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Crystal structure and nontrivial magnetic properties of Cu^{II} binuclear complex based on 4-methyl-2,6-bis{[2-(4,6-dimethylpyrimidin-2-yl)-hydrazono]methyl}phenol

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Experimental details

All chemicals used for the preparative work were of reagent grade. Solvents were dried and distilled before use according to standard procedures. 2,6-diformyl-4-methylphenol was synthesized according to the described procedure.[S1] 2-hydrazino-4,6-dimethylpyrimidine was obtained using the known procedure.[S2] The copper(II) salt ($CuCl_2 \cdot 2H_2O$) was used in its hydrated forms.

Synthesis of bis(4,6-dimethylpyrimidinehydrazone)-2,6-diformyl-4-methylphenol (H_3L). A solution of 2,6-diformyl-4-methylphenol (1 mmol) in butanol (5 ml) was added to a hot solution of 2-hydrazino-4,6-dimethylpyrimidine (2 mmol) in butanol (5 ml) to form a yellow solution. The reaction mixture was refluxed for 3 h. The formed yellow precipitate was filtered off hot and washed with ethanol. The purification was performed by recrystallization from an ethanol–dimethylformamide (3 : 1) mixture. The yield of the yellow amorphous precipitate was 49%; m.p. = 273 °C. Elemental analysis. Calc. for $C_{21}H_{24}N_8O$: C, 62.36; H, 5.98; N, 27.70. Found: C, 62.24; H, 5.87; N, 27.61%. IR (nujol mull), ν/cm^{-1}: 3194 (N-H), 1595 ($C{=}N_{azomethine}$), 1565 ($C{=}N_{heterocycle}$). ^1H NMR (300MHz, DMSO-d_6), δ: 2.2 (s, 3H, CH_3), 2.3 (s, 12H, CH_3), 6.8 (s, $2H_{pyrimidine}$), 7.3 (s, $2H_{diformylphenol}$), 8.2 (s, 2H CH=N), 11.2 (s, 2H, N-H), 12.3 (s, 1H, O-H).

Complex **2** was synthesized by following method. To a hot suspension of the **H_3L** (0.001 M) in methanol (10 ml), a solution of $CuCl_2 \cdot 2H_2O$ (0.002 M) in methanol (10 ml) was added. The mixture was refluxed for 4 h. After cooling to the room temperature, a precipitate was filtered, washed with hot methanol, and dried *in vacuo*.

$[Cu_2H_2L(\mu\text{-}Cl)]Cl_2$ Green solid. Yield 64 %. Elemental analysis. Calc. for $C_{21}H_{23}N_8Cu_2Cl_3$: C, 39.60; H, 3.64; N, 17.59. Found: C, 39.51; H, 3.55; N, 17.48%. IR spectrum (nujol mull), ν/cm^{-1}: 3246 (N-H), 1608 ($C{=}N_{azomethine}$), 1565 ($C{=}N_{heterocycle}$).

Physical measurements

Elemental analyses (C, H, and N) were performed on a Perkin Elmer 240C Analyzer. IR spectra were recorded on a Varian Scimitar 1000 FT-IR spectrophotometer in the range of 4000–400 cm^{-1}. The ^1H NMR spectra were recorded on a 300 MHz Varian Unity-300 spectrometer in DNSO-d^6. Conductance was determined for DMF solutions (10^{-3} M) of the complex **II** using a R38 conductivity bridge at 298 K.

Crystal Data and Structures

General procedure

X-Ray diffraction experiment for single crystals of compounds **1** and **2** was carried out with a Bruker APEX2 CCD (λMoK_α, ω-scans).[S3] Reflection intensities were integrated using SAINT software and adsorption correction was applied semi-empirically using SADABS program.[S3] The structure was solved using the SHELXT software.[S4] The refinement has been performed using SHELXL-2014/7 software.[S4,S5]

Atomic coordinates and thermal parameters are deposited with The Cambridge Crystallographic Data Centre (CCDC № 1845761, 1845762). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk

Special details

Compound **1** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors (gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Compound 1 crystalizes in the monoclinic $P2_1/n$ space group with one (H_3L) moiety and ethanol molecules in the asymmetric unit. The molecule is essentially planar; C(4)N(1)C(1)C(2)C(3)N(2) and C(13)N(7)C(14)C(15)C(16)N(8) pyrimidine rings are unfolded relative to C(6)C(7)C(8)C(9)C(10)C(11) benzene cycle plane on 5.77° and 11.41° ,respectively. The OH group of phenol fragment forms strong intramolecular O(1)–H(1)···N(5) hydrogen bond with parameters: d(D–H) 0.82 Å, d(H···A) 1.89 Å, d(D···A) 2.61 Å with a DHA angle of 145.3°. The ethanol molecule takes part in formation of two hydrogen bonds: O(1S)–H(1S)···N(8)^{i} (d(D–H) 0.82 Å, d(H···A) 2.04 Å, d(D···A) 2.85 Å, (i: x–1/2, –y+1/2, z–1/2) and N(3)–H(3A)···O(1S) (d(D–H) 0.86 Å, d(H···A) 2.06 Å, d(D···A) 2.92 Å, ∠DHA 176.6°). Moreover, the weak hydrogen bond N(6)–H(6A)···N(1)^{ii} (d(D–H) 0.86 Å, d(H···A) 2.42 Å, d(D···A) 3.163 Å, ∠DHA 144.2º is also taking place in the crystal (ii: x+1/2, –y+1/2, z+1/2). Thus**,** bis-hetarylhydrazone **1** crystallizes as an infinite zigzag molecular chain (see Table S2† and Figure. S1†).

Compound 2 $[Cu_2(H_2L)Cl_3]\cdot 0.3H_2O$ single crystals represent very small and thin plates with weak reflection.The location of hydrogen atoms has been calculated. Non-hydrogen atoms were refined in anisotropic approximation, the hydrogen atoms have been refined by rider model with isotropic displacement parameters $U_{iso} = 1.2U_{eqv}$ of corresponding non-hydrogen atom ($1.5U_{eqv}$ for methyl groups). Under refining the thermal ellipsoid of C(21) atom has been restricted to isotropic form. The first two peaks at ~0.5 e height at zero synthesis, which are located in cavities with 72 Å^3 volume, have been interpreted as H_2O molecules. Their population (*q*) was refined under fixed isotropic displacement parameters $U_{iso} = 0.08$ Å^2 and then the water molecules were refined in isotropic approximation at $q = 0.15$. The hydrogen atoms of water molecule were localized in differential synthesis and

were included in rider model's refinement with U_{iso} = 1.2U_{eqv}(O) after O-H(0.85 Å) bond length normalization.

Both six-membered metal-chelate cycles have a 'half-boat' conformation. Cu(1) and Cu(2) atoms deviate from the mean plane of other five atoms by 0.35 and 0.56 Å, respectively. The four-membered Cu(1)O(1)Cu(2)Cl(1) metal-chelate cycle has a roof-shaped conformation. The dihedral angle between Cl(1)Cu(1)O(1) and Cl(1)Cu(2)O(1) planes is 154.55°. The distance between copper atoms is 3.174(2) Å. The value of Cu(1)O(1)Cu(2) valent angle is 106.1(3)°, and Cu(1)Cl(1)Cu(2) valent angle is 85.29(9)°.

Each molecule of complex **2** forms with two neighboring molecules the intermolecular hydrogen bonds N(6)–H(6A)···Cl(2)^{i} and N(3)^{ii}–H(3A)^{ii}···Cl(3) (symmetry operation i = 1–x, 1–y, 1–z, ii = 1–x, 1–y, 2–z; table 2) leading to formation of endless molecule chains oriented along the c crystallographic axis (see Table S3† and Figure S2†).

Moreover, the X-ray analysis of complex **2** revealed that there are the intermolecular stacking interaction between the pyrimidine rings N(7)C(13)N(8)C(16)C(15)C(14) and phenolic rings C(6)^{i}C(7)^{i}C(8)^{i}C(9)^{i}C(10)^{i}C(11)^{i} (symmetry operation i = 1–x, 1–y, 1–z; dihedral angle between average planes 5.63°, intercentroid distance 3.490 Å).

Table S1 Crystal data and unit cell parameters for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{23}H_{30}N_8O_2$	$C_{21}H_{23.60}Cl_3Cu_2N_8O_{1.30}$
Formula weight	450.55	642.31
Crystal size, mm	0.34 × 0.17 × 0.10	0.140 x 0.140 x 0.010
Temperature, K	296(2)	120(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Lattice parameters		
a, Å	17.308(2)	11.230(4)
b, Å	8.2354(12)	20.912(7)
c, Å	17.646(3)	11.507(4)
α, °	90	90
β, °	106.462(3)	98.372(5)
γ, °	90	90
V/Å^3	2412.1(6)	2673.5(15)
Z	4	4
$D_{(calc)}$, mg m^{-3}	1.241	1.596
μ, mm^{-1}	0.084	1.922
F(000)	960	1300
Reflections collected	14686	13205
Independent reflections	4993	2645
Rint	0.0822	0.1533
Θ range for data collection/°	1.45 – 26.76	1.948 to 20.406
Data / restraints / parameters	4993/0/288	2645 / 6 / 329
Goodness-of-fit	1.001	0.998
R_1, wR_2 [I>2σ(I)]	0.0719, 0,1747	0.0507, 0.0996
R_1, wR_2 (all data)	0,1656, 0.2209,	0.1172, 0.1254
Largest diff. peak and hole, e/Å^{-3}	0.594/–0.425	0.504/ -0.376

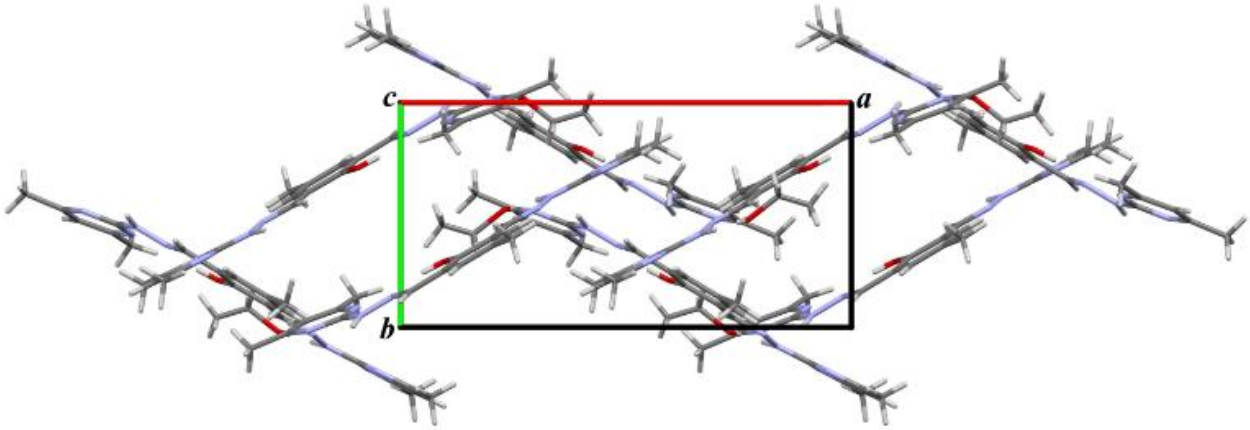


Figure S1 The molecular packing in a single crystal of compound **1** (the view along *c* crystallographic axis).

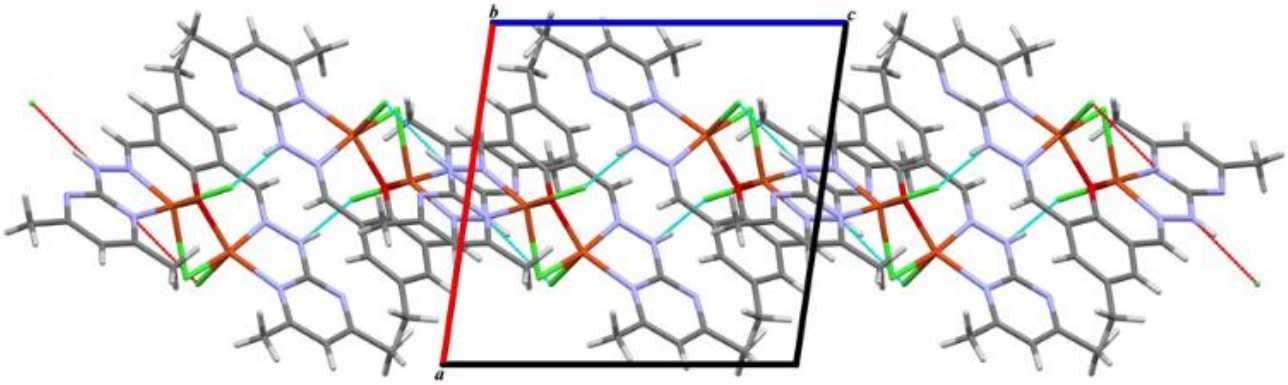


Figure S2 The endless chains of hydrogen-bonded molecules in the crystal of complex **2** (view along the crystallographic axis *b*).
Selected bond lengths [Å] and angles [°]:

Table S2 Parameters of hydrogen bonds for compound **1**.

D–H···A	D–H/Å	H···A/Å	D···A/Å	∠DHA/deg
O(1)–H(1)···N(5)	0.82	1.89	2.61	145.3
N(3)–H(3A)···O(1S)	0.86	2.06	2.92	176.6
N(6)–H(6A)···N(1)^{i}	0.86	2.42	3.16	144.2
O(1S)–H(1S)···N(8)^{ii}	0.82	2.04	2.85	169.6

Symmetry operation: i = x+1/2, -y+1/2, z+1/2, ii = x-1/2, -y+1/2, z-1/2

Table S3 Parameters of intermolecular hydrogen bonds in complex **2.**

D–H···A	D–H/Å	H···A/Å	D···A/Å	∠DHA/deg
N(6)–H(6A)···Cl(2)^{i}	0.88	2.25	3.113(9)	168
N(3)^{ii}–H(3A)^{ii}···Cl(3)	0.88	2.25	3.105(8)	165

Symmetry operation: i = 1–x, 1–y, 1–z, ii = 1–x, 1–y, 2–z.

Magnetic Measurements

The temperature dependence of magnetic susceptibility was measured on the powder sample using a Quantum Design MPMS-XL-5 SQUID magnetometer, from 10 K to 300 K, and in a 1000 Oe magnetic field. The data were corrected for the contributions of the sample holder and for the diamagnetism of the sample estimated from Pascal's constants as well as for temperature independent paramagnetism.

The exchange parameters were calculated according to the HDVV theory[S6-S8] using the Equation 1 and shown in Table S4.

$$\chi'_M = \frac{2N_A g^2 \beta^2}{3kT}\left[(1-f)\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + f\cdot S(S+1)\right] + N_\alpha \qquad (1)$$

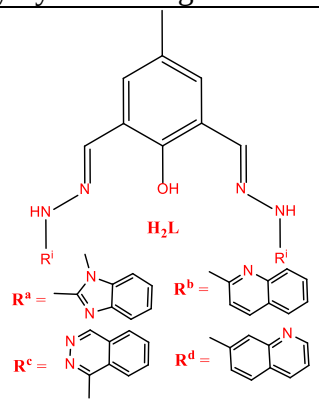
wherein χ'_M, N_A, g, β, k, J, f, and N_α are the molar magnetic susceptibility corrected to diamagnetism of atoms, Avogadro's number, the Landé factor, the Bohr magneton, the Boltzmann constant, the exchange parameter, the molar fraction of the mononuclear impurity, and temperature independent paramagnetism, respectively. The value of Nα was kept fixed at 120×10^{-6} cm^3 mol^{-1} during fitting procedure.[S6]

Table S4 The data of magnetic measurement for complex **2**.

Complex	*T*/K	μ_{eff}/B.M.[a]	$-2J/cm^{-1}$	*g*	*R*
II	295	1.59	193	2.14	1.47
	10.2	0.18			

[a] μ_{eff} were calculated per one copper ion

Table S5 The magnetic properties of Cu(II) binuclear complexes with derivatives of bis-hetarylhydrazone ligands



Complex composition	$-2J/cm^{-1}$	Ref
$[Cu_2(H_2L\text{-}R^a)Cl_3]$	140	S9
$[Cu_2(H_2L\text{-}R^b)Cl_3]$	145	S10
$[Cu_2(H_2L\text{-}R^c)Cl_3]$	70	S11
$[Cu_2(H_2L\text{-}R^d)Cl]\cdot2Cl$	204	S12

Computational studies

Density Functional Theory (DFT) calculations were performed using Gaussian09[S13] software package. Molecular structures were initially obtained at the semi-empirical PM3 level as starting input geometries. All stationary points were identified as minimal (number of imaginary frequencies $N_{imag} = 0$). No symmetry constraints on nuclear coordinates were applied during the geometry optimization procedure. The solvent effects (ethanol) are considered by using the polarizable continuum model.[S14] The hybrid exchange-correlation functional B3LYP[S15] was used for geometry optimizations in combination with 6-311G(d,p) basis set. The IR spectrum was modelled within harmonic oscillator approximation at the same level of theory, calculated frequencies of fundamental vibrations were scaled by 0.967 as recommended in ref.[S16] Data preparation and processing as well as visualization of calculation's results were performed using the ChemCraft.[S17]

Exchange interaction parameter was calculated within 'broken symmetry' approximation (DFT-BS) by Ginsberg, Noodleman, Yamaguchi and others.[S18–S20]

For extraction of *2J* values from the energies of 'broken symmetry' (BS) and high spin states (HS), a non-spin-projected formula (2) proposed by Ruiz *et al.*[S21] was employed:

$$2J = E_{(BS)} - E_{(HS)} \quad (2)$$

wherein $E_{(BS)}$ is the energy of the complex in the BS state and $E_{(HS)}$ is the energy of the complex in the first triple state.

Table S6 The calculated for tautomer **1a**, **1b** and experimental stretching vibration data.

Type of vibration	Experimental data, ν/cm^{-1}	Calculation data for **1a** ν/cm^{-1}	Intensity	Calculation data for **1b** ν/cm^{-1}	Intensity
ν(NH)	3194	3412	18.28	3471	63
		3384	10.02	3470	44
ν(OH)	3194	3265	584	3047	719
$\nu(C=N)_{heterocycle}$	1565	1546	1273	1611	197
		1551	528	1610	202
$\nu(C=N)_{azomethine}$	1595	1610	20.7	1616	2061
		1617	15.9	1623	657

Table S7 The interatomic distances and valence angles between bonds for optimized structure of **1a** molecule in comparison with X-ray data.

Bond	Calc./Å	X-ray data/Å	Angle	Calc.,/deg	X-ray data/deg
N(1)–C(4)	1.35	1.352(4)	C4-N3-N4	121.1	121.1(3)
N(1)–C(1)	1.34	1.343(4)			
N(2)–C(4)	1.34	1.339(4)	N3-N4-C5	115.6	117.6(3)
N(2)–C(3)	1.34	1.335(4)			
N(3)–C(4)	1.38	1.352(4)	N4-C5-C6	121.2	121.2(3)
N(3)–N(4)	1.35	1.377(4)	C15-C14-N8	120.6	121.0(3)
N(4)–C(5)	1.29	1.278(4)	C14-N8-N7	120.2	117.1(3)
N(5)–N(6)	1.35	1.361(3)	N8-N7-C13	118.3	123.6(3)
N(5)–C(12)	1.29	1.280(4)	C8-O1-H12	118.6	120.7(3)
N(6)–C(13)	1.38	1.380(4)	(C4-N1-C13-C2-C1-N2)- (C6-C7-C9-C16-C15-C8)		1.6
N(7)–C(13)	1.34	1.332(4)			
N(7)–C(14)	1.34	1.339(4)	(C6-C7-C9-C16-C15-C8)- (C13-N5-C12-C11-C10-N6)		17.1
N(8)–C(13)	1.35	1.338(4)	C15-C14-N8-N7	179.4	-179.8
N(8)–C(16)	1.34	1.352(4)			
O(1)–C(7)	1.35	1.356(3)			
(C5-C6)	1.46	1.459			
(C14-C15)	1.46	1.445			

Table S8 The comparison of main bond lengths and valent angles (X-ray data and calc.) for **2b** complex.

Bond	X-ray data/Å	Calc./Å	Angle	X-ray data/deg	Calc./deg
Cu(1)-N(4)	1.957(8)	2.09	N(4)-Cu(1)-O(1)	89.0(3)	83.3
Cu(1)-O(1)	1.973(7)	1.98	N(4)-Cu(1)-N(1)	82.2(4)	79.7
Cu(1)-N(1)	1.988(9)	1.98	O(1)-Cu(2)-Cl(1)	83.2(2)	82.5
Cu(1)-Cl(2)	2.315(3)	2.33	N(5)-Cu(2)-O(1)	88.4(3)	83.3
Cu(1)-Cl(1)	2.436(3)	2.46	N(5)-Cu(2)-N(7)	81.6(4)	79.5
Cu(2)-N(5)	1.936(8)	2.07	Cu(2)-Cl(1)-Cu(1)	85.30(10)	83.1
Cu(2)-O(1)	2.001(6)	1.98	N(5)-Cu(2)-Cl(1)	170.7(3)	130.8
Cu(2)-N(7)	2.042(9)	2.02	O(1)-Cu(1)-Cl(1)	78.9(2)	81.0
Cu(2)-Cl(1)	2.245(3)	2.31	N(1)-Cu(1)-Cl(1)	96.5(3)	97.4
Cu(2)-Cl(3)	2.471(3)	2.52	Cl(2)-Cu(1)-Cl(1)	103.58(12)	111.8

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Cartesian coordinates (Å) for B3LYP calculation

1a E_{tot}=-1328,26036 a.u.				**1b** E_{tot}=-1328,22022 a.u.			
O	1.071428	-0.125556	0.00005	C	7.542356	-1.169165	0.000093
H	2.05484	-0.071774	0.000048	C	6.921047	-2.384913	0.000148
N	-5.507032	-2.321707	-0.000011	C	5.486416	-2.405978	0.000039
N	-5.737751	0.067118	-0.000041	N	4.749859	-1.326031	-0.000051
N	-3.655397	-1.003156	0.000036	C	5.361743	-0.096226	-0.000067
H	-3.180197	-1.901958	0.000040	N	6.764301	-0.057411	-0.000048
N	-2.961792	0.150368	0.000015	C	2.826623	2.171554	-0.000024
N	3.427628	1.052634	0.000025	H	3.418461	3.090786	0.000013
N	4.772722	1.009667	0.000007	C	1.380037	2.273924	0.000000
H	5.327648	1.859562	-0.000034	C	0.775668	3.542006	0.000079
N	4.791522	-1.322955	0.000043	H	1.419938	4.416955	0.000104
N	6.805326	-0.017983	-0.000040	C	0.558464	1.116039	-0.000033
C	-6.834340	-2.451744	-0.000038	C	-0.605800	3.703292	0.000134
C	-7.671241	-1.333059	-0.000077	H	7.495090	-3.300490	0.000255
H	-8.748320	-1.439029	-0.000106	N	4.789251	1.070401	-0.000057
C	-7.067077	-0.074655	-0.000077	N	3.417307	1.024923	-0.000052
C	-5.031373	-1.064682	-0.000011	C	-6.876315	-2.433701	-0.000150
C	-1.681141	0.064681	0.000035	C	-7.665538	-1.319938	-0.000026
H	-1.166889	-0.899466	0.000064	C	-7.014547	-0.039628	0.000055
C	-0.843993	1.263423	0.000031	N	-5.718211	0.115757	-0.000008
C	0.560159	1.120689	0.000037	C	-4.908766	-0.997368	-0.000193
C	1.376544	2.278605	0.000024	N	-5.532195	-2.259553	-0.000218
C	0.767258	3.544268	0.000011	C	-1.697683	0.073690	0.000039
H	1.405949	4.423061	-0.000001	H	-1.213440	-0.902398	-0.000141
C	-0.614844	3.700903	0.000011	C	-0.847250	1.263357	0.000040
C	-1.400225	2.546617	0.000017	C	-1.394794	2.550863	0.000120
H	-2.482226	2.619947	0.000009	H	-2.476964	2.623844	0.000182
C	2.826072	2.190331	0.000012	H	-8.743114	-1.402727	0.000024
H	3.389210	3.130417	-0.000011	N	-3.612504	-1.050718	-0.000162
C	5.474283	-0.177791	0.000005	N	-2.979168	0.172781	0.000051
C	5.527021	-2.441170	0.000043	C	-1.241491	5.074249	0.000155
C	6.921779	-2.395254	-0.000006	H	-1.875328	5.220322	0.880532
H	7.511475	-3.302594	-0.000011	H	-0.484991	5.862421	0.000757
C	7.531830	-1.138186	-0.000050	H	-1.874388	5.220785	-0.880827
C	9.026228	-0.972349	-0.000139	O	1.079257	-0.120713	-0.000132
H	9.338118	-0.402866	-0.879565	H	2.071992	-0.037728	-0.000201
H	9.541131	-1.933904	0.000235	C	9.026657	-0.965183	0.000213
H	9.338147	-0.402129	0.878792	H	9.339427	-0.400753	0.884065
C	4.768404	-3.738754	0.000137	H	9.546020	-1.922393	-0.000047
H	4.119532	-3.789193	-0.878055	H	9.339516	-0.400215	-0.883261
H	4.120373	-3.789550	0.878937	C	4.773966	-3.730376	0.000082
H	5.436586	-4.600970	-0.000332	H	5.055024	-4.316466	0.880998
C	-7.373627	-3.856151	0.000018	H	3.697340	-3.571592	0.000007
H	-7.010132	-4.395213	-0.878785	H	5.055133	-4.316576	-0.880726
H	-8.464453	-3.872079	-0.000483	C	-7.384109	-3.843870	-0.000259

H	-7.010986	-4.394809	0.879428	H	-7.028035	-4.383109	0.882981
C	-7.870804	1.196751	-0.000114	H	-8.473158	-3.860748	0.000005
H	-7.616779	1.795538	0.878427	H	-7.028473	-4.382803	-0.883863
H	-8.944174	1.001152	-0.000155	C	-7.860004	1.205774	0.000181
H	-7.616710	1.795531	-0.878638	H	-7.218412	2.084893	0.000344
C	-1.254634	5.069469	0.000035	H	-8.509648	1.229415	-0.880835
H	-1.888490	5.212333	-0.880445	H	-8.509770	1.229161	0.881111
H	-0.501390	5.860324	-0.000302	H	7.169165	0.869473	-0.000068
H	-1.887932	5.212561	0.880883	H	-4.895985	-3.045817	-0.0003040

Complex **2a**

E_{BS}=-5068.4430658 a.u. $<S^2>$ = 0.978932 E_{HS}=-5068.4420301 a.u. $<S^2>$ = 2.004831

C	-0.001158	2.329960	-0.002251	C	-0.001158	2.329960	-0.002251
C	1.183727	3.077367	0.249474	C	1.183727	3.077367	0.249474
C	-1.185341	3.075525	-0.257222	C	-1.185341	3.075525	-0.257222
C	1.146978	4.485724	0.256878	C	1.146978	4.485724	0.256878
C	-1.150129	4.485161	-0.265799	C	-1.150129	4.485161	-0.265799
C	-0.003170	5.221597	-0.001980	C	-0.003170	5.221597	-0.001980
H	2.071246	5.017290	0.463533	H	2.071246	5.017290	0.463533
H	-2.073663	5.015319	-0.478312	H	-2.073663	5.015319	-0.478312
O	-0.000051	0.979839	-0.001254	O	-0.000051	0.979839	-0.001254
C	2.486762	2.505451	0.491527	C	2.486762	2.505451	0.491527
H	3.278215	3.198868	0.776606	H	3.278215	3.198868	0.776606
N	2.788561	1.258222	0.365499	N	2.788561	1.258222	0.365499
C	-2.486315	2.502142	-0.505755	C	-2.486315	2.502142	-0.505755
H	-3.276678	3.194041	-0.797472	H	-3.276678	3.194041	-0.797472
N	-2.787885	1.255135	-0.376395	N	-2.787885	1.255135	-0.376395
N	4.045664	0.805738	0.613159	N	4.045664	0.805738	0.613159
N	-4.043464	0.800113	-0.628100	N	-4.043464	0.800113	-0.628100
C	-4.348306	-0.485741	-0.247153	C	-4.348306	-0.485741	-0.247153
C	-5.926590	-2.088235	0.026636	C	-5.926590	-2.088235	0.026636
C	-3.631108	-2.486094	0.654235	C	-3.631108	-2.486094	0.654235
C	-4.941272	-2.928223	0.563423	C	-4.941272	-2.928223	0.563423
H	-5.195776	-3.920246	0.912250	H	-5.195776	-3.920246	0.912250
N	-5.608786	-0.846079	-0.363109	N	-5.608786	-0.846079	-0.363109
N	-3.313633	-1.233169	0.210175	N	-3.313633	-1.233169	0.210175
Cu	-1.595589	-0.210821	0.054524	Cu	-1.595589	-0.210821	0.054524
Cu	1.595852	-0.210685	-0.055757	Cu	1.595852	-0.210685	-0.055757
C	4.349883	-0.482503	0.240086	C	4.349883	-0.482503	0.240086
C	3.631364	-2.489281	-0.645521	C	3.631364	-2.489281	-0.645521
C	5.928439	-2.085818	-0.027226	C	5.928439	-2.085818	-0.027226
C	4.942077	-2.929993	-0.555364	C	4.942077	-2.929993	-0.555364
H	5.196147	-3.924231	-0.898132	H	5.196147	-3.924231	-0.898132
N	3.314275	-1.233500	-0.209149	N	3.314275	-1.233500	-0.209149
C	2.566881	-3.368441	-1.222662	C	2.566881	-3.368441	-1.222662
H	3.016995	-4.218086	-1.733782	H	3.016995	-4.218086	-1.733782
H	1.913964	-3.758277	-0.438478	H	1.913964	-3.758277	-0.438478

H	1.940572	-2.831590	-1.936549	H	1.940572	-2.831590	-1.936549
N	5.610925	-0.841205	0.354859	N	5.610925	-0.841205	0.354859
C	7.355244	-2.500846	0.116696	C	7.355244	-2.500846	0.116696
H	7.991815	-1.857966	-0.498159	H	7.991815	-1.857966	-0.498159
H	7.680031	-2.363795	1.151377	H	7.680031	-2.363795	1.151377
H	7.515717	-3.537913	-0.174165	H	7.515717	-3.537913	-0.174165
C	-2.567436	-3.360389	1.24022	C	-2.567436	-3.360389	1.240220
H	-1.912474	-3.755479	0.460381	H	-1.912474	-3.755479	0.460381
H	-1.943064	-2.817966	1.951616	H	-1.943064	-2.817966	1.951616
H	-3.018148	-4.206604	1.756491	H	-3.018148	-4.206604	1.756491
C	-7.352865	-2.504944	-0.117783	C	-7.352865	-2.504944	-0.117783
H	-7.989891	-1.864349	0.499118	H	-7.989891	-1.864349	0.499118
H	-7.678537	-2.365940	-1.151837	H	-7.678537	-2.365940	-1.151837
H	-7.511852	-3.542733	0.171347	H	-7.511852	-3.542733	0.171347
H	-4.80065	1.431688	-0.862426	H	-4.800650	1.431688	-0.862426
H	4.802969	1.438685	0.843323	H	4.802969	1.438685	0.843323
Cl	0.000441	-1.840015	0.003414	Cl	0.000441	-1.840015	0.003414
C	-0.00518	6.727992	0.024587	C	-0.005185	6.727992	0.024587
H	-0.848145	7.138512	-0.53269	H	-0.848145	7.138512	-0.532690
H	-0.078083	7.098874	1.051275	H	-0.078083	7.098874	1.051275
H	0.910075	7.137860	-0.406403	H	0.910075	7.137860	-0.406403

Complex **2b**

E_{BS}=-5989.4406404 a.u. $\langle S^2 \rangle$ = 0.980688 E_{HS}=-5989.439751 a.u. $\langle S^2 \rangle$ = 2.005770

C	0.012469	2.253034	0.015432	C	0.012469	2.253034	0.015432
C	1.122636	2.980136	0.530666	C	1.122636	2.980136	0.530666
C	-1.078596	2.991674	-0.518737	C	-1.078596	2.991674	-0.518737
C	1.098845	4.379562	0.524235	C	1.098845	4.379562	0.524235
C	-1.028340	4.393247	-0.539348	C	-1.028340	4.393247	-0.539348
C	0.039977	5.111740	-0.012155	C	0.039977	5.111740	-0.012155
H	1.951746	4.913141	0.937201	H	1.951746	4.913141	0.937201
H	-1.867100	4.934608	-0.970044	H	-1.867100	4.934608	-0.970044
O	-0.003395	0.934653	0.031394	O	-0.003395	0.934653	0.031394
C	2.316325	2.322717	1.033313	C	2.316325	2.322717	1.033313
H	3.027529	2.934635	1.595518	H	3.027529	2.934635	1.595518
N	2.588400	1.092516	0.782265	N	2.588400	1.092516	0.782265
C	-2.275330	2.347952	-1.025784	C	-2.275330	2.347952	-1.025784
H	-2.970448	2.964571	-1.602333	H	-2.970448	2.964571	-1.602333
N	-2.572871	1.122872	-0.770022	N	-2.572871	1.122872	-0.770022
N	3.734452	0.512393	1.207226	N	3.734452	0.512393	1.207226
N	-3.725634	0.563630	-1.207972	N	-3.725634	0.563630	-1.207972
C	-4.141901	-0.603878	-0.616195	C	-4.141901	-0.603878	-0.616195
C	-5.726499	-2.210870	-0.428423	C	-5.726499	-2.210870	-0.428423
C	-3.726736	-2.287510	0.902332	C	-3.726736	-2.287510	0.902332
C	-4.949613	-2.846980	0.540234	C	-4.949613	-2.846980	0.540234
H	-5.284901	-3.762052	1.010769	H	-5.284901	-3.762052	1.010769
N	-5.318555	-1.075159	-1.007775	N	-5.318555	-1.075159	-1.007775

N	-3.318181	-1.145311	0.306085	N	-3.318181	-1.145311	0.306085
Cu	-1.590300	-0.129075	0.547570	Cu	-1.590300	-0.129075	0.547570
Cu	1.547755	-0.178248	-0.501690	Cu	1.547755	-0.178248	-0.501690
C	4.125790	-0.658661	0.603022	C	4.125790	-0.658661	0.603022
C	3.674392	-2.321937	-0.927552	C	3.674392	-2.321937	-0.927552
C	5.700826	-2.268678	0.362301	C	5.700826	-2.268678	0.362301
C	4.904261	-2.887954	-0.601076	C	4.904261	-2.887954	-0.601076
H	5.230638	-3.793319	-1.096071	H	5.230638	-3.793319	-1.096071
N	3.276541	-1.193748	-0.299294	N	3.276541	-1.193748	-0.299294
C	2.769874	-2.900192	-1.962390	C	2.769874	-2.900192	-1.962390
H	3.217108	-3.778587	-2.428215	H	3.217108	-3.778587	-2.428215
H	1.810802	-3.172858	-1.515038	H	1.810802	-3.172858	-1.515038
H	2.551044	-2.147467	-2.725155	H	2.551044	-2.147467	-2.725155
N	5.309478	-1.137734	0.962158	N	5.309478	-1.137734	0.962158
C	7.034250	-2.818705	0.775847	C	7.034250	-2.818705	0.775847
H	7.816279	-2.075214	0.601197	H	7.816279	-2.075214	0.601197
H	7.032627	-3.033282	1.847826	H	7.032627	-3.033282	1.847826
H	7.286937	-3.730922	0.234686	H	7.286937	-3.730922	0.234686
C	-2.838496	-2.894601	1.934636	C	-2.838496	-2.894601	1.934636
H	-1.870024	-3.146360	1.494772	H	-1.870024	-3.146360	1.494772
H	-2.635070	-2.169401	2.727120	H	-2.635070	-2.169401	2.727120
H	-3.288461	-3.791573	2.360671	H	-3.288461	-3.791573	2.360671
C	-7.053818	-2.750538	-0.874002	C	-7.053818	-2.750538	-0.874002
H	-7.836030	-2.005732	-0.705840	H	-7.836030	-2.005732	-0.705840
H	-7.032466	-2.952819	-1.948145	H	-7.032466	-2.952819	-1.948145
H	-7.320515	-3.667719	-0.348236	H	-7.320515	-3.667719	-0.348236
H	-4.368656	1.051799	-1.819634	H	-4.368656	1.051799	-1.819634
H	4.407595	1.000520	1.786289	H	4.407595	1.000520	1.786289
Cl	-1.604374	0.323713	2.815275	Cl	-1.604374	0.323713	2.815275
Cl	1.695096	0.455920	-2.742152	Cl	1.695096	0.455920	-2.742152
Cl	-0.017466	-2.019567	-0.022542	Cl	-0.017466	-2.019567	-0.022542
C	0.050311	6.620829	-0.000254	C	0.050311	6.620829	-0.000254
H	-0.689906	7.030865	-0.690486	H	-0.689906	7.030865	-0.690486
H	-0.178798	7.013995	0.995880	H	-0.178798	7.013995	0.995880
H	1.026530	7.018688	-0.289600	H	1.026530	7.018688	-0.289600