Microporous chiral metal coordination polymers: hydrothermal synthesis, channel engineering and stability of lanthanide tartrates†

Samadara Thushari, John A. K. Cha, Herman H.-Y. Sung, Stephen S.-Y. Chui, Andy L.-F. Leung, Yu-Fong Yen and Ian D. Williams*

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L-Tartrate ions can endure hydrothermal conditions up to 160 °C to form the robust, enantiopure open-framework coordination polymers $[Ln_2(\text{L-TAR})_3(H_2O)_2]3H_2O$, 1; the addition of succinate results in formation of the related $[Ln_2(\text{L-TAR})_2(SUC)(H_2O)_2]5.5H_2O$, 2 with larger channels than 1, whereas racemic D/L-tartrate gives the more condensed $[Ln_2(\text{D/L-TAR})_3(H_2O)_2]$, 3. TAR = $[C_4H_4O_6]^{2-}$.

The preparation and study of metal coordination polymer (MCP) zeotypes is an active area,[1] since they offer potential advantages over zeolites through more facile introduction of channel functionalization[2,3] or chirality.[4–7] The application of hydrothermal and solvothermal conditions[8] to MCP synthesis typically affords different product phases, with less ancillary ligation and higher dimensionality than those formed at ambient conditions for the same metal–ligand systems.[3,9–11] This is of particular value in the construction of stable 3D open frameworks, the formation of which may be precluded by precipitation of meta-stable kinetic phases.[10]

One problem surrounding the use of chiral organic ligands in hydrothermal preparation of MCPs is whether they can survive the rigorous conditions enantiomerically intact. In general use of chiral bases to template chiral inorganic frameworks has been unsuccessful, though Lii *et al.* found that 1,2-*R*,*R*-diaminocyclohexane survived to give a 1D chain gallophosphate with enantiopure organic cations.[12]

L-tartaric acid is a simple and inexpensive chiral ligand source. Kim *et al.* used a tartrate derivative in the synthesis of a highly porous MCP POST-1, which has chiral catalytic properties,[5] whilst recently Lu and co-workers formed chiral lanthano–molybdate–tartrate hybrid solids,[7] however neither of these was prepared hydrothermally.

Through measurement of circular dichroism (CD) spectra,† we have now established that L-tartrate ions are enantiomerically stable in neutral solutions at temperatures of 160 °C for several days. This has led us to investigate the potential of L-tartrate in the hydrothermal preparation of chiral MCPs. Herein we report our findings for the lanthanide–tartrate system and the successful synthesis and X-ray structure determination of the microporous polymers $[Ln_2(\text{L-TAR})_3(H_2O)_2]3H_2O$ **1**, Ln = La–Yb, Y. Compound **1** is formed by hydrothermal reaction of lanthanide acetate, $Ln(OAc)_3.xH_2O$ (1 mmol), L-tartaric acid (225 mg, 1.5 mmol) and potassium hydroxide (110 mg, 2 mmol) in 2 mL water for 2 days at 140 °C. In the case of erbium this affords 550 mg (65% yield) of pink plate-like crystals up to 200 μm dimension and allowed a single crystal X-ray structure determination.‡

Crystals of **1-Er** belong to the triclinic system. Although the lanthanide metals are pseudo-inversion related, refinement in centric *P*-1 is unsatisfactory. The true solution refined in *P*1 shows **1** to be $[Ln_2(\text{L-TAR})_3(H_2O)_2]3H_2O$. This has an enantiopure 3D open-frameework with a low level of ancillary aquation, just one bound aqua group per metal. The handedness of the structure was clearly confirmed by the Flack parameter. The structure has hydrophilic channels of *ca.* 5 × 7 Å dimension bounded by rings of 4 lanthanide ions and 4 L-tartrate ligands, Fig. 1. The channels have a polar chiral arrangement as may be seen in Fig. 2a which shows the packing along the *a*-axis. The projection of the free tartrate OH groups in all channels is in the same sense and creates a clear channel asymmetry.

Apart from its chiral nature, the 3D network of **1** has some other interesting structural features. Both Ln ions have similar 9-coordinate environments. Although the three tartrate ligands are each crystallographically independent, two are chemically similar and may be classed as μ_4, κ^6, that is they bind to four Ln ions using all 6 oxygen atoms of the tartrate. Each half of the tartrate has '1,2-chelation' involving a carboxylate oxygen and the *ortho*-hydroxy group. These two ligands combine with metal ions to form a condensed 2D slab of $[Ln_2(\mu_4,\kappa^6\text{-L-TAR})_2]$ in the *ab* plane. The third tartrate is quite different and bridges only two Ln ions *via* two bidentate carboxylates and may be described as μ_2, κ^4.

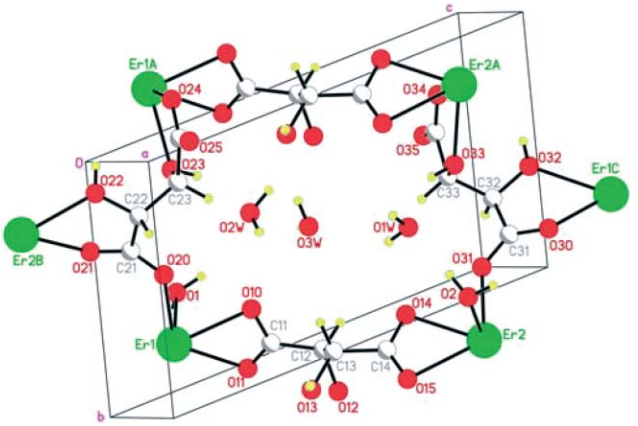


Fig. 1 Asymmetric channel structure in **1** from 4 Er and 4 TAR ligands.

Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China.
E-mail: chwill@ust.hk; Fax: +(852) 3106-3446; Tel: +(852) 2358-7384

† Electronic supplementary information (ESI) available: preparation and characterization details for **1–3**, CD spectra, VT-pXRD data and supplementary figures. See http://dx.doi.org/10.1039/b508574h

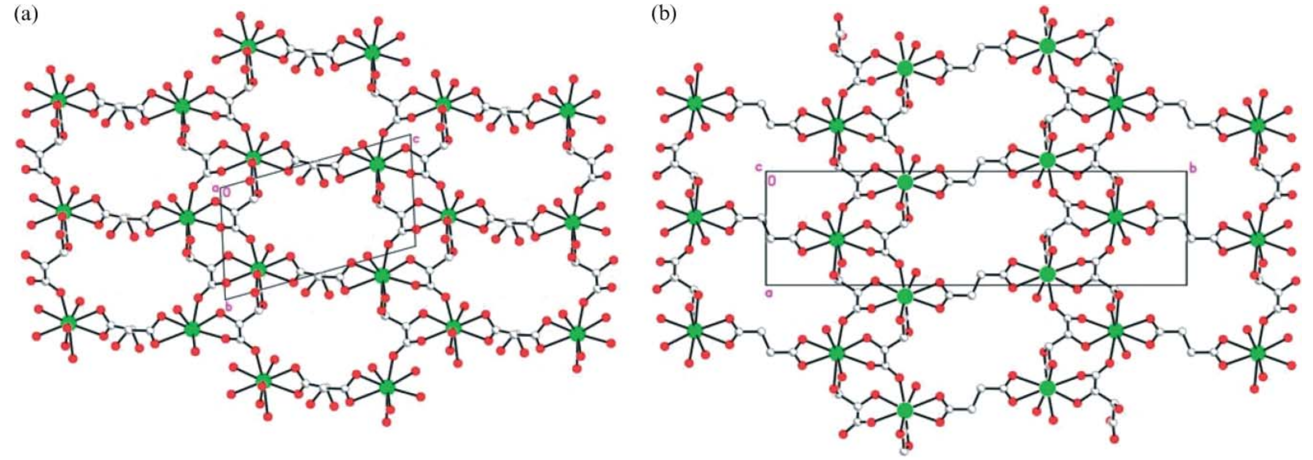
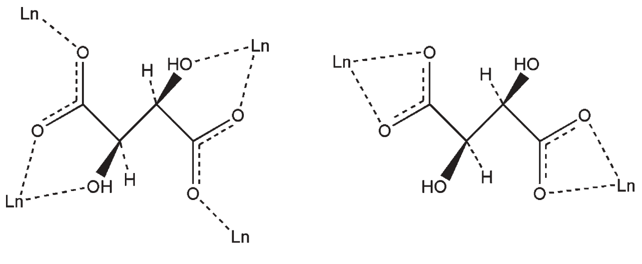


Fig. 2 Packing diagram for a) **1** [Ln_2(L-TAR)$_3$(H_2O)$_2$]3H_2O along the *a*-axis and b) **2** [Ln_2(L-TAR)$_2$(SUC)(H_2O)$_2$]5.5H_2O along the *c*-axis.

These two contrasting binding modes, both previously unreported, are shown in Fig. 3. Whilst μ_4, κ^6- is more stable the lanthanide ions have trouble in coordinating all three tartrates in this way and must settle for one μ_2, κ^4-mode, leading to the rather open nature of the network found in **1**. Since the OH groups in the third tartrate ligand are not utilized, this raised the question of whether the third tartrate might be replaced in the structure by other aliphatic dicarboxylates, thus modifying the channel whilst maintaining the 2D slab component.

To test this idea the hydrothermal reaction of Ln(OAc)$_3$ (Ln = Pr, Er) with L-tartaric acid and succinic acid in 2 : 2 : 1 ratio was carried out at 110 °C for 2 d; this leads to a new phase type **2** with similar but not identical pXRD pattern to **1**. A single crystal X-ray structure determination for Ln = Pr showed that **2** has indeed a mixed ligand network [Ln_2(L-TAR)$_2$(SUC)(H_2O)$_2$]-5.5H_2O with incorporation of the succinate in place of the μ_2-tartrate. Whilst the unit cell and crystal symmetry have changed, the topological relationship of the two structures is clearly shown in Fig. 2. The retention of the strongly bonded [Ln_2(μ_4,κ^6-L-TAR)$_2$] slabs can be seen and the effect of succinate incorporation on channel shape and functionality is also clear. The channels are now enlarged to *ca.* 6 × 9 Å and contain 5.5H_2O rather than 3H_2O per Ln_2 unit.

The preparation of **1** and its analogue **2** again demonstrated the success of hydrothermal crystallization in assisting formation of stable and 3D network MCP structures with optimal ligand binding and low ancillary ligation. This contrasts with numerous previous crystallization attempts in the lanthanide tartrate system under ambient conditions,[13,14] which typically form a kinetic product [Ln(TAR)$_2$H(H_2O)$_x$].[13] Alternatively the use of silica gel to control the crystallization was also found to be ineffective, with different spherulitic aggregates usually formed.[14] The powder diffractograms of these are different from the hydrothermal phases we report herein.



[μ_4, κ^6-2R,3R-$C_4H_4O_6$]

[μ_2, κ^4-2R,3R-$C_4H_4O_6$]

Fig. 3 Tartrate binding modes found in compounds **1** and **2**.

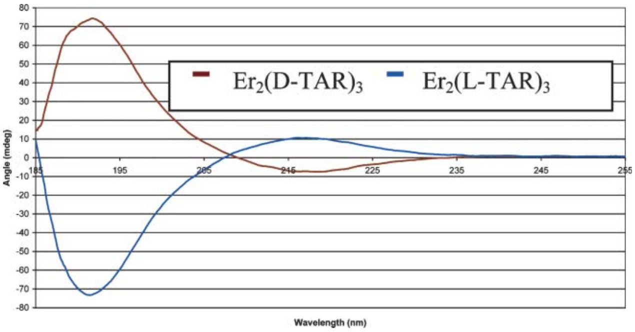


Fig. 4 Circular dichroism spectra of saturated erbium tartrate solutions obtained by sonication of chiral solids **1-D-Er** and **1-L-Er**.

Whilst our single crystal X-ray results were consistent with retention of chirality in the system, based on determination of absolute structure parameter, they were not proof of enantiopurity in the product phase overall. In order to prove this two further experiments were devised. One proof of enantiopurity for **1** came from circular dichroism measurements of sonicated solutions prepared from the solids of **1-Er** prepared separately from natural L-tartaric and unnatural D-tartaric acids. The results are shown in Fig. 4 and show clear optical rotation spectra with mirror image Cotton effects.

A second convincing strategy involved the substitution of the *R*,*R*-configuration L-tartaric acid with either racemic D/L-tartaric acid (*R*,*R*/*S*,*S*) or *meso*-tartaric acid (*R*,*S*) in the original reaction. For erbium this resulted cleanly in formation of two new product phases, **3** and **4** respectively, as found by powder X-ray diffraction, Fig. 5. These findings imply that the extent of chiral racemization under the reaction conditions is minimal, and that the phase **1** isolated from L-TAR is enantiomerically pure, since phase **3** would form before a mixture of **1**-L and **1**-D crystals.

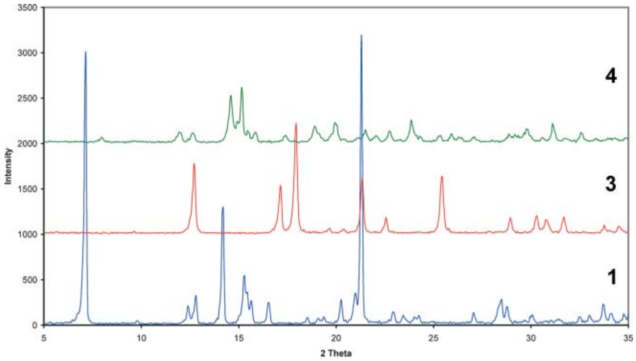


Fig. 5 Powder diffractograms for hydrothermal products of Er(OAc)$_3$ and tartaric acids, 160 °C, 1 d; **1** L-TAR; **3** D/L-TAR; **4** *meso*-TAR.

A structure determination of phase **3** demonstrated it to be [Er$_4$(L-TAR)$_3$(D-TAR)$_3$(H$_2$O)$_4$], Fig. 6. Its space group is *Iba*2 which is non-centrosymmetric, but the crystallographic glide planes require the presence of both L- and D-TAR moieties. The structure of the *meso*-TAR product **4** remains undetermined due to the poor crystallinity as shown in its powder XRD pattern, though its analytical data are consistent with an overall formula of [Er$_2$(*m*-TAR)$_3$]5H$_2$O, isomeric with **1**.

The structural robustness of these new tartrate MCPs has been studied by *in-situ* variable temperature powder XRD.† The condensed framework **3** has an impressive stability up to *ca.* 225 °C. Intriguingly the more open framework **1** retains crystallinity to 250 °C, through it undergoes two structural phase changes at 100 °C (irreversible) and 200 °C (reversible). These high temperature forms retain the original [Ln$_2$(μ_4,κ^6-L-TAR)$_2$] slabs, but the μ_2-tartrate binding is modified. The channels are reduced in size but allow reversible sorption/desorption of water, indicating true microporosity.

In summary we have successfully shown that hydrothermal crystallization of new chiral network polymers using a simple and readily available chiral source is possible at temperatures up to 160 °C. The compact nature of tartrate renders MCPs made solely from it limited in porosity, however the retention of chirality under the forcing conditions and the robustness of the resulting structures have implications for its use in more open chiral frameworks in combination with other spacer ligands, as demonstrated by preparation of our mixed tartrate–succinate compound **2**, or through use of extended tartrate derivatives as in Kim's POST-1.[5]

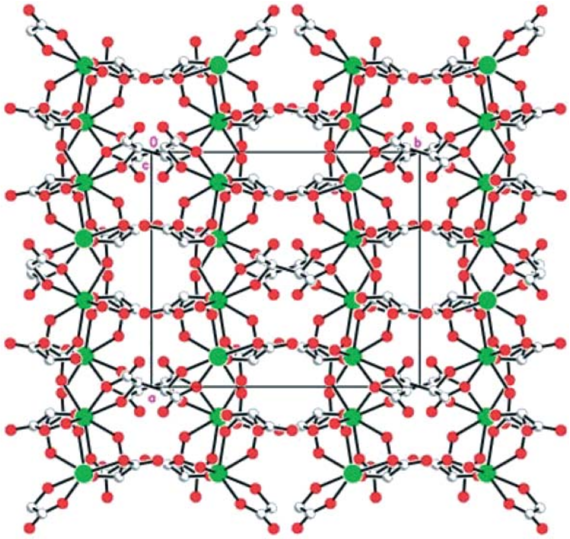


Fig. 6 Packing diagram for [Er$_2$(D/L-TAR)$_3$(H$_2$O)$_2$] along the *c*-axis.

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Notes and references

‡ Crystal data for [Er$_2$(L-TAR)$_3$(H$_2$O)$_2$]3H$_2$O, **1-Er**; C$_{12}$H$_{22}$Er$_2$O$_{23}$, Fw 868.8, T = 100(2) K, λ = 0.71073 Å, triclinic, $P1$, a = 5.9565(4), b = 7.3716(5), c = 13.1769(9) Å, α = 102.925(1), β = 101.637(1), γ = 90.785(1)°, V = 551.28(6) Å^3, Z = 1, Dc = 2.62 Mg/m^3, μ = 7.67 mm^{-1}, 2Θmax = 56.6°, data/restraints/parameters 3301/3/269, S = 1.015, $R1$ = 0.0329, w$R2$ (all) = 0.0814, Flack 0.013(18), Δe +1.54 and −1.83 e.Å^{-3}; for [Pr$_2$(L-TAR)$_2$(SUC)(H$_2$O)$_2$]5.5H$_2$O, **2-Pr**; C$_{12}$H$_{27}$Pr$_2$O$_{23.5}$, Fw 829.16, T = 100 K, λ = 0.71073 Å, orthorhombic, $P2_12_12$, a = 7.5802(6), b = 28.044(2), c = 6.1008(5) Å, V = 1296.9(2) Å^3, Z = 2, Dc = 2.12 Mg/m^3, μ = 3.81 mm^{-1}, 2Θmax = 50°, data/restraints/parameters 2205/0/143, S = 1.057, $R1$ = 0.0368, w$R2$ (all) = 0.0891, Flack 0.01(4), Δe +1.42 and −1.65 e.Å^{-3}; for [Er$_2$(D/L-TAR)$_3$(H$_2$O)$_2$], **3-Er**; C$_{12}$H$_{16}$Er$_2$O$_{20}$, Fw 814.77, T = 223(2) K, λ = 0.71073 Å, orthorhombic, *Iba*2, a = 12.3605(19), b = 14.081(2), c = 10.4021(15) Å, V = 1810.4(5) Å^3, Z = 4, Dc = 2.99 Mg/m^3, μ = 9.33 mm^{-1}, 2Θmax = 50.0°, data/restraints/parameters 1547/1/74, S = 1.086, $R1$ = 0.0326, w$R2$ (all) = 0.0622, Flack 0.06(3), Δe +0.99 and −1.07 e.Å^{-3}. CCDC 276254–276256. See http://dx.doi.org/10.1039/b508574h for crystallographic data in CIF or other electronic format.

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