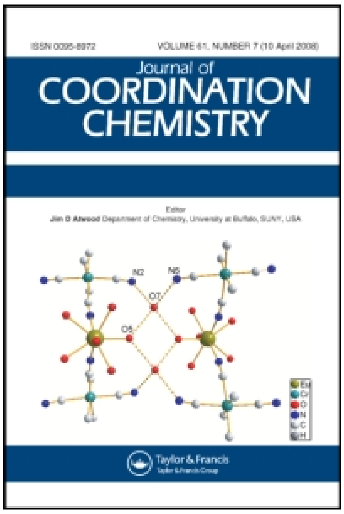

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Unexpected formation of chiral single crystals of {NH(*n*-$C_3H_7)_3[Mn^{II}Cr^{III}(C_2O_4)_3]$}, A 2D oxalate-based material

G. V. Shilov[a]; N. S. Ovanesyan[a]; S. M. Aldoshin[a]; M. Gruselle[b]; C. Train[b]; C. Guyard-Duhayon[b]
[a] Institute of Problems in Chemical Physics, Russian Academy of Science, Moscow Region, 142432 Chernogolovka, Russia [b] Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR-CNRS 7071, Université Pierre et Marie Curie, 4 place Jussieu, F-75252 Paris Cedex 05, France

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UNEXPECTED FORMATION OF CHIRAL SINGLE CRYSTALS OF $\{NH(n\text{-}C_3H_7)_3[Mn^{II}Cr^{III}(C_2O_4)_3]\}$, A 2D OXALATE-BASED MATERIAL

G.V. SHILOV[a], N.S. OVANESYAN[a,*], S.M. ALDOSHIN[a], M. GRUSELLE[b],
C. TRAIN[b] and C. GUYARD-DUHAYON[b]

[a]*Institute of Problems in Chemical Physics, Russian Academy of Science, Moscow Region, 142432 Chernogolovka, Russia;* [b]*Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR-CNRS 7071, Université Pierre et Marie Curie, case courrier 42, 4 place Jussieu, F-75252 Paris Cedex 05, France*

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In an attempt to obtain chiral single crystals of a two-dimensional (2D) bimetallic oxalate-based material by enantioselective auto-assembling of Mn^{2+} and (*rac*)-$[Cr(C_2O_4)_3]^{3-}$ templated by the optically active complex (+)-(*Rp*)-$[1\text{-}CH_2(n\text{-}C_3H_7)_3\text{-}2\text{-}CH_3(C_5H_3)Fe(C_5H_5)]^+$, we obtained the unexpected 2D network species $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$. X-ray diffraction determination of the structure reveals that the complex crystallizes in the enantiomorphous space group $P6_3$. The interlayer spacing of 7.93 Å is the lowest found so far for 2D, bimetallic, oxalate-bridged compounds.

Keywords: Chirality; Oxalate; 2D networks; Enantioselectivity; Self-assembling; Crystal structure

EXPERIMENTAL

Synthesis

The salt (+)-(*Rp*)-$\{[1\text{-}CH_2N(n\text{-}C_3H_7)_3\text{-}2\text{-}CH_3(C_5H_3)Fe(C_5H_5)]^+I^-\}$ was synthesized through a classical asymmetric cyclopalladation reaction [1] followed by carboxylation in methanol. Reduction of the ester group was achieved in two steps using $LiAlH_4$ and then $NaBH_4$ with CF_3CO_2H according to a modified Kursanov–Parnes reaction [2]. The title compound was obtained according to a published method [3].

Single crystals suitable for X-ray determination were obtained using a gel technique. Some 100 mg of $(NH_4)_3Cr(C_2O_4)_3 \cdot 3H_2O$ dissolved in 7 cm^3 of water was added to a mixture of 7 cm^3 of $SiOMe_4$ and 7 cm^3 of MeOH. The final mixture was poured into tubes. After two days at room temperature, a gel was obtained. Subsequently, 22 mg of (+)-(*Rp*)-$\{[1\text{-}CH_2N(n\text{-}C_3H_7)_3\text{-}2\text{-}CH_3(C_5H_3)Fe(C_5H_5)]^+I^-\}$ and 10 mg of $Mn(NO_3)_2 \cdot 6H_2O$ dissolved in 2 cm^3 of MeOH were added to the gels. After several weeks, crystallization of $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$ occurred.

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*Corresponding author. E-mail: ovanesyan@icp.ac.ru

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X-ray Determination

The crystal structure of the compound was determined from single-crystal X-ray diffraction data collected at room temperature. The data were collected on a truncated, pyramidal-shaped single crystal of dimensions 0.05 × 0.05 × 0.15 mm using a KM-4 automated four-circle diffractometer (Mo Kα radiation, $\omega/2\theta$ scan mode in the range $0 < \theta < 35°$, graphite monochromator). Lattice parameters were initially derived from the setting angles of 25 reflections. An experimental array of 450 reflections with $I > 2\sigma(I)$ was used to determine the structure, which was solved by direct methods using SHELXL-93 [4] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97 [5]. Atoms of the anion and the nitrogen of the cation were refined with anisotropic temperature factors while the carbon atoms of the cation were derived from difference Fourier syntheses and refined in the anisotropic approximation with constraints of bond lengths. Crystals of $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$ belong to the hexagonal space group $P6_3$, with $a = 9.353(1)$, $c = 15.850(3)$ Å and $Z = 2$. Crystallographic parameters are listed in Table I, and significant interatomic distances and bond angles are given in Table II.

TABLE I Crystal structure information for $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$

Formula	$C_{15}H_{22}CrMnNO_{12}$
Crystal class	Hexagonal
Space group	$P6_3$
a (Å)	9.353(1)
b (Å)	9.353(1)
c (Å)	15.850(3)
V (Å^3)	1200.8(3)
Z	2
λ (Å)	0.710730
ρ_{calc} (Mg m^{-3})	1.43
M (g mol^{-1})	515.28
μ (Mo Kα) (mm^{-1})	1.03
Temperature (K)	293
Size (mm)	0.015 × 0.015 × 0.15
Color	Pale green
Shape	Pyramidal
Diffractometer type	KM-4
Scan type	$\omega/2\theta$
Reflections measured	2266
*R*int	0.06
Theta min, max	2, 26
*h*min, *h*max	–11, 10
*k*min, *k*max	0, 11
*l*min, *l*max	0, 13
Refinement	on F^2
R factor*	0.0572
Weighted *R* factor**	0.1312
Delta rho min (e Å^{-3})	–0.39
Delta rho max (e Å^{-3})	0.43
Reflections used	727
$\sigma(I)$ limit	2.00
Number of parameters	110
Goodness of fit	1.012

$^*R = \Sigma\|F_0| - |F_c\|/\Sigma|F_0|$. $^{**}Rw = [\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^{\,2}]^{1/2}$.

TABLE II Selected bond lengths (Å) and angles (°) for $\{NH(n\text{-}C_3H_7)_3[MnCr(ox)_3]\}$

Cr(1)–O(1)	1.958(6)	Mn(1)–O(4)	2.172(7)
Cr(1)–O(1^a)	1.958(6)	Mn(1)–O(4^c)	2.172(7)
Cr(1)–O(1^b)	1.958(6)	Mn(1)–O(4^d)	2.172(7)
Cr(1)–O(2)	1.976(7)	Mn(1)–O(3)	2.189(7)
Cr(1)–O(2^a)	1.976(7)	Mn(1)–O(3^c)	2.189(7)
Cr(1)–O(2^b)	1.976(7)	Mn(1)–O(3^d)	2.189(7)
N(1)–C(31)	1.49(3)	O(1)–C(1)	1.256(8)
N(1)–C(31^a)	1.49(3)	O(2)–C(2)	1.282(10)
N(1)–C(31^b)	1.49(3)	O(3)–C(1)	1.229(9)
N(1)–C(61)	1.52(3)	O(4)–C(2)	1.237(11)
N(1)–C(61^a)	1.52(3)	C(2)–C(1)	1.505(13)
N(1)–C(61^b)	1.52(3)		
O(1^a)–Cr(1)–O(1)	94.1(3)	O(4^c)–Mn(1)–O(4)	96.8(3)
O(1^b)–Cr(1)–O(1)	94.1(3)	O(4^c)–Mn(1)–O(4^d)	96.8(3)
O(1^a)–Cr(1)–O(1^b)	94.1(3)	O(4)–Mn(1)–O(3)	76.8(2)
O(1)–Cr(1)–O(2^a)	173.1(3)	O(4)–Mn(1)–O(3^c)	92.8(2)
O(1^a)–Cr(1)–O(2^a)	83.0(2)	O(4^c)–Mn(1)–O(3)	169.0(2)
O(1^b)–Cr(1)–O(2^a)	92.3(2)	O(4^c)–Mn(1)–O(3^c)	76.8(2)
O(1^a)–Cr(1)–O(2)	92.3(2)	O(4^d)–Mn(1)–O(3)	92.8(2)
O(1^b)–Cr(1)–O(2)	173.1(2)	O(4^d)–Mn(1)–O(3^c)	169.0(2)
O(1)–Cr(1)–O(2)	83.0(2)	O(3)–Mn(1)–O(3^c)	94.5(3)
O(2^a)–Cr(1)–O(2)	90.9(4)	O(3)–Mn(1)–O(3^d)	94.5(3)
O(1)–Cr(1)–O(2^b)	92.3(2)	O(3^c)–Mn(1)–O(3^d)	94.5(3)
O(1^a)–Cr(1)–O(2^b)	173.1(2)	O(4)–Mn(1)–O(3^d)	169.0(2)
O(1^b)–Cr(1)–O(2^b)	83.0(2)	O(4^c)–Mn(1)–O(3^d)	92.8(2)
O(2)–Cr(1)–O(2^b)	90.9(4)	O(4^d)–Mn(1)–O(3^d)	76.8(2)
O(2^a)–Cr(1)–O(2^b)	90.9(3)	O(4)–Mn(1)–O(4^d)	96.8(3)

Symmetry transformations used to generate equivalent atoms are $^a -x+y,\ -x+1,\ z$; $^b -y+1,\ x-y+1,\ z$; $^c -y,\ x-y,\ z$; $^d -x+y,\ -x, z$.

RESULTS AND DISCUSSION

Crystal Structure

The crystal structure of $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$ shows a stack of anionic layers parallel to the *ab* crystallographic plane with an interlayer spacing of 7.93 Å. The anionic layer presents a honeycomb structure. The corners of the hexagons are occupied successively by Mn^{II} and Cr^{III} ions. In some previously determined crystal structures of such compounds with bimetallic oxalate networks, the assignment of Mn^{II} and Cr^{III} (or Fe^{III}) to a definite position from interatomic distances was often in question due to crystal twinning phenomena for both racemic and chiral crystals [6]. In the present case, the metal to oxygen distances being 2.17(1) and 1.96 Å (Table II), we can clearly distinguish between the Mn^{II} and Cr^{III} ions. In a given anionic layer, the two metal ions have opposite configurations. According to the value of the Flack parameter [7], Mn^{II} ions adopt a Λ configuration while the Cr^{III} ions adopt a Δ configuration (Fig. 1). Starting from one anionic layer, the second is obtained by a rotation of $2\pi/6$ around Mn^{II} followed by a translation by one-half along *c*. Each metal ion therefore adopts the same configuration in all layers.

As the Mn^{II} ions are located on the helicoidal axis, they lie one above the other while the Cr^{III} ions are situated over a hexagonal cell of a neighboring layer. $NH(n\text{-}C_3H_7)_3$ cations are located between the anionic layers. From a crystallographic point of view, there are two possible positions for the ammonium cation; the nitrogen atom of the

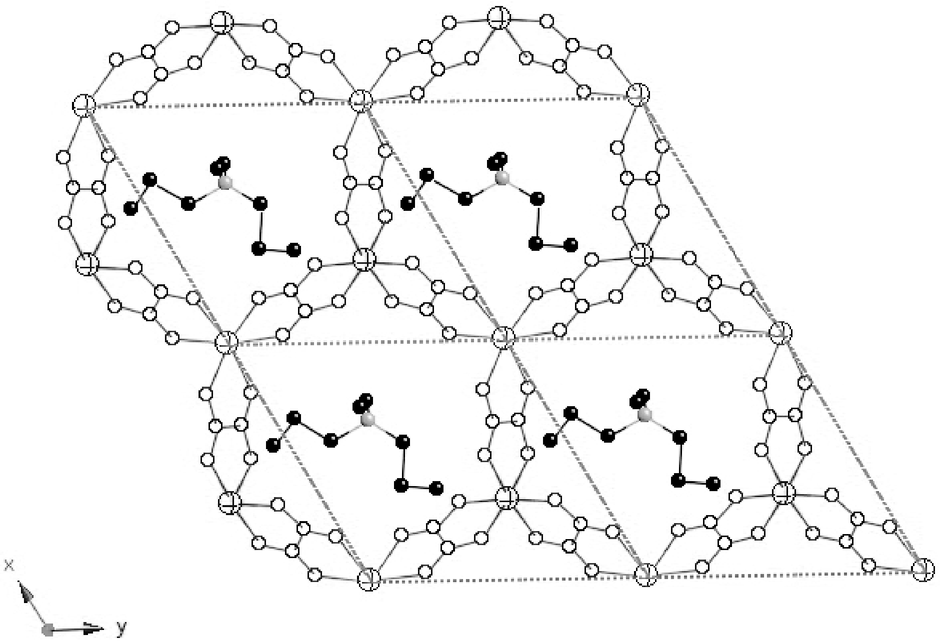

FIGURE 1 View of the $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$ structure along the *c* axis. The *n*-propyl chains of the ammonium cation have been represented in one of their three possible positions (see text).

cation is either above (Fig. 2a) or below (Fig. 2b) the Cr^{III} ion. At the present stage, with available crystal data, we propose two hypotheses to explain this situation: disorder in the ammonium cation or a twinning effect of the crystal (in this case, the two types of cation correspond to two components of the twinned crystal). In both cases, the distance between the nitrogen atom and the Cr^{III} ion is two-thirds of the interlayer distance. One propyl chain of the ammonium cation is embedded in the honeycomb net of a neighboring layer and can adopt three different conformations. The two remaining propyl moieties (we could not localize the hydrogen atoms) are directed towards the oxygen atoms of the oxalate group coordinated to the chromium(III) ion (Fig. 1). The two propyl groups can adopt three different positions and the occupancy of carbon atoms of these groups is thus 2/3. This is due to rotational disorder of the ammonium cation around the helicoidal axis. One of the three possible positions of the cations has been arbitrarily presented in Figs. 1 and 2.

Discussion

The formation of chiral crystals of $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$ starting from the (+)-(*Rp*)-$[1\text{-}CH_2N(n\text{-}C_3H_7)_3\text{-}2\text{-}CH_3(C_5H_3)Fe(C_5H_5)]^+$ cation in the presence of (*rac*)-$[Cr(C_2O_4)_3]^{3-}$ and Mn^{2+} was unexpected. Attempts to obtain such a compound either in powder or as single crystals under the same experimental conditions starting with the $NH(n\text{-}C_3H_7)_3$ cation failed. Therefore, it is likely that in order to obtain the final material, the presence of a starting template cation is necessary. Such a cation is in fact known to be efficient in preparing 2D networks when it is used in either its racemic or its optically active forms [3b]. Because of the long crystallization time,

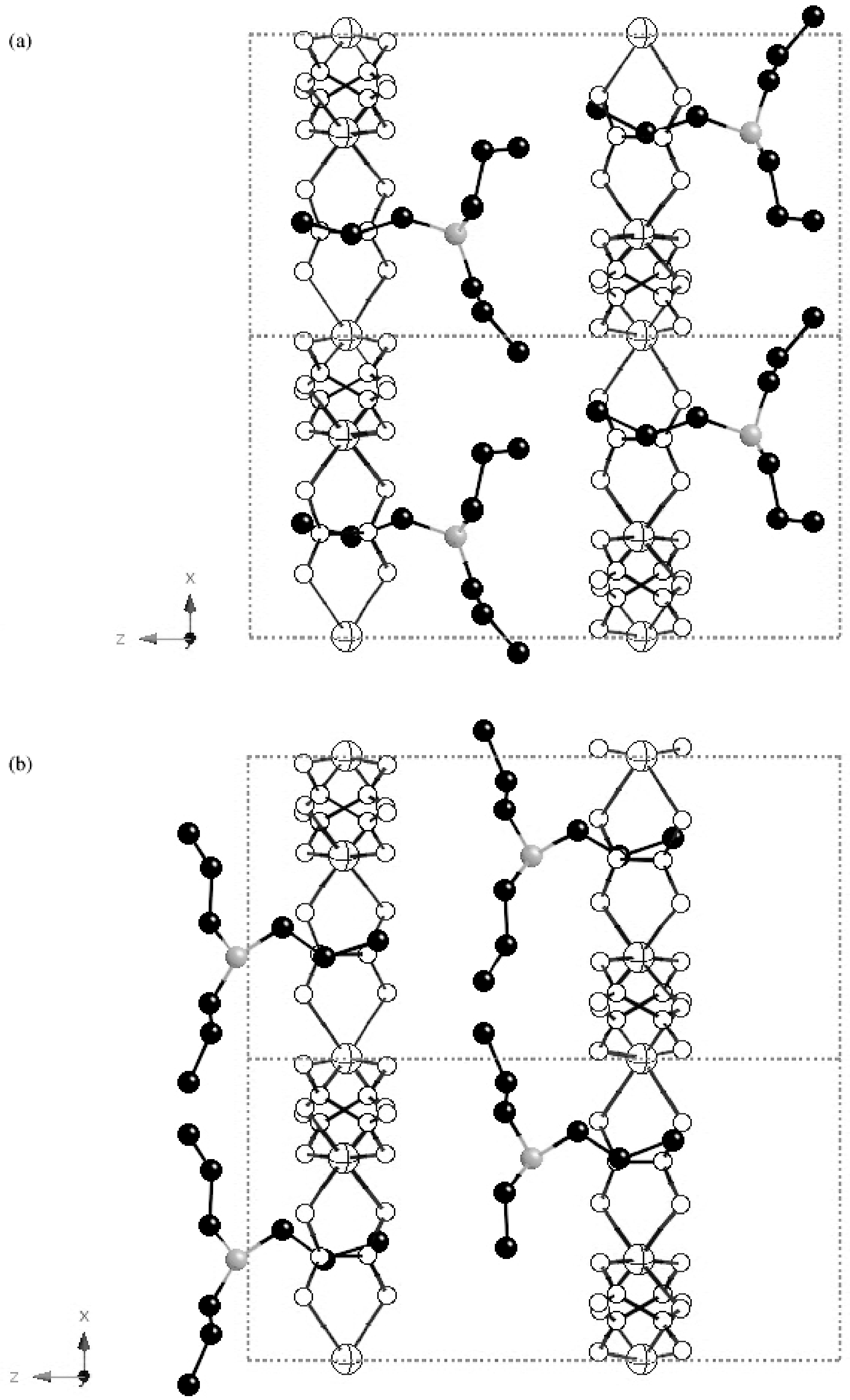

FIGURE 2 View of the *ac* plane of the {$NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]$} structure for an $NH(n\text{-}C_3H_7)_3$ cation situated (a) above or (b) below the Cr^{III} ion. The *n*-propyl chains of the ammonium cation have been represented in one of their three possible positions (see text).

the formation of the network is accompanied by slow hydrolysis of {(*Rp*)-[1-$CH_2N(n\text{-}C_3H_7)_3$-2-$CH_3(C_5H_3)Fe(C_5H_5)]^+$ due to the presence of methanol and water in the gel. This hydrolysis leads to the $NH(n\text{-}C_3H_7)_3$ cation.

The interlayer distance is 8.19 Å in $\{N(n\text{-}C_3H_7)_4[MnCr(C_2O_4)_3]\}$ [6] compared with 7.93 Å in $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$. When going from $[N(n\text{-}C_3H_7)_4]^+$ to $[NH(n\text{-}C_3H_7)_3]^+$, the cation is tilted due to equatorial asymmetry. The second carbon of the axial propyl chain now lies on the threefold axis instead of the first one (as for the $N(n\text{-}C_3H_7)_4$ cation). Consequently, the asymmetry of the $NH(n\text{-}C_3H_7)_3$ cation allows better packing of the anionic layers and the interlayer distance is shortened by 0.26 Å.

Our earlier studies of crystal structures of $\{N(n\text{-}C_3H_7)_4[MnCr(C_2O_4)_3]\}$ and $\{N(n\text{-}C_4H_9)_4[MnCr(C_2O_4)_3]\}$ compounds revealed that space group *R*3c was favored when starting from *rac*-$[Cr(C_2O_4)_3]^{3-}$ [6] and $P6_3$ when starting from Λ- or Δ-$[Cr(C_2O_4)_3]^{3-}$ [8]. For *n*-propyl or *n*-butyl ammonium cations, the formation of a 2D, oxalate-based material crystallizing in a noncentrosymmetric space group relies on the presence of a resolved building block unless the spontaneous resolution is simply fortuitous. The fact that in the present case, despite the use of *rac*-$[Cr(C_2O_4)_3]^{3-}$, we obtained material with the $P6_3$ space group, supports the active role of the resolved ferrocenic ammonium cation in the formation of the chiral salt.

In conclusion we report the unexpected formation of single crystals of a chiral, 2D $[MnCr(C_2O_4)_3]$ network with tripropylammonium as counter-cation. This compound has the smallest interlayer separation reported for 2D, oxalate-based networks. The chirality of the crystal as well as the failure to obtain the material starting from tripropylammonium salts suggests a synthetic process where the starting chiral cation plays an active role. We are currently developing this concept in order to synthesize various other optically active 2D networks.

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Supplementary Material

A CIF file for the crystal structure of $\{NH(n\text{-}C_3H_7)_3[MnCr(C_2O_4)_3]\}$ has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 227403.

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