



A new 3D metal–organic framework with (4, 8)-connected AlB₂ topology constructed from coordinated evolution of a C₃ symmetry ligand

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ABSTRACT

A new 3D lanthanide metal–organic framework, {[Ce(L)(DMF)]·2.5(DMF)·3(H₂O)}_n (1) (H₃L = N,N',N''-tris(4-carboxyphenyl)-1,3,5-benzenetricarboxamide, DMF = N,N'-dimethylformamide) has been synthesized under solvothermal condition. Compound 1 features a 3D non-interpenetrated binodal (4, 8)-connected AlB₂ topology with a Schläfli symbol of (4⁵.6)₂(4¹⁰.6¹⁴.8⁴), where the C₃ symmetry ligand H₃L evolves into an unusual 4-connected node and dinuclear cerium cluster acts as an 8-connected node. Furthermore, compound 1 displays blue emission in the solid state at room temperature.

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The construction of metal–organic frameworks (MOFs) with structural features of metallic or inorganic compounds is of high current interest for their potential applications [1]. The AlB₂ topology structure, featuring the 3⁶ layers alternatively packing with 6³ sheets, is an important and frequently encountered structure type in inorganic compounds [2]. However, only a few MOFs with AlB₂ topology have been reported to date. In particular, highly-connected AlB₂ structures are still rare, such as binodal (4, 8) and (6, 12)-connected frameworks [3], possibly owing to the limited coordination sites of metal centers and the steric hindrance of most commonly used organic ligands [4]. To construct MOFs with such topology, trigonal organic ligands are regarded as good candidates, because they have been extensively used to construct 6³ networks [3,5]. Based on above deduction, we notice a semi-rigid C₃ symmetry aromatic carboxamide ligand, N,N',N''-tris(4-carboxyphenyl)-1,3,5-benzenetricarboxamide (H₃L). Compared to the widely utilized C₃ symmetry tricarboxylic acids, H₃L possesses similar geometric configuration, more coordination sites and the potential to construct higher-connected and intriguing frameworks due to the coordination of carbonyl-oxygen atoms of the amide groups in presence of the induced conditions. On the other hand, lanthanide ions are considered for this construction, not only because of their high tendency to coordinate with oxygen atom donors, but also of their high coordination number, which facilitates the formation of highly-connected frameworks [6].

Herein, we report a 3D lanthanide MOF {[Ce(L)(DMF)]·2.5(DMF)·3(H₂O)}_n (1) with (4, 8)-connected AlB₂ topology. In the

structure, the C₃ symmetry L evolves into a 4-connected node by the coordination of one oxygen atom from amide group, together with dinuclear Ce(III) cluster acting as an 8-connected node. To our knowledge, it is the first example of lanthanide MOF with (4, 8)-connected AlB₂ topology.

Colourless prismatic crystals of 1 were prepared by the reaction of Ce(NO₃)₃·6H₂O, H₃L and 1,1'-(1,4-butanediyl)bis(imidazole) (bbi) under solvothermal condition [7]. Single-crystal X-ray diffraction analysis [8] shows that 1 crystallizes in the monoclinic system, space group P2(1)/c. Each asymmetric unit consists of one Ce(III) ion, one L ligand and one coordinated DMF molecule, but not containing bbi. It should be pointed out that the single-crystal data collected on a laboratory-based diffractometer does not allow the precise determination of disordered solvent molecules. Solvent molecules located in the framework of 1 are determined by considering a combination of elemental analysis and synthesis systems. And it can be inferred that there are two and a half DMF and three H₂O molecules in 1, further evidenced by IR spectra (Fig. S1) and thermogravimetric analysis (TGA) (Fig. S2).

The crystal structure of 1 exhibits a non-interpenetrated 3D framework and exists a heart-like channel along the Z axes (Fig. 1), which possesses 41.1% solvent cavity of the total crystal volume calculated by PLATON [9]. As shown in Fig. 2, each Ce(III) ion is crystallographical and adopts a nine-coordinated slightly distorted tri-capped trigonal-prismatic coordination geometry, coordinated by seven oxygen atoms from deprotonated L ligands, one oxygen atom from monodentate carbonyl-oxygen of the amide group, and one oxygen atom from coordinated DMF. The Ce–O distances present a broad region in range from 2.396(3) to 2.880(4) Å, in which the longest bond length is longer than those in lanthanide compounds bridged by carboxylate group, and can be regarded as a weak

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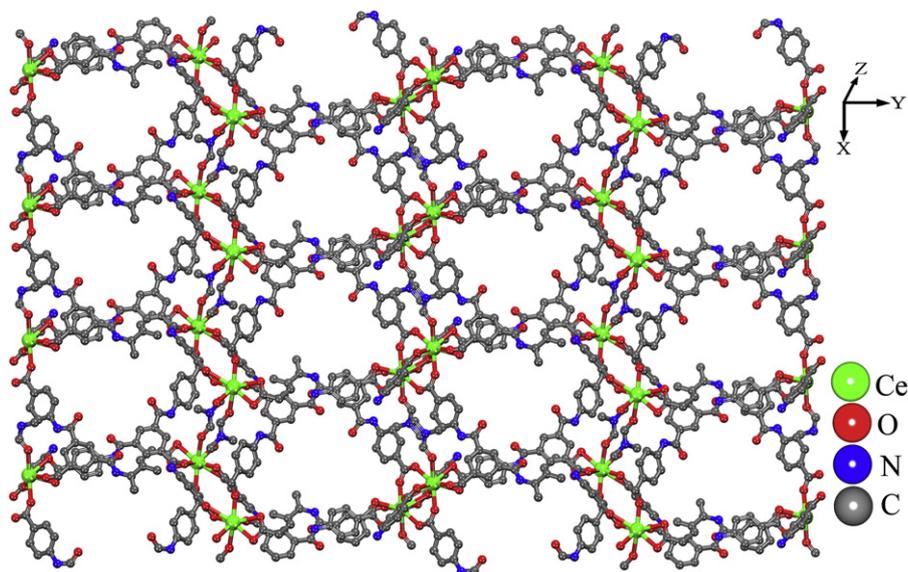


Fig. 1. The 1D heart-like channels viewed along Z axis in the framework of 1.

interaction [10]. Two Ce(III) ions are bridged together by two pairs of carboxylate groups of L ligands to give a dinuclear slightly distorted dodecahedral $[\text{Ce}_2(\text{CO}_2)_4(\text{CONH})_2\text{DMF}_2]$ cluster (Fig. 3b). On the other hand, each crystallographical independent L ligand in turn connects to six Ce(III) ions (Fig. 3a) through its three carboxyl groups and one carbonyl-oxygen atom of the amide group. Such coordination mode makes three longer “legs” of L ligand non-coplanar, with an average dihedral angle between the carboxylate groups and center phenyl rings of 18.4° . Particularly, the C_3 symmetry ligand L evolves from the tripodal node to 4-connected node due to the additional coordination of carbonyl-oxygen atom of the amide group. Each L connects four dinuclear Ce(III) clusters to form an extended 3D framework.

From the topological point of view, compound 1 can be described as an interesting binodal (4, 8)-connected AlB_2 net with a Schläfli

symbol of $(4^5.6)_2(4^{10}.6^{14}.8^4)$ analyzed by Topos3.2 program [11]. The well known structure of AlB_2 contains 3^6 layers of Al atoms alternatively packing with planar 6^3 sheets of B atoms [2]. In the simplified structure of 1, as depicted in Fig. 3c, the 4-connected L with light blue sticks takes the place of aluminum atoms in AlB_2 , forming a 2D 3^6 layers, while other three 4-connected L and three 8-connected dinuclear Ce(III) cluster with red sticks replace the boron atoms in an ordered manner, resulting in a puckered 2D 6^3 sheets, and those two layers lie in alternating fashion. However, it is different from the reported (4, 8)-connected AlB_2 MOFs, where metal centers act as the 4-connected nodes and organic ligands as the 8-connected nodes.

Inspired by Blatov’s statement “Knowing the relations between nets, one can find possible ways of transitions from one net to another” [12], we compare the (4, 8)-connected AlB_2 nets with the well known (3, 6)-connected rutile. The topological relationship between them is schematically illustrated in Fig. 4. Their mutual transformations can be realized by breaking or forming net edges, for example, breaking the blue edges in the initial AlB_2 net results in a rutile net. More interestingly, this structure transition is exemplified between 1 and $[(\text{Zn}_4\text{O})_2\text{L}_4(\text{DMF})_2(\text{H}_2\text{O})_3]$ (2) [13] based on the same L ligand. When the carbonyl-oxygen atoms of the amide groups is not coordinated to metal centers, the L acts as a C_3 tripodal node, which can form some classically (3, 6)-connected networks such as rutile (2). In comparison of their mild synthesis conditions, it can be inferred that high-coordination Ln(III) ions and solvothermal reaction under higher temperature are favor to enhancing the coordination capability of carbonyl-oxygen atoms of the amide type [14], resulting in different structures. This suggests that H_3L might be suitable and promising for the construction of novel architectures through controlling the coordination of amide group. Furthermore, the comparison of the structures of 1 and 2 demonstrates that 1 shows a non-interpenetrated network while 2 displays a two-fold interpenetrated network, possibly due to the high connectivity of 1.

The luminescence spectrum of 1 in the solid state is investigated at room temperature (Fig. S3). It can be observed that 1 exhibits broad blue-light emission band at ca. 438 nm, excitation at ca. 350 nm. For the free H_3L ligand, the emission band at the maximum wavelength of 468 nm under the same condition, is attributable to $\pi^* \rightarrow \pi$ transitions of the intraligands. The similarity between 1 and H_3L implies that the luminescent behavior of 1 is ligand-based emission [15]. However, compared with free H_3L , compound 1 exhibits blue-shift emission peaks. The blue-shift of emission may be attributed to the coordination of H_3L ligand to the Ce(III) centre, which effectively increases the

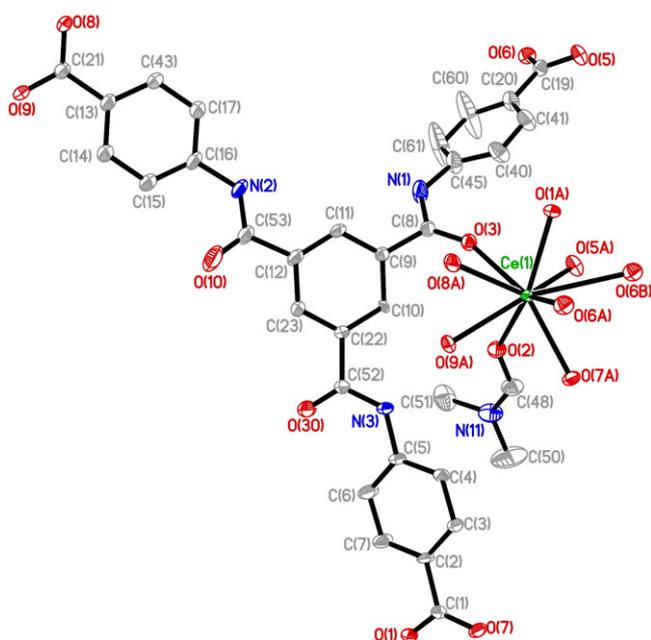


Fig. 2. The coordination environment of the Ce(III) ions in 1. All the hydrogen atoms have been omitted for clarity.

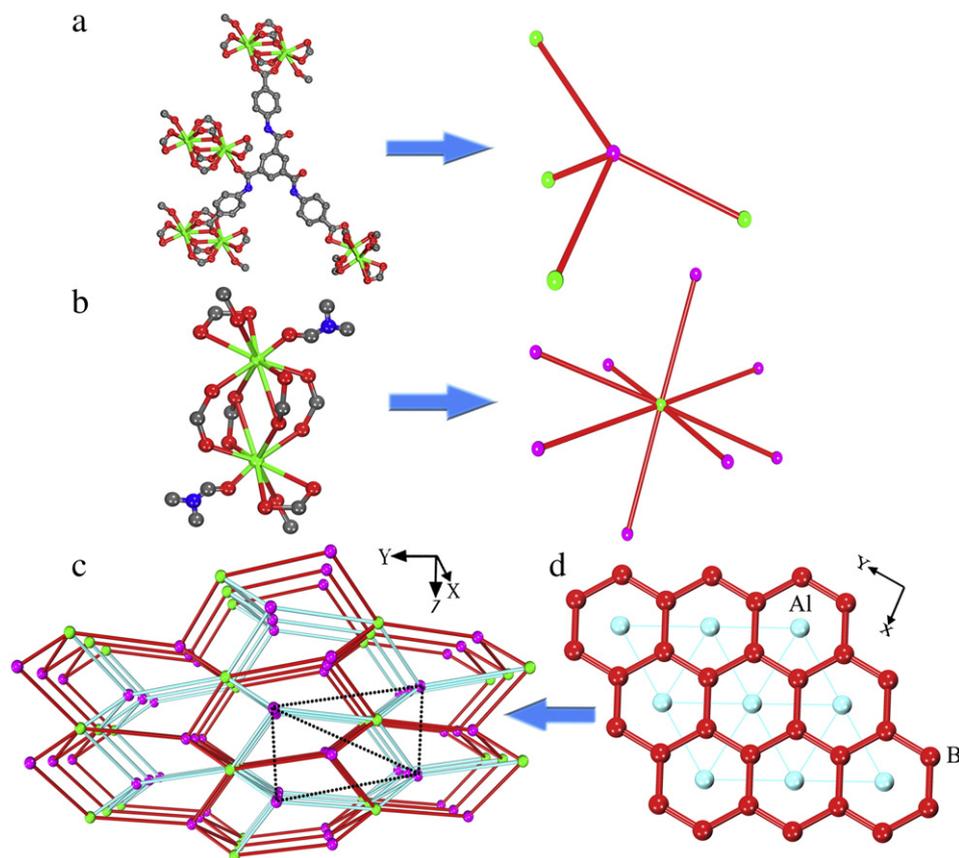


Fig. 3. (a), (b) Ball-and-stick and schematic representations of 4-connected (pink) and 8-connected nodes (green), respectively; (c) Schematic representation with (4, 8)-connected AlB_2 topology of 1 with Schläfli symbol of $(4^5.6)_2(4^{10}.6^{14}.8^4)$ (4-connected with light blue sticks represent 3^6 layers of Al atoms, 4-connected alternating with 8-connected with red sticks represent 6^3 sheets of B atoms), they are in separate layers; (d) Projection of the well known AlB_2 structure along the Z axis. Al and B atoms are in separate layers.

rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state [16]. These observations indicate that 1 may be suitable as a potential candidate of blue-fluorescent material.

To explore whether the framework of 1 would break down on removal of solvent molecules, TGA and powder X-ray diffraction (PXRD) analysis are introduced. The TGA is performed on 1 from 25 to 1000 °C in N_2 atmosphere (Fig. S2). The result indicates that the

weight loss between 25 and 280 °C is classified to the loss of guest molecules (H_2O and DMF). And the PXRD pattern of the yellow residual powder heated at 280 °C reveals that the powder still possesses the important characteristic peaks of as-synthesized 1, which indicates that 1 can retain its framework after removing all guest molecules. Further heating to 440 °C, the coordinated DMF molecule is removed and the PXRD pattern suggests the framework of 1 is collapsed after the loss of coordinated DMF molecule. The sharp

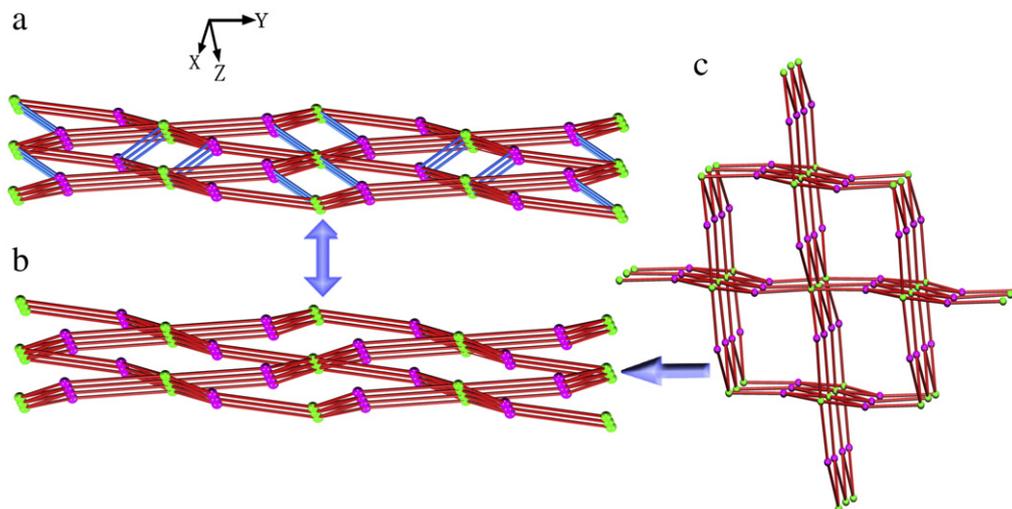


Fig. 4. (a) Schematic representation of the (4, 8)-connected AlB_2 topology of 1. (blue lines represent the coordination of carbonyl-oxygen atoms of the amide groups); (b) Schematic representation of the stretched (3, 6)-connected rutile topology when carbonyl-oxygen atoms of the amide groups is not coordinated to Ce(III); (c) Schematic view of the rutile topology of 2.

weight loss above 440 °C corresponds to the decomposition of the compound and the solid residues heated at 1000 °C consist of C (48.53%) and CeO₂ (PDF # 34-0394), confirmed by the elemental analyses and PXRD analyses (Fig. S5).

In summary, the first lanthanide MOF with (4, 8)-connected AlB₂ topology has been synthesized, where dinuclear Ce(III) cluster acts as eight-connected node and the rational tripodal ligand H₃L acts as four-connected node due to the coordination evolution of one carbonyl-oxygen atom of the amide group. The present work demonstrates that H₃L might be suitable and promising for construction of MOFs with predictable fascinating network topologies through controlling the coordination preference of potential coordinated atoms.

Acknowledgements

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Appendix A. Supplementary material

CCDC 818363 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data to this article can be found online at [doi:10.1016/j.inoche.2011.06.018](https://doi.org/10.1016/j.inoche.2011.06.018).

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- [7] All commercially available chemicals were analytical reagent grade and used as received without further purification. The ligand of H₃L was prepared according to reported procedure [17], and bbi was synthesized by the literature method [18]. Synthesis of compound 1: A mixture of Ce(NO₃)₃·6H₂O (22 mg, 0.05 mmol), H₃L (57 mg, 0.10 mmol), bbi (8 mg, 0.05 mmol) were dissolved in 8 mL of mixed solvents of distilled water and DMF (1:1, v/v) in a Teflon reactor (15 mL) and heated at 130 °C for 3 days. After the mixture was gradually cooled to room temperature, colourless prismatic crystals were obtained and collected by filtration, washed with deionized water, then dried in air, 60–80% yield based on Ce(III). Element analysis, calc for 1 (%): H, 4.82%; C, 47.95%; N, 8.97%. Found: H, 4.60%; C, 48.13%; N, 8.89%. IR (KBr, cm⁻¹): 3299 (w), 3071 (w), 2970 (w), 2930 (w), 1656 (s), 1604 (s), 1517 (s), 1405 (s), 1316 (m), 1254 (s), 1177 (m), 1107 (w), 1047 (w), 1014 (w), 957 (w), 865 (m), 838 (w), 786 (m), 728 (w), 700 (w).
- [8] Crystal data for compound 1 C₃₃H₂₅N₄O₁₀Ce: *M*_r = 777.69, monoclinic, space group P2 (1) / *c*, *a* = 12.288(3) Å, *b* = 36.854(7) Å, *c* = 11.440(2) Å, α = 90°, β = 117.642(2)°, γ = 90°, *V* = 4587.7(17) Å³, *Z* = 4, *D*_c = 1.125 mg/m³, μ = 1.167 mm⁻¹, 42661 reflections measured, 11509 unique, *R* (int) = 0.0506, *R*₁ = 0.0647 with *I* > 2σ(*I*), *wR*₂ = 0.1456 and *GOF* = 1.104. Reflection data were collected on a Bruker Smart CCD diffractometer with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at room temperature. The structures were solved by direct methods and refined by the full-matrix least-squares technique on *F*² using SHELXTL 5.1 [19] package of crystallographic software. All non-hydrogen atoms were refined with anisotropic thermal parameters except highly disordered neutral solvent molecules in the void spaces of the structure of 1. The SQUEEZE [9] model was applied to remove the disordered species. Further detailed crystallographic data and structure refinement parameters are summarized in Table S1, Selected bond lengths (Å) and angles (°) are listed in Table S2, Supplementary material.

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