

A lanthanide-based metal–organic framework with a dynamic porous property†

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Hydrothermal reaction of $\text{La}(\text{NO}_3)_3$, NaHCO_3 and H_3L (H_3L = pyrazole-3,5-dicarboxylic acid) gives a 3D metal–organic framework with a dynamic porous property.

Metal–organic frameworks (MOFs) have received much interest in recent years because of their structural diversity and potential applications in separation, storage, catalysis, and as multifunctional materials.^{1–4} Although a great variety of MOFs with diverse compositions and structures have been reported, those based on lanthanide ions remain less studied. This hiatus is attributable to the high coordination number requirement as well as the flexible coordination geometry of these unique metal ions. However, it is these special features of lanthanide coordination chemistry that make their MOFs particularly attractive, both structurally⁵ and in terms of application. On the one hand, the bulky metal ions generally require, in addition to the framework forming ligands, solvent molecules to achieve saturation of their coordination sphere. On the other hand, their flexible coordination geometry facilitates structural re-organization without disrupting the overall framework structure of the MOF.⁶ Upon removal of coordinated solvent molecules, the metal ions may adjust their coordination geometry to accommodate such changes, but the overall framework integrity is maintained. The unsaturated metal ions are then poised for binding and activation with desired substrates because of their inherent Lewis acidity.^{7,8} The processes of desolvation and guest binding, together with any structural re-organization in between, causes the MOF to be structurally dynamic. We note that current efforts in lanthanide-based MOFs have mainly been focused on their synthesis and determination of their static solid-state structure,^{5–8} and reports on dynamic porous lanthanide-based MOFs remain scarce,⁹ despite such a property playing a key role in the understanding of the catalytic mechanism.¹⁰ Herein, we report the synthesis and crystal structure of $\{[\text{La}_2(\text{HL})_2(\text{H}_2\text{O})_2(\text{CO}_3)](\text{H}_2\text{O})_7\}_\infty$ (**1**), (H_3L = pyrazole-3,5-dicarboxylic acid), a lanthanide-based MOF, as well as its dynamic porous property.†

Complex **1** was prepared through the hydrothermal reaction of H_3L , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and NaHCO_3 . Crystallographic studies reveal that in its asymmetric unit there is one La^{3+} , one HL^{2-} , half a carbonate ion, and four and a half water molecules. As shown in

Fig. 1, the La^{3+} ion is deca-coordinate, featuring coordination by four HL^{2-} , two carbonate, and one aqua ligand. For a particular La^{3+} , only one of the two HL^{2-} carboxylate groups is coordinating, three being monodentate and the fourth one chelating. One of the HL^{2-} ligands, with its carboxylate group monodentate in coordination, uses the N atom *cis* to this carboxylate group to form a five-membered ring with the metal ion. The bond lengths for La–O and La–N are 2.518(2)–2.906(7) and 2.812(7) Å, respectively. These bond distances are within the expected ranges reported for La^{3+} complexes.^{11,12}

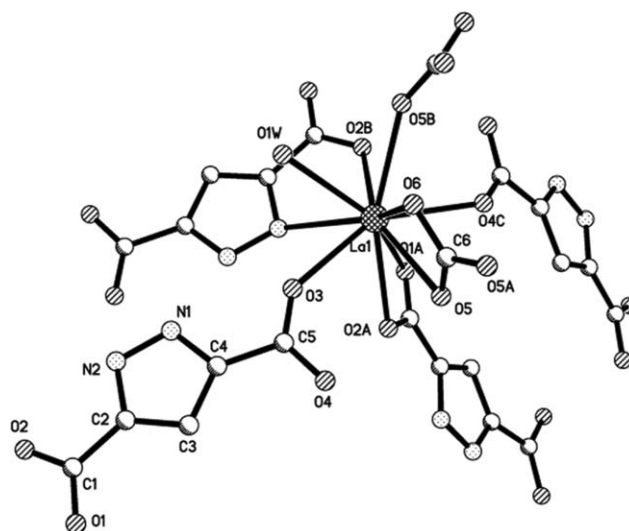


Fig. 1 ORTEP plot showing the coordination environment of the La^{3+} ion in **1**.

For the same La^{3+} ion, one carbonate ligand is monodentate, while the other is chelating. Further, the monodentate ligand uses the same O atom to bridge a neighbouring La^{3+} , thus forming a one dimensional (1D) chain of the deca-coordinate La^{3+} ions. This bridging interaction is reinforced by two HL^{2-} ligands, each using a carboxylate O to connect to a neighbouring La^{3+} ion. Two of such chains are then bridged by the chelating carbonate ligands by sharing a common O, each of these carbonate ligands generates a pair of chelating interactions, affording a 1D tape of two of the above mentioned 1D chains (Fig. 2). Between the two chains, the La^{3+} ions are separated by a shortest distance of 4.92 Å, while the neighbouring La^{3+} ions within the same chain are separated by a distance of 4.39 Å. Individual tapes are linked together *via* La^{3+} –carboxylate coordination using the second carboxylate group of the HL^{2-} ligand, resulting in the sophisticated MOF structure (Fig. 3). Water molecules are located in the pseudo-hexagonal channels and are hydrogen bonded to the carboxylate group of

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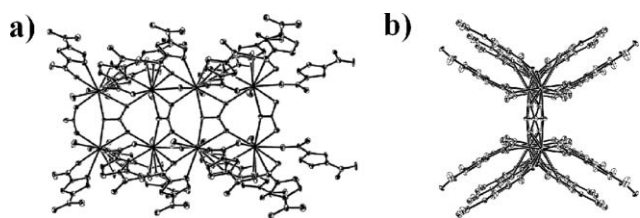


Fig. 2 (a) ORTEP plot showing the 1D tape structure in **1**, (b) side view of (a).

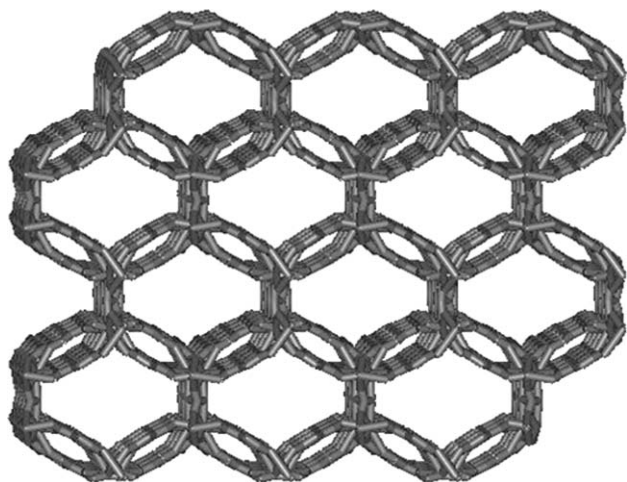


Fig. 3 Ball and stick plot showing the 3D structure of **1** viewed along the *a* axis. Hydrogen atoms and guest water molecules were removed for clarity.

the framework. The total potential solvent area occupied is 30.5% of the cell volume.¹³

Thermogravimetric analysis of complex **1** (ESI, Fig. S1)† reveals an initial weight loss of 15.43% between room temperature and 150 °C, consistent with the loss of lattice water (calcd 15.60%). No further weight loss was observed between 150 and 350 °C, indicating that over this temperature range, the composition of the dehydrated product remains unchanged.

To explore any structural transitions upon temperature change and the possible dynamic behaviour of the MOF structure, variable temperature XRD patterns of **1**, both pristine and dehydrated, were obtained (Fig. 4). Fitting these patterns gives both the space group and unit cell parameters, as shown in Table 1. The samples heated at 25 °C and 80 °C and the sample heated and then cooled to 25 °C are of the same space group, and their cell parameters are similar to those obtained using single-crystal X-ray diffraction. These results suggest that the framework of **1** is maintained during the dehydration process, and re-hydration is possible and regenerates the original hydrated structure. However, the sample

Table 1 The space group and cell parameters for the fitting of X-ray powder diffraction data using the Jade 5 procedure¹⁴ (25* indicates sample cooling to 25 °C in air after going through the heating cycle)

Temp./°C	Space group	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	β /°	<i>V</i> /Å ³
25	<i>Pnma</i>	8.528	15.551	18.778	90	2490.4
80	<i>Pnma</i>	8.396	17.989	15.806	90	2387.2
190	<i>P2₁/c</i>	5.320	16.232	13.771	104.71	1150.3
25*	<i>Pnma</i>	8.485	15.392	18.743	90	2447.9

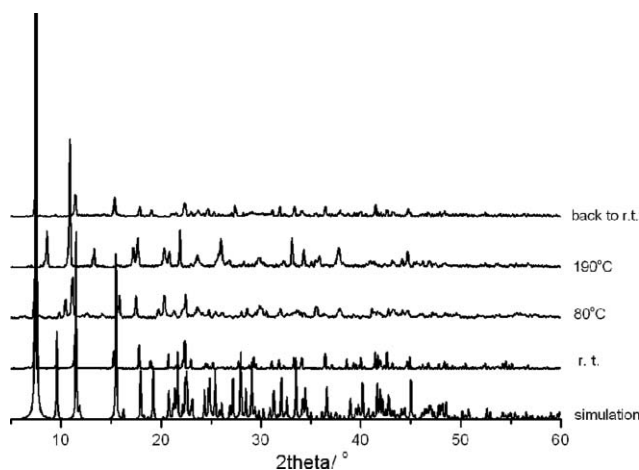


Fig. 4 PXRD patterns for **1** at different temperatures.

heated to 190 °C differs significantly from the other samples. Due to the cracking of the single crystals at such a high temperature, we have not been able to establish its structure using single-crystal X-ray diffraction. Since there is no change in its composition, it is reasonable to attribute such structural changes to the removal of guest water and the following reorganization of the inherently flexible coordination sphere of La³⁺. Similar phenomena have been reported in the complex of Cr(OH)-{O₂CC₂H₄CO₂}-H₂O.¹⁵

In summary, we report the synthesis and crystal structure of a lanthanide-based MOF. TGA and XRD studies reveal that its framework structure is maintained during a dehydration and re-hydration process, and that the removal of the guest water molecule results in a change of its porous shape. Gas adsorption studies of the MOF is under way.

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Notes and references

† Crystal data for **1**: C₁₁H₂₂La₂N₄O₂₀, colourless block, *M* = 808.15, orthorhombic, space group *Pnma* (no 62), *a* = 8.521(2), *b* = 18.477(4), *c* = 15.380(4) Å, *V* = 2421.4(10) Å³, *Z* = 4, *T* = 223(2) K, *D_c* = 2.217 g cm⁻³, μ (MoK α) = 3.579 mm⁻¹, 12529 reflections collected, 2460 are independent (*R_{int}* = 0.0513). The final agreement factors are *R₁* = 0.0595 (*I* > 2 σ (*I*)) with 2254 data and *wR₂* = 0.1204 for 2460 data based on 173 parameters.

- 1 A. Corma, *Chem. Rev.*, 1997, **97**, 2373; J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982.
- 2 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- 3 S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276; D. Braga, *Chem. Commun.*, 2003, 2751; R. H. Wang, M. C. Hong, J. H. Luo, R. Cao and J. B. Weng, *Chem. Commun.*, 2003, 1018.
- 4 D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273; R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, *Nature*, 2005, **436**, 238.
- 5 J. Lu, E. H. Shen, Y. G. Li, D. R. Xiao, E. B. Wang and L. Xu, *Cryst. Growth Des.*, 2005, **5**, 65; X. P. Yang, R. A. Jones, J. H. Rivers and R. P. Lai, *Dalton Trans.*, 2007, **35**, 3936.
- 6 V. Kiritis, A. Michaelides, S. Skoulika, S. Golhen and L. Ouahab, *Inorg. Chem.*, 1998, **37**, 3407; L. Pan, K. M. Adams, H. E. Hernandez,

- X. T. Wang, C. Zheng, Y. Hattori and K. Kaneko, *J. Am. Chem. Soc.*, 2003, **125**, 3062.
- 7 F. Serpaggi and G. Ferey, *J. Mater. Chem.*, 1998, **8**, 2737; T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651.
- 8 T. M. Reineke, M. Eddaoudi, M. O'Keefe and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 1999, **38**, 2590.
- 9 S. Kitagawa, *Chem. Commun.*, 2005, 2436.
- 10 S. Horike, M. Dincă, K. Tamaki and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 5854.
- 11 L. Pan, J. L. Huang, Y. G. Wu and N. W. Zheng, *Angew. Chem., Int. Ed.*, 2000, **39**, 527; J. Xia, B. Zhao, H. S. Wang, W. Shi, Y. Ma, H. B. Song, P. Cheng, D. Z. Liao and S. P. Yan, *Inorg. Chem.*, 2007, **46**, 3450.
- 12 S. A. Cotton, V. Franckevicius, M. F. Mahon, L. L. Ooi, P. R. Raithby and S. J. Teat, *Polyhedron*, 2006, **25**, 1057.
- 13 A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, C34.
- 14 *XRD Pattern Processing and Identification Program Release 5.0*, Materials Data, Inc.
- 15 C. Serre, F. Millange, C. Tnouvenot, M. Nogues, G. Marslier, D. Louer and G. Ferey, *J. Am. Chem. Soc.*, 2002, **124**, 13519; L. G. Beauvais, M. P. Shores and J. R. Long, *J. Am. Chem. Soc.*, 2000, **122**, 2763; S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109.