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Dialkyl substituted monoamidinium-templated oxalate-based non centro-symmetric 2D compounds

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Abstract

1-propyl-2-phenyl-3-methylamidinium (**A**) and 1-hexyl-2-phenyl-3-methylamidinium (**B**) cations are used to template the formation of 2D oxalate-based bimetallic compounds of formula **A**[Mn^{II}Cr^{III}(C₂O₄)₃] (**1**) and **B**[Mn^{II}Cr^{III}(C₂O₄)₃] (**2**). The single-crystal X-rays diffraction analysis reveals that both compounds crystallize in non-centrosymmetric space groups. In both compounds, the bimetallic coordination network is made of slightly corrugated two-dimensional (2D) (6,3) bimetallic honeycomb layers arranged in an eclipsed manner. The monocations are located between the layers without any preferential interaction with the anionic coordination network. The magnetic susceptibility measurements can be fitted using a Curie-Weiss law with Curie-Weiss temperatures of 9.9K for **1** and 9.0K for **2**, revealing that the dominating exchange interaction is ferromagnetic. This favours the onset of a ferromagnetic long-range ordering at 6.0K for **1** and 5.8K for **2**.

Keywords: Template synthesis; Layered compounds; Inclusion compounds; Magnetic properties

1. Introduction

Starting from the seminal work of Tamaki *et al.*, [1] the oxalate anion has been widely investigated for the development of new multifunctional molecule-based magnets. The main reason for the infatuation for this ligand lies in its ability to behave as a bis(bidentate) bridge between two metal ions. In this widely encountered coordination mode, it can build up essentially two types of coordination networks of formula C[M^{II}M^{III}(ox)₃], namely three-dimensional (3D) (10,3) networks [2] and 2D (6,3) compounds presenting a honeycomb-layered structure.[3] The dimensionality of the coordination network is mainly controlled by the nature of the template cation C⁺ though, in the case of 2D compounds, this templating activity must be reinforced using

tris(oxalato)metalate (III) complexes $[M(\text{ox})_3]^{3-}$ ($M = \text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}, \text{Ru}^{\text{III}}, \text{V}^{\text{III}}, \text{Mn}^{\text{III}}$) as ligand. Within the coordination networks, the exchange interaction between the M^{III} and M^{III} paramagnetic centers mediated by the oxalate bridge enables the onset of long-range magnetic ordering with critical temperatures up to 45 K.[1, 4]

For many years, taking advantage of the versatility of this approach, a wellfare of the guest-cations (photochromic molecules,[5] spin transition complexes,[6] organic radical cations,[7] paramagnetic decamethylferrocenium,[8] photochromic,[9] organic π -electron donors [10]) have been intercalated between the 2D coordination layers to yield multifunctional materials associating magnetic ordering with another physical property. Along this line, different functional cations such as hyperpolarisable cationic chromophores have been intercalated between the bimetallic oxalato-bridged magnetic layers to yield second harmonic generation (SHG), electro-optic devices.[5a],[11] But, for these properties to be present, it is necessary to control the arrangement in a non-centrosymmetric manner hence the space group in which the hybrid compound is crystallising. Tries have been made to solve the crystalline structure on powders, with compound exhibiting strong NLO active compounds [12] but the challenge for breaking the symmetry in such crystals, in order to induce the formation of non centrosymmetric crystals remains open. For this purpose, chiral tetraalkyl ammonium cations [13] have been used. Through intermolecular interactions between the alkyl chains and the coordination network, such cations allow to control the absolute configuration within the coordination layers and observe cross-effects such as magneto-chiral dichroism [14] or magnetisation-induced SHG (MSHG) arising from the coordination network itself. Recently, counter-ions presenting H-bonding ability were used to introduce properties due to the template cations themselves like ferroelectricity or proton conduction.[15] But, because H-bonds may compete with coordination ones, this introduction dramatically changed the self-assembly process: instead of the usual networks, discrete clusters or coordination networks with original topologies were observed. With bisamidinium cations known to be active H-bonds donors,[16],[17] we have obtained binuclear [18] or trinuclear [19] complexes but also highly corrugated 2D bimetallic layers.[20]

Herein, two dialkyl-substituted monoamidinium cations, namely 1-propyl-2-phenyl-3-methylamidinium (**A**) and 1-hexyl-2-phenyl-3-methylamidinium (**B**) (Scheme 1) are used to template the formation of layered oxalate-based assemblies. The cations present a low symmetry whereas the alkyl substitution hinders their H-donating ability: these characteristics will be here analysed to the light of previous results obtained with more symmetrical H-bond donor cations.[18]-[20] The synthesis of two 2D layered oxalate-based compounds **A** $[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]$ (**1**) and **B** $[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]$ (**2**) is presented thereafter. The structures of **1** and **2** are described and discussed in details. Finally, their magnetic properties are presented.

Variable temperature (2.0-300 K) magnetic susceptibility measurements were carried out on polycrystalline samples checked by PXRD with a MPMS SQUID magnetometer by applying a 1000 G external magnetic field.

2.3. Structural studies

2.3.1. Powder diffraction studies (PXR)

Powder diffraction studies (PXR) diagrams were collected on polycrystalline samples, on a Bruker D8 diffractometer using monochromatic Cu-K α radiation with a scanning range between 3.8 and 40° using a scan step size of 2°/mn.

2.3.2. Single-Crystal Studies

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-K α ($\lambda = 0.71073$) radiation. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-2013 crystallographic software package. All hydrogen atoms were generated geometrically.[23]

CCDC 1890603-1890604 contain supplementary crystallographic data for the two compounds. They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

3. Results and discussion

3.1. Synthesis

1 and **2** were obtained as crystalline materials suitable for X-ray diffraction by slow evaporation at room temperature of a methanolic solution containing the ammonium salt of tris(oxalato)chromate(III), chosen for its solubility in methanol, manganese(II) chloride and the hexafluorophosphate salt of the amidinium cation **A**⁺ for **1** and tetraphenylborate salt for amidinium cation **B**⁺ for **2**. For **1** and **2**, PXR analysis of the polycrystalline samples (Fig. 1) demonstrated that only one crystalline phase is obtained during the crystallization processes, even if discrepancies in intensity were observed between the observed and simulated patterns, owing to the preferential orientations of the microcrystalline powders.

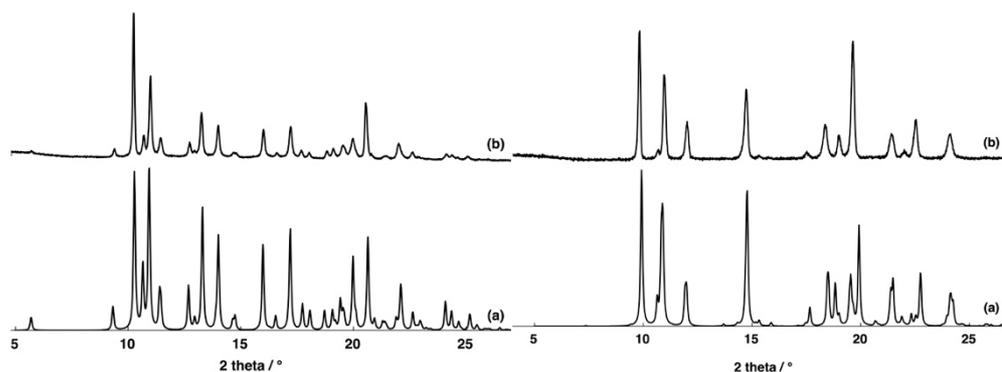


Fig. 1: Comparison of PXRD patterns for **1** (left) and **2** (right) (a) **calculated** and powdered recorded (b).

TGA measurements (Fig. S3) confirm that the products are pure and single-phased. In particular, there are no traces of the ammonium-templated 3D bimetallic networks previously synthesized [15] indicating a stronger templating activity of the amidinium cations. Moreover, the abruptness of the TGA traces (Fig. S3) evidences that, for both compounds, there is no solvent molecule inside the unit cell. This conclusion is supported by the single-crystals XRD analysis.

3.2. Single-Crystal X-ray Diffraction

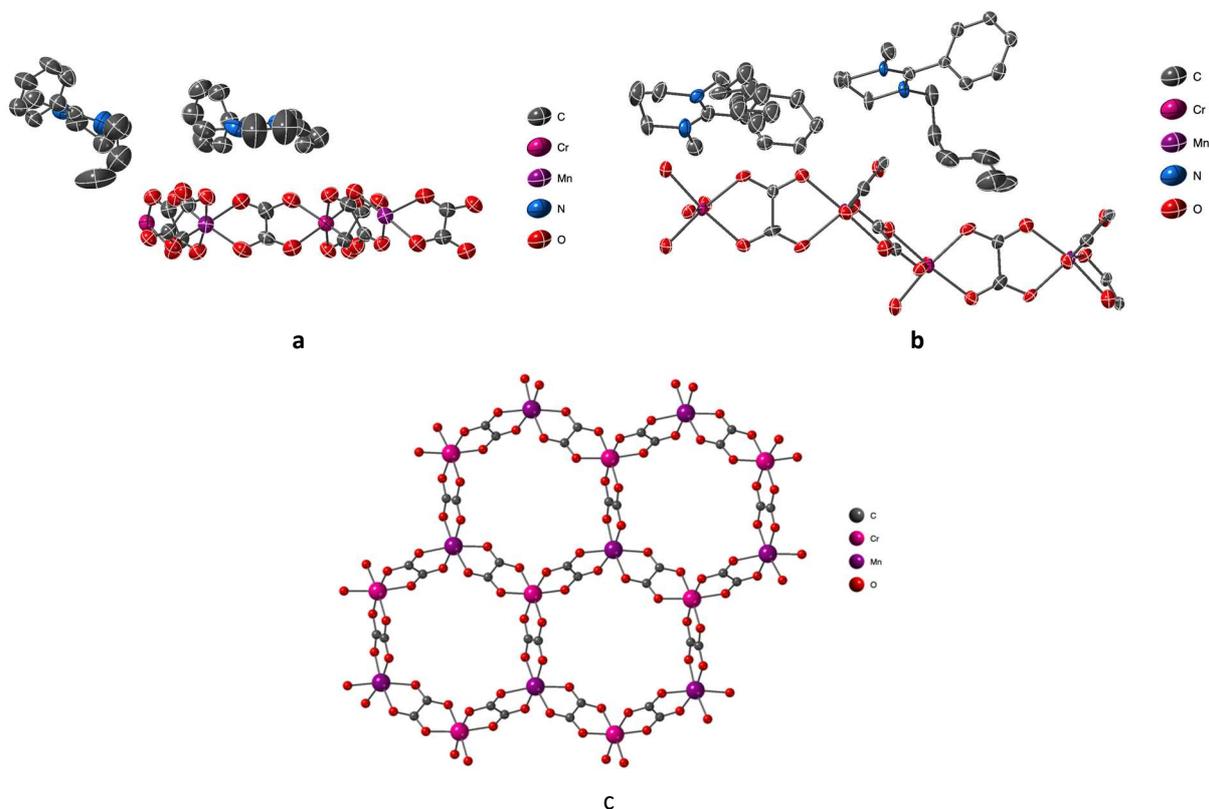


Fig. 2: Asymmetric unit based on monocationic (A^+ or B^+) and $[Mn_2^{II}Cr_2(ox)_6]^{2-}$ dicationic species forming **1** (a) and **2** (b) and their thermal ellipsoid representations, together with the representation of the 2D bimetallic network observed in both compounds (c).

X-ray diffraction on single crystals showed that compounds **1** and **2** crystallize in the polar Pc and chiral $P2_1$ space groups respectively (Table 1). In both compounds, the asymmetric unit is composed of two amidinium monocationic (A^+ or B^+) and a $[Mn_2Cr_2(ox)_6]^{2-}$ dianionic moiety, leading to the formulas $(C_{14}H_{21}N_2)_2[Mn_2Cr_2(C_2O_4)_6]$ for **1** and $(C_{17}H_{27}N_2)_2[Mn_2Cr_2(C_2O_4)_6]$ for **2**, evidencing the absence of solvent molecule in the unit cell (Fig. 2a and 2b).

Table 1. Crystallographic parameters for compounds **1** and **2** recorded at 173 K.

$$^aR_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } P = [\max(F_o^2, 0) + 2F_c^2]/3.$$

	1	2
Formula	$C_{40}H_{42}Cr_2Mn_2N_4O_{24}$ $(Cr_2Mn_2C_{12}O_{24})(C_{14}H_{21}N_2)_2$	$C_{46}H_{54}Cr_2Mn_2N_4O_{24}$ $(Cr_2Mn_2C_{12}O_{24})(C_{17}H_{27}N_2)_2$
Molecular weight	1176.66	1260.81
Crystal system	Monoclinic	Monoclinic
Space group	Pc	$P2_1$
a(Å)	16.033(3)	9.3876(2)
b(Å)	9.4755(19)	17.8144(4)
c(Å)	17.770(4)	16.2318(4)
β (deg)	104.56(3)	90.6230(10)
V(Å ³)	2613.0(9)	2714.36(11)
Z	2	2
Colour	violet	purple
D _{calc} (gcm ⁻³)	1.496	1.543
F(000)	1200	1296
μ (mm ⁻¹)	0.960	0.930
Wavelength (Å)	0.71073	0.71073
Number of data meas.	25554	18508
Number of data with $I > 2\sigma(I)$	10773	10257
Final R1 ^a , wR2 ^b [$I > 2\sigma(I)$]	0.0963, 0.1003	0.0914, 0.1002
R1 ^a , wR2 ^b (all data)	0.2460, 0.2519	0.2459, 0.2566
GOF	1.028	1.062
Largest peak in final difference (eÅ ⁻³)	-0.582 and 1.391	-1.081 and 1.017
Flack parameter	0.18(3)	0.00(4)

Both compounds are both formed of anionic 2D bimetallic oxalate-based networks $[Mn^II Cr^III(ox)_3]^-$, with monocations inserted between the anionic bimetallic layers (Fig. 2c). In contrast with the strong corrugation observed in the networks templated by bis(amidinium) cations,[20] in **1** and **2**, the coordination layers are essentially flat (Fig. 3a and 3b). Moreover, these anionic layers are stacked above one another (Fig. 3c and 3d) rather than staggered as observed in most of the 2D oxalate-based compounds.

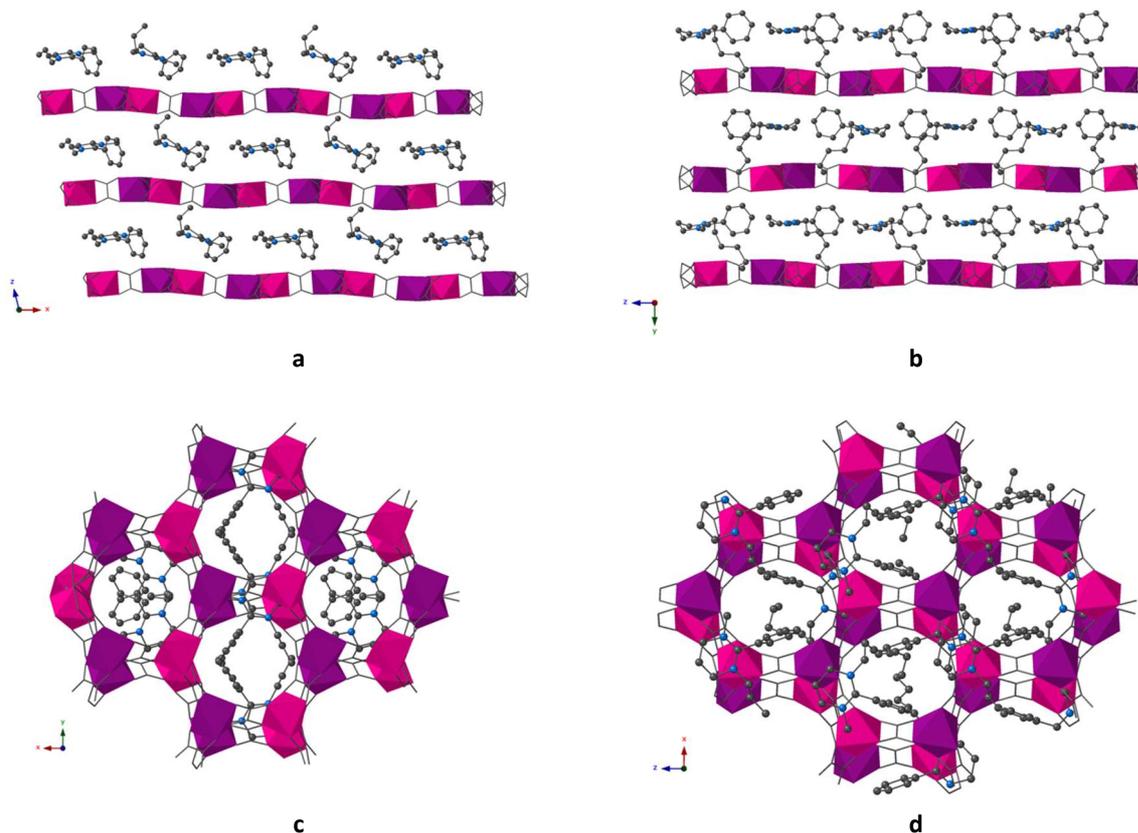


Fig. 3: Location of the cations between the anionic bimetallic planes: A^+ in **1** (a and c, view along the c and b axis respectively) and B^+ in **2** (b and d, view along the a and c axis respectively). The disorder in the alkyl chain for **2** has been omitted for clarity.

In both **1** and **2**, the Cr^{III} and Mn^{II} ions are surrounded by three bidentate oxalate ligands forming slightly deformed octahedral environments with Cr–O and Mn–O bond lengths and the O–Cr–O and O–Mn–O angles in a narrow range (Table 2). According to the heterochiral nature of the 2D bimetallic oxalate-bridged compounds,[24] within a layer, the absolute configuration of the helical tris(bischelated) Cr^{III} and Mn^{II} metal centers is alternating. In **1**, there is an alternation of the absolute configurations of Cr^{III} and Mn^{II} from one layer to the other. On the contrary, in **2**, each metal ion exhibits the same absolute configuration throughout the crystal (Δ for Cr^{III} and Λ Mn^{II} for the described single crystal). Accordingly, a spontaneous resolution occurred during the formation of **2**, leading to the formation of crystals of the two enantiomers in equal proportions, e.g. to a racemate.

Table 2. Distances and angles around the $Cr(III)$ and $Mn(II)$ metallic centres for compounds **1** and **2**.

	1	2
Cr-O (Å)	2.033(5)- 2.070(6)	2.035(7)-2.082(6)
Mn-O (Å)	2.097(6)- 2.144(6)	2.069(7)- 2.120(7)
O-Cr-O (°)	81.2(2)- 95.2(2) 170.8(2)- 172.4(2)	80.0(2)- 95.8(3) 168.0(2)- 171.2(3)
O-Mn-O (°)	78.9(2) -98.56(19) 166.40(19)- 171.7(2)	79.3(2)- 97.1(2) 167.4(3)- 172.1(3)

In both compounds **1** and **2**, there are two independent monocationic units located between the anionic layers. In **2**, there is a disorder in the alkyl chain for one of the two cations. The amidinium-phenyl axis of both cations are pointing in two different directions and there is no specific orientation of the cations towards the hexagonal cavities formed by the honeycomb like network for **1** and **2**. Together with the non-centrosymmetry of the space groups, the situation compares well with the one encountered in the multiferroic oxalate-based compound.[15a]

There are no hydrogen bonds in **1** and **2** but short van der Waals contacts between the pendant alkyl chains of the cations and the bimetallic coordination network as shown in Fig. 2a and 2b. The absence of H-bonds and/or any directional intermolecular interactions avoid the modification of the coordination environment of the two metallic ions as previously observed with H-donating bisamidinium cations.[18]-[20] For the 2D compound,[20] the H-bond between the cation and an oxalate ligand led to a weakening of the coordination ability of this oxalate towards Mn^{II} and to the coordination on this metal ion of a methanol molecule. The seven coordination of the Mn^{II} induced a strong corrugation of the layers that is not observed here for compounds **1** and **2**.

3.3. Physical properties

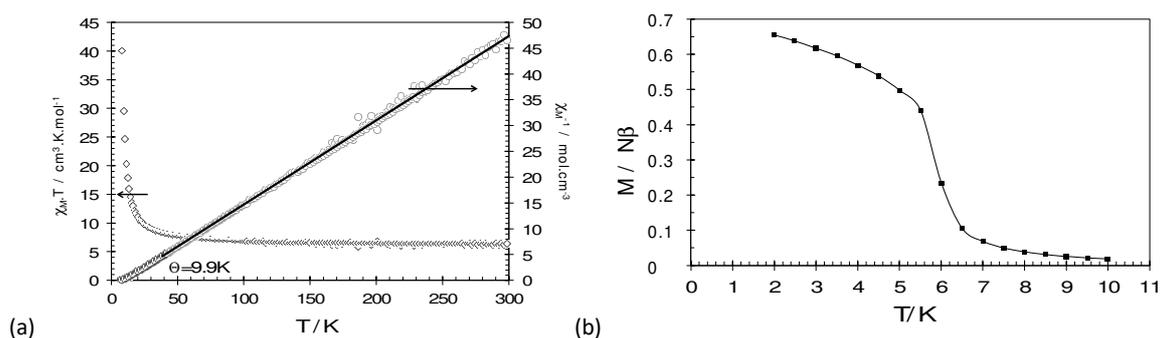


Fig. 4: Thermal variation of $\chi_M T$ and χ_M^{-1} (a) and Field-Cooled Magnetisation (b) for **1**.

The magnetic susceptibility for **1** and **2** has been measured on microcrystalline powder between **2** and 300 K. The thermal variations of $\chi_M T$ and χ_M^{-1} for **1** are shown in Fig. 4a (for **2**, see Fig. S4a). Following the structural similarity of the coordination layers, the magnetic behavior of the two compounds is very similar. At room temperature, the $\chi_M T$ values are 6.40 (**1**) and 6.64 cm³ mol⁻¹ K (**2**), which are close to those expected for the sum of the

corresponding non-interacting isotropic metallic ions ($6.25 \text{ cm}^3 \text{ mol}^{-1}\text{K}$ for $g = 2.00$ for both Cr^{III} and Mn^{II}). Upon cooling, the $\chi_{\text{M}}T$ products for **1** and **2** increase continuously. This evolution indicates that the exchange interactions between the two metallic Cr^{III} and Mn^{II} ions are dominated by ferromagnetic interactions. To quantify the average interaction, the inverse susceptibility (Fig. 4a and S4a) is fitted using a Curie-Weiss law in the 40-300K window and yield Curie-Weiss temperatures of 9.9K for **1** and 9.0K for **2**. Upon further cooling, both compounds enter in a ferromagnetic phase with a Curie temperature 6.0K for **1** and 5.8K for **2** (Fig. 4b and S4b). These results match with those found for previous 2D [MnCr] oxalate-based compounds, the slight modifications being due to slight changes in the metrics of the coordination spheres of each metallic ion that influence the exchange interaction between the two metal ions.

Since the space groups of both compounds are compatible with ferroelectricity,[25] this property has been tested. Due to leakage currents, the ferroelectricity measurements performed using the same procedure as for $\text{C}[\text{MnCr}(\text{C}_2\text{O}_4)_3(\text{CH}_3\text{CH}_2\text{OH})]$ ($\text{C}^+=1$ -hydroxyethyl)-4-(N,N-dimethylamino)pyridinium[15b] were not conclusive.

4. Conclusion

The presented results confirm the ability of amidinium-based cations to template the formation of 2D oxalate-bridged bimetallic [MnCr] networks. Two striking features appear when comparing the templating activity of the mono(amidinium) monocations with the one of the previously used bis(amidinium) dication.[20] Firstly, the absence of H-donating ability of the dialkyl substituted mono(amidinium) monocation limits the intermolecular interaction between the cation and the coordination network and leads solely to non-directional interactions. The absence of competition between coordination and hydrogen bonds led to flattened 2D coordination layers instead of the corrugation previously observed. Most importantly, the asymmetry brought about by the absence of the second amidinium moiety has favored the crystallization of the compounds in non-centrosymmetric space groups and, in the case of **2**, led to a spontaneous resolution process. Accordingly, such template cations open new possibilities towards new multifunctional oxalate-based compounds.

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6. Supplementary material

FT-IR for **1** and **2**, TGA traces for **1** and **2** and Thermal variation of χ_{MT} and χ_M^{-1} and Field-Cooled Magnetisation for **2**.

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Graphical Abstract

