

Supporting Information

Water Stable Triazolyl Phosphonate MOFs; Steep Water Uptake and Facile Regeneration

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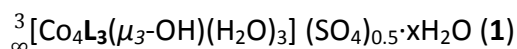
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1 Synthesis

4-(4*H*-1,2,4-triazol-4-yl)phenyl phosphonic acid (**H₂L**) was synthesized as described in reference.^[1]



Solvothermal syntheses were carried out in 23 mL Teflon lined steel autoclaves. The synthesis conditions were optimized in temperature programmable ovens ULE400 (MEMMERT) using the software CELSIUS 2007 (Version 9.2).

A steel autoclave with teflon vessel was charged with 11.2 mg (0.05 mmol) **H₂L**, 14.7 mg (0.05 mmol) **CoSO₄·7H₂O** (Merck), 5.0 ml water and sealed properly. The reaction mixture was heated to 150 °C within two hours. Heating at 150 °C was continued for 8 hours and then the autoclave was cooled down to room temperature within 62 hours. The pink color needle-shaped crystals were filtered, washed and dried in air.

Yield: ~ 6.8 mg (45 %); ${}^3[\text{Co}_4\text{L}_3(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{SO}_4)_{0.5}\cdot 10\text{H}_2\text{O}$ (**1**)

1.1 Elemental Analysis of 1:

CHN found (%): C 26.7; H 3.17; N 12.3 after drying at 105 °C; calculated (%) for ${}^3[\text{Co}_4\text{L}_3(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{SO}_4)_{0.5}\cdot 3\text{H}_2\text{O}$: C 26.7; H 2.90; N 11.7;

found (%): C 23.6; H 4.25; N 10.2 after drying at the air; calculated (%) for ${}^3[\text{Co}_4\text{L}_3(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{SO}_4)_{0.5}\cdot 12\text{H}_2\text{O}$: C 23.2; H 3.98; N 10.2

AAS (Co) and Ion Chromatography (phosphate, sulfate) found (%): Co 17.0; P 6.7; S 1.5 after drying at the air; calculated (%) for ${}^3[\text{Co}_4\text{L}_3(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{SO}_4)_{0.5}\cdot 20\text{H}_2\text{O}$: Co 17.0; P 6.7; S 1.2

For analysis by ion chromatography 20 mg of **1** (dried at 105 °C) was decomposed by conc. HCl (3 mL) and the sample solution was diluted with water to 50 mL. A Dionex ICS 1000 ion chromatography system was used for separation and quantification of sulfate and phosphate ions. The chromatographic conditions include, column (AS12 A, 250 mm x 4 mm), suppressor (ASRS-I, 4 mm), temperature (25 °C), eluent (3,5 mmol/L Sodium carbonat / 1,0 mmol/L Sodium bicarbonate / Water isocratic), eluent flow (1.2 ml/min), sample volume (25 µl), detector (conductivity), elution time (phosphate ions: 8.7 min and sulfate ions: 10.2 min).

2 X-Ray diffraction studies

The single crystal X-ray diffraction data of **1** were measured at 180 K on a diffractometer IPDS-2T (STOE) using Mo-K_α radiation ($\lambda = 71.073$ pm)^[2]. The structure was solved and refined using SHELX-97 and SHELXL-2014/7^[3] and WinGX[®]^[4]. Non-hydrogen atoms of the framework were refined anisotropically except disordered oxygen atoms. Whereas the C, N and P atoms of the ligand and the Co atoms are not disordered, all O atoms are refined on split positions. The $\mu_3\text{-OH}$ group is disordered (above and below the mirror plane through

the Co1 atoms and the atoms of the triazolyl phenyl group). The coordinated water molecule, the μ_3 -OH and phosphonate oxygen atoms are disordered accordingly, consistent with octahedral coordination of Co1 (Fig. S1). Because of the disorder of the O atoms the coordination of Co2 ($\bar{6}$ position) can only approximately be described as trigonal prismatic. The disorder of the donor atoms leads to increased thermal parameters of Co2. Refinement in lower symmetry space groups $P31c$ and $P321$ (subgroups of $P\bar{6}2c$ without mirror plane) lead to the same disorder problems. No additional reflections could be observed that would suggest a larger unit cell. The SO_4^{2-} anions and water molecules are disordered in the pore channels. Therefore the SQUEEZE^[5] routine was applied in order to remove the diffuse residual electron density (305 e^- in a solvent accessible volume of 960 \AA^3). The program DIAMOND 3.2e^[6] was used to visualize the structure.

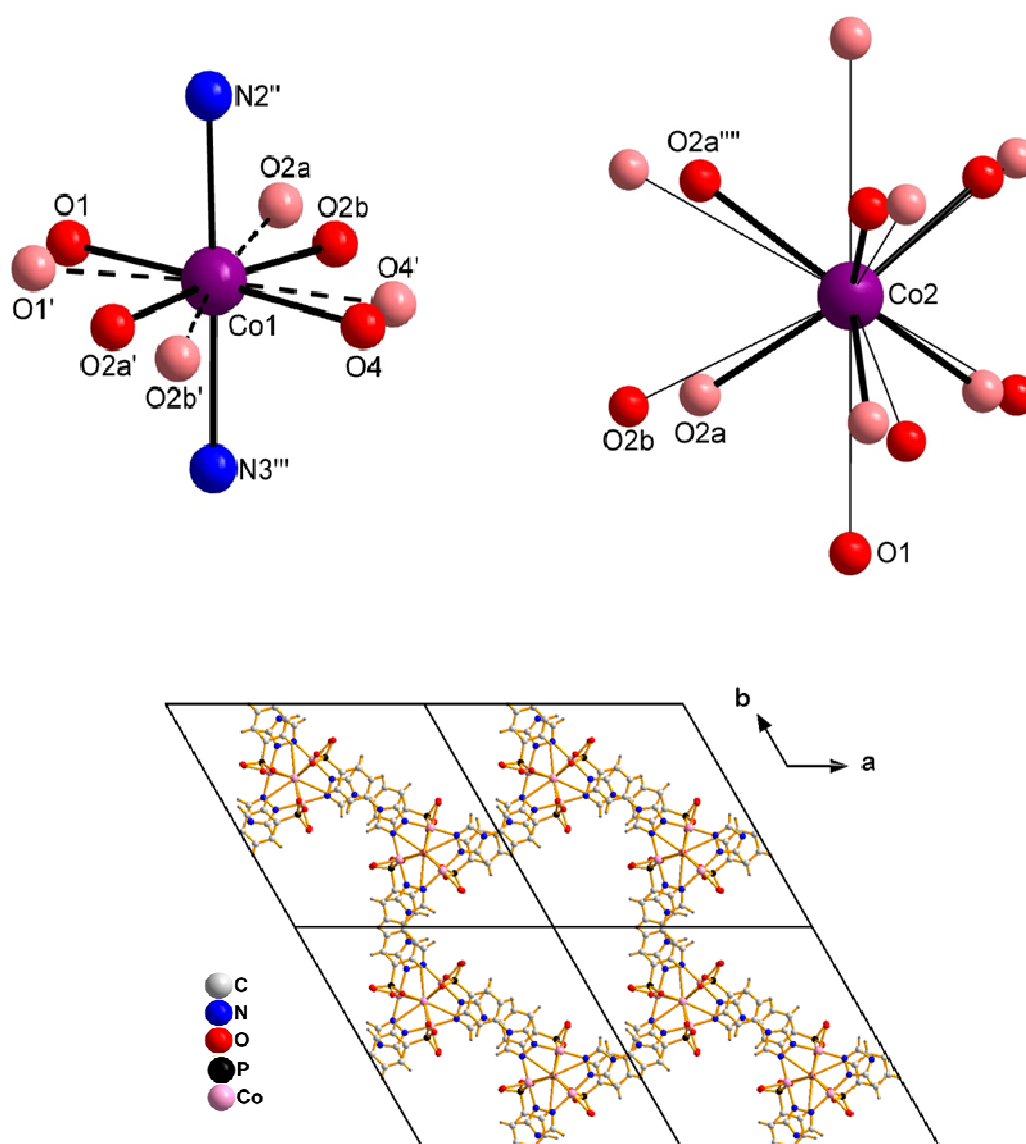


Figure S1: Coordination of the Co1 and Co2 atoms in **1** showing the disorder of O atoms; red and pink spheres represent sets of disordered O atoms coordinating to Co^{2+} (top); fragment of the crystal structure of **1**, view on four unit cells along $[00\bar{1}]$ (bottom). Symmetry operations: ' $x, y, 1.5-z$; '' $x-y, -y, 1-z$; ''' $1-x, 1-x+y, 1-z$; '''' $x, y, 0.5-z$

Table S1: Selected bond lengths in pm

Atoms	bond length	Atoms	bond length	Atoms	bond length	Atoms	bond length
P1-O2A	160.1(9)	Co1-O1	210.0(4)	Co1-O4	211.2(15)	Co2-O2A	219.0(10)
P1-O2B	148.4(16)	Co1-O2A	210.5(8)	Co1-N2	211.9(12)		
P1-O3	155.1(18)	Co1-O2B	204.1(16)	Co1-N3	215.9(12)		

The following notations are used in the manuscript for compound **1**:

1 – Pristine sample ${}^3[\text{Co}_4\text{L}_3(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{SO}_4)_{0.5}\cdot 12\text{H}_2\text{O}$

1' – **1** evacuated at 25 °C under $1\cdot 10^{-2}$ mbar

1'' – **1** evacuated at 130 °C under $1\cdot 10^{-2}$ mbar

PXRD

The X-ray powder diffraction measurements (Fig. S2) were carried out on a STOE STADI-P diffractometer in Debye-Scherrer mode using Cu-K α_1 radiation ($\lambda = 154.0598$ pm) at 25 °C. The samples for these measurements were prepared in glass capillaries (outer diameter 0.5 mm).

X-Ray powder diffraction data (Figures S3 and S4) were collected on a Rigaku RINT-2200HF (Ultima) diffractometer with Cu-K α radiation at 25 °C.

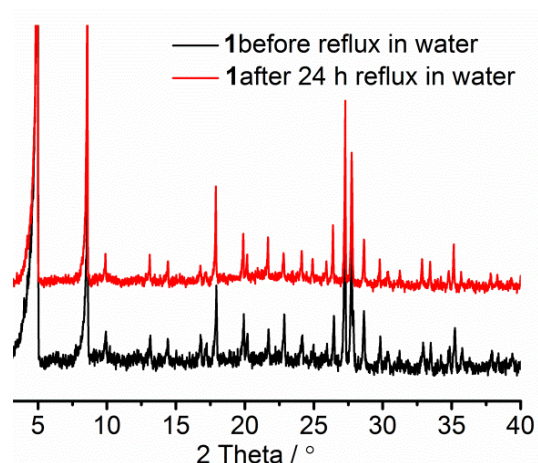


Figure S2: X-ray powder diffraction patterns of **1**; before reflux in water (black) and after 24 hours reflux in water in the presence of air (red).

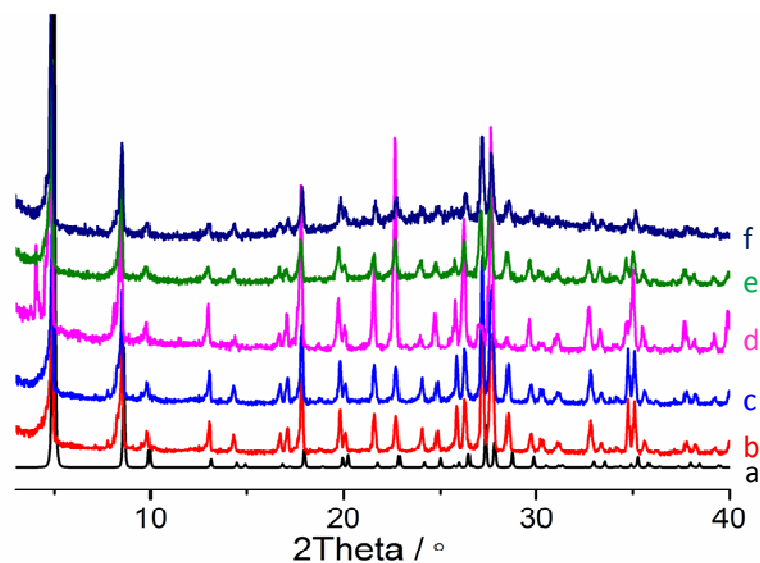


Figure S3: X-ray powder diffraction patterns of **1** after different sample treatments:
a) simulated powder pattern based on single crystal structure data of **1** (black);
b) as-synthesized sample **1** was activated at 25 °C, $1 \cdot 10^{-2}$ mbar (red);
c) after adsorption and desorption of N₂, CO₂ (blue);
d) after H₂O-sorption first cycle (magenta);
e) after impedance measurement (pellet) (green);
f) afterwards the same sample used for water sorption second and third cycle – PXRD recorded after third water sorption cycle (dark blue).

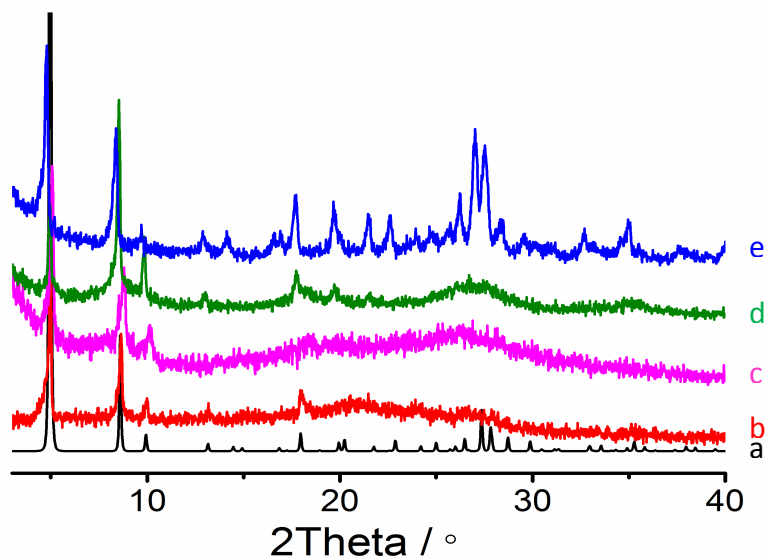


Figure S4: X-Ray powder diffraction patterns of **1''** after different sample treatments:
a) simulated powder pattern based on single crystal structure data of **1** (black);
b) the as-synthesized sample **1''** was activated at 130 °C, $1 \cdot 10^{-2}$ mbar (red);
c) after adsorption and desorption of N₂, CO₂ (magenta);
d) after H₂O-sorption (green);
e) after keeping **1''** at 95% RH at 90 °C for 12 h (blue).

3 Sorption studies

Sorption isotherms for N₂ at 77 K and CO₂ at 195 K were measured using a BEL-mini instrument. Based on N₂ sorption data **1** exhibits BET surface area of 26 m² g⁻¹ with a pore volume of 0.023 cm³ g⁻¹. The H₂O isotherms at 298 K were measured using a BEL-aqua instrument.

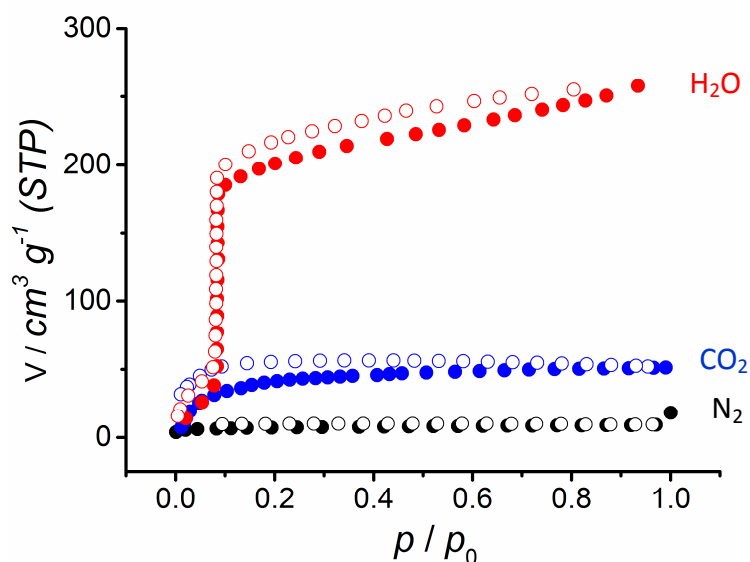


Figure S5: H₂O, CO₂ and N₂ sorption isotherm of **1**' at 298 K, 195 K and 77 K, respectively. Solid and hollow symbols represent adsorption and desorption, respectively.

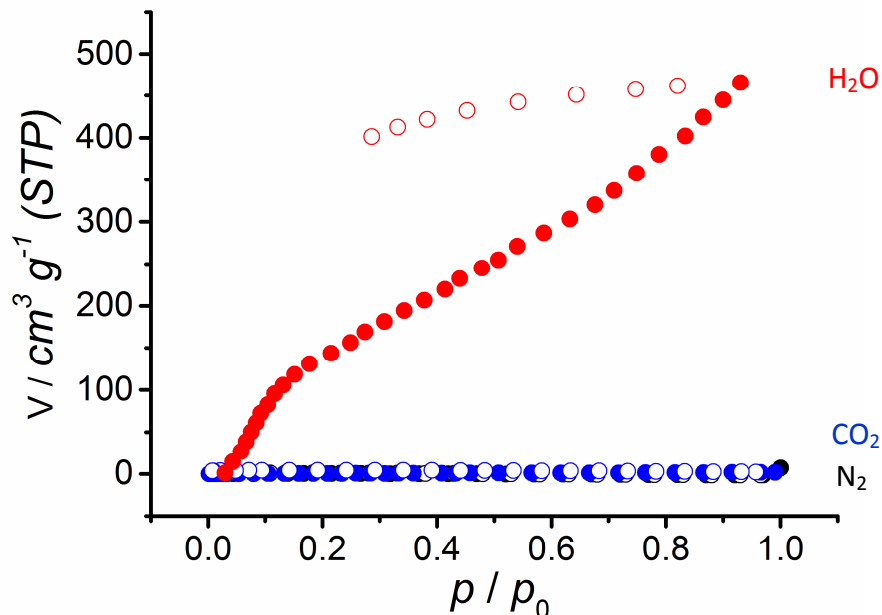


Figure S6: H₂O, CO₂ and N₂ sorption isotherms of **1''** at 298 K, 195 K and 77 K, respectively. Solid and hollow symbols represent adsorption and desorption, respectively.

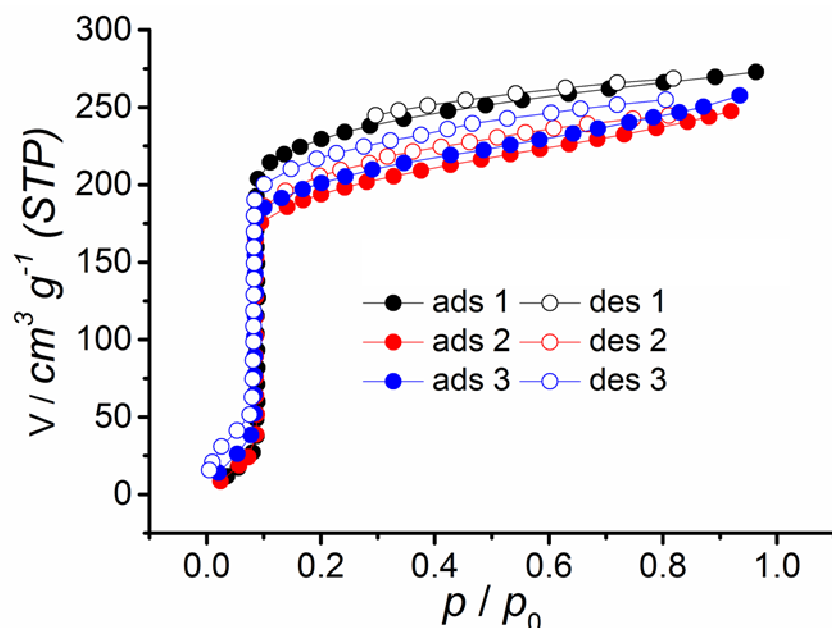


Figure S7: H₂O sorption isotherms of **1'** at 298 K in three consecutive cycles on the same sample. In the first cycle single crystals were used, after the first cycle the sample was grinded and pelletized for impedance measurements and later on used for 2nd and 3rd water sorption cycles. Solid and hollow symbols represent adsorption and desorption, respectively.

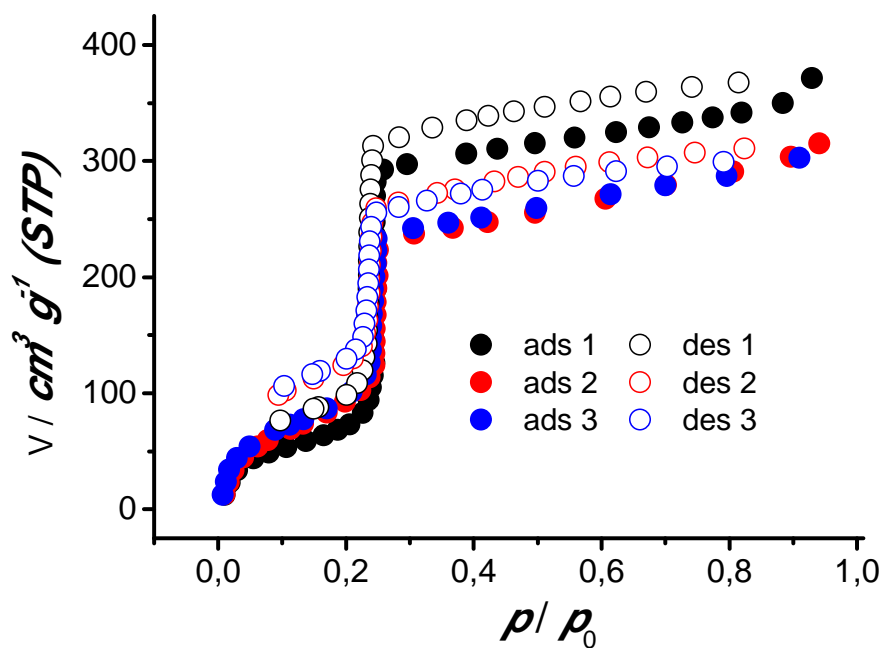


Figure S8: H₂O sorption isotherms of **2'** at 298 K in three consecutive cycles on the same sample. In the first cycle single crystals were used, after the first cycle the sample was grinded and pelletized for impedance measurements and later on used for 2nd and 3rd water sorption cycles. Solid and hollow symbols represent adsorption and desorption, respectively.

4 References

- [1] S. Begum, Z. Wang, A. Donnadio, F. Costantino, M. Casciola, R. Valiullin, C. Chmelik, M. Bertmer, J. Kärger, J. Haase, H. Krautscheid, H. *Chem. Eur. J.* **2014**, *20*, 8862.
- [2] X-Area and X-Red, *Stoe & Cie, Darmstadt, Germany* **2006**.
- [3] G. M. Sheldrick, *Acta Crystallogr.*, **2008**, *A64*, 112; SHELXL-2014/7.
- [4] L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837.
- [5] PLATON, A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7.
- [6] K. Brandenburg, DIAMOND 3.2e, Crystal Impact GbR, Bonn, Germany **2010**.