Electronic Supplementary Information (ESI)

Tetranuclear copper(II) Cubane Complex Derived from Self-Assembled 1,3-Dimethyl-5-(*o*-phenolate-azo)-6-aminouracil: Structures, non-Covalent Interactions and Magnetic Property

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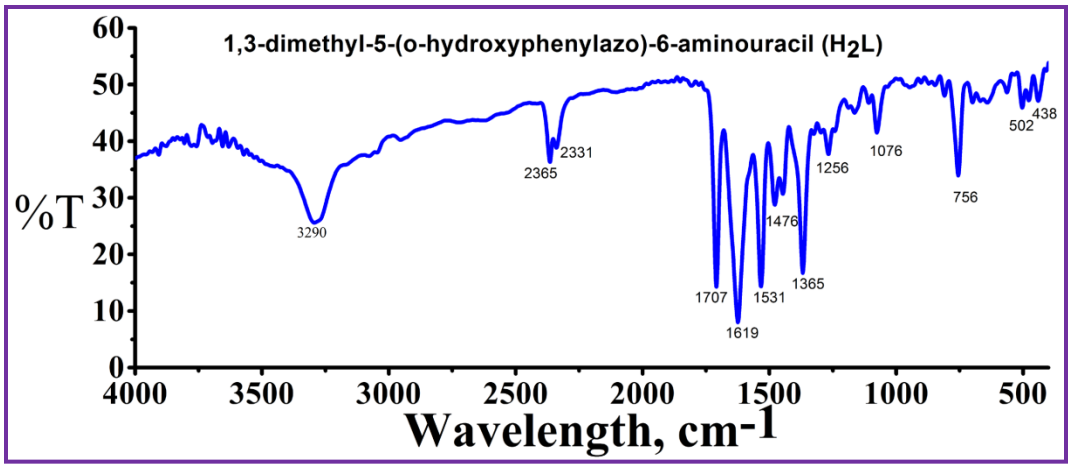


Figure S1. IR spectrum of H_2L, **1**

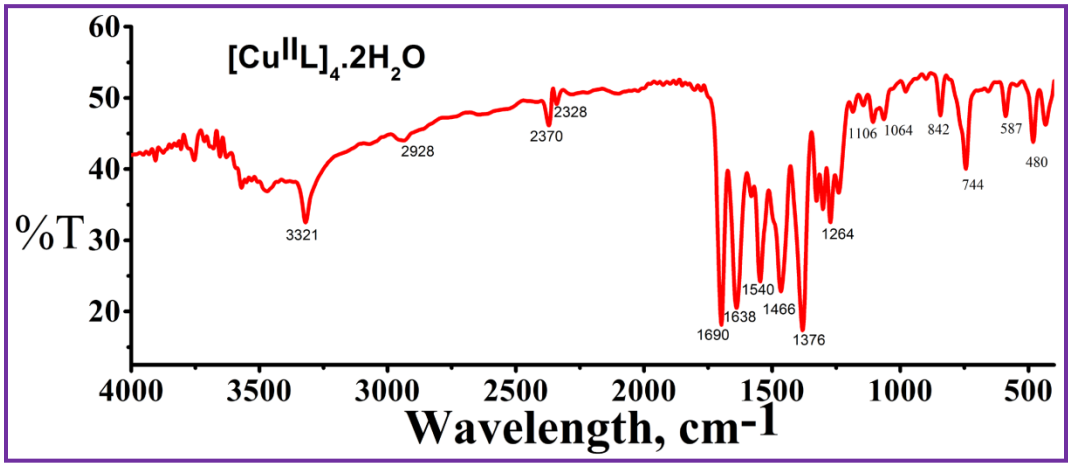


Figure S2. IR spectrum of $[Cu^{II}L]_4\ 2H_2O$, **2**

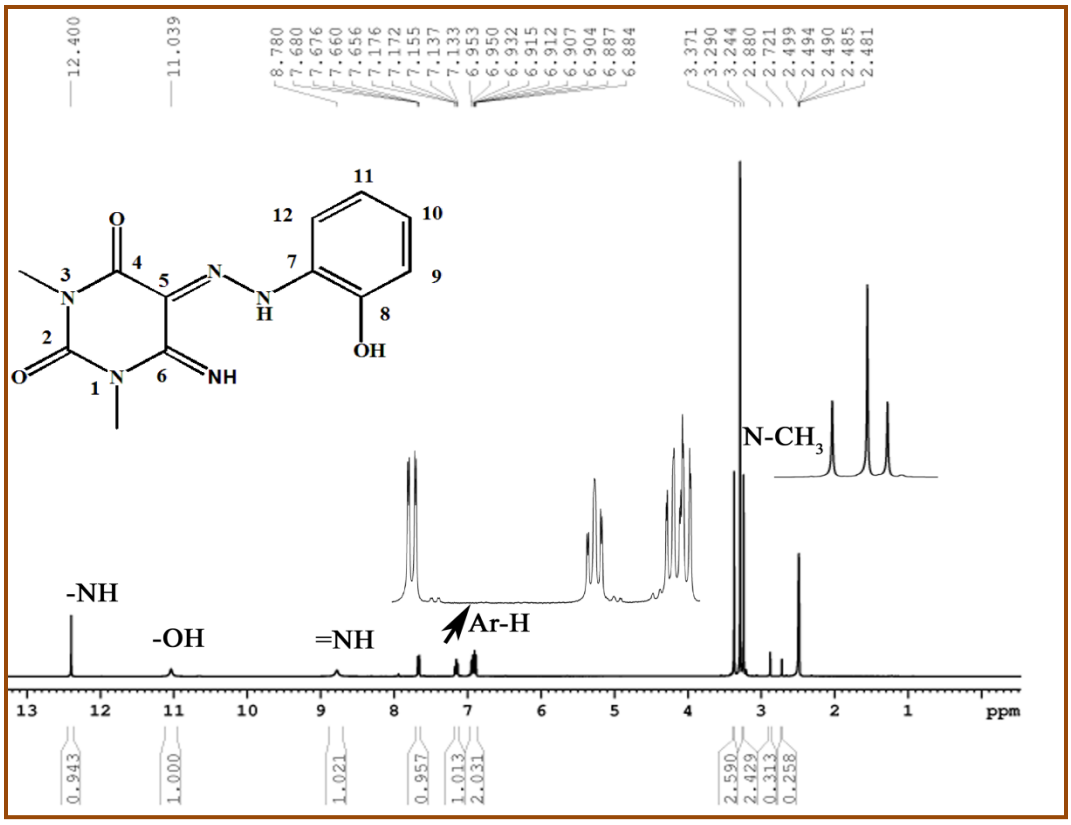


Figure S3. ^{1}H NMR spectrum of H_2L, **1**

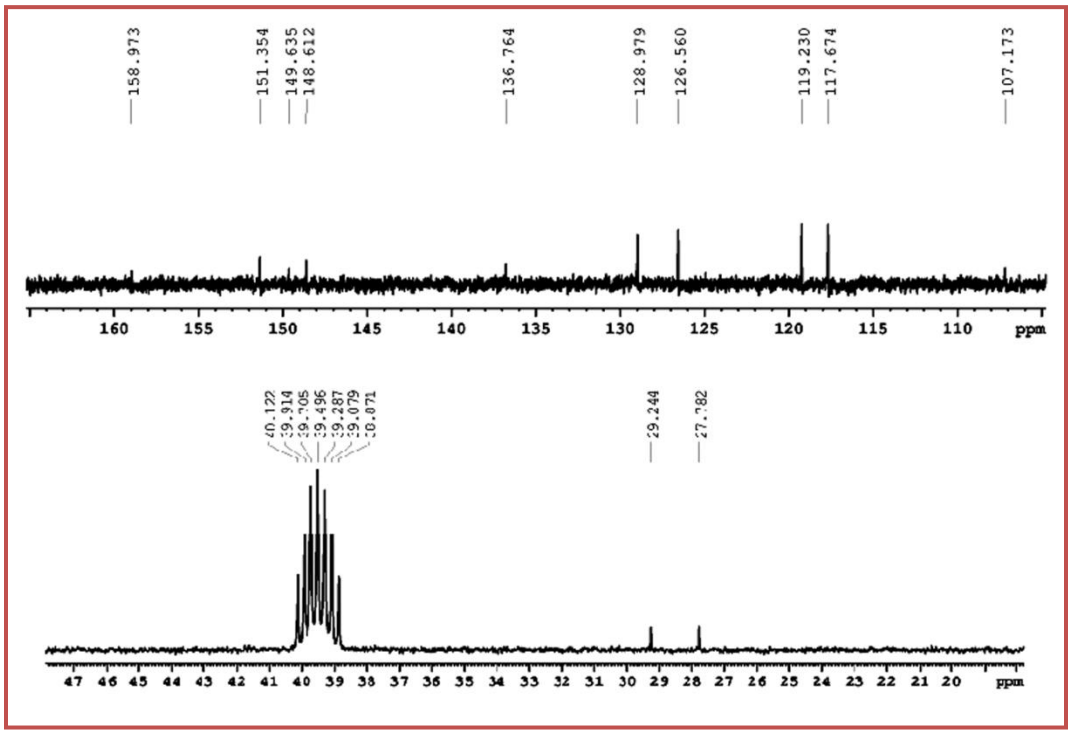
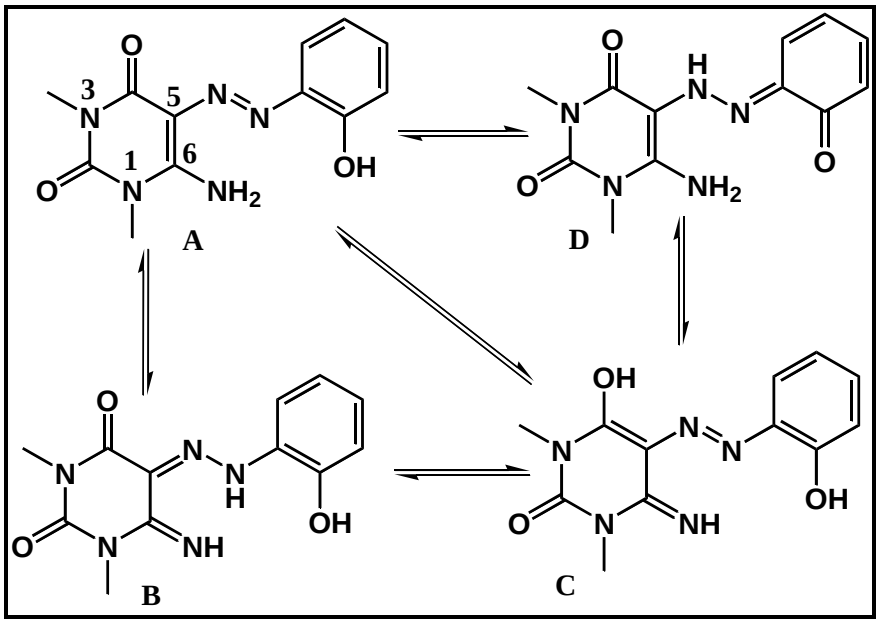


Figure S4. ^{13}C NMR spectrum of H_2L, **1**



Scheme S1. Possible tautomeric forms of H_2L

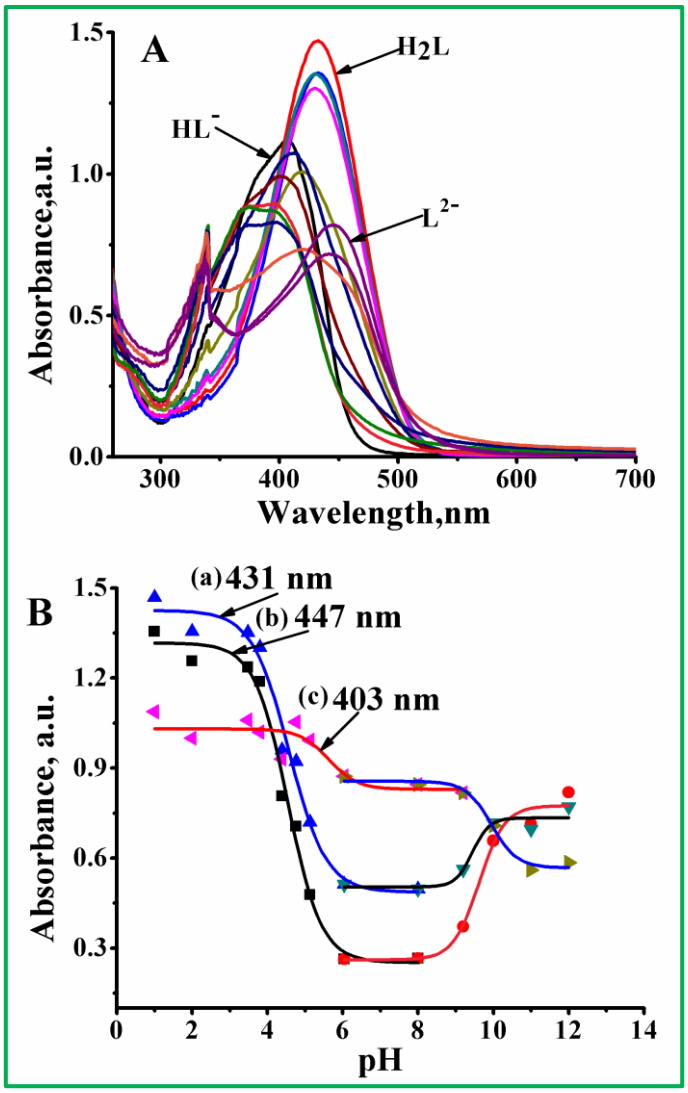


Figure S5. (**A**) UV-vis spectra of H_2L, 1 at different buffer solutions; (**B**) Plot of absorbance vs pH of different buffer solutions at (**a**) 431 nm, (**b**) 447 nm, and (**c**) 403 nm.

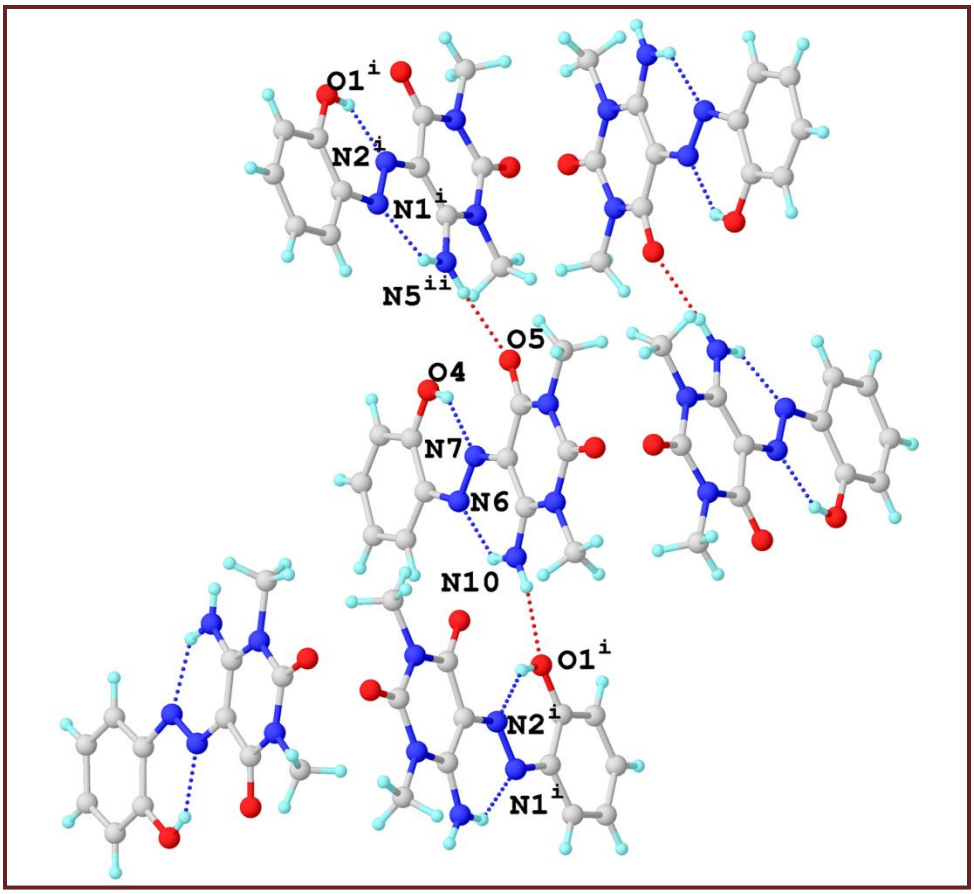


Figure S6. H-bonded network present in H_2L.

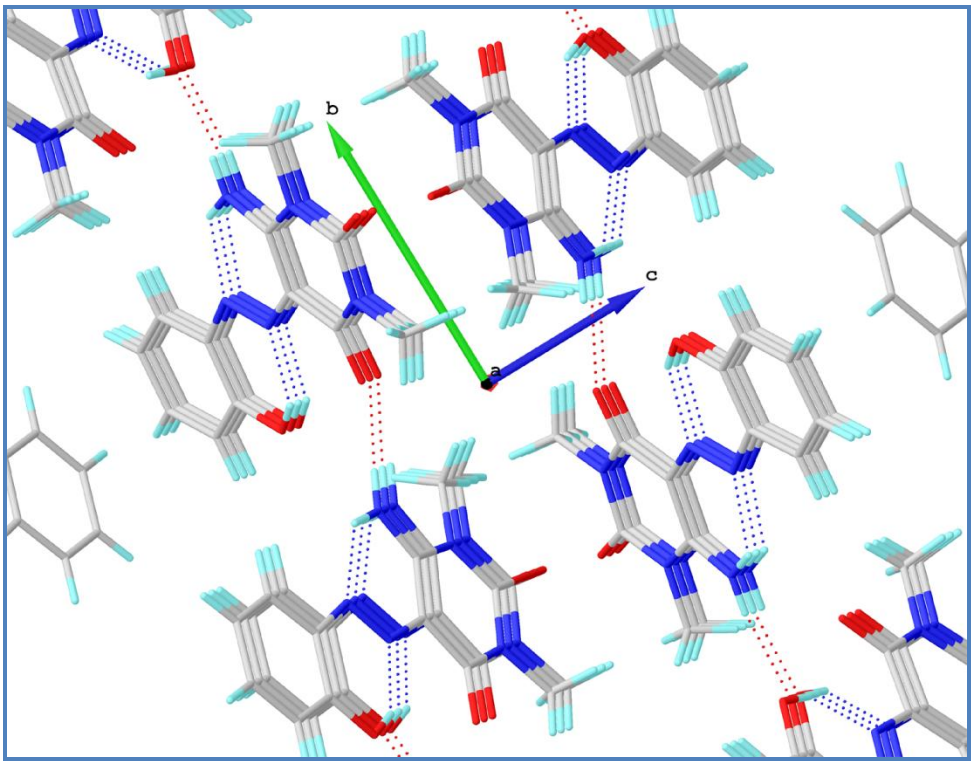


Figure S7. Stacking feature of H_2L.

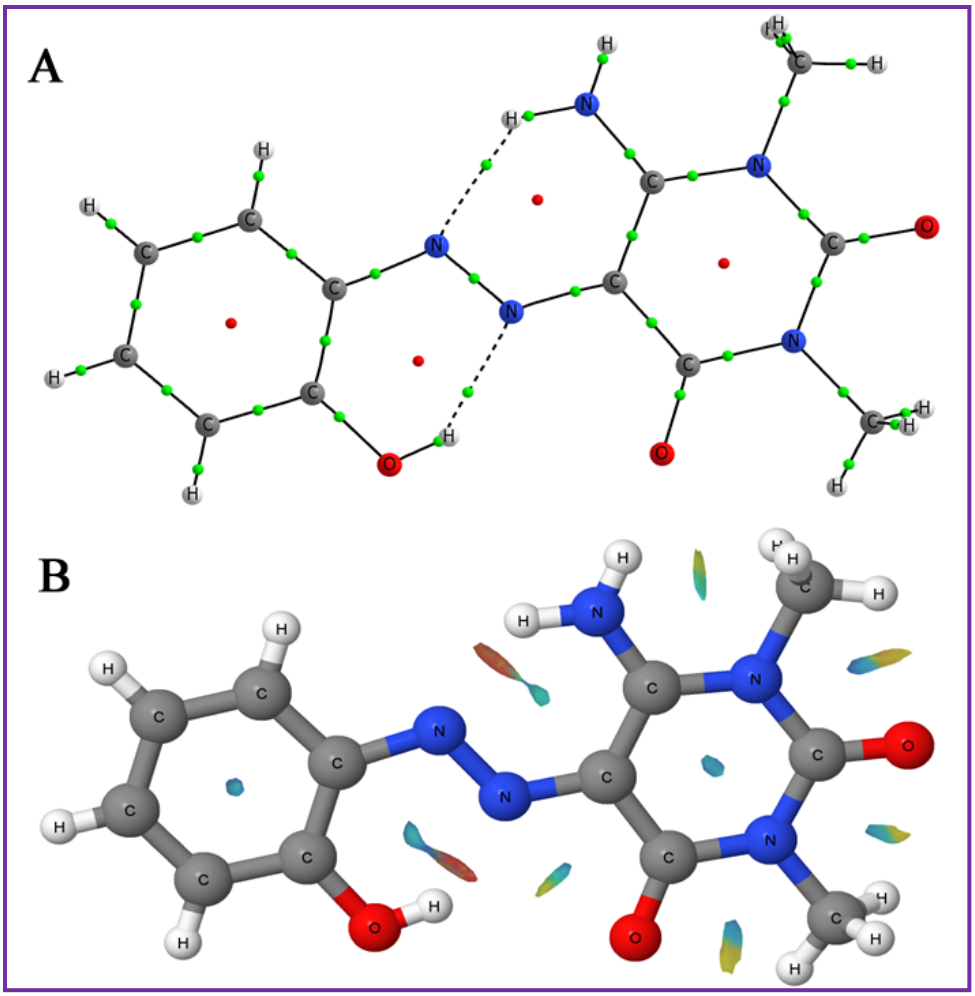


Figure S8. (**A**) AIM molecular graph and (**B**) NCI plot of the intramolecular interaction in the molecule, **1**. The green, red and blue dots in the molecular graph indicate the position of the bond, ring and cage critical points. The green colored isosurface of the NCIplot is an indication of moderate attractive interaction.

Table S1. pKa value of H_2L

H_2L		**Spectrophotometric Half-Height Method**			
pH	**λ_{max}, nm**	**pKa (at λ_{H2L} = 431 nm, hydrazo-phenol)**	**pKa (at λ_{HL^-} = 403 nm, hydrazo anion-phenol)**	**pKa (at $\lambda_{L^{2-}}$ = 447 nm, hydrazo-phenolic dianion)**	**pKa (Mean)**
1	431				
2	431				
3.48	430				
3.8	429	$pK_1 = 4.58$	$pK_1 = 5.60$	$pK_1 = 4.56$	$pK_1 = 4.91$
4.39	419				
4.76	413	and	and	and	and
5.13	403, 371				
6.04	396, 371	$pK_2 = 9.45$	$pK_2 = 9.96$	$pK_2 = 9.62$	$pK_2 = 9.68$
8	396, 371				
9.2	398, 371				
10	422				
11	444				
12	447				

Table S2. Bond lengths (Å) for H_2L.

Bond	**Length (Å)**	**Bond**	**Length (Å)**
C1-C6	1.396(2)	C1-N1	1.410(2)
C1-C2	1.415(2)	C2-O1	1.349(2)
C2-C3	1.392(2)	C3-C4	1.383(3)
C4-C5	1.385(3)	C5-C6	1.388(3)
C7-N2	1.365(2)	C7-C12	1.401(2)
C7-C8	1.446(2)	C8-O2	1.228(2)
C8-N3	1.396(2)	C9-N3	1.467(2)
C10-O3	1.212(2)	C10-N3	1.377(2)
C10-N4	1.393(2)	C11-N4	1.467(2)
C12-N5	1.325(2)	C12-N4	1.369(2)
C13-C18	1.403(2)	C13-N6	1.412(2)
C13-C14	1.413(2)	C14-O4	1.356(2)
C14-C15	1.395(2)	C15-C16	1.380(2)
C16-C17	1.392(3)	C17-C18	1.381(2)
C19-N7	1.366(2)	C19-C24	1.410(2)
C19-C20	1.433(2)	C20-O5	1.234(2)

C20-N8	1.390(2)	C21-N8	1.465(2)
C22-O6	1.212(2)	C22-N8	1.379(2)
C22-N9	1.395(2)	C23-N9	1.468(2)
C24-N10	1.323(2)	C24-N9	1.370(2)
N1-N2	1.2920(19)	N6-N7	1.2852(19)

Table S3. Bond angles (°) for H_2L.

Bond	**Angle (°)**	**Bond**	**Angle (°)**
C6-C1-N1	116.30(15)	C6-C1-C2	119.12(16)
N1-C1-C2	124.58(15)	O1-C2-C3	119.02(16)
O1-C2-C1	121.50(15)	C3-C2-C1	119.48(16)
C4-C3-C2	120.42(17)	C3-C4-C5	120.45(17)
C4-C5-C6	119.97(17)	C5-C6-C1	120.53(17)
N2-C7-C12	125.87(15)	N2-C7-C8	113.15(14)
C12-C7-C8	120.98(15)	O2-C8-N3	120.53(15)
O2-C8-C7	124.33(16)	N3-C8-C7	115.14(14)
O3-C10-N3	121.68(16)	O3-C10-N4	121.49(16)
N3-C10-N4	116.81(14)	N5-C12-N4	119.20(15)
N5-C12-C7	121.85(15)	N4-C12-C7	118.95(15)
C18-C13-N6	115.74(14)	C18-C13-C14	118.96(15)
N6-C13-C14	125.28(15)	O4-C14-C15	117.99(15)
O4-C14-C13	122.78(15)	C15-C14-C13	119.22(15)
C16-C15-C14	120.74(16)	C15-C16-C17	120.46(16)
C18-C17-C16	119.60(16)	C17-C18-C13	120.98(16)
N7-C19-C24	126.34(15)	N7-C19-C20	113.57(14)
C24-C19-C20	120.09(15)	O5-C20-N8	120.09(15)
O5-C20-C19	123.66(15)	N8-C20-C19	116.25(14)
O6-C22-N8	121.76(16)	O6-C22-N9	121.69(16)
N8-C22-N9	116.54(14)	N10-C24-N9	119.63(15)
N10-C24-C19	121.29(15)	N9-C24-C19	119.08(15)
N2-N1-C1	113.27(14)	N1-N2-C7	121.14(14)
C10-N3-C8	125.06(14)	C10-N3-C9	115.26(14)
C8-N3-C9	119.49(14)	C12-N4-C10	122.95(14)
C12-N4-C11	119.93(14)	C10-N4-C11	117.10(14)
N7-N6-C13	113.36(13)	N6-N7-C19	120.53(14)

C22-N8-C20	124.59(14)	C22-N8-C21	116.05(14)
C20-N8-C21	119.01(14)	C24-N9-C22	122.99(14)
C24-N9-C23	120.16(14)	C22-N9-C23	116.84(14)

Table S4. H-bond parameters present in H_2L

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N5H1…N1	0.936	1.927	2.668	134.446
O1H1…N2	0.841	1.763	2.491	143.803
O1H1… O2	0.841	2.658	3.378	144.553
N10H3…O2	0.841	2.951	4.084	115.817
N10H4…O1	0.841	2.016	2.844	168.316
N5H2…O5	0.885	1.966	2.834	166.34
N5H1…O4	0.839	2.819	4.634	124.453
N10H3…N6	0.972	1.924	2.667	131.241
O5H4… N7	2.701	1.836	2.676	69.302
O4H4…N7	0.839	1.836	2.549	11.746
O5H5…N5	0.885	1.965	2.834	166.364

Table S5. Bond lengths (Å) for $[Cu^{II}L]_4$ $2H_2O$.

Bond	**Length (Å)**	**Bond**	**Length (Å)**
Cu1-N5	1.900(4)	Cu1-N1	1.920(4)
Cu1-O1	1.940(3)	Cu1-O1	1.969(3)
C1-O1	1.347(6)	C1-C2	1.394(7)
C1-C6	1.403(6)	C2-C3	1.398(7)
C3-C4	1.386(7)	C4-C5	1.386(7)
C5-C6	1.396(6)	C6-N1	1.408(6)
C7-N2	1.337(6)	C7-C12	1.435(6)
C7-C8	1.465(6)	C8-O2	1.221(6)
C8-N3	1.393(7)	C9-N3	1.471(6)
C10-O3	1.199(6)	C10-N3	1.387(6)
C10-N4	1.393(6)	C11-N4	1.457(6)
C12-N5	1.306(6)	C12-N4	1.388(6)
N1-N2	1.282(5)	O1-Cu1	1.968(3)

Table S6. Bond angles (°) for $[Cu^{II}L]_4$ $2H_2O$.

Bond	Angle (°)	Bond	Angle (°)
N5-Cu1-N1	91.39(16)	N5-Cu1-O1	173.15(15)
N1-Cu1-O1	84.39(15)	N5-Cu1-O1	95.74(15)
N1-Cu1-O1	167.05(15)	O1-Cu1-O1	89.45(14)
O1-C1-C2	122.6(4)	O1-C1-C6	117.6(4)
C2-C1-C6	119.8(4)	C1-C2-C3	119.1(4)
C4-C3-C2	121.2(5)	C3-C4-C5	119.8(4)
C4-C5-C6	119.9(4)	C5-C6-C1	120.3(4)
C5-C6-N1	126.2(4)	C1-C6-N1	113.6(4)
N2-C7-C12	127.4(4)	N2-C7-C8	112.8(4)
C12-C7-C8	119.7(4)	O2-C8-N3	119.6(4)
O2-C8-C7	124.2(5)	N3-C8-C7	116.2(4)
O3-C10-N3	121.8(4)	O3-C10-N4	122.4(5)
N3-C10-N4	115.8(4)	N5-C12-N4	119.9(4)
N5-C12-C7	122.5(4)	N4-C12-C7	117.6(4)
N2-N1-C6	117.1(4)	N2-N1-Cu1	130.5(3)
C6-N1-Cu1	112.4(3)	N1-N2-C7	121.0(4)
C10-N3-C8	125.6(4)	C10-N3-C9	116.1(4)
C8-N3-C9	118.0(4)	C12-N4-C10	124.8(4)
C12-N4-C11	120.0(4)	C10-N4-C11	115.1(4)
C12-N5-Cu1	126.7(3)	C1-O1-Cu1	112.0(3)
C1-O1-Cu1	124.5(3)	Cu1-O1-Cu1	122.14(16)

Table S7. Cu_4 clusters of the present study with the literature (Ref. 24a).

Parameter	Cu_4 cluster, present study	Cu_4 cluster, Ref. 24a
Ligand	1,3-Dimethyl-5-(*o*-hydroxy-phenylazo)-6-aminouracil	1,3-Dimethyl-5-(*o*-carboxy-phenylazo)-6-aminouracil
Bridging group	Phenolate-O	Carboxylate-O
Geometry-around Cu(II)	Distorted square-planar	In between square-pyramidal and TBP
Cu_4-cluster	Doubly opened 4+2 cubane	87%Tetrahedon and 13% square planar
Framework	8-membered	16-membered
Cu---Cu	3.426(11)- 3.498(13) Å	4.15 - 4.8 Å
Crystal	tetragonal	monoclinic
Magnetic property	Antiferromagnetic ground state	Ferromagnetic ground state