A novel hexanuclear Cu(II) complex built from a simple tetra-chelating triazole ligand: synthesis, structure and magnetism

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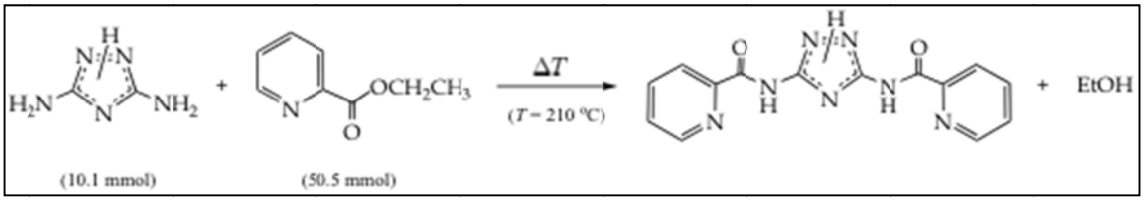
S1 Details on the synthesis and characterization of ligand 3,5-bis(pyridine-2-yl-acetamido)-1,2,4-triazole=3,5-bis(picolinamido)-1,2,4-triazole (**H_3diV**).

An evaporating flask containing 3,5-diamino-1,2,4-triazole=guanazole (10.1 mmol, 1 g) and ethyl 2-picolinate (50.5 mmol, ρ = 1.119 g/mL, 6.8 mL) was connected to a glass oven and the temperature reaction was slowly raised to 210 ºC. At this temperature, the guanazole melted and a dark yellow solution was obtained. Then, the mixture was stirred (rotated) for 4 h. During that time, the yellow solution was gradually becoming dark brown (almost black). At this point, a vacuum pump was connected during 60 minutes to remove the excess of ethyl 2-picolinate. Afterwards, the reaction was brought to room temperature and the mixture solidified. The dark brown solid was isolated and stirred with 50 mL of ethyl acetate for 30 minutes at 50 ºC. Then, the resulting mixture was filtered, washed with hot ethyl acetate, and dried to constant weight. The solid is stable under light and air. The solid was crystallized from hot methanol. In a typical crystallization, 50 mg of the solid were dissolved with 25 mL of hot methanol and the final solution placed on a crystallizing dish. After one-two days, pale brown needles were obtained. Yield: 1.6 g, 51%. Anal. Calc. for $C_{14}H_{11}N_7O_2$ (309.28): C, 54.37; H, 3.58; N, 31.70. Found: C, 54.01; H, 3.52; N, 31.67. Selected *FT*-IR data (KBr pellet) $\tilde{\nu}_{max}$ (cm^{-1}): [ν(N−H) + ν(arC−H)] 3367-3352 d-m, 3180 b, 3066 w; [ν(C=O)] 1703-1689 d-s; [δ(N−H) + $\nu(C{=}N)_{ring}$ + $\nu(C{=}C)_{ring}$] 1557 vs, 1448 m, 1415 s (see spectrum in S13). FAB^+ mass spectra (methanol) (m/z): 310.5 $[M + H]^+$. ^{1}H RMN (300 MHz) (dmso-d_6, δ/ppm): 13.6 (bs, 1H, NH-amide); 11.6 (bs, 1H, NH-amide); 10.6 (bs, 1H, NH-trz); 8.7 (d, 1H, *J* = 4.2 Hz, pyridine); 8.1 (m, 2H, pyridine); 7.7 (m, 1H, pyridine). ^{13}C RMN (75 MHz) (dmso-d_6, δ/ppm): 162.8 (1C, C=O); 148.7, 138.1, 127.4, 122.5 (4C, pyridine). Signals for ^{13}C quaternary-pyridine and ^{13}C quaternary-triazole were not observed. Solubility properties: water (low); ethanol (moderate); methanol (moderate); DMF (soluble); DMSO (soluble).



S2 Details on the synthesis and characterization of complex $[Cu_6(HdiV)_2(ClO_4)_6(H_2O)_{14}](ClO_4)_2 \cdot 10H_2O$ (**1**).

A methanolic solution (10 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.97 mmol, 360 mg) was added dropwise to a hot methanolic solution (30 mL) of H_3diV (0.16 mmol, 50 mg) (reactants ratio is H_3diV/Cu(II) = 1:6). Immediately, a pale green precipitate* was formed. The mixture was stirred for approximately 20 minutes and then filtered. The resulting green solution was brought to room temperature and covered with Parafilm in a crystallizing dish. Sea-blue green prismatic crystals suitable for X-ray analysis were obtained after *ca.* 2 months. The crystals were filtered, washed with methanol and air dried on filter paper to constant weight. Yield: 0.107 g (*ca.* 30 %). Anal. Calc. for $Cu_6C_{28}H_{66}N_{14}O_{60}Cl_8$ (2223.78): C, 15.12; H, 2.99; N, 8.82. Found: C, 15.42; H, 2.73; N, 9.02. Selected *FT*-IR data (KBr pellet) $\tilde{\nu}_{max}$ (cm^{-1}): [ν(O−H) + ν(N−H) + ν(arC−H)] 3464 b-m, 3220 m, 3100 w; [ν(C=O)] 1617 m; [δ(N−H) + ν(N-C=O) + ν(C=N)ring + ν(C=C)ring] 1589 s, 1545 s, 1486 m, 1402 s; [ν(ClO_4)] 1148 s, 1121 sh, 1112-1091 d-vs (see IR/KBr spectrum in S13).

*Information relative to the pale green precipitate removed during synthesis:
Yield: 0.030 g. Proposed formula (a dimeric compound): $[Cu(H_2diV)(ClO_4)]_2 \cdot 8H_2O$. Anal. Calc. for $Cu_2C_{28}H_{36}N_{14}O_{20}Cl_2$ (1086.7): C, 30.95; H, 3.34; N, 18.05. Found: C, 30.83; H, 2.89; N, 17.89. Selected *FT*-IR data (KBr pellet) $\tilde{\nu}_{max}$ (cm^{-1}): [ν(O−H) + ν(N−H) + ν(arC−H)] 3443 b-m, 3088 w; [ν(C=O)] 1614 vw; [δ(N−H) + ν(N-C=O) + ν(C=N)ring + ν(C=C)ring] 1584 s, 1562 s, 1461 s, 1401 m; [ν(ClO_4)] 1093 s, 1054 s (see spectrum in S13).

S3 Details on X-ray measurements for complex **1**.

X-ray details Crystal data for 1: A sea-blue prismatic crystal of $[Cu_6(HdiV)_2(ClO_4)_6(H_2O)_{14}](ClO_4)_2 \cdot 10H_2O$ was mounted on a glass fiber and used for data collection. Crystal data were collected at 298(2) K, using a Bruker SMART CCD 1000 diffractometer. Graphite monochromated MoK(alpha) radiation (lambda = 0.71073 Å) was used throughout. The data were processed with SAINT [1] and corrected for absorption using SADABS (transmissions factors: 1.000 - 0.XXX) [2]. The structure was solved by direct methods using the program SHELXS-97 [3] and refined by full-matrix least-squares techniques againts F^2 using SHELXL-97 [3]. Positional and anisotropic atomic displacement parameters were refined for nonhydrogen atoms. Atoms in the ClO_4^- ions and crystallization water molecules which showed very high thermal motion refined isotropically. Hydrogen atoms were placed geometrically and positional paremeters were refined using a riding model. The H atoms of water molecules were not located. Criteria of a satisfactory complete analysis were the ratios of "rms" shift to standard deviation less than 0.001 and no significant features in final difference maps. Atomic scattering factors from "International Tables for Crystallography" [4]. Molecular graphics from PLATON [5] and DIAMOND [6]. A summary of the crystal data, experimental details and refinement results is listed in S4.

References

[1] Bruker (1997). SMART and SAINT. Area Detector Control and Integration Software, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

[2] G.M. Sheldrick (1997). SADABS. Program for Empirical Absorption Correction of Area Detector Data. University of Goettingen, Germany.

[3] G.M. Sheldrick (2008). Acta Cryst. A64, 112-122.

[4] A. J. C. Wilson (1995). International Tables for Crystallography. Vol. C, Kluwer Academic Publishers: Dordrecht, The Netherlands.

[5] A.L. Spek. (2009), Acta Cryst. D65, 148-155.

[6] K. Brandenburg, H. Putz (2004). DIAMOND 3.x, Crystal Impact GbR, Bonn, Germany.

S4. Summary of Crystallographic Data for **$[Cu_6(HdiV)_2(ClO_4)_6(H_2O)_{14}](ClO_4)_2 \cdot 10H_2O$** (**1**).

Identification code	12acsf01
Empirical formula	C28 H66 Cl8 Cu6 N14 O60
Formula weight	2223.79
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 10.7330(3) A α = 67.589(2) deg. b = 13.2580(3) A β = 76.747(2) deg. c = 15.4740(5) A γ = 71.487(2) deg.
Volume	1915.52(9) A^3
Z, Calculated density	1, 1.928 Mg/m^3
Absorption coefficient	2.041 mm^-1
F(000)	1122
Crystal size	0.15 x 0.11 x 0.07 mm
Theta range for data collection	1.43 to 27.52 deg.
Limiting indices	-13<=h<=13, -14<=k<=17, -17<=l<=20
Reflections collected / unique	13807 / 8744 [R(int) = 0.0339]
Completeness to theta = 27.52	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8703 and 0.7494
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8744 / 0 / 456
Goodness-of-fit on F^2	1.144
Final R indices [I>2sigma(I)]	R1 = 0.0940, wR2 = 0.2984
R indices (all data)	R1 = 0.1333, wR2 = 0.3329
Extinction coefficient	0.0040(17)
Largest diff. peak and hole	3.026 and -1.887 e.A^-3

S5. Table of bonds lengths (Å) and angles (°) for **$[Cu_6(HdiV)_2(ClO_4)_6(H_2O)_{14}](ClO_4)_2 \cdot 10H_2O$** (**1**).

Cu(1)-O(17)	1.923(5)
Cu(1)-O(27)	1.954(5)
Cu(1)-N(2)	1.957(6)
Cu(1)-N(1)	1.963(6)
Cu(1)-O(1)	2.428(8)
Cu(1)-O(11)	2.809(9)
Cu(2)-N(11)	1.985(7)
Cu(2)-O(2)	1.984(6)
Cu(2)-O(3)	1.995(6)
Cu(2)-N(18)	2.028(5)
Cu(2)-O(4)	2.332(8)
Cu(2)-O(21)	2.519(7)
Cu(3)-N(21)	1.978(6)
Cu(3)-O(5)	1.989(6)
Cu(3)-O(7)	1.991(5)
Cu(3)-N(28)	2.035(6)
Cu(3)-O(6)	2.269(7)
Cu(3)-O(31)	2.577(7)

O(17)-Cu(1)-O(27)	83.0(2)
O(17)-Cu(1)-N(2)	169.3(2)
O(27)-Cu(1)-N(2)	86.8(2)
O(17)-Cu(1)-N(1)	87.0(2)
O(27)-Cu(1)-N(1)	169.1(2)
N(2)-Cu(1)-N(1)	102.8(2)
O(17)-Cu(1)-O(1)	89.0(3)
O(27)-Cu(1)-O(1)	89.4(3)
N(2)-Cu(1)-O(1)	94.4(3)
N(1)-Cu(1)-O(1)	94.9(3)
O(17)-Cu(1)-O(11)	92.2(3)
O(27)-Cu(1)-O(11)	96.0(3)
N(2)-Cu(1)-O(11)	85.3(3)
N(1)-Cu(1)-O(11)	79.9(3)
O(1)-Cu(1)-O(11)	174.6(3)
N(11)-Cu(2)-O(2)	167.2(3)
N(11)-Cu(2)-O(3)	93.5(3)
O(2)-Cu(2)-O(3)	89.1(2)
N(11)-Cu(2)-N(18)	82.0(2)
O(2)-Cu(2)-N(18)	95.9(2)
O(3)-Cu(2)-N(18)	174.7(2)
N(11)-Cu(2)-O(4)	103.3(3)
O(2)-Cu(2)-O(4)	89.2(3)
O(3)-Cu(2)-O(4)	90.2(3)
N(18)-Cu(2)-O(4)	88.1(3)
N(11)-Cu(2)-O(21)	83.6(3)
O(2)-Cu(2)-O(21)	84.6(3)
O(3)-Cu(2)-O(21)	79.5(3)
N(18)-Cu(2)-O(21)	102.7(2)
O(4)-Cu(2)-O(21)	168.0(3)
N(21)-Cu(3)-O(5)	94.3(3)
N(21)-Cu(3)-O(7)	170.6(3)
O(5)-Cu(3)-O(7)	87.6(2)
N(21)-Cu(3)-N(28)	82.7(3)
O(5)-Cu(3)-N(28)	176.8(2)

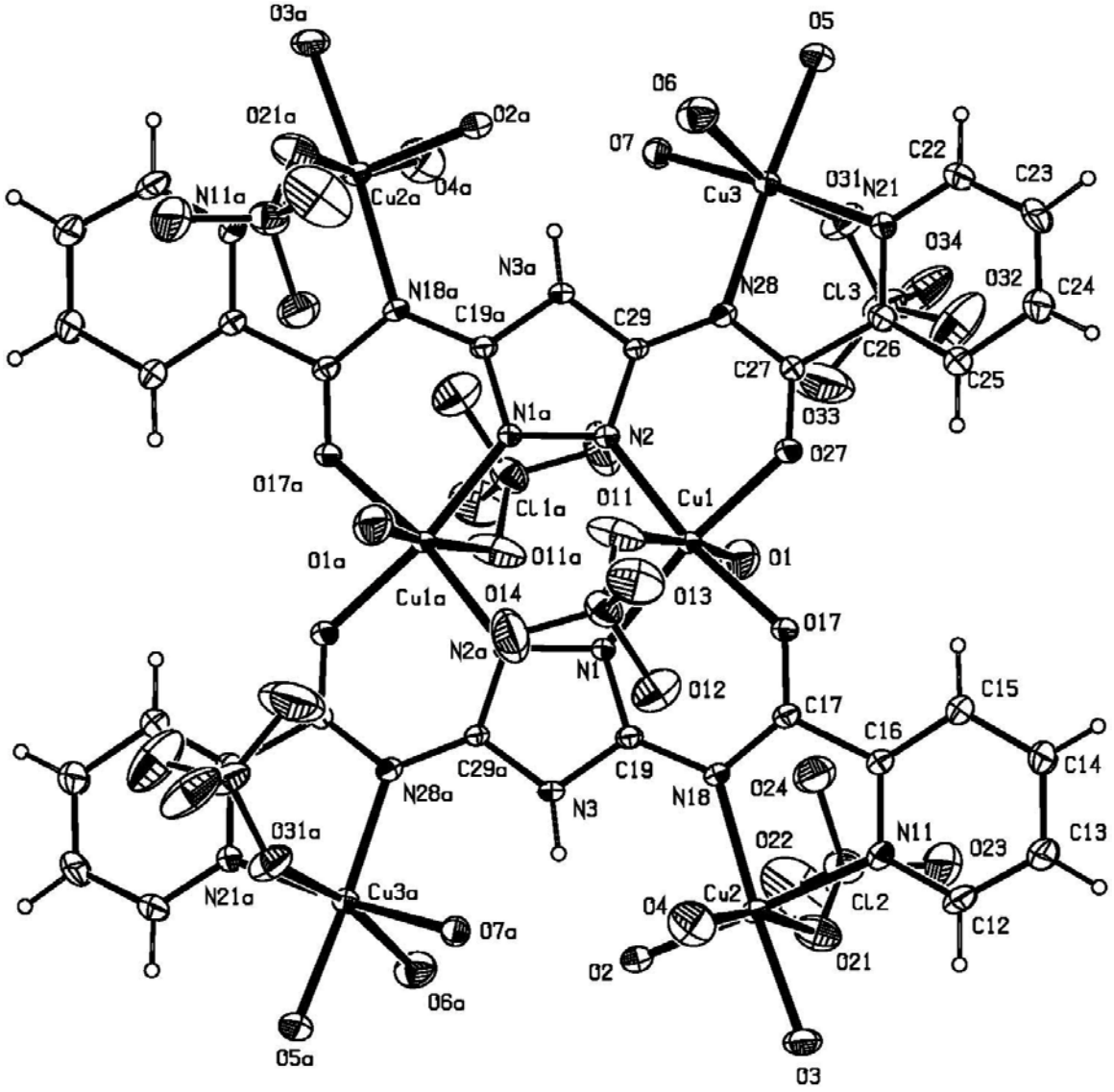
O(7)-Cu(3)-N(28)	95.2(2)
N(21)-Cu(3)-O(6)	98.6(3)
O(5)-Cu(3)-O(6)	86.8(3)
O(7)-Cu(3)-O(6)	90.7(3)
N(28)-Cu(3)-O(6)	94.8(3)
N(21)-Cu(3)-O(31)	88.8(3)
O(5)-Cu(3)-O(31)	80.9(3)
O(7)-Cu(3)-O(31)	82.4(3)
N(28)-Cu(3)-O(31)	97.8(3)
O(6)-Cu(3)-O(31)	166.1(3)

S6. Table of selected H-bonds (lengths (Å), angles (°)) for complex **1**.

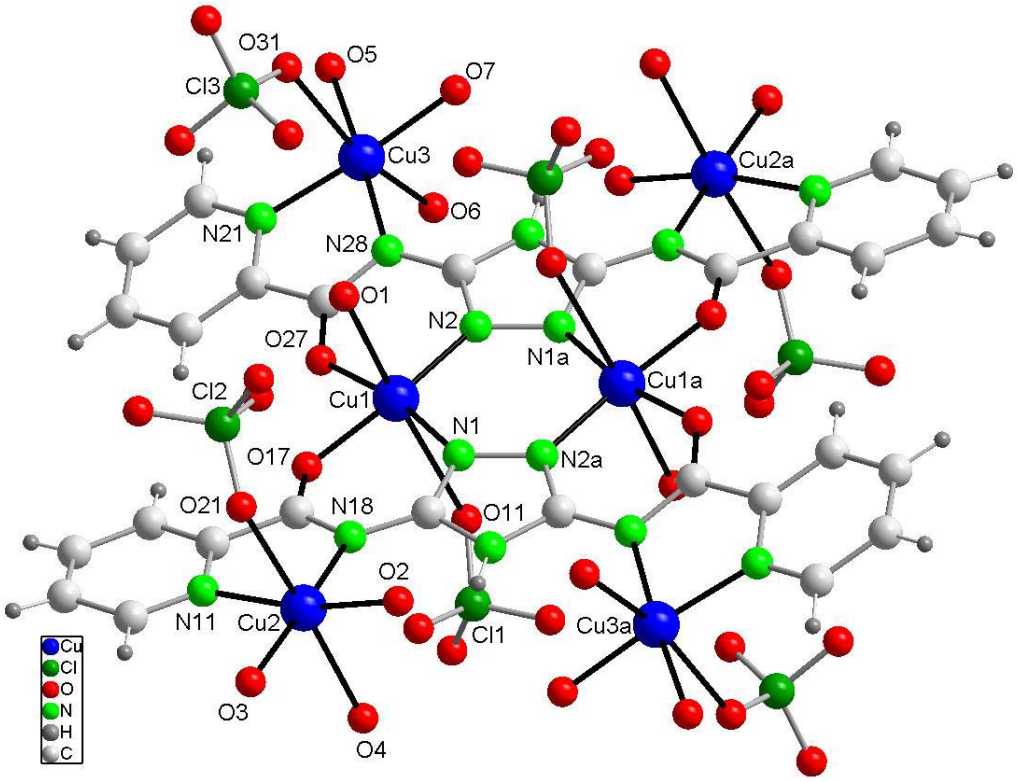
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(2)	0.90	2.03	2.785(8)	140.8
N(3)-H(3)...O(7)#1	0.90	2.29	2.810(8)	116.7
O1 - O14#1			3.032(14)	
O2 - O52#4			2.676(12)	
O2 - O53#4			2.681(13)	
O3 - O54#2			2.727(13)	
O3 - O13#3			2.755(11)	
O3 - O21			2.915(10)	
O4 - O41#2			2.899(11)	
O4 - O42#2			3.055(10)	
O4 - O54#4			2.942(15)	
O5 - O55#5			2.720(13)	
O5 - O31			2.995(10)	
O5 - O43#5			2.951(07)	
O5 - O51#5			2.748(11)	
O6 - O55#5			2.828(14)	
O7 - O51#8			2.698(11)	
O7 - O31			3.041(09)	
O7 - O34#9			2.857(12)	
O55 - O44			3.073(12)	

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z
#2 -x+1, -y+1, -z
#3 x-1, y, z
#4 x, y, z-1
#5 x+1, y, z
#8 -x+1, -y, -z+1
#9 -x+2, -y, -z+1

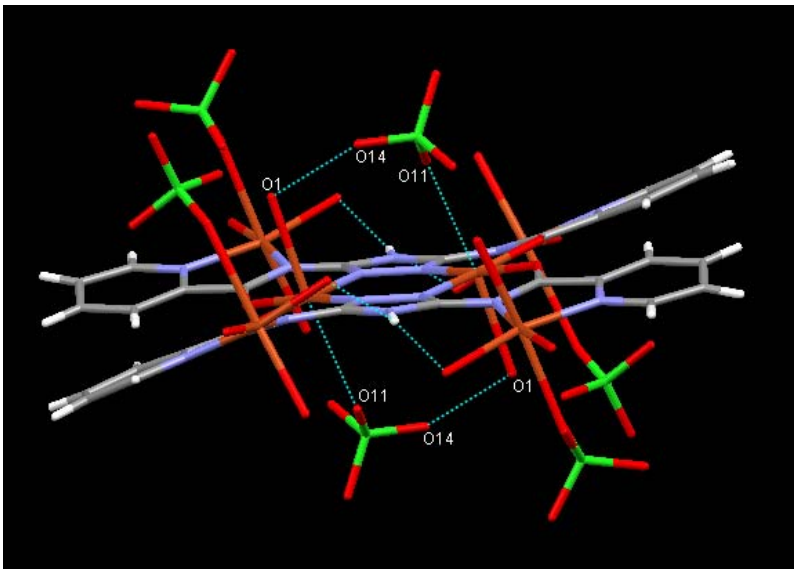
S7. ORTEP view of **1** with full atomic labeling scheme.



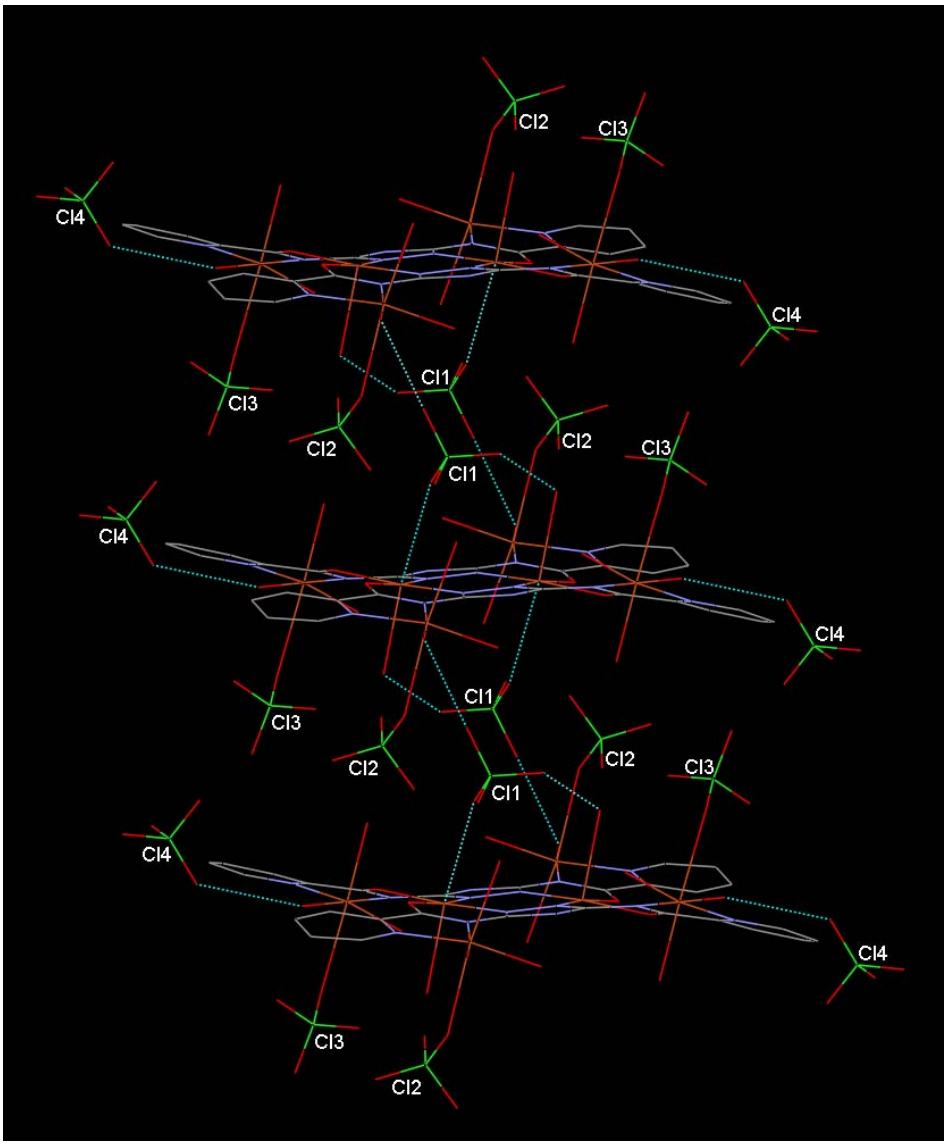
S8. Drawing of **1** including the 6 (weakly) bonded perchlorate anions (*Cl*1, *Cl*2, *Cl*3).



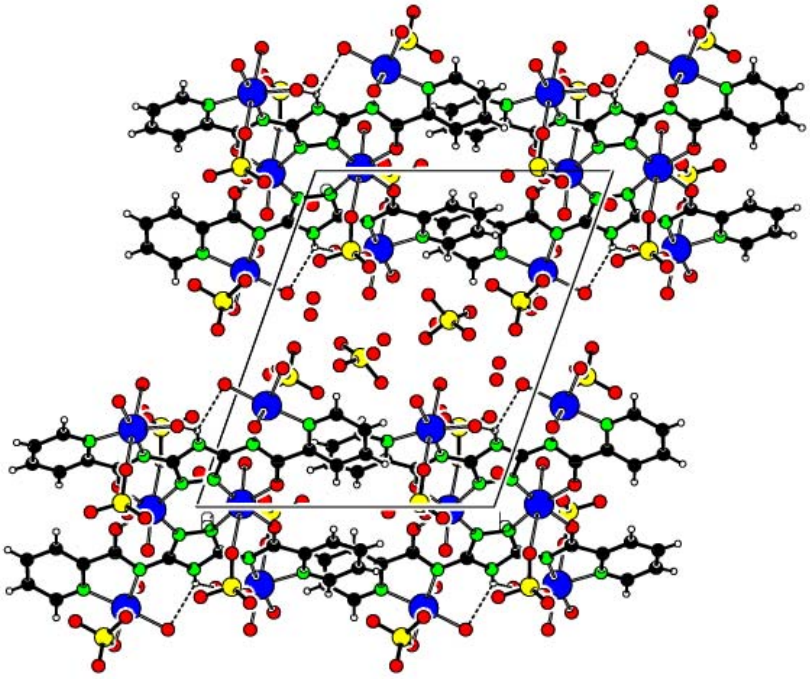
S9. Drawing of **1** showing the (weak) interaction of the perchlorate anion *Cl*1 with Cu1.



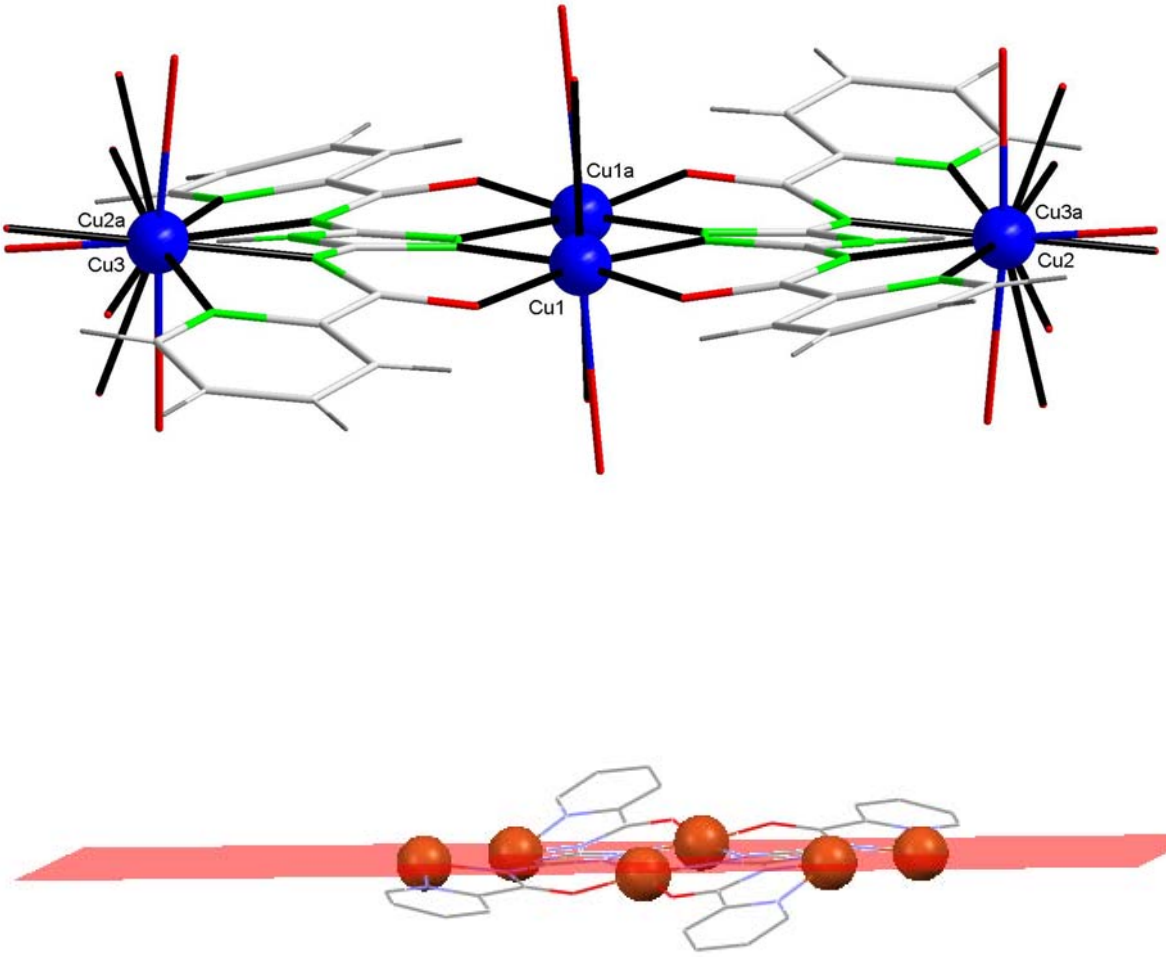
S10. Packing view of **1** showing the connection between hexanuclear units through H-bonds established by the perchlorate anions *Cl*1 and *Cl*4.



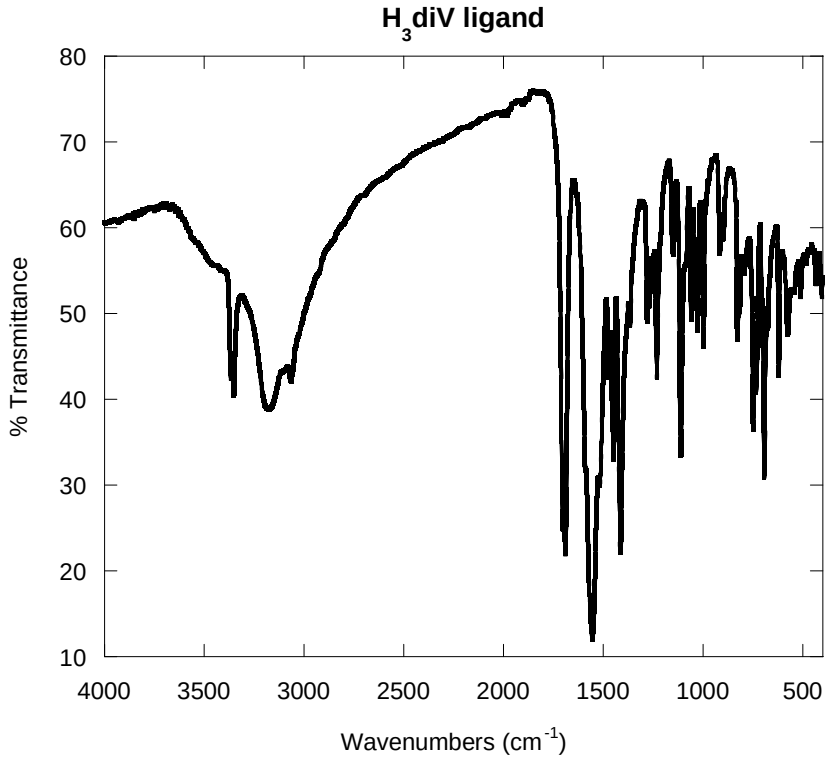
S11. A view of the unit-cell contents of **1** in projection down the *a* axis.

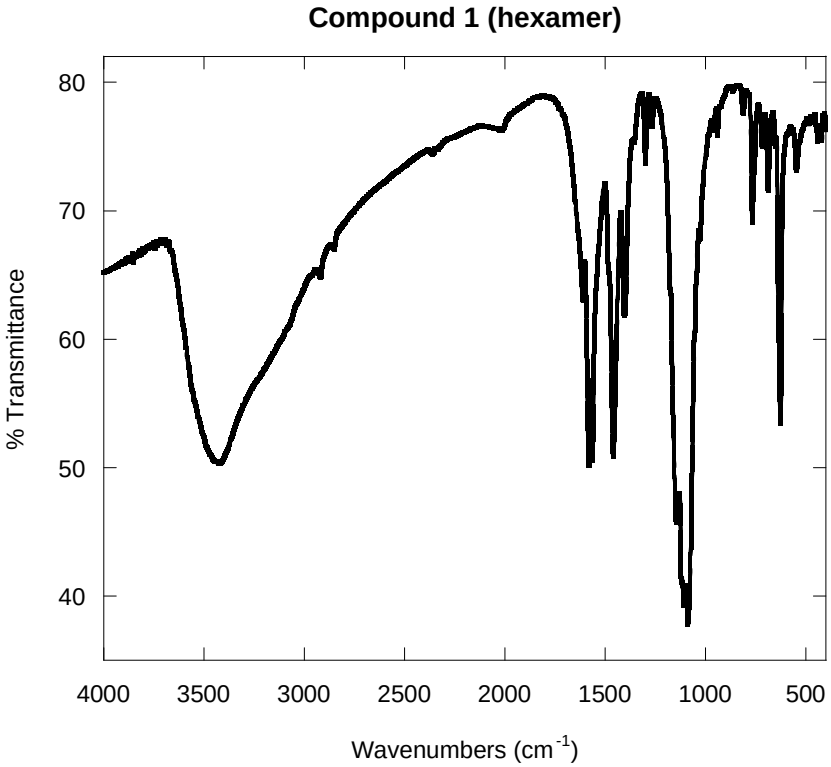


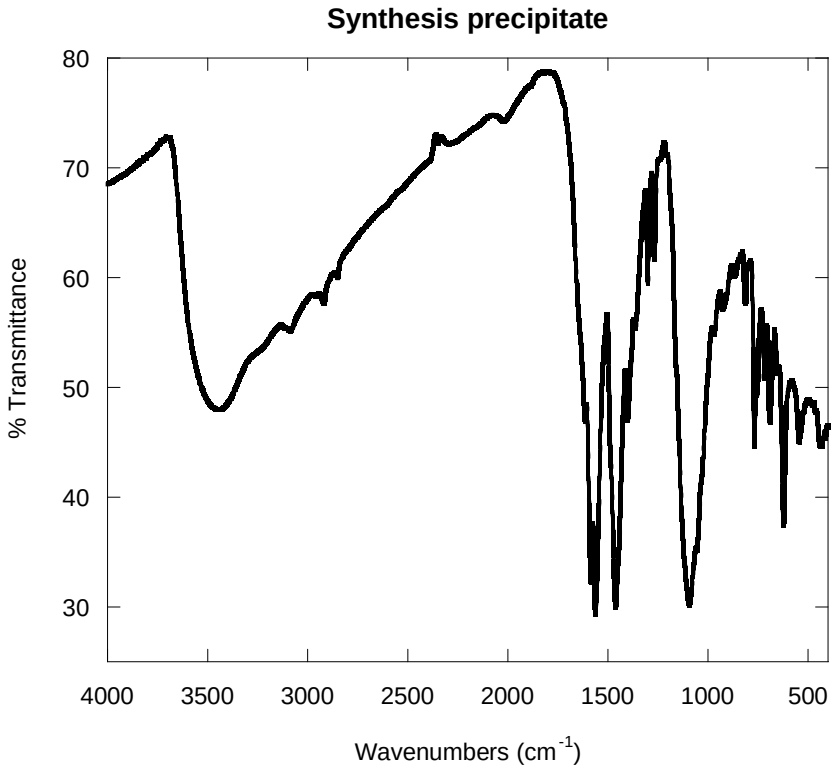
S12. Views of **1** showing the Cu_6 plane.



S13 IR spectra (KBr) of ligand, compound **1** and synthesis precipitate






Synthesis precipitate
% Transmittance
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)