Synthesis, characterization and CO_2 uptake of a chiral Co(II) Metal-Organic Framework containing a thiazolidine-based spacer

Andrea Rossin,[a] Barbara Di Credico,[a] Giuliano Giambastiani,[a] Maurizio Peruzzini,*[a] Gennaro Pescitelli,[b] Gianna Reginato,[a] Elisa Forfecchia,[c] Diego Gianolio,[c] Carlo Lamberti,[c] Silvia Bordiga[c]*

[a] Istituto di Chimica dei Composti Organometallici (ICCOM - CNR), Via Madonna del Piano 10, 50019, Sesto Fiorentino, (Italy)

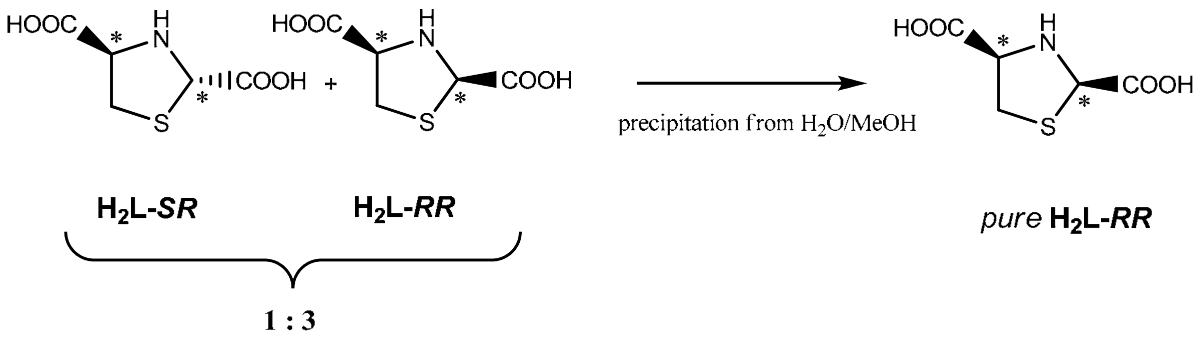
[b] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, 56126 Pisa, Italy.

[c] Dipartimento di Chimica IFM and NIS Centre of Excellence, Università di Torino, INSTM UdR Università, Via Pietro Giuria 7, 10125 Torino, Italy

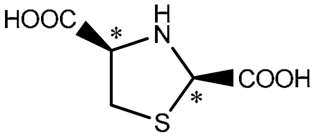
Electronic Supplemenary Information

Preparation of H_2L and resolution of (*2R,4R*)-thiazolidine-2,4-dicarboxylic acid (H_2L-*RR*) and (*2S,4R*)-thiazolidine-2,4-dicarboxylic acid (H_2L-*SR*).

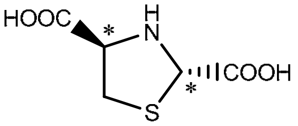
Diethyl thiazolidine-2(*R,S*),4(*R*)-dicarboxylate (4.0 g, 17.0 mmol)[S1] was dissolved in MeOH (170.0 mL). A solution of cesium carbonate (22.20 g, 68.0 mmol) in H_2O (170.0 mL) was added and the mixture was stirred at room temperature overnight. The reaction mixture was then concentrated *in vacuo* to remove methanol. The aqueous phase was washed with ethyl acetate and acidified with concentrated HCl ($1 \leq pH \leq 4$), to let **H_2L** gradually precipitate out of the solution. The solid was collected by filtration, washed with EtOH (3 x 15 mL), H_2O (3 x 15mL) and Et_2O (3 x 15mL) to afford 3.0 g (100%) of **H_2L** as a white solid. The diastereoisomeric mixture was separated by successive crystallizations from H_2O/MeOH.



Scheme S1. Diastereomeric enrichment of **H_2L**.



H_2L-*RR*: IR (KBr, cm^{-1}): $\tilde{\nu} = 3295$ (NH), 1682 (CO). ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ 4.88 (s, 1H); 3.82 (dd, ABX spin system, $J_{AB} = 6.0$, $J_{BX} = 10.0$ Hz, 1H); 3.31 (dd, ABX spin system, $J_{AX} = 10.0$, $J_{AB} = 6.0$ Hz, 1H); 2.74-2.67 (bt, $J_{app} = 6.0$ Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 25 °C): δ 172.53; 65.89; 55.38; 37.43. ESI-MS, *m/z* (%): 177(2) [M^+]. Anal. Calcd for $C_5H_7NO_4S$ (177.18): C, 33.89; H, 3.98; N, 7.91. Found: C, 33.84; H, 4.00; N, 7.89.



H_2L-*SR*: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3295 (NH), 1684 (CO). ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): δ 4.88 (s, 1H); 4.24-4.19 (bt, J_{app} = 6.0 Hz, 1H); 3.14 (dd, ABX spin system, J_{AB} = 6.0, J_{BX} = 10.0 Hz, 1H); 2.90 (dd, ABX spin system, J_{AX} = 10.0, J_{AB} = 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C): δ 172.53; 65.89; 55.38; 37.43. ESI-MS, *m/z* (%): 177(2) [M$^+$]. Anal. Calcd for $C_5H_7NO_4S$ (177.18): C, 33.89; H, 3.98; N, 7.91. Found: C, 33.86; H, 3.95; N, 7.93.

Thiazolidine-2,4-dicarboxylic acid was prepared by condensation of cysteine with ethyl glyoxalate in aqueous methanol containing potassium bicarbonate and obtained as a 3:1 (*R,R*)/(*S,R*) diastereomeric mixture. Condensation reactions with aldehydes gave mixtures of two diastereoisomers, in 1:1 to 1:3 diastereomeric ratio, due to the presence of a new stereogenic centre generated at the C-2 atom of the thiazolidine ring. Ester saponification with Cs_2CO_3 in aqueous methanol afforded the corresponding carboxythiazoles, which were isolated after crystallization from acidic water and (remarkably) obtained as pure isomers after fractional crystallization from MeOH/H_2O.

The two diastereomers **H_2L-*RR*** and **H_2L-*SR*** had similar UV absorption spectra consisting of a broad band with a maximum at 245 nm in H_2O. More interestingly, the two electronic CD spectra had also similar shapes but mirror image-like appearance (Figure S1). Thus, the CD spectrum of the (2*R*,4*R*) diacid shows two negative bands with maxima at 250 and 213 nm followed by a positive high-energy tail, while the opposite signs are observed for the corresponding bands of the (2*S*,4*R*) diacid. The observed CD bands are likely to be allied with transitions centered on the sulfide moiety, as chiral sulfides show three distinct CD bands in the 200-240 nm region.[S2] Therefore, it is conceivable that the chiral center closest to the sulfide group will contribute in a larger extent to the observed CD spectrum. In fact, the two diastereomers, differing in the configuration at C-2, show CD bands in similar positions but with opposite sign.

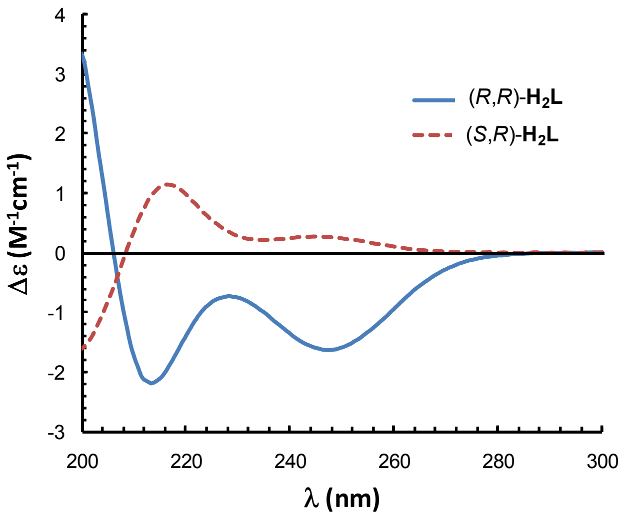


Figure S1. CD spectra of (*2R,4R*)-$\mathbf{H_2L}$ and (*2S,4R*)-$\mathbf{H_2L}$ (solid line: *R,R* diastereomer; dashed line: *S,R* diastereomer), 9.1 mM in H_2O; 0.1 cm cell.

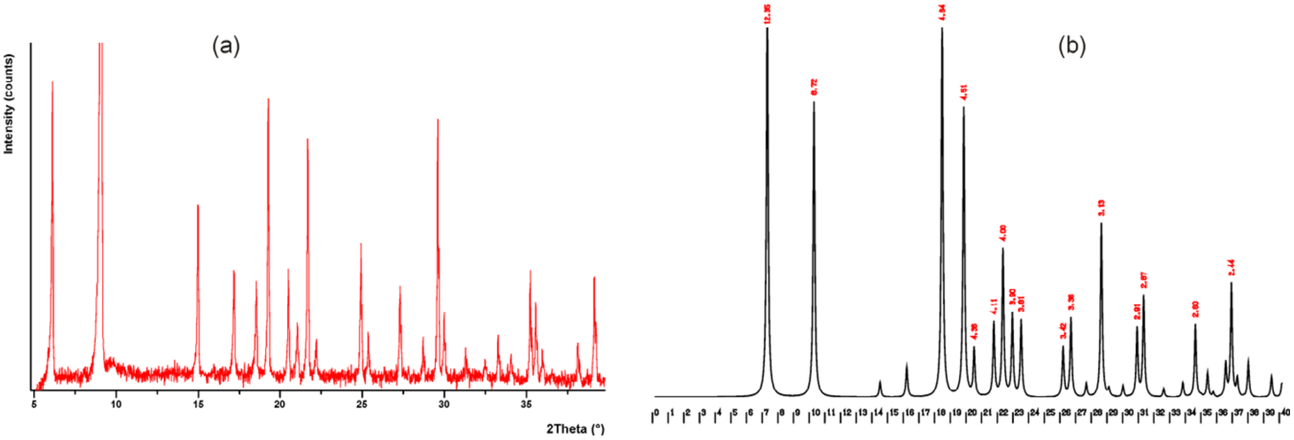
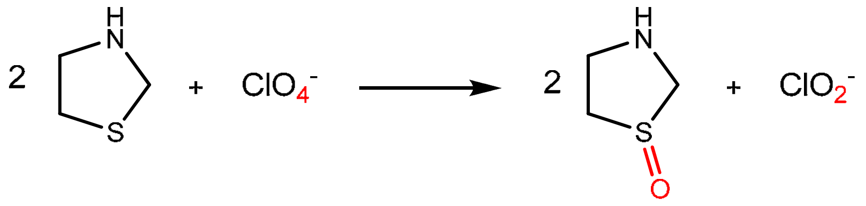


Figure S2. (a) Experimental and (b) simulated powder X-ray diffractogram of **1**. The red numbers on the simulated pattern indicate the corresponding *d*-spacing. The experimental peak intensity at 2θ = 9° is out of scale.



Scheme S2. Formation of the chlorite anion as a result of a redox reaction between the thiazolidine ring and perchlorate salts.

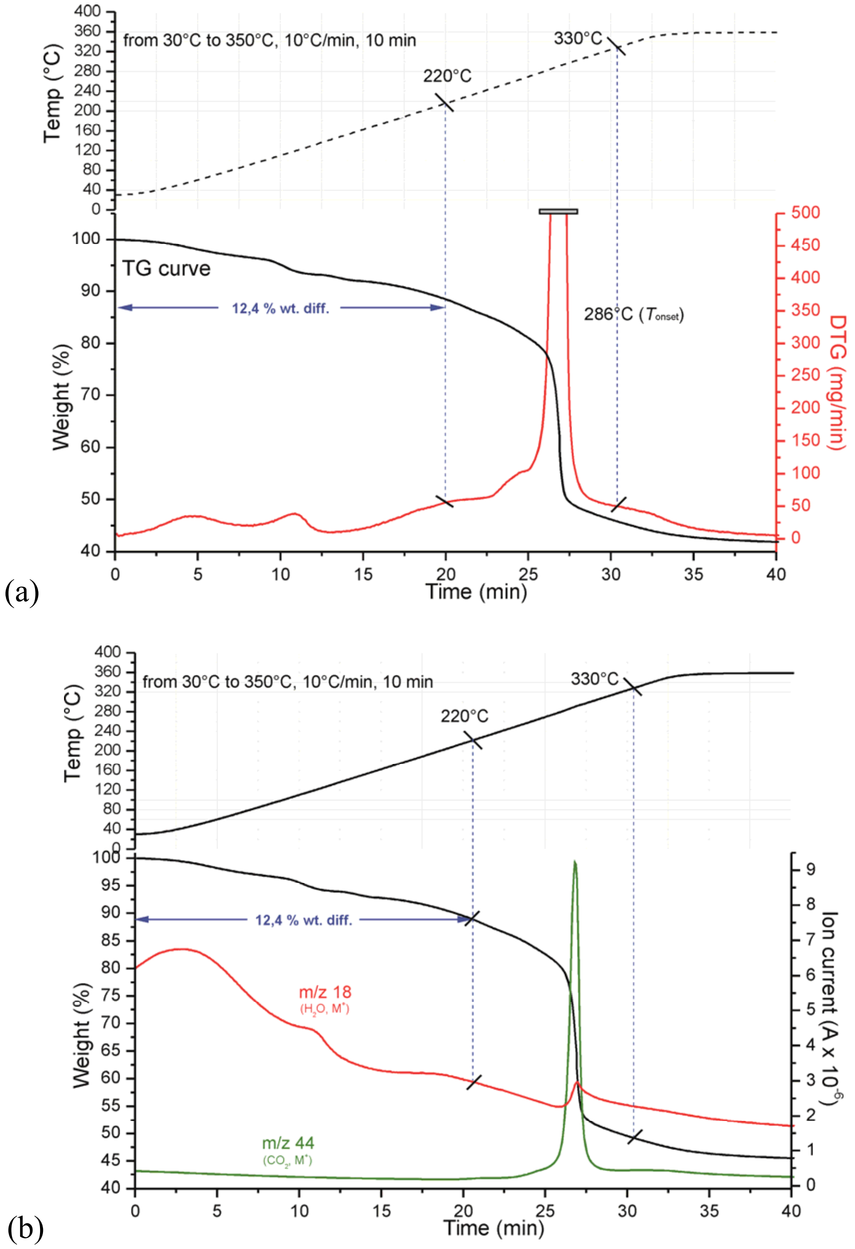


Figure S3. (a) TG-DTG and (b) related MS spectra of **1**.

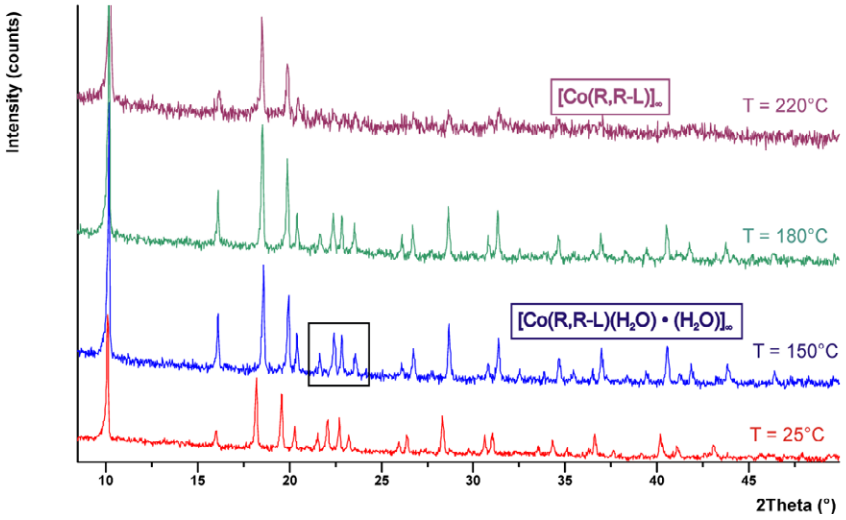


Figure S4. VT-PXRD spectra of **1**. The black square indicates the peaks that disappear upon dehydration, occurring between 180 and 220 °C. Compare with Figures S2(b) and S3.

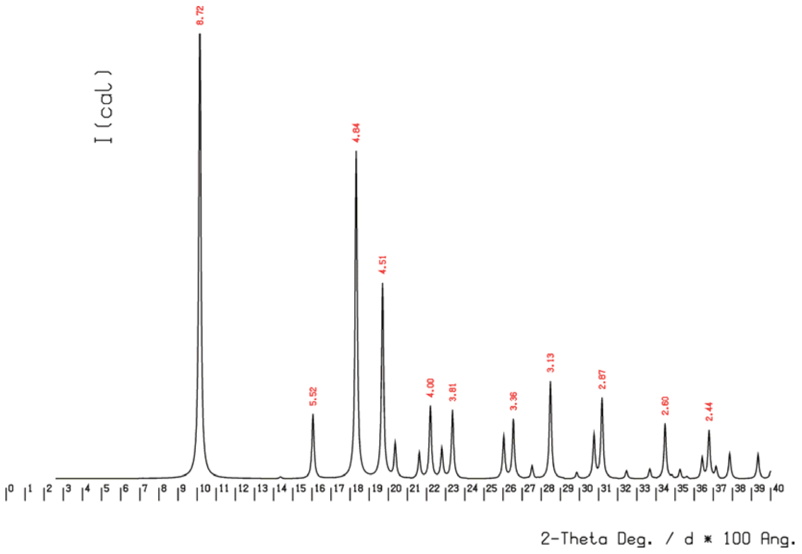


Figure S5. PXRD simulated pattern of the anhydrous [Co(**L-*RR***)]$_\infty$ phase ($\mathbf{1_{act}}$) built from the single crystal data. Compare with Figure S2(b).

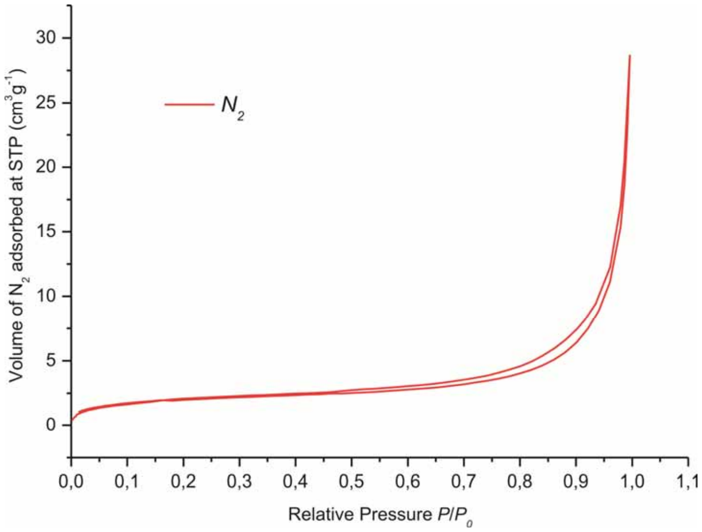


Figure S6. N_2 adsorption isotherm recorded on $\mathbf{1_{act}}$ at 77 K.

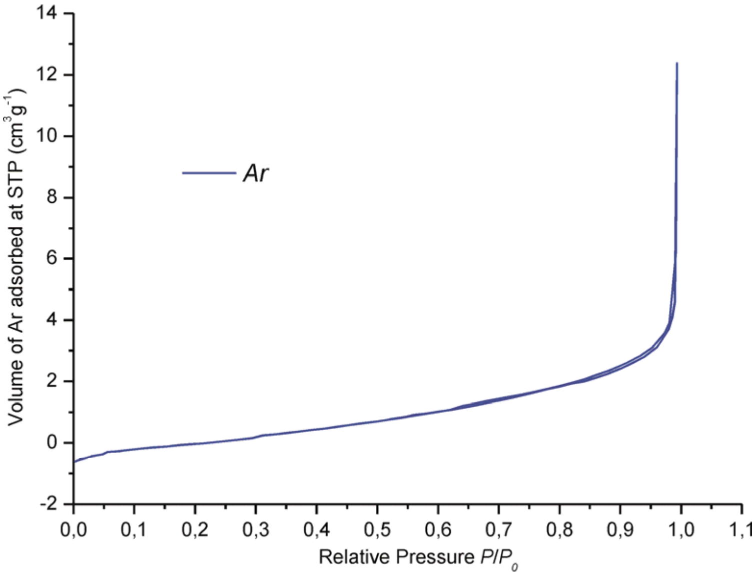


Figure S7. Ar adsorption isotherm recorded on $\mathbf{1_{act}}$ at 87 K.

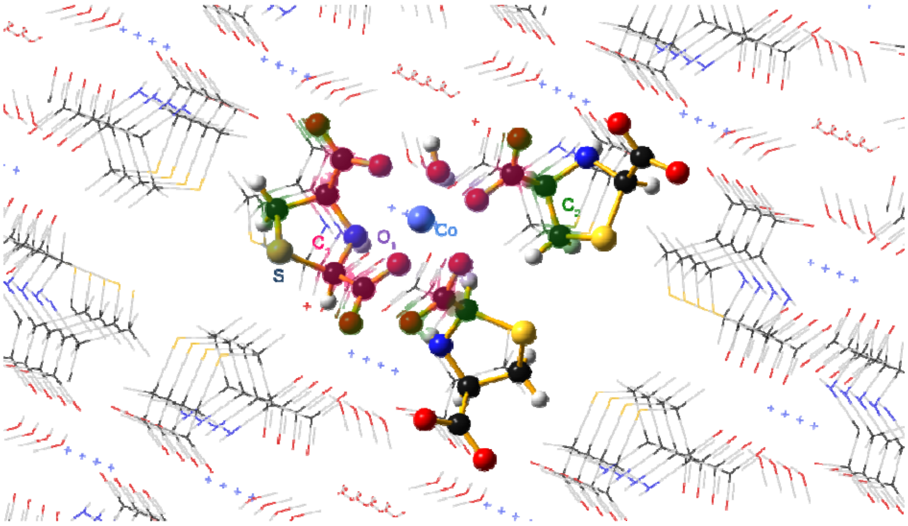


Figure S8. Structure of **1** obtained from the single crystal XRD refinement used as the starting point for the fitting procedure of the EXAFS data. Atoms included in the cluster used to compute phases and amplitudes are represented as spheres with the following color code: Co light blue, C black, O red, H white, N blue, S yellow. The three different shells of low Z atoms and the high Z Co and S atoms contributing to EXAFS signal are highlighted by different colored halos.

Details of the fitting procedure: given the similar electronic number for C, O, and N ($\Delta Z = 2$ or 1), their scattering amplitude (and the related contribution to the overall EXAFS scattering) will be very similar. Thus, these atoms were treated in the same way, optimizing from all of them the same displacement from the atomic coordinates (ΔR_i, i = 1, 2 or 3) and the same Debye-Waller factor (σ_i^2, i = 1, 2 or 3). On the other hand, a different approach was required for the higher-Z atoms such as S and Co (different form the absorber), which needed a special set of ΔR and σ^2 parameters. Including an energy shift ΔE and an amplitude factor shared among all SS and MS paths, the complete fitting model needed 12 independent parameters. As for the MS paths, the ΔR were calculated according to geometrical constrains starting from the ΔR of the involved atoms, while the Debye-Waller factors were summed according to the following rule: $\sigma_{MS}^2 = \sigma_1^2 + \sigma_2^2$, where $\sigma_{1,}$ σ_2 corresponds to the Debye-Waller factors of the atoms involved in the MS. For $\mathbf{1}_{\mathbf{act}}$, a similar procedure was applied, after removal of the water molecule from the Co(II) coordination sphere of **1** to get the initial guess structure for the data refinement. We tried to distinguish between the signal coming from the ligand N atom or the water molecule O atom (in the as-synthesized sample) and that due to the remaining four O atoms of the organic ligand. Even using different parameters, we obtained the same results in the fit, concluding that the discrimination is impossible because of the very similar Z and distances from the absorber. The low-R region, indicatively up to 2.5 Å, is well reproduced adding to the first shell also the SS paths related to the second shell atoms. In the region 2.5-4 Å, different SS and MS paths contribute to the overall signal. In the high-R region (distances longer than 4 Å), the dominant contribution is assigned to Co-Co SS. Looking at the optimized parameters resulting from the fits, we obtained for both samples comparable energy shifts and S_0^2 parameters equal to 1 within the experimental error. The Debye-Waller factors assume values comparable with the errors in the two fits for all the different atom shells; generally, the values are proportional to the distance from the absorber and to the number of electrons of the scattering atom.

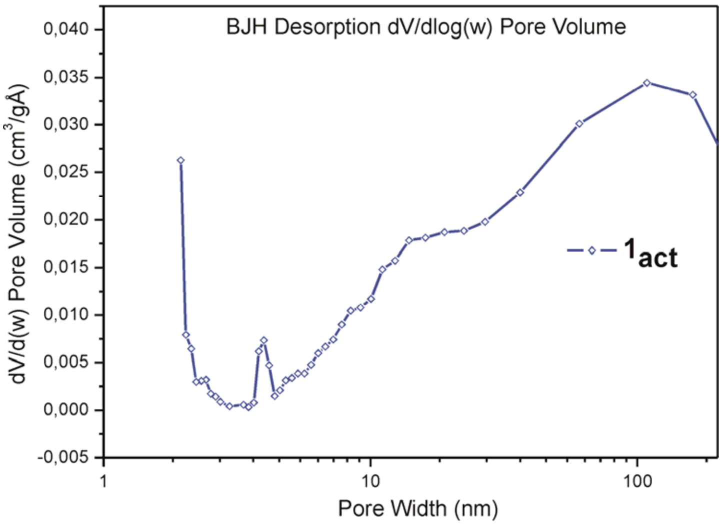


Figure S9. BJH pore size distribution of **1_{act}** derived from the N_2 adsorption experiment at 77 K.

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

CCDC	855629	
Empirical formula	$C_5 H_9 Co N O_6 S$	
Formula weight	270.13	
Temperature	100(2) K	
Wavelength	0.71069 Å	
Crystal system	Tetragonal	
Space group	$P\,4_1$	
Unit cell dimensions	a = 12.335(4) Å	α= 90.°.
	b = 12.335(4) Å	β= 90°.
	c = 5.265(3) Å	γ = 90°.
Volume	801.1(9) Å^3	
Z	4	
Density (calculated)	2.165 Mg/m^3	
Absorption coefficient	2.398 mm^{-1}	
F(000)	528	
Crystal size	0.05 x 0.05 x 0.1 mm^3	
Theta range for data collection	4.21 to 28.95°.	
Index ranges	$-15 \leq h \leq 16$, $-15 \leq k \leq 16$, $-7 \leq l \leq 7$	
Reflections collected	4373	
Independent reflections	1769 [R(int) = 0.0325]	
Completeness to theta = 28.95°	87.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1769 / 3 / 131	
Goodness-of-fit on F^2	0.996	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0610	
R indices (all data)	R1 = 0.0333, wR2 = 0.0627	
Absolute structure parameter	– 0.010(17)	
Largest diff. peak and hole	0.551 and – 0.421 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2954(2)	-2057(2)	7195(6)	10(1)
C(2)	3448(3)	-3186(2)	7393(6)	13(1)
C(3)	4756(3)	-1694(2)	9008(6)	10(1)
C(4)	5016(3)	1048(3)	6402(6)	11(1)
C(5)	1866(2)	2062(2)	11684(6)	9(1)
N(1)	3837(2)	-1259(2)	7506(5)	10(1)
O(1)	4168(2)	1287(2)	7570(4)	13(1)
O(2)	4315(2)	-332(2)	12112(4)	11(1)
O(3)	2078(2)	-1009(2)	10465(4)	14(1)
O(4)	2081(2)	518(2)	6625(5)	19(1)
O(5)	2569(2)	1323(2)	11920(5)	12(1)
O(6)	26(7)	-137(6)	9637(17)	58(2)
S(1)	4397(1)	-3077(1)	9999(2)	13(1)
Co(1)	3212(1)	155(1)	9414(1)	9(1)

Table S3. (Selected) bond lengths [Å] and angles [°] for **1**. Refer to Figure 1(a) for the atom numbering.

C(1)-N(1)	1.477(4)
C(1)-C(2)	1.523(4)
C(1)-C(5)#1	1.537(4)
C(2)-S(1)	1.809(3)
C(3)-N(1)	1.483(4)
C(3)-S(1)	1.839(3)
C(4)-O(1)	1.250(4)
C(5)-O(5)	1.264(4)
N(1)-Co(1)	2.154(3)
N(1)-H(1)	0.80(4)
O(1)-Co(1)	2.069(2)
O(2)-Co(1)	2.056(2)
O(3)-Co(1)	2.080(2)
O(4)-Co(1)	2.075(3)
O(4)-H(4A)	0.840(19)

O(4)-H(4B)	0.812(19)
O(5)-Co(1)	2.109(2)
N(1)-C(1)-C(2)	107.9(2)
C(1)-C(2)-S(1)	104.0(2)
N(1)-C(3)-S(1)	107.6(2)
C(1)-N(1)-C(3)	112.4(2)
C(1)-N(1)-Co(1)	109.11(19)
C(3)-N(1)-Co(1)	108.53(19)
C(4)-O(1)-Co(1)	123.3(2)
C(5)-O(5)-Co(1)	133.6(2)
C(2)-S(1)-C(3)	90.56(15)
O(2)-Co(1)-O(1)	98.32(9)
O(2)-Co(1)-O(4)	175.48(10)
O(1)-Co(1)-O(4)	84.56(10)
O(2)-Co(1)-O(3)	93.42(9)
O(1)-Co(1)-O(3)	166.89(9)
O(4)-Co(1)-O(3)	83.38(10)
O(2)-Co(1)-O(5)	90.93(10)
O(1)-Co(1)-O(5)	92.68(9)
O(4)-Co(1)-O(5)	92.42(11)
O(3)-Co(1)-O(5)	92.96(9)
O(2)-Co(1)-N(1)	81.32(11)
O(1)-Co(1)-N(1)	97.11(10)
O(4)-Co(1)-N(1)	94.90(11)
O(3)-Co(1)-N(1)	78.84(10)
O(5)-Co(1)-N(1)	168.29(10)

Symmetry transformations used to generate equivalent atoms:

#1 y,-x,z-1/4 #2 -x+1,-y,z+1/2 #3 -x+1,-y,z-1/2 #4 -y,x,z+1/4

Table S4. Anisotropic displacement parameters (Å^{2}x 10^3)for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	9(2)	13(2)	9(2)	-2(1)	-1(1)	-4(1)
C(2)	12(2)	14(2)	13(2)	-3(1)	0(1)	-1(1)
C(3)	9(2)	11(2)	10(2)	2(1)	1(1)	1(1)

C(4)	11(2)	11(2)	10(2)	-2(1)	-2(1)	-4(1)
C(5)	10(2)	10(2)	7(2)	-1(1)	0(1)	1(1)
N(1)	9(1)	12(1)	9(1)	1(1)	2(1)	-2(1)
O(1)	10(1)	11(1)	18(1)	2(1)	5(1)	1(1)
O(2)	12(1)	11(1)	11(1)	-3(1)	-2(1)	0(1)
O(3)	14(1)	12(1)	17(1)	-2(1)	4(1)	-3(1)
O(4)	16(1)	29(1)	13(1)	11(1)	-3(1)	-3(1)
O(5)	15(1)	10(1)	11(1)	-1(1)	0(1)	4(1)
S(1)	14(1)	9(1)	16(1)	1(1)	-3(1)	0(1)
Co(1)	8(1)	9(1)	10(1)	0(1)	0(1)	0(1)

Table S5. Hydrogen bonds for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(2)#5	0.80(4)	2.32(4)	3.117(4)	173(4)
O(4)-H(4A)...O(6)#1	0.840(19)	2.01(2)	2.830(8)	164(4)
O(4)-H(4A)...O(6)#6	0.840(19)	2.09(3)	2.841(9)	149(4)
O(4)-H(4A)...O(6)	0.840(19)	2.44(3)	3.098(9)	135(4)
O(4)-H(4B)...O(5)#5	0.812(19)	1.924(19)	2.735(4)	178(4)
O(4)-H(4B)...O(3)#7	0.812(19)	2.51(3)	3.027(4)	122(3)

Symmetry transformations used to generate equivalent atoms:

#1 y,-x,z-1/4 #2 -x+1,-y,z+1/2 #3 -x+1,-y,z-1/2 #4 -y,x,z+1/4 #5 x,y,z-1 #6 -x,-y,z-1/2 #7 -y,x,z-3/4

References

[S1] B. Di Credico, G. Reginato, L. Gonsalvi, M. Peruzzini and A. Rossin, *Tetrahedron*, 2011, **67**, 267-274.

[S2] G. Pescitelli, T. Kurtan, U. Florke and K. Krohn, *Chirality*, 2009, **21**, E181-E201.