

Two new Cerium–Organic Frameworks with unusual network topologies constructed by racemic tartaric acid involving in situ reaction

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ABSTRACT

Hydrothermal reactions of CeO₂ with racemic tartaric acid (H₂tar) at different temperature yielded two novel Cerium–Organic Frameworks, [Ce₂(tar)₂(C₂O₄)(H₂O)₂]_n·4nH₂O (**1**) and [Ce₂(tar)₂(C₂O₄)(H₂O)₄]_n (**2**). **1** displays an unprecedented fsx-4,5-*P2*₁/*c* topology, which contains hydrophilic channels constructed by triple helical chains along *a* axis; **2** exhibits a 2D layer framework with a binodal (3,4)-connected V₂O₅ network. Notably, in both **1** and **2**, the oxalate ligands were in situ synthesized from H₂tar.

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Over the past few decades, exploratory synthesis and research on metal–organic frameworks (MOFs) have been attractive fields due to the potential applications of MOFs, as well as their intriguing variety of architectures and topologies [1]. Hydrothermal synthesis is one of powerful techniques for synthesizing new MOFs with diverse structural architectures. Under relatively high temperature and pressure, the problems associated with solubility can be well-solved; thus the reactivity of reactants in the crystallization process is efficiently enhanced [2]. This technique has earned enormous importance due to its simplicity and the tremendous results regarding the new production of MOFs [3]. The hydrothermal reactions are affected by a variety of parameters such as reaction time, pH value and temperature [4]; these reactions are often quite complicated and may involve some in situ metal/ligand reactions such as hydrolysis, substitution and oxidation [5]. Although it is not always possible to exert synthetic control, a fascinating variety of novel MOFs have been obtained from hydrothermal reactions [6].

Racemic tartaric acid (H₂tar) is a cheap hydroxy dicarboxylic acid. As one of prominent ligands, this compound has six coordination sites which are helpful to get high dimensional structure. So far, a few examples of lanthanide–tartrate–frameworks have been obtained through hydrothermal synthesis [7]. Herein we report the hydrothermal synthesis and structural characterization of two new Cerium–Organic Frameworks: [Ce₂(tar)₂(C₂O₄)(H₂O)₂]_n·4nH₂O (**1**) and [Ce₂(tar)₂(C₂O₄)(H₂O)₄]_n (**2**). These two MOFs were synthesized based on H₂tar and CeO₂ under hydrothermal conditions at different

temperature (Scheme S1) [8]. The syntheses of **1** and **2** indicate that in situ decomposition of H₂tar in the presence of cerium ions lead to the formation of oxalate C₂O₄^{2−} ligand. In general, to transform H₂tar into C₂O₄^{2−}, there should be other reagents such as strong oxidizers like H₂SO₄ taking part in the reaction; it was reported that tartaric acid can endure hydrothermal conditions up to 160 °C to form the robust framework [7a]. Although there are several examples involving decomposing of organic chemical into oxalate [9], there is no reported case about this in situ decomposition of H₂tar into oxalate during hydrothermal reaction to the best of our knowledge [10]. Besides, it is noteworthy that as an oxidant CeO₂ only part of the H₂tar is oxidized to oxalate ligand, both unoxidized H₂tar and oxalate ligands are coordinated with Ce(III) ions and construct the frameworks of **1** and **2** together.

X-ray analysis [11] revealed that **1** crystallizes in the monoclinic space group *P2*₁/*c*, and the asymmetric unit consists of one Ce(III) cation, one tar^{2−} ligand, a half oxalate anion (C₂O₄^{2−}), one coordinated water and two lattice water molecules. As illustrated in Fig. S1, the Ce(III) center is nine-coordinated in a distorted tricapped trigonal prism with one water molecule, two oxygen atoms from one oxalate anion (C₂O₄^{2−}) and six oxygen atoms from four carboxyl groups and two α -hydroxyl groups of four tar^{2−} ligands, the Ce–O bond lengths are in the range of 2.4705(18)–2.7052(18) Å, which are comparable to the previously reported cerium MOFs [12]. The tar^{2−} ligand can be classified as μ_4, κ^6 (Scheme S2), which binds to four Ce(III) ions through six oxygen atoms from four bidentate carboxyl groups, and two α -hydroxyl groups to form a 2D layer in the (110) plane; and the C₂O₄^{2−} anion acts as a μ_2 -bridge ligand and interconnects the neighboring layers to give a 3D network with hydrophilic channels along [100] direction. Water molecules occupy these hydrophilic

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channels, which provide multiple intermolecular hydrogen bonds among lattice waters and stabilize the crystal structure (Fig. 1a). As shown in Fig. 2, it is remarkable that the hydrophilic channels are constructed by triple helical chains along [100] direction, each triple helical chain is interwoven by three similar single helical chains ($\text{Ce}-\text{C}_2\text{O}_4^{2-}-\text{Ce}-\text{COO}^- - \text{Ce}-\text{tar}^{2-}-\text{Ce}-\text{C}_2\text{O}_4^{2-}-\text{Ce}-\text{COO}^- - \text{Ce}-\text{tar}^{2-}-\text{Ce}$) with 2_1 screw axis and a pitch of 18.2991 Å. These triple helical chains are alternately arranged in a right- and left-handed sequence, as illustrated in Fig. 1b, so the whole 3D structure does not show chirality.

In the topological view, each Ce(III) cation serves as a 5-connected node by combining four tar^{2-} ligands and one $\text{C}_2\text{O}_4^{2-}$ anion, each tar^{2-} ligand is linked to four Ce(III) cations to represent a 4-connected node and each $\text{C}_2\text{O}_4^{2-}$ anion acts as 2-connected node by connecting to two Ce(III) cations. Hence, a binodal 4,5-connected topology network is formed with Schläfli symbol of $(4^2.6^4)_2(4^2.6^7.8)$ (Fig. 3), the vertex symbol using TOPOS 4.0 [13a] calculation gives (4. 6₂. 4. 6₄. 6₃. 6₄) for the 4-connected node and (4. 4. 6₂. 6₂. 6₂. 6₂. 6₂. 6₃. 6₄. 10₅) for the 5-connected node, and is thus corresponding to the topology type with transformation symbol [13a,b] $\text{fsx}/I4/mmm- P2_1/c$ ($-\mathbf{a}, \mathbf{b}, \mathbf{a} + \mathbf{c}$); Bond sets: **1, 3, 4, 5, 6: fsx**. As the maximal symmetry of this unique net is $P2_1/c$, this long notation can be reduced to a short s-d-G-n symbol: $\text{fsx-4,5-}P2_1/c$. In the TTD collection [13a], there are 85

binodal nets derived from (5,6)-connected **fsx** net, only 10 of them was found in real structures to date, such as: **fsx-3,4-}C2/c-1**; **fsx-3,4-}C2/c-2**; **fsx-3,4-}Fd-3m**; **fsx-3,4-}Pccn**; **fsx-4,5-}C2/c**; **fsx-4,5-}C2/c**; **fsx-4,5-}Cmce-1**; **fsx-4,5-}Cmce-2**; **fsx-4,5-}P2_12_12_1**; **fsx-4,5-}P6_3/mmc**, **fsx-4,5-}R-3m**. To the best of our knowledge, there is no known crystal structure about topology **fsx-4,5-}P2_1/c** in any compilations and databases [13]. The discovery of this new topology is fundamental in the crystal engineering of coordination networks.

Single-crystal X-ray diffraction study reveals that **2** crystallizes in the triclinic space group $P-1$. The asymmetric unit of **2** consists one Ce(III) cation, one tar^{2-} ligand, a half oxalate anion ($\text{C}_2\text{O}_4^{2-}$) and two coordinated water molecules. As illustrated in Fig. S2, the Ce(III) center is nine-coordinated in a distorted tricapped trigonal prism with two water molecule, two oxygen atoms from one oxalate anion ($\text{C}_2\text{O}_4^{2-}$) and five oxygen atoms from three carboxyl groups and two α -hydroxyl groups of four tar^{2-} ligands, the Ce–O bond lengths are in the range of 2.4245(17)–2.6216(16) Å, which are comparable to those in **1**. The tar^{2-} ligand in the μ_3, τ^5 coordination mode (Scheme S3) combines with three Ce(III) ions to form a infinite chain along [100] direction, the oxalate anions bridge two neighboring Ce(III) cations to form chains along [010] direction. These chains run along the [100] and [010] directions, and further interweave into a 2D layer network (Fig. S3). Furthermore, there are extensive hydrogen bonding

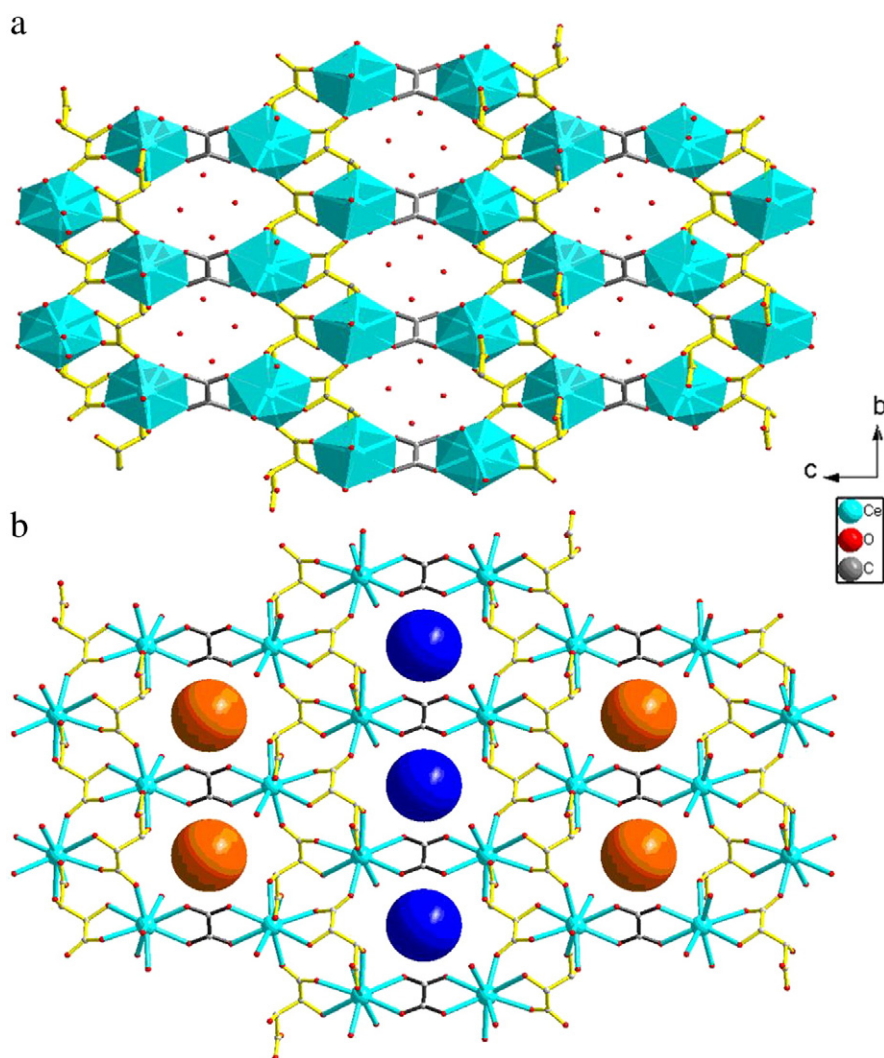


Fig. 1. (a) Polyhedral representation of **1** down [100] direction, all H atoms are omitted for clarity; (b) View of the 3D structure of **1** down [100] direction, all H atoms and lattice water molecules are omitted for clarity. (Blue and orange axes represent the axes of L and R helical chains).

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