

(S)-(–)-(2-MeBu)N(Pr)₂MeI Salt as Template in the Enantioselective Synthesis of the Enantiopure Two-dimensional (S)-(–)-(2-MeBu)N(Pr)₂Me[ΔMnΔCr(C₂O₄)₃] Ferromagnet

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ABSTRACT We describe herein the synthesis of (*rac*)- or enantiopure (S)-(–)-(2-MeBu)N(Pr)₂MeI ammonium salts. These racemic and enantiopure ammonium salts were used as cationic templates to obtain new two-dimensional (2D) ferromagnets [(*rac*)-(2-MeBu)N(Pr)₂Me][MnCr(C₂O₄)₃] and [(S)-(–)-(2-MeBu)N(Pr)₂Me][ΔMnΔCr(C₂O₄)₃]. The absolute configuration of the hexacoordinated Cr(III) metallic ion in the enantiopure 2D network was determined by a circular dichroism measurement. The structure of [(2-MeBu)N(Pr)₂Me][MnCr(C₂O₄)₃], established by single crystal X-ray diffraction, belongs to the chiral *P*6₃ space group. According to direct current (dc) magnetic measurements, these compounds are ferromagnets with a temperature T_c = 6°K. *Chirality* 00:000–000, 2013. © 2013 Wiley Periodicals, Inc.

KEY WORDS: ammonium salts; ferromagnets; 2D chiral networks

INTRODUCTION

Our interest in optically active ammonium salts is part of a general strategy to synthesise optically active molecular magnets.^{1–3} One of the goals of this approach is to study the magnetochiral dichroism (MChD)^{4–7} resulting from the simultaneous breaking of spatial and time symmetries in the studied material. Recently we have discovered that 2D optically active single crystals belonging to the *P*6₃ space group are efficient materials to study the MChD effect along the *c*-axis of the crystal.^{8,9} In these single crystals of formula [(S)-NMe(Pr)₂(*sec*-Bu)][ΔMnΔCr(C₂O₄)₃] and [(R)-NMe(Pr)₂(*sec*-Bu)][ΔMnΔCr(C₂O₄)₃], the asymmetric hexacoordinated Cr^{III} centres show a Cotton effect at 550 nm resulting from the Cr–Cr* transition. They are also interacting with Mn^{II} centres through the oxalate ligands giving birth to a long-range ferromagnetic ordering (LRFO) below 7°K. This latter point is of first importance because it causes a dramatic magnification of the MChD at low temperature. Moreover, following the association of a non-centrosymmetric space group and LRFO, this material also exhibits a large magnetization-induced second harmonic generation.¹⁰

The chemistry of 2D [Mn^{II}Cr^{III}] oxalate-based networks is very well documented.^{2,11} These 2D networks are composed of anionic layers alternating with cationic ones. In these structures the relative configurations of the adjacent coordinated M₁ and M₂ metallic ions are opposite (Δ, Λ)* leading to a honeycomb (6,3) organisation (Fig. 1).

We have previously demonstrated that such 2D bimetallic networks of general formula [NR₄][M^{II}M^{III}(C₂O₄)₃], in which metallic ions are connected by oxalate ligands, can be chiral¹² and obtained in their enantiopure forms.^{8,13,14} In this latter case a diastereomeric relationship exists between the absolute configurations of the cationic template and the hexacoordinated Cr^{III} ion in the adjacent anionic network. Such enantiopure

2D networks can be reached using either optically active K₃Cr(C₂O₄)₃ anionic bricks or cationic templates.¹⁴ The cationic templates used in the reaction: C⁺ + M(II)²⁺ + [M^{III}(C₂O₄)₃]³⁻ = [C][M^{II}M^{III}(C₂O₄)₃] are usually tetra-alkyl ammonium salts of the general formula NR¹R²R³R⁴I.² Because of the fast racemisation of K₃Cr(C₂O₄)₃ in solution,¹⁵ we chose to develop enantioselective templated-assembly of these compounds starting from enantiopure chiral template cations. Taking in account the difficult resolution of chiral ammonium salts in which the chiral centre is the nitrogen atom itself, we decided to synthesise ammonium salts with a chiral carbon centre located on an alkyl chain on the nitrogen atom as is the case for (S)-NMe(Pr)₂(*sec*Bu)I and (R)-NMe(Pr)₂(*sec*Bu)I.¹⁶

In this way we have previously prepared optically active single crystals of opposite configurations [(S)-NMe(Pr)₂(*sec*-Bu)][ΔMnΔCr(C₂O₄)₃] and [(R)-NMe(Pr)₂(*sec*-Bu)][ΔMnΔCr(C₂O₄)₃].⁸ In these compounds, the ammonium cations were disordered. In order to increase the crystallographic discrimination between the alkyl side chains, we decided to synthesise [(S)-(–)-(2-MeBu)N(Pr)₂Me][ΔMnΔCr(C₂O₄)₃] using the (S)-(–)-(2-MeBu)N(Pr)₂MeI ammonium salt as template (unfortunately the (R)-amine is not available). We describe here our efforts in this perspective.

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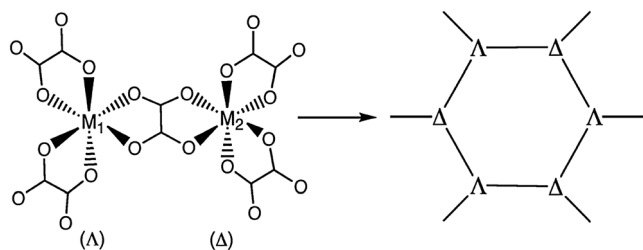


Fig. 1. Heterochiral configurational arrangement of the adjacent hexacoordinated metal ions ($M_1 = \text{Fe}^{\text{II}}, \text{Mn}^{\text{II}}; M_2 = \text{Cr}^{\text{III}}$) leading to a 2D honeycomb structure.

MATERIALS AND METHODS

All the chemicals used for the present study were purchased from commercial sources and were used without any further purification. Elemental analyses were carried out at the IPCP, Chernogolovka, Moscow region for C, H, N and I. The infra-red (IR) spectra were recorded in KBr pellets with a Bio-Rad IRFT spectrophotometer in the 4000–400 cm^{-1} range. $^1\text{H-NMR}$ spectra were recorded on a Bruker AC 300 spectrometer.

XRD studies were performed on a CCD diffractometer Agilent XCalibur with a detector EOS (Agilent Technologies UK, Yarnton, Oxfordshire, England). Collection, data processing, and refinement of unit cell parameters were performed with CrysAlis PRO program.¹⁷

The magnetization of the powder sample was measured using a Quantum Design MPMS-XL7 SQUID magnetometer down to 2°K and up to 7 T. The data were corrected from the diamagnetic contributions of both the sample and the PVC film wrapping it.

Synthesis

(rac)-(2-methylbutyl)dipropylamine. To a mixture of 2.02 g (0.02 mol) of dipropylamine in 5 mL of methanol and 5 mL of dichloromethane cooled in an ice bath and slowly stirred was added dropwise a solution of 2 g (0.023 mol) of 2-methylbutanol in 5 mL of methanol. The reaction mixture was stirred for 30 min at room temperature, then cooled and 5.3 g (25 mmol) of sodium triacetoxyborohydride $[\text{NaBH}(\text{OAc})_3]$ were added in small portions. The mixture was stirred for 1 hour at room temperature and then three small portions were added, alternately, of 2-methylbutanol (~0.4 mL) and $\text{NaBH}(\text{OAc})_3$ (~0.16 g). The mixture was stirred for additional 3 hours. Then the pH was adjusted to 14 by addition of 11 mL of 10% vol. aqueous NaOH. The product was extracted with diethyl ether (3 × 15 mL). The organic phase was dried with anhydrous sodium sulfate. The solvent and volatile byproducts were distilled at atmospheric pressure. The residue was distilled under vacuum. The fraction (2 g) with a boiling point of 44–45°C under 1 mm Hg, identified as the (2-methylbutyl)dipropylamine, was obtained in 58% yield.

Analysis: calculated for $\text{C}_{11}\text{H}_{25}\text{N}$ %: C 77.12; H 14.71; N 8.18. Found: C 77.06; H 14.59; N 8.56.

IR, $\nu \text{ cm}^{-1}$: 2959 ($\nu_{\text{as}} \text{CH}_3$), 2934 ($\nu_{\text{as}} \text{CH}_2$), 2874 ($\nu_{\text{sym}} \text{CH}_3$), 2799 ($\nu_{\text{sym}} \text{CH}_2$), 1463 ($\delta_{\text{as}} \text{CH}_3 + \delta \text{CH}_2$), 1379 ($\delta_{\text{sym}} \text{CH}_3$).

(rac)-(2-methylbutyl)dipropylmethylammonium iodide. To a solution of 2 g (0.0117 mol) (2-methylbutyl)dipropylamine in 50 mL of toluene was added a solution of 1.8 g (0.0126) of iodomethane in 50 mL of toluene. The reaction mixture was refluxed for 3 hours. During the reaction, the (2-methylbutyl)dipropylmethylammonium iodide salt precipitated. The final product was filtered and dried. The yield in (2-methylbutyl)dipropylmethylammonium iodide was 2.9 g (79%).

Analysis: calculated for $\text{C}_{12}\text{H}_{28}\text{NI}$ %: C 46.01; H 9.01; N 4.47; I 40.51. Found: C 45.77; H 9.11; N 4.45; I 40.10.

$^1\text{H-NMR}$ (CDCl_3), δ (ppm): 0.97 (t, 3H, $\delta\text{-CH}_3$, 2-MeBu); 1.04 (m, 6H, $\gamma\text{-CH}_3$, Pr); 1.14 (d, 3H, $\gamma\text{-CH}_3$, 2-MeBu); 1.40 (m, 1H, $\gamma\text{-CH}_2$, 2-MeBu); 1.53 (m, 1H, $\gamma\text{-CH}_2$, 2-MeBu); 1.76 (m, 4H, $\beta\text{-CH}_2$, Pr), 1.98 (m, 1H, $\beta\text{-CH}$, 2-MeBu); 3.2 (a, 3H, N-CH₃); 3.20–3.40 (m, 6H, N-CH₂).

IR, $\nu \text{ cm}^{-1}$: 2967 ($\nu_{\text{as}} \text{CH}_3$), 2937 ($\nu_{\text{as}} \text{CH}_2$), 2878 ($\nu_{\text{sym}} \text{CH}_3$), 1464 ($\delta_{\text{as}} \text{CH}_3$), 1383 ($\delta_{\text{sym}} \text{CH}_3$).

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(S)-(2-methylbutyl)dipropylmethylammonium iodide. This compound was synthesised starting from the (S)-2-methylbutylamine according to Reference 16.¹⁶ A 3 mL methanolic solution of propanal (0.72 g, 12.5 mmol) was added dropwise to an ice-cooled solution of (S)-2-methylbutylamine (1 g, 11.5 mmol) in methanol (3 mL). After an hour of stirring at room temperature, the resulting (S)-(2-methylbutyl)propylamine was reduced with sodium borohydride (0.47 g, 12.5 mmol), which was added in small portions to the ice-cooled solution. The resulting mixture was stirred for 2 hours at room temperature, to give (S)-(2-methylbutyl)propylamine. The pH of the solution was set to 14 by adding 0.8g of NaOH dissolved in 20 mL of water. The secondary amine was extracted with diethyl ether and purified by distillation.

A 2.5 mL methanolic solution of propanal (0.72 g, 12.5 mmol) was added dropwise to an ice-cooled solution of (S)-(2-methylbutyl)propylamine dissolved in a mixture of methanol (2.5 mL) and dichloromethane (5 mL). After half an hour of stirring at room temperature, sodium triacetoxyborohydride (3 g) was added in small portions, to the ice-cooled solution. After 15 min, three extra portions of propanal (0.03 g) and $[\text{NaBH}(\text{OAc})_3]$ (0.16 g) were alternately added over a period of 1 hour. The resulting mixture was stirred for 3 hours at room temperature to give (S)-(2-methylbutyl)dipropylamine. The pH of the solution was set to 14 by adding 1.6 g of NaOH dissolved in 40 mL of water. The tertiary amine was extracted with diethyl ether and purified by distillation.

The quaternary ammonium salt (1.4 g; 70% yield) was obtained in the same way as the racemic one. IR and $^1\text{H NMR}$ spectra are consistent with those obtained for the racemic salt. The absolute rotation was found as $[\alpha]_{\text{D}}^{20} = -19.8$ (0.5, CH_2Cl_2).

$[(2\text{-MeBu})\text{N}(\text{Pr})_2\text{Me}][\text{MnCr}(\text{C}_2\text{O}_4)_3]$. To a solution of 0.205 g (0.5 mmol) $(\text{NH}_4)_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 2 \text{H}_2\text{O}$ in 1 mL of water, were added 0.125 g (0.5 mmol) of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and a solution 0.235 g (0.75 mmol) of $[(2\text{-MeBu})(\text{Pr})_2\text{NMe}]\text{I}$ in 1 mL of methanol. The reaction mixture was left for one day. The resulting precipitate was separated, washed with methanol-water (1: 2) mixture and air-dried (yield 0.176 g (63%) of product).

IR, $\nu \text{ cm}^{-1}$: 1630 ($\nu_{\text{as}} \text{C}=\text{O}$), 1388 ($\nu_{\text{sym}} \text{C}=\text{O}$); 1259, 1078, 812.

Crystals for X-ray analysis were obtained using a gel technique. To a solution of 0.12 g (0.3 mmol) of $(\text{NH}_4)_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 2 \text{H}_2\text{O}$ and 0.08 g (0.32 mmol) of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 1 mL of water was added 1 mL of $\text{Si}(\text{OCH}_3)_4$ and then 1 mL of methanol. The mixture was stirred until obtention of a homogenous solution, then divided into 2 equal portions. A day was necessary to obtain a gel. To each portion of the gel, a solution of 0.055 g (0.18 mmol) of $[(2\text{-MeBu})(\text{Pr})_2\text{NMe}]\text{I}$ in 30 drops of methanol + 10 drops of water was added. After a few days crystals suitable for X-ray diffraction were obtained.

Single Crystal X-ray Diffraction

Crystals of compound $[(2\text{-MeBu})\text{NPr}_2\text{Me}][\text{MnCr}(\text{C}_2\text{O}_4)_3]$ synthesised from the racemic ammonium (2-MeBu) NPr_2Me I salt are twinned and formed as thin hexagonal-shaped plates.

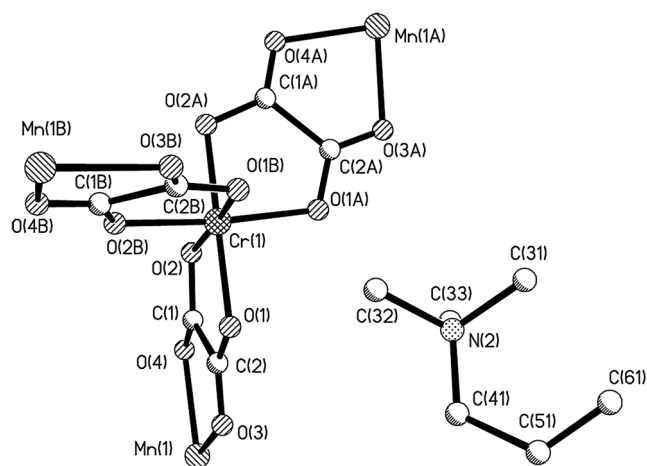
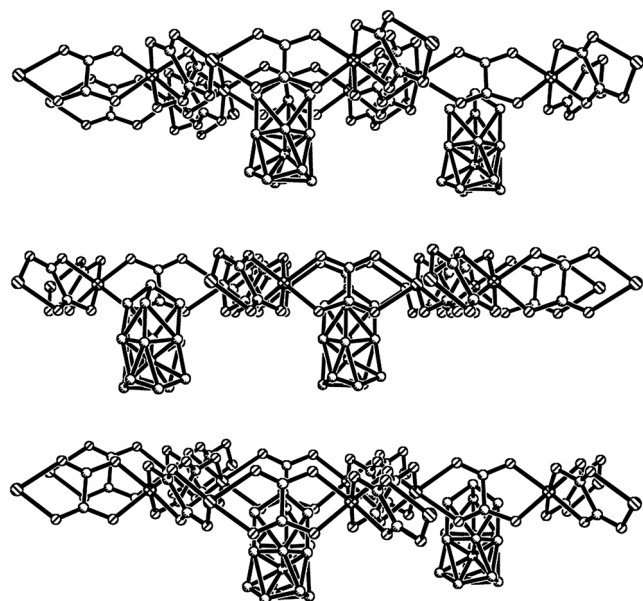
The single crystal X-ray diffraction experiments were performed at 100, 150 and 260°K. The quality of the crystals decreases slightly when decreasing the temperature but, in this temperature range, no structural change related to a phase transition was observed. The evolution of the cell parameters, which is more important for the *c* parameter, is solely related to the thermal expansion (Table 1).

The chiral space group found at 100, 150 and 260°K indicates that a spontaneous resolution takes place during the crystal growth. According to powder X-ray diffraction, this statement also holds for microcrystalline powders.

The refinement of the structure shows that the anionic part is a honeycomb network. Due to the poor quality of the crystals and the location of the asymmetric cation on the third order axis, correct coordinates of the ammonium cation cannot be obtained. The analysis of Fourier syntheses revealed that the crystal is a racemic twin. For one chiral anionic layer, two types of cations are present on either side of the layer. The cations are located over the Cr atoms. Figure 2 shows a fragment of a possible variant of the cation and Figure 3 shows a portion of the crystal structure.

TABLE 1. Thermal evolution of the crystallographic parameters of [(2-MeBu)NPr₂Me][MnCr(C₂O₄)₃]

T / K	100	150	260
space group	<i>P</i> 6 ₃	<i>P</i> 6 ₃	<i>P</i> 6 ₃
<i>a</i> = <i>b</i> / Å	9.36501(5)	9.3625(4)	9.3780(5)
<i>c</i> / Å	16.541(1)	16.608(1)	16.916(1)
$\alpha = \beta$ / °	90	90	90
γ / °	120	120	120

**Fig. 2.** View of a part of the anionic layer and the related cation.**Fig. 3.** A variant of the *bc* projection of crystal structure along the *a*-axis. The cations are orientationally disordered along the *c*-axis.

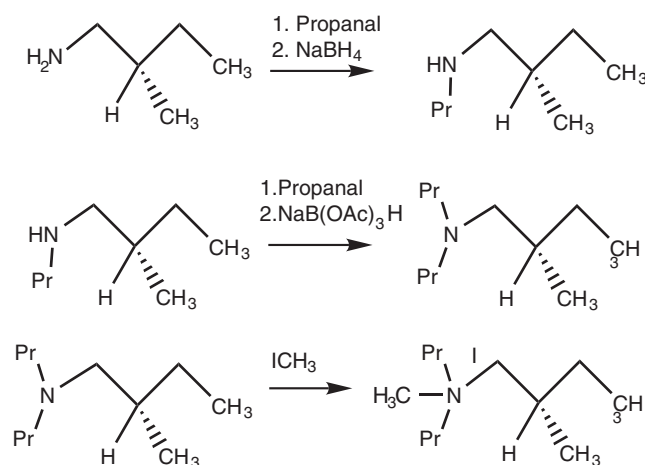
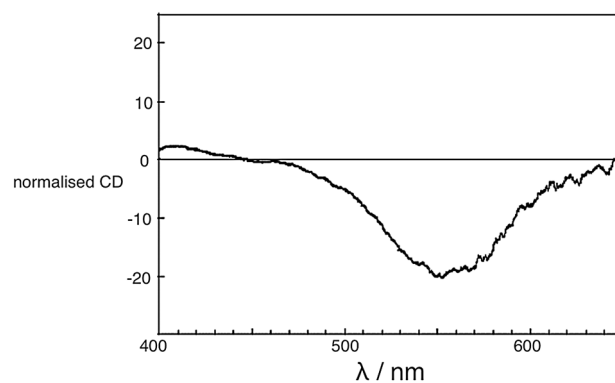
Selected bond distances (T = 260K) Cr(1)-O(1) 2.00(1) Å, Cr(1)-O(2) 1.96(1) Å, Mn(1)-O(3) 2.20(1) Å, Mn(1)-O(4) 2.16(1) Å, O(1)-C(2) 1.27(1) Å, O(2)-C(1) 1.35(1) Å, O(3)-C(2) 1.19(1) Å, O(4)-C(1) 1.27(1) Å, C(1)-C(2) 1.59(2) Å. Atoms Cr and N lie on the crystallographic 3-fold axis. Distance between Cr(1) and N(2) is 5.27 Å, it is ~2/3 of the distance between two anionic layers.

RESULTS AND DISCUSSION

The syntheses of the ammonium salts were performed for the racemic and the (*S*) configuration starting from the dipropylamine or the (*S*)-(-)-2-methylbutylamine respectively. For the racemic compounds the addition of 2-methylbutanal to the dipropylamine leads to the imine addition product which is reduced in the tertiary amine using [NaH(OAc)₃]. Finally the ammonium salt is obtained by quaternisation of the tertiary amine using methyl iodide. Synthesis of the enantiopure ammonium salt differs by the starting amine. In this case, it is the (*S*)-(-)-2-methylbutylamine. Two successive additions of propanal followed by hydride reduction and subsequent quaternisation lead to expected (*S*)-ammonium iodide (Scheme 1).

The ammonium salts were obtained in 50% overall yield and used after crystallisation using a Et₂O/CH₂Cl₂ mixture. The absolute rotation of the (*S*)-(-)-2-MeBuN(Pr)₂MeI was found as $[\alpha]_D^{20} = -19.8$ (0.5, CH₂Cl₂).

Starting from the racemic or the optically active ammonium salt, the crystals obtained in the reaction with Mn(NO₃)₂ and (NH₄)₃Cr(C₂O₄)₃ salts using the gel technique belong to the chiral *P*6₃ space group. Using the optically active ammonium salt leads to optically active network in which the absolute configuration of the hexacoordinated Cr^{III} ions was assessed

**Scheme 1.** Synthesis of the enantiopure (*S*)-(-)-2-MeBuN(Pr)₂Me Iodide.**Fig. 4.** CD curve obtained for the [(*S*)-(-)-2-MeBuN(Pr)₂Me][AMnΔCr(C₂O₄)₃] (2.5 mg in 150 mg KBr).

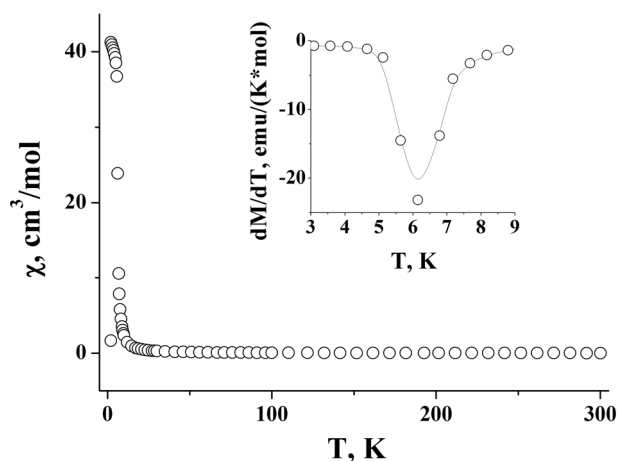


Fig. 5. Temperature dependence of magnetic susceptibility χ . Inset: temperature dependence of the derivative of magnetisation on temperature.

by CD measurements showing a negative Cotton effect at 555 nm attributed to the Cr-Cr* transition (Figure 4). This result confirms that (S)-(-)-(2-MeBu)N(Pr)₂MeI ammonium salt in which the length of the stereogenic chain differs only by one carbon and by the relative position β or γ from the nitrogen atom of the chiral centre from the (S)-NMe(Pr)₂(*sec*-Bu)I, previously used, has the same enantioselective templating effect in the network building: the (S) configuration of the stereogenic centre leads to the Δ configuration for the hexacoordinated Cr^{III} ions in the 2D network and consequently to the opposite Λ configuration for the hexacoordinated Mn^{II} ions.

Magnetic Measurements

At room temperature, the χT product, χ being the molar magnetic susceptibility per Mn-Cr unit, is equal to 6.6 cm³/(mol K). This is close to the calculated value of 6.25 cm³/(mol K) for paramagnetic non-interacting Mn²⁺ ($S = 5/2$) and Cr³⁺ ($S = 3/2$) ions assuming $g = 2$ for both ions. Temperature dependence of magnetic susceptibility χ at $T = 300$ – 20 K obeys the Curie-Weiss law with a Weiss temperature $\Theta = 6.55$ K. This is the signature of nearest neighbours ferromagnetic interaction between the Cr^{III} and Mn^{II} ions. A sharp increase of the susceptibility is observed below 20 K due to a transition

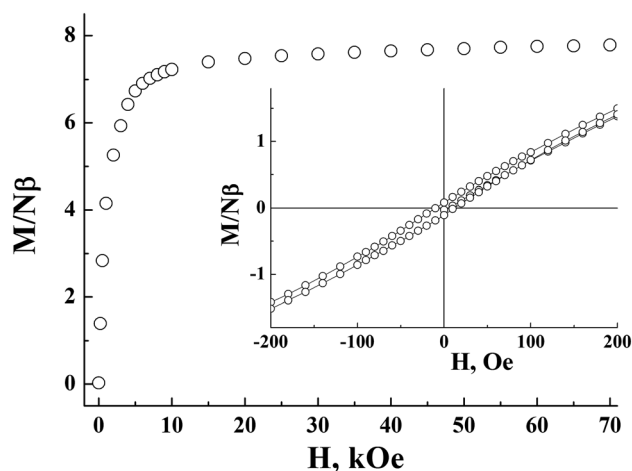


Fig. 6. Field dependence of magnetisation at $T = 2$ K. Inset: low-field part of hysteresis loop.

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to LRFO (Fig. 5). The Curie temperature determined at the minimum position of $(dM/dT)^{-1}$ thermal dependence is equal to 6 K (inset of Fig. 5).

Field dependence of the magnetisation at $T = 2$ K shows a sharp increase of the magnetisation that rapidly reaches a saturation value of 7.8 μ_B (Fig. 6). This saturation value is in good agreement with the value of 8 μ_B expected for ferromagnetically aligned Mn²⁺ and Cr³⁺ ions. The small value of coercivity $H_c = 10$ Oe points out the magnetic softness of the material (inset of Fig. 6).

CONCLUDING REMARKS

We have described the synthesis of a new ammonium iodide salt both in its racemic and optically active forms. This salt is able to template enantioselectively the formation of a bimetallic oxalate-bridged network. The diastereomeric relation between the stereogenic centre of the ammonium and the hexacoordinated Cr atom in the 2D network was established as (S)- Δ . The interaction between Cr^{III} and Mn^{II} centres is ferromagnetic and the transition from paramagnetic to ferromagnetic state occurs at 6 K.

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