New mix-ligand copper(I) and copper(II) pyrazolate complexes with 2,2′-bipyridine

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Materials and methods. ^{1}H, ^{19}F and ^{31}P NMR measurements were carried out on Bruker Avance 400 spectrometer. Infrared (IR) spectra were collected on a Shimadzu IRPresige 21 FT-IR spectrometer using KBr pellets. Steady-state luminescence and excitation spectra were recorded on Fluorolog FL 3-22 Horiba-Jobin-Yvon photon counting emission spectrometer equipped with a 450 W xenon source and double monochromators for excitation and emission. The luminescence spectra observed were corrected for the nonlinear response of the instrument using predetermined factors. The crystals for these measurements were packed in quartz capillaries.

Synthetic procedures.

Bis(2,2'-bipyridine)(hydroxo)tricopper(II) pentakis[3,5-bis(trifluoromethyl)pyrazol-1-ide] **1**. A mixture of [Cu((CF$_3$)$_2$Pz)]$_3$ (50 mg, 0.0625 mmol) and 2,2'-bipyridine (9.8 mg, 0.0625 mmol) was dissolved in toluene (3 ml). The crimson solution was stirred overnight at room temperature in air to become blue. Then, hexane (3 ml) was layered on the surface of the reaction solution. The solution obtained was refrigerated at 5 °C. Within one hour, the blue crystals have formed which were isolated by filtration, washed with hexane and Et$_2$O, and dried under vacuum yielding 21 mg of **1**. IR (KBr, cm^{-1}): 3636 (ν(OH)), 3152, 3114 (ν(CH^{Pz})), 3087, 2956, 2920, 2851 (ν(CH)^{biPy}), 1612, 1605 (δ(CN^{bipy})), 1525, 1456, 1253, 1100. Anal. calc./found: C, 35.20/35.52; H, 1.44/1.58; N, 12.77/12.68.

[Bis(diphenylphosphino)methane](2,2'-bipyridine)dicopper(I) bis[3,5-bis(trifluoromethyl)-pyrazol-1-ide] **2**: To a solution of [Cu((CF$_3$)$_2$Pz)]$_3$ (30 mg, 0.0375 mmol) in toluene (2 ml) was added dppm (14.4 mg, 0.0375 mmol). The colourless solution was stirred for 1 h, and a solution of 2,2'-bipyridine (5.85 mg, 0.0375 mmol) in toluene (1.5 ml) was added dropwise. The yellow solution was stirred at 60 °C for 3 h. After cooling to room temperature, hexane (3 ml) was added. The product was crystallized at -15 °C, isolated by filtration, washed with cold hexane, and dried under vacuum yielding 27 mg of **2**. ^{1}H NMR (CD$_2$Cl$_2$, ppm): δ = 3.45 (t, 2H, CH_2 dppm), 6.89 (s, 2H, CH^{Pz}), 6.95-7.36 (m, 22H, CH^{Ph} and 5,5′-CH^{biPy}), 7.83 (t, 2H, 4,4′-CH^{biPy}), 8.00 (d, 2H, 6,6′-CH^{biPy}), 8.90 (d, 2H, 3,3′-CHL). IR (KBr, cm^{-1}): 3155, 3147 (ν(CH^{Pz})), 3075, 3060, 3020, 3001, 2920 (ν(CH$^{ph/bipy}$)), 1600, 1594 (δ(CN^{bipy})), 1436, 1252, 1039. Anal. calc./found: C, 50.33/50.27; H, 3.00/3.18; N, 7.83/7.74.

X-ray diffraction study.

The structures were solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methylene and aromatic fragments were calculated according to their idealized geometry and refined with constraints applied to C-H and O-H bond lengths and equivalent displacement parameters ($U_{eq}(H) = 1.2U_{eq}(X)$, X - cental atom of XH_2 group. All structures were solved with the ShelXT [S1] program and refined with the ShelXL [S2] program. Molecular graphics was drawn using OLEX2 [S3] program.

Table S1. Crystal data, data collection and structure refinement parameters for **1** and **2**.

datablock	1	2
Formula moiety	$C_{45}H_{22}Cu_3F_{30}N_{14}O$	$C_{45}H_{32}Cu_2F_{12}N_6P_2$
Brutto formula	$C_{45}H_{22}Cu_3F_{30}N_{14}O$	$C_{45}H_{32}Cu_2F_{12}N_6P_2$
Formula weight	1535.38	1073.78
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD
Scan mode	ϕ and ω scans	ϕ and ω scans
Anode [Wavelength, Å]	MoKα [0.71073]	MoKα [0.71073]
Crystal Dimensions, mm	$0.08 \times 0.18 \times 0.28$	$0.08 \times 0.13 \times 0.25$
Crystal color	colourless	yellow
Crystal system	monoclinic	triclinic
a, Å	12.9719(6)	10.4244(14)
b, Å	12.2711(5)	14.4627(19)
c, Å	33.9803(15)	15.325(2)
α, °	90	87.963(2)
β, °	93.4930(10)	78.566(2)
γ, °	90	80.011(2)
Volume, Å³	5398.9(4)	2230.2(5)
Density, g cm⁻³	1.889	1.599
Temperature, K	120	120.0
Tmin/Tmax	0.6545/0.7461	0.5745/0.7461

μ, mm^{-1}	1.328	1.117
Space group	P2$_1$/c	P-1
Z	4	2
F(000)	3020	1080
Reflections collected	95470	29778
Independent reflections	16653	13780
Reflections (I>2σ(I))	12061	9964
Parameters	842	622
R$_{int}$	0.0551	0.0435
2θmin - 2θmax, °	3.146 - 61.392	2.860 - 61.680
wR$_2$ (all reflections)[a]	0.0899	0.1580
R$_1$(I>σ(I))[b]	0.0358	0.0526
GOF	1.008	1.055
ρ_{min}/ρ_{max}, e Å^{-3}	-0.800/1.142	-0.842/1.199

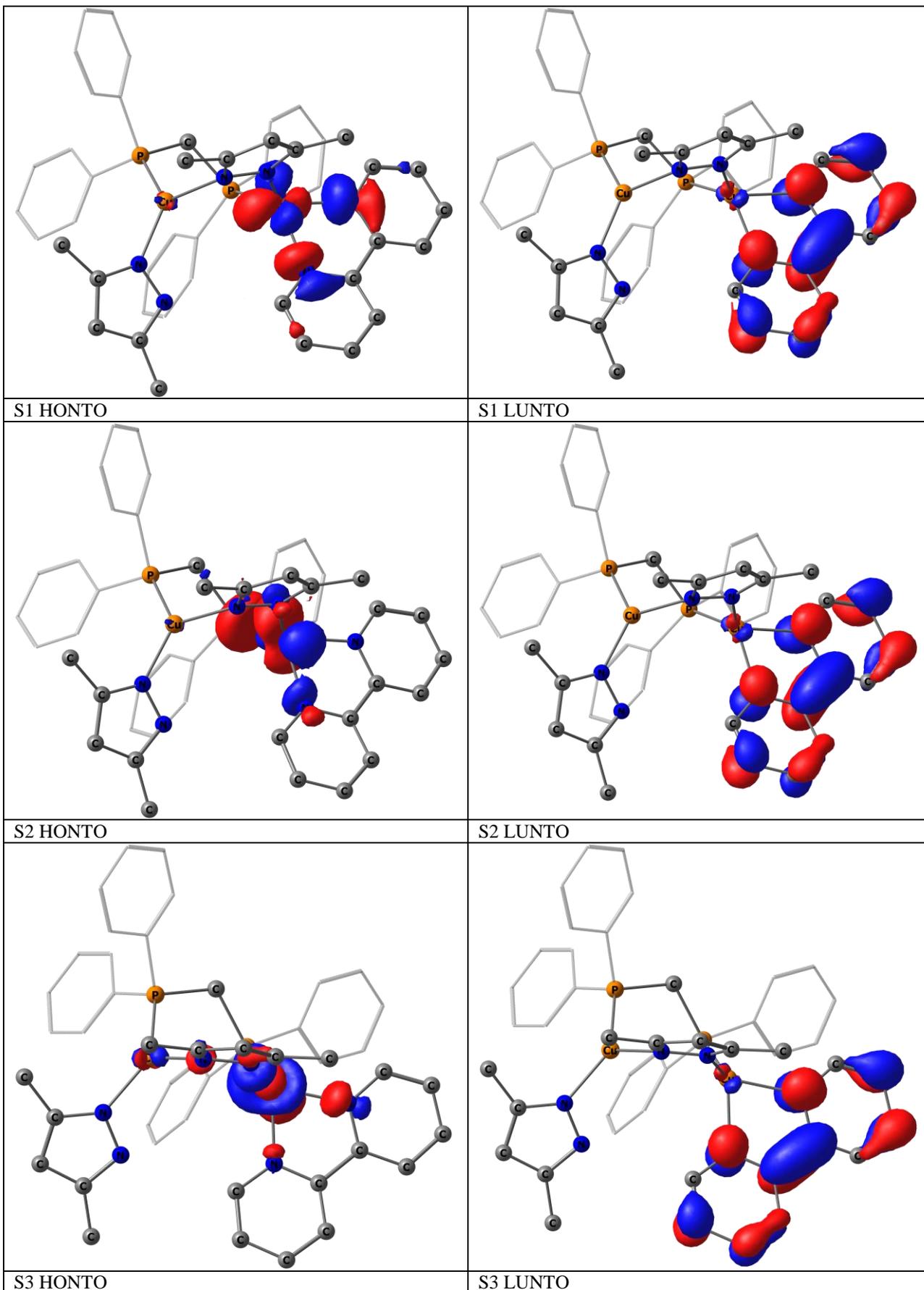[a] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

[b] $R_1 = \Sigma\left||F_o| - |F_c|\right|/\Sigma|F_o|$

Computation details.

The excited states' similarity was analyzed by the approach suggested by Chen [S4]:

$$s_{H/E} = 1 - \frac{\sum_i |a_i - b_i|}{2}$$

where a_i and b_i are contributions of the i atom to the hole (s_H) or electron (s_E) in the states a and b.

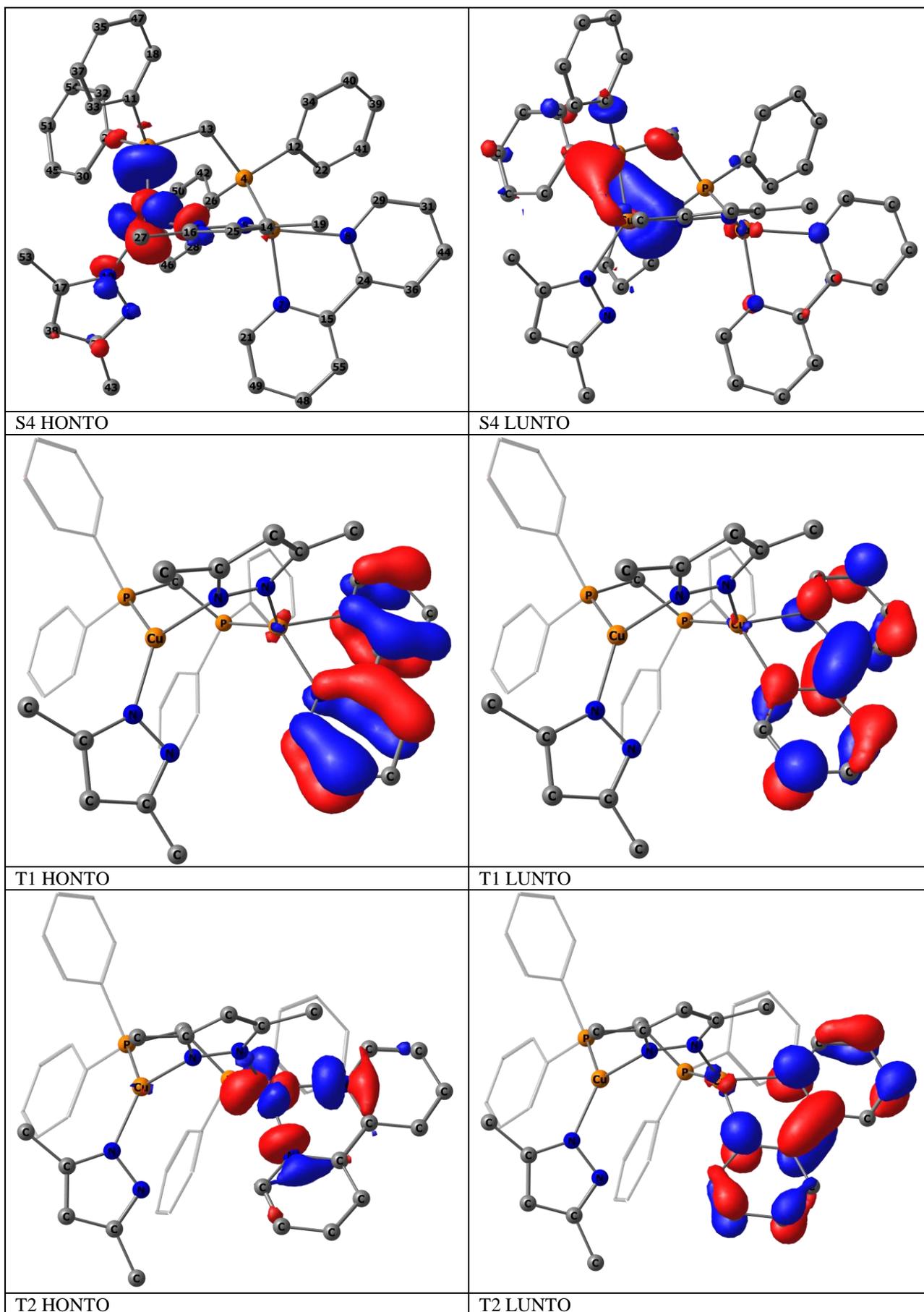| S1 HONTO | S1 LUNTO |
| S2 HONTO | S2 LUNTO |
| S3 HONTO | S3 LUNTO |

Figure S1. Natural transition orbitals of **2** as isosurface at 0.05 a.u.
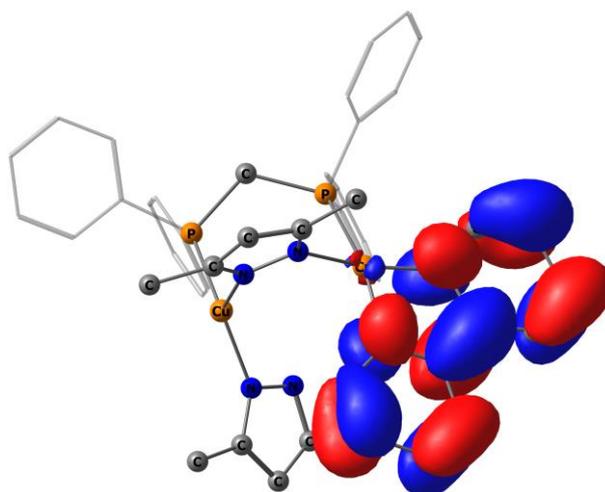
Figure S2. Highest energy SOMO of optimized triplet state of **2**.

Table S2. Energies of 20 lowest energy vertical $S_0 \rightarrow S_X$ transitions with oscillator strengths, and energies of 20 lowest energy forbidden $S_0 \rightarrow T_n$ transitions.

	singlets				triplets	
	nm	eV	f		nm	eV
S1	347.5	3.568	0.0121	T1	397.9	3.116
S2	319.6	3.880	0.0442	T2	375.0	3.306
S3	309.4	4.007	0.0211	T3	355.2	3.491
S4	279.4	4.437	0.0159	T4	351.5	3.528
S5	273.4	4.536	0.0058	T5	349.8	3.545
S6	273.0	4.542	0.0032	T6	348.4	3.559
S7	266.6	4.651	0.0479	T7	345.3	3.590
S8	265.3	4.673	0.0002	T8	325.4	3.810
S9	262.7	4.721	0.0018	T9	303.7	4.083
S10	261.5	4.742	0.0501	T10	298.8	4.150
S11	259.8	4.772	0.0139	T11	295.8	4.191
S12	259.0	4.787	0.0226	T12	283.8	4.369
S13	257.3	4.819	0.2135	T13	281.4	4.406
S14	255.1	4.861	0.0417	T14	278.3	4.455
S15	252.6	4.908	0.0377	T15	277.5	4.468
S16	251.8	4.924	0.0006	T16	275.4	4.503
S17	247.0	5.020	0.0028	T17	274.6	4.515
S18	244.3	5.076	0.0460	T18	274.3	4.520
S19	241.1	5.142	0.0347	T19	274.1	4.524
S20	239.3	5.182	0.0168	T20	273.6	4.532

Table S3. XYZ coordinates of DFT optimized complex **2**.

2, singlet, E= -7224.81103100 Ha

29	2.014491000	-0.210894000	0.174941000
29	-1.447417000	-0.204905000	0.653475000
15	-1.488119000	2.023570000	0.339928000
15	1.302597000	1.619516000	-0.929071000
9	3.431097000	-1.312901000	4.717212000
9	3.884223000	-1.877369000	2.687403000
9	3.694508000	0.205682000	3.205827000
9	-4.627066000	-0.033433000	0.633976000
9	-1.916740000	-1.802134000	5.020599000
9	-1.455913000	-3.420024000	-3.901913000
9	-3.182988000	-4.664765000	-3.530927000
9	-1.346970000	-4.997796000	-2.445496000
7	1.182255000	-0.686226000	1.997885000
7	-0.141225000	-0.857088000	2.079795000
7	2.398817000	-2.125244000	-0.677079000
7	4.170923000	-0.285788000	0.121345000
7	-1.776523000	-2.312588000	-1.243365000
7	-2.473144000	-1.592301000	-0.365716000
9	-4.882575000	-1.929794000	1.618606000
9	-6.034301000	-1.480728000	-0.144018000
9	-2.693749000	-0.738361000	3.304182000
6	-2.060809000	2.983130000	1.786197000
6	2.714210000	2.728095000	-1.297088000
6	0.184766000	2.732528000	0.021069000
1	0.114297000	3.713680000	-0.449003000
1	0.649529000	2.848645000	1.000958000
6	1.713831000	-1.073410000	3.165509000
6	3.689217000	-2.467664000	-0.746667000
9	-2.244166000	-2.839714000	3.160459000
6	-0.424704000	-1.350188000	3.288831000
6	-3.769515000	-1.934063000	-0.463387000
6	-1.497838000	4.186485000	2.198094000
1	-0.656940000	4.611904000	1.667264000
6	3.171078000	-1.014556000	3.437423000
6	-2.638575000	-3.101691000	-1.884674000
6	1.467619000	-3.032294000	-0.958368000
1	0.432652000	-2.713794000	-0.899424000
6	3.550055000	2.413403000	-2.366575000
1	3.311626000	1.572690000	-3.005409000
6	-2.504548000	2.695421000	-1.022041000
6	4.669867000	-1.403551000	-0.412027000
6	0.729323000	-1.508155000	4.033198000
1	0.834178000	-1.868569000	5.039885000
6	0.500094000	1.442818000	-2.554293000
6	-1.816835000	-1.683922000	3.688284000
6	0.041254000	0.190142000	-2.939584000
1	0.152986000	-0.659321000	-2.280256000
6	4.997639000	0.694356000	0.463766000
1	4.543810000	1.573725000	0.899189000
6	-3.133582000	1.809478000	-1.885728000
1	-3.008487000	0.744699000	-1.744015000
6	6.365052000	0.620547000	0.288637000
1	6.995407000	1.445357000	0.587642000
6	-2.684643000	4.063769000	-1.206388000
1	-2.225025000	4.770805000	-0.527332000
6	-3.139162000	2.469611000	2.501340000
1	-3.582816000	1.528129000	2.206931000
6	3.049207000	3.811778000	-0.493063000
1	2.429911000	4.082056000	0.350923000
6	-3.079131000	4.345895000	3.995524000
1	-3.471511000	4.872792000	4.855245000
6	6.033214000	-1.547951000	-0.634061000
1	6.425543000	-2.444761000	-1.087631000
6	-3.647109000	3.148673000	3.594246000
1	-4.483563000	2.732526000	4.139549000
6	-3.935016000	-2.908079000	-1.429796000
1	-4.842344000	-3.390117000	-1.745343000
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1	5.878875000	4.842362000	-2.034440000
6	4.182192000	4.567296000	-0.755549000
1	4.421495000	5.410277000	-0.120513000
6	4.677089000	3.168138000	-2.631357000
1	5.307906000	2.911479000	-3.472268000
6	0.318465000	2.525893000	-3.412474000
1	0.673404000	3.508977000	-3.130618000
6	-2.162987000	-4.035896000	-2.931398000
6	6.888906000	-0.525367000	-0.277706000
1	7.953501000	-0.624158000	-0.442786000
6	-3.922131000	2.282084000	-2.923052000
1	-4.407807000	1.580185000	-3.587608000
6	-0.588840000	0.017491000	-4.162921000
1	-0.948185000	-0.963964000	-4.440576000
6	-2.002125000	4.862447000	3.296434000
1	-1.550166000	5.795678000	3.606151000
6	3.109055000	-4.693762000	-1.388633000
1	3.394748000	-5.701450000	-1.659578000
6	1.779918000	-4.329776000	-1.324339000
1	0.984251000	-5.024079000	-1.550636000
6	-0.305780000	2.353677000	-4.631629000
1	-0.444307000	3.201100000	-5.289933000
6	-4.090715000	3.642282000	-3.102141000
1	-4.711180000	4.011155000	-3.908473000
6	-0.758085000	1.096841000	-5.009099000
1	-1.247355000	0.964144000	-5.965285000
6	-4.817847000	-1.350557000	0.408652000
6	-3.470163000	4.535023000	-2.240632000
1	-3.607851000	5.600516000	-2.370692000
6	4.077312000	-3.752271000	-1.095180000
1	5.120527000	-4.026480000	-1.122487000

2, triplet, E= -7224.74033174 Ha

29	1.461398000	0.521270000	1.086638000	6	-1.484939000	-0.091775000	-3.626125000
29	-1.308337000	-1.114165000	-0.071732000	1	-0.833619000	-0.785095000	-3.107930000
15	-2.331605000	0.601064000	-1.088121000	6	5.071876000	2.458169000	-0.081948000
15	0.311598000	2.156435000	-0.382560000	1	5.373343000	3.440364000	-0.413337000
9	0.130214000	2.578450000	4.653875000	6	-3.165009000	1.625178000	-3.583175000
9	1.082135000	0.827195000	5.461690000	1	-3.849564000	2.259727000	-3.034849000
9	1.769467000	1.663704000	3.589523000	6	-4.904039000	-0.274988000	-0.692523000
9	-2.272726000	-4.422877000	-0.175005000	1	-4.486598000	-1.234715000	-0.971041000
9	-4.295352000	-0.673892000	2.846988000	6	0.087389000	4.123254000	1.548789000
9	2.209880000	-2.618172000	-4.226727000	1	-0.426117000	3.359358000	2.118191000
9	3.331151000	-4.089531000	-3.114826000	6	-6.788007000	1.035100000	0.001491000
9	3.477791000	-1.992132000	-2.607692000	1	-7.837369000	1.107465000	0.254554000
7	-0.145869000	0.247781000	2.278389000	6	5.573236000	0.200464000	0.527843000
7	-1.170520000	-0.519281000	1.902847000	1	6.274933000	-0.606921000	0.675429000
7	2.329709000	-1.176466000	1.621927000	6	-6.247548000	-0.181195000	-0.382105000
7	3.301412000	1.008901000	0.604734000	1	-6.870885000	-1.064104000	-0.426703000
7	0.789336000	-2.071836000	-1.644514000	6	1.002490000	-4.304154000	-1.477300000
7	-0.164331000	-2.517012000	-0.825363000	1	1.351846000	-5.312479000	-1.604366000
9	-0.869708000	-4.315741000	1.451089000	6	0.945824000	6.357950000	1.424451000
9	-0.751791000	-5.944654000	0.038466000	1	1.095266000	7.331242000	1.872366000
9	-3.270961000	-2.241637000	1.777234000	6	0.271914000	5.367855000	2.120583000
6	-4.081634000	0.847642000	-0.637714000	1	-0.101995000	5.558295000	3.117523000
6	0.566630000	3.847749000	0.269371000	6	1.435915000	6.092111000	0.158623000
6	-1.530736000	2.145818000	-0.475200000	1	1.970528000	6.857109000	-0.388741000
1	-1.852633000	3.021870000	-1.039012000	6	0.380577000	3.079207000	-3.036756000
1	-1.874761000	2.268895000	0.552703000	1	-0.345036000	3.826026000	-2.741892000
6	-0.286145000	0.531768000	3.582119000	6	2.620540000	-2.959430000	-2.986038000
6	3.670660000	-1.208060000	1.341607000	6	6.007547000	1.408838000	0.083318000
9	-3.376616000	-2.285608000	3.937829000	1	7.055000000	1.568295000	-0.132937000
6	-1.951534000	-0.707369000	2.966002000	6	-1.464904000	-0.030316000	-5.010382000
6	-0.054377000	-3.850363000	-0.713583000	1	-0.800018000	-0.681183000	-5.562163000
6	-4.633905000	2.063048000	-0.250499000	6	2.216201000	1.164712000	-3.834948000
1	-4.023124000	2.953514000	-0.191165000	1	2.917650000	0.400941000	-4.141110000
6	0.678127000	1.391988000	4.320556000	6	-5.978759000	2.155029000	0.069637000
6	1.494604000	-3.130378000	-2.036273000	1	-6.393059000	3.107030000	0.374378000
6	1.733021000	-2.263951000	2.131741000	6	3.778389000	-3.479993000	2.118363000
1	0.672139000	-2.186224000	2.316065000	1	4.338144000	-4.385939000	2.308675000
6	1.249617000	4.845389000	-0.416800000	6	2.400574000	-3.424111000	2.401421000
1	1.648423000	4.652858000	-1.402428000	1	1.866328000	-4.270939000	2.803948000
6	-2.332338000	0.740156000	-2.903555000	6	0.812900000	3.042427000	-4.346625000
6	4.207709000	-0.013768000	0.816184000	1	0.422874000	3.754029000	-5.061931000
6	-1.433677000	-0.056271000	4.074641000	6	-2.293484000	0.852277000	-5.679197000
1	-1.826025000	-0.021993000	5.075369000	1	-2.283452000	0.891896000	-6.760712000
6	0.872418000	2.163779000	-2.105705000	6	1.736299000	2.086116000	-4.745370000
6	-3.220566000	-1.483255000	2.877334000	1	2.071154000	2.056210000	-5.773993000
6	1.785553000	1.201250000	-2.518228000	6	-0.980458000	-4.629142000	0.141886000
1	2.149608000	0.458619000	-1.824044000	6	-3.144467000	1.681634000	-4.964042000
6	3.762692000	2.203543000	0.187847000	1	-3.801095000	2.366110000	-5.485054000
1	3.028218000	2.986558000	0.076868000	6	4.401571000	-2.389254000	1.594453000
				1	5.455251000	-2.423994000	1.362141000

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