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Supplementary Material

A Cu_{12} Metallacycle Assembled from Four C_3-Symmetric Spin Frustrated Triangular Units

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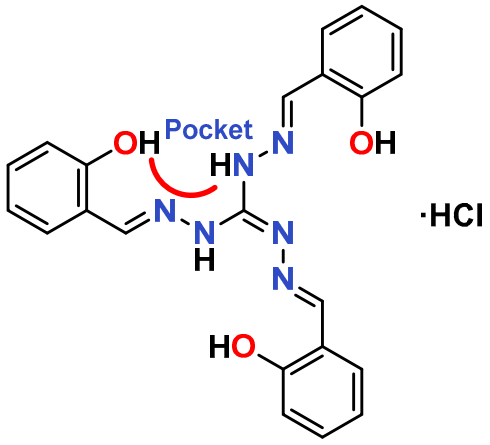
S1. Crystallographic data & structure of ligand $H_5L{\cdot}HCl$

Table S1. Crystal data and structure refinement parameters for **Cu12**.

Compound	Cu12
Empirical formula	$C_{168}H_{140}Cu_{12}N_{52}O_{12}$
Formula weight	3841.79
Temperature [K]	120.0
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	15.683(3)
b [Å]	16.188(3)
c [Å]	19.864(3)
α [°]	102.157(5)
β [°]	92.572(6)
γ [°]	117.967(5)
Volume [Å^3]	4293.4(13)
Z	1
ρ_{calc} [gcm^{-3}]	1.486
μ [mm^{-1}]	1.528
$F(000)$	1956
Radiation	MoK_α (λ = 0.71073 Å)
Reflections collected	54021
Independent reflections	14660; R_{int} = 0.1212, R_{sigma} = 0.1126
Data / Restraints / Parameters	14660/238/1075
Goodness-of-fit on F^2	1.042
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.1299, wR_2 = 0.3834
Final R indexes [all data]	R_1 = 0.1685, wR_2 = 0.4134
CCDC number	2248078



Scheme S1. Structure of the ligand [H_6L]Cl with three coordination pockets.

S2. Molecular structures

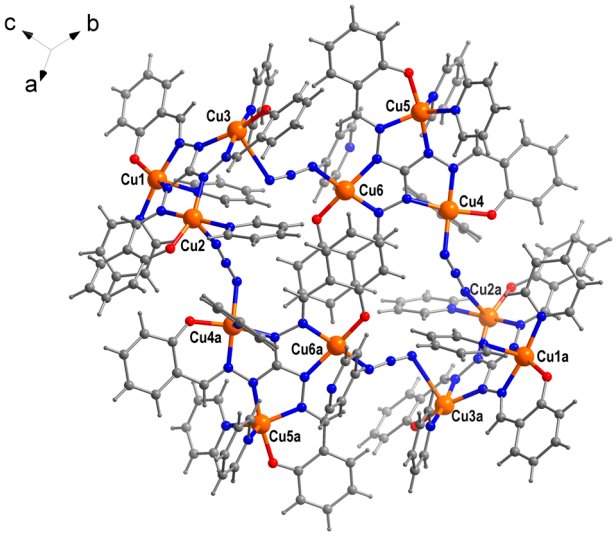


Figure S1. The molecular structure of **Cu**$_{12}$, hydrogen atoms and two free pyridine molecules have been omitted for clarity. Color code: orange, Fe; red, O; blue, N; grey, C and light grey, H.

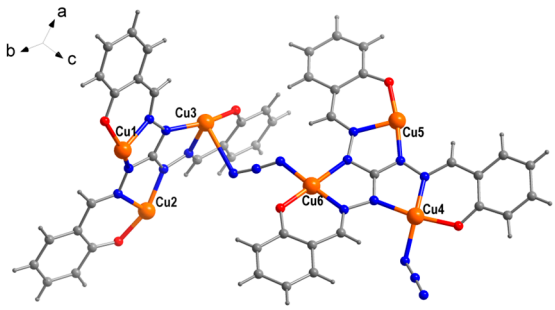


Figure S2. The asymmetric unit of **Cu**$_{12}$ in giving direction, the coordinated and free pyridine molecules have been omitted for clarity. Color code: orange, Fe; red, O; blue, N; grey, C and light grey, H.

S3. Structural details of Cu_{12}

Table S2. Selected bond lengths (Å) and angles (°) for **Cu_{12}**.

Cu_1-O_2	1.918(10)	Cu_3-O_3	1.915(10)	Cu_5-O_5	1.887(12)
Cu_1-N_5	1.994(12)	Cu_3-N_2	1.978(12)	Cu_5-N_{11}	1.946(14)
Cu_1-N_6	1.976(12)	Cu_3-N_4	1.946(13)	Cu_5-N_{15}	1.982(13)
Cu_1-N_7	1.993(13)	Cu_3-N_{12}	2.003(14)	Cu_5-N_{25}	2.240(12)
Cu_1-N_{14}	2.342(14)	Cu_4-O_4	1.935(11)	Cu_5-N_{26}	2.097(9)
Cu_2-O_1	1.918(11)	Cu_4-N_9	2.245(14)	Cu_6-N_{13}	1.937(13)
Cu_2-N_1	1.931(11)	Cu_4-N_{16}	1.987(13)	Cu_6-O_6	1.914(12)
Cu_2-N_3	1.989(12)	Cu_4-N_{17}	1.930(15)	Cu_6-N_{18}	2.015(14)
Cu_2-N_8	1.996(12)	Cu_4-N_{20}	2.016(15)	Cu_6-N_{23}	1.977(16)
O_2-Cu_1-N_6	92.7(5)	O_3-Cu_3-N_4	93.2(5)	O_5-Cu_5-N_{15}	93.9(5)
O_2-Cu_1-N_7	151.9(5)	O_3-Cu_3-N_{12}	89.9(5)	O_5-Cu_5-N_{25}	90.0(6)
O_2-Cu_1-N_{14}	96.7(5)	N_2-Cu_3-N_{12}	99.4(5)	O_5-Cu_5-N_{26}	91.0(5)
N_5-Cu_1-N_{14}	88.3(5)	N_4-Cu_3-N_2	79.9(5)	N_{11}-Cu_5-N_{15}	79.7(5)
N_6-Cu_1-N_5	171.7(5)	N_4-Cu_3-N_{12}	171.0(5)	N_{11}-Cu_5-N_{25}	91.0(6)
N_6-Cu_1-N_7	79.2(5)	O_4-Cu_4-N_9	91.2(5)	N_{11}-Cu_5-N_{26}	94.5(5)
N_6-Cu_1-N_{14}	86.4(5)	O_4-Cu_4-N_{16}	169.0(5)	N_{15}-Cu_5-N_{25}	113.1(6)
N_7-Cu_1-N_5	96.6(5)	O_4-Cu_4-N_{20}	90.6(5)	N_{15}-Cu_5-N_{26}	132.2(6)
N_7-Cu_1-N_{14}	109.4(5)	N_{16}-Cu_4-N_9	94.8(5)	N_{26}-Cu_5-N_{25}	114.5(5)
O_1-Cu_2-N_1	92.4(5)	N_{16}-Cu_4-N_{20}	97.7(6)	N_{13}-Cu_6-N_{18}	80.5(5)
O_1-Cu_2-N_3	156.4(5)	N_{17}-Cu_4-O_4	90.8(5)	N_{13}-Cu_6-N_{23}	175.9(7)
O_1-Cu_2-N_8	93.2(5)	N_{17}-Cu_4-N_9	103.5(6)	O_6-Cu_6-N_{13}	93.1(6)
N_1-Cu_2-N_3	79.9(5)	N_{17}-Cu_4-N_{16}	78.9(6)	O_6-Cu_6-N_{18}	166.6(6)
N_1-Cu_2-N_8	170.5(5)	N_{17}-Cu_4-N_{20}	158.1(6)	O_6-Cu_6-N_{23}	90.4(6)
N_3-Cu_2-N_8	97.8(5)	N_{20}-Cu_4-N_9	98.3(6)	N_{23}-Cu_6-N_{18}	96.4(6)
O_3-Cu_3-N_2	162.7(5)	O_5-Cu_5-N_{11}	173.4(5)		

S4. Coordination geometry

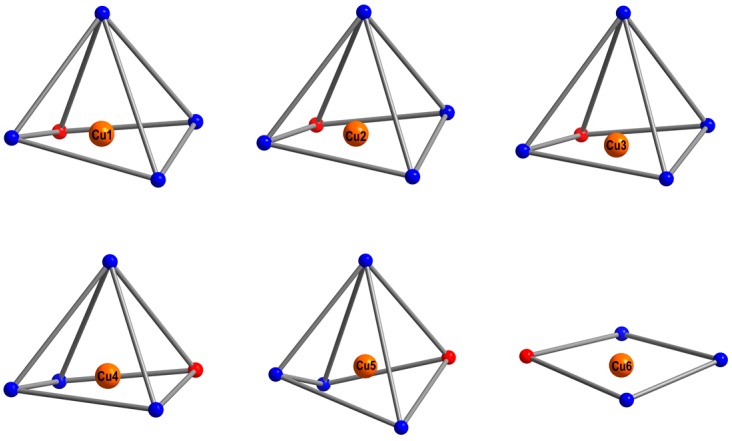


Figure S3. Representation of copper environment geometries for **Cu_{12}**.

Table S3. Calculated geometries of **Cu12** by *SHAPE* 2.1 software[1].

Cu center	Pentagon (D_{5h})	Vacant octahedron (C_{4v})	Trigonal bipyramid (D_{3h})	Spherical square pyramid (C_{4v})	Johnson trigonal bipyramid J12 (D_{3h})
Cu1	31.543	3.143	2.252	2.491	5.457
Cu2	32.501	3.180	2.599	2.411	6.305
Cu3	33.698	3.355	3.575	2.365	7.466
Cu4	31.406	1.853	3.751	1.092	6.894
Cu5	34.450	5.718	0.865	3.647	5.267
Cu center	Square (D_{4h})	Tetrahedron (T_d)	Seesaw (C_{2v})		
Cu6	0.727	27.843	14.856		

S5. Magnetic susceptibility measurement

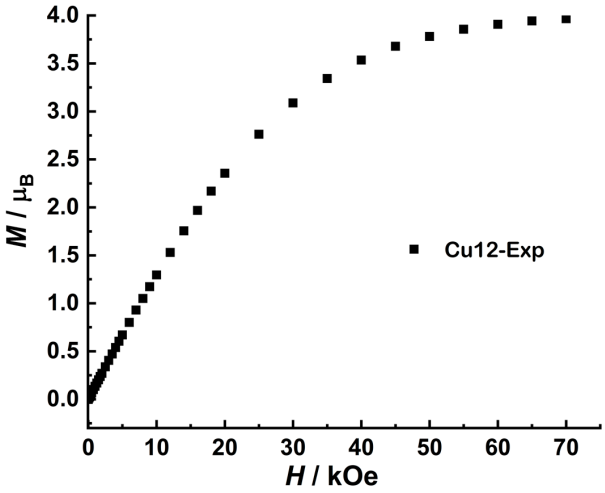


Figure S4. Magnetization curve for **Cu12** at 2 K.

S6. Theoretical calculations

Table S4. Principal magnetic coupling constants (J in cm^{-1}) for **Cu12** calculated at the DFT level with the B3LYP, B3LYP* and PBE0 functionals. The atom labels correspond to those used in **Figure 1**.

	B3LYP	PBE0	B3LYP*
Cu_1-Cu_2 J_{intra}	−330	−275	−403
Cu_1-Cu_3 J_{intra}	−305	−256	−371
Cu_2-Cu_3 J_{intra}	−337	−282	−412
Cu_4-Cu_5 J_{intra}	−236	−200	−286
Cu_4-Cu_6 J_{intra}	−389	−320	−485
Cu_5-Cu_6 J_{intra}	−205	−170	−250
Cu_2-Cu_{4a} J_{azido}	+3	+3	+3
Cu_3-Cu_6 J_{azido}	+7	+6	+8

Table S5. Calculated energy gap ΔE_{ES1-GS} (cm^{-1}) between the first excited state (ES1) and the ground state (GS), and the electronic *g*-factors for the ground state of the different metal centers in **Cu12**.

	ΔE_{ES1-GS}	g_x	g_y	g_z
Cu1	11895	2.07	2.10	2.39
Cu2	13195	2.07	2.09	2.37
Cu3	13738	2.08	2.08	2.37
Cu4	12202	2.06	2.10	2.39
Cu5	11981	2.36	2.21	2.01
Cu6	13914	2.07	2.08	2.38
Cu7	11895	2.06	2.11	2.39
Cu8	13195	2.06	2.10	2.37
Cu9	13737	2.07	2.09	2.37
Cu10	13910	2.07	2.08	2.37
Cu11	11982	2.36	2.21	2.01
Cu12	12202	2.07	2.10	2.39

Table S6. Relative energy (in cm^{-1}) of the 20 lowest states of the spin Hamiltonian used in this work.

		J_{azido} (J_{intra} = −250 cm^{-1})			
States	B3LYP	0 cm^{-1}	−2 cm^{-1}	−5 cm^{-1}	−15 cm^{-1}
1	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.7806	0.0004	0.4353	0.6063	1.4873
3	0.7923	0.0004	0.9632	2.3698	6.8771
4	0.7970	0.0008	0.9645	2.3713	6.8826
5	1.5166	0.0014	0.9658	2.3730	6.8852
6	1.5182	0.0018	1.0798	2.5398	7.4928
7	1.5212	0.0020	1.0805	2.5408	7.4977
8	2.2897	0.0021	1.0815	2.5443	7.5062
9	2.2924	0.0031	1.1809	2.6920	7.6633
10	2.2969	0.0044	1.1930	2.6933	7.6700
11	2.3083	0.0045	1.1933	2.6973	7.6778
12	2.3086	0.0051	1.1960	2.9665	8.9167
13	2.4105	0.0054	1.3782	3.3076	9.8370
14	2.4136	0.0060	1.3786	3.3719	9.9414
15	2.4151	0.0065	1.3809	3.3722	10.0169
16	2.4246	0.0093	1.3864	3.3762	10.0194
17	29.2526	0.1801	1.4773	3.4374	10.0225
18	29.2541	0.1801	1.4789	3.4877	10.2403
19	29.2543	0.1802	1.4818	3.4910	10.2514
20	29.2585	0.1803	1.5506	3.4923	10.2579

References

1. D. Casanova, M. Llunell, P. Alemany and S. Alvarez, Chem. Eur. J., 2005, 11, 1479-1494.