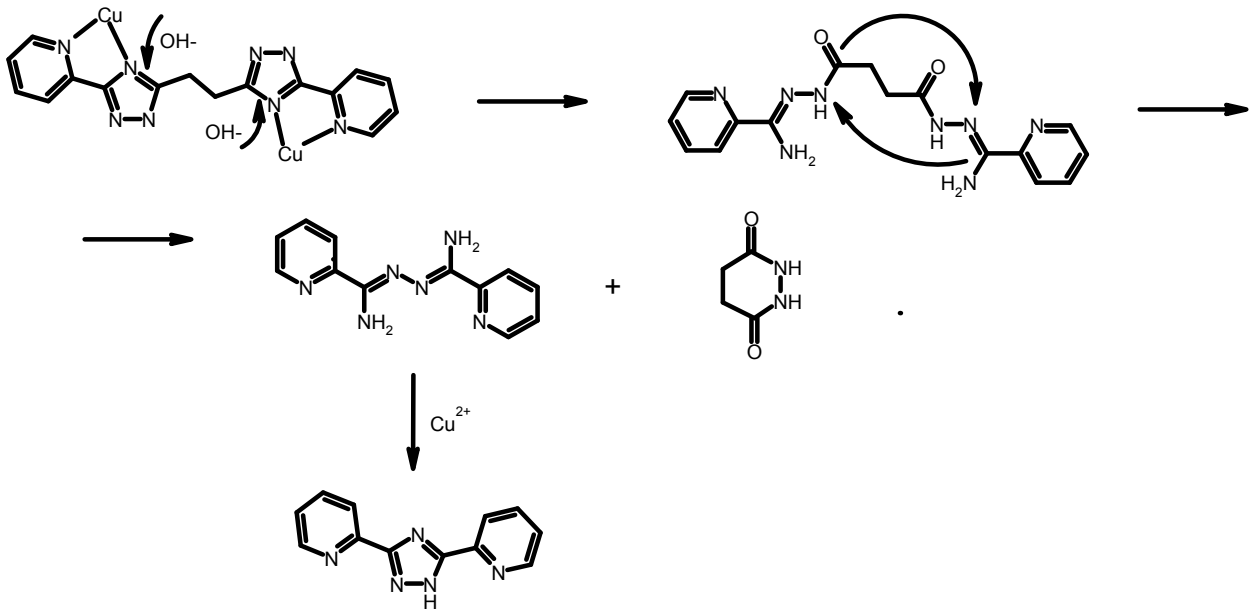
Supplementary Information

Copper(II)) self-assembled clusters of bis((pyridin-2-yl)-1,2,4-triazol-3-yl)alkanes. Unusual rearrangement of ligand upon reaction condition.

Table S1. Crystal data and structure refinements for **1-4**.

Parameter/Complex	**1**	**2**	**3**	**4***
Molecular formula	$[Cu_2(H_2L1)Cl_2]Cl_2 \cdot 6.5$ MeOH	$[Cu_4L1_4] \cdot 6H_2O \cdot 2.8$ MeOH	$[Cu(H_2L2)(ClO_4)_2]$	$[Cu_3(OH)Na_2(L')_6] \cdot (ClO_4)$ $11H_2O$
Formula	$C_{36.5}H_{50}Cl_4Cu_2N_{16}O_{6.5}$	$C_{62.8}H_{57.6}Cu_4N_{32}O_{8.8}$	$C_{16}H_{14}Cl_2CuN_4O_8$	$C_{72}H_{70}ClCu_3N_{30}Na_2O_{16}$
Crystal system	Monoclinic	Tetragonal	Monoclinic	Triclinic
Space group	*C2/c*	$I\bar{4}$	*C2/c*	$P\bar{1}$
a, Å *b*, Å *c*, Å	19.725(3) 18.998(3) 12.833(2)	13.1705(9) 13.1705(9) 19.6437(14)	13.0990(11) 11.6970(7) 14.5274(12)	15.506(3) 16.160(3) 20.311(4)
α ° β° γ°	90 95.971(5) 90	90 90 90	90.0 112.745(10) 90.0	86.840(3) 89.884(3) 61.689(3)
V, Å ^{3} Z	4783.0(14) 4	3407.4(5) 2	2052.8(3) 4	4472.5(16) 2
μ_{Mo}. mm^{-1}	1.175	1.314	1.392	0.824
Parameters	328	254	159	1124
No. unique	5761	4536	1819	14633
No. I > 2σ(I)	4107	3931	1595	4410
GOF	1.017	1.058	1.084	0.713
R(I > 2σ(I))	0.0531	0.0371	0.0250	0.0658
wR_2	0.1544	0.0939	0.0695	0.1459

* the formula does not include masked solvent



Scheme S1. Proposed mechanism for the rearrangement of the ligand H_2L2 to afford the 3,5-bis-(pyridin-2-yl)-1,2,4-triazole

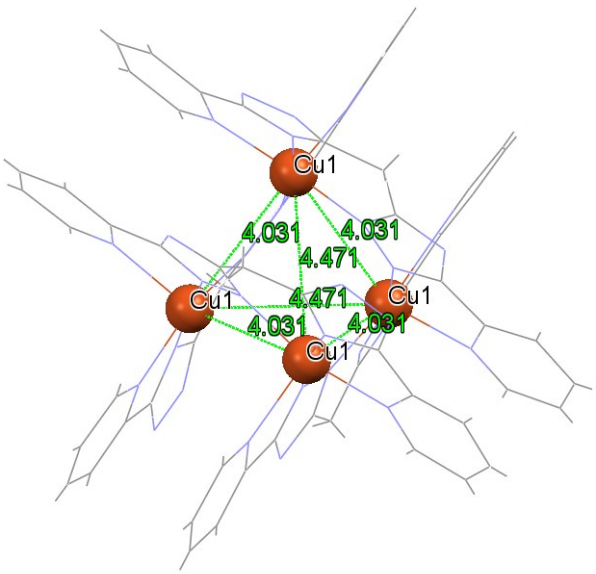


Figure.S1. Copper-copper distances in tetranuclear core of complex **2**.

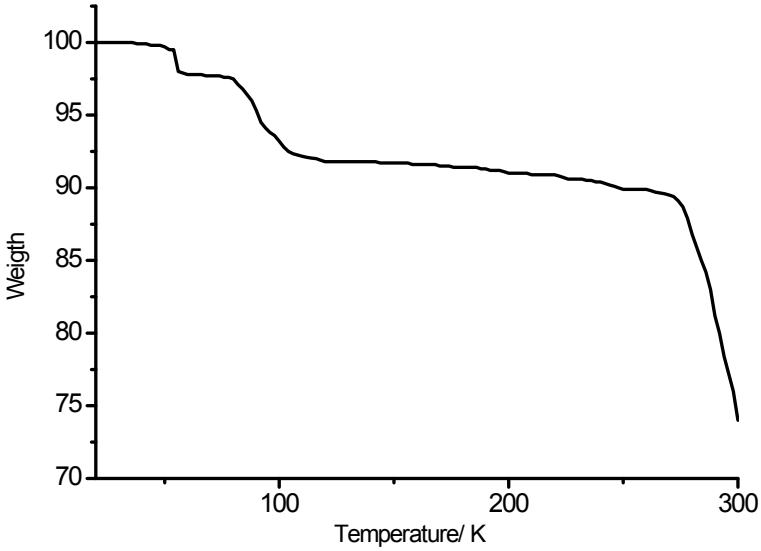


Figure S2. TG curve of **4**.

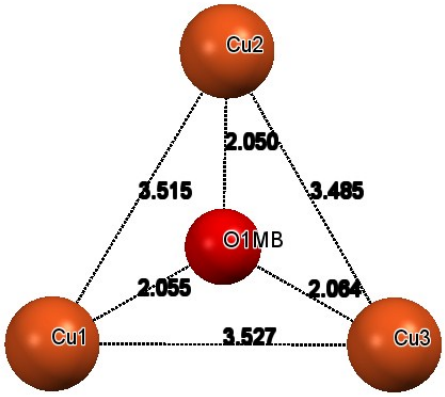


Figure S3. Structure of trinuclear Cu_3OH core in complex **4**.

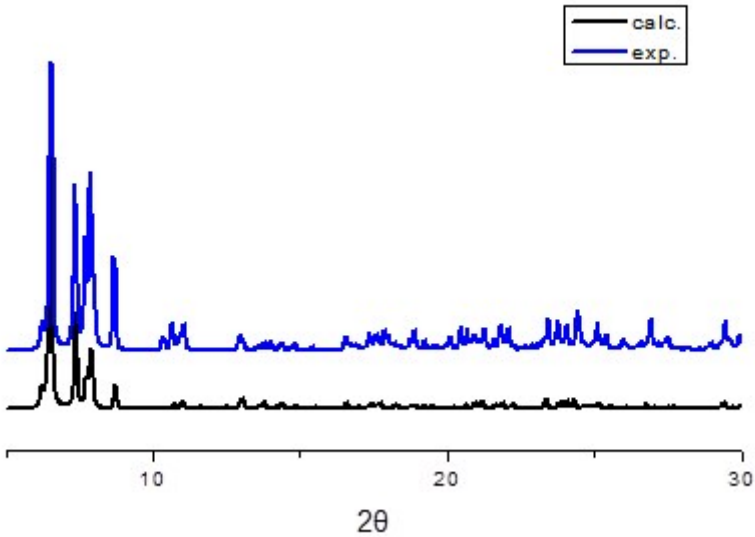


Figure S4. XRPD curve of **4**.

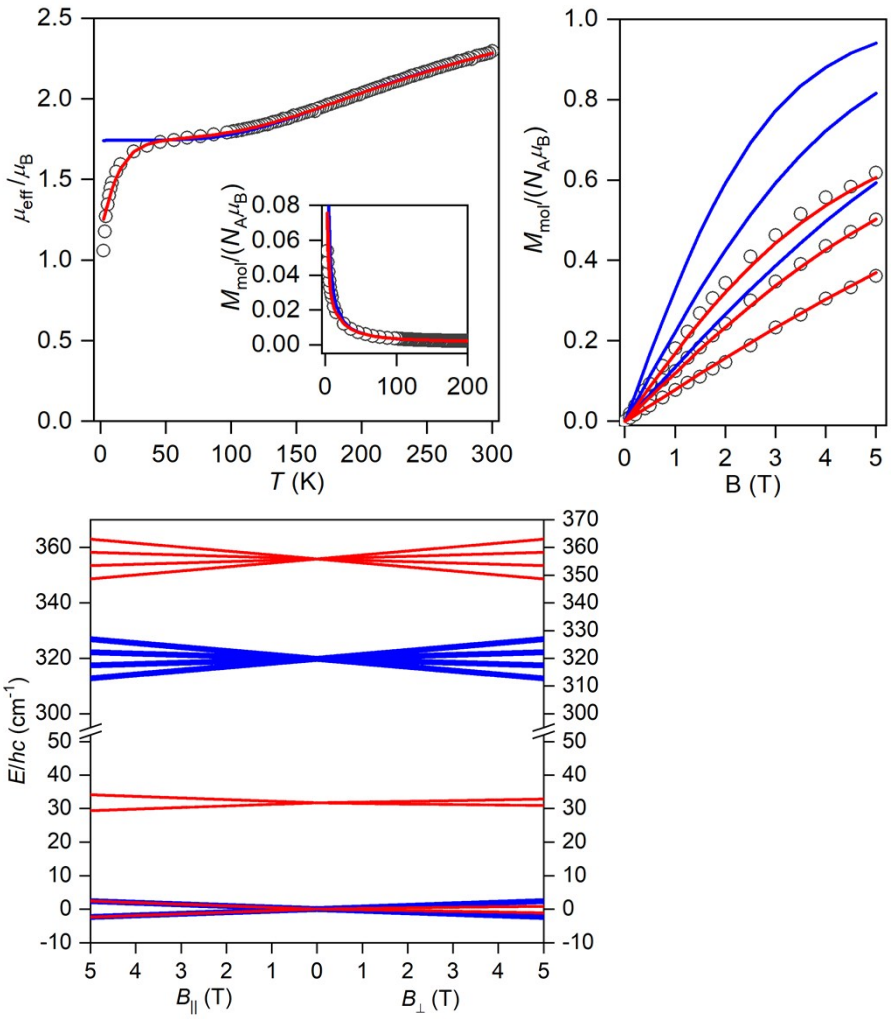


Figure S5. *Top*: Temperature dependence of the effective magnetic moment (calculated from magnetization at B = 0.5 T) of **4** with the low-temperature region expanded in the inset and the isothermal magnetization data measured at T = 2, 3 and 5 K. Circles are experimental points, blue lines are calculated using the best-fit parameters: J = -213 cm^{-1} and g = 2.02, red lines = calculated using the best-fit parameters: J_{12} = -218 cm^{-1}, J_{13} = J_{23} = -231 cm^{-1}, g = 2.05

and $|d_z|$ = 16.7 cm^{-1}. *Bottom*: the calculated energy levels in magnetic field using J = -213 cm^{-1} and g = 2.02 (blue color) and J_{12} = -218 cm^{-1}, $J_{13} = J_{23}$ = -231 cm^{-1}, g = 2.05 and $|d_z|$ = 16.7 cm^{-1} (red color).

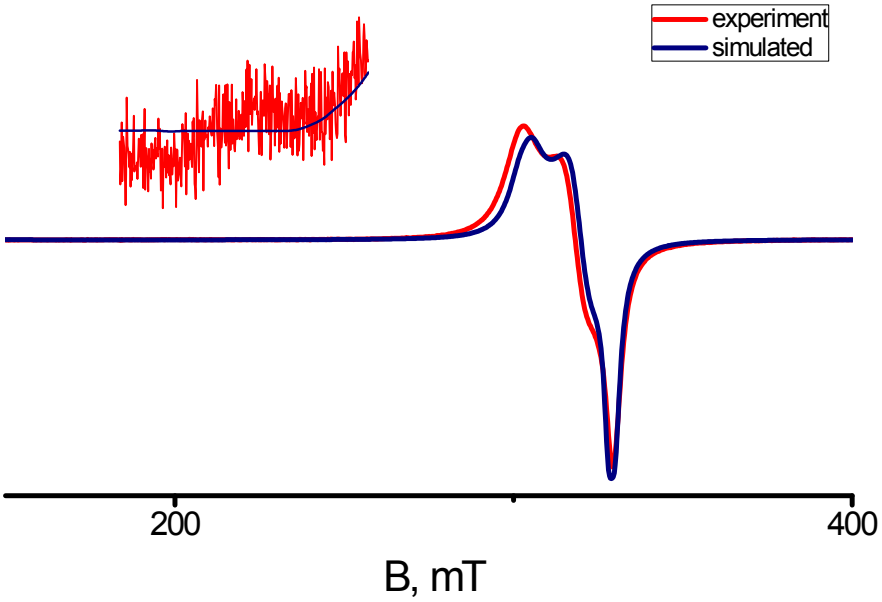


Figure S6. Experimental and simulated X-Band EPR spectra of a polycrystalline sample of complex **1** at 50 K

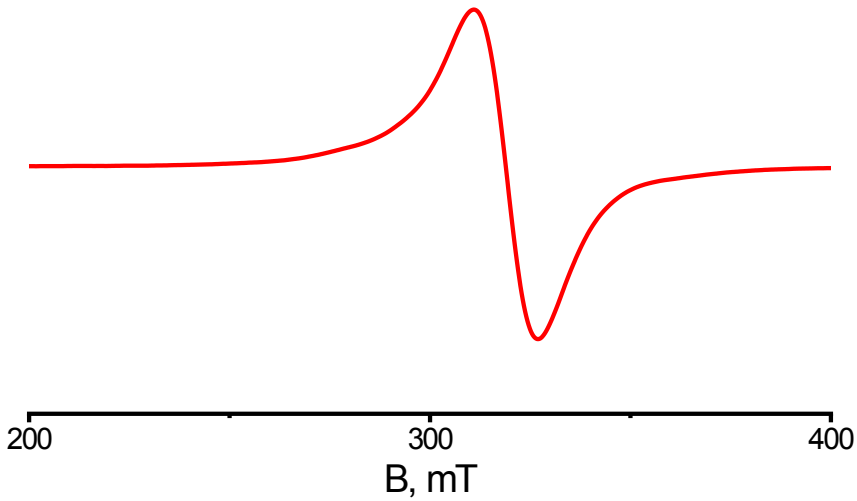


Figure S7. Experimental X-Band EPR spectra of a polycrystalline sample of complex **4** at 294 K