Supporting Information

Accurate modeling of spin state energetics in spin-crossover systems with modern density functional theory

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Computational details:

All computations in this work were carried out with the ORCA program package.[1] Geometry optimizations of the HS and LS states for each complex were performed with the BP86 density functional.[2] Since BP86 geometries are usually superior to those predicted by B3LYP and can be obtained more efficiently it is usually the method of choice.[3,4] The TZVPP[5] (Fe), TZVP (O and N) and SV(P) (other elements) basis sets[6] were applied in the geometry optimization step. Subsequent frequency calculations using the same basis sets yield the zero-point energies (ZPE). Single point energy calculations were carried out with one representative density functional from each type of widely used DFT methods: GGA(BP86[2]), OPTX-GGA (OPBE[7]), meta-GGA(TPSS[8]), hybrid-GGA (B3LYP[9]) and double hybrid (B2PLYP[10]). Unless mentioned otherwise, the 'new' default basis sets of quadruple-ζ quality including high exponent polarization functions (def2-QZVPP)[11] have been used together with tight SCF convergence criteria in the single point calculations. The basis sets are flexible enough to adequately recover the dynamic correlation energy required by the MP2 step. This implies that calculations with more than 2500 basis functions had to be handled in the MP2 step of the B2PLYP calculations but are efficiently handled by the ORCA software. The density fitting and "chain of spheres" approximations (RIJCOSX)[12] were used in the B3LYP and the SCF part of B2PLYP calculations. For the PT2 correction in B2PLYP the density fitting (RI) approximation[13] has been employed as well in conjunction with the def2-QZVPP/C auxiliary basis set.[14]. The computational cost of B2PLYP is roughly as ~1.5 times as that for B3LYP. For

example it takes ~10 hours to finish the B3LYP single point calculation of the LS state for **1** using four processors vs. ~16 hours employing B2PLYP. Thus, for the medium-size metal complexes such calculations are still affordable even employing the very extensive basis set.

In order to probe the basis set dependence of the HS-LS energy difference, we calculate the HS-LS energy splitting for **4** and **5** using the B3LYP and B2PLYP functionals in conjunction with a series of basis sets (Table S1). As expected for many body perturbation theory, a remarkable basis set dependence was observed for B2PLYP. The calculations employing the SV(P) basis sets even yield qualitatively wrong results for both complexes, thus large and flexible basis sets are a prerequisite for obtaining qualitatively correct results. The COSMO solvation model[15] with ε = 7.25 (THF) has been tested and shown to lead to only marginal changes in the computed numbers. Thus the incorrect prediction of ground state spin multiplicities for these two complexes is intrinsic to the B3LYP functional

Table S1. The basis dependence of the LS-HS energy differences for 4 and 5 employing B3LYP and B2PLYP density functionals.

	4		**5**	
	B3LYP	B2PLYP	B3LYP	B2PLYP
SV(P)	−6.5	−8.8	−7.1	−5.6
TZVP	−5.3	−2.9	−5.8	1.9
TZV(2D, P)	−4.2	−1.1	−4.5	4.3

TZVPP	−3.6	0.3	−3.7	−0.4
Def2-TZVPP	−2.1	4.3	−2.3	3.3
Def2-TZVPP + COSMO	−4.1	10.1	−2.6	6.5
Def2-QZVPP	−2.3	12.4	−2.3	11.1

Table S2. Structural data for the complexes [Fe(N_HS_4)L], [Fe(phen)$_2$(SCN)$_2$], FePCl and experimental data[a] in parentheses.

L	NH_3		N_2H_4		CO		NO^+		PM_3		PH_3	
	S=2	S=0	S=2	S=0	S=2	S=0	S=2	S=0	S=2	S=0	S=2	S=0
Fe-S	2.354(2.397)	2.341	2.341(2.381)	2.315	2.455	2.329(2.298)	2.422	2.346	2.440	2.324(2.307)	2.447	2.333
Fe-S	2.357(2.394)	2.341	2.368(2.402)	2.340	2.416	2.329(2.305)	2.391	2.349	2.445	2.330(2.309)	2.399	2.319
Fe-S	2.712(2.588)	2.294	2.669(2.602)	2.249	2.535	2.259(2.251)	2.569	2.327	2.497	2.241(2.231)	2.484	2.246
Fe-S	2.707(2.586)	2.294	2.714(2.602)	2.256	2.544	2.247(2.225)	2.523	2.310	2.570	2.229(2.229)	2.568	2.228
Fe-N	2.392(2.244)	2.064	2.302(2.255)	2.080	2.403	2.130(2.072)	2.300	2.107	2.388	2.120(2.067)	2.345	2.098
Fe-X	2.203(2.189)	2.028	2.197(2.192)	2.046	1.970	1.739(1.753)	1.923	1.637	2.504	2.230(2.215)	2.538	2.189

Fe(phen)$_2$(NCS)$_2$	S=2	S=0	S=2 (ZORA)	S=0 (ZORA)
Fe-N(phen)	2.229(2.199)	1.996(2.005)	2.195(2.199)	1.985(2.005)
Fe-N(phen)	2.327(2.213)	2.011(2.014)	2.238(2.213)	1.995(2.014)
Fe-N(phen)	2.231(2.199)	1.996(2.005)	2.196(2.199)	1.984(2.005)
Fe-N(phen)	2.336(2.213)	2.011(2.014)	2.241(2.213)	1.995(2.014)
Fe-N(NCS)	1.995(2.057)	1.961(1.958)	2.035(2.057)	1.927(1.958)
Fe-N(NCS)	1.995(2.057)	1.961(1.958)	2.035(2.057)	1.928(1.958)

FePCl	S=5/2	S=3/2	$Fe(L)(CN)_2$	S=2	S=0
Fe-N	2.107 (2.060)	2.026	Fe-N(py)	2.055(2.107)	1.809
Fe-N	2.107 (2.066)	2.026	Fe-N	2.180(2.203)	2.018
Fe-N	2.107 (2.077)	2.026	Fe-N	2.217(2.203)	1.907
Fe-N	2.107 (2.078)	2.026	Fe-C(CN)	2.093(2.163)	1.934
Fe-Cl	2.226 (2.211)	2.270	Fe-C(CN)	2.094(2.163)	1.933
			Fe-O	2.426(2.334)	2.454
			Fe-O	2.495(2.334)	3.294

[a] (i) Gallois, B.; Real, J.-A.; Hauw, C.; Zarembowitch, J. *Inorg. Chem.* **1990**, *29*, 1152-1158.(ii) Sellmann, D.; Hoffmann, T.; Knoch, F. *Inorg. Chim. Acta* **1994**, *224*, 61-71. (iii) Sellmann, D.; Soglowek, W.; Knoch, F.; Ritter, G.; Dengler, J. *Inorg. Chem.* **1992**, *31*, 3711-3717. (iv) Sellmann, D.; Kunstmann, H.; Moll, M.; Knoch, F. *Inorg. Chim. Acta* **1988**, *154*, 157-167. (v) Scheidt, W. R.; Finnegan, M. G. *Acta Cryst.* **1989**, *C45*, 1214-1216. (vi) Guionneau, P.; Costa, J. S.; Létard, J-F. Acta Cryst. **2004**, *C60*, m587-m589.

$[Fe(NO)N_HS_4]^+$ S=2

Fe	0.603207	-0.054677	-0.492931
S	1.390480	1.587480	1.105156
S	0.250522	-1.873557	-2.004910
S	-0.493572	1.999935	-1.640886
S	0.986358	-1.782625	1.305267
C	-2.180634	1.075796	0.466717
H	-3.236108	0.979212	0.790604
H	-1.613828	1.541849	1.288191
C	-2.144754	1.939897	-0.790248
H	-2.443924	2.977621	-0.577690
H	-2.830953	1.542728	-1.559081
C	1.146944	3.159225	0.335591
C	0.861435	5.733223	-0.806134
C	0.347214	3.361012	-0.817841
C	1.792834	4.281250	0.898712
C	1.644345	5.550500	0.339942
C	0.221451	4.635338	-1.388668
H	2.418621	4.141999	1.784202
H	2.154181	6.403316	0.797653
H	-0.377410	4.767703	-2.294226
H	0.755298	6.725174	-1.253929
C	0.517410	-3.319765	-1.009516
C	0.870599	-5.742801	0.417936
C	0.763701	-3.315772	0.387981
C	0.463416	-4.569408	-1.665208
C	0.627463	-5.761232	-0.961056
C	0.953066	-4.518927	1.085004
H	0.288492	-4.591897	-2.744152
H	0.576483	-6.713684	-1.496785
H	1.177328	-4.494615	2.155580
H	1.014140	-6.675583	0.970127
N	-1.591580	-0.246783	0.167949
H	-2.014268	-0.588646	-0.704754
C	-1.806019	-1.313690	1.182240
H	-1.966515	-2.258256	0.638560
H	-2.724879	-1.114002	1.765931
C	-0.637919	-1.488690	2.144667
H	-0.828531	-2.332915	2.827303
H	-0.457452	-0.590534	2.758870
N	2.333425	0.206710	-1.290641
O	3.052353	0.705804	-2.022823

$[Fe(NO)N_HS_4]^+$ S=0

Fe	0.698184	0.012364	-0.347523
S	1.087224	1.578957	1.355467
S	0.175186	-1.574966	-1.997678
S	-0.177232	1.734456	-1.644961
S	1.206732	-1.685917	1.133953
C	-2.087282	0.978829	0.259477
H	-3.153110	0.756294	0.457155
H	-1.716118	1.649011	1.049361
C	-1.951329	1.606077	-1.117167
H	-2.381649	2.618414	-1.158473
H	-2.430304	0.989589	-1.897159
C	0.951988	3.119958	0.487806
C	0.759427	5.604925	-0.858709
C	0.400621	3.215516	-0.804475
C	1.400112	4.307742	1.098643
C	1.295661	5.530252	0.434745
C	0.318239	4.440206	-1.486044
H	1.841374	4.262083	2.098133
H	1.653942	6.438445	0.928570
H	-0.085580	4.477278	-2.502327
H	0.698099	6.563671	-1.380313
C	0.346872	-3.106562	-1.106226
C	0.651426	-5.600564	0.203847
C	0.762862	-3.183343	0.237284
C	0.077523	-4.316256	-1.779369
C	0.221084	-5.540934	-1.129897
C	0.936541	-4.418724	0.884370
H	-0.242081	-4.285219	-2.824832
H	0.005921	-6.464523	-1.675409
H	1.299516	-4.452156	1.916412
H	0.778112	-6.564032	0.704633
N	-1.288488	-0.273663	0.293596
H	-1.584151	-0.842958	-0.514332
C	-1.504951	-1.118871	1.518008
H	-1.963633	-2.067112	1.197148
H	-2.219450	-0.616323	2.190752
C	-0.215349	-1.397132	2.276355
H	-0.312577	-2.279283	2.930035
H	0.105206	-0.541744	2.891782
N	2.224409	0.161803	-0.919366
O	3.279434	0.252125	-1.310572

$Fe(CO)N_HS_4$ S=2

Fe	0.814495	-0.004241	-0.641323
S	1.396016	1.616623	1.108362
S	0.314507	-1.854953	-2.111957
S	-0.362056	1.965972	-1.718666
S	1.245037	-1.770635	1.139112
C	-2.057953	1.005606	0.369580
H	-3.124176	0.910457	0.705386
H	-1.501551	1.552348	1.161825
C	-2.042483	1.798224	-0.937926
H	-2.454813	2.818737	-0.796855
H	-2.657449	1.287623	-1.714242
C	1.072156	3.191590	0.375870
C	0.621181	5.795742	-0.721907
C	0.320777	3.373938	-0.822920
C	1.582976	4.361555	1.001617
C	1.358198	5.636186	0.467643
C	0.110820	4.658761	-1.365706
H	2.171389	4.244401	1.925966
H	1.772114	6.519321	0.983141
H	-0.456521	4.759181	-2.305844
H	0.453327	6.796897	-1.150986
C	0.425889	-3.298051	-1.089838
C	0.578392	-5.731443	0.412563
C	0.796766	-3.297823	0.289505
C	0.137679	-4.560398	-1.679993
C	0.205438	-5.749633	-0.945746
C	0.882927	-4.504144	1.017644
H	-0.143898	-4.584289	-2.745247
H	-0.027311	-6.706649	-1.442641
H	1.202813	-4.471511	2.072737
H	0.646701	-6.666745	0.991504
N	-1.428471	-0.305050	0.168357
H	-1.794946	-0.737951	-0.692445
C	-1.543687	-1.279917	1.270923
H	-1.764485	-2.274810	0.827908
H	-2.402949	-1.026932	1.940113
C	-0.281543	-1.400533	2.127517
H	-0.411154	-2.194622	2.894881
H	-0.034444	-0.448496	2.645800
C	2.639384	0.239351	-1.342937
O	3.740908	0.336315	-1.670773

$Fe(CO)N_HS_4$ S=0

Fe	0.755426	-0.003402	-0.383286
S	1.213057	1.548224	1.293130
S	0.195103	-1.574755	-2.008040
S	-0.049111	1.681588	-1.655644
S	1.267074	-1.653803	1.052912
C	-2.018018	0.977741	0.211275
H	-3.104105	0.798162	0.408557
H	-1.629251	1.669362	0.989211
C	-1.852118	1.573074	-1.181787
H	-2.292614	2.588151	-1.260813
H	-2.312797	0.922821	-1.959428
C	0.973384	3.105966	0.504333
C	0.628704	5.626002	-0.795383
C	0.430187	3.203467	-0.801627
C	1.326335	4.320413	1.152922
C	1.151702	5.553347	0.513385
C	0.273271	4.440496	-1.455853
H	1.753896	4.276253	2.168128
H	1.442695	6.478833	1.038802
H	-0.125013	4.468852	-2.484447
H	0.511647	6.598513	-1.300160
C	0.314301	-3.107405	-1.125517
C	0.552678	-5.606334	0.237815
C	0.760794	-3.181167	0.219335
C	-0.018491	-4.331365	-1.767763
C	0.092575	-5.553421	-1.095273
C	0.900904	-4.414177	0.887944
H	-0.364298	-4.302932	-2.814315
H	-0.173118	-6.485857	-1.621561
H	1.288847	-4.435938	1.920873
H	0.652771	-6.571763	0.759684
N	-1.248196	-0.282910	0.283771
H	-1.515688	-0.874548	-0.528444
C	-1.440644	-1.092224	1.527233
H	-1.928353	-2.051265	1.250373
H	-2.131126	-0.559164	2.217481
C	-0.124355	-1.374935	2.252190
H	-0.206373	-2.255757	2.925055
H	0.217624	-0.500563	2.845892
C	2.373074	0.144724	-1.003871
O	3.457620	0.237696	-1.417091

$Fe(PMe_3)N_HS_4$ S=2

Fe	0.638838	0.072601	-0.628058
S	1.218957	1.784319	1.012232
S	0.107794	-1.881264	-1.997017
S	-0.654592	1.903277	-1.730778
S	1.256530	-1.648554	1.178341
C	-2.257388	0.939234	0.422758
H	-3.311396	0.781634	0.774505
H	-1.750538	1.597398	1.162461
C	-2.316308	1.622228	-0.943954
H	-2.835662	2.601201	-0.881475
H	-2.865466	0.989094	-1.677907
C	0.702901	3.310564	0.288782
C	-0.050194	5.840713	-0.831654
C	-0.102404	3.398662	-0.886504
C	1.106224	4.540554	0.880919
C	0.736654	5.775848	0.335835
C	-0.461757	4.645741	-1.439882
H	1.727074	4.501053	1.790869
H	1.072260	6.705586	0.826391
H	-1.070372	4.670264	-2.359488
H	-0.334735	6.812311	-1.267419
C	0.267943	-3.272744	-0.909029
C	0.483755	-5.631794	0.708391
C	0.732586	-3.210975	0.440660
C	-0.080650	-4.560348	-1.408065
C	0.018795	-5.711644	-0.619565
C	0.847391	-4.380395	1.224224
H	-0.438508	-4.633049	-2.448181
H	-0.263992	-6.688129	-1.048644
H	1.237622	-4.298193	2.252879
H	0.575477	-6.537129	1.330394
N	-1.515247	-0.322420	0.329103
H	-1.839929	-0.866383	-0.485247
C	-1.519983	-1.188725	1.524509
H	-1.777189	-2.222560	1.207526
H	-2.313120	-0.867153	2.242611
C	-0.183023	-1.227076	2.271506
H	-0.228962	-1.962479	3.104380
H	0.087044	-0.232562	2.688656
P	2.803890	0.322897	-1.859695
C	2.654482	0.367675	-3.711183
H	3.649979	0.409203	-4.207561

H	2.061102	1.258957	-4.010546
H	2.110733	-0.541470	-4.047367
C	3.868892	1.802444	-1.517747
H	4.803852	1.788715	-2.122039
H	4.117988	1.823071	-0.435806
H	3.294848	2.726050	-1.745411
C	3.990693	-1.082468	-1.609838
H	4.911294	-0.965255	-2.224814
H	3.481508	-2.031310	-1.884121
H	4.272829	-1.135171	-0.536091

$Fe(PMe_3)N_HS_4$ S=0

Fe	0.574541	0.082432	-0.487965
S	1.102283	1.737089	1.055970
S	-0.073055	-1.616323	-1.946027
S	-0.432258	1.647085	-1.737966
S	1.307454	-1.441307	0.964248
C	-2.184153	0.952926	0.321996
H	-3.232394	0.716471	0.633528
H	-1.776883	1.719060	1.016149
C	-2.187055	1.465519	-1.112244
H	-2.702089	2.443319	-1.210310
H	-2.665638	0.736364	-1.804675
C	0.668300	3.243664	0.255185
C	0.000125	5.676836	-1.092005
C	0.002207	3.245406	-0.998845
C	0.978450	4.510506	0.824716
C	0.647952	5.698709	0.163137
C	-0.318416	4.439779	-1.672556
H	1.493626	4.541408	1.799320
H	0.908041	6.665158	0.628090
H	-0.819302	4.393429	-2.655124
H	-0.245291	6.615913	-1.614095
C	0.216379	-3.089826	-1.000527
C	0.724897	-5.480079	0.480224
C	0.805577	-3.052701	0.290762
C	-0.118150	-4.368214	-1.526588
C	0.126410	-5.537233	-0.797456
C	1.075168	-4.231799	1.014416
H	-0.576285	-4.423707	-2.528254
H	-0.145369	-6.513794	-1.233314
H	1.565621	-4.166145	2.001188
H	0.926566	-6.403218	1.047708

N	-1.322951	-0.248090	0.399349
H	-1.636779	-0.912901	-0.335741
C	-1.354232	-0.969526	1.711187
H	-1.848280	-1.953880	1.561630
H	-1.975800	-0.397020	2.434354
C	0.041378	-1.175992	2.302268
H	0.067667	-2.031732	3.010999
H	0.406677	-0.265139	2.822501
P	2.513462	0.246622	-1.577776
C	2.397656	0.583595	-3.402797
H	3.404562	0.564690	-3.875573
H	1.937145	1.580656	-3.571821
H	1.751451	-0.188391	-3.871815
C	3.749119	1.531933	-1.057409
H	4.657092	1.489007	-1.699666
H	4.028086	1.366098	0.003848
H	3.288309	2.539585	-1.130304
C	3.571727	-1.282007	-1.574583
H	4.481802	-1.140188	-2.198853
H	2.981089	-2.134469	-1.971874
H	3.882081	-1.517538	-0.533766

$Fe(PH_3)N_HS_4$ S=2

Fe	0.739482	-0.011457	-0.655099
S	1.410604	1.608446	1.052458
S	0.376233	-1.858762	-2.142344
S	-0.384949	1.921369	-1.736771
S	1.250777	-1.799002	1.116266
C	-2.098282	0.955055	0.327656
H	-3.167680	0.836439	0.644424
H	-1.574090	1.536399	1.117519
C	-2.079437	1.717797	-0.997396
H	-2.529465	2.726299	-0.887103
H	-2.656982	1.169198	-1.776334
C	1.004360	3.183769	0.358984
C	0.439857	5.783763	-0.702609
C	0.239500	3.353028	-0.833216
C	1.465664	4.366928	0.999759
C	1.186618	5.637973	0.483325
C	-0.026212	4.635162	-1.358748
H	2.058561	4.262892	1.923036
H	1.563934	6.530868	1.010417
H	-0.603358	4.724523	-2.294299
H	0.229007	6.783126	-1.116908

C	0.367899	-3.295973	-1.102443
C	0.343784	-5.721288	0.424103
C	0.720512	-3.307896	0.281253
C	0.005080	-4.543213	-1.684150
C	-0.012675	-5.727558	-0.939037
C	0.719335	-4.510122	1.021524
H	-0.265938	-4.559280	-2.752414
H	-0.301175	-6.672281	-1.430553
H	1.028294	-4.488135	2.080356
H	0.344499	-6.653678	1.011923
N	-1.426923	-0.343792	0.177609
H	-1.775128	-0.819472	-0.668596
C	-1.523181	-1.273082	1.323609
H	-1.775880	-2.281539	0.931459
H	-2.355775	-0.974441	2.006198
C	-0.235840	-1.380789	2.145121
H	-0.352430	-2.148874	2.940651
H	0.036276	-0.414623	2.623176
P	3.082177	0.407302	-1.535546
H	4.152292	-0.141018	-0.740243
H	3.630940	1.739122	-1.614790
H	3.605217	-0.051262	-2.805384

$Fe(PH_3)N_HS_4$ S=0

Fe	0.668598	-0.012850	-0.426748
S	1.245576	1.550346	1.208981
S	0.077928	-1.577705	-2.030571
S	-0.168318	1.664438	-1.668691
S	1.243825	-1.649433	0.970875
C	-2.057521	0.982575	0.268505
H	-3.131923	0.794938	0.516421
H	-1.638710	1.677797	1.027291
C	-1.957104	1.575960	-1.130712
H	-2.397012	2.592521	-1.192350
H	-2.452921	0.924573	-1.885617
C	0.949412	3.108244	0.435344
C	0.515388	5.623994	-0.848889
C	0.341783	3.197135	-0.843973
C	1.321322	4.328577	1.063695
C	1.103700	5.558887	0.433161
C	0.139370	4.433293	-1.488144
H	1.794141	4.289745	2.059098

H	1.408260	6.488332	0.943985
H	-0.314030	4.455640	-2.494105
H	0.360819	6.594718	-1.347296
C	0.221851	-3.116883	-1.160862
C	0.501478	-5.613815	0.200928
C	0.711091	-3.188347	0.169789
C	-0.130474	-4.342821	-1.789517
C	0.001915	-5.563636	-1.118808
C	0.868900	-4.419629	0.837118
H	-0.510750	-4.315631	-2.824291
H	-0.280375	-6.497381	-1.634402
H	1.285833	-4.437990	1.859028
H	0.615181	-6.578164	0.722317
N	-1.278247	-0.275954	0.308701
H	-1.587619	-0.868797	-0.487934
C	-1.432482	-1.084143	1.561998
H	-1.940845	-2.037569	1.302911
H	-2.092387	-0.542425	2.275073
C	-0.093615	-1.381374	2.236773
H	-0.156991	-2.267569	2.904596
H	0.275868	-0.513657	2.823826
P	2.696383	0.261981	-1.205595
H	3.817920	-0.197463	-0.419328
H	3.198321	1.595825	-1.439989
H	3.111964	-0.314364	-2.465751

$Fe(NH_3)N_HS_4$ S=2

Fe	0.040534	0.000726	0.107231
S	0.750151	-1.716386	1.554274
S	0.801738	1.710480	1.539460
S	-0.787798	-2.138298	-1.340255
S	-0.803746	2.142856	-1.317531
C	-2.166251	-2.454951	-0.138813
H	-1.699958	-2.679376	0.844458
H	-2.749830	-3.335359	-0.482971
C	-2.156384	2.453784	-0.085438
H	-1.669020	2.656881	0.892379
H	-2.737136	3.345630	-0.404050
N	1.895053	-0.014847	-1.082016
H	2.657645	0.002658	-0.377555
H	2.033744	0.810257	-1.697115
H	2.039082	-0.864399	-1.661776

C	1.085007	3.121177	0.500418
C	1.659112	5.395301	-1.145778
C	0.418911	3.330848	-0.745657
C	2.027176	4.108949	0.896569
C	2.312083	5.218792	0.090455
C	0.705155	4.450653	-1.554244
H	2.546962	3.975340	1.859687
H	3.057253	5.958257	0.430482
H	0.165246	4.577327	-2.507486
H	1.883231	6.267233	-1.781927
C	0.425323	-3.325580	-0.747346
C	2.306062	-5.211319	0.121772
C	1.062081	-3.120556	0.514906
C	0.734199	-4.440071	-1.555143
C	1.682173	-5.383374	-1.130050
C	1.998559	-4.107105	0.927239
H	0.216371	-4.563774	-2.520950
H	1.924093	-6.250991	-1.765577
H	2.495649	-3.976812	1.902707
H	3.046177	-5.949840	0.474644
N	-2.337159	-0.005368	0.372168
H	-2.231438	-0.027131	1.404903
C	-3.063355	1.232612	-0.014507
H	-3.511589	1.050493	-1.015999
H	-3.912628	1.443531	0.681527
C	-3.062830	-1.226583	-0.063781
H	-3.481393	-1.015898	-1.072561
H	-3.933156	-1.445771	0.603520

$Fe(NH_3)N_HS_4$ S=0

Fe	-0.107566	-0.000506	0.025237
S	0.709992	-1.544274	1.582811
S	0.709075	1.540956	1.583590
S	-0.813978	-1.842746	-1.129658
S	-0.807393	1.839554	-1.133975
C	-2.307733	-2.340676	-0.024291
H	-2.071988	-3.339773	0.390475
H	-3.173237	-2.437462	-0.716338
C	-2.569724	-1.289409	1.068775
H	-3.658553	-1.262770	1.322159
H	-1.977544	-1.496692	1.981373
N	-2.123171	0.001595	0.496855

H	-2.536982	-0.001525	-0.459440
C	-2.570427	1.296225	1.059922
H	-3.659393	1.270818	1.312858
H	-1.978726	1.510112	1.971315
C	-2.308652	2.339453	-0.040588
H	-2.080738	3.343578	0.366378
H	-3.171355	2.425299	-0.737635
N	1.789335	-0.002799	-0.690574
H	2.406080	0.006177	0.150621
H	2.047089	0.829730	-1.258449
H	2.049563	-0.845479	-1.242183
C	0.985977	2.987260	0.615551
C	1.456467	5.261107	-1.056172
C	0.362837	3.129120	-0.654583
C	1.836390	4.045829	1.037292
C	2.064930	5.155874	0.213574
C	0.591235	4.241326	-1.485518
H	2.327121	3.972908	2.022167
H	2.739403	5.956158	0.563763
H	0.083900	4.304144	-2.463216
H	1.651699	6.132905	-1.701541
C	0.360146	-3.130389	-0.656225
C	2.068296	-5.155096	0.204650
C	0.987253	-2.988543	0.612108
C	0.587364	-4.241677	-1.488748
C	1.455882	-5.260226	-1.063223
C	1.840634	-4.046211	1.030151
H	0.076630	-4.304651	-2.464660
H	1.650513	-6.131106	-1.710016
H	2.334220	-3.973512	2.013611
H	2.745201	-5.954607	0.551895

$Fe(N_2H_4)N_HS_4$ S=2

Fe	0.486396	0.010184	0.083197
S	1.119402	-1.716107	1.536814
S	0.986231	1.800297	1.553913
S	-0.077439	-1.985208	-1.591687
S	-0.524411	2.039129	-1.392698
C	-1.881618	-2.091882	-1.201879
H	-2.202359	-3.146072	-1.339972
H	-2.382775	-1.485540	-1.988483
C	-2.011432	2.162075	-0.287915

H	-1.655225	2.522117	0.700921
H	-2.716395	2.905651	-0.716987
N	2.393141	0.231564	-0.987247
H	2.456931	1.146163	-1.478805
H	2.560901	-0.467883	-1.738552
C	1.110855	3.250403	0.533737
C	1.426345	5.609347	-1.062558
C	0.482002	3.380753	-0.742103
C	1.879531	4.357988	0.984075
C	2.038174	5.509931	0.202756
C	0.641750	4.542914	-1.526227
H	2.366656	4.287112	1.970608
H	2.651769	6.343366	0.585306
H	0.137935	4.603961	-2.505193
H	1.552394	6.513790	-1.679885
C	0.561919	-3.406262	-0.676418
C	1.576234	-5.668409	0.631669
C	1.072568	-3.254987	0.645679
C	0.578011	-4.657431	-1.329987
C	1.078085	-5.795036	-0.680317
C	1.574611	-4.426236	1.277387
H	0.194683	-4.729627	-2.361852
H	1.086639	-6.769513	-1.195484
H	1.972701	-4.334960	2.301410
H	1.978129	-6.551816	1.156668
N	-1.780700	-0.213773	0.431710
H	-1.713918	-0.045963	1.453221
C	-2.681881	0.798560	-0.167731
H	-2.980442	0.438287	-1.176407
H	-3.623362	0.900241	0.427069
C	-2.228765	-1.607123	0.207748
H	-3.332582	-1.707175	0.366364
H	-1.716004	-2.245178	0.957216
N	3.604194	0.175469	-0.135036
H	3.454307	-0.700189	0.417551
H	3.405202	0.906294	0.586929

$Fe(N_2H_4)N_HS_4$ S=0

Fe	0.291053	0.005068	-0.081564
S	0.970712	-1.557653	1.487251
S	0.812821	1.644074	1.507540
S	-0.132425	-1.683052	-1.502962
S	-0.437321	1.707432	-1.368508

C	-1.926653	-2.017441	-1.089920
H	-2.126475	-3.099441	-1.231316
H	-2.525490	-1.453267	-1.838338
C	-1.973329	2.125295	-0.373715
H	-1.627205	2.673001	0.527125
H	-2.639968	2.775298	-0.979761
N	2.213982	0.230873	-0.747784
H	2.333118	1.190390	-1.132979
H	2.426320	-0.386550	-1.556350
C	1.073818	3.071835	0.493609
C	1.536228	5.315028	-1.218803
C	0.577055	3.116130	-0.839254
C	1.784753	4.211878	0.954062
C	2.012996	5.306880	0.108846
C	0.802123	4.213306	-1.689239
H	2.172179	4.216250	1.986514
H	2.584641	6.170534	0.489490
H	0.398049	4.200814	-2.715745
H	1.733010	6.174385	-1.880167
C	0.596871	-3.170252	-0.750275
C	1.657669	-5.456536	0.444320
C	1.044482	-3.083189	0.592879
C	0.691720	-4.361495	-1.494127
C	1.223941	-5.515244	-0.897640
C	1.571512	-4.266801	1.178033
H	0.348104	-4.379455	-2.542883
H	1.306762	-6.451032	-1.474062
H	1.922074	-4.231873	2.223078
H	2.079785	-6.356640	0.923152
N	-1.679558	-0.183584	0.553002
H	-1.588395	-0.020998	1.574305
C	-2.649200	0.817227	-0.008506
H	-3.105001	0.369861	-0.917304
H	-3.478301	0.996660	0.715979
C	-2.194751	-1.572323	0.344800
H	-3.288204	-1.626179	0.570922
H	-1.656634	-2.232023	1.055381
N	3.394919	0.073136	0.132303
H	3.195306	-0.830245	0.621280
H	3.191289	0.759147	0.895863

$Fe(phen)_2(NCS)_2$ S=2

Fe	0.003942	0.848343	0.026990
N	1.909022	0.393665	1.090144
C	2.352998	1.069664	2.162008
H	1.663956	1.843416	2.548623
C	3.607409	0.809551	2.762658
H	3.910714	1.404095	3.644578
C	4.439446	-0.187007	2.243722
H	5.424359	-0.413207	2.695564
C	3.997303	-0.909925	1.097602
C	2.717480	-0.568568	0.552754
C	2.251617	-1.246885	-0.638406
C	3.076498	-2.250379	-1.244509
C	4.349486	-2.594267	-0.652948
H	4.962521	-3.376710	-1.138118
C	4.795979	-1.943425	0.478026
H	5.776897	-2.189579	0.925936
N	1.051096	-0.859304	-1.156361
C	0.636104	-1.427963	-2.293260
H	-0.328870	-1.061198	-2.691977
C	1.376772	-2.431054	-2.964591
H	0.976882	-2.861343	-3.901969
C	2.600535	-2.857637	-2.442347
H	3.204129	-3.637770	-2.945026
N	-1.049603	-0.939663	1.100069
C	-0.635822	-1.584825	2.195505
H	0.328975	-1.246584	2.619506
C	-1.377394	-2.631631	2.795981
H	-0.978709	-3.125275	3.702128
C	-2.600503	-3.021058	2.244247
H	-3.204966	-3.833567	2.691587
C	-3.074712	-2.333590	1.089910
C	-2.249206	-1.290998	0.554709
C	-2.714620	-0.532701	-0.588023
C	-3.994726	-0.835906	-1.154685
C	-4.792868	-1.910317	-0.608629
H	-5.773468	-2.125612	-1.072808
C	-4.346785	-2.637341	0.474983
H	-4.959657	-3.451643	0.904841
N	-1.906865	0.463854	-1.059105
C	-2.352723	1.213624	-2.079947
H	-1.664077	2.012338	-2.412513
C	-3.608240	0.996473	-2.695148

H	-3.913100	1.651747	-3.532346
C	-4.438837	-0.034557	-2.246572
H	-5.424463	-0.228435	-2.711680
N	-0.594530	2.023483	1.524332
C	-1.049573	2.672864	2.425969
S	-1.671676	3.563396	3.664841
N	0.591320	2.121626	-1.392055
C	1.043306	2.833748	-2.246698
S	1.661662	3.809193	-3.421785

$Fe(phen)_2(NCS)_2$ S=0

Fe	-0.000942	0.481482	0.167488
N	-1.577464	0.845331	-1.000717
C	-1.825988	1.915068	-1.768927
H	-1.022980	2.672051	-1.796783
C	-3.033210	2.065014	-2.478096
H	-3.174270	2.974425	-3.088671
C	-4.022718	1.094581	-2.399980
H	-4.977961	1.202340	-2.947568
C	-3.798134	-0.041035	-1.580723
C	-2.553308	-0.106663	-0.903348
C	-2.270406	-1.203503	-0.031542
C	-3.229582	-2.235532	0.141282
C	-4.475829	-2.161528	-0.574263
H	-5.213576	-2.970836	-0.429352
C	-4.750883	-1.103417	-1.401772
H	-5.714901	-1.041855	-1.937750
N	-1.065987	-1.162963	0.618845
C	-0.785782	-2.165459	1.463580
H	0.178451	-2.098864	1.995100
C	-1.671243	-3.234746	1.685298
H	-1.378601	-4.024486	2.399938
C	-2.895679	-3.284797	1.033517
H	-3.607357	-4.112810	1.209110
N	1.070899	-0.528124	-1.199656
C	0.795109	-0.791993	-2.484839
H	-0.168743	-0.412560	-2.864013
C	1.684430	-1.492013	-3.318686
H	1.395545	-1.669107	-4.370001
C	2.907800	-1.933428	-2.834097
H	3.622282	-2.473332	-3.482910
C	3.237287	-1.661995	-1.482601
C	2.274370	-0.960809	-0.710490
C	2.553665	-0.636111	0.653247

C	3.797849	-1.000558	1.229488
C	4.753730	-1.723778	0.434530
H	5.717031	-2.005184	0.896362
C	4.482570	-2.043956	-0.870854
H	5.223075	-2.588815	-1.483250
N	1.575597	0.052651	1.314648
C	1.820517	0.421462	2.579409
H	1.015683	0.999890	3.065428
C	3.026323	0.102584	3.233126
H	3.164475	0.441373	4.275197
C	4.018268	-0.612165	2.575574
H	4.972455	-0.864379	3.075407
N	0.899608	2.112512	-0.445850
C	1.787165	2.799390	-0.851490
S	2.991854	3.777232	-1.426315
N	-0.907346	1.383067	1.654267
C	-1.796040	1.689883	2.389092
S	-3.001539	2.120850	3.437547

FePCl S=5/2

Fe	0.031403	0.000080	-0.405146
Cl	0.006756	0.000405	-2.631267
N	2.084318	0.000001	0.067831
N	-2.010860	-0.000007	0.111133
N	0.036649	2.047685	0.089832
C	2.913234	1.106516	0.096574
C	2.475883	2.438871	0.106312
H	3.254607	3.217343	0.129192
C	1.143497	2.876280	0.115492
C	-1.069469	2.876301	0.138199
C	-0.650251	4.262531	0.188880
H	-1.330422	5.123987	0.235664
C	0.725393	4.262523	0.174891
H	1.406362	5.123983	0.207853
C	-2.401660	2.439027	0.155245
H	-3.179731	3.217524	0.194088
C	-2.839161	1.106541	0.155563
C	-2.838982	-1.106610	0.157016
C	-4.224691	-0.687937	0.226753
H	-5.085590	-1.368556	0.277141
C	-4.224805	0.687810	0.225533
H	-5.085857	1.368391	0.273771

C	4.300051	0.687750	0.137555
H	5.161890	1.368322	0.168793
C	4.299988	-0.687992	0.137305
H	5.161756	-1.368654	0.168523
C	2.913213	-1.106598	0.096116
C	2.475847	-2.438870	0.105764
H	3.254574	-3.217380	0.127077
C	1.143639	-2.876278	0.113570
N	0.036739	-2.047647	0.088799
C	-1.069417	-2.876241	0.136991
C	-0.650131	-4.262633	0.187741
H	-1.330268	-5.124023	0.236216
C	0.725537	-4.262640	0.173030
H	1.406540	-5.123963	0.208782
C	-2.401600	-2.438710	0.158422
H	-3.179714	-3.217129	0.197913

FePCl S=3/2

Fe	0.033981	-0.000003	-0.166967
Cl	0.010367	-0.000048	-2.437032
N	2.042330	0.000013	0.096377
N	-1.968441	-0.000005	0.138034
N	0.036936	2.005486	0.117277
C	2.883716	1.101145	0.102757
C	2.468988	2.432040	0.105499
H	3.247188	3.210202	0.107314
C	1.138160	2.846758	0.120984
C	-1.063994	2.846767	0.143429
C	-0.649358	4.230685	0.167964
H	-1.336016	5.087535	0.194523
C	0.724104	4.230681	0.153994
H	1.411151	5.087539	0.166516
C	-2.394852	2.432046	0.155296
H	-3.172871	3.210193	0.172880
C	-2.809537	1.101135	0.161366
C	-2.809532	-1.101147	0.161532
C	-4.193082	-0.686780	0.204202
H	-5.049696	-1.373663	0.232567
C	-4.193080	0.686771	0.204082
H	-5.049689	1.373659	0.232421
C	4.267846	0.686769	0.117222
H	5.124855	1.373654	0.128098

C	4.267836	-0.686780	0.117107
H	5.124830	-1.373686	0.127908
C	2.883704	-1.101129	0.102597
C	2.468968	-2.432028	0.105142
H	3.247161	-3.210198	0.106759
C	1.138151	-2.846748	0.120764
N	0.036928	-2.005479	0.117302
C	-1.063993	-2.846759	0.143627
C	-0.649352	-4.230666	0.168032
H	-1.336006	-5.087516	0.194697
C	0.724106	-4.230665	0.153763
H	1.411156	-5.087519	0.166382
C	-2.394843	-2.432053	0.155518
H	-3.172852	-3.210208	0.173216

$Fe(L)(CN)_2$ S=2

N	0.305099	-0.026956	1.097934
C	1.395855	0.045733	1.916278
C	1.257512	0.267855	3.297868
H	2.146111	0.330809	3.943933
C	-0.030648	0.413416	3.844927
H	-0.164063	0.603430	4.921245
C	-1.146123	0.297332	2.999558
H	-2.160775	0.394889	3.413776
C	-0.954517	0.067435	1.623940
C	2.690323	-0.120128	1.219080
C	-2.029097	-0.085821	0.624196
N	-1.608162	-0.170077	-0.607661
N	2.587209	-0.269323	-0.068931
C	-3.486293	-0.171953	1.011998
H	-3.644288	-0.141753	2.107113
H	-3.926055	-1.122598	0.635004
H	-4.071368	0.661676	0.561196
C	3.978622	-0.089651	2.008006
H	4.157059	0.929796	2.419817
H	4.855608	-0.358515	1.386909
H	3.938593	-0.792450	2.868519
C	3.714864	-0.404691	-0.984112
H	4.549904	-1.009750	-0.560494
H	4.104449	0.616904	-1.201552
C	-2.506822	-0.356540	-1.740882
H	-3.497168	0.132951	-1.593875
H	-2.679164	-1.451988	-1.864608
C	-1.865466	0.188817	-3.023014
H	-1.731010	1.294374	-2.962609

H	-2.511942	-0.059954	-3.900169
C	3.260187	-1.048856	-2.297346
H	4.092565	-1.006164	-3.040778
H	2.961198	-2.111662	-2.137438
O	2.136847	-0.288589	-2.764704
O	-0.598072	-0.460658	-3.138571
C	1.573631	-0.759637	-4.002083
H	2.270734	-0.534930	-4.845568
H	1.401626	-1.860475	-3.948125
C	0.251278	-0.037842	-4.210305
H	0.393202	1.067760	-4.184582
H	-0.187341	-0.337439	-5.194012
Fe	0.546215	-0.223581	-0.933724
C	0.527657	1.795756	-1.484904
C	0.568609	-2.311144	-1.097478
N	0.414908	2.913974	-1.827719
N	0.573567	-3.486217	-1.113113

$Fe(L)(CN)_2$ S=0

N	0.322231	-0.051337	1.146449
C	1.419817	0.025712	1.980614
C	1.236150	0.102401	3.375114
H	2.110277	0.160567	4.041260
C	-0.063329	0.087205	3.904125
H	-0.218324	0.136236	4.993302
C	-1.167546	0.002951	3.037285
H	-2.190020	-0.014151	3.442149
C	-0.955862	-0.060790	1.648066
C	2.651797	-0.013286	1.215685
C	-1.942032	-0.137163	0.578892
N	-1.417052	-0.183522	-0.631645
N	2.424854	-0.178555	-0.079609
C	-3.423629	-0.144644	0.867311
H	-3.624687	-0.241330	1.952223
H	-3.928928	-0.993269	0.356770
H	-3.912197	0.794349	0.520019
C	4.020377	0.145336	1.823686
H	4.592254	0.956385	1.320585
H	4.622437	-0.789365	1.746256
H	3.954436	0.405575	2.899222
C	3.522523	-0.240703	-1.041914
H	4.444429	-0.673817	-0.594596
H	3.745094	0.798950	-1.376276
C	-2.341833	-0.215767	-1.775644
H	-3.270264	0.348161	-1.539381

H	-2.624527	-1.279101	-1.960178
C	-1.758809	0.351617	-3.063912
H	-1.260517	1.329449	-2.869589
H	-2.599411	0.516941	-3.785645
C	3.096253	-1.077492	-2.240640
H	3.874732	-1.012755	-3.038346
H	2.943829	-2.145461	-1.956256
O	1.869443	-0.504945	-2.705656
O	-0.843082	-0.608080	-3.571358
C	1.450853	-0.960808	-4.000831
H	2.277318	-0.784914	-4.732355
H	1.210617	-2.050178	-3.971784
C	0.225619	-0.154251	-4.390943
H	0.429693	0.930219	-4.231121
H	-0.004411	-0.320008	-5.473665
Fe	0.600089	-0.226638	-0.632677
C	0.628735	1.636526	-1.152208
C	0.540070	-2.158502	-0.659039
N	0.648822	2.749340	-1.530653
N	0.538767	-3.333524	-0.670157

Table S3. The calculated energies for all investigated complexes using def2-QZVPP basis sets.

	BP86 (Eh)	OPBE (Eh)	TPSS (Eh)	TPSSh (Eh)	B3LYP (Eh)	B2PLYP (Eh)	ZPE (kcal/mol)
1 S=2	-3390.140922	-3389.396436	-3990.156321	-3389.949628	-3388.870175	-3388.777985	239.5
1 S=0	-3390.168925	-3389.400793	-3390.188299	-3389.965358	-3388.866148	-3388.778853	245.9
2 S=2	-3361.868981	-3661.255152	-3661.756573	-3661.587766	-3660.679949	-3660.527985	200.7
2 S=0	-3661.926315	-3661.306056	-3661.813018	-3661.629514	-3660.698179	-3660.608326	202.5
3 S=2	-3645.469615	-3644.859643	-3645.360241	-3645.213256	-3644.322379	-3644.197077	200.4
3 S=0	-3645.534280	-3644.917646	-3645.422587	-3645.255040	-3644.338974	-3644.242430	202.1
4 S=2	-3993.310743	-3992.643179	-3993.199939	-3993.057492	-3992.061089	-3991.916842	268.1
4 S=0	-3993.356698	-3992.677165	-3993.244453	-3993.080656	-3992.057468	-3991.936649	267.6
5 S=2	-3875.296247	-3874.679168	-3875.162024	-3875.031156	-3874.127308	-3873.982111	212.6
5 S=0	-3875.341124	-3874.716020	-3875.208006	-3875.053704	-3874.123587	-3873.999770	214.0
6 S=2	-3644.036601	-3643.429442	-3643.921305	-3643.782059	-3642.883270	-3642.755924	231.1

6 S=0	-3644.059003	-3643.436442	-3643.944848	-3643.785878	-3642.862735	-3642.747878	232.2
7 S=2	-3588.685804	-3588.112470	-3588.567360	-3588.435793	-3587.568437	-3587.440714	218.4
7 S=0	-3588.684813	-3588.094385	-3588.568126	-3588.417029	-3587.526101	-3587.408458	219.3
8 S=5/2	-2713.160259	-2712.681247	-2713.137855	-2712.983458	-2712.164651	-2712.089093	181.5
8 S=3/2	-2713.173057	-2712.676617	-2713.151086	-2712.988085	-2712.162147	-2712.085793	181.2
9 S=2	-1722.333669	-1722.132388	-1722.191378	-1722.126760	-1721.863698	-1721.770397	100.0
9 S=0	-1722.289306	-1722.050378	-1722.153431	-1722.079580	-1721.810236	-1721.711738	97.6
10 S=2	-1603.105002	-1602.994752	-1602.976889	-1602.925724	-1602.642533	-1602.547019	150.0
10 S=0	-1603.105411	-1602.962862	-1602.981380	-1602.916540	-1602.620714	-1602.513923	150.0
11 S=2	-1621.712067	-1621.571226	-1621.580963	-1621.500970	-1621.200367	-1621.079186	128.5
11 S=1	-1621.728591	-1621.571494	-1621.600581	-1621.513112	-1621.202417	-1621.086559	129.3
12 S=2	-2349.099477	-2348.580887	-2349.111062	-2348.955246	-2348.170646	-2348.092718	240.1
12 S=0	-2349.142639	-2348.611271	-2349.150972	-2348.972451	-2348.167725	-2348.100653	250.6

Table S4. $<S^2>$ value for each complex.

	BP86	OPBE	TPSS	TPSSh	B3LYP	B2PLYP
1 S=2	6.24	6.30	6.18	6.10	6.07	6.24
1 S=0	1.00	1.00	1.00	1.00	1.00	1.00
2 S=2	6.19	6.21	6.20	6.23	6.65	7.02
2 S=0	1.00	1.00	1.00	1.00	1.00	1.00
3 S=2	6.05	6.09	6.04	6.04	6.05	6.03
3 S=0	1.00	1.00	1.00	1.00	1.00	1.00
4 S=2	6.03	6.04	6.03	6.02	6.02	6.02
4 S=0	1.00	1.00	1.00	1.00	1.00	1.00
5 S=2	6.03	6.04	6.03	6.02	6.02	6.02
5 S=0	1.00	1.00	1.00	1.00	1.00	1.00
6 S=2	6.02	6.04	6.02	6.02	6.02	6.02

6 S=0	1.00	1.00	1.00	1.00	1.00	1.00
7 S=2	6.02	6.03	6.01	6.02	6.02	6.01
7 S=0	1.00	1.00	1.00	1.00	1.00	1.00
8 S=5/2	8.76	8.76	8.76	8.76	8.76	8.77
8 S=3/2	3.78	3.80	3.78	3.79	3.79	3.80
9 S=2	6.00	6.01	6.00	6.00	6.01	6.01
9 S=0	1.00	1.00	1.00	1.00	1.00	1.00
10 S=2	6.00	6.01	6.00	6.00	6.01	6.01
10 S=0	1.00	1.00	1.00	1.00	1.00	1.00
11 S=2	6.03	6.04	6.02	6.06	6.06	6.61
11 S=1	2.01	2.02	2.01	2.01	2.02	2.02
12 S=2	6.24	6.32	6.22	6.22	6.21	6.09
12 S=0	1.00	1.00	1.00	1.00	1.00	1.00

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