Spontaneous resolution upon crystallization of chiral La(III) and Gd(III) MOFs from achiral dihydroxymalonate†

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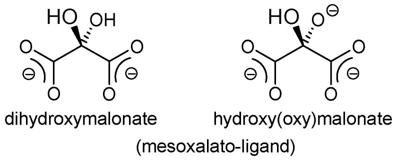
The achiral chelating and bridging dihydroxymalonato (mesoxalato) ligand is a new enantiopurity enforcer in extended structures by yielding the Λ/Δ-metal configured homochiral MOFs 2D-[Ln_2(μ-mesoxalato)$_3$(H_2O)$_6$] (Ln = La(III), Gd(III)) through self-resolution during crystal growth.

The combination of lanthanoid(III) ions with carboxylate-containing bridging ligands has produced a great variety of extended metal–organic frameworks (MOFs) which are of special importance since they exhibit interesting properties such as porosity, luminescence, magnetism, catalytic activity and chirality.[1–3] The synthesis of chiral materials is of particular attention since they may lead to enantioselective catalysis.[4] The synthesis of chiral MOFs can be induced by chiral templating or the use of chiral ligands. Also, homochiral MOFs are prepared from totally achiral components *via* spontaneous resolution during crystal growth.[4] In this approach a stereogenic center must be created in the complexation of the metal ions by the achiral ligands in the construction and crystallization of the MOF. If all the metal centers in the crystal keep the same Λ- or Δ-configuration the crystal will be chiral, the reaction yielding equivalent quantities of both crystal enantiomorphs (opposite handedness) of MOFs. We have followed this strategy for the synthesis of 2D-[La_2(μ-mesoxalato)$_3$(H_2O)$_6$] (**1**) and 2D-[Gd_2(μ-mesoxalato)$_3$-(H_2O)$_6$] (**2**) in which a doubly deprotonated, dinegative mesoxalato ligand assembles only metal centers of the same Λ- or Δ-configuration within a single crystal. A CSD search[5] revealed just three examples of metal complexes with the hydroxyl(oxy)- or dihydroxymalonato ligand (Scheme 1),[6,7] with only one of them being an extended 1D coordination polymeric structure.[8]



Scheme 1

In isostructural **1** and **2** each Ln atom is surrounded by 9 O atoms from three chelating mesoxalato and three aqua ligands. The Ln coordination polyhedron is a tri-capped (slightly distorted) trigonal prism (Fig. 1). Depending on the crystal investigated the chelate-ring planes of the three chelating mesoxalato ligands form either a left- or right handed propeller around each Ln atom, akin to the Λ- or Δ-configuration in an octahedron (Fig. 1). In the absence of inversion symmetry elements in the Sohncke space group $R32$ the crystal is homochiral (enantiopure) with all Ln atoms of the same Λ or Δ configuration. The overall ensemble of the crystals in a batch of **1** or **2** can be expected to be racemic, that is, to contain crystals of Λ- and Δ-configured Ln atoms, respectively, in equal amounts.[9] For **1** one crystal was shown to contain the Λ and a second crystal the Δ-configuration (Fig. 1).‡ In principle crystals of space group $R32$ in the non-centrosymmetric crystal class 32 should be enantiomorphic and, thus, could be separated by hand.[10]

The Ln atom sits on a three-fold proper rotation axis, the central carbon atom on a two-fold proper rotation axis (Fig. S4 in ESI†), so that only half of the mesoxalato ligand and one aqua ligand is unique.

Each mesoxalato ligand bridges between two Ln atoms in a bis-chelate mode (Fig. 1 and 2). This bis-chelate bridging action involves both ends of the mesoxalato ligand with its chelate-ring planes then forming a dihedral angle of about 80°. The mesoxalato bridging action is akin to the oxalato bridging action in 2D or 3D $[M_2(ox)_3]^{n-}$ (6,3)-honeycomb or (10,3)-a nets. In the planar 2D-$[M_2(ox)_3]^{n-}$ (6,3)-nets the M atoms alternate with opposite Λ-/Δ-configuration. In the 3D-$[M_2(ox)_3]^{n-}$ (10,3)-a nets a single (10,3)-a net is homochiral

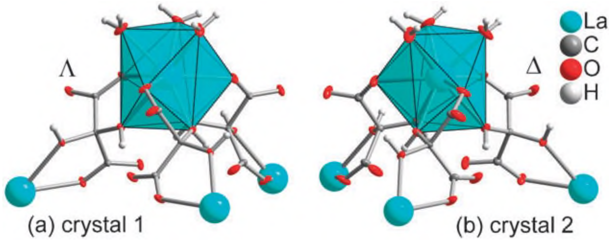


Fig. 1 La coordination sphere in (a) Λ-**1** and (b) Δ-**1** from two different crystals in a polyhedral presentation to illustrate the tri-capped trigonal prism; also showing the bridging action of the mesoxalato ligand to the next La atoms (50% thermal ellipsoids for C and O). For another view, atom labeling and the Gd coordination in **2** see Fig. S2 and S3 in ESI.†

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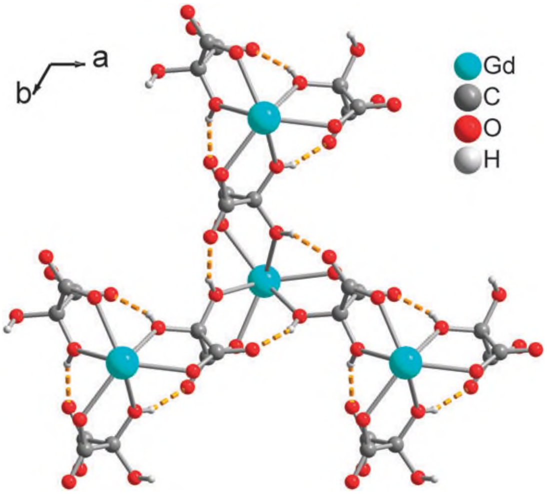

Fig. 2 Bridging actions of the trigonally-arranged mesoxalato ligands around an Ln atom in **1** and **2** with hydrogen bonds (dashed orange lines, Table S3 in ESI†); aqua ligands are not shown for clarity. Note again the homochiral Λ configuration around each Gd atom.

(enantiopure), thus, all M atoms in the net have the same Λ- or Δ-configuration.[11]

The Ln atoms are covalently connected by the mesoxalato ligands into a corrugated grey arsenic-type (6,3)-net[12] (or layer) with chair-shaped six-membered rings (Fig. 3 and 4). Yet, the mesoxalato ligand combines only Ln atoms of the same handedness (Λ- or Δ-configuration) in such a neutral 2D-[M_2(mesox)$_3$] net.

The aqua ligands on the Ln atoms then connect adjacent layers to a 3D hydrogen-bonded framework of the pcu[12b] α-Po type (Fig. 4, Table S3 in ESI†). Noteworthy, also adjacent nets contain Ln atoms of the same handedness. Thus, the interlayer hydrogen-bonds transmit the 2D net homochirality into the third dimension.[9] The hydrogen bonds in **1** and **2** are of the type (aqua or mesoxalato)O–H$\cdots{}^{-}$O(mesoxalato) and, hence, are "charge-assisted", with here the hydrogen bond acceptor carrying a negative ionic charge. The enhancement of hydrogen bond strength—which may be linked to robustness—by ionic charge has long been recognized and some of the strongest hydrogen bonds are "charge-assisted".[13]

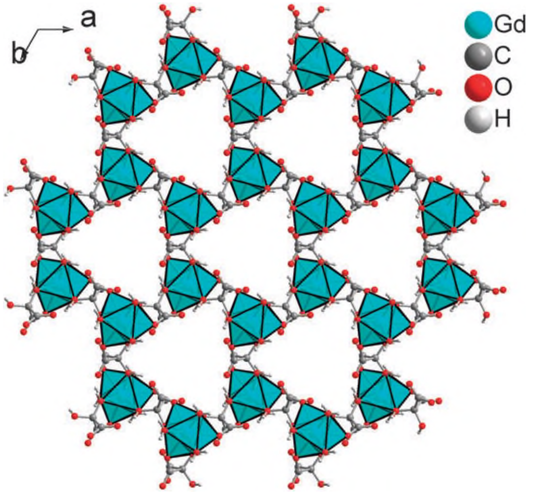

Fig. 3 (6,3)-Net in isostructural **1** and **2**, of the corrugated grey-arsenic type with chair-shaped six-membered rings (*cf.* Fig. 4) instead of the planar honeycomb type.

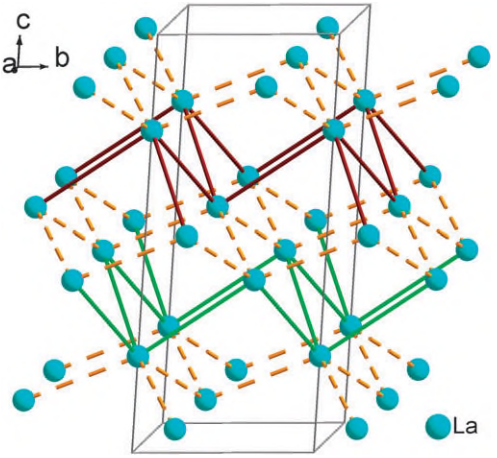

Fig. 4 Inter-layer hydrogen-bonding interactions (dashed orange lines) between two adjacent nets (differentiated by green and brown colored topological Ln–Ln connections along the mesoxalate bridges); inner-layer H-bonds (*cf.* Fig. 2) are not drawn for clarity. The schematic view shows only the Ln atoms with their covalent and hydrogen-bonded topological connectivity to emphasize the connection of the covalent corrugated (6,3)-nets into a 3D supramolecular pcu, α-polonium framework.[12]

Also, in the other known extended structure of $\{Na[Mn(mesox)(H_2O)_2]\}_n$[8] with 1D coordination polymeric $[Mn(mesox)(H_2O)_2]^-$ strands, the bis-chelated Mn atoms within a strand all have the same Λ- or Δ-configuration. Furthermore, adjacent strands connected by H-bonds into a supramolecular 2D double layer still have all Mn atoms of the same configuration. Thus, the interstrand hydrogen-bonds transmit the 1D chain homochirality into the second dimension. The configuration only changes from layer to layer where intermittent Na^+ ions weaken the interlayer hydrogen-bonding interactions (Fig. S5 in ESI†).

The temperature dependence of the χT product [χ is the magnetic susceptibility per two Gd(III) ions] is shown in Fig. 5. At room temperature, χT is 15.78 cm^3 mol^{-1} K, a value which

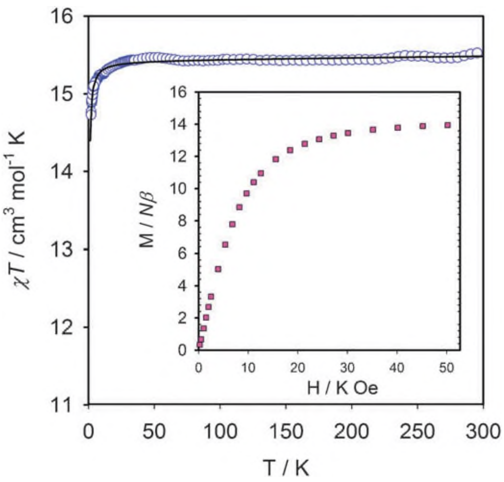

Fig. 5 Temperature dependence of the χT product of **2**, (blue circles); the solid line (—) corresponds to the best fit to the honey-comb model (see text). The inset shows the *M* (pink squares) *vs.* *H* plot at 2 K.

is as expected for two magnetically isolated Gd(III) ions [$\chi T = 2 \times (N\beta^2 g^2/3kT)\, S(S+1) = 15.78$ cm^3 mol^{-1} K with $g = 2.00$ and $S = 7/2$].[14] Upon cooling, χT remains almost constant until 10 K and then slightly decreases at lower temperatures. This curve is indicative of the occurrence of weak antiferromagnetic interactions amongst the Gd(III) ions. As described in the structural part, the gadolinium atoms are covalently connected by the mesoxalato ligands into a corrugated grey arsenic-type (6,3)-net[12] (or layer). In this framework each Gd(III) ion is connected to three others by means of a diol bridge displaying the magnetic exchange pathway shown in Fig. 1 and 2.

In agreement with its structure, the magnetic susceptibility data have been analyzed by means of the expression for a two-dimensional Heisenberg classical honeycomb lattice (details given in ESI†).[15,16] The best fit parameters are $g = 2.01(1)$, $J = -0.0039(1)$ cm^{-1} and $R = 3.6 \times 10^{-6}$. R is the agreement factor defined as $\Sigma_i[(\chi T)_{\text{obs}}(i) - (\chi T)_{\text{calc}}(i)]^2/\Sigma_i[(\chi T)_{\text{obs}}(i)]^2$. A good agreement between the experimental and calculated data has been obtained as can be seen in Fig. 5. To our knowledge, this is the first time in which Gd(III) ions are bridged by a diol bridge and precludes comparison with other related species. However, the value is smaller but comparable with the antiferromagnetic coupling observed through a bis-chelating oxalate occurring in [$Gd_2(ox)_3(H_2O)_6$] for which a magnetic coupling of $J = -0.0050(2)$ cm^{-1} is found.[16] In this latter compound the shorter Gd–Gd distance [6.524(3) A] and the higher efficiency of the double *anti–anti* carboxylate bridge explain the higher intensity of the coupling. On the other hand, the larger Gd–Gd distance [6.9291(4) A], the deviation from the planarity and the expected lower efficiency of the diol bridge account for the lower intensity of the antiferromagnetic coupling in **2**.

Chiral lanthanoid(III) containing MOFs have been prepared with the achiral mesoxalato ligand. All Ln atoms in an enantiopure single crystal have the same Λ- or Δ-configuration through spontaneous resolution based on the mesoxalato chelating and bridging action together with the strong hydrogen bonding between the corrugated grey arsenic-type (6,3) 2D-[$Ln_2(\mu\text{-mesoxalato})_3(H_2O)_6$] homochiral nets. The Gd compound shows an antiferromagnetic coupling between the paramagnetic centers.

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Notes and references

‡ Single crystals of the complexes suitable for X-ray analysis were formed by slow diffusion of an aqueous solution of Ln(III) nitrate and 2-dihydroxymalonic acid, see ESI† for details. Crystal data, all compounds: trigonal, space group $R32$, $Z = 3$, 63 parameters; for Λ-**1**: $T = 123(2)$ K, $C_9H_{18}La_2O_{24}$ (788.05) $a = b = 9.75040(10)$, $c = 21.2854(15)$ A, $V = 1752.50(13)$ A^3, $D_c = 2.240$ g cm^{-3}, $F_{000} = 1134$, $\mu = 3.714$ mm^{-1}, 46 805 refl. measd, 2409 unique (R_{int} 0.0145), final $R_1 = 0.0126$, w$R_2 = 0.0297$ (all data), absolute structure parameter (Flack value) −0.004(11); for Δ-**1**: $T = 203(2)$ K, $C_9H_{18}La_2O_{24}$ (788.05) $a = b = 9.7580(3)$, $c = 21.2982(15)$ A, $V = 1756.29(15)$ A^3, $D_c = 2.235$ g cm^{-3}, $F_{000} = 1134$, $\mu = 3.706$ mm^{-1}, 20627 refl. measd, 2432 unique (R_{int} 0.0388), final $R_1 = 0.0200$, w$R_2 = 0.0381$ (all data), Flack value −0.002(13); for **2**: $T = 294(2)$ K, $C_9H_{18}Gd_2O_{24}$ (824.73), $a = b = 9.6396(8)$, $c = 20.7433(16)$ A, $V = 1669.3(2)$ A^3, $D_c = 2.461$ g cm^{-3}, $F_{000} = 1176$, $\mu = 6.020$ mm^{-1}, 10186 refl. measd, 1427 unique (R_{int} 0.0345), final $R_1 = 0.0190$, w$R_2 = 0.0411$ (all data), Flack value −0.026(16).

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