

Porous lanthanide–organic framework with zeolite-like topology†

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Two novel isomorphous porous frameworks of Ln(III), $\{[Ln_2(\text{imdc})_2(\text{H}_2\text{O})_3](\text{H}_2\text{O})\}_m$ [Ln = Gd(III) (**1**) and Er(III) (**2**)] have been synthesized hydrothermally using multifunctional 4,5-imidazoledicarboxylic acid (imdc) as a connector; they have a zeolite-like network topology which can provide another form upon dehydration, and exhibit selective adsorption properties for H₂O over N₂, CO₂ and MeOH.

The crystal engineering of coordination polyhedra and networks with different geometrical and topological characteristics has developed rapidly during the past decade.¹ In particular “node and spacer” methodology has proven to be remarkably successful in the rational design of metal–organic architectures with novel functionalities like gas storage, heterogeneous catalysis, and optoelectronic properties.² Metal–organic hybrid frameworks with lanthanide ions are of great interest due to their unique physical and chemical properties attributable to the high coordination number of lanthanide ions with structural flexibility and thermodynamic stability, magnetic and photo-luminescent properties.³ To satisfy the high coordination number lanthanide frameworks always contain ancillary ligands like water molecules and often collapse of the framework occurs when such ancillary ligands are removed from the coordination site. However, in some cases stable frameworks are prepared as porous solids with coordinatively unsaturated and Lewis-acidic lanthanide ions having the potential for sorption and catalytic activity,⁴ which to date are rare in the literature.⁵ In this work we have employed a single multifunctional ligand, 4,5-imidazoledicarboxylic acid (imdc), which has multiple coordination sites for rigid and stable higher dimensional structures. In particular, imdc is a proton donor, providing various acid–base type coordination modes. Of most significance is the arrangement of the two N atoms with the N–X–N angle of about 144° (X = center of the imide ring), which is very close to the Si–O–Si angle of 145° in zeolites. Here we report two novel isomorphous 3D hybrid frameworks of Ln(III), $\{[Ln_2(\text{imdc})_2(\text{H}_2\text{O})_3](\text{H}_2\text{O})\}_m$ [Ln = Gd(III) (**1**) and Er(III) (**2**)], having a zeolite-like network topology along with their sorption and magnetic properties. Most interestingly the porous framework displays sorption properties, with preference for water molecules over methanol, although the latter has capability of not only coordination to the metal but also hydrogen bonding.

The frameworks **1** and **2** have been synthesized by hydrothermal techniques using Ln(NO₃)₃·6H₂O and imdc in the presence of KOH. The molecular structure of **1** was determined by X-ray crystallography† and Fig. 1 shows the coordination environment

of Gd(III) with the atom numbering scheme. There are two crystallographically independent octa-coordinated Gd(III) ions (Gd1 and Gd2) in the asymmetric unit with different coordination environments. There are also two crystallographically independent tri-anionic imdc ligands (L1 = O1/O2/O3/O4/N1/N2; L2 = O5/O6/O7/O8/N3/N4) with different coordination modes to each other: L1 shows hepta-dentate and L2 shows hexa-dentate binding mode. The Gd1 is octa-coordinated with two chelated L2 and one L1 imdc ligands (O5, O7/O1, N1/N3*, O6*; * = 3/4 – y, 1/4 + x, 1/4 + z) and two water molecules (O2w and O3w) (Fig. 1(a)). The Gd2 is coordinated to (O2, O3/N2*, O4*/N4ⁱ, O8ⁱ; i = –1/4 + y, 3/4 – x, 3/4 + z) from two chelated L1 and one L2 imdc ligands and one water molecule (O1w) and the octa-coordinated geometry is completed by a bridging oxygen (O2ⁱⁱ; ii = 1/2 – x, 1/2 – y, 3/2 – z) (Fig. 1(b)). The Gd1–O bond distances are in the range 2.313(5)–2.614(5) Å, slightly shorter than those of Gd2–O with the range 2.349(5)–2.699(6) Å. Each Gd1 is attached to two different Gd1 and Gd2 whereas each Gd2 is attached to three different Gd1 and two different Gd2 ions through *syn–syn* as well as *syn–anti* carboxylate bridges constructing the wall of the column structure along the z-axis (Fig. S1(a)†). It is interesting to note that the

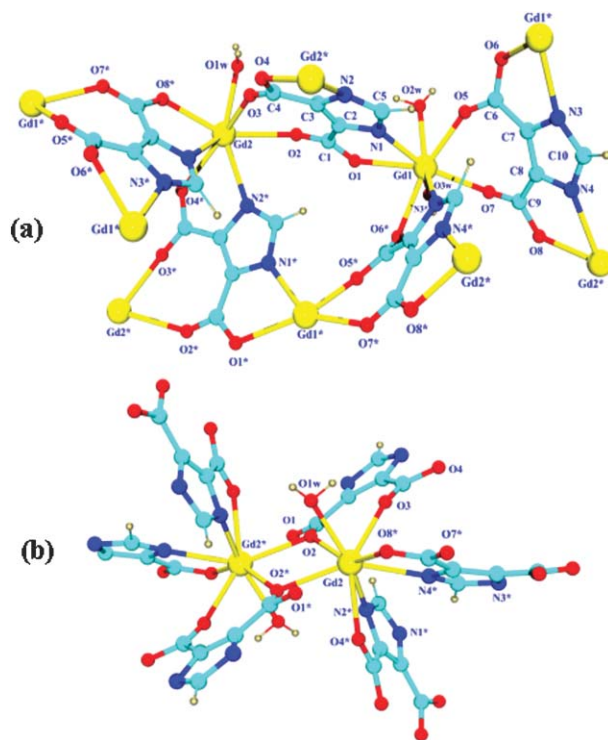


Fig. 1 View of the coordination environment of (a) Gd1 and (b) Gd2 in framework **1** with atom numbering.

† Electronic supplementary information (ESI) available: experimental details, view of the column structure, TG analyses and $\chi_{\text{M}}T$ vs. T curves for frameworks **1** and **2**. See http://www.rsc.org/suppdata/cc/b5/b500971e/*kitagawa@sbchem.kyoto-u.ac.jp

column structure with ligand L1 creates a nanotube like form (Fig. S1(b)†), which is obstructed by the imidazole part of L2 (Fig. S1(c)†). The columns are doubly bridged by Gd2–O2–Gd2ⁱⁱⁱ (Gd2–O2–Gd2ⁱⁱⁱ 114.6(2)°; iii = 1/2 – x, 1/2 – y, 3/2 – z) connectivity, forming a high-density three-dimensional network (Fig. 2). The resultant three dimensional networks contain one-dimensional channels (3.68 × 3.68 Å²; V_{void} = 10.1% of the total crystal volume)^{6,7} along the crystallographic *c*-axis and occupied by four water molecules, which are strongly H-bonded to the coordinated water molecules as well as with the carboxylate oxygen atoms (O–H···O: 2.671(7)–3.044(11) Å) (Fig. 2). The dehydrated framework provides 19.7% void space of the total crystal volume with the channel dimension of 5.88 × 5.88 Å² (Fig. 3). It is worth noting that the Gd1–N1(imid)N2–Gd2* and Gd1*–N3(imid)N4–Gd2* angles are 147.56° and 159.91° respectively, which are close to the Si–O–Si angle 145° in zeolite, providing a zeolite-like network topology (Fig. 3), and are also consistent with recent reports of an imidazole-containing

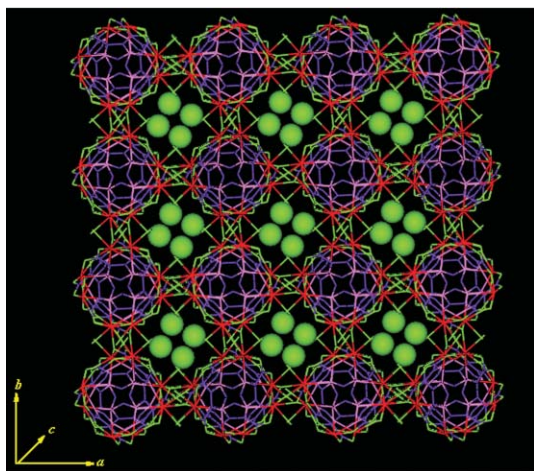


Fig. 2 View of the 3D environment of framework **1** with water (O = green) filled channel along the crystallographic *c*-axis.

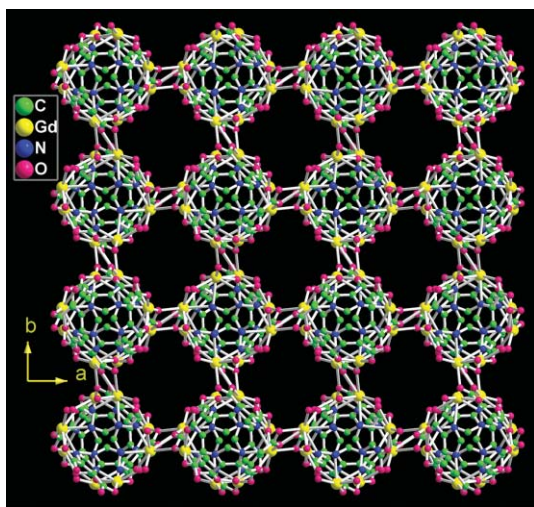


Fig. 3 View of the 3D open zeolite-like network topology of **1** in the crystallographic *ab*-plane. Guest and coordinated water molecules have been removed for clarity.

zeolite-like network with the two N-atoms at 144°.⁸ The X-ray powder diffraction, IR, elemental and thermal analysis shows that **2** is isomorphous with framework **1**, affording the formula $\{[\text{Er}_2(\text{imidc})_2(\text{H}_2\text{O})_3](\text{H}_2\text{O})\}_n$ (**2**) (Fig. 4).

The TGA curve indicates that the guest and coordinated water molecules are removed in a single step in the temperature range ~25–180 °C and ~25–190 °C for frameworks **1** and **2**, respectively (Fig. S2 & S3†). The release of the water molecules up to a high temperature is ascribed to the strong cooperative H-bonding interaction between the coordinated and guest water molecules. The decomposition of the framework starts at ~290 °C and ~315 °C for **1** and **2**, respectively, and no weight loss was observed in between these temperatures, indicating the presence of a stable dehydrated framework over a wide range of temperatures. The XRPD patterns of the dehydrated framework of **1**, *i.e.*, **1a** shows that some new peaks appeared, whereas peaks at $2\theta = 8.78$ (200), 12.44 (220), and 17.74(312) remained unaltered (Fig. 4). This indicates that the resulting solid Gd₂(imidca)₂ (**1a**) retains crystallinity and a certain structural change or distortion occurs after removal of the coordinated and guest water molecules, forming a porous metal–organic framework with coordinatively unsaturated lanthanide ions. Dehydration with the structural transformation corroborates the flexibility of the frameworks and the structural stability was conferred by the chelated imidc ligand.

Based on well-defined **1a** and **2a**, Ln₂(imidca)₂, adsorption isotherms of samples of Gd₂(imidca)₂ were measured for sorption of O₂, N₂, Ar and CO₂ and solvent molecules H₂O and MeOH. The adsorption isotherms of O₂ (surface area: 14.1 Å²),^{9,10} N₂ (16.3 Å²), Ar (14.7 Å²) (at 77 K) and CO₂ (17.9 Å²) (at 195 K) are shown in Fig. 5 and clearly indicate no occlusion except surface adsorption, therefore, these molecules cannot diffuse into the micropores. On the other hand, H₂O (10.5 Å²) and MeOH (18.0 Å²) sorptions were also measured at 298 K (Fig. 5), and indicate that MeOH cannot diffuse but H₂O molecules can go inside the framework. The DR analysis suggests that there are 3.16 molecules of H₂O per two Gd(III) in the framework and the surface area based on the H₂O cross section is 372.13 m² g⁻¹. The adsorption selectivity is chiefly associated with the structural

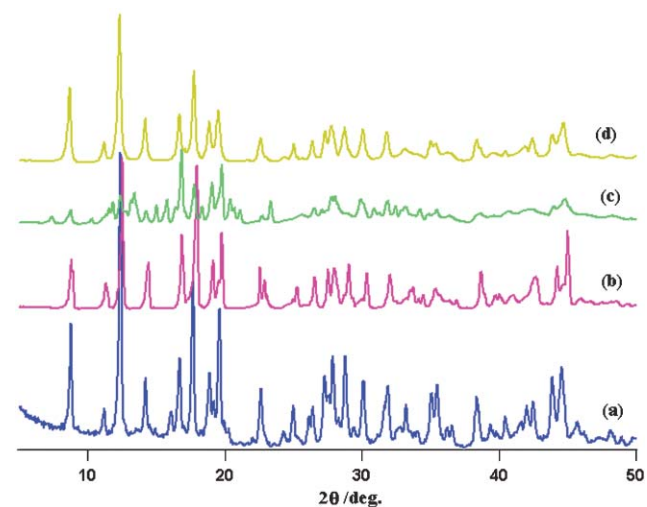


Fig. 4 XRPD patterns of (a) as-synthesized $\{[\text{Gd}_2(\text{imidc})_2(\text{H}_2\text{O})_3](\text{H}_2\text{O})\}_n$ (**1**); (b) as-synthesized $\{[\text{Er}_2(\text{imidc})_2(\text{H}_2\text{O})_3](\text{H}_2\text{O})\}_n$ (**2**); (c) dehydrated **1**, **1a** at 190 °C; (d) rehydrated **1**.

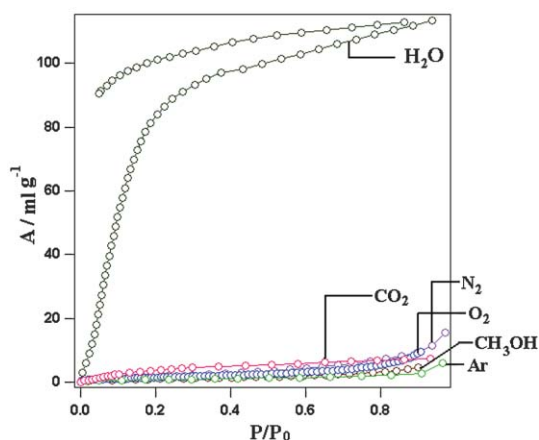


Fig. 5 Adsorption isotherms of different adsorbates measured for **1** in dehydrated state.

transformation after the dehydration, which implies that after dehydration the effective aperture of the channel becomes smaller compared to the kinetic diameter of the related adsorbate.^{5,11} The adsorption studies corroborate the observation that the framework responded with highest affinity towards H₂O compared to MeOH and other gas molecules.

Measurement of the temperature dependent magnetic properties of both frameworks was carried out in the temperature range 300–2 K. The temperature dependence of the $\chi_M T$ values (χ_M = molar magnetic susceptibility) for **1** and **2** are shown in Fig. S4 & S5, respectively.† At 300 K, the $\chi_M T$ is equal to 13.83 cm³ mol⁻¹ K for **1**, which is a little lower than the value attributable to two non-interacting Gd³⁺ spin carriers ($\chi_M T$ = 15.7 cm³ mol⁻¹ K). Upon lowering the temperature $\chi_M T$ decreases and it reaches 9.72 cm³ mol⁻¹ K at 2 K. On the other hand, for **2**, the $\chi_M T$ value at 300 K is equal to 20.75 cm³ mol⁻¹ K, which is also smaller than the value expected for two magnetically isolated Er³⁺ ions in the ⁴I_{15/2} ground state ($\chi_M T$ = 22.2 cm³ mol⁻¹ K). As the temperature decreases, it reaches a minimum of 8.29 cm³ mol⁻¹ K. A 1/ χ_M vs. T (Curie) plot shows a straight line down to very low temperatures for both the frameworks **1** and **2**. Fitting this curve to the Curie–Weiss law gives a Curie constant C = 13.85 cm³ mol⁻¹ K and Weiss temperature θ = -0.199 K for **1**, and for **2**, C = 20.92 cm³ mol⁻¹ K and θ = -1.700 K. The negative θ value in both cases is indicative of (weak) antiferromagnetic interactions, in agreement with the decrease in $\chi_M T$ on going to low temperatures.

In conclusion we have synthesized two isomorphous 3D porous frameworks of Gd(III) and Er(III), by rationally choosing a multi-connectivity ligand, which exhibit zeolite-like network topology. The framework shows flexible behavior, *i.e.*, after dehydration a framework transformation occurs which is shown by the XRPD patterns. The dehydrated frameworks only selectively adsorb H₂O molecules from among a number of adsorbates.

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Notes and references

‡ Crystal Data: C₁₀H₁₀Gd₂N₄O₁₂; Formula weight, 692.72; Tetragonal; Space group, *I4₁/a* (No. 88); $a = b = 20.1321(15)$; $c = 16.1402(12)$ Å; $V = 6541.7(8)$ Å³; $Z = 16$; $\rho_{\text{calc}} = 2.813$ g cm⁻³; $\mu(\text{MoK}\alpha) = 8.118$ mm⁻¹; $F(000) = 5152$; $T = 223$ (K); $\lambda(\text{MoK}\alpha) = 0.71069$ Å; $\theta_{\text{max}} = 27.5^\circ$; Total data = 23671; Unique data = 3751 ($R_{\text{int}} = 0.136$); Observed data [$I > 2\sigma(I)$] = 2806; $R = 0.0442$; $wR = 0.1122$, GOF = 0.95. CCDC 261754. See <http://www.rsc.org/suppdata/cc/b5/b500971e/> for crystallographic data in CIF or other electronic format.

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