

Supplementary Data

Crystal chemistry, optic and magnetic characterizations of a new copper based material templated by hexahydrodiazepine.

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Table S1: Crystal data and structure refinement for (DAP-H₂)[CuBr₄].

Empirical formula	(C ₅ H ₁₄ N ₂)[CuBr ₄]
Crystal color /shape	black/ prism
Formula weight (g mol ⁻¹)	485.36
Volume (Å ³)	1299.6(4)
ρ _{calc} (Mg m ⁻³)	2.481
Crystal system	monoclinic
Space group	C2/c
Z	4
a(Å)	11.658(19)
b(Å)	11.241(2)
c(Å)	10.419(17)

β (°)	107.883(6)
θ range for data collection (°)	2.6< θ <27.5
Temperature (k)	295
λ (Moka) (Å)	0.71073
Absorption correction	Multi-scan
Crystal size (mm ³)	0.41 * 0.25 * 0.14
h, k, l range	-15≤h≤15 -14≤k≤14 -13≤l≤13
Diffractometer	D8 VENTURE Bruker AXS
Programs systems	SHELXT-2015 and SHELXL-2018
No. of reflections collected	5613
No. of independent reflections	1495
No. of reflections observed (I > 2s(I))	1194
Rint	0.0714
F(000)	908
No. of parameters	49
Goodness of fit	1.048
Transmission factors	Tmax = 0.188, Tmin = 0.015
Rindices	R1=0.0544, wR2= 0.1496

Table S2: Selected bond distances (Å) and angles (°) for (C₅H₁₄N₂)[CuBr₄].

CuBr ₄ tetrahedron anion		C ₅ H ₁₄ N ₂ organic cation	
Cu-Br1	2.3697 (10)	C1—C7	1.512 (16)
Cu-Br2	2.4049 (11)	C3—C4	1.448 (19)
Br1—Cu1—Br2	99.55 (3)	C4—C5	1.482 (18)
Br1—Cu1—Br1 ⁱ	138.44 (8)	C1—N2	1.489 (12)
Br1—Cu1—Br2 ⁱ	99.34 (3)	C5—N6	1.473 (10)
Br1 ⁱ —Cu1—Br2	99.34 (3)	N2—C3	1.473 (10)
Br2 ⁱ —Cu1—Br2	124.87 (8)	N6—C7	1.490 (12)
		C3—C4—C5	121.7 (13)
		C4—C3—N2	120.0 (10)
		N6—C7—C1	115.2 (8)
		N2—C1—C7	115.1 (8)
		N6—C5—C4	117.0 (10)
		C3—N2—C1	119.1 (8)
		C5—N6—C7	119.1 (8)

Symmetry code: (i) $-x+1, y, -z+3/2$.

Table S3: Intermolecular hydrogen bonds parameters (Å, °) in (C₅H₁₄N₂)[CuBr₄].

D—H...A	D—H	H...A	D—A	D— \hat{H} —A
N2—H2A...Br1 ^{iv}	0.89	2.94	3.441 (9)	117.7
N2—H2A...Br2 ^{iv}	0.89	2.52	3.367 (9)	158.3
N2—H2B...Br1 ⁱ	0.89	2.98	3.637 (9)	132.3
N2—H2B...Br2	0.89	2.64	3.351 (9)	137.5
N6—H6A...Br1 ⁱⁱⁱ	0.89	2.94	3.441 (9)	117.7
N6—H6A...Br2 ⁱⁱⁱ	0.89	2.52	3.367 (9)	158.3
N6—H6B...Br1 ^v	0.89	2.98	3.637 (9)	132.2
N6—H6B...Br2 ^{vi}	0.89	2.64	3.351 (9)	137.5

Symmetry codes: (i) $-x+1, y, -z+3/2$; $y+1/2, z$, (iii) $-x+3/2, -y+3/2, -z+1$; (iv) $x+1/2, -y+3/2, z+1/2$; (v) $x+1, y, z$, (vi) $-x+2, y, -z+3/2$.

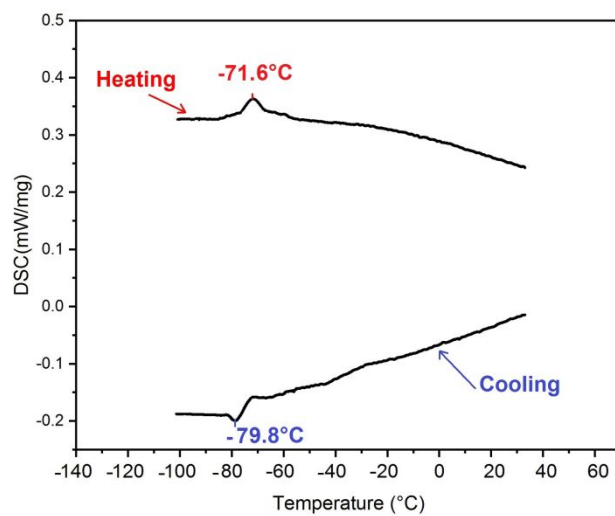


Figure S1: DSC curves of $(C_5H_{14}N_2)[CuBr_4]$ recorded at low temperature .

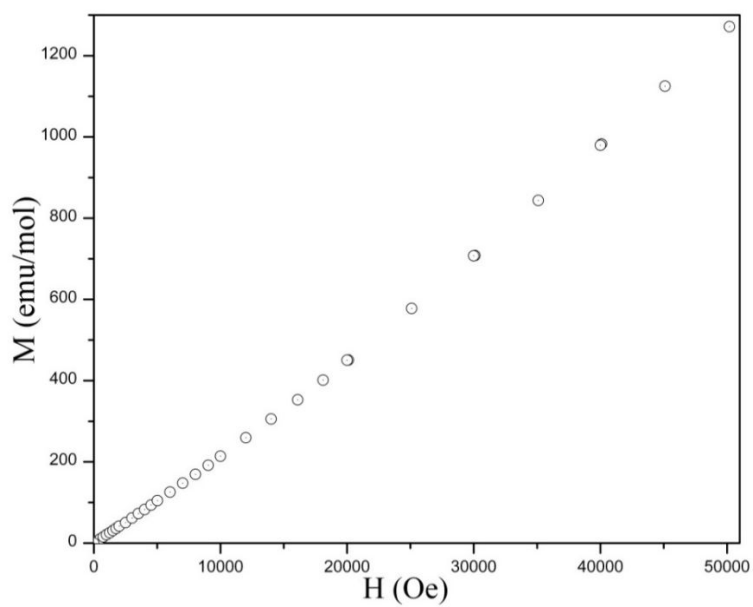


Figure S2 – M(H) for compound 1.

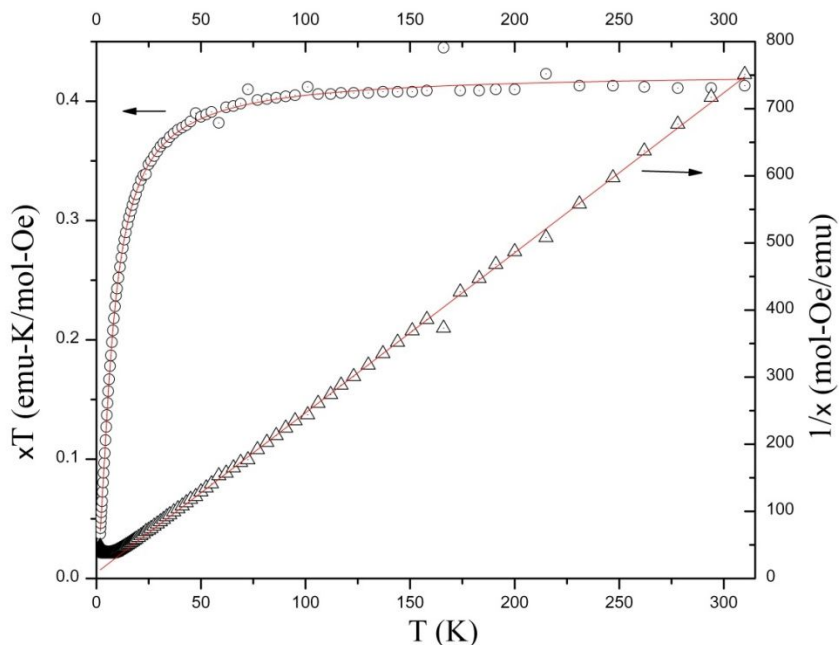


Figure S3 – $\chi T(T)$ (o) and $1/\chi(T)$ (Δ) for compound **1**. The solid lines are the best fit to the 1D-uniform chain model [$\chi T(T)$] (all data) or the Curie-Weiss law [$1/\chi(T)$] (35 -310 K).

Infrared Spectroscopy

Figure S1 represents the major selected absorptions in the IR spectra of the title compound with their respective assignments (Table S3). These attributions were made by comparison with the experimental results reported in a similar compounds $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$, $(C_5H_{14}N_2)[CuCl_4]$ and $(C_5H_{14}N_2)[CdCl_4]$.^{29,31,32} The broad band observed in the range 3250-2500 cm^{-1} is due to the overlap of broad peaks resulting from N-H stretching, of the NH_2 groups

involved in hydrogen bonds, with the CH stretching vibrations. The band around 1628 cm^{-1} is attributed to NH_2 scissoring vibrations and that at 1554 cm^{-1} can be assigned to $\delta_{\text{as}}(\text{C-N-H})$ asymmetric bending. The bands which appear at approximately 1465 and 1450 cm^{-1} result from the scissoring vibration $\delta(\text{CH}_2)$. The bands situated at 1280 and 1223 cm^{-1} , they are assigned to the C-N stretching. Concerning the vibrational band at 1065 cm^{-1} is associated to C-C stretching. The rocking vibration $\rho(\text{NH}_2)$ is located at 915 cm^{-1} . The frequencies at 804 and 756 cm^{-1} can be related to the $\delta(\text{C-C-C})$ ring bending vibrations. Finally, the bands located at 700 and 635 cm^{-1} correspond to $\delta(\text{C-C-N})$ deformation vibrations and the $\delta(\text{C-N-C})$ scissoring mode is observed at 525 cm^{-1} .

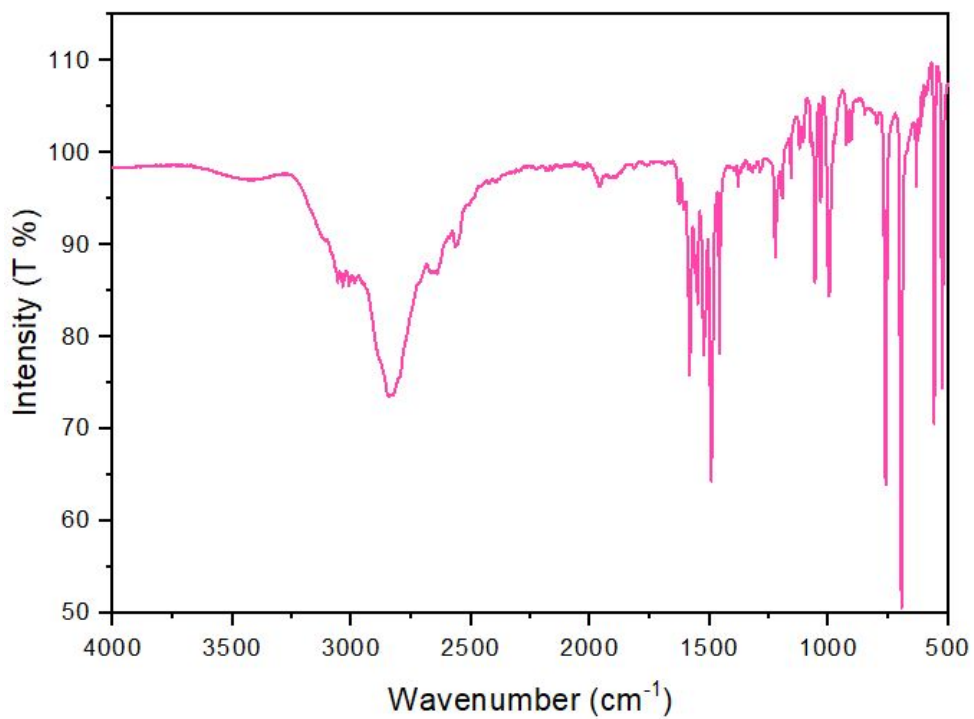


Figure S4: Infrared absorption spectra of $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{CuBr}_4]$.

Table S4: IR bands assignment of $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{CuBr}_4]$.

observed	Assignment
3250-2500	$\nu_{\text{as}}(\text{N-H}), \nu_{\text{a}}(\text{C-H})$
2643	$\nu_{\text{a}}(\text{C-H})$
1628	$\delta(\text{NH}_2)$
1554	$\delta_{\text{as}}(\text{C-N-H})$
1465	$\delta(\text{CH}_2)$

1450	$\delta(\text{CH}_2)$
1280	$\nu_{\text{as}}(\text{C-N})$
1223	$\nu_{\text{as}}(\text{C-N})$
1065	$\nu_{\text{as}}(\text{C-C})$
915	$\rho(\text{NH}_2)$
804	$\delta(\text{C-C-C})$
756	$\delta(\text{C-C-C})$
700	$\delta(\text{C-C-N})$
635	$\delta(\text{C-C-N})$
525	$\delta(\text{C-N-C})$

Abbreviations: ν - stretching; δ - bending; ρ - rocking; s: Symmetric; as: Asymmetric.

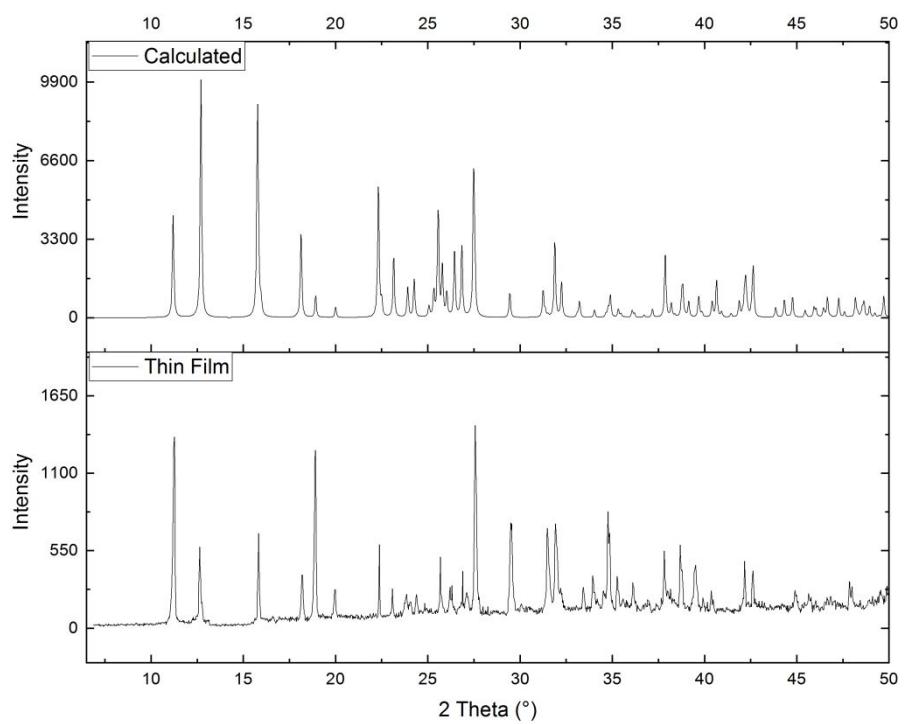


Figure S5: X-ray diffraction patterns of $(C_5H_{14}N_2)[CuBr_4]$.