Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Carbonic anhydrase-mimicking metal-organic frameworks built from amino acid and cadmium ions

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1. Materials.

All chemicals and solvents employed were commercially purchased and used without further purification. L-histidine (HIS) hydrochloride monohydrate (99%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2$•$4H_2O$, 99.9%) were purchased from Fisher.

2. Synthesis

Compound 1 [α-Cd(HIS)]: 0.1270 g (0.4117 mmol) $Cd(NO_3)_2$•$4H_2O$ was mixed with 0.1020 g (0.04866 mmol) L-histidine hydrochloride monohydrate and 0.50 mL 0.5 M KOH in 2.0 mL DI water. The mixture was transferred to a 45 mL Teflon-lined autoclave, sealed and heated at 130 ℃ for 168 hours. The colorless crystals of **1** were collected by filtration and dried in air (0.0813 g, yield 74.9% based on Cd). CHN analysis (%) exp (clc): C: 26.41 (27.14); H: 2.644 (2.657); N: 15.28 (15.82). IR (cm^{-1}): 3344 (w), 3289 (w), 3161, 3136 (w), 3117, 2932, 2895, 1563 (m), 1472, 1439, 1419, 1233, 1317, 1112, 1040, 972, 889, 850, 822, 798, 658.

Compound 2 [β-Cd(HIS)]: 0.1243 g (0.4029 mmol) $Cd(NO_3)_2$•$4H_2O$ was mixed with 0.1001 g (0.4775 mmol) L-histidine hydrochloride monohydrate and 5.0 mL 0.5 M KOH in 10.0 mL DI water and 5 mL EtOH. The mixture was transferred to a 45 mL Teflon-lined autoclave, sealed and heated at 130 ℃ for 72 hours. The colorless crystals of **1** were collected by filtration and dried in air (0.0361 g, yield 34.0% based on Cd). CHN analysis (%) exp (clc): C: 27.24 (27.14); H: 2.648 (2.657); N: 15.875 (15.82). IR (cm^{-1}): 3336 (w), 3280 (w), 3161, 3113, 2926, 2897, 1563(s), 1409, 1318, 1239, 1113, 1050, 882, 820, 775, 662(s).

3. PXRD

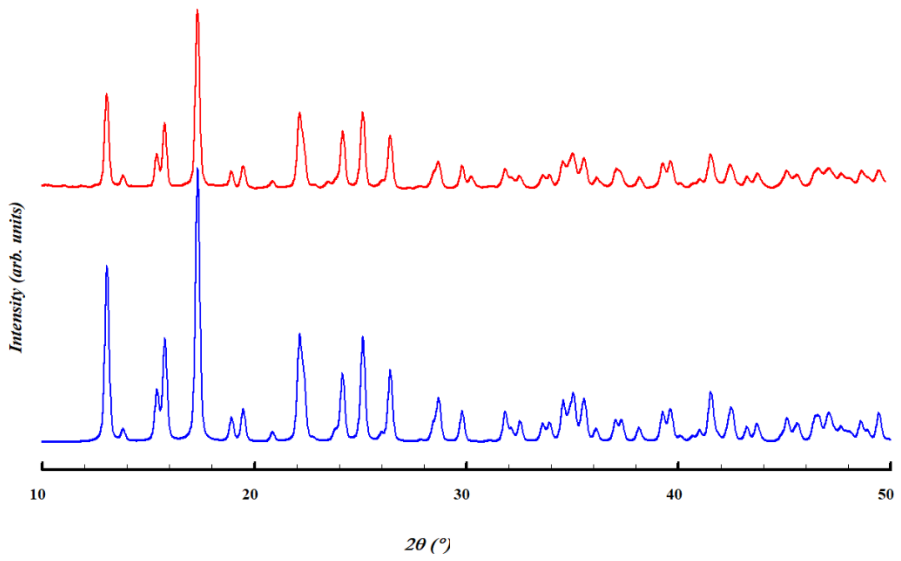

Fig. s1, Simulated PXRD (blue, bottom) from single-crystal XRD and experimented (red, top) PXRD of [α-Cd(HIS)] (**1**).

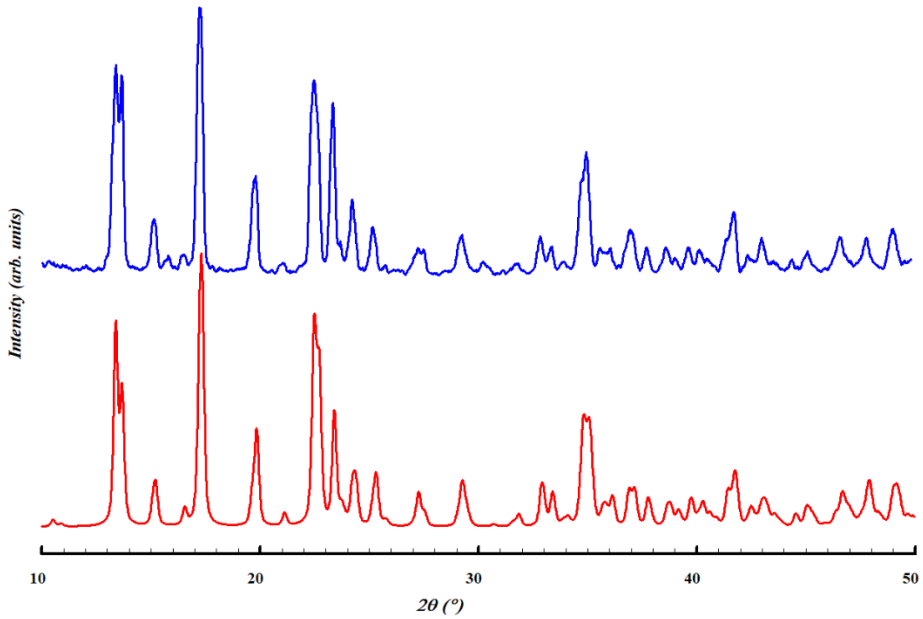

Fig. s2, Simulated PXRD (red, bottom) from single-crystal XRD and experimented (blue, top) PXRD of [β-Cd(HIS)] (**2**).

4. TGA

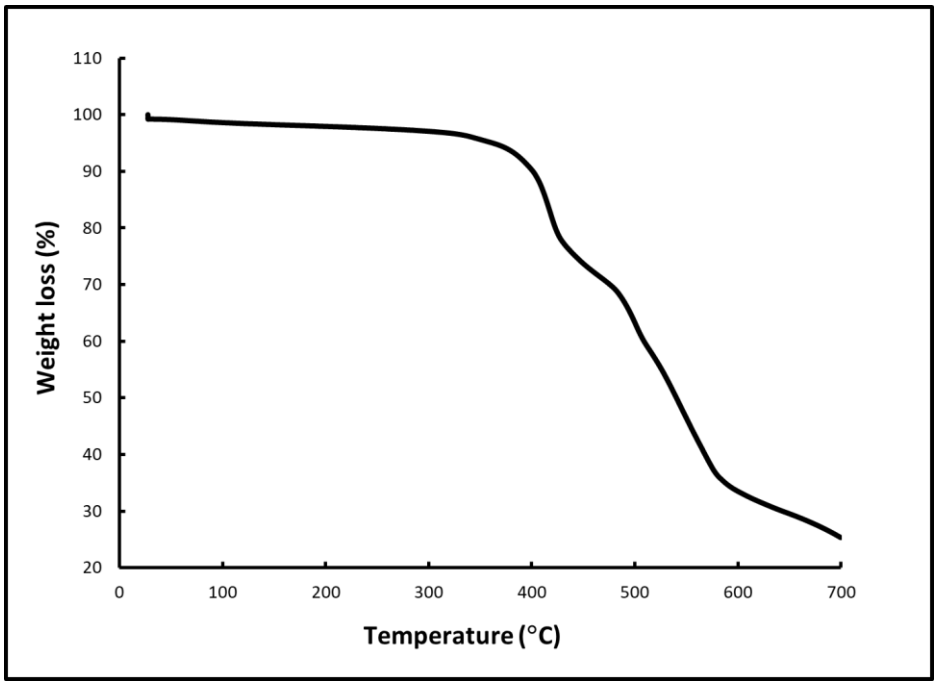

Fig. s 3. TGA plot of compound [α-Cd(HIS)] (**1**).

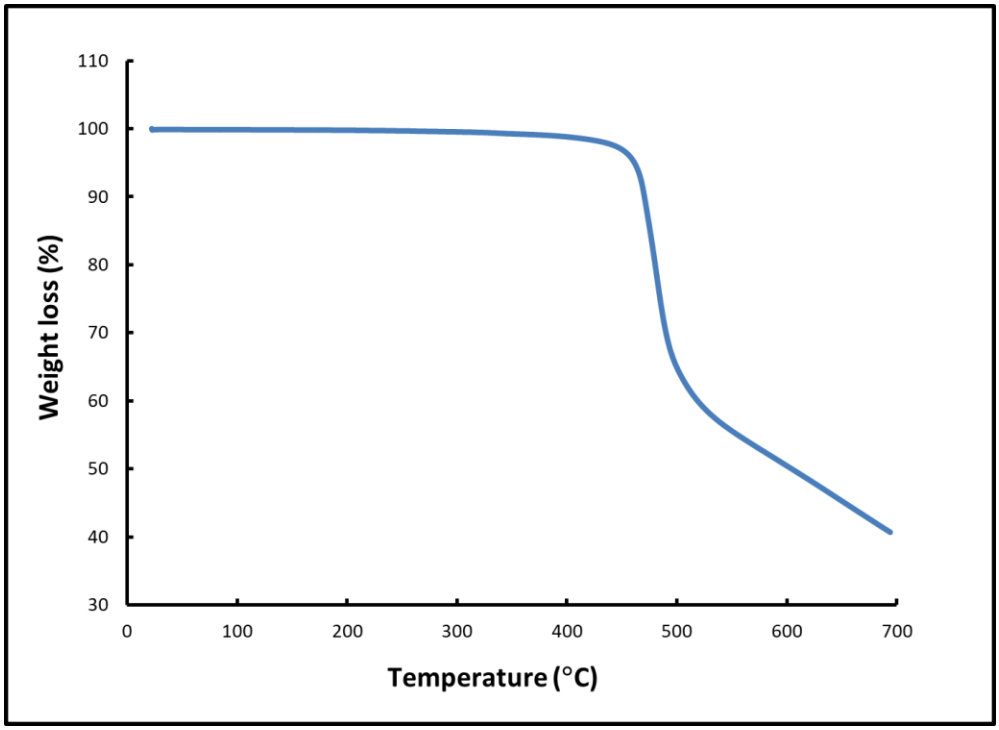

Fig. s4, TGA plot of compound [β-Cd(HIS)] (**2**).

5. X-Ray crystallography

X-ray diffraction data for the title compound were collected on a Bruker Quazar diffractometer with an Apex II CCD area detector. The data were processed with the SAINT software[1] and corrected for absorption with SAD-ABS.[2] The structures were solved by direct methods using SHELXTL V.6.10 package[3] and were refined against F^2 by weighted full-matrix least-squares calculations.[4] All nonhydrogen atoms were refined allowing for anisotropic displacement. Hydrogen atoms of the organic ligand were placed at calculated positions and refined using a riding model. Atomic scattering factors were taken from the International Tables for Crystallography.[5] The crystal data and bond lengths for compounds **1** and **2** are shown in Table s1. Selected hydrogen bonds are shown in Tables s2 and s3.

Table s1. Crystal data and structure refinements

	1	**2**
Formula	$C_6H_7N_3O_2Cd$	$C_{12}H_{14}N_6O_4Cd_2$
Mol. wt.	265.55	531.09
Crystal system	orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a (Å)	7.7921(8) Å	8.13520(10)
b(Å)	8.5071(5) Å	10.7178(2)
c(Å)	11.2218(8) Å	8.41520(10)
α(°)	90	90
β(°)	90	90.4940(10)°
γ(°)	90	90
V(Å^3)	743.9(1)	733.706(19)
Z	4	2
ρ (Mg/m^3)	2.371	2.404
μ (mm^{-1})	2.891	2.932
Wavelength(Å)	0.71073	0.71073
Temperature(K)	296	296
Reflections collected/unique [R_{int}]	1707/0.0186	5292/0.0534
Goodness-of-fit(F^2)	1.108	1.028
Final R indices [$I > 2\sigma(I)$]	R_1=0.0091, wR_2= 0.0243	R_1 = 0.0256, wR_2 = 0.0423
R indices (all data)	R_1=0.0091, wR_2= 0.0243	R_1 = 0.0323, wR_2 = 0.0444
Flack parameter/Friedel coverage (%)	0.01(2)	0.015(18)
Largest diff. peak and hole (e/Å^3)	0.202 and -0.198	0.515 and -0.490

Table s2, Selected hydrogen bonds [Å and °] for compound **1**

D-H…A	d(D-H)	d(H…A)	d(D…A)	∠DHA
N(3)-H(1N)…O(1)#2	0.82	2.54	3.198	138
C(1)-H(009)…O(1)#1	0.93	2.44	3.278	150
C(1)-H(009)…O(2)#3	0.93	2.55	3.121	120

Symmetry transformations used to generate equivalent atoms:

#1= -1+x,y,z

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

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

Table s3, Selected hydrogen bonds [Å and °] for compound **2**

D-H…A	d(D-H)	d(H…A)	d(D…A)	∠DHA
N(3)-H(3A)…O(1)#1	0.90	2.45	3.0258	122
N(3)-H(3B)…O(4)#2	0.90	2.27	3.1660	170
N(6)-H(6B)…N(5)	0.90	2.32	3.0938	144

Symmetry transformations used to generate equivalent atoms:

#1 = 1-x,1/2+y,1-z

#2 = x,y,1+z

6. Biomimetic catalysis study

The catalytic properties were carried out in an HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer solution (50 mM, pH = 8), which was prepared by dissolving 5.96 g of HEPES in 400 mL DI water. KOH pellets were added to adjust the pH of the buffer to 8 before adding water to make the 500 mL solution. The calibration curve for *p*-NP concentrations was plotted using UV-vis absorptions at 402 nm of various known concentrations (5, 10, 25, 50, 100 μM) of *p*-NP solutions, which were prepared using HEPES buffer (50 mM, pH 8.0).

In a 100 mL beaker, 4.9 mg of *p*-NPA was dissolved in 2.5 mL of acetonitrile. Then, 47.5 mL of HEPES buffer (50 mM, pH = 8), and 10 mg of the catalyst was added to this solution. The absorbance at 402 nm of the mixture was measured with a UV-vis spectrometer every 5 minutes. The blank control was carried out under the same conditions without adding the catalyst.

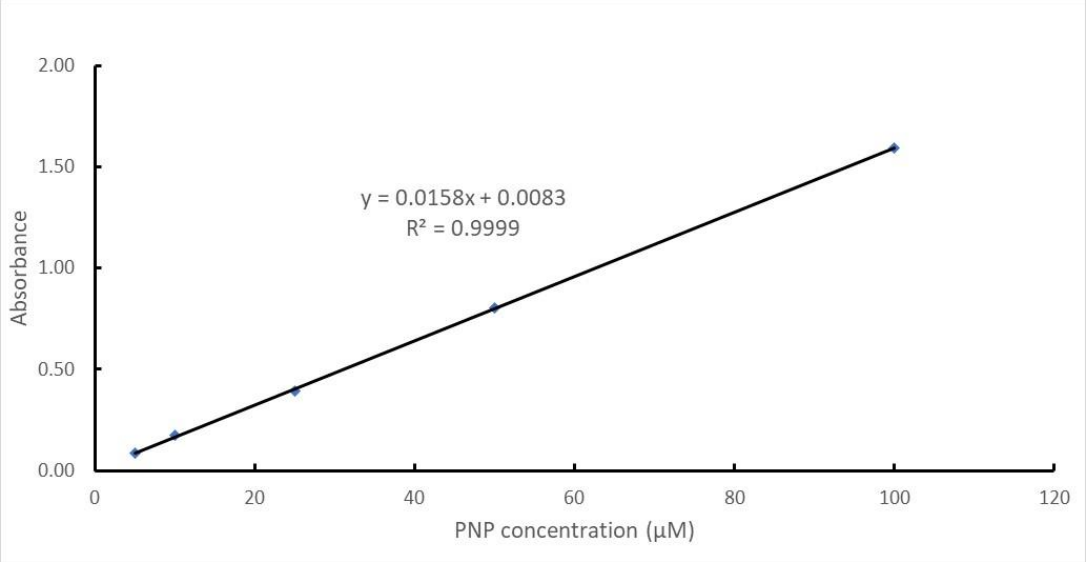

Fig. s5. Calibration curve of PNP.

7. FTIR

The FT-IR spectra were obtained on Spectra One spectrometer from a powder sample of 4000–400 cm^{-1} range.

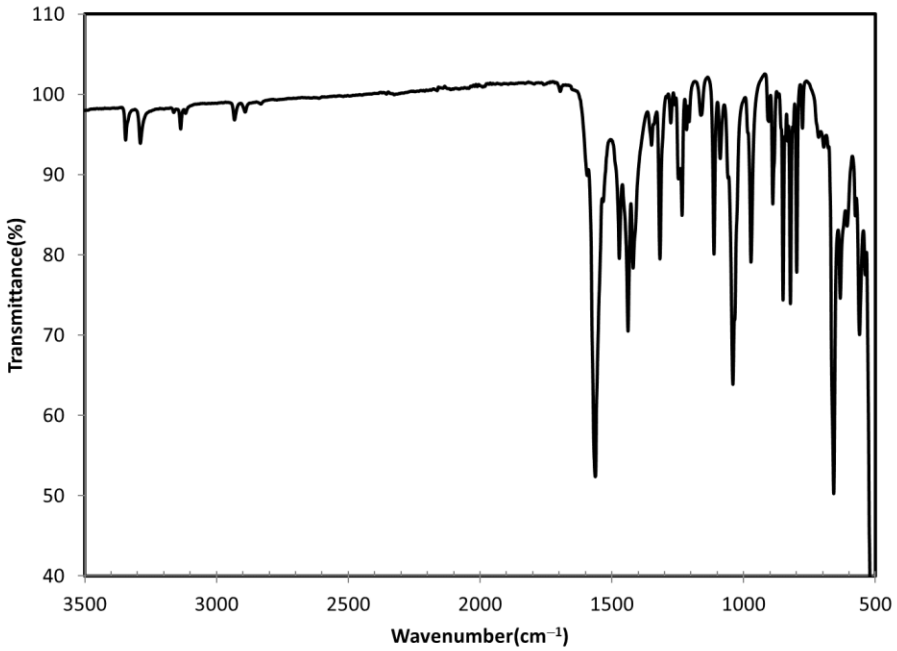

Fig s6, IR spectrum of compound [α-Cd(HIS)] (**1**)

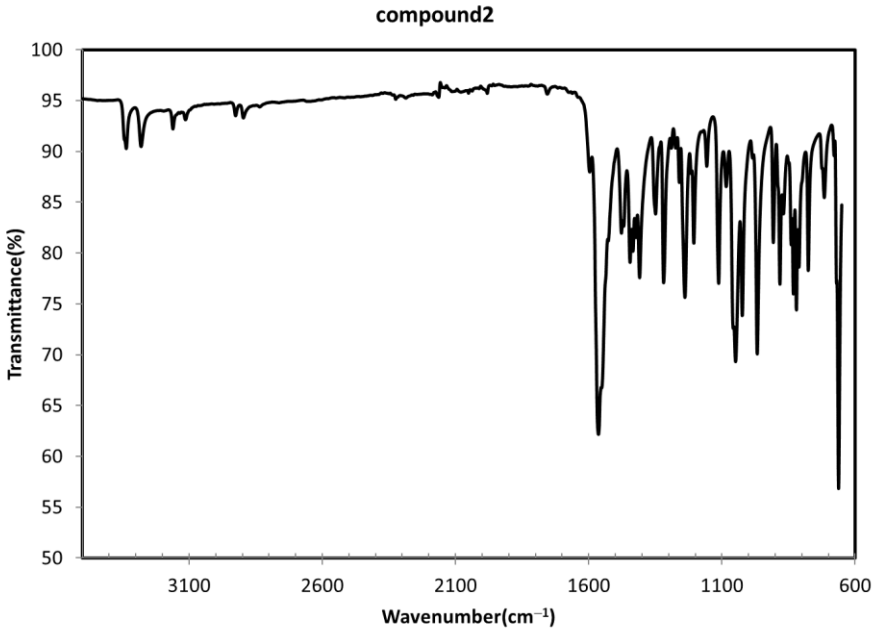

Fig s7, IR spectrum of [β-Cd(HIS)] **(2)**

8 Stability in buffer solution.

The stability of the catalyst in HEPES buffer (50 mM, pH 8.0) was evaluated. ~45 mg of the catalyst was added to 20.0 mL of HEPES buffer (50 mM, pH 8.0). The mixture was stirred at room temperature for 2 hours. Subsequently, the solids were separated by centrifugation, and dried at 120 °C for 12 hours for PXRD analysis.

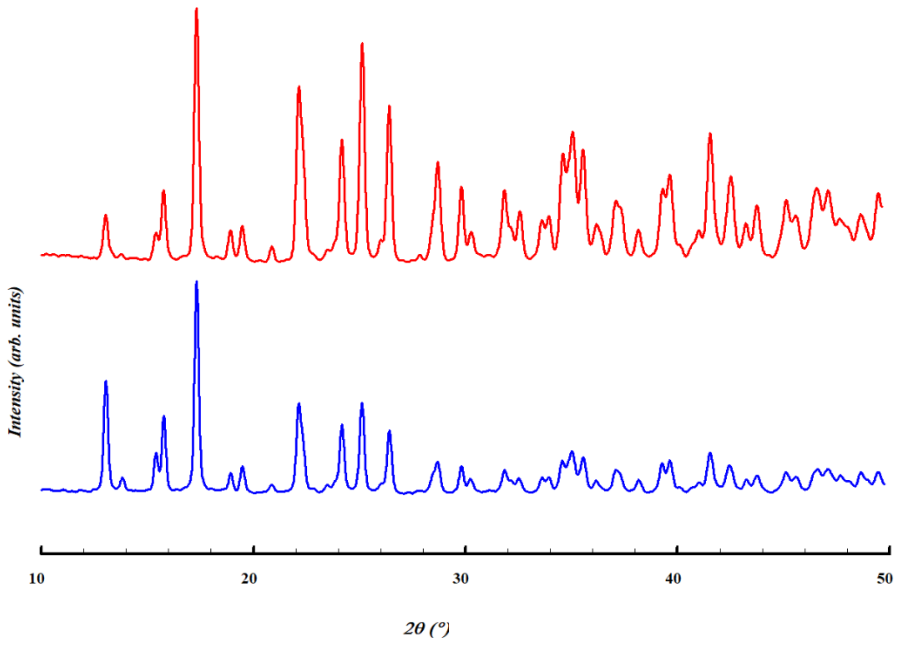

Fig. s8, Experimented PXRD of [α-Cd(HIS)] (**1**) before (bottom, blue) and after (top, red) stirred in buffer solution.

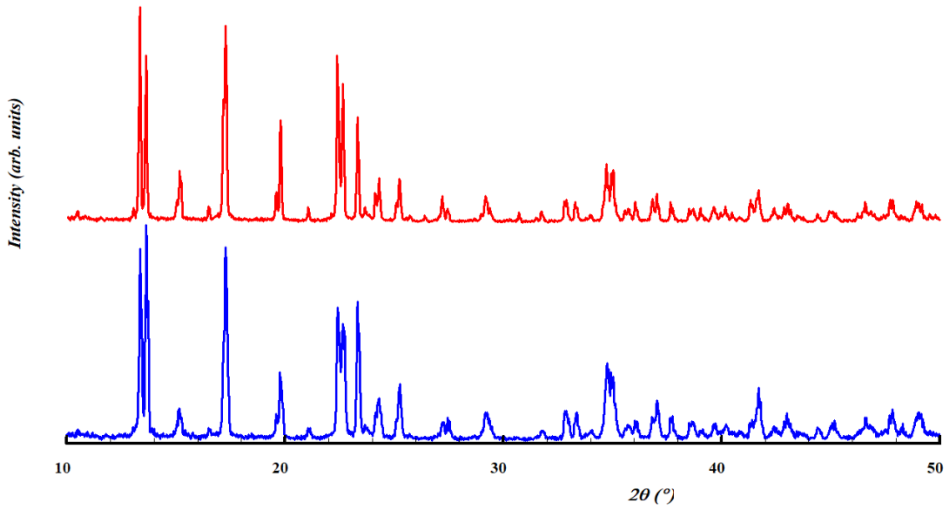

Fig. s9, Experimented PXRD of [β-Cd(HIS)] (**2**) before (bottom, blue) and after (top, red) stirred in buffer solution.

9. References

1. *SAINT Frame Integration Software;*, Bruker AXS Inc.: Madison, WI, 2000.

2. Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption (and other) Correction* Univ. of Göttinger, Göttinger, Germany, 1998.

3. *SHELXTL ver. 6.14, Reference Manual, Bruker Industrial Automation, Analytical Instrument,* , Madison, WI 53719, 2000.

4. Sheldrick, G., A short history of SHELX. *Acta Crystallographica Section A* **2008,** *64* (1), 112-122.

5. Wilson, A. J. C., *International Tables for Crystallography, Vol C*. Kluwer Academic Publishers: Holland, 1995.