Electronic Supplementary Material (ESI) for Dalton Transactions.

Spin-frustration with two quasi-degenerated spin states of a copper(II) heptanuclear complex obtained from an amino acid ligand

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Electronic Supporting Information

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Scheme S1. Schematic representation of the synthesis of the amino acid ligand and **Cu_7atac** complex and its crystals.

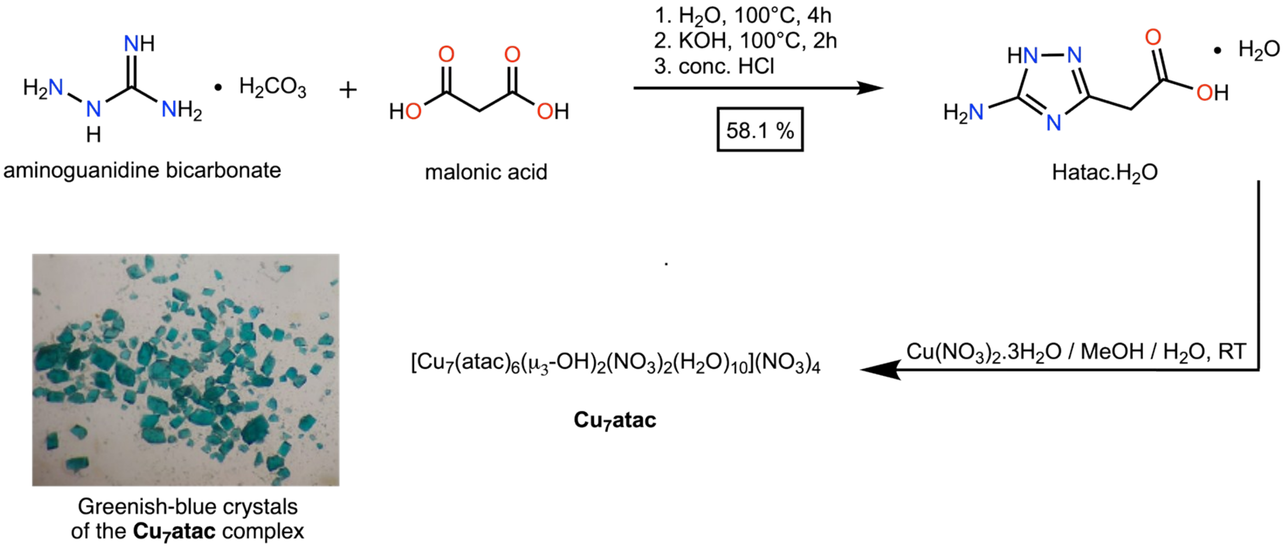


Table S1. Crystal data and structure refinement for the zwitterionic form of the amino acid ligand Hatac and the heptanuclear **Cu_7atac**.

Compound	**Ligand**	**Cu_7atac**
Empirical formula	$C_4H_6N_4O_2.H_2O$	$[Cu_{3.5}(atac)_3(\mu_3\text{-}OH)(NO_3)(H_2O)_5](NO_3)_2$
Formula weight	160.14	938.87
Temperature/K	293(2)	293(2)
Crystal system	Tetragonal	Triclinic
Space group	$P4_3$	$P\bar{1}$
Unit cell dimensions	$a = 5.0341(7)$ Å	11.1571(3)
	$b = 5.0341(7)$ Å	11.6296(4)
	$c = 27.005(5)$ Å	13.2772(3)
	$\alpha = \beta = \gamma = 90°$	$\alpha = 109.647(1)$; $\beta = 105.502(1)$; $\gamma = 102.936(1)$
Volume/Å^3	684.4(2)	1467.04(8)
Z	4	2
ρ calc./g cm^{-3}	1.554	2.147
μ/mm^{-1}	0.13	2.626
$F(000)$	336.00	945.0
Crystal size/mm^{-3}	-	0.337x0.324x0.213
Theta range for data collection	5.052 to 27.511 °	2.83 to 26.01 °
Index ranges	-4 =< h =< 6, -6 =< k =< 5, -27 =< l =< 35,	-4 =< h =< 6, -6 =< k =< 5, -27 =< l =< 35
Reflections collected	6726	17404
Independent reflections	6796 [R(int) = 0.0367, R(sigma) = 0.0354]	5320 [R(int) = 0.0249, R(sigma) = 0.0246]
Data/restraints/ parameters	1457/6/125	5320/36/514
Goof = S	1.046	1.019
Final R indexes [I $\geq 2\sigma$ (I)]	$R_1 = 0.0342$, w$R_2 = 0.0621$	$R_1 = 0.0306$, w$R_2 = 0.0785$
Final R indexes [all data]	$R_1 = 0.0519$, w$R_2 = 0.0574$	$R_1 = 0.0412$, w$R_2 = 0.0846$

Structural Description of the amino acid ligand Hatac. Crystal data and structural refinement of the ligand are shown in Table S1. The bond distances, angles, torsion angles, and the most relevant supramolecular interactions are summarized in Tables S2-S5. The structural refinement suggests the ligand Hatac crystallises in its *zwitterionic* form in the tetragonal space group $P4_3$ with 4 molecules per unit cell (Table S1 and Fig. S1). The structure shows two *synthons* stabilised by three types of hydrogen bonds numbered as I, II and III (Fig. S2b). The hydrogen bond I (N4–H5···O1) is formed between the hydrogen atom of the amino group of the triazole ring and the oxygen atom from an adjacent molecule with H5···O1 distance of 2.09(3) Å (Fig. S2b and Table S5). Hydrogen bonds II (N1–H1···O1) and III (N1–H1···O2) result bifurcated (three-centred) hydrogen bonds between the hydrogen atom (H1) (Fig. S2b). The interactions I and II are responsible for $R_2^1(6)$ supramolecular *synthon* (highlighted in blue), while II and III are responsible for $R_1^2(4)$ supramolecular *synthon* (highlighted in grey) (Fig. S2b and Table S5). The hydration water molecules are able to form three types of hydrogen bonds indicated as IV (N3–H3···O3), V (O3–H3W···N2), and VI (O3–H4W···O1) (Fig. S2b, S2c and Table S5). These interactions contribute to the extended supramolecular network of the amino acid ligand shown in Fig. S2d.

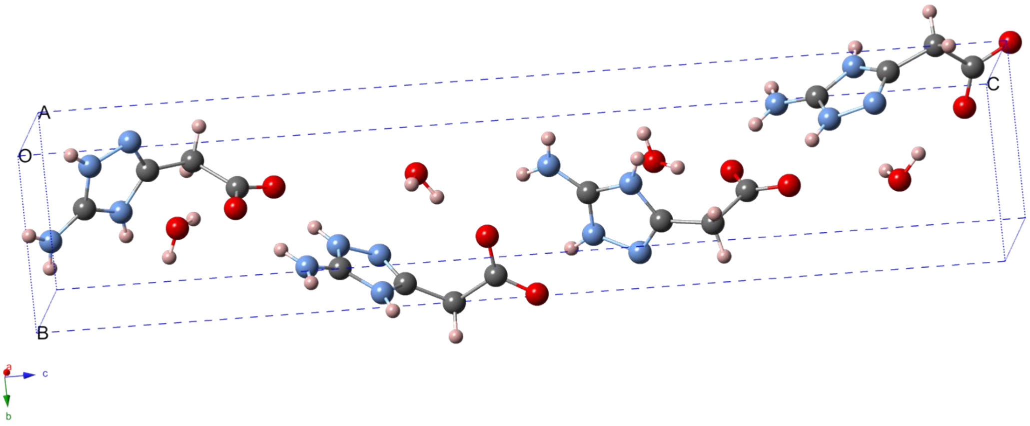
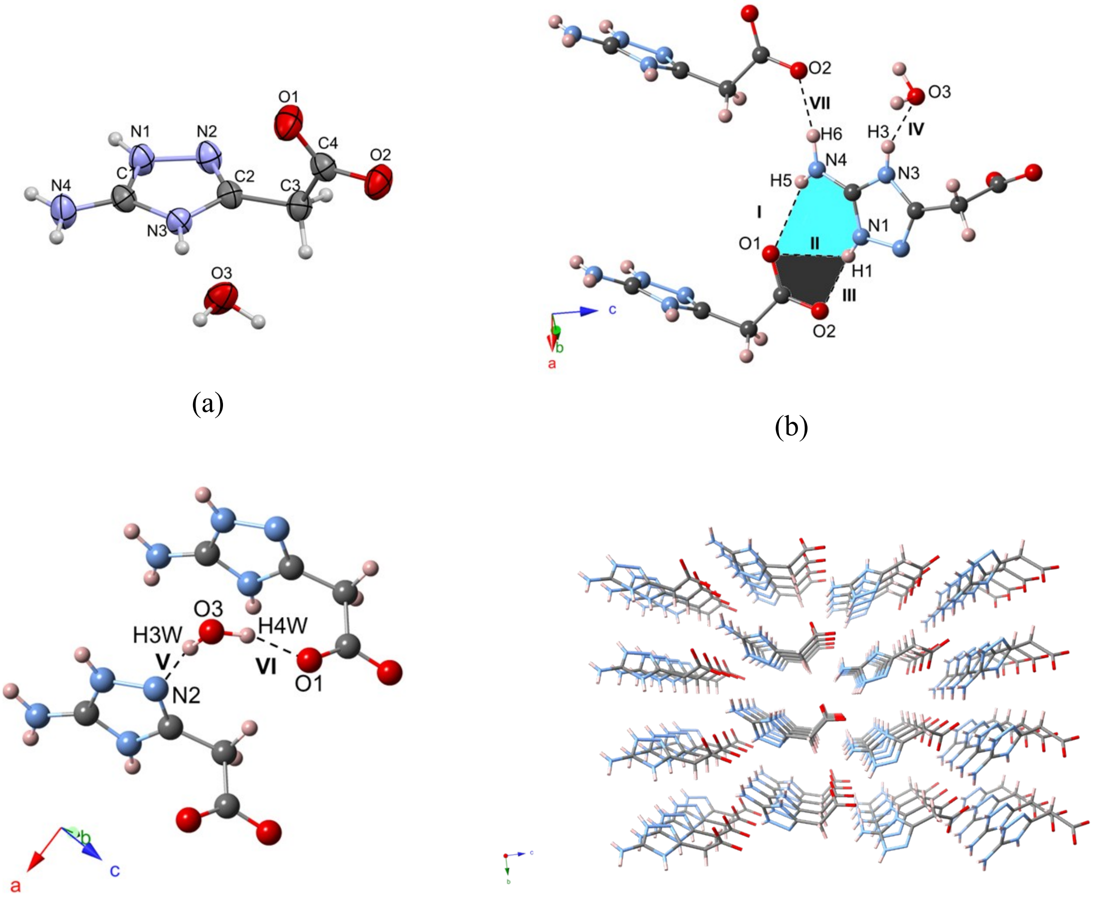


Fig. S1. Unit cell of the amino acid ligand Hatac Hatac.H_2O.



(a)

(b)

(c)

(d)

Fig. S2. (a) ORTEP representation of the amino acid ligand Hatac in its zwitterionic form; (b) representation of its supramolecular interactions and synthons; (c) the main hydrogen bonds and (d) the supramolecular network.

Table S2. Bond distances (Å) for the zwitterionic form of the amino acid ligand Hatac.H_2O.

O3-H4W	0.94(3)	O2-C4	1.253(3)
O3-H3W	0.94(3)	N3-C1	1.346(3)
H3-N3	0.90(4)	N3-C2	1.369(3)
H6-N4	0.82(3)	N4-C1	1.323(4)
H1-N1	0.94(3)	N1-C1	1.326(3)
H5-N4	1.00(3)	C3-H3A	0.97
O1- C4	1.249(3)	C3-H3B	0.97
N2-N1	1.386(3)	C3-C4	1.526(4)
N2-C2	1.291(3)	C3-C2	1.489(4)

Symmetry transformations used to generate equivalent atoms:
i = x, y, z; ii = - x, - y, 1/2 + z; iii = - y, x, 3/4 + z; iv = y, - x, 1/4 + z

Table S3. Bond angles (°) for the zwitterionic form of the amino acid ligand Hatac.H_2O.

H4W-O3-H3W	106(2)	H3A-C3-C2	108.7
N1-N2-C2	105.0(2)	H3B-C3-C4	108.8
H3-N3-C1	128(2)	H3B-C3-C2	108.7
H3-N3-C2	124(2)	C4-C3-C2	114.0(2)
C1-N3-C2	107.1(2)	N3-C1-N4	127.5(2)
H6-N4-H5	124(3)	N3-C1-N1	106.4(2)
H6-N4-C1	120(2)	N4-C1-N1	126.1(2)
H5-N4-C1	116(2)	O1-C4-O2	124.2(2)
H1-N1-N2	121(2)	O1-C4-C3	119.4(2)
H1-N1-C1	128(2)	O2-C4-C3	116.4(2)
N2-N1-C1	110.5(2)	N2-C2-N3	111.0(2)
H3A-C3-H3B	107.7	N2-C2-C3	125.4(2)
H3A-C3-C4	108.8	N3-C2-C3	123.6(2)

Symmetry transformations used to generate equivalent atoms:
i = x, y, z; ii = - x, - y, 1/2 + z; iii = - y, x, 3/4 + z; iv = y, - x, 1/4 + z

Table S4. Torsion angles (°) for the zwitterionic form of the amino acid ligand Hatac.H_2O.

C2-N2-N1-H1	177(2)	H1-N1-C1-N3	-177(3)
C2-N2-N1-C1	0.0(3)	H1-N1-C1-N4	3(3)
N1-N2-C2-N3	0.2(3)	N2-N1-C1-N3	-0.2(3)
N1-N2-C2-C3	-177.6(2)	N2-N1-C1-N4	179.5(3)
H3-N3-C1-N4	10(3)	H3A-C3-C4-O1	110.6
H3-N3-C1-N1	-170(3)	H3A-C3-C4-O2	-68.9
C2-N3-C1-N4	-179.4(3)	H3B-C3-C4-O1	-132.4
C2-N3-C1-N1	0.3(3)	H3B-C3-C4-O2	48.2
H3-N3-C2-N2	170(3)	C2-C3-C4-O1	-10.9(3)
H3-N3-C2-C3	-12(3)	C2-C3-C4-O2	169.6(2)
C1-N3-C2-N2	-0.3(3)	H3A-C3-C2-N2	-21.1
C1-N3-C2-C3	177.5(2)	H3A-C3-C2-N3	161.4
H6-N4-C1-N3	1(2)	H3B-C3-C2-N2	-138
H6-N4-C1-N1	-179(2)	H3B-C3-C2-N3	44.5
H5-N4-C1-N3	178(2)	C4-C3-C2-N2	100.5(3)
H5-N4-C1-N1	-2(2)	C4-C3-C2-N3	-77.1(3)

Symmetry transformations used to generate equivalent atoms:
i = x, y, z; ii = - x, - y, 1/2 + z; iii = - y, x, 3/4 + z; iv = y, - x, 1/4 + z

Table S5. Hydrogen bonds and short contacts of the zwitterionic form of amino acid ligand Hatac.H_2O (distances are given in Å and angles in °).

Type of interaction	*d* (*D*–H···*A*)	*d* (*D*–H)^{a}	*d* (H···*A*)^{b}	*d* (*D*···*A*)^{c}	Angle (*D*–H···*A*)
I	N4–H5···O1^{i}	1.00(3)	2.09(3)	2.990(3)	148(3)
II	N1–H1···O1^{i}	0.94(3)	2.36(3)	3.052(3)	130(2)
III	N1–H1···O2^{i}	0.94(3)	1.82(3)	2.739(3)	166(2)
IV	N3–H3···O3^{ii}	0.89(3)	1.81(3)	2.654(3)	158(3)
V	O3–H3W···N2^{iii}	0.94(3)	1.84(2)	2.770(3)	170(3)
VI	O3–H4W···O1	0.94(2)	1.77(2)	2.691(3)	165(2)

Symmetry codes for: (i) 1-y,x,-1/4+z; (ii) -1+x,y,z; (iii) x,1+y,z; (iv) -y,1+x,-1/4+z

[a] Distance between the donor atom and the hydrogen atom.

[b] Distance between the acceptor atom and the hydrogen atom.

[c] Distance between the donor atom and the acceptor atom.

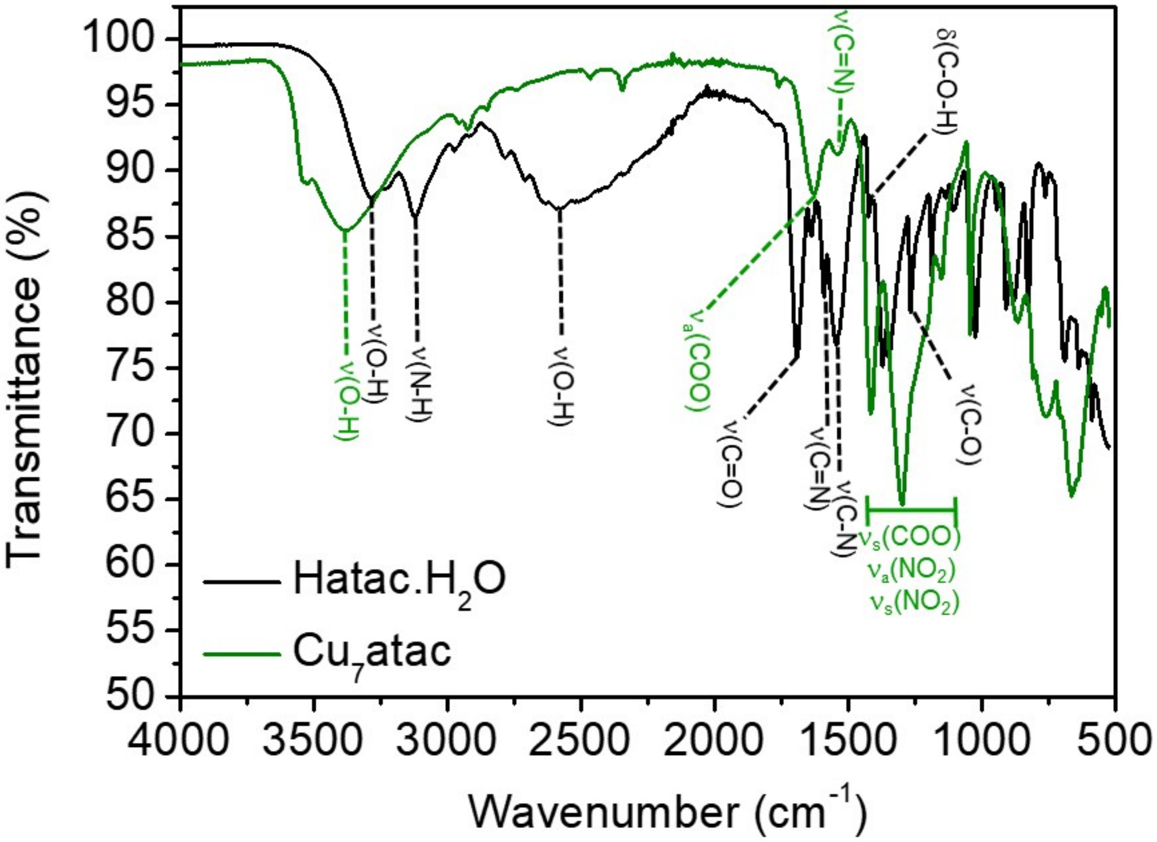
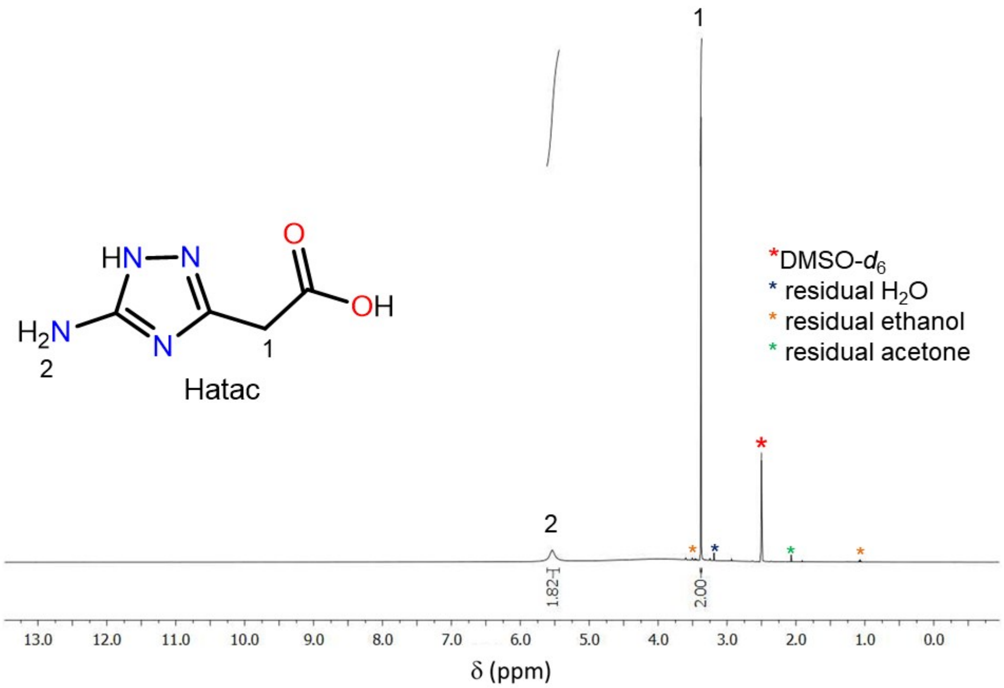


Fig. S3. ATR-FTIR spectra of the amino acid ligand Hatac.H_2O and **Cu_7atac** complex.

Table S6. Assignments of the main ATR-FTIR bands of the amino acid ligand Hatac.H_2O and the **Cu_7atac** complex.

Hatac.H_2O (cm^{-1}) ^{1}	**Cu_7atac (cm^{-1})^2**	**Assignments**
3284	3383	ν(O-H)
3121	-	ν(N-H)
2584	-	ν(O-H)
1691	-	ν(C=O)
1638	-	$\sigma(NH_2)$
1424	-	δ(C-O-H)
1591	1541	ν(C=N)
1544	-	ν(C-N)
1267	-	ν(C-O)
-	1630	ν_a(COO)
-	1446-1125	ν_s(COO), $\nu_a(NO_2)$ and $\nu_s(NO_2)$

(a)


1
*DMSO-d_6
* residual H_2O
* residual ethanol
* residual acetone
HN
N
O
OH
H_2N
N
2
1
Hatac
*
2
1.82
2.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

(b)

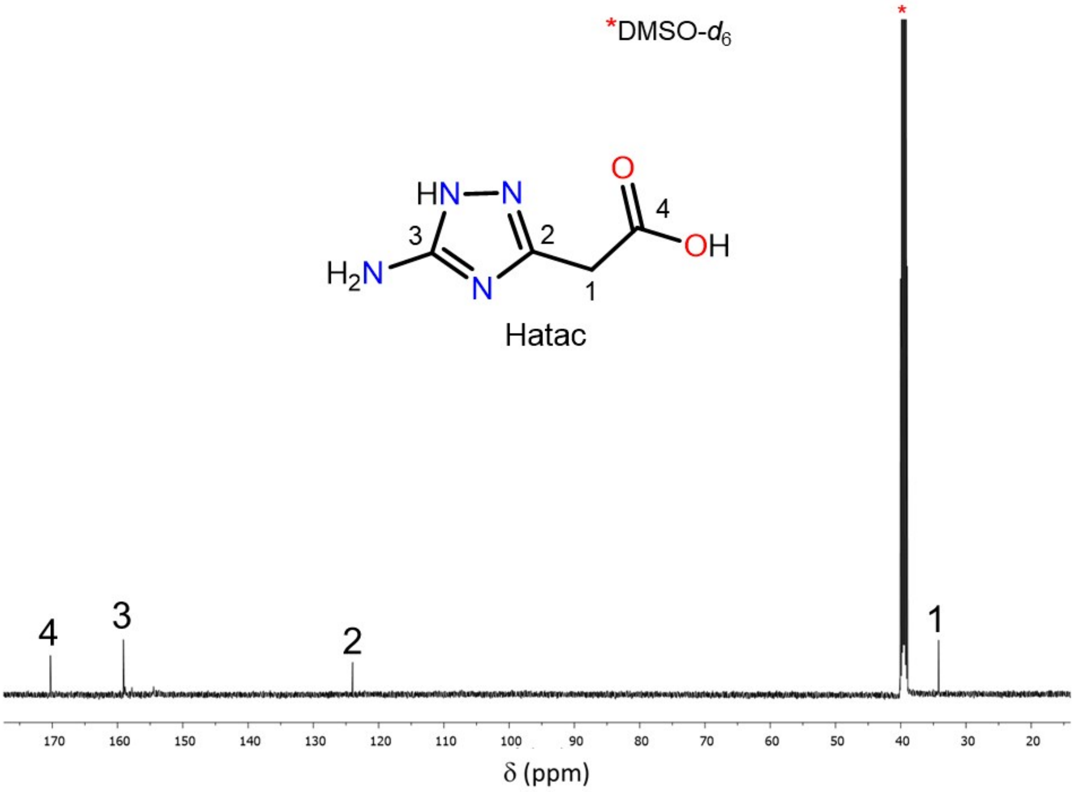

*DMSO-d_6
*
HN
N
O
4
OH
3
2
H_2N
N
1
Hatac
4
3
2
1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
δ (ppm)

Fig. S4. (a) ^1H NMR (298 K, 500 MHz, DMSO-d_6) and (b) ^{13}C NMR (298 K, 125 MHz, DMSO-d_6) of the amino acid ligand.

In the ^1H NMR (Fig. S4a) spectrum of the amino acid ligand, the absence of the signals related to carboxyl group (COOH) and N-H from the triazol ring can be related to deuterium exchange of these labile protons in DMSO-d_6 containing residual D_2O and H_2O. We added molecular sieves to DMSO-d_6 to remove the water, but the exchange was still observed in the ^1H NMR spectrum because the ligand contains one water molecule in its structure. ^{13}C NMR spectrum showed all expected signals for the ligand (Fig. S4b) and elemental analysis confirmed the purity of the ligand (calculated for $C_4H_6N_4O_2.H_2O$ was C, 30.00 %; H, 5.04 %; N, 34.99 %; and experimentally found was C, 29.90 %; H 5.07 %; N 34.80 %).

Table S7. Selected bond distances (Å) for the **Cu$_7$atac** complex.

Cu1-O5	1.958(2)	Cu4-O4	2.122(3)
Cu1-O7	2.001(2)	Cu4-O16	1.952(2)
Cu1-O8	2.411(2)	Cu4-O18A	2.435(13)
Cu1-N5	1.966(3)	Cu4-O19	2.098(15)
Cu1-N9	1.940(3)	Cu4-O4^i	2.122(3)
Cu1-O20A	2.703(9)	Cu4-O16^i	1.952(2)
Cu2-O3	2.000(3)	Cu4-O18A^i	2.435(13)
Cu2-O7	2.017(2)	Cu4-O19^i	2.098(15)
Cu2-O9	2.251(3)	Cu4-O4	2.122(3)
Cu2-N1	1.977(3)	Cu4-O16	1.952(2)
Cu2-N6	1.948(3)	Cu4-O18A	2.435(13)
Cu3-O2	1.947(3)	Cu4-O19	2.098(15)
Cu3-O7	1.997(2)	Cu4-O4^i	2.122(3)
Cu3-O17	2.512(3)	Cu4-O16^i	1.952(2)
Cu3 N2	1.941(3)	Cu4-O18A^i	2.435(13)
Cu3-N10	1.968(3)	Cu4-O19^i	2.098(15)

Symmetry transformations used to generate equivalent atoms: i = -x-1, -y, -z

Table S8. Selected bond angles (°) for the **Cu$_7$atac** complex.

O5-Cu1-N9	89.48(12)	O4-Cu4-O16	87.99(11)
O7-Cu1-O8	91.14(9)	O4-Cu4-O18A	81.7(3)
O7-Cu1-N9	88.88(11)	O4-Cu4-O4^{i}	180
O8-Cu1-N5	87.51(11)	O4-Cu4-O16^{i}	92.01(11)
O8-Cu1-N9	92.92(12)	O4-Cu4-O18A^{i}	98.3(3)
N5-Cu1-N9	178.38(12)	O4-Cu4-O19^{i}	101.3(4)
O3-Cu2-O7	159.67(12)	O16-Cu4-O18A	98.7(3)
O3-Cu2-N1	92.35(13)	O4^{i}-Cu4-O16	92.01(11)
O3-Cu2-N6	89.37(13)	O16-Cu4-O16^{i}	180
O7-Cu2-O9	100.81(11)	O16Cu4O18A ^{i}	81.3(3)
O7-Cu2-N1	88.39(12)	O16-Cu4-O19^{i}	92.7(4)
O7-Cu2-N6	87.93(12)	O4^{i}-Cu4-O18A	98.3(3)
O9-Cu2-N1	91.19(12)	O16^{i}-Cu4-O18A	81.3(3)
O9-Cu2-N6	94.39(12)	O18A-Cu4-O18A^{i}	180
N1-Cu2-N6	173.81(14)	O4^{i}-Cu4-O19	101.3(4)
O2-Cu3-O7	174.72(11)	O16^{i}-Cu4-O19	92.7(4)
O2-Cu3-O17	89.09(11)	O19-Cu4-O19^{i}	180
O2-Cu3-N2	90.11(13)	O4^{i}-Cu4-O16^{i}	87.99(11)
O2-Cu3-N10	91.56(13)	O4^{i}-Cu4-O18A^{i}	81.7(3)
O7-Cu3-O17	96.01(9)	O4^{i}-Cu4-O19^{i}	78.7(4)
O7-Cu3-N2	88.12(11)	O16^{i}-Cu4-O18A^{i}	98.7(3)
O7-Cu3-N10	90.09(11)	O16^{i}-Cu4-O19^{i}	87.4(4)

Symmetry transformations used to generate equivalent atoms: i = -x-1, -y, -z

Table S9. Selected torsion angles (°) for the **Cu$_7$atac** complex.

O8-Cu1-O5-C11	103.4(3)	O3-Cu2-N6-N5	-166.8(3)
N5-Cu1-O5-C11	-169.0(3)	O7-Cu2-N6-C6	166.1(3)
O8-Cu1-O7-Cu2	66.27(13)	O9-Cu2-N6-C6	-93.2(3)
O8-Cu1-O7-Cu3	-75.32(12)	O17-Cu3-O2-C3	106.8(4)
N5-Cu1-O7-Cu3	-162.82(14)	N10-Cu3-O2-C3	-166.4(4)
N9-Cu1-O7-Cu2	159.17(15)	O17-Cu3-O7-Cu1	67.93(14)
O5-Cu1-N5-N6	-168.7(3)	O17-Cu3-O7-Cu2	-73.75(13)
O7-Cu1-N5-C5	-165.5(4)	N2-Cu3-O7-Cu1	162.37(14)
O8-Cu1-N5-N6	-74.4(3)	N10-Cu3-O7-Cu2	-160.63(14)
O8-Cu1-N5-C5	103.3(4)	O2-Cu3-N2-N1	179.2(3)
O5-Cu1-N9-N10	176.5(3)	O7-Cu3-N2-C2	166.1(4)
O7-Cu1-N9-C10	170.4(3)	O17-Cu3-N2-N1	90.1(3)
O8-Cu1-N9-N10	82.2(3)	O17-Cu3-N2-C2	-98.1(4)
O8-Cu1-N9-C10	-98.5(3)	O2-Cu3-N10-N9	-171.8(3)
O3-Cu2-O7-Cu1	101.0(3)	O7-Cu3-N10-C9	-170.6(4)
O3-Cu2-O7-Cu3	-117.5(3)	O17-Cu3-N10-N9	-82.8(3)
N6-Cu2-O7-Cu3	159.95(14)	O17-Cu3-N10-C9	93.4(4)
O3-Cu2-N1-N2	-179.1(3)	O16-Cu4-O4-C7	122.4(4)
O7-Cu2-N1-C1	-166.5(4)	O18A-Cu4-O4-C7	-138.5(5)

O9-Cu2-N1-N2	-79.5(3)	O16^{i}-Cu4-O4-C7	-57.6(4)
O9-Cu2-N1-C1	92.7(4)	O18A^{i}-Cu4-O4-C7	41.5(5)

Symmetry transformations used to generate equivalent atoms: i = -x-1, -y, -z

Table S10. Hydrogen bonds and short contacts in **Cu$_7$atac** complex (distances are given in Å and angles in °).

Type of interaction	*d* (*D*–H···*A*)	*d* (*D*–H)[a]	*d* (H···*A*)[b]	*d* (*D*···*A*)[c]	Angle (*D*–H···*A*)
I	N8–H8A···O5	0.86	2.17	2.861(4)	137
II	N12–H12A···O2	0.86	2.08	2.796(5)	140
III	N4–H4B···O3	0.86	2.13	2.859(4)	142
IV	O17–H17A···O1^{iv}	0.82	2.03	2.847(5)	167
V	O8–H8E···O6^{ii}	0.87	1.87	2.719(4)	164
VI	O16–H16B···O6^{i}	0.86	1.81	2.651(4)	166

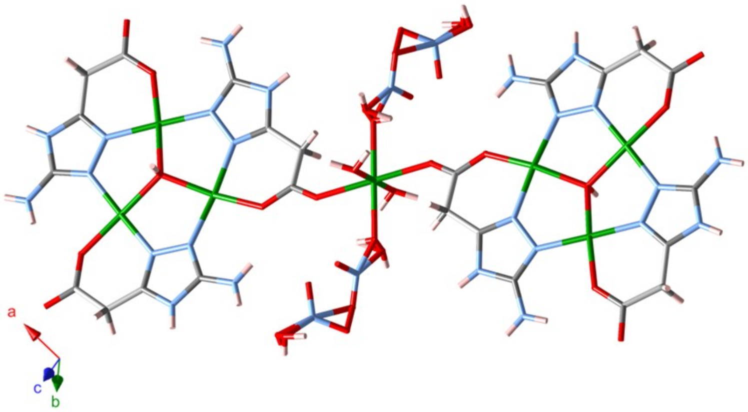
Symmetry codes for: (i) -x,-y,-z; (ii) 1-x,1-y,-z; (iii) -x,1-y,-z; (iv) 1-x,2-y,1-z; (v) -x,1-y,1-z

[a] Distance between the donor atom and the hydrogen atom.

[b] Distance between the acceptor atom and the hydrogen atom.

[c] Distance between the donor atom and the acceptor atom.

(a)



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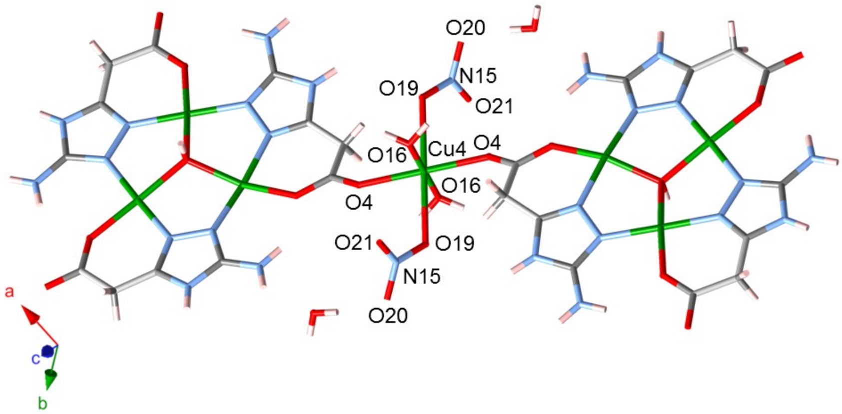


(c)

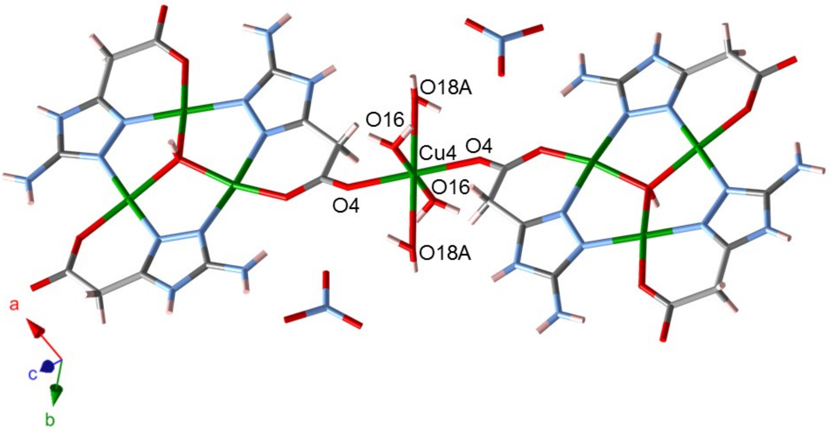


Fig. S5. Structural representation of **Cu₇atac** complex in which is shown (a) all disordered molecules superposed around Cu4; (b) one group of disordered molecules around Cu4 and (c) another group of disordered molecules around Cu4.

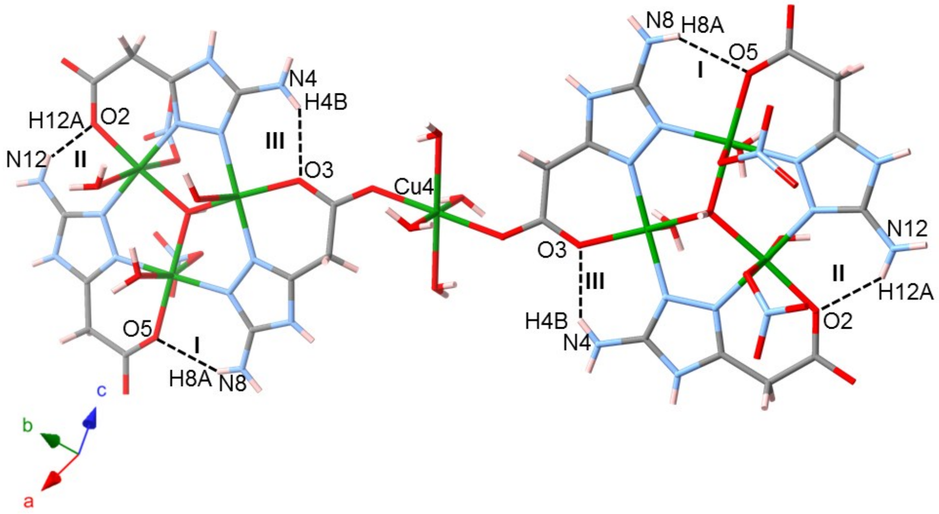


Fig. S6. Hydrogen bonds I (N8–H8A···O5), II (N12–H12A···O2) and III (N4–H4B···O3) in the triangular subunits of the **Cu_7atac** complex.

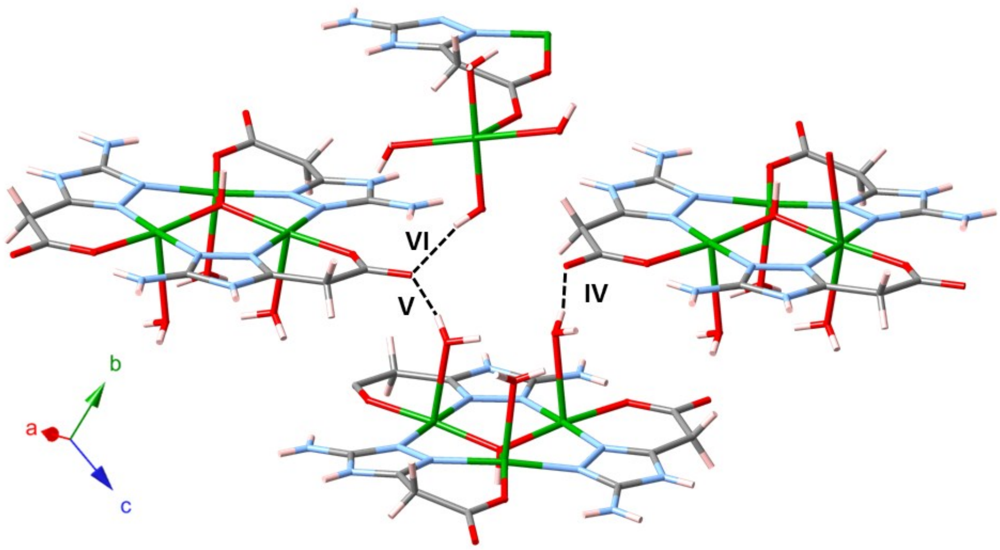


Fig. S7. Supramolecular interactions IV (O17–H17A···O1), V (O8–H8E···O6) and VI (O16–H16B···O6) between discrete units of the **Cu_7atac** complex.

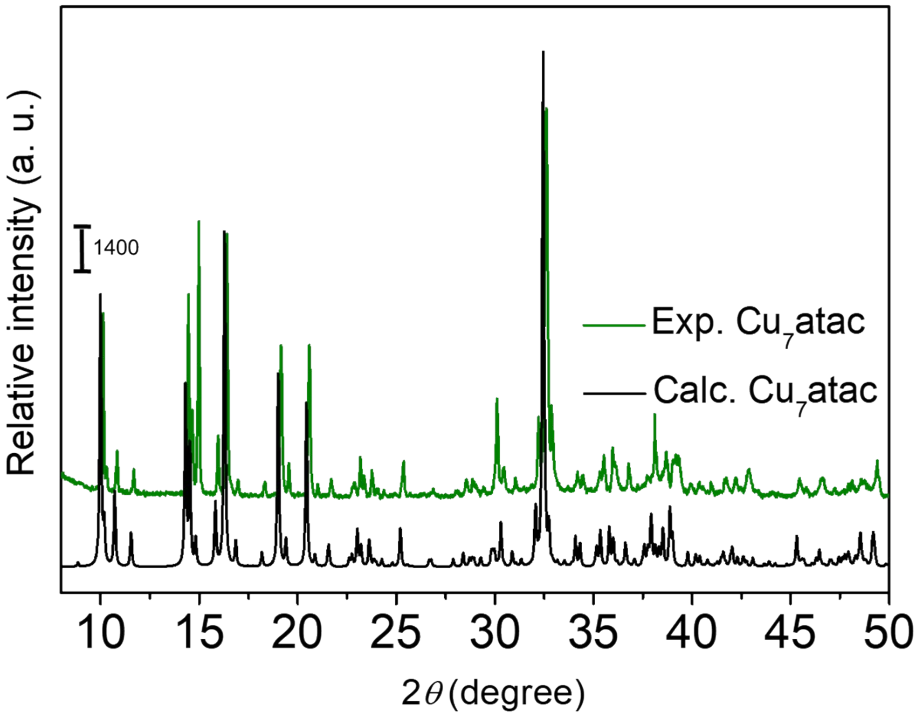
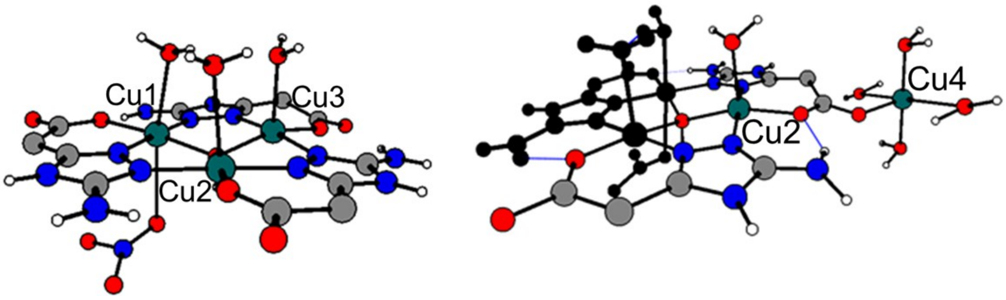


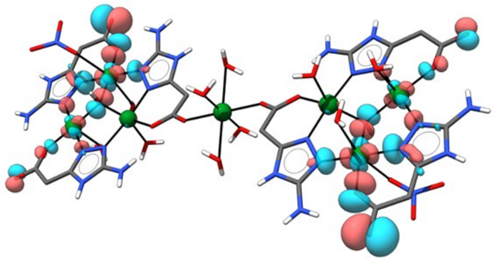
Fig. S8. Calculated PXRD pattern obtained from single crystal X-ray diffraction data of the **Cu_7atac** complex (Calc.) compared to the experimental pattern of the polycrystalline sample of **Cu_7atac** complex (Exp.).



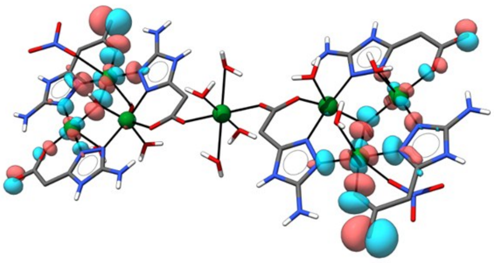
(a) Fragment A

(b) Fragment B

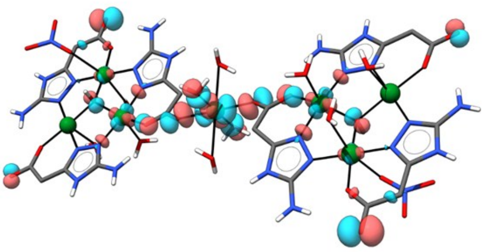
Fig. S9. (a) Representation of the fragment A containing the triangular unit with a nitrate coordinated to Cu1. (b) Fragment B is representative of the coupling between Cu4 and Cu2 on the triangle (atoms in black are not taken into account for this coupling). The colors for the atoms are: grey = C, red = O, blue = N, olive = Cu, white = H.



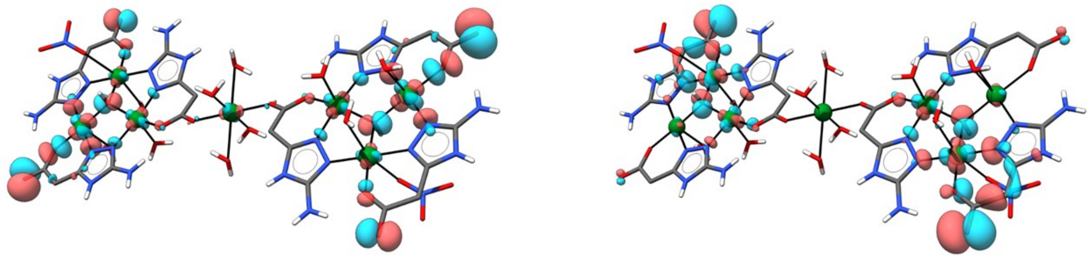
SOMO



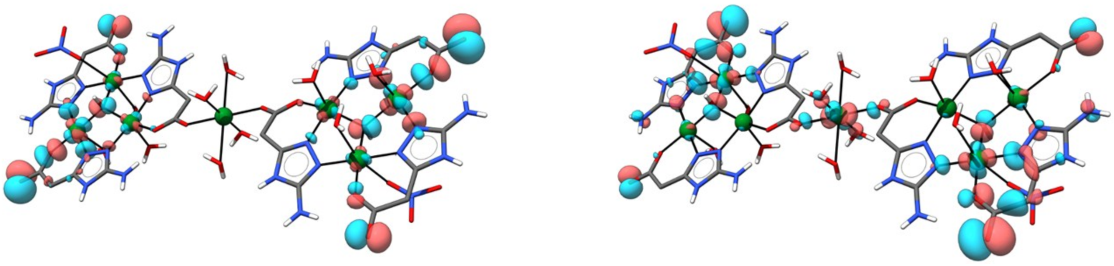
SOMO-1



SOMO-4

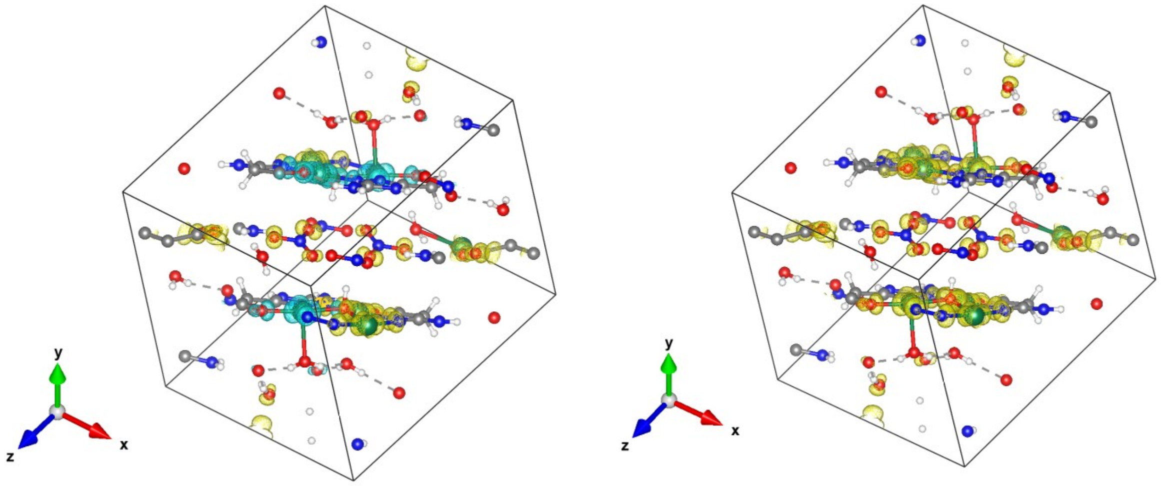


SOMO-2 SOMO-5



SOMO-3 SOMO-6

Fig. S10. Representation of the seven magnetic orbitals in **Cu_7atac** complex with isosurface cutoff σ = 0.03 e/Bohr^3.



(a) (b)

Fig. S11. Spin moment in the unit cell of the **Cu_7atac** complex for (a) doublet state (E_{BS}) and (b) octet state (E_{HS}). Atoms are represented by CPK color scheme: grey = C, red = O, blue = N, olive = Cu, white = H, yellow = up spin density, blue = down spin density.

Table S11. Spin moment values calculated for the doublet and octet states of the **Cu$_7$atac** complex.

Duplet state					
Spin Density					
Trimer -1					
Cu1	**O7**	**N29**	**O31**	**N67**	**O142**
-0.63153	-0.07924	-0.09106	-0.06881	-0.06881	0.03051
Cu3	**O37**	**N47**	**O31**	**N49**	
0.6217	0.074627	0.073612	-0.08631	0.085928	
Cu5	**O39**	**N53**	**O31**	**N57**	**O149**
-0.62093	-0.10682	-0.08731	-0.08631	-0.06869	0.071299
Trimer -2					
Cu2	**O8**	**N30**	**O32**	**N68**	**N143**
-0.62005	-0.07875	-0.09046	0.066509	-0.06722	0.031428
Cu4	**O38**	**N48**	**O32**	**N50**	
0.632931	0.076781	0.075897	0.066509	0.08732	
Cu6	**O40**	**N54**	**O32**	**N58**	**O148**
0.619325	0.105808	0.084811	0.066509	0.069044	0.074212
Central Cu(II)-Cu4					
Cu7	**O132**	**O133**	**O134**	**O135**	
0.496101	0.048604	0.049063	0.044054	0.043256	
Octet state					
Spin Density					
Trimer -1					
Cu1	**O7**	**N29**	**O31**	**N67**	**N142**
0.6419	0.080964	0.09229	0.069347	0.069347	0.041565
Cu3	**O37**	**N47**	**O31**	**N49**	
0.647406	0.077712	0.077345	0.254644	0.085928	
Cu5	**O39**	**N53**	**O31**	**N57**	**N149**
0.633903	0.10946	0.086677	0.254644	0.070255	0.076411
Trimer -2					
Cu2	**O8**	**N30**	**O32**	**N68**	**N143**
0.641901	0.080964	0.09229	0.254643	0.069347	0.041558
Cu4	**O38**	**N48**	**O32**	**N50**	
0.647409	0.077711	0,077346	0.254643	0.085928	
Cu6	**O40**	**N54**	**O32**	**N58**	**N148**
0.633903	0.109461	0.086677	0.254643	0.070255	0.076413
Central Cu(II)-Cu4					

Cu7	**O132**	**O133**	**O134**	**O135**
0.504362	0.050546	0.050546	0.042332	0.042332

Reference

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2. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, New Jersey, 6th ed., **2009**.