Cis and *Trans* linkage of spin frustrated Copper triangles creating Cu_6 clusters

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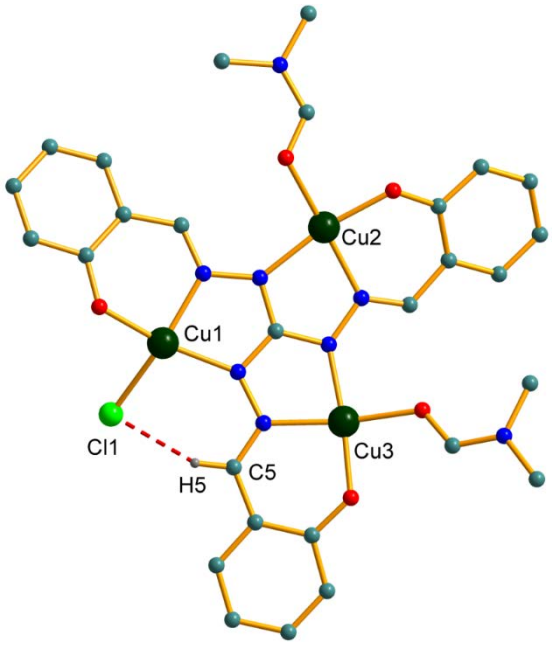

Figure S1. The asymmetric unit of **Cu_6Cl**, hydrogen atoms have been omitted for clarity.

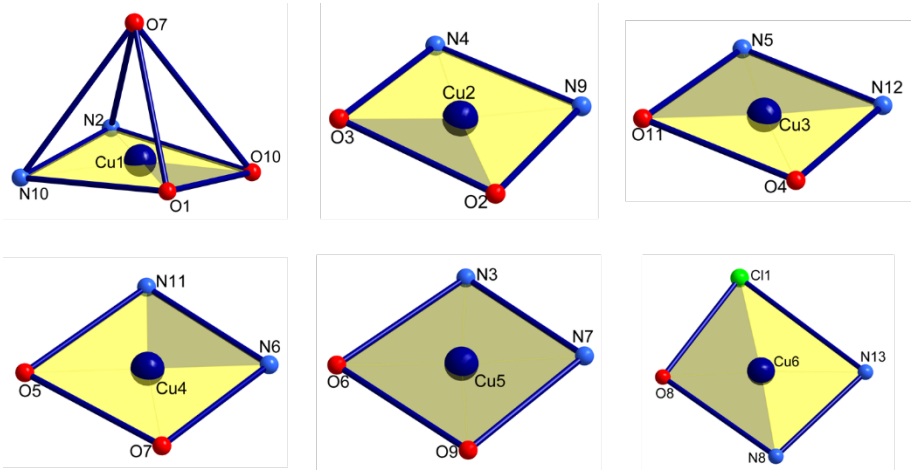

Figure S2. Representation of geometries for **Cu_6**.

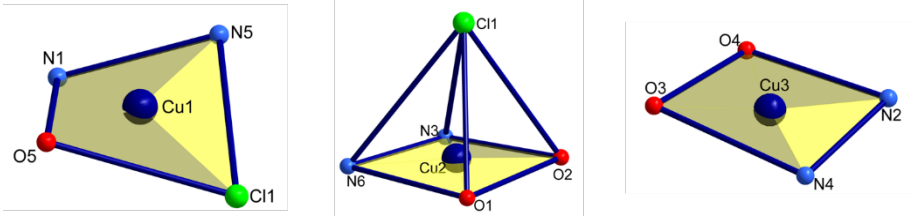

Figure S3. Representation of geometries for **Cu_6Cl**.

Table S1. Crystal data and structure refinement parameters for **Cu_6** and **Cu_6Cl**.

Compound	**Cu_6**	**Cu_6Cl**
Formula	$C_{58}H_{61}ClCu_6N_{16}O_{12}$	$C_{56}H_{58}Cl_2Cu_6N_{16}O_{10}$
FW($gmol^{-1}$)	1590.91	1567.32
Temperature (K)	173.15	170(2)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	14.0806(12)	9.6347(9)
b/Å	16.0032(13)	12.3396(13)
c/Å	16.2677(13)	13.0755(13)
α/°	118.409(4)	93.388(3)
β/°	104.542(4)	91.539(3)
γ/°	92.002(5)	101.347(3)
Volume ($Å^3$)	3069.2(5)	1520.3(3)
Z	2	1
$\rho_{calc}(gcm^{-3})$	1.721	1.712
μ/mm^{-1}	2.161	2.220
Wavelength/Å	0.71073	0.71073
Radiation type	MoK_a	MoK_a
Reflections collected	49067	17935
Independent reflections	10858	4818
GOF on F^2	1.065	1.087
*R_1, wR_2 ($I \geq 2\sigma(I)$)	0.0636, 0.1347	0.0399, 0.0858
*R_1, wR_2 (all data)	0.1280, 0.1705	0.0702, 0.1053

*$R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$ for $Fo > 2\sigma(Fo)$; $wR_2 = (\Sigma w(Fo^2-Fc^2)^2/\Sigma(wFc^2)^2)^{1/2}$ all reflections, $w = 1/[\sigma^2(Fo^2)+(0.1557P)^2]$ where $P = (Fo^2+2Fc^2)/3$

Table S2. Selected bond lengths (Å) and angles (°) for **Cu_6**.

Cu1-O1	1.953(5)	Cu4-O5	1.945(6)
Cu1-O7	2.378(6)	Cu4-O7	1.892(5)
Cu1-O10	1.900(5)	Cu4-N6	1.948(6)
Cu1-N2	1.953(6)	Cu4-N11	1.975(7)
Cu1-N10	1.994(6)	Cu5-O6	1.978(6)
Cu2-O2	1.881(5)	Cu5-O9	1.874(5)
Cu2-O3	1.961(5)	Cu5-N3	1.960(6)
Cu2-N4	1.958(6)	Cu5-N7	1.946(6)
Cu2-N9	1.942(6)	Cu6-Cl1	2.269(3)
Cu3-O4	1.874(5)	Cu6-O8	1.893(6)
Cu3-O11	1.966(5)	Cu6-N8	1.951(6)
Cu3-N5	1.956(6)	Cu6-N13	2.005(6)
Cu3-N12	1.945(6)		
O1-Cu1-O7	88.5(2)	N12-Cu3-O11	176.8(2)
O1-Cu1-N10	99.3(2)	N12-Cu3N5	81.2(2)
O10-Cu1-O1	87.6(2)	O5-Cu4-N6	176.6(3)
O10-Cu1-O7	101.7(2)	O5-Cu4-N11	97.3(3)
O10-Cu1-N2	93.5(2)	O7-Cu4-O5	89.1(2)
O10-Cu1-N10	162.1(3)	O7-Cu4-N6	93.5(2)
N2-Cu1-O1	178.6(2)	O7-Cu4-N11	173.6(3)
N2-Cu1-O7	90.6(2)	N6-Cu4-N11	80.2(3)
N2-Cu1-N10	79.8(2)	O9-Cu5-O6	87.2(2)
N10-Cu1-O7	94.9(2)	O9-Cu5-N3	173.9(3)
O2-Cu2-O3	87.9(2)	O9-Cu5-N7	93.3(3)
O2-Cu2-N4	173.4(3)	N3-Cu5-O6	98.3(3)
O2-Cu2-N9	93.5(2)	N7-Cu5-O6	176.2(3)
N4-Cu2-O3	98.2(2)	N7-Cu5-N3	81.4(3)
N9-Cu2-O3	174.5(3)	O8-Cu6-Cl1	85.38(19)
N9-Cu2-N4	80.7(2)	O8-Cu6-N8	92.8(3)
O4-Cu3-O11	89.4(2)	O8-Cu6-N13	170.7(3)
O4-Cu3-N5	174.4(2)	N8-Cu6-Cl1	175.1(2)
O4-Cu3-N12	93.4(2)	N8-Cu6-N13	79.5(3)
N5-Cu3-O11	96.0(2)	N13-Cu6-Cl1	102.7(2)

Table S3. Selected bond lengths (Å) and angles (°) for **Cu_6Cl**.

Cu1-Cl1	2.279(14)	Cu2-N3	1.960(4)
Cu1-O5	1.886(3)	Cu2-N6	1.985(4)
Cu1-N1	1.960(4)	Cu3-O3	1.974(3)
Cu1-N5	1.957(4)	Cu3-O4	1.866(3)
Cu2-Cl1	2.690(14)	Cu3-N2	1.951(4)
Cu2-O1	2.023(4)	Cu3-N4	1.929(4)
Cu2-O2	1.905(3)	-	-
O5-Cu1-Cl1	90.74(11)	O2-Cu2-Cl1	89.10(11)
O5-Cu1-N1	92.02(16)	O2-Cu2-O1	89.73(14)
O5-Cu1-N5	162.27(16)	O2-Cu2-N3	90.61(15)
N1-Cu1-Cl1	154.76(12)	O2-Cu2-N6	168.82(16)
N5-Cu1-Cl1	102.80(12)	N3-Cu2-Cl1	103.63(12)
N5-Cu1-N1	80.64(16)	N3-Cu2-O1	170.47(16)
O1-Cu2-Cl1	85.90(11)	N3-Cu2-N6	79.85(16)
N6-Cu2-Cl1	98.76(12)	N6-Cu2-O1	98.71(15)
O4-Cu3-O3	91.67(15)	N2-Cu3-O3	166.28(16)
O4-Cu3-N2	94.29(15)	N4-Cu3-O3	94.58(15)
O4-Cu3-N4	173.32(15)	N4-Cu3-N2	80.12(16)

Table S4. Calculated geometries of **Cu_6** by *SHAPE* 2.1[1] software.

Cu center	**Pentagon (D_{5h})**	**Vacant octahedron (C_{4v})**	**Trigonalbipyramid (D_{3h})**	**Spherical square pyramid (C_{4v})**	**Johnson trigonalbipyramid J12 (D_{3h})**
Cu1	30.035	1.901	3.733	**1.366**	6.917
Cu center	**Square (D_{4h})**	**Tetrahedron (T_d)**	**Seesaw (C_{2v})**		
Cu2	**0.501**	30.121	16.861		
Cu3	**0.290**	32.354	18.168		
Cu4	**0.350**	32.276	18.398		
Cu5	**0.451**	30.858	17.184		
Cu6	**1.371**	30.083	16.185		

Table S5. Calculated geometries of **Cu_6Cl** by *SHAPE* 2.1[1] software.

Cu center	Pentagon (D_{5h})	Vacant octahedron (C_{4v})	Trigonalbipyramid (D_{3h})	Spherical square pyramid (C_{4v})	Johnson trigonalbipyramid J12 (D_{3h})
Cu2	30.013	3.136	6.662	**1.782**	1 0.438

Cu center	Square (D_{4h})	Tetrahedron (T_d)	Seesaw (C_{2v})
Cu1	**4.190**	18.942	10.207
Cu3	**0.814**	27.235	14.866

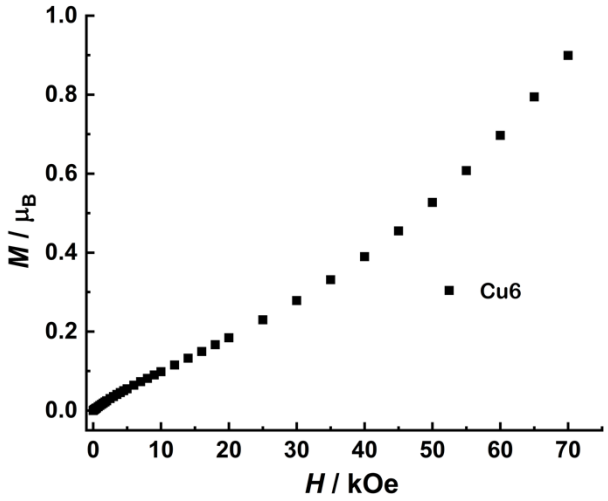

Figure S4. Magnetization curve for **Cu_6** at 2 K.

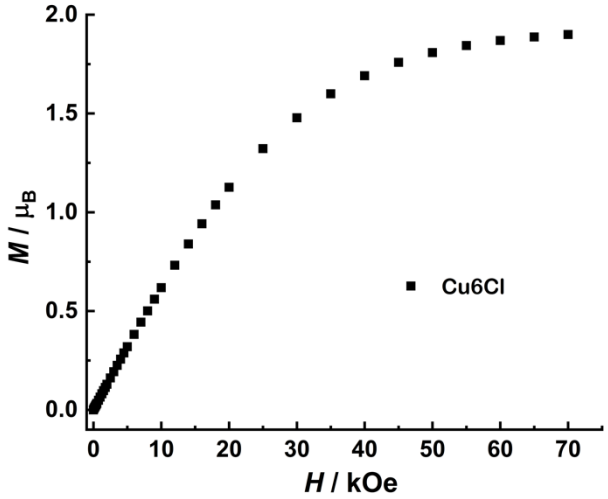

Figure S5. Magnetization curve for **Cu_6Cl** at 2 K.

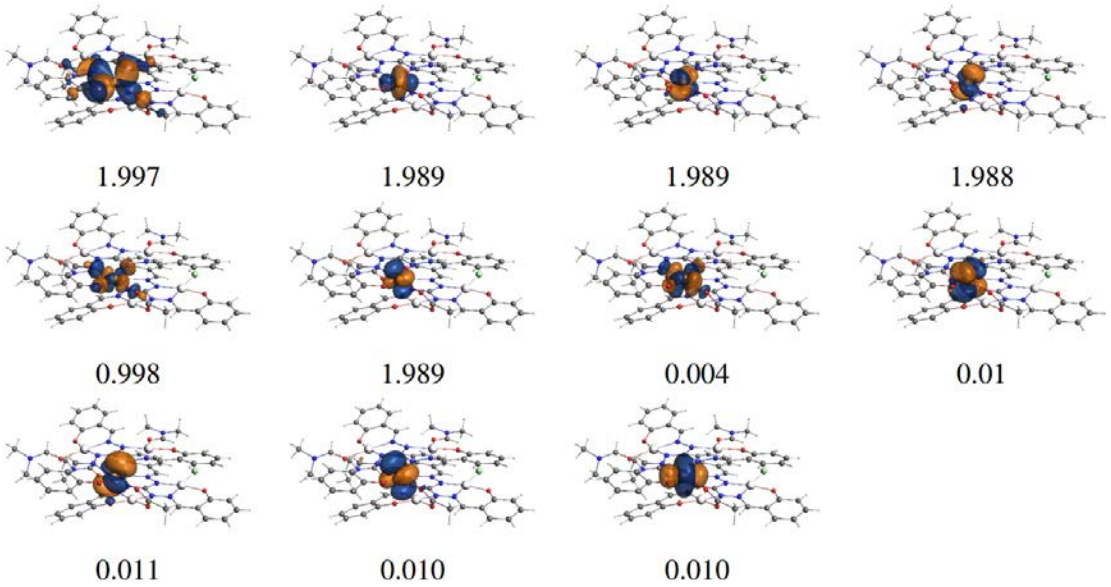

Figure S6. Natural Orbitals of the spin-orbit GS of one Cu^{II} center in compound **Cu_6**. CAS(11,11)SCF-SO Results. Iso-surface value, 0.03 au.

Table S6. Calculated energy gap (ΔE, cm^{-1}) between the ground state (GS) and the first excited state (ES1) and electronic g-factors for the ground state of the different metal centers in **Cu_6** and **Cu_6Cl**.

	ΔE GS -ES1	gx	gy	gz
Cu_6				
Cu1	12965	2.39	2.08	2.08
Cu2	14826	2.35	2.06	2.08
Cu3	11854	2.44	2.07	2.09
Cu4	14457	2.36	2.07	2.08
Cu5	14779	2.35	2.06	2.08
Cu6	13532	2.38	2.09	2.06
Cu_6Cl				
Cu1	14711	2.35	2.06	2.08
Cu2	12762	2.41	2.11	2.07
Cu3	12446	2.40	2.05	2.11
Cu4	12762	2.40	2.10	2.06
Cu5	14709	2.35	2.06	2.09
Cu6	12446	2.39	2.11	2.06

Table S7. Magnetic coupling constants (J in cm^{-1}) for **Cu_6** and **Cu_6Cl** calculated at the DFT level with the B3LYP and PBE0 functionals.

	Cu_6		**Cu_6Cl**	
	B3LYP	PBE0	B3LYP	PBE0
Cu1-Cu2	**-371.7**	**-304.9**	**-180.5**	**-157.5**
Cu1-Cu3	**-258.0**	**-214.8**	**-383.8**	**-312.8**
Cu1-Cu4	-23.1	-19.7	-0.1	0.3
Cu1-Cu5	0.1	0.6	-0.7	0.1
Cu1-Cu6	0.2	0.2	0.7	0.6
Cu2-Cu3	**-277.4**	**-235.1**	**-185.8**	**-156.8**
Cu2-Cu4	-0.0	0.1	-0.2	0.0
Cu2-Cu5	-0.3	0.3	0.1	0.0
Cu2-Cu6	0.2	0.1	5.9	4.9
Cu3-Cu4	-0.3	-0.5	6.1	4.9
Cu3-Cu5	-0.0	0.4	0.8	0.7
Cu3-Cu6	-0.8	-1.2	1.9	0.9
Cu4-Cu5	**-246.0**	**-210.6**	**-180.6**	**-157.5**
Cu4-Cu6	**-283.4**	**-235.1**	**-185.8**	**-156.8**
Cu5-Cu6	**-365.8**	**-298.8**	**-383.8**	**-312.8**

Table S8. Relative energy (in cm^{-1}) of the 8 lowest state in **Cu_6** and **Cu_6Cl** calculated with the Hamiltonian in the main text.

	Cu_6		**Cu_6Cl**	
States	B3LYP	PBE0	B3LYP	PBE0
1	0.000	0.000	0.000	0.000
2	3.108	3.616	0.161	0.039
3	3.128	3.633	0.166	0.044
4	3.159	3.662	0.172	0.051
5	98.540	77.486	196.938	153.101
6	107.290	80.755	196.940	153.108
7	107.314	80.780	197.004	153.161
8	107.331	80.798	198.527	153.216

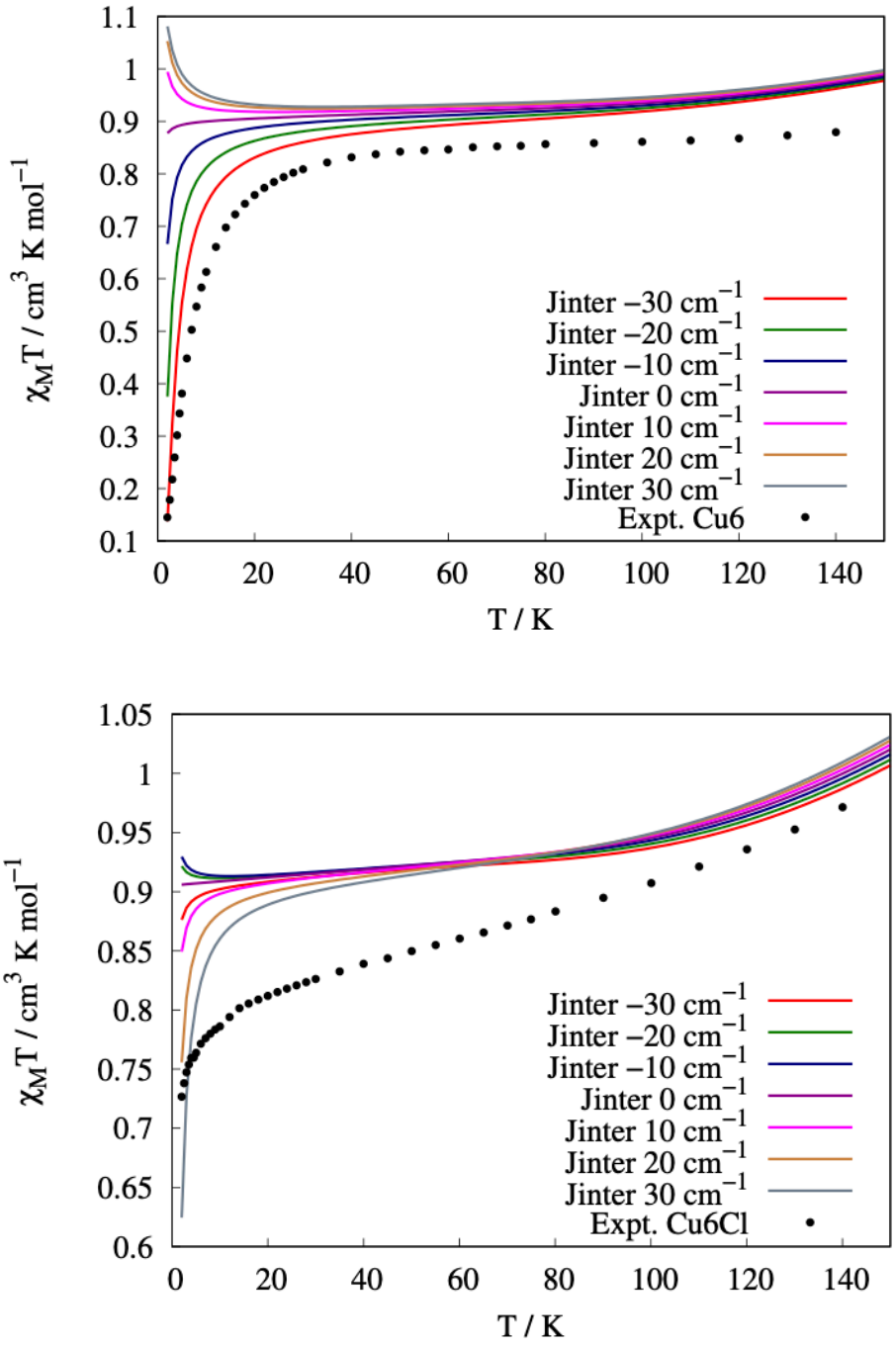

Figure S7. Calculated (plain lines) and experimental (filled circles) magnetic susceptibility ($\chi_M T$) as a function of the temperature for the **Cu_6** (top) and **Cu_6Cl** (bottom) complexes. Results are shown for different values of the Jinter.

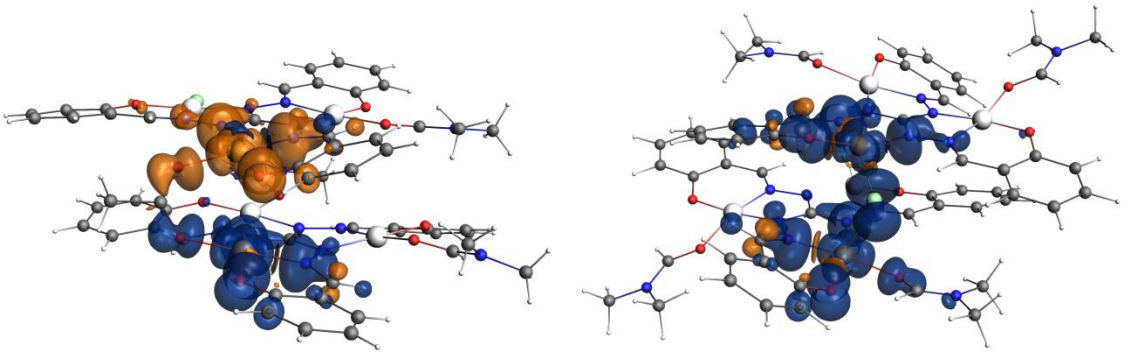

Figure S8. Spin density plots for the broken symmmetry solution of **Cu_6** (left) and the triplet state of **Cu_6Cl** (right). Iso-surface value, 0.001 au.

References

(1) Casanova, D.; Llunell, M.; Alemany, P.; Alvarez, S. The rich stereochemistry of eight-vertex polyhedra: A continuous shape measures study. *Chem. Eur. J.* **2005,** *11*, 1479-1494.