Electronic Supplementary Information (ESI)

Antiferromagnetic Cyclic Tetrameric Copper(II) complex and 8-Azaxanthine derived from 1,3-Dimethyl-5-(5'-methyl-3'-isoxazolyl-azo)-6-aminouracil: Structures, Non-Covalent Interactions and Magnetism

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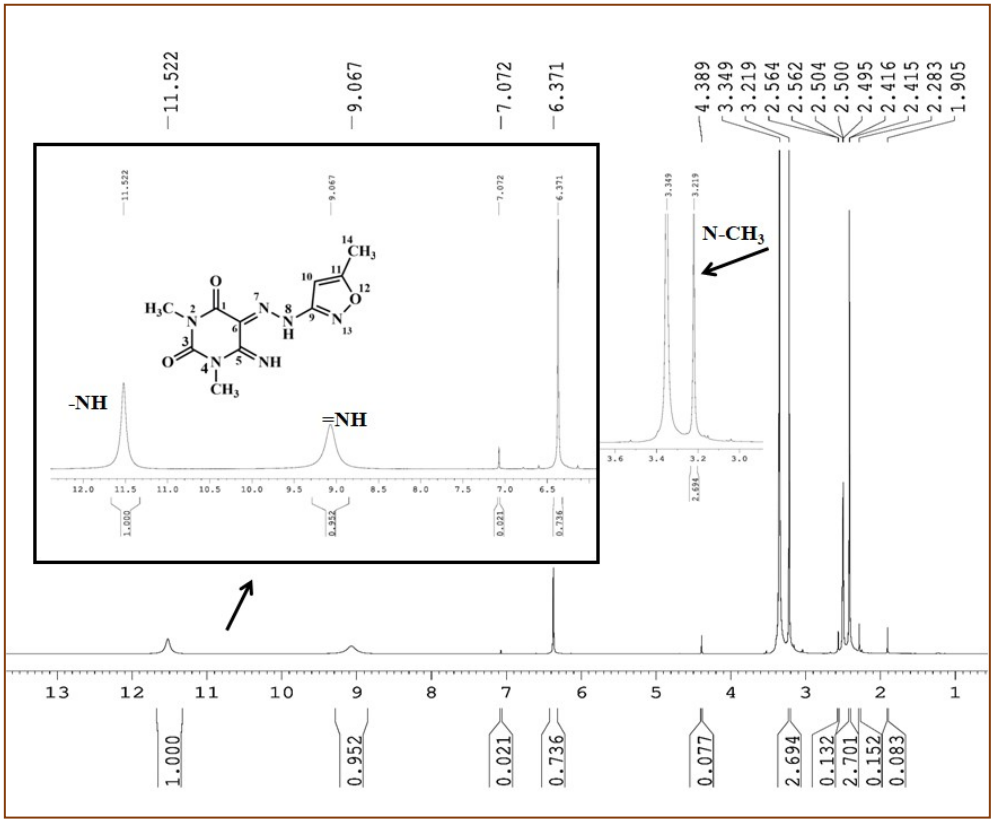

Figure S1. ^{1}H NMR spectrum of H_2L (**1**).

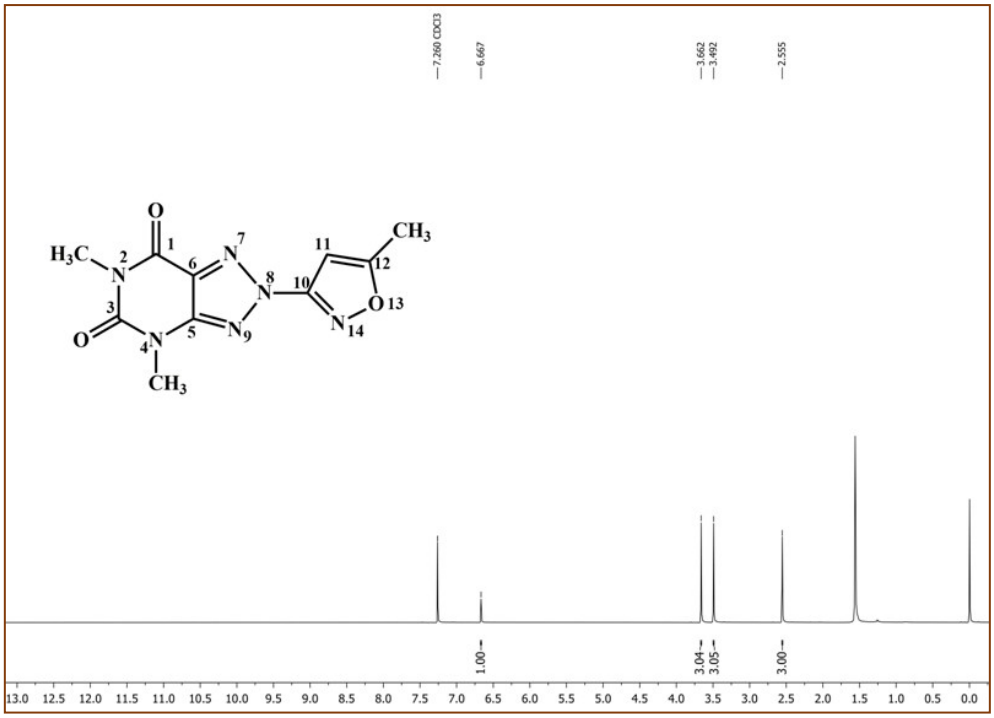

Figure S2. ^{1}H NMR spectrum of 8-azaxanthine derivative (**2**).

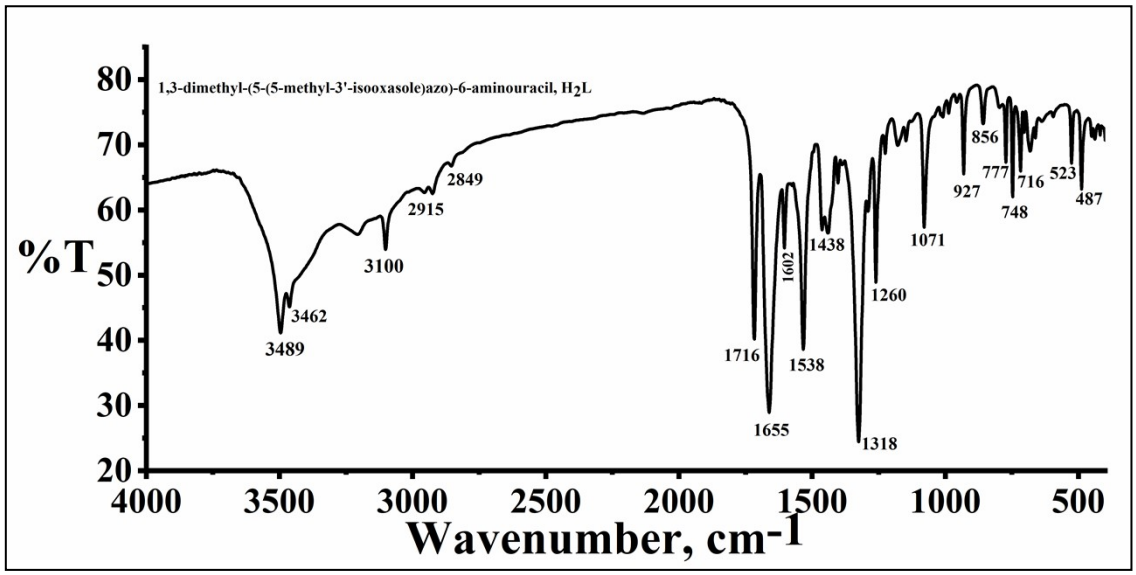

Figure S3. FT-IR spectrum of H_2L (**1**).

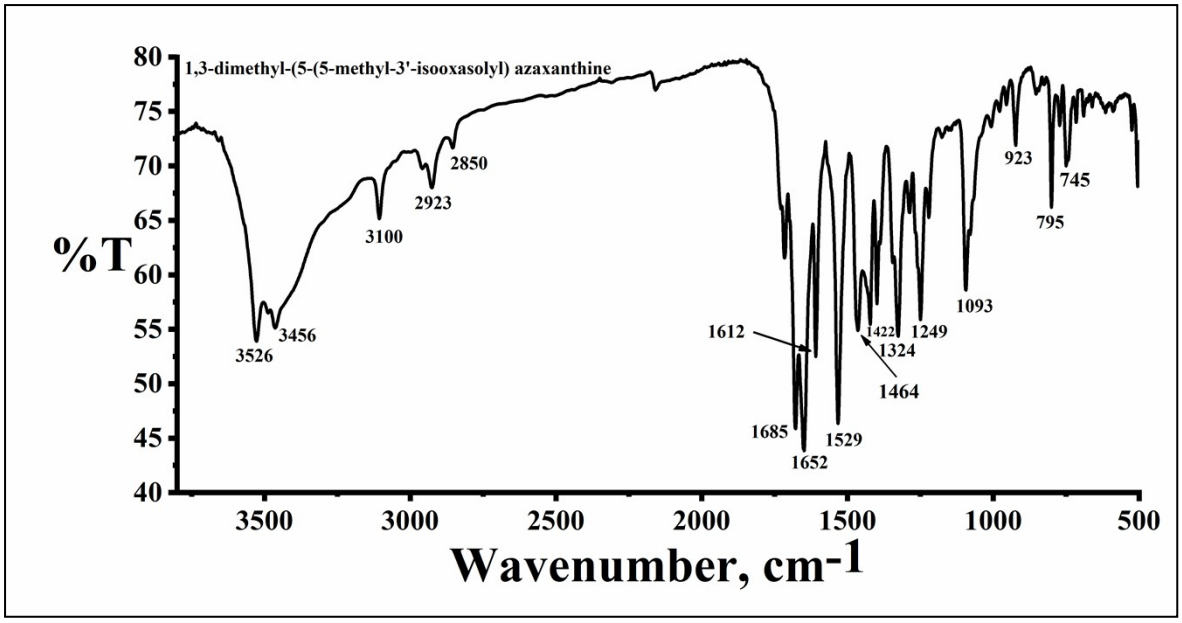

Figure S4. FT-IR spectrum of 8-azaxanthine derivative (**2**).

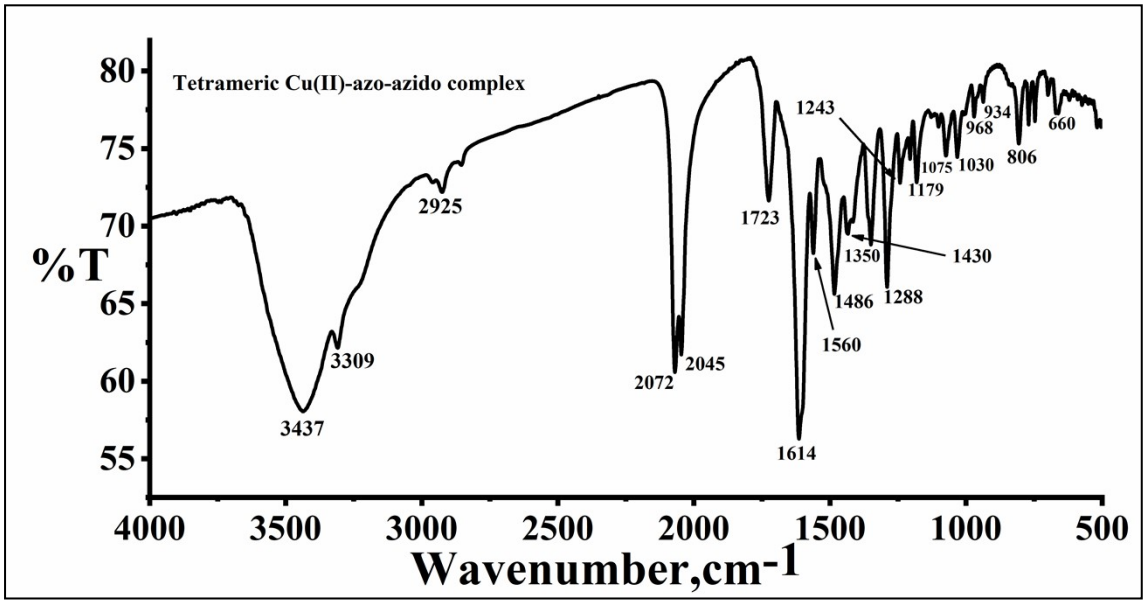

Figure S5. FT-IR spectrum of Cu(II) complex (**3**).

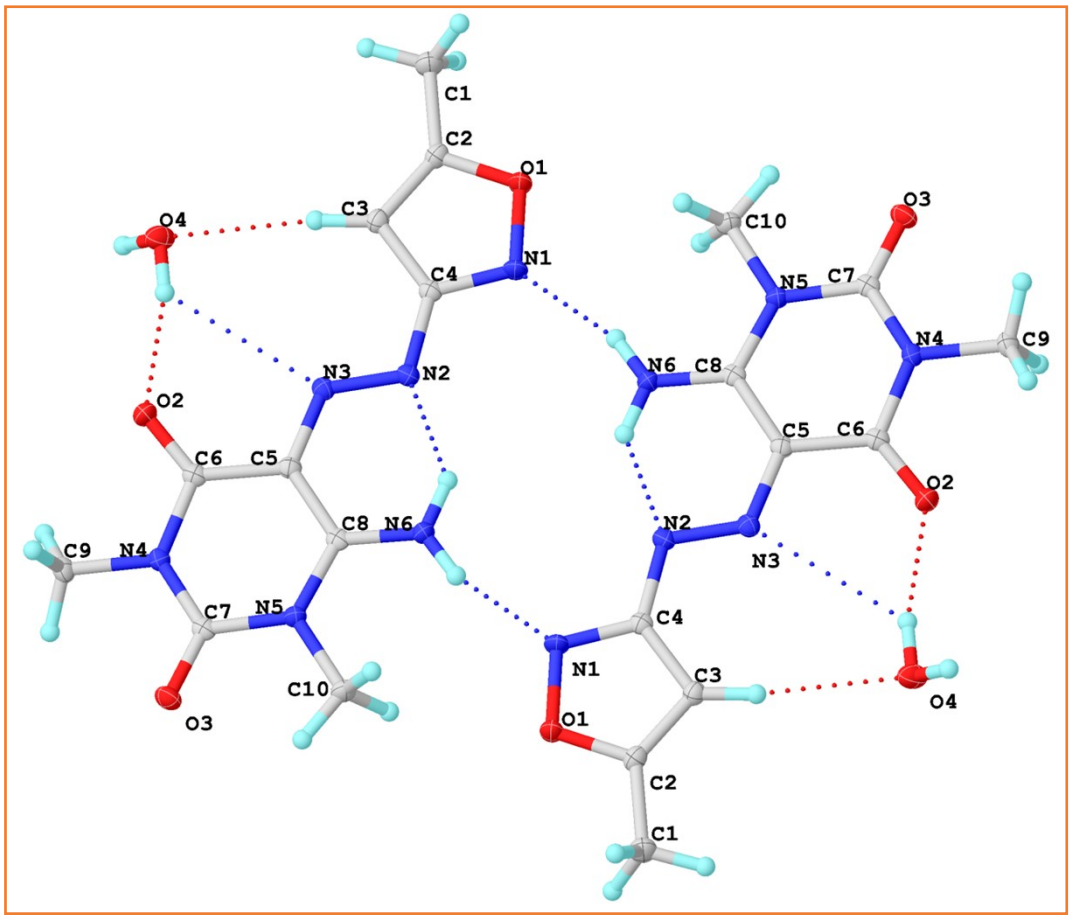

Figure S6. H-bonding interactions exist in H_2L (**1**).

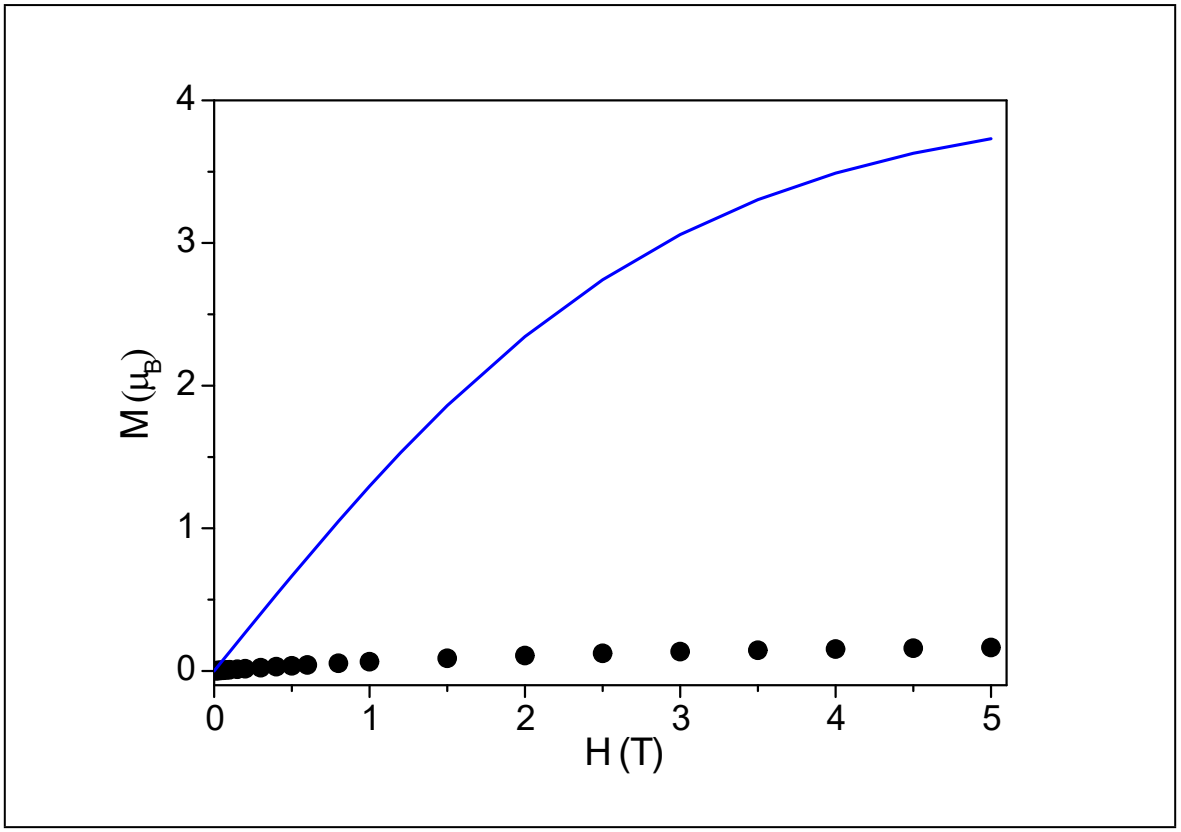

Figure S7. The field dependence of the magnetization (*M* per Cu^{II}_4 entity) at 2 K for **3** (●). The solid line is the Brillouin function curve calculated for a defined number of uncoupled copper(II) ions in **3.**

Table S1. Bond length of H_2L(**1**), **2** and Cu(II) complex (**3**).

H_2L(1)		**2**		**Complex (3)**	
Bond	**Length/Å**	**Bond**	**Length/Å**	**Bond**	**Length/Å**
O1-N1	1.4043(12)	O1-N1	1.4070(14)	Cu1-O1	1.916(2)
O1-C2	1.3664(14)	O1-C3	1.3577(15)	Cu1-O4	2.299(2)
O2-C6	1.2240(14)	O2-C6	1.2202(15)	Cu1-N1	1.949(2)
O3-C7	1.2121(14)	O3-C7	1.2114(16)	Cu1-N5	1.991(3)
N1-C4	1.3156(14)	N1-C1	1.3096(16)	Cu1-N7	2.041(3)
N2-N3	1.2951(14)	N2-N3	1.3568(14)	Cu2-O3	2.041(3)
N2-C4	1.4027(15)	N2-N4	1.3323(14)	Cu2-N4	1.996(3)
N3-C5	1.3548(14)	N2-C1	1.4087(16)	Cu2-N6	1.910(2)
N4-C6	1.3944(15)	N3-C8	1.3302(16)	Cu2-N7[1]	2.394(3)
N4-C7	1.3755(14)	N4-C5	1.3336(16)	Cu2-N8[1]	2.947(3)
N4-C9	1.4642(15)	N5-C6	1.3943(16)	Cu2-N10	1.958(3)
N5-C7	1.4046(14)	N5-C7	1.4146(17)	O1-C9	1.279(4)
N5-C8	1.3668(15)	N5-C9	1.4675(16)	O2-C2	1.211(4)
N5-C10	1.4714(14)	N6-C7	1.3817(16)	O3-C3	1.256(4)
N6-C8	1.3197(14)	N6-C8	1.3643(16)	N1-C1	1.290(4)

C1-C2	1.4844(16)	N6-C10	1.4692(17)	N2-C1	1.387(4)
C2-C3	1.3488(16)	C1-C2	1.4097(17)	N2-C2	1.391(4)
C3-C4	1.4250(15)	C2-C3	1.3549(17)	N2-C5	1.476(4)
C5-C6	1.4500(15)	C3-C4	1.4808(18)	N3-C2	1.397(5)
C5-C8	1.4214(15)	C5-C6	1.4557(17)	N3-C3	1.345(4)
		C5-C8	1.4006(17)	N3-C6	1.477(5)
				N4-N5	1.302(3)
				N4-C4	1.322(4)
				N5-C7	1.425(4)
				N6-C7	1.317(4)
				N7-N8	1.218(3)
				N8-N9	1.156(4)
				N10-N11	1.216(5)
				N11-N12	1.172(5)
				C1-C4	1.449(5)
				C3-C4	1.454(5)
				C7-C8	1.411(5)
				C8-C9	1.382(5)
				C9-C10	1.510(5)

[1]1-X,1-Y,1-Z

Table S2. Bond angles of the H_2L(**1**), **2** and Cu(II) complex (**3).**

Ligand, H_2L		**2**		**Complex(3)**	
Bond	**Angle /°**	**Bond**	**Angle /°**	**Bond**	**Angle /°**
N1-O1-C2	108.33(8)	N1-O1-C3	109.60(9)	O1-Cu1-O4	87.60(9)
O1-N1-C4	105.42(8)	O1-N1-C1	103.25(10)	O1-Cu1-N1	176.08(11)
N3-N2-C4	110.96(8)	N3-N2-N4	117.21(9)	O1-Cu1-N5	91.86(11)
N2-N3-C5	118.92(9)	N3-N2-C1	121.81(10)	O1-Cu1-N7	86.67(11)
C6-N4-C7	124.70(9)	N4-N2-C1	120.98(10)	O4-Cu1-N1	92.59(9)
C6-N4-C9	117.12(9)	N2-N3-C8	101.19(9)	O4-Cu1-N5	101.14(9)
C7-N4-C9	11703(9)	N2-N4-C5	102.34(10)	O4-Cu1-N7	97.02(9)
C7-N5-C8	122.83(9)	C6-N5-C7	127.80(10)	N1-Cu1-N5	91.95(10)
C7-N5-C10	117.00(9)	C6-N5-C9	117.05(10)	N1-Cu1-N7	89.41(10)
C8-N5-C10	120.16(9)	C7-N5-C9	115.13(11)	N5-Cu1-N7	161.71(11)
O1-C2-C1	115.71(10)	C7-N6-C8	119.09(11)	O3-Cu2-N4	79.64(10)
O1-C2-C3	110.22(10)	C7-N6-C10	119.01(11)	O3-Cu2-N6	154.78(11)

C1-C2-C3	134.06(11)	C8-N6-C10	121.80(11)	O3-Cu2-N7[1]	87.42(10)
C2-C3-C4	103.85(10)	N1-C1-N2	119.36(11)	O3-Cu2-N8[1]	68.47(9)
N1-C4-N2	116.44(9)	N1-C1-C2	114.49(11)	O3-Cu2-N10	98.38(13)
N1-C4-C3	112.18(10)	N2-C1-C2	126.14(11)	N4-Cu2-N6	78.22(11)
N2-C4-C3	131.36(10)	C1-C2-C3	102.93(11)	N4-Cu2-N7[1]	88.77(10)
N3-C5-C6	114.12(9)	O1-C3-C2	109.73(11)	N4-Cu2-N8[1]	98.61(9)
N3-C5-C8	126.64(10)	O1-C3-C4	116.786(11)	N4-Cu2-N10	176.80(12)
C6-C5-C8	119.24(10)	C2-C3-C4	133.51(12)	N6-Cu2-N7[1]	103.96(10)
O2-C6-N4	119.13(10)	N4-C5-C6	129.14(11)	N6-Cu2-N8[1]	126.86(9)
O2-C6-C5	125.02(11)	N4-C5-C8	109.08(11)	N6-Cu2-N10	103.17(13)
N4-C6-C5	115.85(9)	C6-C5-C8	121.78(11)	N7[1]-Cu2-N8[1]	23.58(7)
O3-C7-N4	122.71(10)	O2-C6-N5	122.73(11)	N7[1]-Cu2-N10	93.67(11)
O3-C7-N5	120.72(10)	O2-C6-C5	126.23(11)	N8[1]-Cu2-N10	82.90(10)
N4-C7-N5	116.57(10)	N5-C6-C5	111.03(10)	Cu1-O1-C9	128.2(2)
N5-C8-N6	119.30(10)	O3-C7-N5	120.66(11)	Cu2-O3-C3	110.5(2)
N5-C8-C5	119.56(9)	O3-C7-N6	121.96(12)	Cu1-N1-C1	128.7(2)
N6-C8-C5	121.14(10)	N5-C7-N6	117.39(11)	C1-N2-C2	123.4(3)
		N3-C8-N6	127.01(11)	C1-N2-C5	119.6(3)
		N3-C8-C5	110.18(11)	C2-N2-C5	117.0(3)
		N6-C8-C5	122.81(11)	C2-N3-C3	123.8(3)
				C2-N3-C6	118.1(3)
				C3-N3-C6	118.1(3)
				Cu2-N4-N5	117.9(2)
				Cu2-N4-C4	115.6(2)
				N5-N4-C4	126.1(3)
				Cu1-N5-N4	124.4(2)
				Cu1-N5-C7	125.7(2)
				N4-N5-C7	109.9(3)
				Cu2-N6-C7	116.6(2)
				Cu1-N7-Cu2[1]	116.92(11)
				Cu1-N7-N8	115.5(2)
				Cu2[1]-N7-N8	104.64(19)

				Cu2[1]-N8-N7	51.79(16)
				Cu2[1]-N8-N9	127.5(2)
				N7-N8-N9	178.9(3)
				Cu2-N10-N11	122.2(2)
				N10-N11-N12	176.7(3)
				N1-C1-N2	123.8(3)
				N1-C1-C4	120.5(3)
				N2-C1-C4	115.8(3)
				O2-C2-N2	121.6(3)
				O2-C2-N3	120.2(3)
				N2-C2-N3	118.1(3)
				O3-C3-N3	120.9(3)
				O3-C3-C4	121.8(3)
				N3-C3-C4	117.2(3)
				N4-C4-C1	128.4(3)
				N4-C4-C3	110.6(3)
				C1-C4-C3	121.1(3)
				N5-C7-N6	116.7(3)
				N5-C7-C8	119.7(3)
				N6-C7-C8	123.6(3)
				C7-C8-C9	126.8(3)
				O1-C9-C8	126.1(3)
				O1-C9-C10	114.8(3)
				C8-C9-C10	119.1(3)

[1]1-X,1-Y,1-Z

Table S3. Comparison of apical bond length for SP geometry with similar kind of Cu(II) system

Cu(II)-azo system	**Geometry around Cu(II)**	**Apical bond parameter**		**Ref.**
		Bond length	**Length/Å**	
Cu(II)-azo-isothiocyanato complex	Square Pyramidal(SP)	$Cu1\text{-}O3_{(water)}$	2.2698(13)	[14a]
Homometallic Cu(II)-	SP	$Cu1\text{-}O3_{(uracil\text{-}o)}$	2.5525(13)	[14a]

azo-azido polymer				
Cu(II)-azo-diaquo complex	SP	$Cu\text{-}O3_{(water)}$	2.2207(13)	[14d]
Cu(II)-azo-azido complex	SP	$Cu1\text{-}O3_{(water)}$	2.3303(15)	[14b]
1D homometallic Cu(II)-azo-thiocyanato polymer	SP	$Cu1\text{-}S_{SCN}$	2.6650(5)	[14b]
$\{(pmtpm)Cu(Cl)\}_2\mu\text{-}Cl](ClO_4)$ and $[\{(pmtpm)Cu_2(\mu\text{-}Cl)_2](ClO_4)_2$	SP	Cu–Cl	2.5597(9) and 2.7037(12)	[31b]
$[Cu(L)Cl_2]$ L=piperidin-2-ylmethyl-pyridin-2-ylmethylene-amine	SP	Cu–Cl	2.505	[36]
$Cu(C_{10}H_{24}N_4)Br]Br$	SP	Cu-Br	2.6028 (6)	[31a]
$[Cu_2(PaPy_3H)_2](ClO_4)_4$	SP	$Cu(II)\text{-}O_{carbonyl}$	2.260(2)	[35a]
$[Cu(Py_3P)]$	SP	Cu-N5	2.172(2)	[35b]
[Cu(L′)(dpa)] and $[Cu(L^1)(dpa)]$	SP	Cu-N(26)	2.234(2) and 2.189(2)	[15f]
Cu(II) tetramer (3)	SP	$Cu1\text{-}O4_{(water)}$ $Cu2\text{-}N7_{(azide)}$	2.299(2) 2.394(3)	Present work

Table S4. Cartesian atomic coordinates for model structures.

Atom	X	Y	Z
1			
O	7.993820	-1.296299	10.228915
O	7.304351	3.784629	14.539839
O	4.030206	6.786685	13.737284
N	6.977226	-0.328808	10.177301
N	6.321547	1.550437	11.352101
N	6.674875	2.299427	12.347817
N	5.787802	5.372167	14.006887
N	4.120347	4.960776	12.381053
N	4.207075	3.089151	11.015634

C	9.934876	-1.948230	11.508506
C	8.814969	-1.001076	11.280350
C	8.390626	0.117222	11.903626
C	7.227953	0.495263	11.171648
C	5.920337	3.382441	12.653003
C	6.404289	4.140281	13.790461
C	4.615207	5.776114	13.412156
C	4.733518	3.802506	11.993168
C	6.273369	6.172911	15.132420
C	2.878026	5.395729	11.723368
H	9.586850	-2.863616	11.541352
H	10.374878	-1.735120	12.357788
H	10.582188	-1.870746	10.776920
H	8.776732	0.551412	12.655154
H	3.429825	3.293938	10.600377
H	4.652071	2.338579	10.815435
H	5.866479	5.849612	15.963128
H	6.030586	7.112328	14.993806
H	7.248251	6.093375	15.193614
H	3.055107	5.575313	10.776334
H	2.548954	6.212180	12.154461
H	2.202663	4.690169	11.801376
O	7.993820	-7.157399	10.228915
O	7.304351	-2.076471	14.539839
O	4.030206	0.925585	13.737284
N	6.977226	-6.189908	10.177301
N	6.321547	-4.310663	11.352101
N	6.674875	-3.561673	12.347817
N	5.787802	-0.488933	14.006887
N	4.120347	-0.900324	12.381053
N	4.207075	-2.771949	11.015634
C	9.934876	-7.809330	11.508506
C	8.814969	-6.862176	11.280350
C	8.390626	-5.743878	11.903626
C	7.227953	-5.365837	11.171648
C	5.920337	-2.478659	12.653003
C	6.404289	-1.720819	13.790461
C	4.615207	-0.084986	13.412156
C	4.733518	-2.058594	11.993168
C	6.273369	0.311811	15.132420
C	2.878026	-0.465371	11.723368
H	9.586850	-8.724716	11.541352
H	10.374878	-7.596220	12.357788
H	10.582188	-7.731846	10.776920
H	8.776732	-5.309688	12.655154
H	3.429825	-2.567162	10.600377
H	4.652071	-3.522521	10.815435
H	5.866479	-0.011488	15.963128

H	6.030586	1.251228	14.993806
H	7.248251	0.232275	15.193614
H	3.055107	-0.285787	10.776334
H	2.548954	0.351080	12.154461
H	2.202663	-1.170931	11.801376
2			
O	10.056766	13.198864	3.591242
O	11.039208	5.781072	4.265690
O	7.128544	5.050911	1.999686
N	9.359390	12.038294	3.208507
N	9.745798	9.732605	3.416749
N	8.619328	9.415334	2.730205
N	10.474885	8.723372	3.890841
N	9.046516	5.447865	3.174357
N	7.734068	7.222174	2.259187
C	10.136358	11.069936	3.625325
C	11.311931	11.501440	4.272640
C	11.209172	12.851423	4.219444
C	12.059133	13.958709	4.713518
C	9.774448	7.657813	3.500353
C	10.057073	6.245300	3.709999
C	7.910864	5.863918	2.440764
C	8.642134	8.087005	2.796634
C	9.177958	3.996788	3.349518
C	6.619212	7.690173	1.424481
H	12.005689	10.975169	4.652636
H	12.357185	14.504566	3.956067
H	12.839627	13.589613	5.177117
H	11.543266	14.514784	5.333900
H	8.305738	3.615527	3.582420
H	9.818035	3.811145	4.068007
H	9.497984	3.594724	2.515012
H	6.856025	7.592850	0.478503
H	6.437640	8.632983	1.620493
H	5.820069	7.156724	1.617619
O	9.504064	5.049086	6.932741
O	10.486505	12.466878	7.607189
O	6.575842	13.197039	5.341185
N	8.806688	6.209656	6.550005
N	9.193096	8.515345	6.758247
N	8.066626	8.832616	6.071703
N	9.922183	9.524578	7.232339
N	8.493814	12.800085	6.515855
N	7.181366	11.025776	5.600686
C	9.583656	7.178014	6.966824
C	10.759229	6.746510	7.614139
C	10.656470	5.396527	7.560942
C	11.506431	4.289241	8.055016

C	9.221746	10.590137	6.841852
C	9.504371	12.002650	7.051497
C	7.358162	12.384032	5.782263
C	8.089432	10.160945	6.138132
C	8.625256	14.251162	6.691017
C	6.066510	10.557777	4.765979
H	11.452987	7.272781	7.994134
H	11.804483	3.743384	7.297565
H	12.286925	4.658337	8.518616
H	10.990564	3.733166	8.675399
H	7.753036	14.632423	6.923919
H	9.265332	14.436805	7.409506
H	8.945282	14.653226	5.856511
H	6.303323	10.655100	3.820001
H	5.884938	9.614967	4.961992
H	5.267367	11.091226	4.959118
3			
Cu	0.437946	2.873026	5.081721
Cu	3.828229	5.365801	7.333606
O	0.631042	3.470747	3.271208
O	0.689001	1.904501	11.468248
O	3.267165	4.878569	9.234744
O	-1.465292	4.156801	5.200847
N	0.175074	2.159157	6.876528
N	0.496664	1.914445	9.203217
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C	2.165965	5.257132	3.557507
C	1.266355	4.493184	2.838560
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H	-0.160080	0.114075	8.546742
H	4.023453	6.304542	5.037630
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H	2.000836	3.560447	12.377751
H	2.584309	4.853002	11.636235
H	2.575343	5.979440	3.096125
H	1.680522	5.455385	1.068764
H	0.111139	5.297346	1.339591
H	0.970519	4.037065	0.855640
Cu	4.263186	1.689165	6.551723
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O	4.012131	2.657691	0.165195
O	1.433967	-0.316378	2.398700
O	6.166424	0.405391	6.432596
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N	2.737771	1.153400	1.276189
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C	2.149851	0.688481	0.003490
C	2.160541	-0.512657	6.727620
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C	3.434778	0.069007	8.794883
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H	4.861212	4.448117	3.086702
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O	0.218677	10.450669	11.468248
O	2.796841	13.424737	9.234744
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N	1.740956	12.803724	6.957962
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C	0.547189	10.928469	10.404952
C	1.912251	12.533862	9.218341
C	1.273641	12.110889	7.982869
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C	0.511491	13.398850	1.399503
H	-0.885356	10.055922	6.946096
H	-2.291611	12.759263	5.959813
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H	-1.789964	9.565221	9.177042
H	-0.737549	8.832286	10.134125
H	-0.630404	8.660243	8.546742
H	3.553129	14.850710	5.037630
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H	1.530512	12.106615	12.377751
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H	2.105019	14.525608	3.096125
H	1.210198	14.001553	1.068764
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H	0.500195	12.583234	0.855640
Cu	3.792862	10.235333	6.551723

Cu	0.402579	7.742559	4.299837
O	3.599766	9.637612	8.362235
O	3.541807	11.203859	0.165195
O	0.963643	8.229790	2.398700
O	5.696100	8.951559	6.432596
N	4.055734	10.949202	4.756915
N	3.734144	11.193915	2.430226
N	2.267447	9.699568	1.276189
N	2.019528	8.850803	4.675481
N	2.418452	8.945603	5.910953
N	0.703195	7.379064	6.150601
N	4.669103	11.909472	7.323253
N	5.082999	11.806650	8.464493
N	5.481822	11.730983	9.546404
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N	-3.304827	7.426477	3.364392
C	3.481513	10.597098	3.656391
C	3.213295	10.726059	1.228492
C	1.848233	9.120666	2.415103
C	2.486843	9.543638	3.650575
C	4.617234	12.374173	2.362752
C	1.679527	9.234649	0.003490
C	1.690217	8.033511	6.727620
C	2.064843	7.851228	8.075936
C	2.964453	8.615175	8.794883
C	3.248993	8.255678	10.233940
H	4.645840	11.598606	4.687347
H	6.052095	8.895265	5.673630
H	5.568060	8.181309	6.742744
H	5.550448	12.089307	2.456402
H	4.498033	12.822242	1.499318
H	4.390888	12.994285	3.086702
H	0.207355	6.803818	6.595813
H	0.771664	9.592712	-0.086785
H	2.229972	9.547912	-0.744308
H	1.646499	8.255358	-0.002792
H	1.655465	7.128920	8.537319
H	2.550286	7.652974	10.564679
H	4.119669	7.811014	10.293852
H	3.260289	9.071294	10.777804