

Supporting Information

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

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

^a *Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, China*

E-mail: zouyang@zstu.edu.cn

^b *Ulsan Natl Inst Sci & Technol, Interdisciplinary Sch Green Energy, Ulsan 689798,
South Korea.*

E-mail: molah@unist.ac.kr

Materials

The following chemicals were used as received with no further purification: *p*-phthaloyl chloride, 5-amino isophthalic acid, triethylamine, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, *N,N'*-dimethylformamide (DMF), *N,N'*-dimethylacetamide (DMA), methanol and acetone from Aladdin-reagent, Inc.

General procedures

All the reagents were purchased from commercial sources and were used without further purification. Infrared spectra were recorded using KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$ employing a Nicolet FT-IR 400 system. Thermogravimetric analysis (TGA) was performed in a nitrogen stream using an Pyris Diamond system with a heating rate of $10^\circ\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) data was recorded by a Bruker D8 ADVANCE automated diffractometer. The adsorption isotherms were measured at 195 K for CO_2 and 77 K for N_2 using a Micrometric ASAP2020M system and ultra-pure gases (99.999%). The temperature-dependent magnetic susceptibility of **1** was measured with crystalline powder samples on a Quantum Design MPMS XL-7 Squid magnetometer in a magnetic field of 100 Oe under the temperature range 3–300K.

Preparation of bis-(3,5-dicarboxy-phenyl) terephthalamide (H_4L): The synthesis of bis-(3,5-dicarboxy-phenyl) terephthalamide (H_4L) was achieved by using a modified version of a previously reported procedure¹. 3.05g (15.00 mmol) sample of *p*-phthaloyl chloride is added to a solution of 5.62g (31 mmol) of 5-amino isophthalic acid and 1mL of triethylamine in 60 mL of DMA. The mixture is stirred for 16 hrs, and then 500 mL water was added. White precipitate formed was filtered and the solid was washed with acetone, water, methanol and finally ether and further dried in vacuum. Yield = 5.9 g (79.9%). IR (KBr): ν/cm^{-1} : 3380(b), 1716(vs), 1677(s), 1614(s), 1552(vs), 1510(s), 1385(s), 1336(s), 1286(m), 1253(m), 1200(s), 928(m), 760(vs), 715(m), 665(m), 615(m). Elemental analysis: Calcd. for $\text{H}_4\text{L} \cdot 1.5\text{H}_2\text{O}$. ($\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_{11.5}$, fw = 519.4): C, 55.50; H, 3.69; N, 5.39%. Found: C, 55.12; H, 3.75; N, 5.36%.

Preparation of $\{[\text{Co}_2(\text{L})(\text{H}_2\text{O})_3] \cdot \text{S}_x\}_n$ 1: A solvothermal reaction of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0322 g, 0.11 mmol) and H_4L (0.0240 g, 0.05 mmol) in 6 mL DMF- H_2O (10 : 1 volume ratio) was performed at 85°C for 5 days. The blue block crystals of **1** were obtained in 50% yield (based on ligand). The crystals were soaked in DMF overnight and in methanol for 7 days and filtered and dried in vacuum at 150°C overnight to obtain **1a**. IR (KBr, cm^{-1}): 3396(b), 1614(vs), 1550(vs), 1423(vs), 1382(vs), 1284(s), 1241(w), 1220(w), 1018(w), 877(w), 781(m), 719(m), 617(w) Elemental analysis: Calcd. for

$[(\text{Co}_2\text{L}(\text{H}_2\text{O})_3)\cdot 4\text{DMF}\cdot 6\text{H}_2\text{O}] \cdot (\text{C}_3\text{H}_6\text{N}_2\text{O}_2)_2$, fw = 1064.7): C, 40.61; H, 5.87; N, 7.89%. Found: C, 41.3; H, 5.69; N, 8.03%.

Crystallographic data collections and refinements of structure

A crystal was coated with paratone oil and the diffraction data were measured at 115 K on a Siemens SMART CCD diffractometer equipped with a graphite monochromatic Mo K α ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects (SAINT), and multi-scan absorption corrections based on equivalent reflections were applied (SADABS).

Crystal structure of **1**: Light blue block shaped crystal, 0.23 x 0.16 x 0.08 mm³, C₄₈H₅₇N₄O₃₆Co₄, fw = 1501.70 g·mol⁻¹, monoclinic, space group *P21*, a = 10.152(3) Å, b = 17.953(6) Å, c = 18.062(6) Å, $\beta = 94.62(1)^\circ$, V = 3281.3(18) Å³, Z = 1, $\mu = 0.544$ mm⁻¹, 18179 reflections were collected, 11482 were unique [$R_{\text{int}} = 0.065$]. The structure was solved by direct methods and refined by full-matrix least-squares on F² (SHELXTL)². The contributions of the disordered DMF molecules were removed from the diffraction data using the SQUEEZE routine of PLATON software.³ Since the DMF molecules are badly disordered, we can not find all DMF molecules and their exact location and amount, as well as the anisotropic refinement for this badly disordered solvent molecules seems also impossible. Thereby, in '1.cif' file, we only defined partly solvent molecules that is refined by isotropic refinement, resulting in the high R1=0.1020 and $\omega R2=0.2662$ values. Then, we carry out Platon Squeeze program towards these badly disordered solvent molecules, leading to the better R1=0.0547 and $\omega R2=0.1163$ values, which is reported as '1squeeze.cif' file.

References

- (1) Y. Zou, M. Park, S. Hong and M. S. Lah, *Chem. Comm.* 2008, 2340
- (2) G. M. Sheldrick, SHELXTL-Plus, Crystal Structure Analysis Package; Bruker Analytical X-Ray; Madison, WI, USA, 1997.
- (3) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2001.

Table S1. Crystal data and structure refinement for **1**.

| | | |
|-----------------------------------|--|----------------|
| Empirical formula | C ₄₈ H ₅₇ N ₄ O ₃₆ Co ₄ | |
| Formula weight | 1501.70 | |
| Temperature | 115(2) K | |
| Crystal system | Monoclinic | |
| Space group | <i>P21</i> | |
| Unit cell dimensions | a = 10.152(3) Å | α = 90°. |
| | b = 17.953(6) Å | β = 94.62(1)°. |
| | c = 18.062(6) Å | γ = 90°. |
| Volume | 3281.3(18) Å ³ | |
| Z | 1 | |
| Density (calculated) | 0.756 g/cm ³ | |
| Absorption coefficient | 0.544 mm ⁻¹ | |
| F(000) | 765 | |
| Crystal size | 0.23 x 0.16 x 0.08mm ³ | |
| Theta range for data collection | 2.3 to 26.00°. | |
| Index ranges | -12 ≤ h ≤ 12, -22 ≤ k ≤ 19, -22 ≤ l ≤ 20 | |
| Reflections collected | 18179 | |
| Independent reflections | 11482 [R(int) = 0.065] | |
| Completeness to theta = 26.00° | 99.7 % | |
| Absorption correction | Empirical | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 11482 / 1 / 349 | |
| Goodness-of-fit on F ² | 0.99 | |
| Final R indices [I > 2σ(I)] | R1 = 0.1020, wR2 = 0.2662 | |
| R indices (all data) | R1 = 0.1503, wR2 = 0.2951 | |
| Largest diff. peak and hole | 0.76 and -0.63 e·Å ⁻³ | |

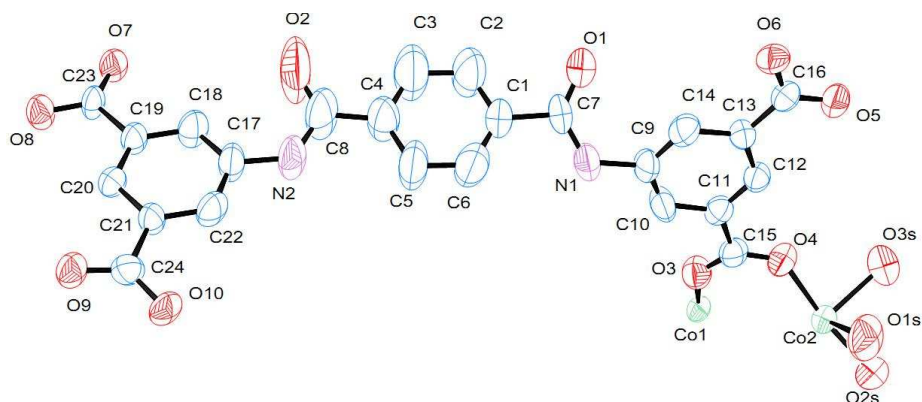


Figure S1. ORTEP picture of the asymmetric unit in crystal structure of **1** with 50% of thermal ellipsoid probability displacement. Hydrogen atoms are omitted for clarity. Atom colours shown as carbon - black, nitrogen - violet, oxygen - red and cobalt- green.

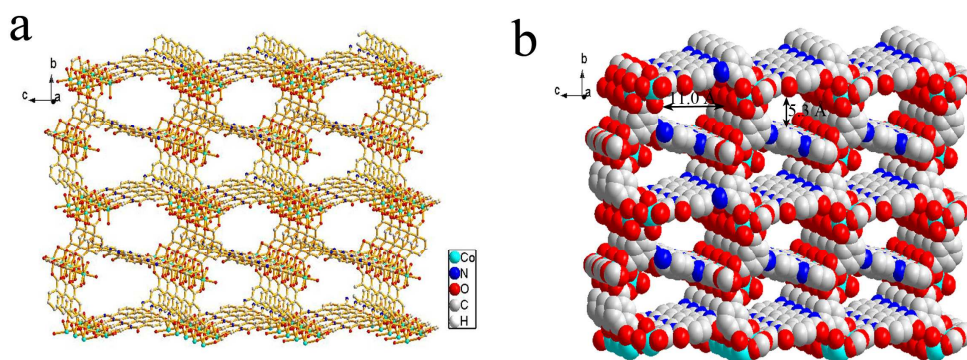


Figure S2. a) X-ray crystal structures of **1** with the **lon** net showing channels along the *a* axis. b) CPK model picture of the **1** illustrating the dimensions of the channel windows (11.0 Å x 5.3 Å) along the *a* axis. Guest molecules and hydrogen atoms are omitted for clarity.

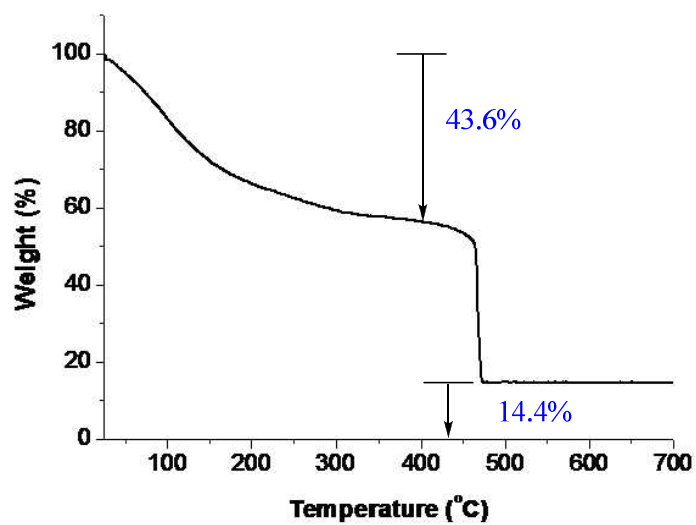


Figure S3. TGA curve of complexes 1.

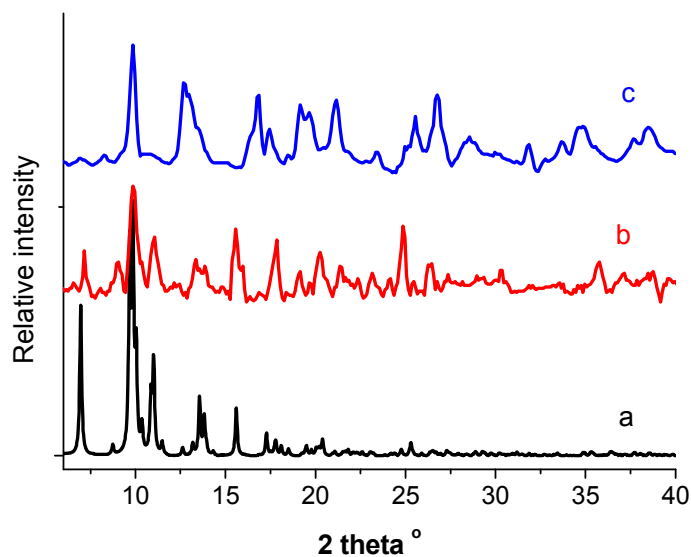


Figure S4. PXRD patterns of **1** and **1a**. (a) Simulated PXRD pattern from the single crystal structure of **1**, (b) as synthesized, **1** and (c) activated, **1a**.

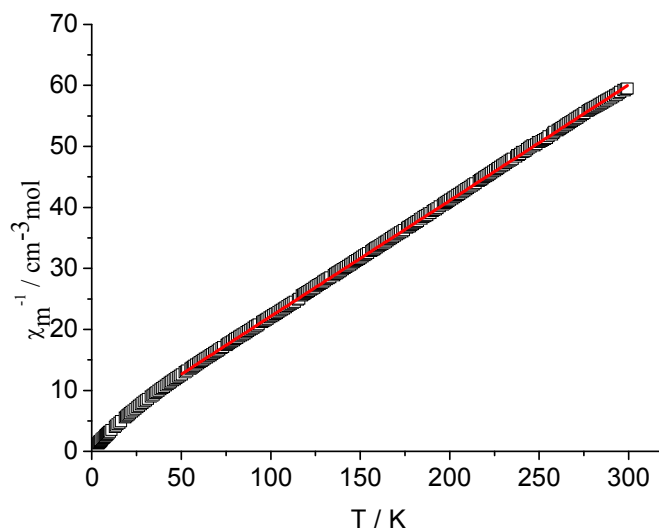


Figure S5. Plots of the χ_m^{-1} vs T for **1**, the red line shows the Curie–Weiss fitting (50–300K).