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Trinuclear Copper(II) Bromide Complex $[C_3H_5N_3Br]_{2n}[Cu_3Br_8]_n$. Structure, Magnetic Properties and DFT calculations.

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Table S1. Crystal data and structure refinement for $[HL]_{2n}[Cu_3Br_8]_n$

Empirical formula	$C_6H_{10}Br_{10}Cu_3N_6$
Formula weight	1155.92
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	3.9511(3)
b/Å	12.1653(10)
c/Å	12.6022(10)
α/°	67.660(3)
β/°	89.706(4)
γ/°	86.172(4)
Volume/Å^3	558.89(8)
Z	1
ρ_{calc}g/cm^3	3.434
μ/mm^{-1}	20.708
F(000)	525.0
Crystal size/mm^3	0.467 × 0.139 × 0.107
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.628 to 59.28
Index ranges	$-5 \le h \le 5$, $-16 \le k \le 16$, $-17 \le l \le 11$
Reflections collected	6108
Independent reflections	3148 [R_{int} = 0.0439, R_{sigma} = 0.0689]
Data/restraints/parameters	3148/0/115
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.1054
Final R indexes [all data]	R_1 = 0.0523, wR_2 = 0.1108
Largest diff. peak/hole / e Å^{-3}	1.29/-1.76

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for [HL]2n[Cu3Br8]n. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Br3A	3728.5(13)	10511.3(5)	6216.2(4)	9.87(13)
Br4A	582.2(13)	7977.3(5)	6416.1(4)	11.37(13)
Br2A	4384.5(13)	6501.1(5)	9087.6(4)	12.15(14)
Br1A	7860.0(13)	9168.4(5)	8829.3(4)	13.01(14)
Br1C	8072.0(15)	3405.9(6)	5703.0(5)	19.10(15)
Cu2	0	10000	5000	11.7(2)
Cu1	3894.5(16)	8531.8(6)	7778.6(5)	11.53(16)
N2	10942(13)	3643(5)	8645(4)	19.8(11)
N1	9320(14)	4745(5)	8125(4)	23.7(12)
C2	9028(13)	3813(5)	6955(4)	11.8(11)
C1	10772(14)	3035(5)	7955(4)	13.2(11)
N3	12232(14)	1941(5)	8199(4)	24.2(13)
C3	8169(15)	4845(6)	7105(5)	20.3(13)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for $[HL]_{2n}[Cu_3Br_8]_n$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br3A	12.5(2)	9.0(3)	7.1(2)	-2.0(2)	-1.26(18)	-0.4(2)
Br4A	15.2(3)	8.9(3)	8.2(2)	-1.3(2)	-2.29(19)	-0.9(2)
Br2A	14.1(3)	9.4(3)	9.8(2)	-0.5(2)	-1.25(19)	1.2(2)
Br1A	14.9(3)	14.3(3)	9.3(2)	-4.0(2)	-2.14(19)	-0.6(2)
Br1C	25.4(3)	19.5(3)	13.5(3)	-7.6(2)	-5.6(2)	-0.3(2)
Cu2	15.7(5)	9.3(5)	7.7(4)	-0.5(4)	-3.8(3)	-1.5(4)
Cu1	14.7(3)	9.7(4)	7.9(3)	-0.9(3)	-3.6(2)	-0.4(3)
N2	25(3)	25(3)	11(2)	-9(2)	-1.3(19)	2(2)
N1	35(3)	20(3)	22(3)	-16(2)	-3(2)	4(2)
C2	12(2)	17(3)	7(2)	-5(2)	2.8(18)	-5(2)
C1	18(3)	10(3)	10(2)	-2(2)	2(2)	-1(2)
N3	44(3)	18(3)	10(2)	-7(2)	-3(2)	7(3)
C3	25(3)	22(4)	14(3)	-7(3)	1(2)	-1(3)

Table S4. Bond Lengths for $[HL]_{2n}[Cu_3Br_8]_n$

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Br3A	Cu2	2.4035(5)		Cu2	Br4A[1]	2.4255(6)
Br3A	Cu1	2.4609(9)		N2	N1	1.363(7)
Br4A	Cu2	2.4255(6)		N2	C1	1.343(7)
Br4A	Cu1	2.4774(8)		N1	C3	1.324(7)
Br2A	Cu1	2.3881(9)		C2	C1	1.405(7)
Br1A	Cu1	2.4023(9)		C2	C3	1.360(8)
Br1C	C2	1.871(5)		C1	N3	1.337(7)
Cu2	Br3A[1]	2.4035(5)				

[1]-X,2-Y,1-Z

Table S5. Bond Angles for $[HL]_{2n}[Cu_3Br_8]_n$

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cu2	Br3A	Cu1	94.46(3)		Br1A	Cu1	Br3A	89.81(3)
Cu2	Br4A	Cu1	93.50(3)		Br1A	Cu1	Br4A	169.54(4)
Br3A	Cu2	Br3A[1]	180.0		C1	N2	N1	109.5(5)
Br3A	Cu2	Br4A[1]	93.095(19)		C3	N1	N2	108.4(5)
Br3A[1]	Cu2	Br4A[1]	86.906(19)		C1	C2	Br1C	123.6(4)
Br3A	Cu2	Br4A	86.905(19)		C3	C2	Br1C	128.9(4)
Br3A[1]	Cu2	Br4A	93.095(19)		C3	C2	C1	107.4(5)
Br4A[1]	Cu2	Br4A	180.0		N2	C1	C2	105.9(5)
Br3A	Cu1	Br4A	84.53(3)		N3	C1	N2	124.1(5)
Br2A	Cu1	Br3A	171.45(4)		N3	C1	C2	129.9(5)
Br2A	Cu1	Br4A	90.35(3)		N1	C3	C2	108.8(6)
Br2A	Cu1	Br1A	94.17(3)					

[1]-X,2-Y,1-Z

Table S6. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for [HL]2n[Cu3Br8]n

Atom	*x*	*y*	*z*	U(eq)
H2	11945	3372	9326	24
H1	9079	5296	8418	28
H3A	13393	1575	8847	29
H3B	12032	1586	7713	29
H3	6945	5526	6567	24

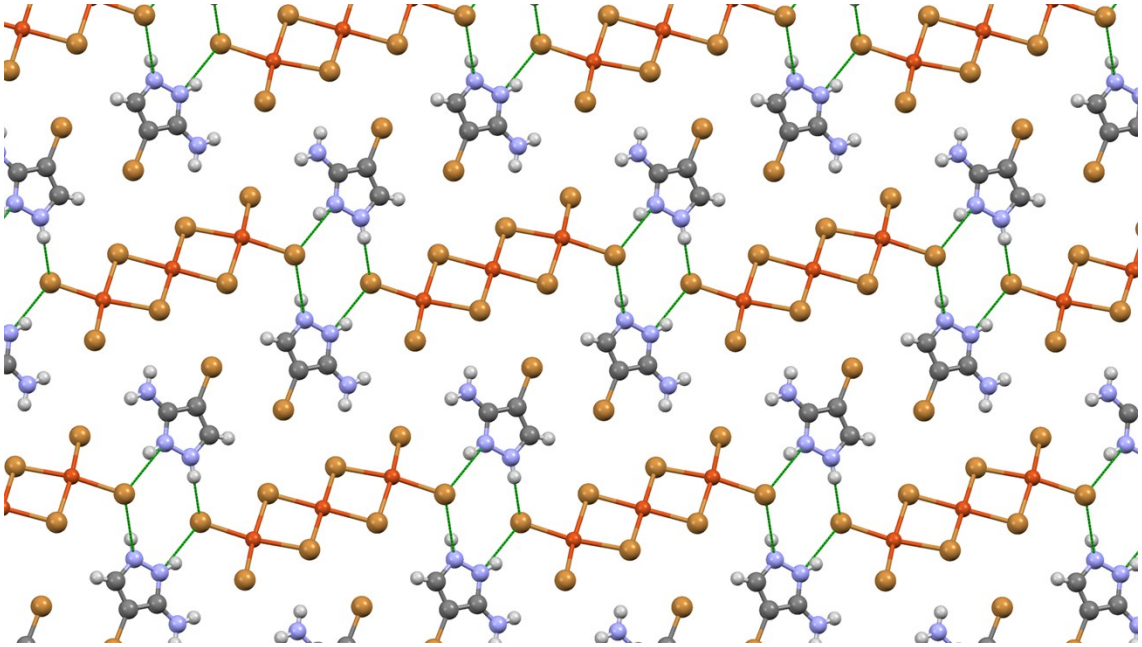

Fig. S1. Crystal structure of the $[HL^a]_{2n}[Cu_3Br_8]_n$ compound. Green dashed lines indicate the H-bonds

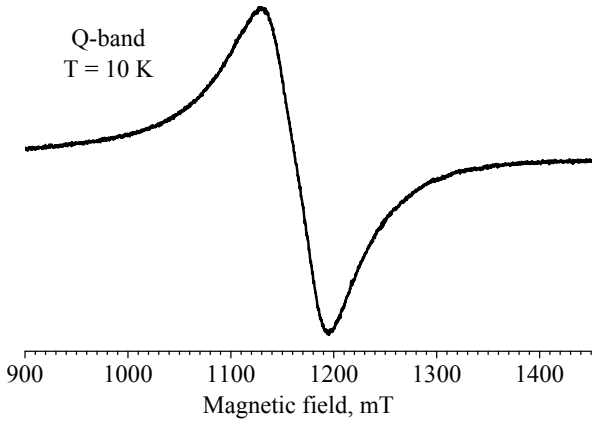

Fig. S2. The Q-band EPR powder spectrum of the $[HL]_{2n}[Cu_3Br_8]_n$ measured at 10 K. The microwave power of 0.2 mW and modulation amplitude of 0.25 mT were applied. The EPR spectrum was recorded with a Bruker Elexsys E580 spectrometer

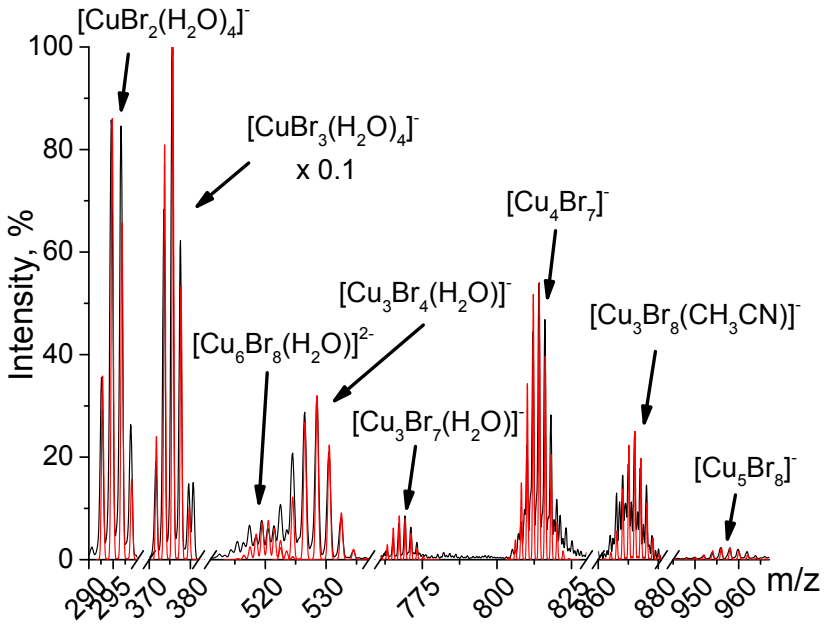

Fig. S3. Negative ion mode ESI MS of the $[HL]_{2n}[Cu_3Br_8]_n$ in water/acetonitrile solution. The simulated isotopic patterns of the species are shown

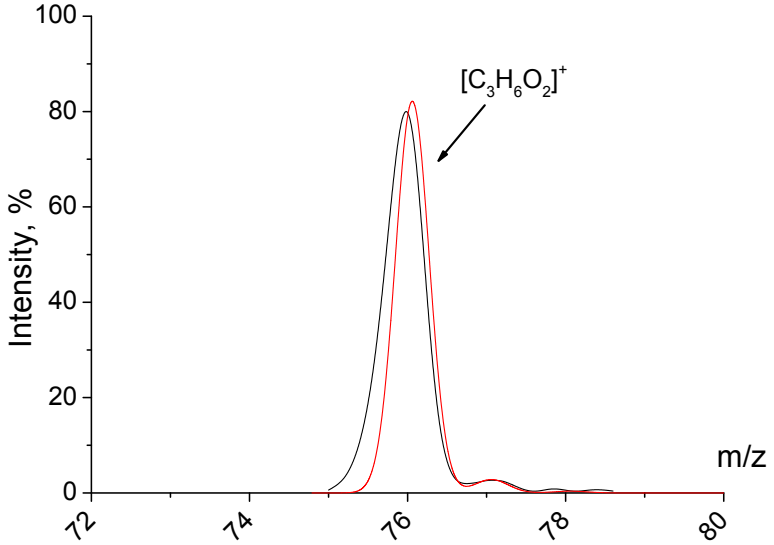

Fig. S4. Positive ion mode ESI MS of the $[HL]_{2n}[Cu_3Br_8]_n$ initial growth solution diluted with water/acetonitrile mixture. The simulated isotopic pattern of the $[C_3H_6O_2]^+$ are shown

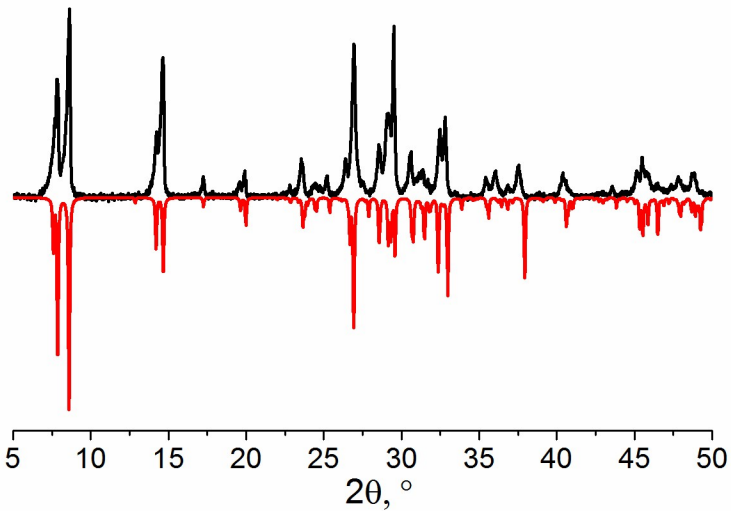

Fig. S5. Powder XRD pattern of the $[HL]_{2n}[Cu_3Br_8]_n$: experimental (black) and simulated from single crystal structure data (red). The single-crystal and powder XRD data were collected at 150 K and 300 K respectively that could explain the dissimilarities in peak positions observed.

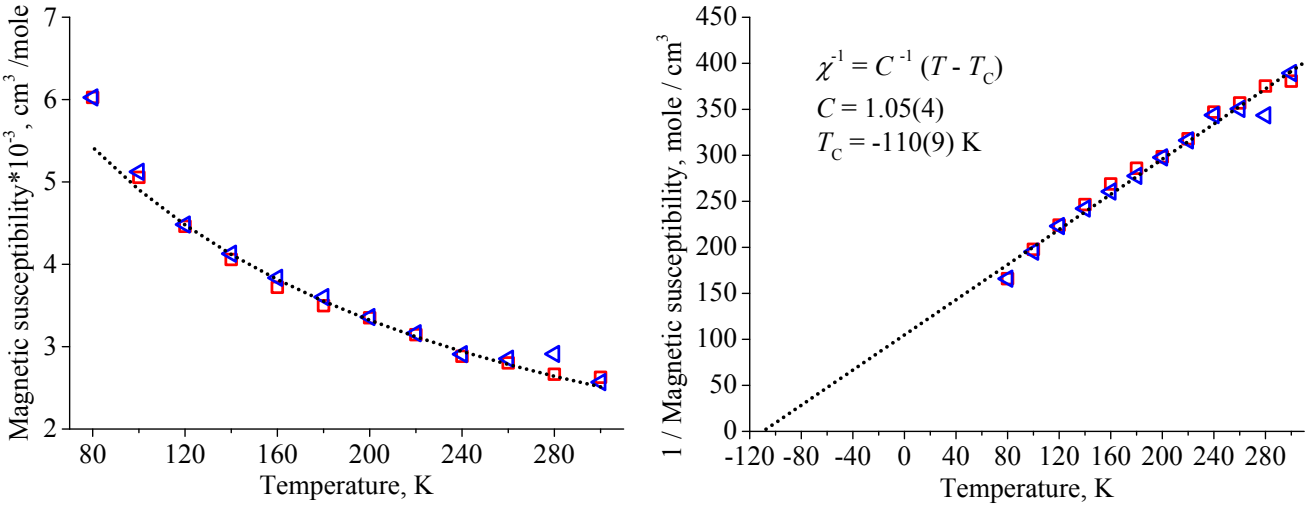

Fig. S6. Measured χ and χ^{-1} vs T for the $[HL]_{2n}[Cu_3Br_8]_n$ compound. The data are fitted with the Curie–Weiss law (Curie temperature T_C = -110(9) K, Curie constant C = 1.05(4)).