

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

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Syntheses of the complexes:

An aqueous solution of 2-dihydroxymalonic acid (0.3 mmol in 3 mL) is placed in a sample tube and an aqueous solution of the Lanthanoid (La, Gd) nitrate hexahydrate (0.2 mmol in 3 mL) is added with a Pasteur pipette from the bottom of the tube without mixing both solutions. A small amount of precipitate is formed immediately which is allowed to stand. X-ray suitable single crystals are obtained within five days (Fig. S1). As the starting material is achiral the reaction yields equivalent quantities of both crystal enantiomorphs (opposite handedness).

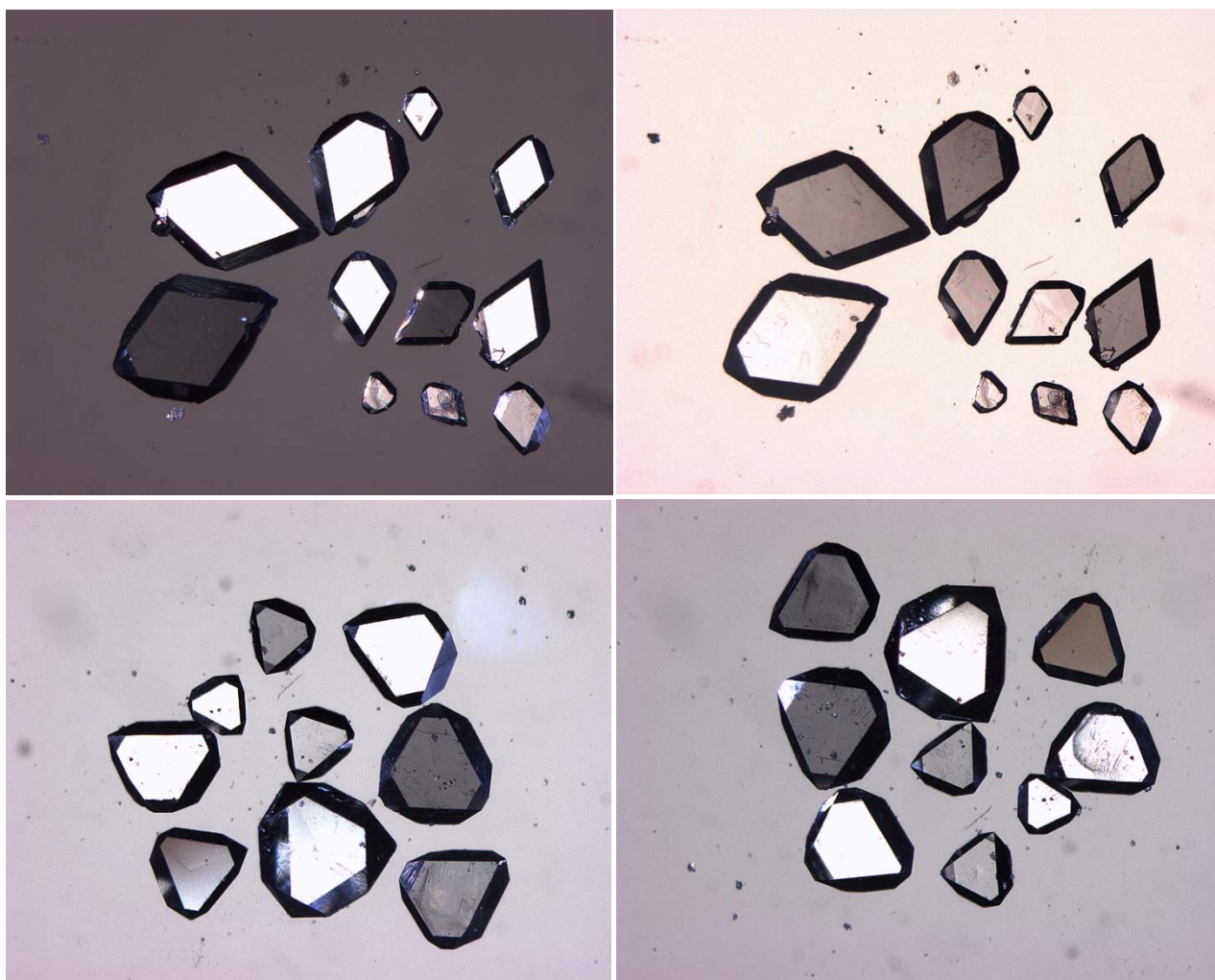


Fig. S1a Crystal photographs from the batch of $[\text{La}_2(\mu\text{-mesoxalato})_3(\text{H}_2\text{O})_6]$ (**1**).

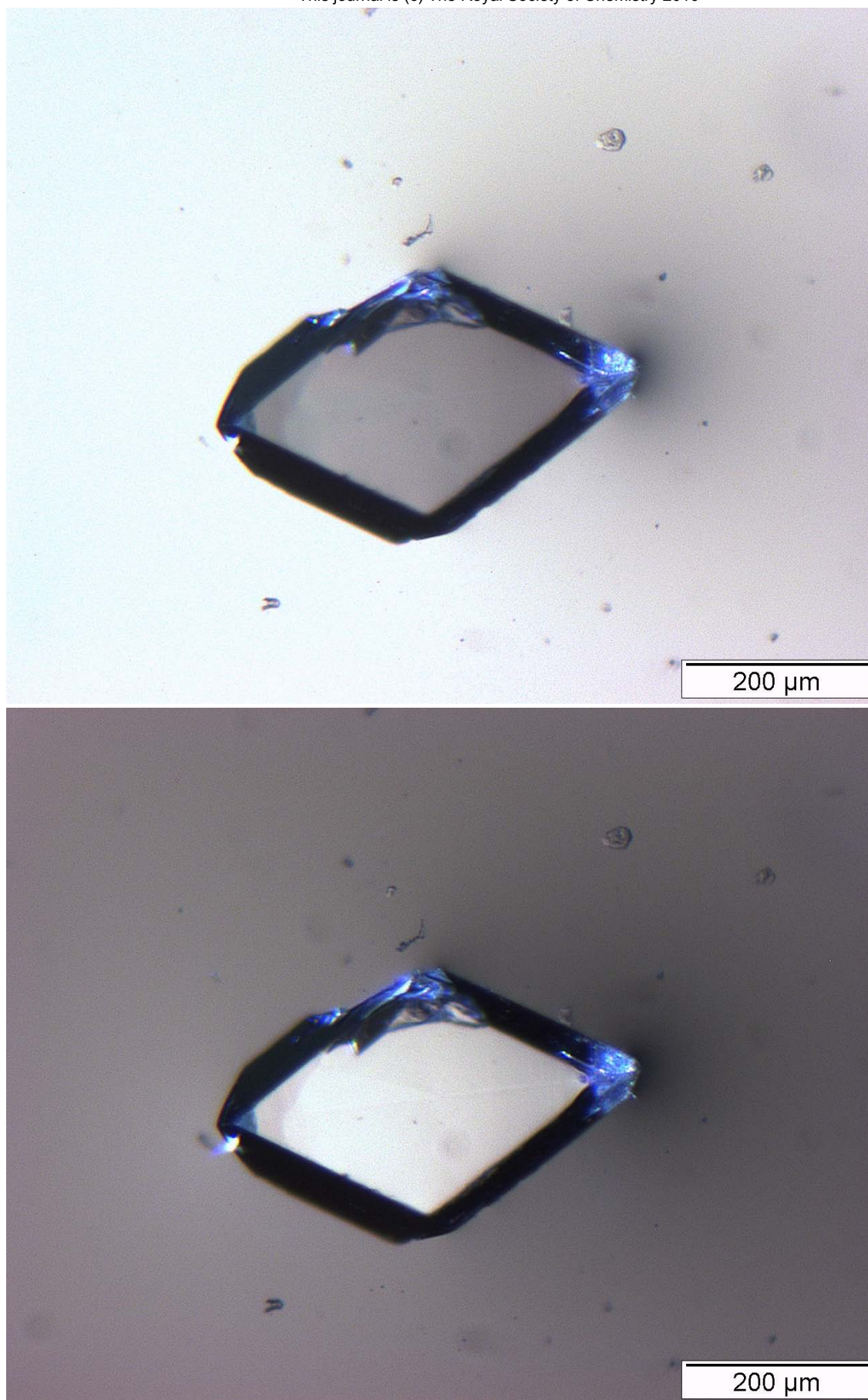


Fig. S1b Crystal photograph for the crystal of Δ -1 (ketb).

Details of crystal structure solution and refinement:

The crystal structure of the first data set (which was the one of **1** in the Δ configuration) could not be solved directly in the final space group $R32$ (no. 155) but in the monoclinic one $P1$. After obtaining a basic structure model, this was transformed to $R32$.

A suitable single crystal was carefully selected under a polarizing microscope.

Data Collection: Rigaku R-axis Spider image plate detector diffractometer, Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), graphite monochromator, double-pass method ω -scan. Data collection, cell refinement and data reduction with CrystalClear,¹ empirical (multi-scan) absorption correction with ABSCOR.² *Structure Analysis and Refinement:* The structure was solved by direct methods (SHELXS-97);³ refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite. All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms of the aqua ligands and on the hydroxyl groups of the mesoxalato ligand were found and refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Graphics were drawn with DIAMOND (Version 3.2c).⁴ Network analysis was carried out using the program package TOPOS.⁵

Crystal data and details on the structure refinement are given in Table S1.

1 CrystalClearSM 1.4.0, Rigaku Corporation, Tokyo, Japan. 2007.

2 T. Higashi, ABSCOR. Rigaku Corporation, Tokyo, Japan. 1995.

3 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.

4 K. Brandenburg, *Diamond* (Version 3.2c), Crystal and Molecular Structure Visualization, Crystal Impact – K. Brandenburg & H. Putz Gbr, Bonn (Germany) 2009; <http://www.crystalimpact.com/diamond>.

5 TOPOS program package for multipurpose crystallochemical analysis, version 4.0, <http://www.topos.ssu.samara.ru>; V. A. Blatov, *IUCr Compcomm. Newsletter* 2006, 7, 4; <http://www.iucr.org/iucr-top/comm/ccom/newsletters>

Table S1 Crystal data and structure refinement for [La₂(μ-mesoxalato)₃(H₂O)₆] (**1**) and [Gd₂(μ-mesoxalato)₃(H₂O)₆] (**2**)

Compound (identifier)	1 (2laketo_c)	1 (ketb)	2 (gdketo)
Empirical formula	C ₉ H ₁₈ La ₂ O ₂₄	C ₉ H ₁₈ La ₂ O ₂₄	C ₉ H ₁₈ Gd ₂ O ₂₄
<i>M</i> /g mol ⁻¹	788.05	788.05	824.73
Crystal size/mm	0.38 x 0.29 x 0.28	0.62 x 0.47 x 0.28	0.19 x 0.10 x 0.08
Crystal appearance	prism, colorless	prism, colorless	block, colorless
Temperature/K	123(2)	203(2)	294(2)
2θ range/° (completeness)	8.36 – 79.98 (98.8%)	6.16 – 79.96 (99.8%)	6.26 – 66.28 (99.8%)
<i>h</i> ; <i>k</i> ; <i>l</i> range	±17; ±17; -35, 37	±17; ±17; -38, 32	±14; -13, 12; -31, 29
Crystal system	trigonal	trigonal	trigonal
Space group	<i>R</i> 32 (no. 155)	<i>R</i> 32 (no. 155)	<i>R</i> 32 (no. 155)
<i>a</i> /Å	9.75040(10)	9.7580(3)	9.6396(8)
<i>b</i> /Å	9.75040(10)	9.7580(3)	9.6396(8)
<i>c</i> /Å	21.2854(15)	21.2982(15)	20.7433(16)
<i>α</i> [deg]	90	90	90
<i>β</i> [deg]	90	90	90
<i>γ</i> [deg]	120	120	120
<i>V</i> /Å ³	1752.50(13)	1756.29(15)	1669.3(2)
<i>Z</i>	3	3	3
<i>D</i> _{calc} /g cm ⁻³	2.240	2.235	2.461
<i>F</i> (000)	1134	1134	1176
<i>μ</i> /mm ⁻¹	3.714	3.706	6.020
Max/min transmission	0.4228/0.3327	0.4235/0.2072	0.6445/0.3942
Reflections collected	46805	20627	10186
Indep. reflections (<i>R</i> _{int})	2409 (0.0145)	2432 (0.0338)	1427 (0.0345)
Obs. reflect [<i>I</i> > 2σ(<i>I</i>)]	2401	2295	1391
Parameters refined	63	63	63
Max./min. Δρ ^a /e Å ⁻³	1.263/-1.246	0.964/-1.058	0.977/-1.088
<i>R</i> _T / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.0125/0.0296	0.0178/0.0378	0.0182/0.0408
<i>R</i> _T / <i>wR</i> ₂ (all reflect.) ^b	0.0126/0.0297	0.0200/0.0381	0.0190/0.0411
Goodness-of-fit on <i>F</i> ^{2c}	1.189	1.101	1.209
Weight. scheme <i>w</i> ; <i>a</i> / <i>b</i> ^d	0.0099/3.5048	0.0171/0.6499	0.0102/1.7470
Flack parameter ^e	-0.004(11)	-0.002(13)	-0.026(16)

^a Largest difference peak and hole. – ^b $R_1 = [\sum(|F_o| - |F_c|)] / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$. – ^c Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$. – ^d $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2) / 3$. – ^e Absolute structure parameter.⁶

6 (a) H. D. Flack and G. Bernardinelli, *Chirality*, 2008, **20**, 681-690. (b) H. D. Flack and G. Bernardinelli, *Acta Crystallogr. A*, 1999, **55**, 908-915. (c) H. D. Flack, *Acta Crystallogr. A*, 1983, **39**, 876-881.

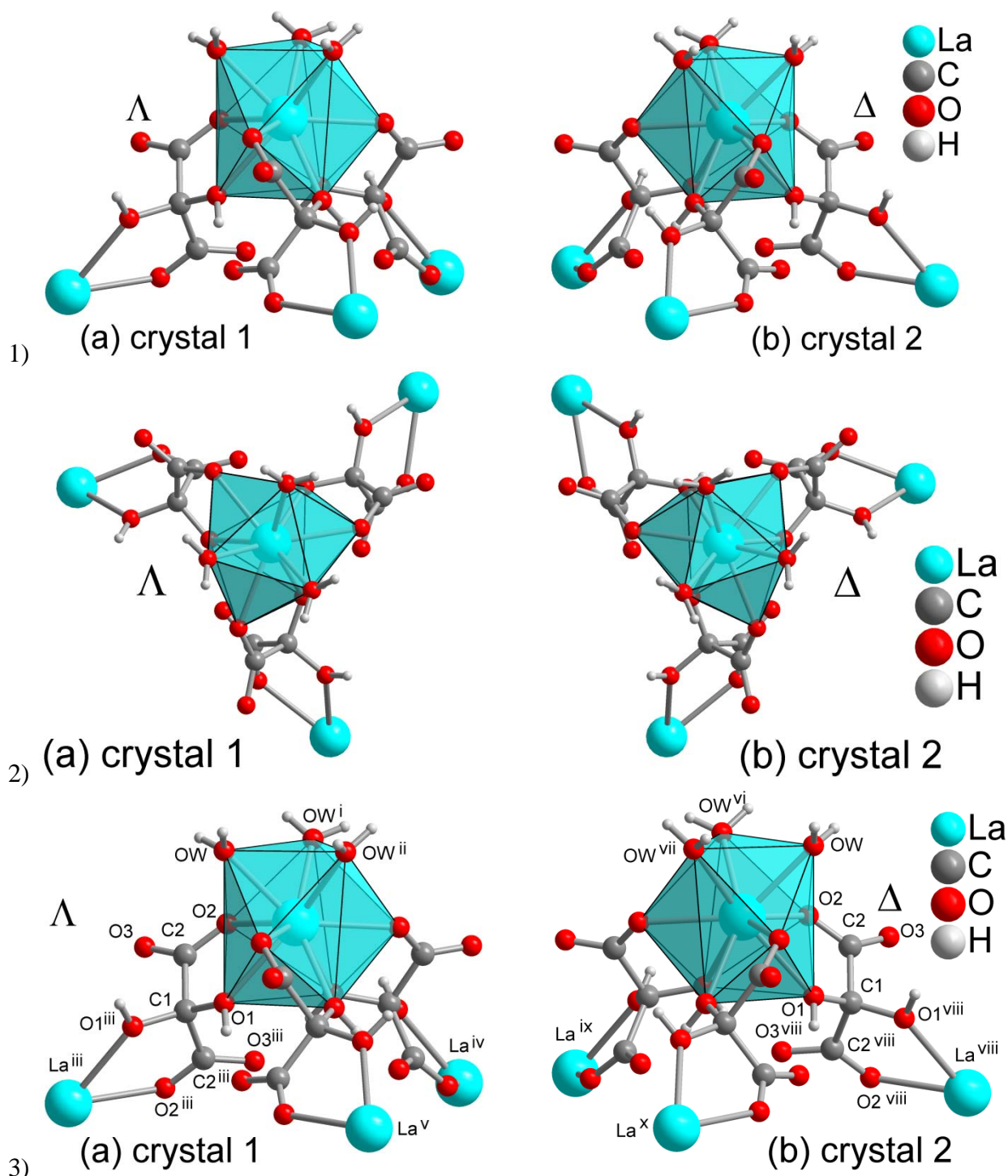


Fig. S2 La coordination sphere in (a) Λ -1 and (b) Δ -1 in a polyhedral presentation to illustrate the tri-capped trigonal prism, also showing the bridging action of the mesoxalato ligand to the next La atoms.

- 1) - ball-and-stick representation, side view,
 2) - ball-and-stick representation, top view
 3) - ball-and-stick representation with atom labels.

Symmetry transformations in (a) Λ -1: i = $1-x+y, 2-x, z$; ii = $2-y, 1+x-y, z$; iii = $2/3+x-y, 1+1/3-y, 1+1/3-z$; iv = $2/3+x-y, 2+1/3-y, 1+1/3-z$; v = $1+2/3+x-y, 2+1/3-y, 1+1/3-z$.

Symmetry transformations in (b) Δ -1: vi = $-x+y, -x, z$; vii = $-y, x-y, z$; viii = $1/3+x-y, 2/3-y, 2/3-z$; ix = $1/3+x-y, -1/3-y, 2/3-z$; x = $-2/3+x-y, -1/3-y, 2/3-z$.

Table S2 Bonds lengths (Å) and angles (°) in **1** and **2**.

	Δ - 1 (Ln = La)	Δ - 1 (Ln = La)	2 (Ln = Gd)
Ln–O1	2.5738(8)	2.5737(10)	2.4727(19)
Ln–O2	2.5175(10)	2.5189(12)	2.422(2)
Ln–OW	2.4994(11)	2.5003(13)	2.391(2)
C1–O1	1.3972(12)	1.3972(14)	1.395(3)
C1–C2	1.5616(14)	1.5639(18)	1.564(3)
C2–O2	1.2582(14)	1.2574(18)	1.254(3)
C2–O3	1.2475(14)	1.2425(18)	1.240(3)
OW–Ln–OW ^{i/vi}	73.66(5)	73.83(7)	75.21(11)
OW–Ln–O2 ^{i/vi}	138.52(4)	138.65(5)	137.36(9)
OW–Ln–O2 ^{ii/vii}	70.98(3)	71.17(4)	69.59(8)
OW–Ln–O2	76.17(4)	75.85(5)	73.20(9)
O2–Ln–O2 ^{i/vi}	119.285(7)	119.287(8)	119.789(9)
OW–Ln–O1 ^{i/vi}	149.28(4)	149.03(5)	146.78(8)
O2–Ln–O1 ^{i/vi}	73.16(3)	73.23(4)	73.60(7)
OW–Ln–O1 ^{ii/vii}	131.12(3)	131.24(4)	131.87(7)
O2–Ln–O1 ^{ii/vii}	126.81(3)	126.84(4)	130.32(7)
OW–Ln–O1	94.58(4)	94.40(5)	92.21(9)
O2–Ln–O1	60.15(3)	60.08(3)	62.31(6)
O1–Ln–O1 ^{i/vi}	71.57(3)	71.62(4)	73.29(8)

Symmetry transformations in Δ -**1** and **2**: i = 1–x+y, 2–x, z; ii = 2–y, 1+x–y, z.
 Symmetry transformations in Δ -**1**: vi = –x+y, –x, z; vii = –y, x–y, z.

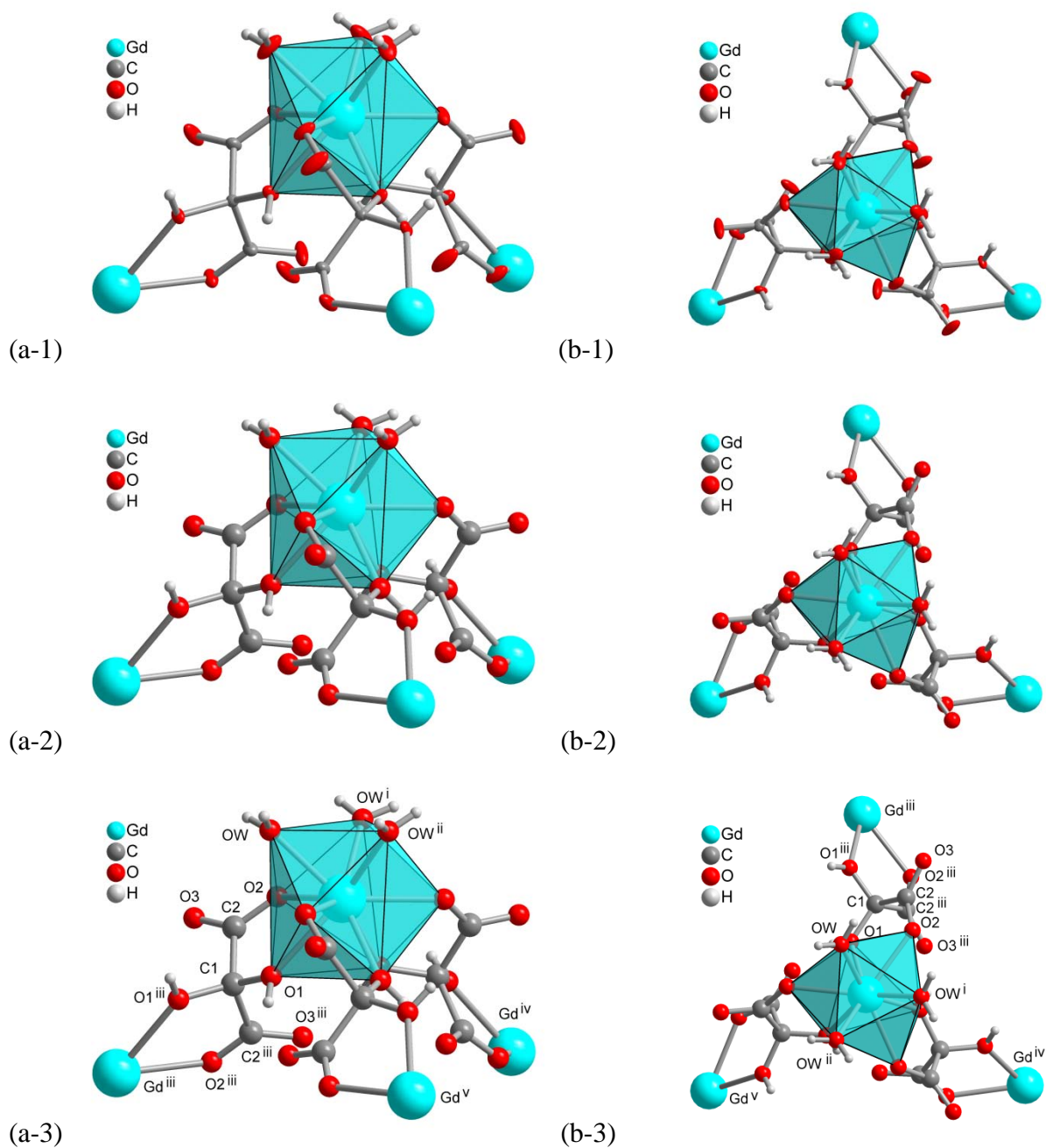


Fig. S3 Gd coordination sphere in **2** (Λ -configuration) in a polyhedral presentation to illustrate the tri-capped trigonal prism, (a) side view, (b) top view; also showing the bridging action of the mesoxalato ligand to the next Gd atoms.

1) - thermal ellipsoids (50% probability) for C and O,

2) - ball-and-stick representation,

3) - ball-and-stick representation with atom labels; symmetry transformations: i = 1-x+y, 2-x, z; ii = 2-y, 1+x-y, z; iii = 2/3+x-y, 1+1/3-y, 1+1/3-z; iv = 2/3+x-y, 2+1/3-y, 1+1/3-z; v = 1+2/3+x-y, 2+1/3-y, 1+1/3-z.

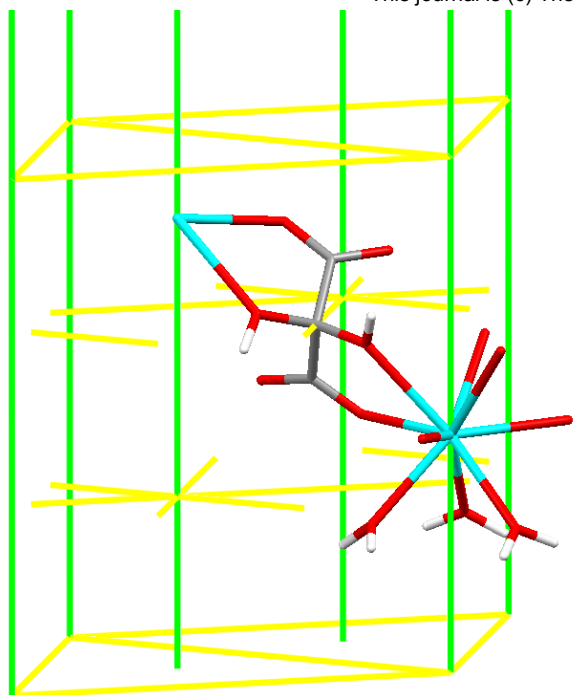


Fig. S4 The proper rotation axes (yellow 2-fold, green 3-fold) in space group *R* 32 with a unit of **1** or **2** (not shown are the 2-fold and 3-fold screw axes).

Table S3 Hydrogen bonding interactions in **1** and **2**.^a

D-H...A	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
Λ-1:				
intra-layer:				
O1-H1-O3 ^{xi}	0.860(15)	1.755(16)	2.6038(13)	169(2)
inter-layer:				
OW-HW2-O3 ^{xii}	0.825(16)	1.974(18)	2.7153(15)	149(2)
OW-HW1-O2 ^{xiii}	0.871(15)	2.073(17)	2.9095(17)	161(2)
Δ-1:				
intra-layer:				
O1-H1-O3 ^{xiv}	0.838(16)	1.804(17)	2.6083(16)	160(2)
inter-layer:				
OW-HW2-O3 ^{xv}	0.851(15)	1.916(17)	2.7158(18)	156(2)
OW-HW1-O2 ^{xvi}	0.900(16)	2.066(18)	2.926(2)	160(2)
Λ-2:				
intra-layer:				
O1-H1-O3 ^{xi}	0.78(3)	1.85(3)	2.592(3)	159(4)
inter-layer:				
OW-HW2-O3 ^{xii}	0.79(2)	1.98(3)	2.700(3)	150(4)
OW-HW1-O2 ^{xiii}	0.80(2)	2.19(3)	2.969(3)	165(3)

^a D = Donor, A = acceptor. For found and refined atoms the standard deviations are given.

Symmetry relations:

xi = $y+2/3, x+1/3, -z+4/3$; xii = $-x+4/3, -x+y+2/3, -z+5/3$; xiii = $x-y+4/3, -y+5/3, -z+5/3$;

xiv = $y-2/3, x-1/3, -z+2/3$; xv = $-x+2/3, -x+y+1/3, -z+1/3$; xvi = $x-y-1/3, -y+1/3, -z+1/3$.

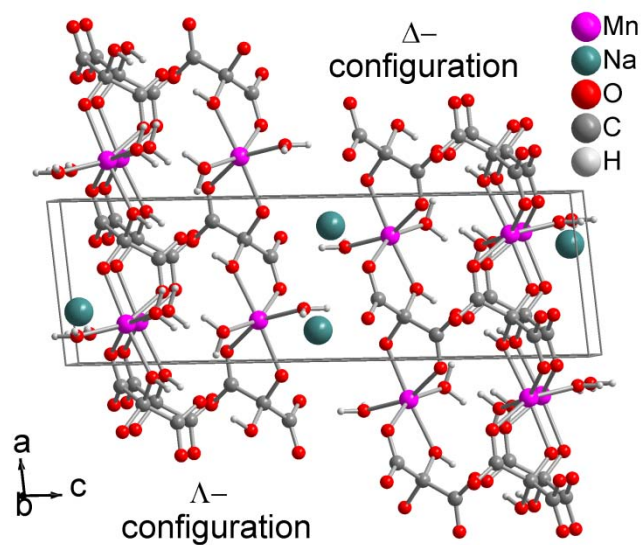


Fig. S5 Packing diagram of $\{Na[Mn(mesox)(H_2O)_2]\}_n$ (Refcode: AZESON).¹ The bis-chelated Mn atoms in a supramolecular 2D layer parallel to the ab plane all have the indicated Λ^- or Δ^- configuration.

¹ J.-M. Shi, S.-C. Zhu and W.-D. Liu, *Trans. Met. Chem.* 2004, **29**, 358-360; catena-(sodium (μ -hydroxy(oxy)malonato)-diaqua-manganese(II)).

Details of magnetic measurements:

Magnetic susceptibility measurements on polycrystalline samples were carried out in the temperature range 1.9-300 K by means of a Quantum Design SQUID magnetometer operating at 500 Oe ($T < 15$ K) and 5000 Oe ($T > 15$ K). Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants¹ and experimental susceptibilities were also corrected for the magnetization of the sample holder. The magnetic susceptibility data have been analyzed by means of the expression for a two-dimensional Heisenberg classical honeycomb lattice.^{2,3} The best fit parameter 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 $\sum_i [(\chi T)_{\text{obs}}(i) - (\chi T)_{\text{calc}}(i)]^2 / \sum_i [(\chi T)_{\text{obs}}(i)]^2$. Almost an identical result [$g = 1.98(1)$, $J = -0.0040(1)$ cm⁻¹ and $R = 3.63 \times 10^{-6}$] is obtained analyzing the magnetic susceptibility data by means of the high-temperature series expansion derived from the two-dimensional Heisenberg model for a $S = 7/2$ honey comb lattice.⁴ N the Avogadro's number 6.0221367×10^{23} mol⁻¹, g the Landé factor, β the Bohr magneton $4.66864374 \times 10^{-5}$ cm⁻¹ G⁻¹, k the Boltzmann's constant 0.69503877 K⁻¹ cm⁻¹

$$\chi = [Ng^2\beta^2 / (3kT)] \cdot X \cdot \left(1 + \sum_{n=1}^8 A_n(X) K^n \right)$$

with

$$A_n(X) = \sum_{i=1}^n a_n X^i$$

$$X = S(S+1)$$

and

$$K = J/kT$$

A_n and a_n are the coefficients for the honey comb lattice and J is the intra-layer magnetic coupling between the local spins of the nearest-neighbours. The a_n coefficients are taken from ref 4, p 179

$$H = -\sum_i J (S_i \cdot S_{i+1})$$

- 1 R. L. Carlin, *Magnetochemistry*; Springer-Verlag: Berlin, Heidelberg, 1986.
- 2 J. Curely, F. Lloret and M. Julve, *Phys. Rev. B*, 1998, **58**, 11465
- 3 L. Cañadillas-Delgado, J. Pasan, O. Fabelo, M. Hernández-Molina, F. Lloret, M. Julve and C. Ruiz-Pérez, *Inorg. Chem.*, 2006, **45**, 10585.
- 4 R. Navarro, *Application of High- and Low-Temperature Series Expansions to Two-dimensional Magnetic Systems*, ed. L. J. de Jongh, Kluwer Academic Publishers, The Netherlands, 1990.
- 5 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993