

A supramolecular self-assembled flexible open framework based on the coordination of honeycomb layers possessing octahedral and tetrahedral Co^{II} geometries†

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Yang Zou,^{*a} Yuanyuan Li,^a Chaoyong Yu,^a Fei Yin^a and Myoung Soo Lah^{*b}

A flexible open framework, $\{[\text{Co}_2(\text{L})\text{Cl}(\text{DMF})_2(\text{H}_2\text{O})] \cdot \text{S}_x\}_n$ ($\text{H}_3\text{L} = 4,4',4''$ -[1,3,5-benzenetriyltris(carbonylimino)]-trisbenzoic acid, DMF = dimethylformamide), was constructed based on a honeycomb coordination subunit with both octahedral and tetrahedral Co^{II} sites, showing moderate MeOH sorption and antiferromagnetic properties.

The self-assembly of coordination polymers has attracted great interest not only because of the judicious design involved in controlling the self-assembly processes, but also, for the construction of functional materials with novel redox, optical, catalytic, biomedical, and magnetic properties.^{1,2} In general, supramolecular coordination complexes can be assembled through two major chemical processes: coordinate chemistry and supramolecular chemistry, which are characterized by fundamental interactions at the molecular level. Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) represent a large proportion of the former category, and the major interaction between building blocks is coordination bonds.³ In the latter category, weaker intermolecular forces (such as strong hydrogen bonding, C–H hydrogen bonding, π – π stacking interactions, *etc.*) act to stabilize certain architectures and to guide the self-assembly of molecular species.^{4,5} Both strategies have proven to be successful.⁶ Recently, the combined coordination chemistry and hydrogen bonding approach have been frequently used as a powerful crystal engineering tool to generate interesting supramolecular systems.⁷

A wide variety of architectures, with high structural stability, have been prepared by connecting rigid metallic building blocks, referred to as secondary building units (SBUs), with organic

linkers *via* strong covalent bonds. The use of multidentate carboxylate ligands as the organic linkers to join the metallic SBU cores has been studied extensively.^{1b,8} Numerous open MOFs with classic SBUs motifs, such as $\text{Zn}_4\text{O}(\text{RCO}_2)_6$ or $\text{Cu}_2(\text{RCO}_2)_4$, have been synthesized with the metal-carboxylate family of complexes.^{3c,9} Compared to $\text{M}_2(\text{RCO}_2)_4$ SBUs, the $\text{M}_2(\text{RCO}_2)_3$ SBUs are quite rare in the construction of functional MOFs.¹⁰ Furthermore, compounds that possess tetrahedral and octahedral metal centers are also rare and are limited to tetrahedral Hg^{II} S-bound to a thiocyanate bridged to M^{II} ($\text{M} = \text{Co}, \text{Ni}$) forming two-dimensional layers with the $\mu_{1,3}$ -NCS motif.¹¹ To the best of our knowledge, $\{[\text{Co}_2(\text{L})\text{Cl}(\text{DMF})_2(\text{H}_2\text{O})] \cdot \text{S}_x\}_n$ **1** (**S** is either DMF or a water molecule and x is the number of solvent molecules in the crystal) is the first example of an $\text{M}_2(\text{RCO}_2)_3$ SBU with both tetrahedral and octahedral geometries in its structure.

We are interested in the construction of porous coordination material with interesting properties based on nano-sized ligands with conformational flexibility.¹² Here, we chose 4,4',4''-[1,3,5-benzenetriyltris(carbonylimino)]-trisbenzoic acid (H_3L , Scheme S1†) as a bridging ligand because it provides the following advantages: (1) the ligand, a substituted carboxylate group, can provide rigidity and thus permit metal coordination geometry to guide the propagation between building blocks; (2) the flexibility around the amide group can allow the sway of the three phenyl rings of the H_3L ligand to meet the coordination requirement of metal ions and direct the final structures; (3) the amide group is well known to form supramolecular synthons through strong hydrogen bonds (it can provide two types of hydrogen bonding sites, with the –NH moiety acting as an electron acceptor, and the C=O group acting as an electron donor) and an interesting functional group for pore surface modification.^{12b,13} In this communication we report the synthesis and characterization of $\{[\text{Co}_2(\text{L})\text{Cl}(\text{DMF})_2(\text{H}_2\text{O})] \cdot \text{S}_x\}_n$ **1** with honeycomb topology based on a 3-connected $[\text{Co}_2(\text{RCO}_2)_3]$ cluster and a nano-sized tricarboxylate ligand. Additional intermolecular forces (N–H \cdots O, N–H \cdots Cl, C–H \cdots Cl hydrogen bonds and π – π interactions, *etc.*) generate interesting supramolecular architectures with one-dimensional channels.

^aDepartment of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, China. E-mail: zouyang@zstu.edu.cn

^bInterdisciplinary School Green Energy, Ulsan National Institute Science & Technology, Ulsan 689798, South Korea. E-mail: mslah@unist.ac.kr

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The use of a slight excess of cobalt chloride combined with the ligand H_3L in a solvent mixture of N,N' -dimethylformamide (DMF) and water (20 : 1) at 85 °C yielded blue crystals of $\{[Co_2(L)Cl(DMF)_2(H_2O)] \cdot S_x\}_n$ **1**,¹⁴ after 7 days. The asymmetric unit of **1** consists of two crystallographically different cobalt ions (Co1 and Co2) and one L^{3-} ligand (Fig. 1). The number of uncoordinated water molecules and uncoordinated DMF molecules cannot be accurately determined because of the badly disordered structure of DMF, so these are more accurately determined using the Platon Squeeze program.¹⁵ Co1 is four-coordinated in a tetrahedral geometry, while Co2 is six-coordinated in an octahedral geometry, as depicted in Fig. S1.† The Co1 ion is surrounded by one chloride (Co–Cl distance: 2.247(3) Å) and three oxygen atoms from the carboxylate groups of three different L^{3-} ligands, with the Co–O distance ranging from 1.943(6) to 1.972(7) Å. The equatorial plane of the Co2 ion is occupied by four oxygen atoms from two different carboxylates, one water molecule, and one DMF molecule. The axial position is coordinated by an oxygen atom from one carboxylate group and one DMF molecule, with Co–O distances of 2.045(7) and 2.113(8) Å. Each carboxyl group of L is deprotonated and adopts a bidentate bridging coordination mode connecting two Co atoms to generate the $Co_2(COO)_3$ SBUs with a Co–Co distance of 3.565(2) Å. Comparatively, in the MOFs with the same L^{3-} , a ligand: copper MOF adopts paddle-wheel $Cu_2(COO)_4$ SBUs,^{13d} a manganese MOF adopts linear $Mn_3(COO)_6$ SBUs,^{13e} a cadmium MOF adopts $Cd(COO)_3$ SBUs^{13g} and rare earth metal ($Ln = Y, La, Ce, Nd, Eu, Tb, Dy, Ho$ and Tm) MOFs adopt $Ln(COO)_6$ SBUs.^{13g}

On the basis of the above connection modes, each ligand connects three adjacent dinuclear $Co(II)$ units and can be simplified as a 3-connected node. Similarly, each dinuclear $Co(II)$ unit connects the three carboxylate groups of the ligand

and serves as a 3-connected node. Thus, the framework has a honeycomb (hcb) topology (Fig. 1b and S2†). The honeycomb layers are parallel to each other, and arrayed in an orderly fashion in a staggered ABAB-packing pattern viewed along the crystallographic a -axis (Fig. 1c). Two adjacent ligands combine to form a ligand dimer by hydrogen bonds ($N-H \cdots O$) and π - π stacking interactions, with face to face distances of 3.45 Å, which is also known as a “Piedfort unit”.¹⁶ All of the coordinated Cl^- ions were located on the outside of the bilayers (Fig. S3†).

An attractive feature of the packing diagram in **1** is the linkage of the bilayer unit through $N-H \cdots Cl$ and $C-H \cdots Cl$ hydrogen-bonding interactions¹⁷, between Co–Cl and the two ligands in the adjacent bilayer unit. As a consequence, the bilayer units are assembled into a 3D network with 1D prismatic channels (Fig. S4†). The $C-H \cdots Cl$ distances observed in **1** falls in the range 2.72–2.79 Å (Table S2†), clearly indicating the presence of intermediate interactions [according to the classification of Brammer and co-workers,¹⁸ the intermolecular contacts were categorized as short (≤ 2.52 Å), intermediate (2.52–2.95 Å) and long 2.95–3.15 Å; the sum of van der Waals radii for $H \cdots Cl = 2.95$ Å]. PLATON calculations suggest that the resulting effective free volume, after removal of guest DMF and water molecules, is 41.6% of the crystal volume (5731.0 Å³ out of the 2382.2 Å³ unit cell volume).¹⁹ Based on the crystallographic data and the van der Waals radii of atoms, the pore cross sections are calculated to be ~ 7 Å in diameter along the a axis in **1**.

The PXRD patterns of **1** (Fig. S6†) show that the diffraction patterns match the simulated one, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.²⁰ The desolvated samples **1a** (under vacuum at 90 °C overnight after soaking in DMF for 1 day and then in MeOH for 3 days) exhibit an amorphous PXRD pattern. This crystalline-to-amorphous transformation is accompanied by loss of the H_2O and DMF guest molecules in the channels, and such structural behavior has also been observed in other compounds.²¹ However, when amorphous **1a** is immersed in methanol, it cannot be restored to its original crystalline phase but changes to a new crystalline phase, which was detected by PXRD.

The adsorption and desorption behaviors of N_2 and MeOH were examined. **1a** showed no N_2 adsorption at 77 K, as shown in Fig. 2. This result indicates that **1a** does not retain channels available for N_2 (kinetic diameter = 3.64 Å).²² Because the PXRD pattern of **1a** changes when it is immersed in methanol, methanol adsorption and desorption experiments were carried out on this compound. The adsorption and desorption isotherms for methanol at 298 K are shown in Fig. 2. The adsorption isotherm showed a gradual uptake to P/P_0 0.93. Conversely, the desorption isotherm did not trace the adsorption profile and decreased slightly, with a large-range hysteresis loop. This characteristic adsorption profile shows the conversion of amorphous **1a**. The interaction between the host framework and methanol is strong enough to transform and maintain the channel structure, so that the large hysteresis profile appears.^{12b} The amount of adsorbed methanol is 2.07 molecules per L^{3-} ligand at P/P_0 0.93. This result also supports the hypothesis that the adsorbed methanol is bound to the

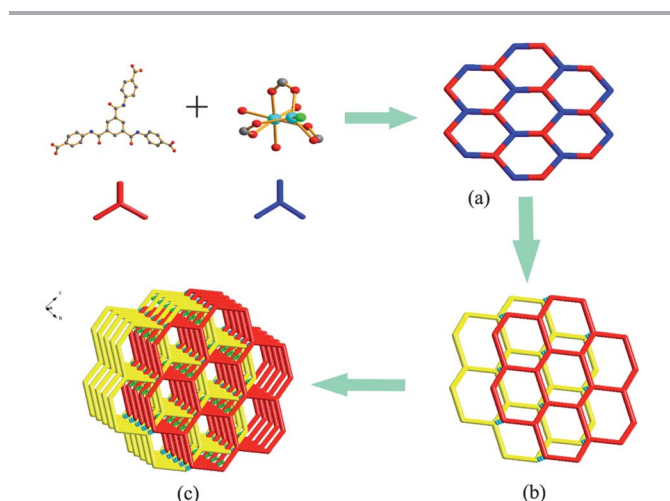


Fig. 1 The crystal structure of **1** is composed of a ligand L^{3-} (red node) and a binuclear cobalt cluster (blue node) as a tri-node, which assemble into (a) the 2D (6,3) honeycomb layer; (b) two layers connected by hydrogen bonds and π - π interactions (cyan dashed line); and (c) bilayers that were further connected by the $C-H \cdots Cl$ and $N-H \cdots Cl$ hydrogen bonds (green dashed line) to form a 3D network with 1D channels. All hydrogen atoms are omitted for clarity. Color codes: cobalt, cyan; carbon, gray; nitrogen, blue; oxygen, red.

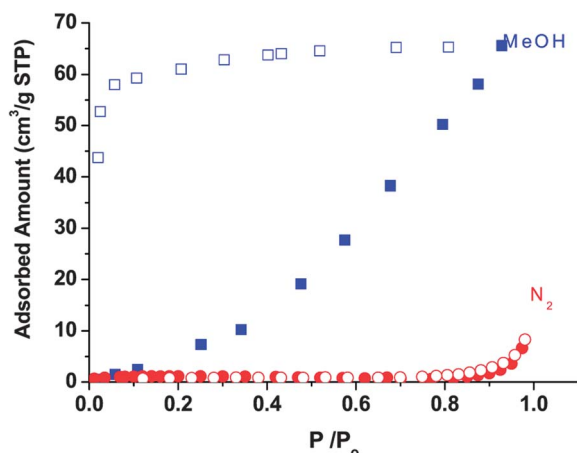


Fig. 2 Gas adsorption-desorption isotherms for the uptake of N₂ and MeOH. P_0 is the saturated vapor pressure, 102.3 kPa, of N₂ (77 K), and 16.94 kPa, of methanol (298 K).

amide groups of **1a** in a 2 : 3 ratio. From these results, we may conclude that the amide groups on the channel surfaces function effectively and give rise to an attractive interaction with the methanol guest molecules *via* hydrogen bonding.

Solid-state magnetic susceptibility measurements for **1** were performed in the range of 2–300 K under a field of 1000 Oe. At 300 K, the $\chi_M T$ value is 5.47 cm³ K mol^{−1} and is higher than the spin-only expectation of 3.75 cm³ K mol^{−1} for two $S = 3/2$ sites (the tetrahedral Co^{II} cations contain three unpaired electrons in the t_2 levels, while the octahedral Co^{II} cations have one unpaired electron in a t_{2g} orbital set and two unpaired electrons in the e_g symmetry orbitals). The χ_M at 20–300 K displays a continuous slow increase concurrent with a decrease in temperature, and then sharply increases when the temperature is lowered from 20–2 K (Fig. 3). At 2 K, the χ_M value is 0.815 cm³ mol^{−1}. The magnetic data were modeled by expressions for (a) independent spins antiferromagnetically coupled (θ) for two $S = 3/2$ Co^{II} sites with the Curie–Weiss equation, (b) the inclusion of zero field splitting, D , for this independent spin model (eqn (1)),²³ and (c) strong intradimer coupling with the dinuclear $S = 3/2 \pm 3/2$ Bleaney–Bowers-like equation (eqn (2)).^{23a}

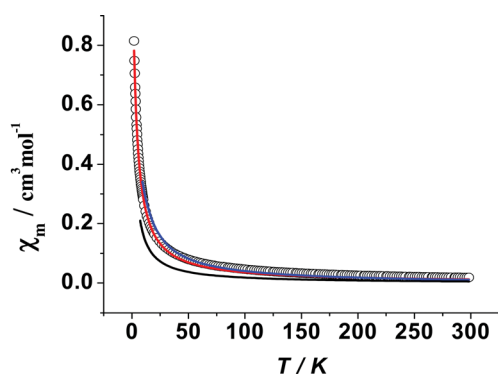


Fig. 3 χ_M – T data of **1** (O) and Curie–Weiss (red), zero-field-splitting (black), and Bleaney–Bowers (blue) fitting expressions.

For all three equations, N , g , β and k_B are the Avogadro constant, Landé factor, Bohr magneton and Boltzmann constant, respectively.

$$\chi_M = \frac{N\beta^2 g^2}{3k_B(T-\theta)} \left(\frac{1+9e^{-2D/k_BT}}{4(1+e^{-2D/k_BT})} \right) + \frac{2N\beta^2 g^2}{3k_B(T-\theta)} \left(\frac{1+\frac{3T}{4D}(1-e^{-2D/k_BT})}{1+e^{-2D/k_BT}} \right) \quad (1)$$

$$\chi_M = \frac{N\beta^2 g^2}{3k_B(T-\theta)} \left(\frac{2e^{J/k_BT} + 10e^{3J/k_BT} + 28e^{6J/k_BT}}{1+3e^{J/k_BT} + 5e^{3J/k_BT} + 7e^{6J/k_BT}} \right) + \text{TIP} \quad (2)$$

The magnetic susceptibility from 2 K to 300 K obeys the Curie–Weiss law with a Weiss constant θ of −14.6 K and a Curie constant C of 5.92 cm³ K mol^{−1}, in accordance with other octahedral and tetrahedral cobalt(II) complexes.²⁴ The negative θ value indicates antiferromagnetic coupling. Above 20 K, the χ_M – T data can be fitted to eqn (1) with the parameters $g = 2.09$, $D/k_B = 25.2$ K, and $\theta = -8.7$ K. The D parameter for this dinuclear complex is comparable to those for one-dimensional chains of cobalt complexes reported in the literature.²⁵ Because of the dinuclear structure, eqn (2) was identified to be a plausible model for the data (the data were fitted above 30 K, $g = 2.2$, $J = -3.05$ cm^{−1}, $\theta = -1.35$, and $\text{TIP} = 426 \times 10^{-6}$ cm³ mol^{−1}). The coupling parameters for the dinuclear complex indicate antiferromagnetic coupling within the dinuclear species.

In conclusion, we have synthesized a porous coordination polymer $\{[\text{Co}_2(\text{L})\text{Cl}(\text{DMF})_2(\text{H}_2\text{O})]\cdot\text{S}_x\}_n$ **1**, using an amide-linked tricarboxylic ligand under solvothermal conditions. The framework of **1** is constructed from trigonal L ligands and 3-connected Co₂ clusters, forming a honeycomb layer structure. π – π interactions, hydrogen bonds and the inorganic synthon X–H \cdots Cl[−]Co(II) (X = N or C) play a significant role in the stabilization of 3D crystalline supramolecular architectures. The Cl[−], together with the flexibility of the ligand, results in the unique tetrahedral and octahedral Co^{II} site in the structure. The desolvated solid **1a** exhibits moderate MeOH uptake and the powder sample of **1** shows antiferromagnetic properties.

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