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Article

Synthesis, Structure, and Magnetic Properties of [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]][Mn(CH_3CN)$_{2/3}$Cr(ox)$_3$]·(CH_3CN)_(solvate), a 2D Chiral Magnet Containing a Quaternary Ammonium Chiral Cation

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The synthesis, structure, and magnetic properties of a novel oxalate-based bimetallic magnet obtained by using the chiral (*S*)-trimethyl-(1-phenyl-ethyl)-ammonium, ((*S*)-[PhCH(CH_3)N(CH_3)$_3$]$^+$), cation as template is reported. This compound can be formulated as [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]][Mn(CH_3CN)$_{2/3}$Cr(ox)$_3$]·(CH_3CN)_(solvate), and it crystallizes in the chiral trigonal space group *P*3. It shows a distorted two-dimensional honeycomb structure formed by Mn^{II} and Cr^{III} ions connected through oxalate anions with [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]$^+$ cations and solvent molecules intercalated between the oxalate layers. Two-thirds of the Mn^{II} ions of the honeycomb anionic network are heptacoordinated. This compound behaves as a soft ferromagnet with an ordering temperature of 5.6 K.

Introduction

The preparation of chiral molecular magnets has received considerable interest since the first experimental evidence of the magneto-chiral dichroic effect reported by Rikken et al.[1] The coexistence of magnetic ordering and chirality has been achieved by using two different strategies. Most of the examples reported in the literature are based on the use of chiral ligands to induce the formation of chiral magnetic structures. Numerous examples of chiral magnets have been reported in the past few years following this strategy.[2] Another possible strategy is the use of the chiral inductive effect of resolved building blocks such as chiral octahedral tris-bidentate complexes. Most of the chiral magnets obtained using this strategy are oxalate-based compounds. The main advantage of this second strategy is that chirality is centered in the magnetic lattice and not in the ligand.

The tris(oxalato) metalate complexes $[M(ox)_3]^{3-}$ (M = Cr^{III}, Fe^{III}, Ru^{III}, V^{III}, Mn^{III}) can be assembled with divalent metal cations to build bimetallic extended networks. The 2D compounds of formula $A[M^{II}M^{III}(ox)_3]$ (A = tetraalkylamonium derivative) present a honeycomb-layered structure[3] and ferro- and ferrimagnetism with ordering magnetic temperatures between 6 and 45 K.[4] Taking advantage of the layered structure of these oxalate-based magnets, researchers have introduced different electroactive cations between the oxalate layers leading to multifunctional magnetic materials.[5–10] Very recently, a 2D oxalate-based network has been obtained in the absence of a bulky templating cation. In this case solvent coordinated Mn^{II} ions are intercalated between the 2D bimetallic layers.[11] An important feature of this structure is the presence of heptacoordinated Mn^{II} ions into the 2D

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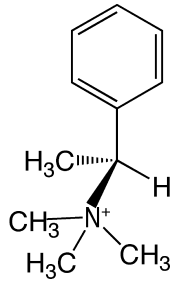
oxalate network. In general, the 2D honeycomb structure is characterized by adjacent M^{II} and M^{III} octahedral tris-bidentate sites of alternated chirality. Thus, the preparation of chiral 2D oxalate-based magnets is a complicated problem.[12] Still, some of these 2D structures induce chirality in some initially achiral cations such as tetraphenylphosphonium[12] or stilbazolium.[6,12,13] Furthermore, resolved enantiomers of ferrocenic ammonium cations are able to template the formation of a powdered optically active compound, which adopts the 2D structure.[14] In any case, the crystallization of a chiral 2D oxalate-based magnet is still a challenge.[12]

Most of the chiral magnets based on the oxalate ligand present a different type of structure, the 3D structure. In contrast to 2D compounds, that admit a large variety of cations, in the 3D structures the templating cation must have the appropriate symmetry (D_3), size, and charge. The general formulas of this class of compounds are $[Z(bpy)_3]X[MM'(ox)_3]$,[15–18] $[Ru(ppy)(bpy)_2][MM'(ox)_3]$,[19] and $[Ir(ppy)_2(bpy)][MM'(ox)_3]$[20] ($Z = Ru^{II}$, Fe^{II}, Co^{II} and Ni^{II}; $X = ClO_4^-$, BF_4^-, PF_6^-; $M, M' = Li^I$, Na^I, Mn^{II}, Ni^{II}, Co^{II}, Fe^{II}, Cu^{II}, Zn^{II}, Rh^{III}, Co^{III}, Cr^{III}, and Fe^{III}; bpy = bipyridine, ppy = phenylpyridine). Thus, chiral tris(bipyridine) metal cations induce the spontaneous resolution of 3D chiral lattices formed by tris(oxometalate) sites of the same chirality as the tris(bipyridine) metal cations. With this strategy, enantiomerically pure compounds have been prepared.[19,21,22]

Chart 1



In this paper, the chiral alkylammonium cation, (*S*)-trimethyl-(1-phenyl-ethyl)-ammonium, ((*S*)-$[PhCH(CH_3)N(CH_3)_3]^+$), (Chart 1) has been used as templating cation to prepare a new oxalato-based bimetallic compound. We have chosen this cation because it is similar to the tetraalkylammonium templating cations that have been shown to lead to 2D honeycomb-layered structures, but chiral. The aim of this work is to study the effect of the chirality of this cation on the final structure of the oxalate network.

Experimental Section

Synthesis. (*S*)-Trimethyl-(1-phenyl-ethyl)-ammonium iodide ((*S*)-$[PhCH(CH_3)N(CH_3)_3]I$) was prepared from the commercial amine following a published procedure.[23] $Ag_3[Cr(ox)_3]$ was prepared by metathesis from the corresponding potassium salt.[24] All other materials and solvents were commercially available and used without further purification.

[(*S*)-$[PhCH(CH_3)N(CH_3)_3]][Mn(CH_3CN)_{2/3}Cr(ox)_3]\cdot(CH_3CN)$_(solvate). Crystals of this compound were obtained by slow diffusion of two solutions. The first solution was prepared by adding 0.05 g of $MnCl_2.4H_2O$ to a suspension of 0.108 g of $Ag_3[Cr(ox)_3]$ in 6 mL of methanol. The AgCl precipitate was filtered. The second solution was obtained by dissolving 0.049 g of [(*S*)-$[PhCH(CH_3)N(CH_3)_3]I$ in 6 mL of acetonitrile. After one week, prismatic violet crystals were obtained. These crystals lose crystallinity very quickly because of the evaporation of the solvent. Because of this, they were kept in contact with the mother liquor prior to the measurements.

Structural Characterization. Crystal data and other details of the structure analyses are presented in Table 1. Violet prismatic single crystals of [(*S*)-$[PhCH(CH_3)N(CH_3)_3]][Mn(CH_3CN)_{2/3}Cr(ox)_3]\cdot(CH_3CN)$_(solvate) were collected and mounted on a Nonius Kappa CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). X-ray diffraction data were collected at 180 K immediately after mounting the crystal. The Denzo and Scalepack programs were used for cell

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Table 1. Crystal Data and Structure Refinement Details for $[(S)\text{-}[PhCH(CH_3)N(CH_3)_3]][Mn(CH_3CN)_{2/3}Cr(ox)_3]\cdot(CH_3CN)\cdot(solvate)$

empirical formula	$C_{61}H_{69}Cr_3Mn_3N_8O_{36}$
formula weight	1811.06
temperature (K)	180(1)
wavelength (Å)	0.71073
crystal system	trigonal
space group	$P3$
a (Å)	15.966(2) Å
b (Å)	15.966(2) Å
c (Å)	9.3600(19) Å
α (°)	90
β (°)	90
γ (°)	120
Z	1
ρ_{calc} (Mg/cm^3)	1.455
Crystal size (mm)	0.40 × 0.30 × 0.30
V (Å^3)	2066.3(6)
θ range of data collection (°)	1.47 to 25.24
reflection collection/unique	4980/4980
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	4980/5/336
goodness-of-fit on $F2$	0.978
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0655$, $wR_2 = 0.1555$

refinements and data reduction.[25] The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[26] The structure was solved in the chiral space group $P3$ based on statistical analyses of the diffraction data. Restraints were employed to stabilize the donor MeCN groups (distance and thermal parameters). Initial refinements revealed the presence of a substantial volume of unresolvable solvent (MeCN and H_2O) molecules. The subroutine SQUEEZE[27] was used to remove the diffracting component of disordered solvents resulting in a void of about 216 Å^3 and 146 electrons/cell omitted. This corresponds to about 4.5 MeCN+H_2O molecules per cell. The data was also refined as a rotational twin using the twin law, "−1, −1, 0, 0, 1, 0, 0, 0, −1", and a refined structure factor of 0.114(2). All non-hydrogen atoms were refined anisotropically.

Physical Measurements. Magnetic susceptibility measurements were performed on a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID sensor. Variable-temperature measurements were carried out in the temperature range 2−300 K. The alternating current (AC) measurements were performed in the range 2−10 K at different frequencies with an oscillating magnetic field of 0.395 mT. The magnetization and hysteresis studies were performed between 5 and −5 T, cooling the samples at zero field. The Mn:Cr ratios were measured on a Philips ESEM X230 scanning electron microscope equipped with an EDAX DX-4 microsonde.

Results and Discussion

Synthesis and Structure. The method used to prepare $[(S)\text{-}[PhCH(CH_3)N(CH_3)_3]][Mn(CH_3CN)_{2/3}Cr(ox)_3]\cdot(CH_3\text{-}CN)$_(solvate) is analogous to that used to prepare the oxalate-based 3D $[M^{II}M^{III}(ox)_3]$ compounds.[18,20] It is based in the use of $Ag_3[Cr(ox)_3]$ to avoid the presence of alkali ions in the structure. In contrast to the synthesis of the 3D systems that are prepared with one solvent in a H-type tube, two different solvents were used to prepare the title compound. Thus, methanol was used to dissolve Mn^{2+} and $[Cr(ox)_3]^{3-}$ ions while acetonitrile was used to dissolve the $[(S)\text{-}[PhCH(CH_3)N(CH_3)_3]^+$ cation. Slow diffusion of these two solutions led to crystals after a few days. The composition of these crystals was checked by microanalysis. These measurements showed that the Mn/Cr ratio is 1:1.

The structure of the compound was solved by single-crystal X-ray diffraction. Attempts to obtain analogous compounds with other paramagnetic M^{2+} ions (M = Ni, Fe, Co, and Cu) were unsuccessful. This can be explained by the presence of heptacoordinated Mn^{2+} ions in the structure (see below). This coordination geometry is difficult to achieve with the other divalent metals that present a smaller size. Therefore, the presence of Mn^{2+} ions seems to be crucial to obtain this structure.

The structure of this compound is formed by bimetallic anionic sheets in the *ab* plane presenting a honeycomb pseudohexagonal structure alternating with layers containing $[(S)\text{-}[PhCH(CH_3)N(CH_3)_3]^+$ cations and solvent molecules. (Figure 1a).

The anionic layer is formed by an extended network of Mn^{II} and Cr^{III} ions linked through oxalate bridges in such a way that each Mn^{II} is surrounded by three neighboring Cr^{III} and vice versa (Figure 1b). The asymmetric unit contains one Cr atom in a general position with an occupancy of 1 and three Mn atoms on 3-fold axes with occupancies of 1/3 each. Two of the three Mn (Mn2 and Mn3) ions adopt heptacoordination by addition of a coordinated acetonitrile molecule. The third Mn atom, Mn1, lies at the origin and is hexacoordinated. The heptahedral coordination of 2/3 of the Mn^{II} ions distorts the honeycomb structure in such a way that the Mn^{II} ions are out of the plane defined by the Cr^{III} ions in contrast to other 2D oxalate structures. This effect is more important for the two heptacoordinated Mn^{II} ions (Mn2 and Mn3) that are clearly above and below the plane defined by the Cr^{III} ions (Figure 1a). The acetonitrile solvent molecules coordinated to these two Mn^{II} sites are perpendicular to the oxalate layers pointing to opposite neighboring layers (see Figure 1a). The presence of coordinated acetonitrile molecules contrasts with the other 2D oxalate network containing heptacoordinated Mn^{II} ions reported in the literature that presents also a distorted honeycomb structure. In this case, the heptacoordination is achieved by addition of one methanol solvent molecule.[11] The hexacoordinated Mn1 ion has a strong trigonal distortion of its octahedral coordination. Thus, it presents O3−Mn1−O4 angles of 147.6(2)° instead of the 180° expected for an octahedral coordination. The Mn−O distances are 2.172(6) Å (Mn1−O4) and 2.217(6) Å (Mn1−O3) Å which are similar or lightly longer to other Mn−O distances found in 2D oxalate compounds reported in the literature.[3,5] The coordination polyhedra around the heptacoordinated Mn2 and Mn3 are better described as a pointed octahedron. Thus, for both ions the six O from the three oxalate ligands form a distorted octahedron at Mn−O mean distances of 2.275(6) Å for Mn2 and 2.292(6) Å for Mn3. These distorted heptahedra are each capped with an acetonitrile molecule with Mn−N distances of 2.309(11) Å for Mn2 and 2.390(11) Å for Mn3.

These oxalate-based layers are stacked one over the other

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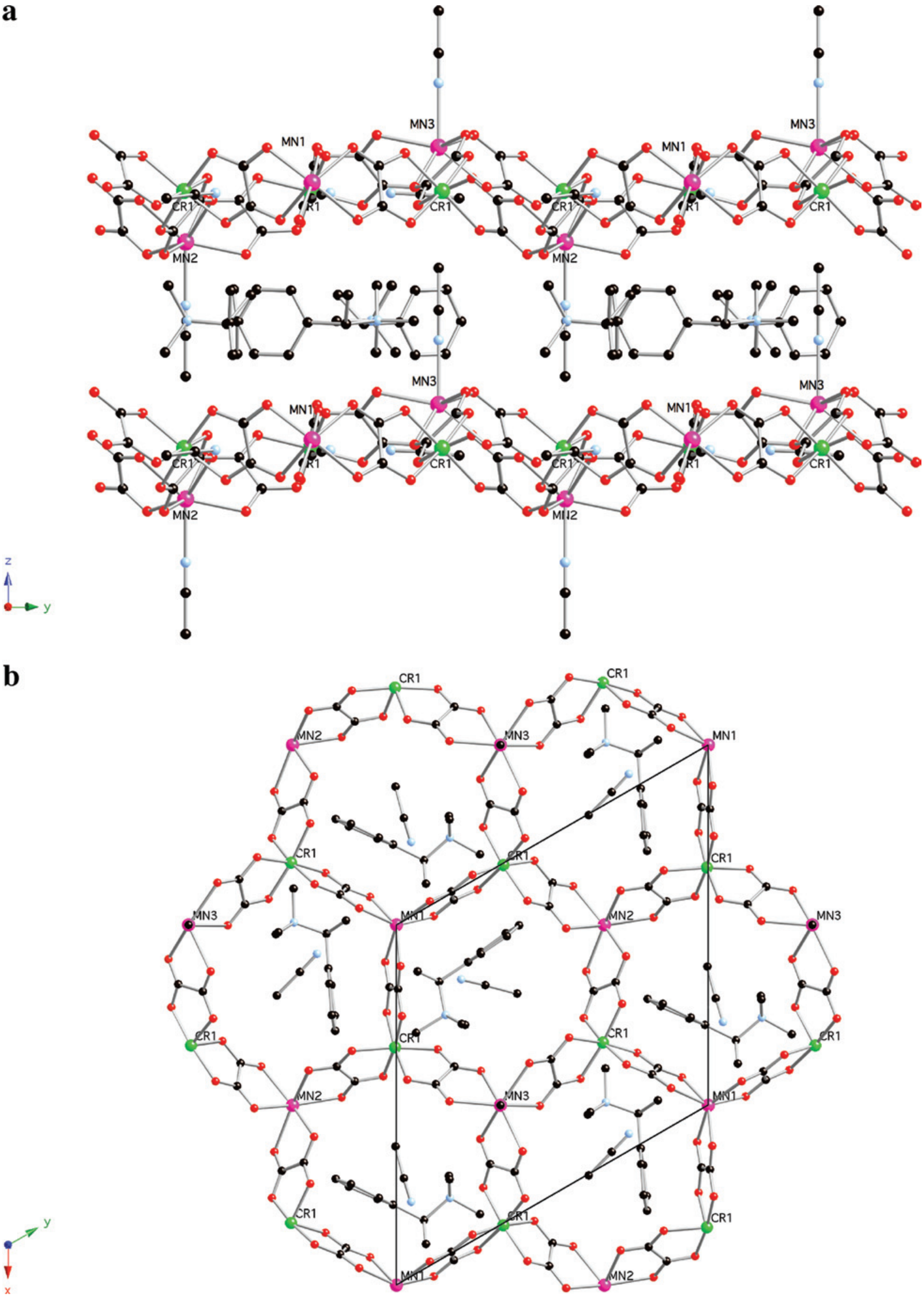

Figure 1. (a)Projection on the *bc* plane of the structure of [(*S*)-[PhCH(CH$_3$)N(CH$_3$)$_3$]][Mn(CH$_3$CN)$_{2/3}$Cr(ox)$_3$]$\cdot$(CH$_3$CN)$\cdot$(solvate). (b). Projection on the *ab* plane of the structure of [(*S*)-[PhCH(CH$_3$)N(CH$_3$)$_3$]][Mn(CH$_3$CN)$_{2/3}$Cr(ox)$_3$]$\cdot$(CH$_3$CN)$\cdot$(solvate). Disordered solvent molecules have not been drawn for clarity. Cr (green), Mn (pink), C (black), N (blue), O (red).

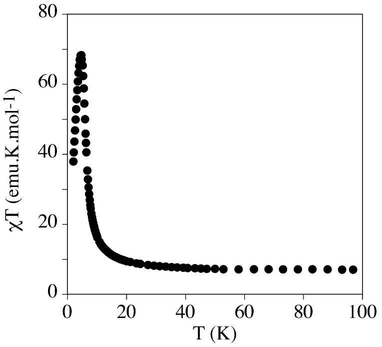

Figure 2. Temperature dependence of the χT product at 0.1 T for the [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]][Mn(CH_3CN)$_{2/3}$Cr(ox)$_3$]·(CH_3CN)·(solvate) compound.

Table 2. Magnetic Parameters for the Compound [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]][Mn(CH_3CN)$_{2/3}$Cr(ox)$_3$]·(CH_3CN)_(solvate)

T_c (K)	θ (K)	C (emu K mol^{-1})	$C_{\text{spin-only}}$ (emu K mol^{-1})	M (μ_B) at 5 T	H_{coer} (mT) at 2 K
5.6	3.8	6.27	6.25	7.35	2

in a *AA*... fashion defining hexagonal channels that are occupied by an acetonitrile molecule which is placed in the middle of the hexagonal rings of the honeycomb structure. The minimum distance between metals of different layers is 9.36 Å which is similar to that found in other oxalate-based 2D compounds with decamethylferrocenium or alkylammonium cations.[5a]

The cationic layer intercalated between these oxalate layers is formed by [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]$^+$ cations and disordered solvent molecules. The plane of the aromatic ring of [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]$^+$ cations lies perpendicular to the oxalate layer whereas the longer axis of the molecule is parallel to the oxalate layers (see Figure 1b). The aromatic ring of the [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]$^+$ cation is placed in the hexagonal channels defined by the oxalate layers. Disordered solvent molecules occupy the holes between the cations and the bimetallic oxalate network.

Magnetic Properties. Figure 2 shows the temperature dependence of the product of the magnetic susceptibility times the temperature (χT) under an applied field of 1000 G. A χT value of 6.4 emu K mol^{-1} is obtained at 300 K in agreement to the expected value for isolated paramagnetic Mn^{II} and Cr^{III} ions. A gradual increase of the χT product upon cooling is observed from 300 to 50 K. Below this temperature there is a sharp increase of the χT product. The magnetic susceptibility follows a Curie−Weiss law between 50 to 300 K with a C value of 6.27 emu K mol^{-1} and a θ value of 3.8 K (see Table 2). This indicates the presence of ferromagnetic interactions between neighboring M^{II}−Cr^{III} magnetic ions and the onset of long-range ferromagnetic ordering, as observed for other Mn^{II}Cr^{III} 2D oxalate compounds. To confirm the presence of long-range magnetic ordering and to determine precisely the critical temperature (T_c), AC susceptibility measurements were carried out. As expected for a sample presenting an ordered state, a maximum in the in-phase signal (χ') near T_c and an out-of-phase signal (χ'') that starts to appear at temperatures just below T_c is observed (Figure 3). These signals are almost frequency independent. From these data the T_c of the compound is 5.6 K. This value is in the range of those found in other Mn^{II}Cr^{III} 2D oxalate compounds. Thus, the T_c of [FeCp*$_2$][MnCr(ox)$_3$] is 5.1 K[5a] while that of of [NBu$_4$][MnCr(ox)$_3$] is 6 K,[4a] and that of ET is 5.4 K.[8] The ferromagnetic ordering is also confirmed by the field dependence of the magnetization at 2 K. It shows a sharp increase at low fields and tends to saturation above 2 T. It reaches a maximum value of 7.35 μ_B at 5 T which is slightly lower than the expected spin-only saturation value of 8 μ_B due to spin canting as usual for this type of systems.[5] The hysteresis loop at 2 K with a coercive field of 2 mT shows that this compound behaves as a soft ferromagnet (Figure 4).

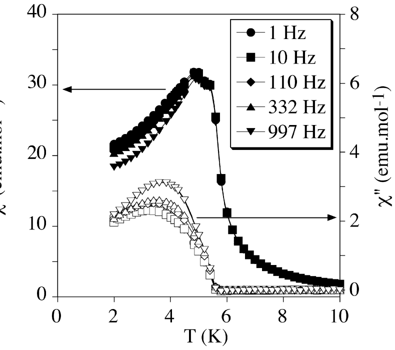

Figure 3. Frequency dependence of the in-phase AC susceptibility (χ', filled symbols) and out-of-phase AC susceptibility (χ'', empty symbols) for the [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]][Mn(CH_3CN)$_{2/3}$Cr(ox)$_3$]·(CH_3CN)·(solvate) compound.

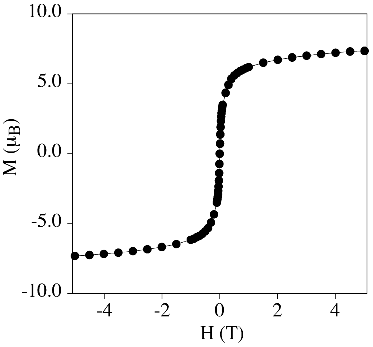

Figure 4. Field dependence of the magnetization (M) for the [(*S*)-[PhCH(CH_3)N(CH_3)$_3$]][Mn(CH_3CN)$_{2/3}$Cr(ox)$_3$]·(CH_3CN)·(solvate) compound.

All these data suggest that the magnetic behavior of this compound is very similar to that reported for other 2D oxalate networks. The different distances and angles of this distorted 2D oxalate network and the changes in symmetry of the magnetic orbitals caused by the heptacoordination of 2/3 of Mn^{II} ions do not cause any significant change in the magnetic properties. Thus, this compound behaves as a soft ferromagnet with a T_c very close to that of other Mn^{II}Cr^{III} 2D oxalate networks. This contrasts to that observed for the other 2D oxalate network containing heptacoordinated Mn^{II} ions that presents antiferromagnetic interactions between neighboring Mn^{II} and Cr^{III} centers.[11] This is explained by the fact that one of the oxalate Mn−Cr bridges of this last compound is not a pure bis-bidentate but it is close to a bis-monodentate-bridge. Mn−Cr interaction has been found to be antiferromagnetic in other oxalate-based compounds with the oxalate bridging in a bis-monodentate mode.[28] Therefore, it seems that the different connectivity of the oxalate ligand has stronger influence in the magnetic behavior of the oxalate network than the changes in symmetry of the magnetic orbitals caused by heptacoordination of Mn^{II} ions. This is not unexpected as in Mn^{II} the five magnetic orbitals are active, so the exchange interactions involving this isotropic ion should not be very sensitive to the distortion of the metal site.

Conclusion

The title compound is the first chiral compound presenting a 2D oxalate structure. The use of a chiral quaternary ammonium templating cation results in a novel structure that contains only one of the two enantiomers of the $[Cr(ox)_3]^{3-}$ anion due probably to chiral recognition with the chiral templating cation. To confirm this point the synthesis of the analogous compound with the (*R*)-enantiomer of the templating cation is under progress. On the other hand, the chirality (opposite) of the neighboring Mn centers observed in the typical 2D oxalate network is lost in this structure. This is due to the addition of solvent molecules (acetonitrile) that give rise to heptacoordination of 2/3 of the Mn and to the trigonal distortion of the remaining 1/3 of Mn that are hexacoordinated. The presence of acetonitrile molecules coordinated to Mn is also a novel structural aspect of this compound. Still, these structural differences with the other well-known 2D networks (chirality, distortions in the 2D honeycomb lattice and heptacoordination around Mn) seem to have little effect on the magnetic properties. The search for new magnetic effects derived from the chirality of the lattice, such as the magneto-chiral effect predicted by Rikken et al.[1] remains to be explored. In this context, the preparation of the analogous antiferromagnet $Fe^{III}Mn^{II}$ should be of major interest because it should provide the opportunity to measure the spin canted structure in this chiral and very distorted structure.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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