Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Where is the Unpaired-Electron Density? A Combined Experimental and Theoretical Finding on Geometric and Electronic Structures of Co(III) and Mn(IV) Complexes of Unsymmetrical Non-innocent Pincer ONS Ligand

Prasenjit Sarkar[a], Amrit Sarmah[b,c] and Chandan Mukherjee*[a]

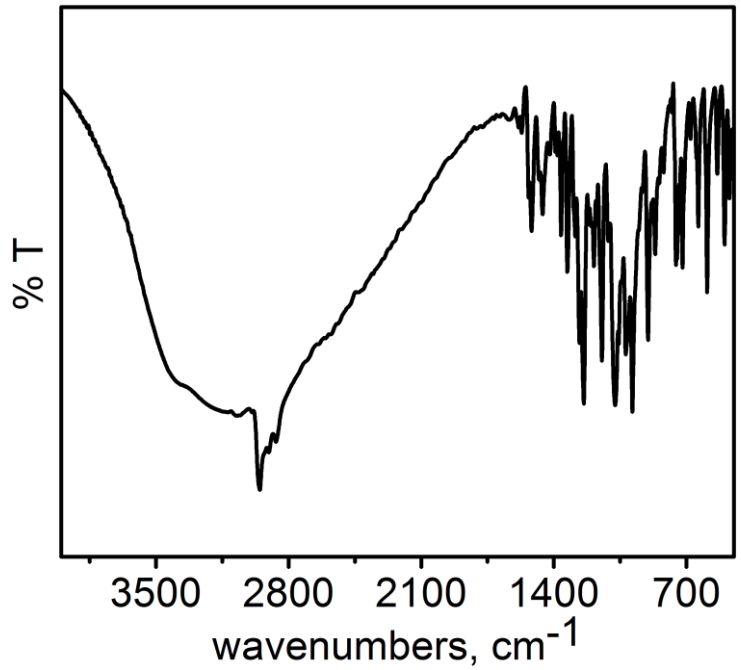

Figure S1. Infrared spectrum of complex **1**.

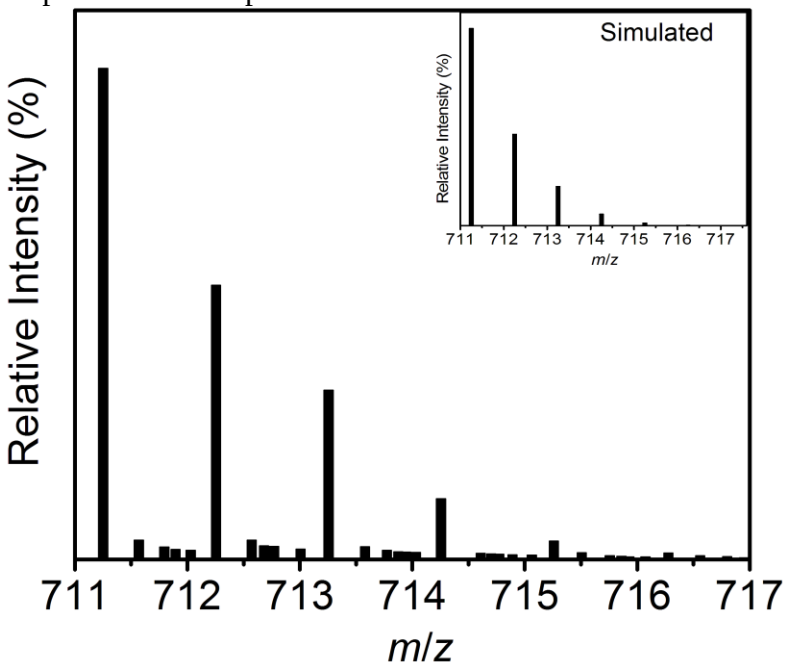

Figure S2. Experimental and simulated mass spectra for complex **1** = $[C_{40}H_{48}N_2O_2S_2Co]^+$ have been shown.

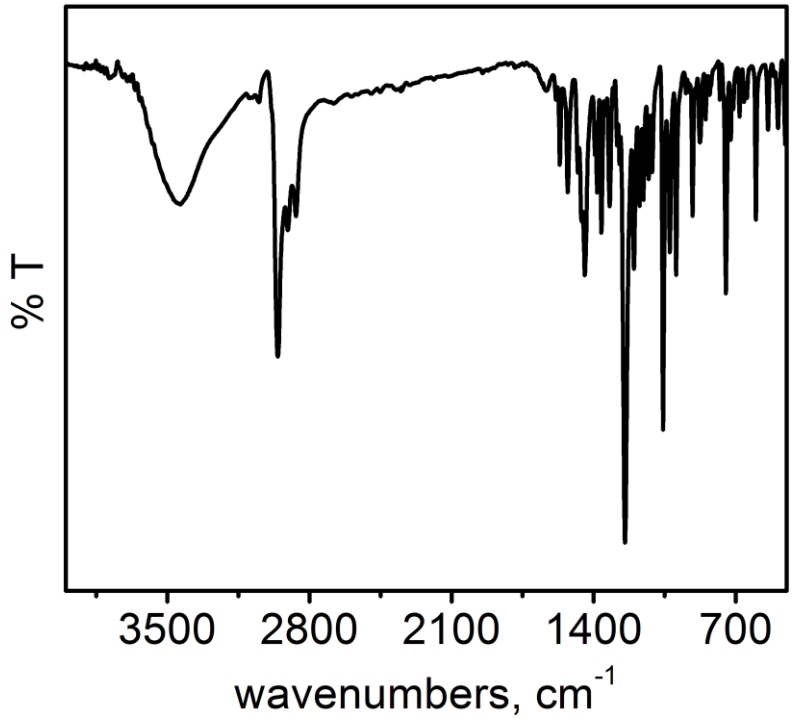

Figure S3. Infrared spectrum of complex **2**.

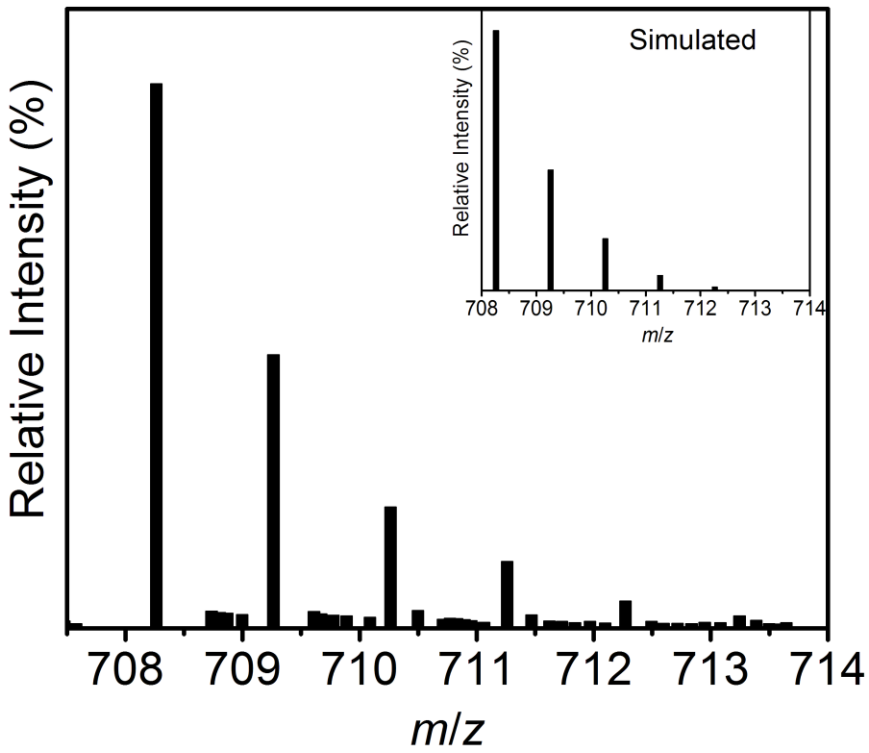

Figure S4: Experimental and simulated mass spectra for complex **2** = $[C_{40}H_{48}N_2O_2S_2Mn +H]^+$ have been shown.

Table S1: Selected bond distances (Å) and bond angles (°) for complex **1**.

Co1–N1	1.863(2)	C1–C6	1.413(4)
Co1–N2	1.870(2)	C15–C16	1.408(4)
Co1–O1	1.9532(19)	C16–C17	1.361(4)
Co1–O2	1.9386(18)	C17–C18	1.392(4)
Co1–S1	2.2188(8)	C19–C18	1.368(4)
Co1–S2	2.2071(8)	C20–C19	1.394(4)
N1–C1	1.354(3)	C20–C15	1.405(4)
N1–C15	1.392(3)	C21–C22	1.430(4)
N2–C21	1.353(3)	C22–C23	1.422(4)
N2–C35	1.393(3)	C24–C23	1.384(5)
O1–C2	1.288(3)	C25–C24	1.415(6)
O2–C22	1.298(3)	C25–C26	1.363(5)
S1–C20	1.741(3)	C26–C21	1.408(4)
S2–C36	1.746(3)	C36–C35	1.393(4)
C1–C2	1.457(4)	C36–C37	1.394(5)
C2–C3	1.428(4)	C38–C37	1.380(5)
C4–C3	1.362(4)	C38–C39	1.368(5)
C4–C5	1.428(4)	C39–C40	1.370(5)
C5–C6	1.350(4)	C35–C40	1.411(4)
N1–Co1–N2	172.42(10)	O1–Co1–S1	171.47(6)
N1–Co1–O2	93.76(8)	N1–Co1–S2	93.48(7)
N2–Co1–O2	84.48(8)	N2–Co1–S2	88.21(7)
N1–Co1–O1	84.08(9)	O2–Co1–S2	172.69(6)
N2–Co1–O1	88.43(8)	O1–Co1–S2	94.20(6)
O2–Co1–O1	85.54(8)	S1–Co1–S2	89.65(3)
N1–Co1–S1	88.10(7)	O2–Co1–S1	91.60(6)
N2–Co1–S1	99.30(7)	C36–S2–Co1	108.21(16)
C20–S1–Co1	95.12(10)		

Table S2: Selected bond distances (Å) and bond angles (°) for complex **2**.

Mn1–N1	1.926(2)	C1–C6	1.413(4)
Mn1–N2	1.918(2)	C15–C16	1.408(4)
Mn1–O1	1.9419(18)	C16–C17	1.361(4)
Mn1–O2	1.9523(19)	C17–C18	1.392(4)
Mn1–S1	2.2713(8)	C19–C18	1.368(4)
Mn1–S2	2.2721(9)	C20–C19	1.394(4)
N1–C1	1.370(3)	C20–C15	1.405(3)
N1–C15	1.401(3)	C21–C22	1.430(4)
N2–C21	1.368(4)	C22–C23	1.422(4)
N2–C35	1.397(4)	C24–C23	1.384(5)
O1–C2	1.303(3)	C25–C24	1.415(6)
O2–C22	1.298(3)	C25–C26	1.363(5)
S1–C20	1.740(3)	C26–C21	1.408(4)
S2–C36	1.744(3)	C36–C35	1.393(4)
C1–C2	1.430(4)	C36–C37	1.397(5)
C2–C3	1.428(4)	C38–C37	1.380(5)
C4–C3	1.362(4)	C38–C39	1.368(5)
C4–C5	1.428(4)	C39–C40	1.370(5)
C5–C6	1.350(4)	C35–C40	1.411(4)
N1–Mn1–N2	173.15(9)	O1–Mn1–S1	163.93(6)
N1–Mn1–O2	104.48(9)	N1–Mn1–S2	90.51(7)
N2–Mn1–O2	80.98(9)	N2–Mn1–S2	84.39(8)
N1–Mn1–O1	81.04(8)	O2–Mn1–S2	164.45(6)
N2–Mn1–O1	103.63(8)	O1–Mn1–S2	91.73(7)
O2–Mn1–O1	86.65(8)	S1–Mn1–S2	95.20(3)
N1–Mn1–S1	84.41(6)	O2–Mn1–S1	90.43(6)
N2–Mn1–S1	91.48(7)	C36–S2–Mn1	96.97(11)
C20–S1–Mn1	97.11(9)		

Table S3: Crystallographic parameters and refinement data for complex **1**.

Empirical formula	C40 H48 N2 O2 S2 Co
Formula weight	711.85
CCDC Number	2178435
Crystal habit, colour	Block, violet
Crystal size, mm^3	$0.33 \times 0.31 \times 0.28$
Temperature, T	100.01(11)
Wavelength, λ (Å)	0.71073
Crystal system	triclinic
Space group	'P -1'
Unit cell dimensions	a = 10.2996(5) Å b = 13.3878(8) Å c = 13.7436(8) Å α = 85.804(5)°, β = 83.910(4)° γ = 80.738(5)°,
Volume, V ($Å^3$)	1856.79(18)
Z	2
Calculated density, $Mg \cdot m^{-3}$	1.273
Absorption coefficient, μ (mm^{-1})	0.611
F(000)	754
θ range for data collection	2.4930° to 28.4220°
Limiting indices	$-11 \leq h \leq 12$, $-15 \leq k \leq 15$, $-16 \leq l \leq 12$
Reflection collected/unique	13882/6538 [R(int)= 0.0406]
Completeness to θ	99.9% (θ = 25.00°)
Max. and min. transmission	1.0000/0.807
Refinement method	'SHELXL-2018/3 (Sheldrick, 2018)'
Data/restraints/parameters	6538/0/436
Goodness–of–fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1093
R indices (all data)	R1 = 0.0548, wR2 = 0.1187
Largest diff. peak and hole	0.88 and –0.46 $e \cdot Å^{-3}$

Table S4: Crystallographic parameters and refinement data for complex **2**.

Empirical formula	C40 H48 N2 O2 S2 Mn
Formula weight	707.86
CCDC Number	2178436
Crystal habit, colour	Block, green
Crystal size, mm^3	$0.35 \times 0.31 \times 0.28$
Temperature, T	293(2)
Wavelength, λ (Å)	0.71073
Crystal system	monoclinic
Space group	'P 21/c'
Unit cell dimensions	a = 21.3127(10) Å b = 18.3726(8) Å c = 10.8905(5) Å α = 90.00°, β = 103.952(4)° γ = 90.00°,
Volume, V ($Å^3$)	4138.6(3)
Z	4
Calculated density, $Mg \cdot m^{-3}$	1.136
Absorption coefficient, μ (mm^{-1})	0.452
F(000)	1500
θ range for data collection	2.938° to 24.997°
Limiting indices	$-22 \leq h \leq 25$, $-21 \leq k \leq 19$, $-12 \leq l \leq 12$
Reflection collected/unique	20446/7267 [R(int)= 0.0387]
Completeness to θ	99.8% (θ = 25.00°)
Max. and min. transmission	1.0000/0.44486
Refinement method	'SHELXL-2018/3 (Sheldrick, 2018)'
Data/restraints/parameters	7267/471/452
Goodness–of–fit on F^2	1.043
Final R indices [I>2sigma(I)]	$R1$ = 0.0492, $wR2$ = 0.1220
R indices (all data)	$R1$ = 0.0669, $wR2$ = 0.1305
Largest diff. peak and hole	0.27 and –0.32 $e \cdot Å^{-3}$

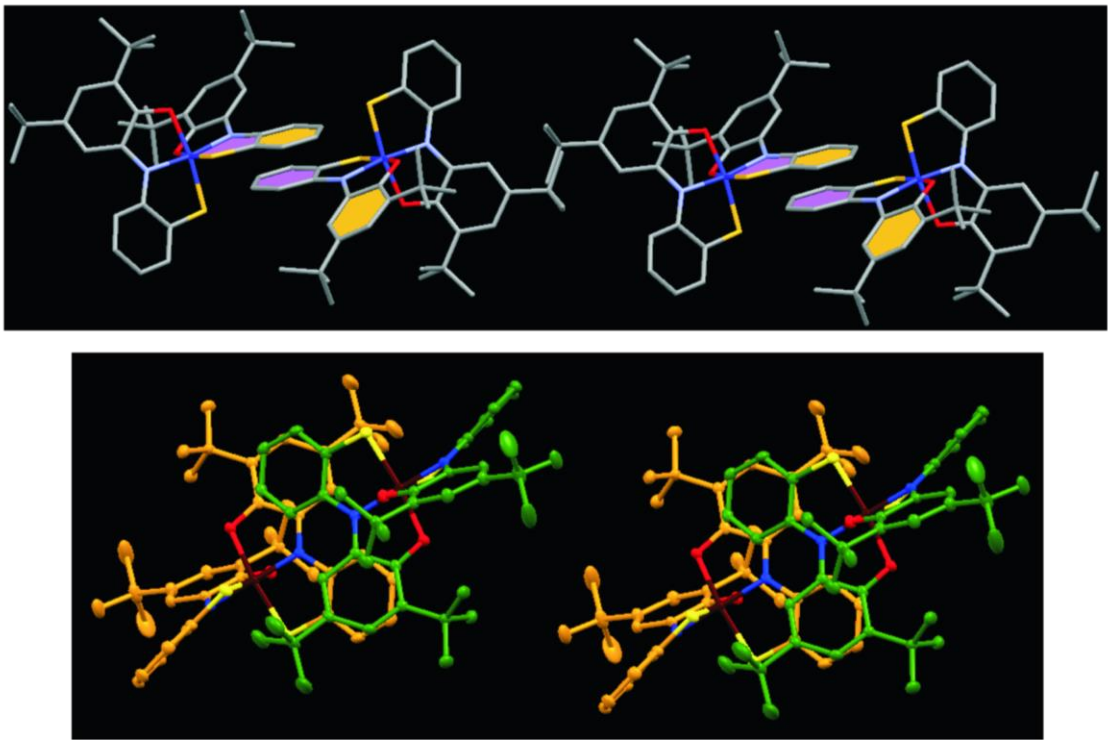

Figure S5: *Showing intermolecular interaction of* complex **1** *at 100 K crystal lattice.*

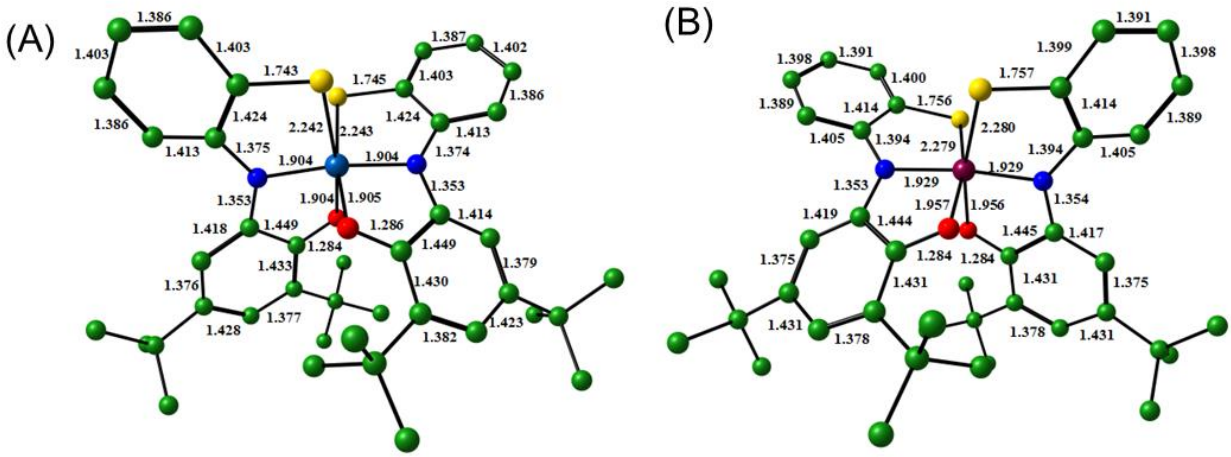

Figure S6: Optimized bond distances of (A) complex **1** and (B) complex **2**.

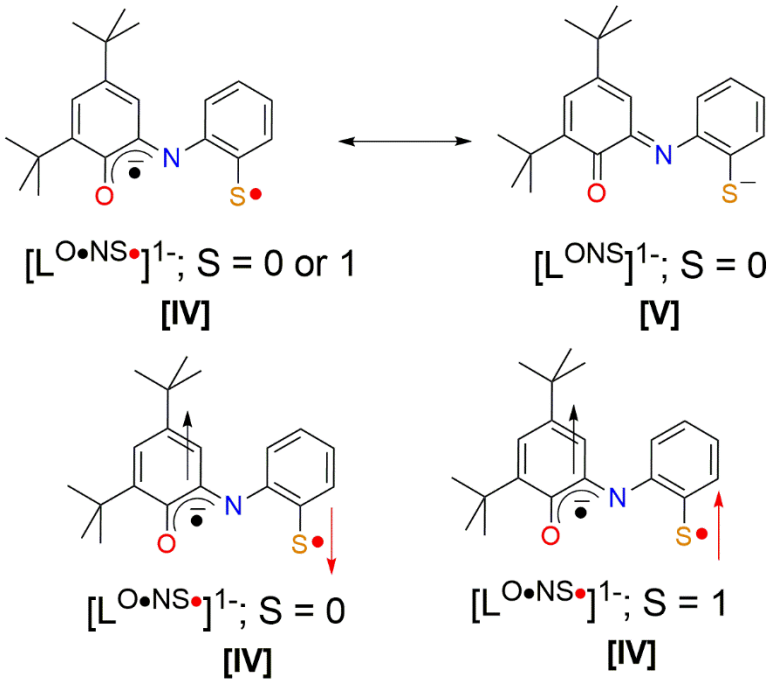

Figure S8: Possible different spin states of the composition **[IV]**.

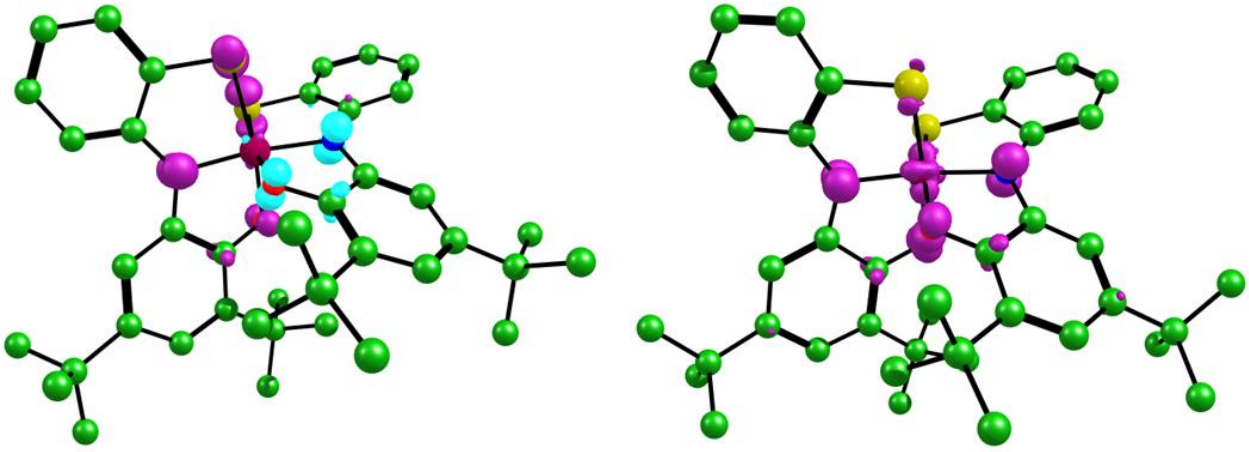

Figure S8: Doublet (left) and quartet(right) spin density maps of complex **1**. (positive electron density = purple and negative electron density = blue)

Table S5: Optimized coordinates of complex **1**

Co	4.9573	8.5484	10.1349
S	6.5172	7.9017	11.5715
S	4.5891	6.4418	9.5879
O	5.0665	10.3954	10.7476
O	3.7921	9.2497	8.7272
N	3.4737	8.4565	11.2725

N	6.3058	8.7772	8.8631
C	1.9726	6.9817	12.6092
H	1.6595	7.6867	13.1297
C	7.7591	7.6943	10.3798
C	2.9166	7.2225	11.5967
C	2.9579	9.6918	11.5149
C	3.9097	10.7391	11.2301
C	3.4198	6.1409	10.8445
C	7.5446	8.1537	9.0607
C	2.4243	10.9288	6.759
C	1.5133	5.7059	12.8313
H	0.8802	5.5496	13.4949
C	9.9331	6.9129	9.6998
H	10.7522	6.5282	9.9164
C	1.3014	11.3239	12.1172
C	4.5951	13.2157	11.2151
C	3.5688	12.1057	11.4836
C	4.5119	9.8535	7.8451
C	3.9442	10.6943	6.8299
C	8.9958	7.0839	10.6755
H	9.1739	6.7963	11.5422
C	5.9508	9.6239	7.8683
C	1.6481	10.0228	11.9224
H	1.0206	9.3496	12.0573
C	8.5049	7.9248	8.0577
H	8.3413	8.1899	7.1815
C	6.7911	10.3152	6.9662
H	7.7133	10.2076	7.0125
C	6.2511	11.1382	6.0314
C	4.8286	11.2906	5.9796
H	4.48	11.8378	5.3132
C	2.9263	4.855	11.0993
H	3.2392	4.1338	10.6019
C	2.2918	12.3328	11.9115
H	2.0478	13.2139	12.0818
C	9.6878	7.3057	8.3861
H	10.327	7.1493	7.7293
C	1.9874	4.6512	12.0723
H	1.6633	3.7933	12.2262
C	1.7347	9.585	6.4988
H	2.0267	9.2329	5.6553
H	0.7829	9.7123	6.4797
H	1.961	8.9676	7.1978
C	5.0582	13.1982	9.7584
H	5.4765	12.3553	9.5662

H	5.6881	13.9076	9.6126
H	4.3015	13.3179	9.1806
C	5.7977	13.0227	12.1458
H	5.5052	13.0665	13.0602
H	6.4437	13.7146	11.9837
H	6.1979	12.1665	11.9796
C	7.0851	11.9591	5.0434
C	2.0692	11.8898	5.6185
H	2.4771	12.7444	5.782
H	1.1163	11.9933	5.5721
H	2.3942	11.5345	4.7886
C	8.5848	11.7713	5.2805
H	8.824	12.1458	6.1308
H	9.0761	12.2154	4.5855
H	8.7949	10.8342	5.2723
C	4.0026	14.6059	11.4945
H	3.2533	14.7569	10.914
H	4.6706	15.2775	11.335
H	3.7137	14.6538	12.4088
C	1.8978	11.5305	8.0591
H	2.0617	10.9216	8.7827
H	0.9528	11.6864	7.9787
H	2.3458	12.3611	8.2308
C	6.7534	13.4538	5.2301
H	5.8226	13.6014	5.0461
H	7.2854	13.9778	4.625
H	6.9466	13.7157	6.1336
C	6.7626	11.4998	3.6248
H	6.9528	10.5616	3.5403
H	7.299	11.9923	2.9993
H	5.8337	11.6542	3.4408
C	-0.12762	11.70094	12.55004
C	-0.36884	13.16181	12.26864
C	-0.31339	11.37391	14.00948
H	-0.22538	13.37848	11.18269
H	-1.41008	13.45036	12.55152
H	0.34042	13.7974	12.85208
H	-0.12955	10.28781	14.19214
H	0.39743	11.96284	14.63829
H	-1.35318	11.61596	14.33773
C	-1.09394	10.84927	11.70596
H	-0.84507	10.94863	10.67006
H	-1.01078	9.82265	11.99587
H	-2.09738	11.18477	11.86548

Table S6: Optimized coordinates of complex **2**

Mn	0.00296	1.34088	0.00823
S	0.01148	2.88797	1.71796
S	0.01717	2.87855	-1.70966
O	-0.38534	-0.0662	1.26683
O	0.36806	-0.08841	-1.23406
N	1.92056	1.30001	0.22695
N	-1.91558	1.3187	-0.22
C	2.57097	2.3534	0.85946
C	3.94218	2.65879	0.7155
H	4.55115	2.0778	0.03412
C	2.47766	0.14338	-0.24851
C	1.56581	-0.59092	-1.08679
C	3.75777	-0.38471	0.0498
H	4.38279	0.12993	0.76427
C	1.73988	3.20421	1.642
C	3.26598	-2.23254	-1.42335
H	3.60761	-3.15631	-1.87123
C	-2.55271	2.36917	-0.86744
C	2.32397	4.27205	2.33833
H	1.69391	4.9106	2.94911
C	5.50955	-2.24299	-0.20029
C	4.15997	-1.57397	-0.52524
C	4.49178	3.73428	1.39633
H	5.54454	3.96716	1.27263
C	1.98729	-1.79439	-1.72566
C	-2.48262	0.16621	0.25434
C	-1.70865	3.21064	-1.64662
C	-1.58275	-0.56684	1.10637
C	6.39264	-1.37366	0.714
H	6.59165	-0.39406	0.26462
H	7.35443	-1.87053	0.88098
H	5.9332	-1.21785	1.69593
C	3.68615	4.52788	2.22771
H	4.12111	5.36364	2.76776
C	-2.01217	-1.7689	1.742
C	-3.75707	-0.36399	-0.06072
H	-4.3755	0.14885	-0.78153
C	1.04512	-2.53352	-2.69323
C	-4.45983	3.75774	-1.43203
H	-5.51252	3.99723	-1.32112
C	1.70398	-3.79436	-3.28846
H	2.6218	-3.55715	-3.83814

H	1.00944	-4.26748	-3.99096
H	1.94305	-4.53351	-2.51508
C	-2.27863	4.27952	-2.35369
H	-1.63804	4.91122	-2.96103
C	-0.24182	-2.97544	-1.95309
H	-0.00057	-3.67361	-1.14521
H	-0.91596	-3.48516	-2.65216
H	-0.77001	-2.12302	-1.52396
C	-3.2844	-2.21218	1.42016
H	-3.63457	-3.13049	1.87281
C	-3.9239	2.68274	-0.73954
H	-4.54195	2.1111	-0.05832
C	6.29953	-2.50163	-1.50657
H	5.7729	-3.17625	-2.18771
H	7.26699	-2.9606	-1.2723
H	6.48618	-1.56281	-2.03921
C	-4.16333	-1.55607	0.50722
C	0.67726	-1.58301	-3.85993
H	0.17872	-0.68325	-3.4952
H	0.00403	-2.09504	-4.55793
H	1.57517	-1.28239	-4.41188
C	-3.64021	4.54427	-2.25675
H	-4.06519	5.37993	-2.80463
C	-1.07898	-2.50677	2.718
C	-0.724	-1.56652	3.89758
H	-0.21977	-0.66343	3.55067
H	-0.06387	-2.08712	4.60174
H	-1.62975	-1.26978	4.43894
C	5.24138	-3.5889	0.51744
H	4.69518	-3.42308	1.45214
H	6.18649	-4.09185	0.75548
H	4.64488	-4.26599	-0.10307
C	-5.51366	-2.2188	0.17777
C	0.21276	-2.93909	1.98044
H	-0.02395	-3.64577	1.17851
H	0.89423	-3.43663	2.68149
H	0.73121	-2.08305	1.54553
C	-1.74079	-3.77176	3.29961
H	-2.66109	-3.53523	3.84588
H	-1.0496	-4.24985	4.00228
H	-1.97654	-4.50573	2.52054
C	-6.30339	-2.46329	1.48644
H	-7.26583	-2.93708	1.26168
H	-6.50041	-1.51881	2.00517
H	-5.7652	-3.12055	2.17621

C	-5.25087	-3.57212	-0.52731
H	-4.67642	-4.25344	0.10853
H	-4.68888	-3.42297	-1.45543
H	-6.19969	-4.06297	-0.7745
C	-6.38466	-1.34918	-0.74888
H	-5.90296	-1.17769	-1.71752
H	-6.60689	-0.37611	-0.29633
H	-7.33767	-1.85365	-0.94044

Table S7: Mulliken charges (I) and spin densities (II) of complex **1** for doublet state.

Atom	I	II
Co1	0.317071	-0.020959
S1	0.109577	0.466437
S2	-0.018513	0.238994
O2	-0.369388	0.153318
O1	-0.330643	-0.160672
N2	-0.261669	0.370259
N1	-0.245447	-0.182056
C40	-0.050271	0.099027
C20	-0.099535	-0.130399
C35	0.181242	-0.079796
C21	0.145025	0.006883
C22	0.196275	0.169242
C36	-0.072948	0.088811
C15	0.193342	0.153209
C7	-0.329390	0.002337
C39	-0.003268	-0.036893
C18	0.023522	-0.118341
C25	0.104698	0.031685
C27	-0.327039	0.000776
C23	0.024568	-0.037650
C2	0.207666	-0.123714
C3	0.018690	-0.008598
C19	0.014674	0.115833
C1	0.158927	-0.113494
C26	-0.150083	0.042028
C16	-0.039227	-0.132431
C6	-0.145468	0.055169
C5	0.103356	-0.120526
C4	-0.098226	-0.055658
C37	-0.024348	-0.041029

C24	-0.112440	0.130702
C17	0.016478	0.137649
C38	0.018858	0.099024
C8	0.130047	-0.000177
C30	0.120834	-0.000070
C28	0.120165	-0.000187
C11	-0.355991	0.009647
C10	0.129162	0.000323
C12	0.145248	0.000061
C29	0.127438	-0.000395
C9	0.135120	-0.000941
C13	0.130450	-0.004803
C14	0.126288	-0.005034
C31	-0.353348	-0.002078
C34	0.141484	0.001103
C32	0.116740	0.001579
C33	0.130298	0.001806

Table S8: Mulliken charges (I) and spin densities (II) of complex **1** for the quartet state:

Atom	I	II
Co1	0.242033	0.216992
S1	0.075238	0.273767
S2	0.072496	0.265556
O2	-0.329579	0.212708
O1	-0.330780	0.211086
N2	-0.275863	0.306777
N1	-0.277151	0.305461
C40	-0.047498	0.059084
C20	-0.086388	0.064648
C35	0.196871	-0.026550
C21	0.169928	0.084025
C22	0.187490	0.149428
C36	-0.085367	0.067172
C15	0.198376	-0.025121
C7	-0.329921	-0.002493
C39	0.005711	0.005385
C18	0.018671	0.068052
C25	0.113056	0.129195
C27	-0.332464	-0.003901
C23	0.035056	0.026532
C40	0.188680	0.156712
C3	0.020210	0.006511

C19	-0.013689	-0.011167
C1	0.186665	0.092785
C26	-0.158271	-0.022105
C16	-0.047312	0.058033
C6	-0.156882	-0.023884
C5	0.109176	0.123380
C4	-0.109062	0.086903
C37	-0.014575	-0.013750
C24	-0.110992	0.074938
C17	0.006264	0.007597
C38	0.019106	0.070062
C8	0.127934	0.002380
C30	0.129329	-0.000015
C28	0.127286	0.002949
C11	-0.356643	-0.010218
C10	0.128359	-0.000258
C12	0.146256	-0.000089
C29	0.130083	-0.000221
C9	0.129518	-0.000483
C13	0.128673	0.005413
C14	0.125120	0.005657
C31	-0.358492	-0.009229
C34	0.146771	0.001345
C32	0.121548	0.004059
C33	0.135026	0.004896