This result opens the way for more investigations about this class of molecule-based magnets, playing with weaker supramolecular interactions, such as hydrogen bonding, and not only with cation−anion interactions. This approach could be useful for the development of other oxalate complexes and also for other families of molecular magnets. The solubility of **1** in water and polar solvents is also remarkable. Obviously, the solutions do not retain the ferromagnetic properties of the material in the solid state, but the ferromagnetic material is easily rebuilt by evaporation of the solvents. This peculiar characteristic is rare in molecule-based magnets and turns it into an excellent candidate for materials processing.

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

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