Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electrocatalytic Reduction of Protons to Hydrogen by a Copper Complex of the Pentadentate Ligand Dmphen-DPA in Nonaqueous Electrolyte

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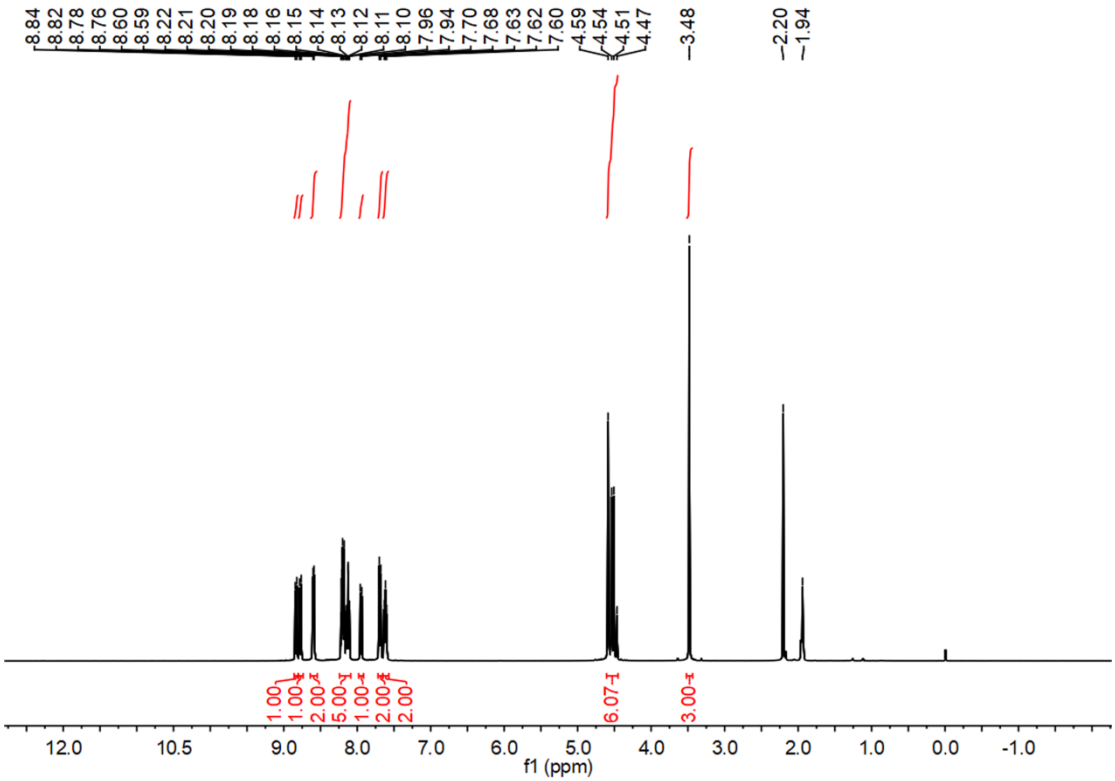

Figure S1. 1H-NMR of the prepared complex **2**

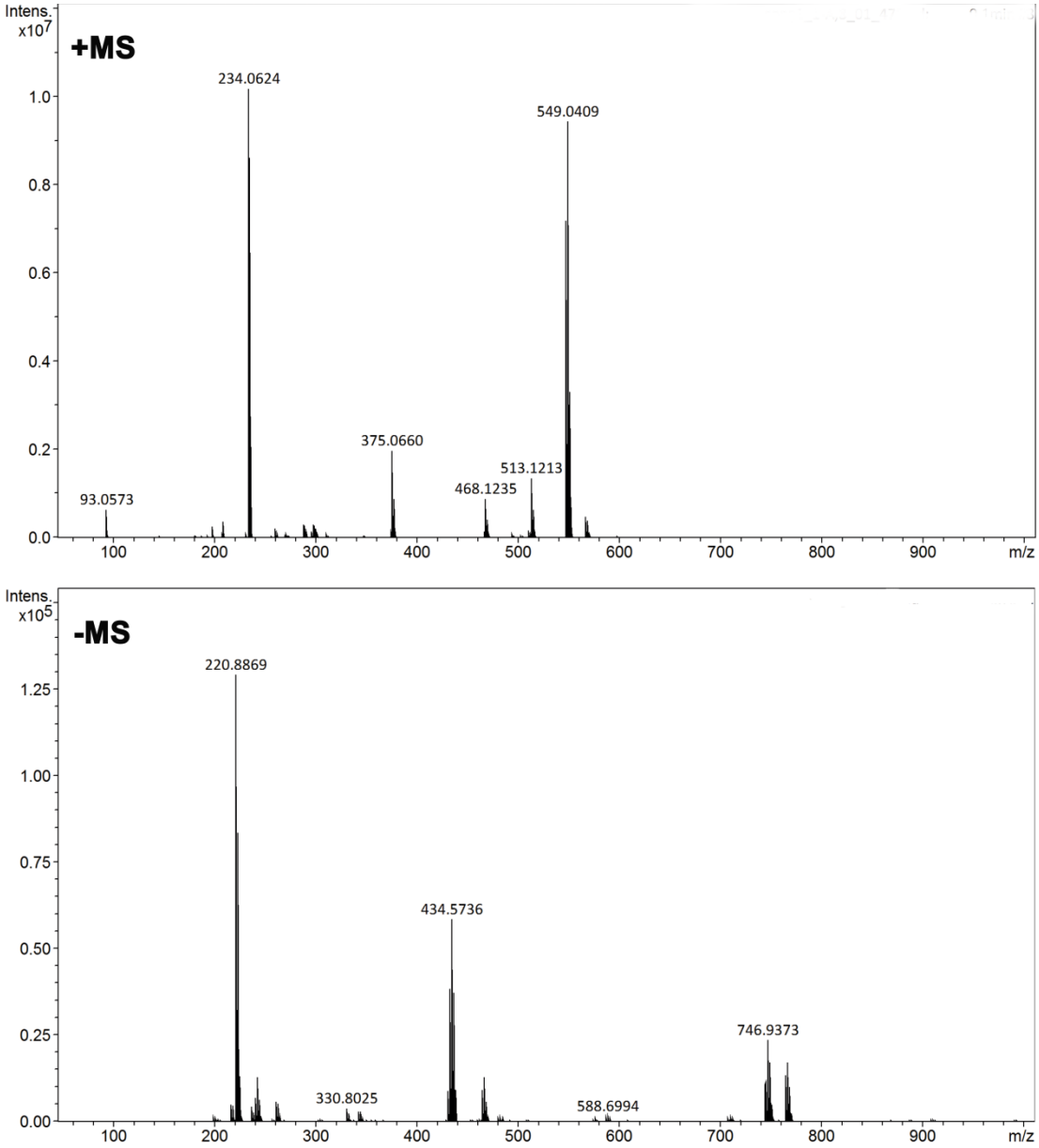

Figure S2. The high-resolution mass spectrometry of the prepared complex **1**

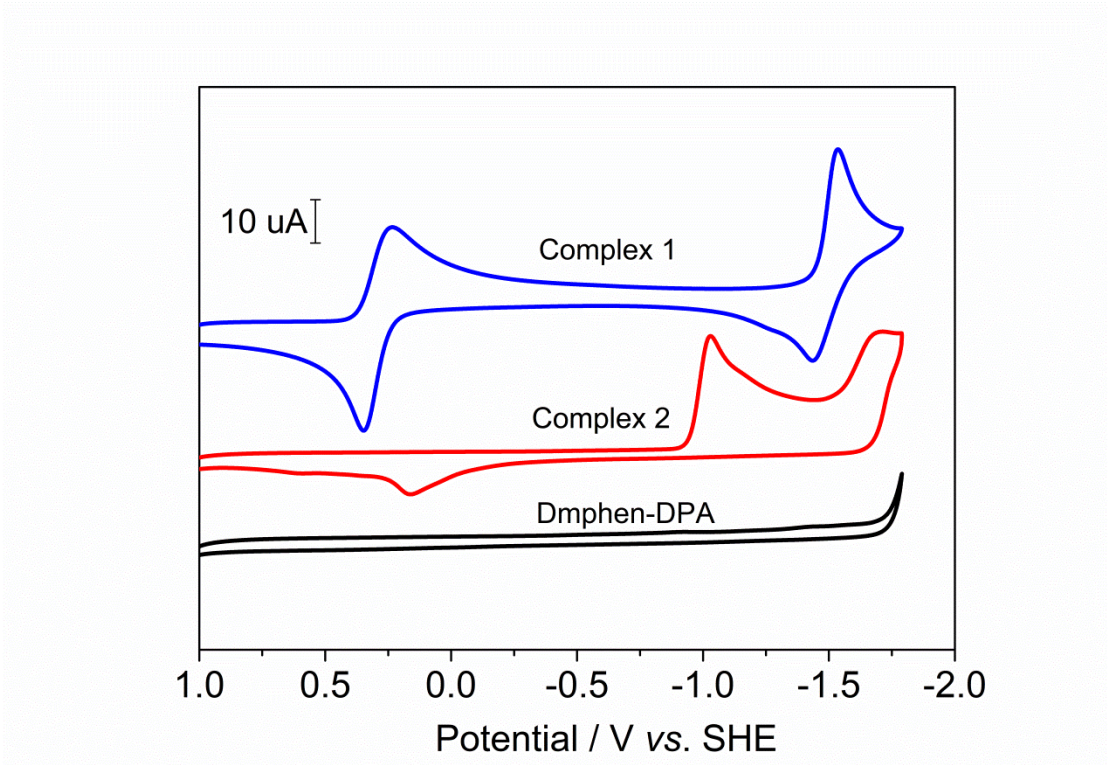

Figure S3. Cyclic voltammograms of **1** (1.2 mM), **2** (1 mM) and the ligand Dmphen-DPA measured in acetonitrile (0.1 M NBu_4PF_6, ν = 100 mV s^{-1}).

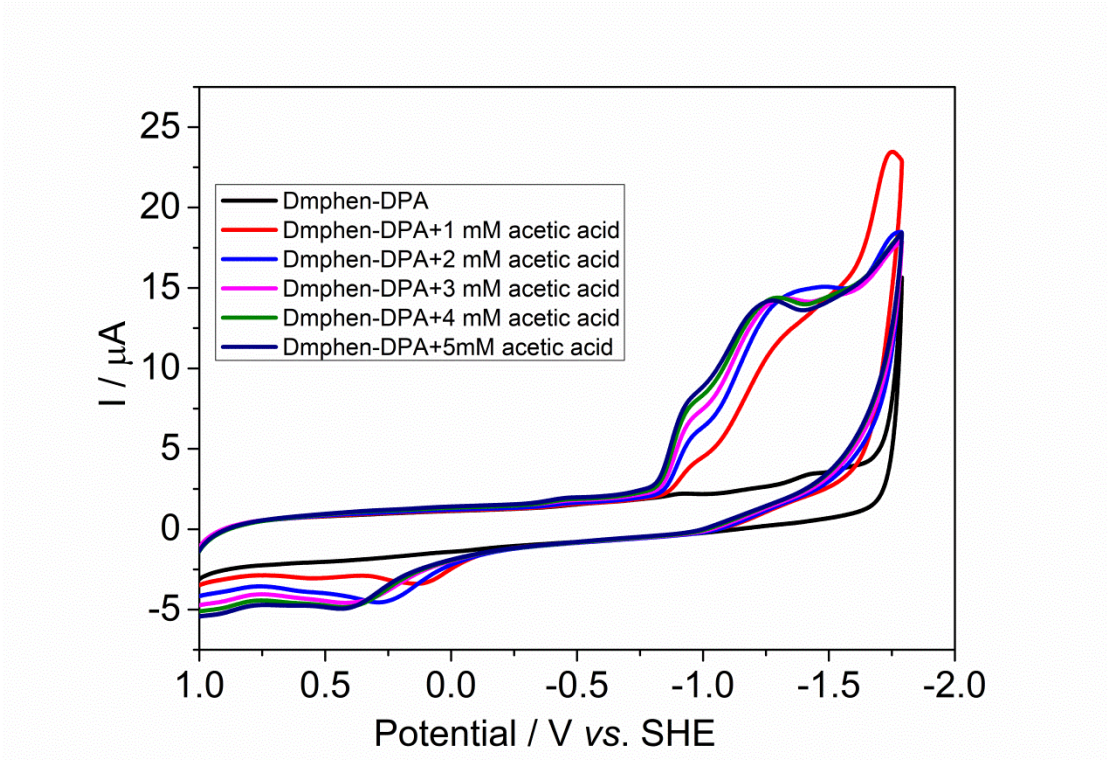

Figure S4. Electrochemical response of 1.0 mM Dmphen-DPA to addition of acetic acid (0, 1, 2, 3, 4, 5 mM) in acetonitrile (0.1 M NBu_4PF_6, ν = 100 mV s^{-1}).

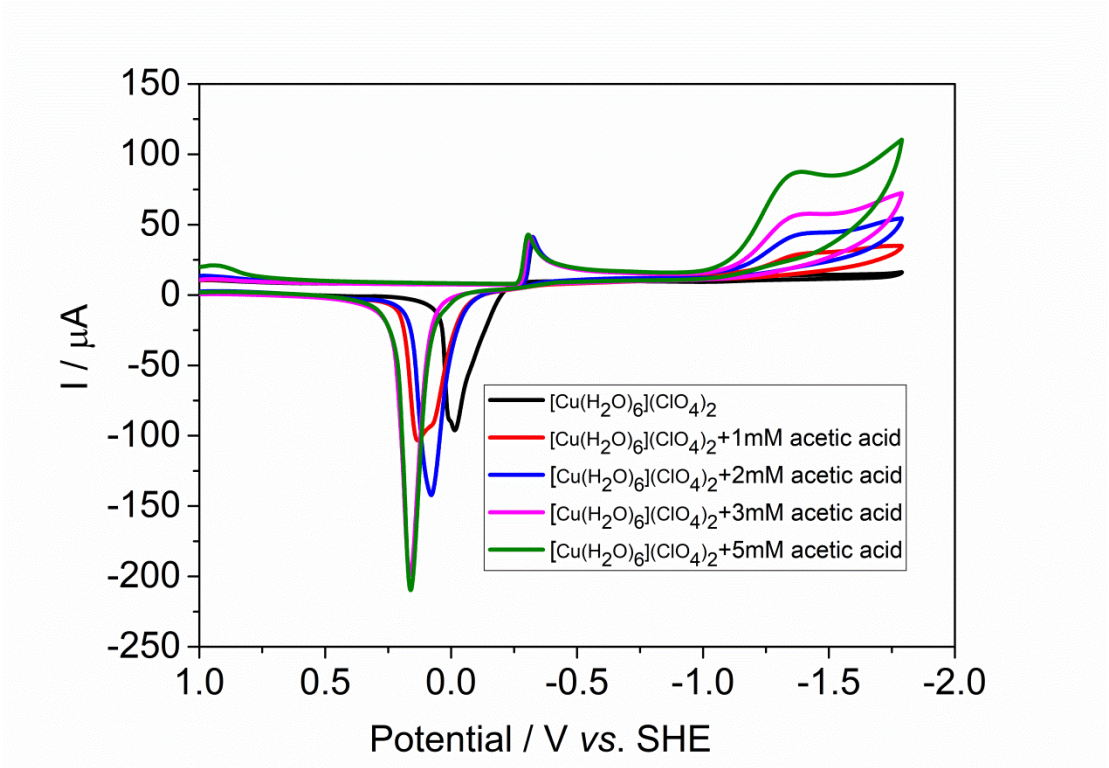

Figure S5. Electrochemical response of 1.0 mM $Cu(H_2O)_6(ClO_4)_2$ to addition of acetic acid (0, 1, 2, 3, 4, 5 mM) in acetonitrile (0.1 M NBu_4PF_6, ν = 100 mV s^{-1}).

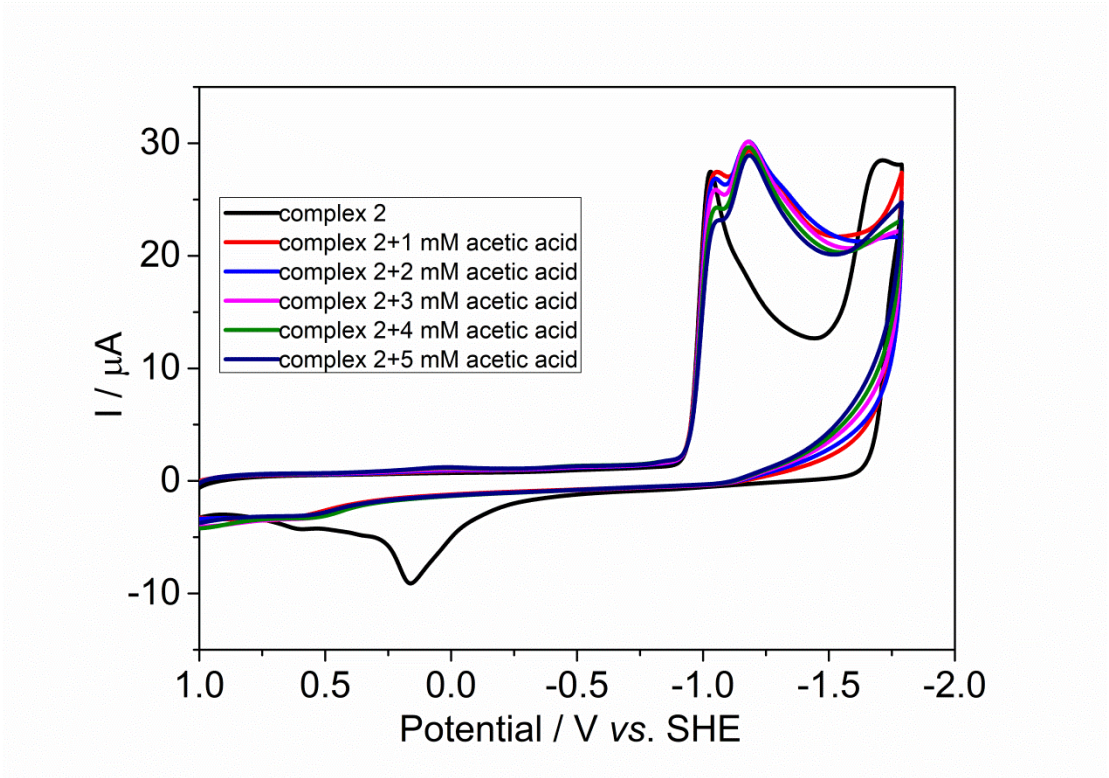

Figure S6. Electrochemical response of 1.0 mM complex **2** to addition of acetic acid (0, 1, 2, 3, 4, 5 mM) in acetonitrile (0.1 M NBu_4PF_6, ν = 100 mV s^{-1}).

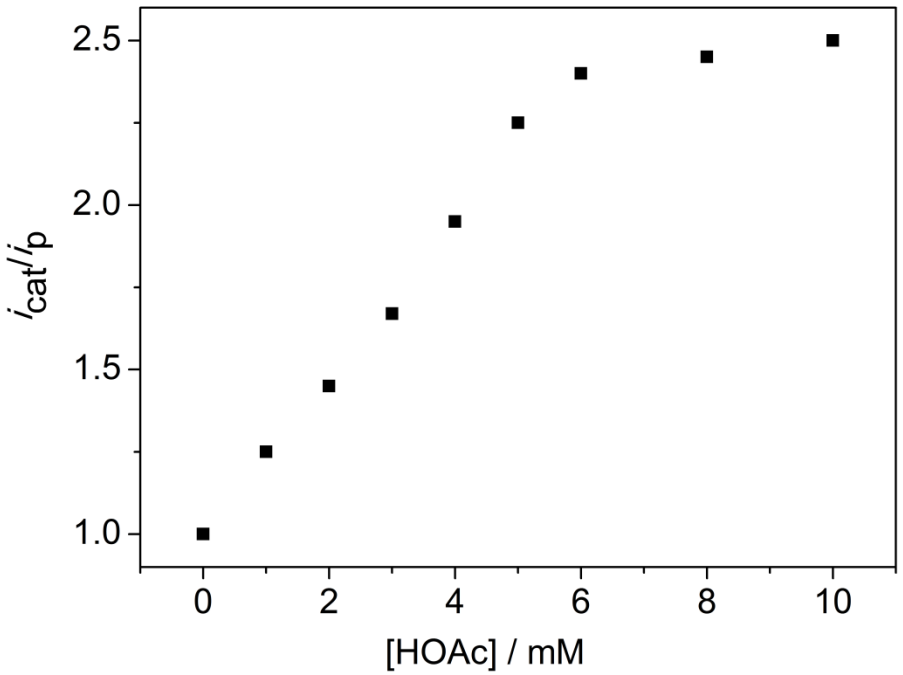

Figure S7. Plots of the i_{cat}/i_p ratio as a function of the concentration of HOAc for **1** (1 mM). i_{cat}/i_p values were measured at the potential of pinnacle. (0.1 M NBu_4PF_6, ν = 100 mV s^{-1})

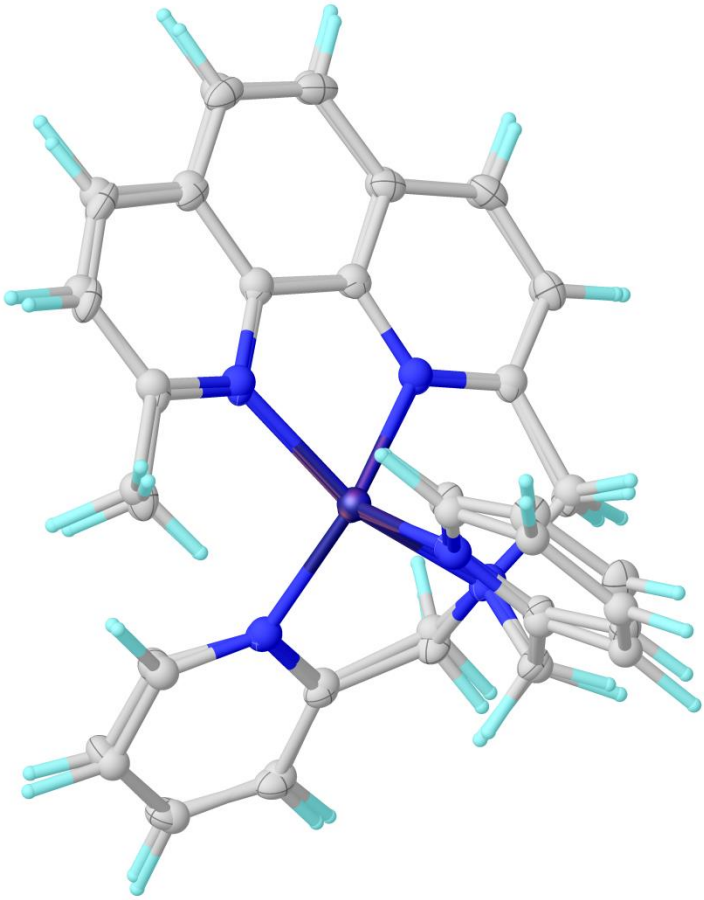

Figure S8. Overlay of the optimized structure and the crystal structure for the complex **1**.

Table S1. Selected bond lengths (Å) and angles (°) for **1** and **2**

1					
Cu(1)-N(4)	1.927(2)	Cu(1)-N(2)	2.043(2)	Cu(1)-N(5)	2.0494(18)
Cu(1)-N(3)	2.0677(19)	Cu(1)-N(1)	2.099(2)	N(4)-Cu(1)-N(2)	128.25(8)
N(4)-Cu(1)-N(5)	81.82(8)	N(2)-Cu(1)-N(5)	107.80(8)	N(4)-Cu(1)-N(3)	80.33(8)
N(2)-Cu(1)-N(3)	82.84(8)	N(5)-Cu(1)-N(3)	162.14(8)	N(4)-Cu(1)-N(1)	109.09(8)
N(2)-Cu(1)-N(1)	116.35(8)	N(5)-Cu(1)-N(1)	105.04(7)	N(3)-Cu(1)-N(1)	81.79(8)
2					
Zn(1)-N(4)	2.009(4)	Zn(1)-N(2)	2.023(5)	Zn(1)-N(1)	2.028(4)
Zn(1)-N(5)	2.148(4)	Zn(1)-N(3)	2.273(4)	N(4)-Zn(1)-N(2)	119.60(17)
N(4)-Zn(1)-N(1)	112.95(16)	N(2)-Zn(1)-N(1)	117.36(17)	N(4)-Zn(1)-N(5)	79.58(15)
N(2)-Zn(1)-N(5)	110.84(17)	N(1)-Zn(1)-N(5)	109.88(16)	N(4)-Zn(1)-N(3)	76.89(15)
N(2)-Zn(1)-N(3)	80.88(18)	N(1)-Zn(1)-N(3)	80.13(16)	N(5)-Zn(1)-N(3)	156.47(15)

Cartesian coordinates of optimized geometries

M1 (Doublet, G = - 2916.838501 a. u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.386450	0.097552	0.123802
2	7	0	-1.459839	-1.208883	1.362221
3	7	0	-1.418543	1.802870	-0.453929
4	7	0	-1.667054	-0.783954	-1.351261
5	7	0	0.918687	-0.832957	-1.020379
6	7	0	1.373017	0.713826	1.068637
7	6	0	-1.103977	-1.658945	2.583820
8	1	0	-0.228280	-1.186432	3.034058
9	6	0	-1.798491	-2.672510	3.244809
10	1	0	-1.475650	-2.998370	4.234572
11	6	0	-2.897893	-3.256401	2.609271
12	1	0	-3.460964	-4.056683	3.093647
13	6	0	-3.261681	-2.807864	1.334433
14	6	0	-2.524920	-1.780142	0.742793
15	6	0	-2.886835	-1.194495	-0.605695
16	1	0	-3.493944	-1.898869	-1.200701
17	1	0	-3.494564	-0.287156	-0.450515
18	6	0	-1.915168	0.317327	-2.315924
19	1	0	-2.769311	0.076896	-2.973650
20	1	0	-1.019828	0.398354	-2.956097
21	6	0	-2.120513	1.634755	-1.606108
22	6	0	-2.924304	2.644383	-2.138701
23	1	0	-3.483887	2.468669	-3.059706
24	6	0	-2.993002	3.877202	-1.481697
25	1	0	-3.612878	4.682447	-1.880870
26	6	0	-2.257318	4.057485	-0.307329
27	1	0	-2.277466	5.002690	0.236881
28	6	0	-1.490057	2.996849	0.173438
29	1	0	-0.908377	3.095543	1.089810
30	6	0	-0.943553	-1.930259	-1.989959
31	1	0	-1.350535	-2.136479	-2.994800
32	1	0	-1.122744	-2.826220	-1.371954
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34	6	0	1.513364	-2.206848	-2.867874
35	1	0	1.210632	-2.870232	-3.680231
36	6	0	2.858231	-1.901381	-2.666064
37	1	0	3.616280	-2.324904	-3.329528

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41	6	0	4.857422	0.123233	-0.178741
42	1	0	5.886965	0.388067	0.073233
43	6	0	3.801515	0.627426	0.659761
44	6	0	2.463215	0.306578	0.334353
45	6	0	2.213684	-0.531603	-0.794396
46	6	0	3.995729	1.420358	1.819807
47	1	0	5.004412	1.711428	2.123119
48	6	0	2.898815	1.801216	2.570480
49	1	0	3.028146	2.391774	3.479734
50	6	0	1.580766	1.428782	2.187132
51	6	0	0.409487	1.804295	3.046475
52	1	0	0.337092	2.897657	3.161731
53	1	0	-0.534532	1.418494	2.637698
54	1	0	0.538777	1.398191	4.062701
55	1	0	-4.108840	-3.249838	0.805849

M2 (Singlet, G = -2916.998884 a. u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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7	6	0	-1.071772	-1.134421	2.826030
8	1	0	-0.211413	-0.552294	3.165372
9	6	0	-1.688665	-2.062833	3.663731
10	1	0	-1.317591	-2.210881	4.679052
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12	1	0	-3.278992	-3.534822	3.788532
13	6	0	-3.187889	-2.561791	1.853422
14	6	0	-2.526053	-1.606951	1.074212
15	6	0	-2.985377	-1.299187	-0.343728
16	1	0	-3.677584	-2.095926	-0.687003
17	1	0	-3.576313	-0.367013	-0.307708
18	6	0	-2.079728	-0.095672	-2.304838
19	1	0	-2.946742	-0.335224	-2.956871
20	1	0	-1.185631	-0.115900	-2.953606
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22	6	0	-3.071767	2.231310	-2.430737
23	1	0	-3.666593	1.894369	-3.282952
24	6	0	-3.144168	3.553235	-1.985468
25	1	0	-3.798002	4.272773	-2.482197
26	6	0	-2.365333	3.928536	-0.887196
27	1	0	-2.383204	4.946855	-0.495853
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37	1	0	3.378231	-2.969346	-3.007465
38	6	0	3.135890	-1.406875	-1.512337
39	6	0	4.517193	-1.057298	-1.347853

40	1	0	5.268674	-1.583780	-1.941164
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43	6	0	3.921177	0.611834	0.340632
44	6	0	2.542846	0.302035	0.193174
45	6	0	2.153872	-0.714008	-0.752069
46	6	0	4.258268	1.599172	1.298129
47	1	0	5.304382	1.877824	1.447551
48	6	0	3.253775	2.190155	2.042918
49	1	0	3.490919	2.943798	2.796906
50	6	0	1.900080	1.818954	1.842094
51	6	0	0.811069	2.444467	2.669122
52	1	0	0.729369	3.524667	2.463817
53	1	0	-0.156679	1.967768	2.453177
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55	1	0	-4.024023	-3.119136	1.424627

M3 (Doublet, G = -2917.106903 a. u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	7	0	-1.137904	1.678775	-0.935745
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5	7	0	0.767276	-1.152723	-0.650443
6	7	0	1.579610	0.802468	1.010528
7	6	0	-1.399951	-0.788412	2.879891
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14	6	0	-2.750691	-1.313134	1.053539
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22	6	0	-2.769106	2.232012	-2.633107
23	1	0	-3.428347	1.880573	-3.431631
24	6	0	-2.715599	3.587397	-2.293315
25	1	0	-3.337500	4.319626	-2.811961
26	6	0	-1.837419	3.976607	-1.266455
27	1	0	-1.737732	5.021197	-0.965558
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30	6	0	-1.201715	-2.315755	-1.443146
31	1	0	-1.543929	-2.887981	-2.333019
32	1	0	-1.422086	-2.939873	-0.555675
33	6	0	0.296953	-2.086761	-1.513017
34	6	0	1.150420	-2.815100	-2.345001
35	1	0	0.731112	-3.553755	-3.033754
36	6	0	2.539881	-2.605795	-2.274866
37	1	0	3.223567	-3.173697	-2.910311
38	6	0	3.052938	-1.633124	-1.379996

39	6	0	4.445450	-1.320641	-1.229598
40	1	0	5.170453	-1.874600	-1.833006
41	6	0	4.876450	-0.347889	-0.352592
42	1	0	5.942985	-0.127671	-0.251691
43	6	0	3.946660	0.396289	0.435344
44	6	0	2.547796	0.114600	0.304196
45	6	0	2.107696	-0.912529	-0.590788
46	6	0	4.315555	1.411225	1.344485
47	1	0	5.372970	1.659517	1.475281
48	6	0	3.335354	2.082970	2.062603
49	1	0	3.600310	2.867589	2.774869
50	6	0	1.965384	1.751785	1.868999
51	6	0	0.893830	2.467615	2.650369
52	1	0	0.952986	3.559259	2.506451
53	1	0	-0.101115	2.119466	2.333891
54	1	0	1.004226	2.281894	3.732257
55	1	0	-4.336900	-2.728416	1.385747

M4 (Doublet, G = -2917.536914 a. u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.476432	0.022754	-0.659295
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4	7	0	2.177470	0.532070	1.177163
5	7	0	-0.408763	-0.417986	1.201296
6	7	0	-1.646114	-0.434324	-1.205530
7	6	0	1.657706	-2.739550	-1.232526
8	1	0	0.629989	-2.910137	-1.563836
9	6	0	2.655591	-3.692999	-1.432284
10	1	0	2.417647	-4.639234	-1.920678
11	6	0	3.950768	-3.405051	-0.989304
12	1	0	4.759816	-4.125473	-1.125932
13	6	0	4.191173	-2.181913	-0.357395
14	6	0	3.139280	-1.272340	-0.198831
15	6	0	3.355342	0.088291	0.439634
16	1	0	4.277711	0.062755	1.058477
17	1	0	3.528393	0.818004	-0.372217
18	6	0	2.101649	1.961936	1.446216
19	1	0	3.100715	2.405562	1.628441
20	1	0	1.537279	2.102976	2.384819
21	6	0	1.379535	2.779314	0.379981
22	6	0	1.628018	4.154849	0.269250
23	1	0	2.403931	4.616167	0.885356
24	6	0	0.874724	4.918877	-0.623087
25	1	0	1.053419	5.991558	-0.722482
26	6	0	-0.107621	4.282422	-1.390175
27	1	0	-0.725262	4.835933	-2.099075
28	6	0	-0.270032	2.906435	-1.247102
29	1	0	-0.994606	2.353323	-1.850066
30	6	0	1.764248	-0.317684	2.288370
31	1	0	2.163980	0.019079	3.266112
32	1	0	2.168333	-1.331318	2.123046
33	6	0	0.250863	-0.439366	2.363111
34	6	0	-0.421114	-0.607396	3.594663
35	1	0	0.151437	-0.609809	4.524896
36	6	0	-1.797864	-0.760012	3.606032
37	1	0	-2.337464	-0.883372	4.548513
38	6	0	-2.515552	-0.751555	2.385400
39	6	0	-3.938561	-0.903928	2.300735

40	1	0	-4.509088	-1.030616	3.223803
41	6	0	-4.571621	-0.892358	1.085385
42	1	0	-5.656543	-1.008901	1.025521
43	6	0	-3.832461	-0.734554	-0.134138
44	6	0	-2.420418	-0.575949	-0.090260
45	6	0	-1.757603	-0.577529	1.192239
46	6	0	-4.437039	-0.728887	-1.415456
47	1	0	-5.520962	-0.838850	-1.504035
48	6	0	-3.645459	-0.588308	-2.538072
49	1	0	-4.088215	-0.587771	-3.536223
50	6	0	-2.236063	-0.452061	-2.411547
51	6	0	-1.372489	-0.354935	-3.634750
52	1	0	-1.837045	0.282079	-4.402145
53	1	0	-0.376538	0.030774	-3.368949
54	1	0	-1.239477	-1.354924	-4.082381
55	1	0	5.186310	-1.928890	0.015645
56	1	0	1.082735	0.348463	-2.058574
