

A 3-dimensional coordination polymer with a rare lonsdaleite topology constructed from a tetrahedral ligand†

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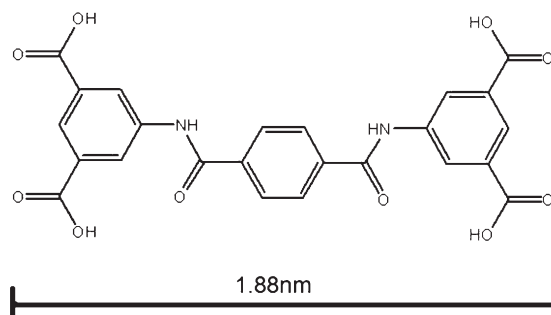
A new 3D coordination polymer was solvothermally synthesized. The coordination polymer possesses a lon network built from 4-connecting Co₂ clusters and tetracarboxylate ligands, and exhibits selective gas sorption behavior as well as antiferromagnetic interactions.

Crystal engineering provides a powerful tool for the construction of metal–organic frameworks (MOFs).^{1,2} Various organic ligands and secondary building units have been specifically designed for the synthesis of MOFs with desirable characteristics (gas storage/separation,³ photoactive material,⁴ magnetism,⁵ catalysis,⁶ etc.). In particular, MOFs which have novel topologies and special applications attract the most attention. With the fundamental contributions by A. F. Wells, M. O’Keeffe and R. Robson,⁷ great efforts have been devoted to design and understand the network structure/topology of MOFs. Up to now, a large number of MOFs have been reported, while the large majority of 3-D MOFs with uninodal nets usually possess low connected structural topology and are dominated by the 4-connected nodes^{6a,7} such as diamond (**dia**), SrAl₂ (**sra**), quartz (**qtz**), square (**sql**), NbO (**nbo**), CdSO₄ (**cds**), and PtS (**pts**) net. From both zeolite chemistry and crystal engineering points of view, the frameworks built from 4-connected tetrahedral centers can generate larger cavities and bigger access windows than those based on octahedral centers and might result in 3D porous frameworks with a low framework density. So there has been increasing interest in the use of tetrahedral four-connected centers as basic structural units for the construction of open-framework materials. For tetrahedral nodes, two types of topologies are possible, namely, diamond (**dia**) and lonsdaleite (**lon**) nets.⁸ Although the two structures are composed of fused 6-membered rings, all such rings in diamond have the chair conformation while those in the lonsdaleite assume both chair and boat conformations. As the natural choice for porous material, the topology of **dia** networks is noticeably classic and widely reported

in MOFs, whereas the **lon** network is still very difficult to realize in MOFs: this remains a great challenge.⁹

Meanwhile, surface modification is a useful tool for introducing new functionalities for MOFs and received much attention. Recently several MOFs have been constructed with amide decorated multiple carboxylate ligands,¹⁰ which are proved to have guest-accessible functional amide sites in the channel and some materials show high CO₂ adsorption capacities due to these functional groups.¹¹ Given the above concerns, we prepared a new ligand containing four carboxylate groups as coordination sites and four amide groups as functional sites (bis-(3,5-dicarboxy-phenyl) terephthalamide, H₄L Scheme 1). We expected that the amide groups might influence the gas sorption properties. Herein we report the synthesis and characterization of {[Co₂(L)(H₂O)₃]·S_x}_n (S is either DMF or water molecule and *x* is number of solvent molecules in the crystal) with a rare **lon** topology based on 4-connected Co₂ cluster and nano-sized tetracarboxylate ligand.

The use of a slight excess of cobalt nitrate combined with the ligand H₄L in a solvent mixture of *N,N'*-dimethylformamide (DMF) and water (9 : 1) at 85 °C yielded blue crystals of {[Co₂(L)(H₂O)₃]·S_x}_n **1** (ESI†) after 5 days. **1** crystallizes in monoclinic space group *P*2₁, and the asymmetric unit consists of two crystallographically cobalt ions (Co1 and Co2) and one L ligand (Fig. S1, ESI†). The solvent molecules cannot be accurately determined, because of the badly disordered structure of them that are further treated by the Platon Squeeze program.¹² Both of the Co ions are six-coordinated in an octahedral geometry, as depicted in Fig. 1b. The Co1 ion is surrounded by six oxygen atoms from



Scheme 1 Nano-sized tetracarboxylic ligand: bis-(3,5-dicarboxy-phenyl) terephthalamide.

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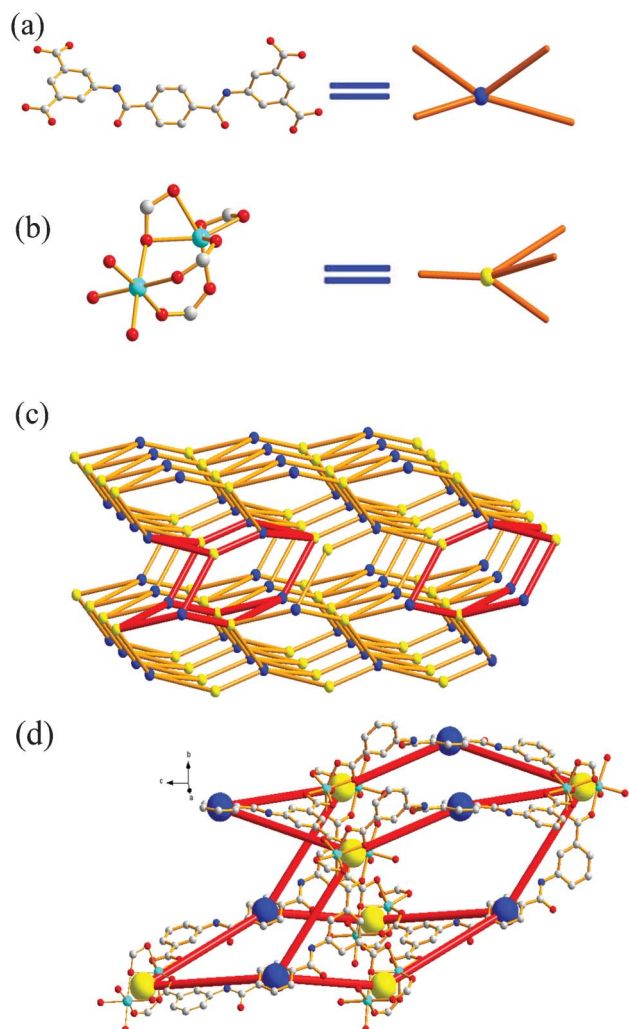


Fig. 1 The crystal structure of **1** is composed of (a) ligand L⁴⁻ and (b) binuclear cobalt cluster Co₂(COO)₄(H₂O)₃ as tetranode, which assemble into (c) a network of **lon** topology. (d) A simplified view of the iceane-like cavity in **lon** net constructed by Co₂ cluster (yellow node) and tetracarboxylate ligand (blue node). All hydrogen atoms are omitted in (a), (b) and (d) for clarity. Color codes: cobalt, cyan; carbon, gray; nitrogen, blue; oxygen, red. The units outlined in red are the natural tiles for **lon** structure.

four different carboxylates of L with the range of Co–O distance from 2.003(2) to 2.239(3) Å. The equatorial plane of the Co₂ ion is occupied by four oxygen atoms from two different carboxylates and two aqua molecules, the axial position is coordinated by the O atom from one carboxylate and one water molecule with Co–O distance 2.137(3), 2.111(2) Å. Each carboxyl group of L is deprotonated and adopts a bidentate bridging coordination mode connecting two six-coordinated Co atoms to generate the Co₂(COO)₄(H₂O)₃ SBUs with a Co–Co distance of 3.484(2) Å. Each bdc unit of the ligand links two such bimetal units.

On the basis of the above connection modes, each ligand connects four adjacent dinuclear Co(II) units and can be simplified as a 4-connected node. Similarly, each dinuclear Co(II) unit connects four ligands and serves as a 4-connected node. Thus the framework has the **lon** topology (Fig. 1c,d), which has both chair and boat conformations in fused six-membered rings. Although

both **dia** and **lon** topologies are expected to be energetically very similar, **dia** topology is overwhelmingly dominant for tetrahedral nodes based on the experimental results, which may be due to the fact that the **dia** network represents the simplest, highest symmetry structure (it is the only regular tetrahedral structure). So it is necessary to construct the **lon** structure by deconstructing the **dia** structure into more elaborate building blocks of chair and boat rings rather than of single tetrahedra.^{6a,8,13} The amide groups in the ligand increase the arms of the ligand, which could potentially generate a large inner cavity in a MOF, and also increase the flexibility of the ligand, which might help to form both the chair and boat conformations in the **lon** network. PLATON calculation suggests that the resulting effective free volume, after removal of guest DMF and water molecules, is 70.3% of the crystal volume (2305.2 Å³ out of the 3281.3 Å³ unit cell volume).¹⁴ Based on the crystallographic data and the van der Waals radii of atoms, the pore cross sections are calculated to be 11.0 × 5.3 Å² along the *a* axis in **1** (Fig. S2, ESI†).

The thermal stability of fresh samples of **1** have been investigated and it was found to be stable up to 450 °C (Fig. S3, ESI†). TG analysis of complex **1** shows a first weight loss of 43.6% from 25 °C to 400 °C, corresponding to a loss of 4 DMF and 9 water molecules (calcd 43.2%). The second step from 460 °C to 478 °C is attributed to the decomposition of the L organic ligands. The remaining weight of 14.4% is likely to be that of CoO (calcd 14.2%). The PXRD patterns of **1** (Fig. S4, ESI†) show that the diffraction patterns are almost the same as the simulated ones, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.¹⁵ The PXRD pattern of the desolvated sample **1a** (under vacuum at 100 °C overnight after soaking in DMF for 1 day and then in MeOH for 7 days) exhibits a decrease in intensity, and the position of partial peaks change, suggesting that a crystal of the coordination network was gradually distorted as a result of the crystal transformation after the loss of coordinated solvent molecules.¹⁶

The seemingly high thermal stability of the framework of **1** inspires us to study its adsorption properties. Gas sorption experiments towards N₂ at 77 K and CO₂ at 195 K were carried

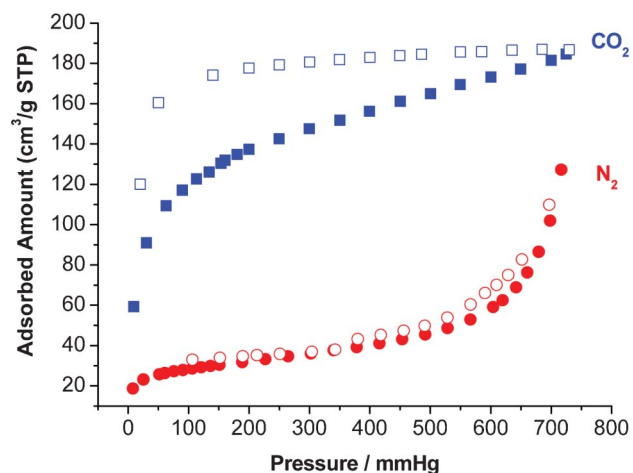


Fig. 2 Gas CO₂ (195 K) and N₂ (77 K) adsorption/desorption isotherms of **1a**.

out. As seen from Fig. 2, desolvated solid **1a** adsorbs N_2 gas to show a type I isotherm at low pressure, indicating the permanent microporosity of **1a**. The gas sorption shows a little hysteresis between sorption–desorption curves and obvious capillary condensation at relatively high pressure, suggesting a small amount of mesoporosity present in the desolvated material, which is attributed to nanosized intercrystalline voids or mesopores within the mosaic pseudomorphs that remain after desolvation.¹⁷ In total, **1** only adsorbs $110 \text{ cm}^3 \text{ g}^{-1}$ (STP) N_2 at $P/P_0 = 0.9$. The Langmuir surface area is estimated as $145.7 \text{ m}^2 \text{ g}^{-1}$ (BET $106.6 \text{ m}^2 \text{ g}^{-1}$) and the pore volume estimated by applying the t -Plot is merely $0.015563 \text{ cm}^3 \text{ g}^{-1}$. These results imply that the pores in **1a** have been destroyed to a large extent during desolvation, showing obvious degradation of crystallinity and structural changes upon escape of solvent molecules. For CO_2 uptake, the sorption increases abruptly at the beginning and reaches $186.8 \text{ cm}^3 \text{ g}^{-1}$ (STP) at $P/P_0 = 0.98$. The gas sorption isotherms show distinct hysteresis between the adsorption–desorption curves, indicating strong interactions of CO_2 molecules with the host solid **1a** and apparent structural changes upon uptake of CO_2 .

Solid-state magnetic susceptibility measurements for **1** were performed in the range of 3–300 K under a field of 100 Oe. The χ_M at 16–300 K displays a continuous slow increase with decrease of temperature and then sharply increase when lowering the temperature from 16 to 3 K (Fig. 3). At 3 K, the χ_M value is $0.803 \text{ cm}^3 \text{ mol}^{-1}$. The $\chi_M T$ value of $5.04 \text{ cm}^3 \text{ K mol}^{-1}$ per Co_2 unit at 300 K is much larger than that ($3.76 \text{ cm}^3 \text{ K mol}^{-1}$) expected for two magnetically isolated high-spin Co^{II} ions with $S = 3/2$, due to the spin–orbit coupling at high temperature. Upon lowering the temperature, the $\chi_M T$ value first slowly decreases to about 50 K and then rapidly decreases to the value of $2.79 \text{ cm}^3 \text{ K mol}^{-1}$ at 3 K. The magnetic susceptibility from 50 K to 300 K obeys the Curie–Weiss law with a Weiss constant θ of -16.6 K and a Curie constant C of $5.27 \text{ cm}^3 \text{ K mol}^{-1}$ (Fig. S5, ESI†). The decrease of the $\chi_M T$ value or the negative θ value can be induced by antiferromagnetic coupling interactions within and between dimeric units as well as strong spin–orbit coupling. In order to estimate the strength of the antiferromagnetic exchange interaction, the following simple phenomenological equation can be used, considering the strong spin–orbit coupling in this compound.¹⁸

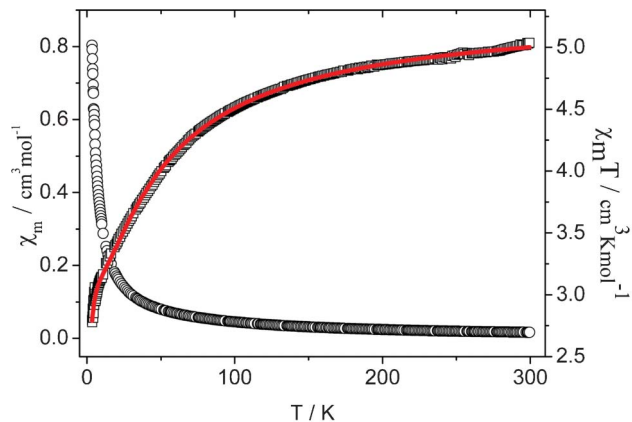


Fig. 3 Plots of the χ_M vs. T and $\chi_M T$ vs. T for **1**. The red line corresponds to the best fit according to the parameters in eqn (1) given in the text.

$$\chi_M T = A \exp(-E_1/kT) + B \exp(-E_2/kT)$$

In this equation, $A + B$ equals the Curie constant, E_1 and E_2 represent the activation energies corresponding to the spin–orbit coupling and the antiferromagnetic exchange interactions, respectively. This equation is in good agreement with the experimental data (Fig. 3). The best fitting results are: $A + B = 5.32 \text{ cm}^3 \text{ K mol}^{-1}$, $E_1/k = 50.6 \text{ K}$ and $-E_2/k = -0.62 \text{ K}$ ($R = \sum[(\chi_M T)_{\text{obs}} - (\chi_M T)_{\text{calc}}]^2 / \sum[(\chi_M T)_{\text{obs}}]^2 = 3.8 \times 10^{-3}$). The obtained value of $A + B$ is very close to that from the Curie–Weiss law equation ($5.27 \text{ cm}^3 \text{ K mol}^{-1}$). The small E_2 value indicates the presence of weak antiferromagnetic interaction.¹⁹

In conclusion, we have successfully synthesized a porous coordination polymer $\{[Co_2(L)(H_2O)_3] \cdot S_x\}_n$, **1**, using an amide linked tetracarboxylic ligand under solvothermal conditions. The framework of **1** is constructed from 4-connected tetrahedral L ligands and 4-connected Co_2 clusters, forming a lonsdaleite network, one of rare topologies in MOFs. Besides the unusual topology, the desolvated solid **1a** exhibits moderate CO_2 uptake and the powder sample of **1** shows antiferromagnetic properties.

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