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Supporting Information

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

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Materials

The following chemicals were used as received with no further purification: *p*-phthaloyl chloride, 5-amino isophthalic acid, triethylamine, $Co(NO_3)_2{\cdot}6H_2O$, *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 4000-400 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^oC 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-pheny1) terephthalamide (H_4L): The synthesis of *bis*-(3,5-dicarboxy-pheny1) terephthalamide (H_4L) was achieved by using a modified version of a previously reported procedure[1]. 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 H_4L ·$1.5H_2O$. ($C_{24}H_{19}N_2O_{11.5}$, fw = 519.4): C, 55.50; H, 3.69; N, 5.39%. Found: C, 55.12; H, 3.75; N, 5.36%.

Preparation of $\{[Co_2(L)(H_2O)_3]{\cdot}S_x\}_n$ 1: A solvothermal reaction of $Co(NO_3)_2{\cdot}6H_2O$(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^oC 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^oC 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

[([Co_2L (H_2O)$_3$]·4DMF·6H_2O. ($C_{36}H_{62}N_6O_{23}Co_2$, 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 Ka (λ= 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 mm^3, $C_{48}H_{57}N_4O_{36}Co_4$, 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, β = 94.62(1)°,V = 3281.3(18) $Å^3$, Z = 1, μ = 0.544 mm^{-1}, 18179 reflections were collected, 11482 were unique [R_{int} = 0.065]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (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	$C_{48}H_{57}N_4O_{36}Co_4$	
Formula weight	1501.70	
Temperature	115(2) K	
Crystal system	Monoclinic	
Space group	*P21*	
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>2sigma(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·$Å^{-3}$	

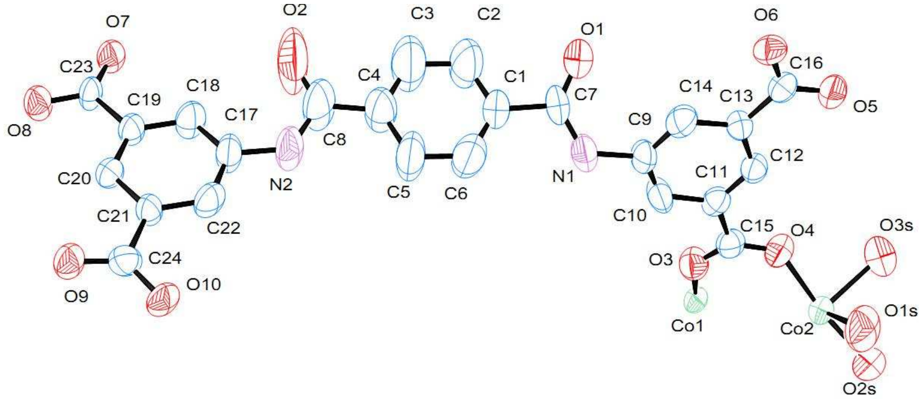

Figure S1. ORTEP picture of the asymmetric unit in crystal structure of **1** with 50% of thermal ellipsoid probability displacement. Hydrogen atoms are omitted for clarity. Atom colours shown as carbon - black, nitrogen - violet, oxygen - red and cobalt- green.

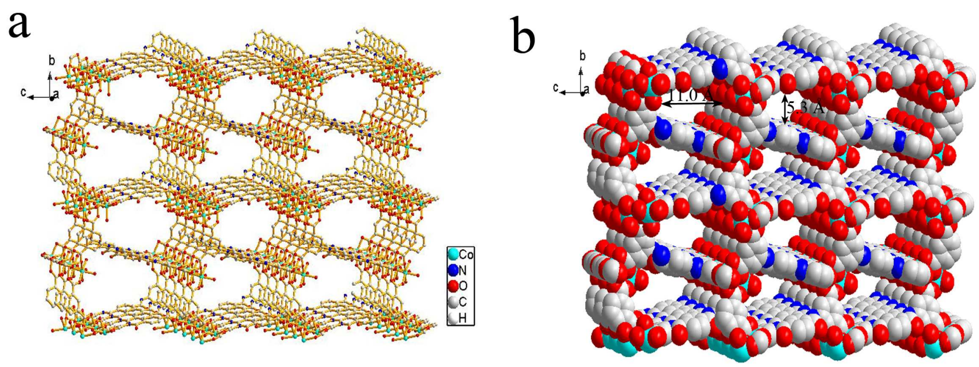

Figure S2. a) X-ray crystal structures of **1** with the **lon** net showing channels along the *a* axis. b) CPK model picture of the **1** illustrating the dimensions of the channel windows (11.0 Å x 5.3 Å) along the *a* axis. Guest molecules and hydrogen atoms are omitted for clarity.

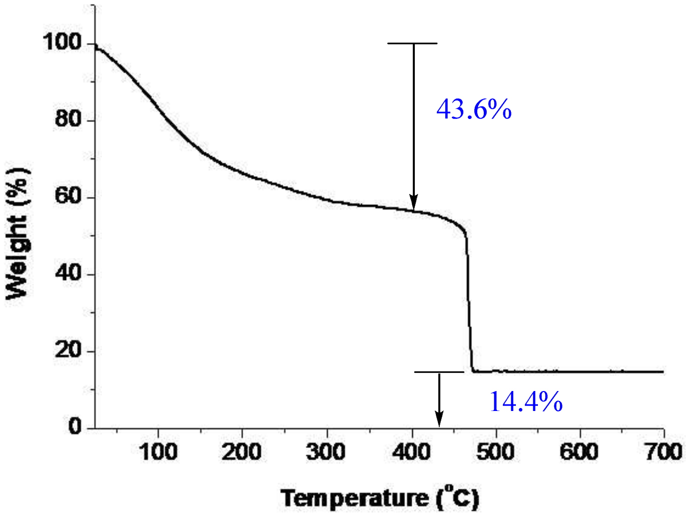

Figure S3. TGA curve of complexes **1**.

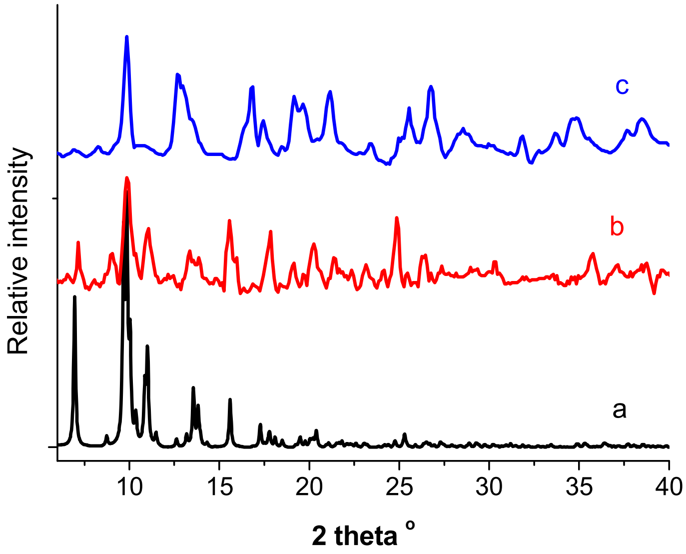

Figure S4. PXRD patterns of **1** and **1a**. (a) Simulated PXRD pattern from the single crystal structure of **1**, (b) as synthesized, **1** and (c) actived, **1a**.

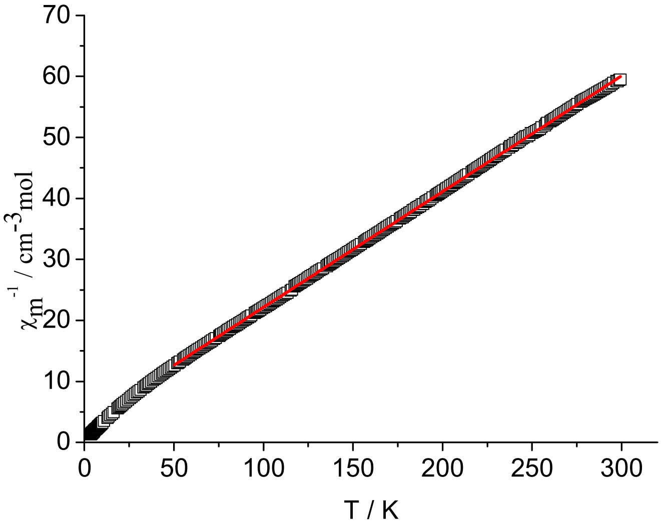

Figure S5. Plots of the χ_m^{-1} vs T for **1**, the red line shows the Curie–Weiss fitting (50-300K).