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Synthesis and structure of nickel and copper chelate complexes with coumarin azo ligand

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Elemental analysis was performed on a Carlo Erba TCM 480 instrument. The IR spectra were taken on a Varian Excalibur-3100 FT-IR instrument for a powder *via* the frustrated total internal reflection method. The electron absorption spectra were recorded on a Varian Cary 1E spectrophotometer in DMSO solution. X-ray diffraction analysis of single crystal **4** was done on a Bruker SMART APEXII diffractometer equipped with a CCD detector [λ (Mo*K*α) 0.71073 Å], a graphite monochromator.

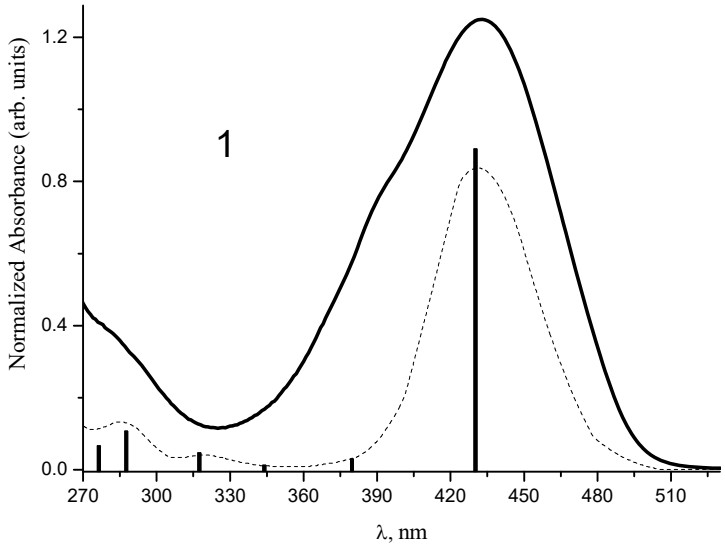


Figure S1 EAS for compound **1** in DMSO solution, the experimental data corresponds to solid line, while theoretical data are presented by dotted one, wave lengths of electron transitions are shown by vertical lines, the values of oscillator strength corresponding to the electron transition are ordinates of lines. The energy shift of theoretical EAS is +15 nm.

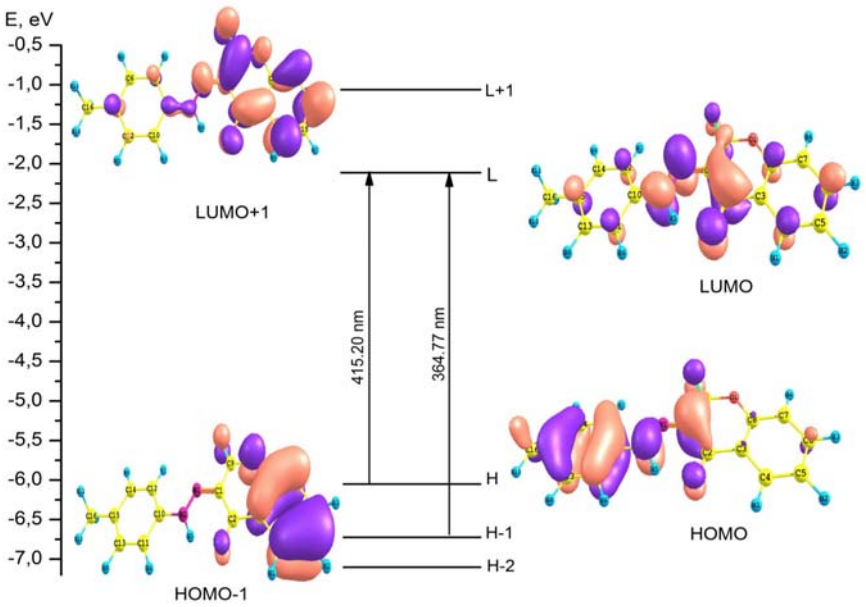


Figure S2 Energy diagrams and view of isosurfaces of frontier MO participating in the formation of EAS bands of compound **1**.

Table S1 Calculated wave lengths λ, energy E of electron transitions between appropriate MO, contributions of distinct electron transitions and oscillator strengths (f) for compound **1** obtained from TDDFT calculations.

λ, nm	E, eV	Electron transitions (contributions, %)	f
415.20 (433[a])	2.9861	HOMO→LUMO (82 %)	0.89
364.77	3.3990	HOMO-1→LUMO (94 %)	0.03

[a]experimental value

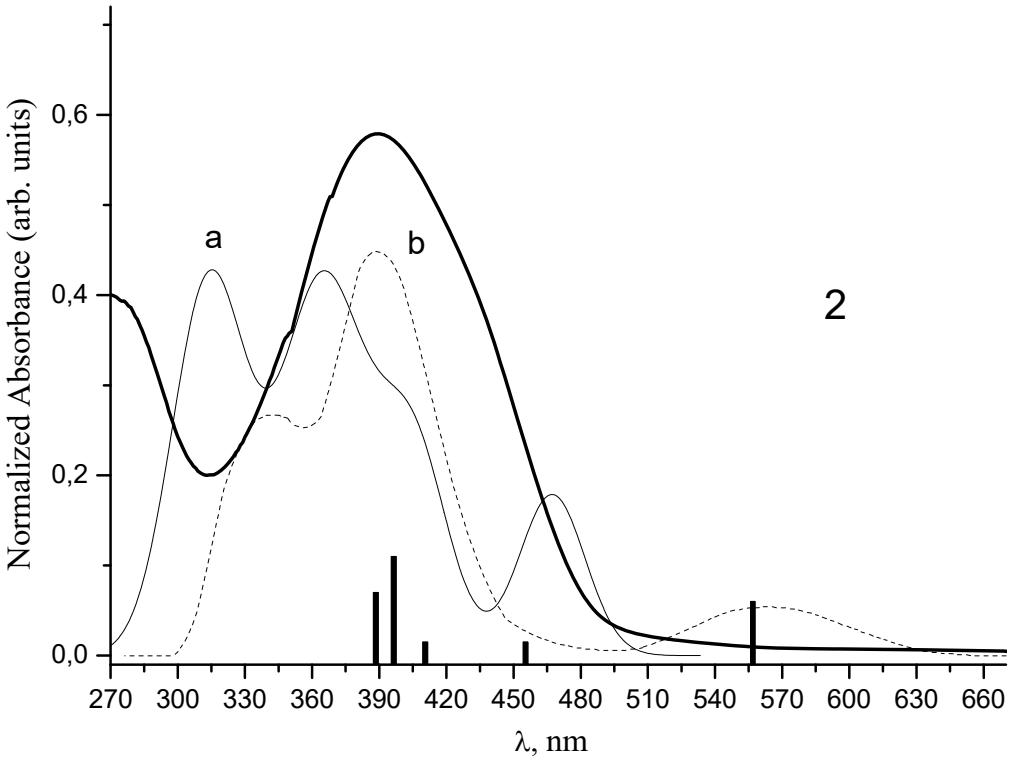


Figure S3 EAS for nickel complex solution in DMSO, experimental data corresponds to bold solid line, while theoretical data are presented by *a*) thin solid line for complex **2a**, *b*) dotted line for complex **4**. The wave lengths of electron transitions are shown by vertical lines, the values of oscillator strength corresponding to electron transitions for complex **4** are the ordinates of lines. The energy shift of theoretical EAS is +25 nm.

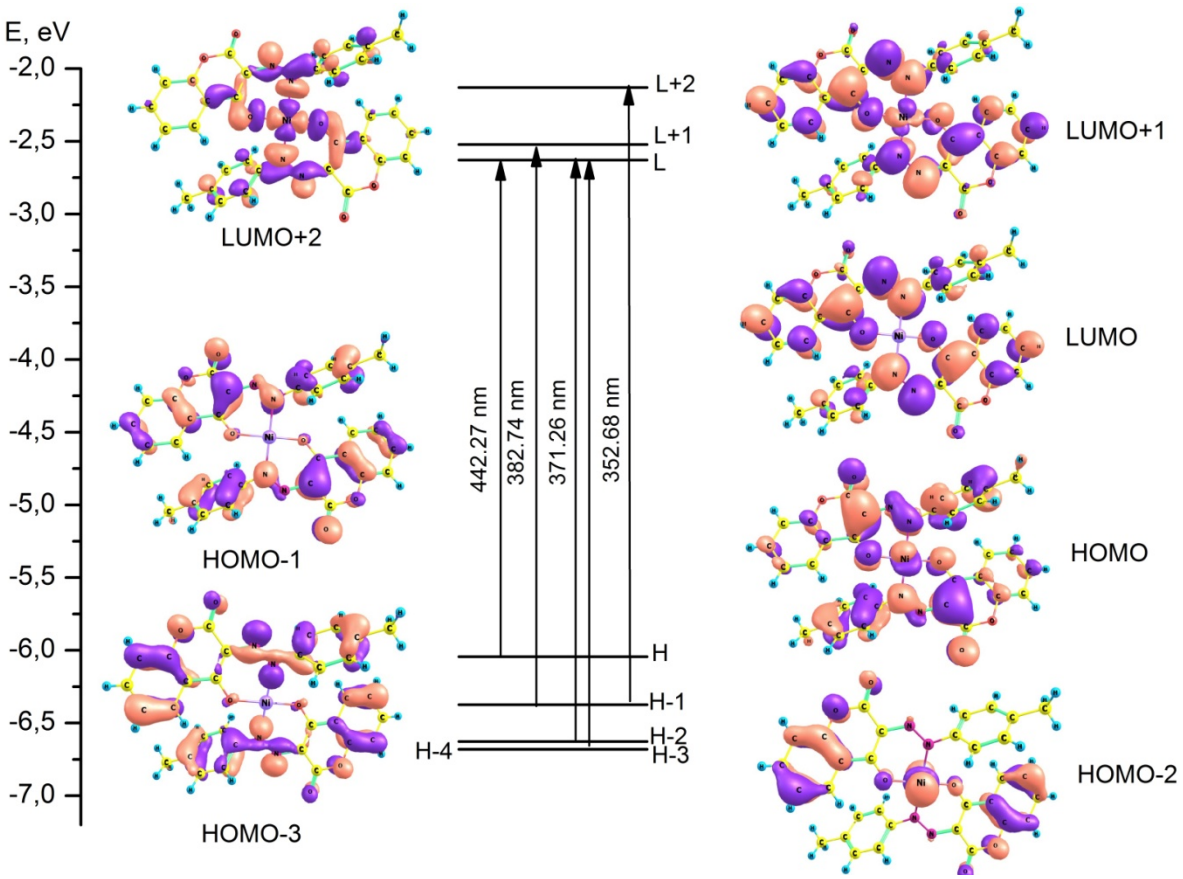


Figure S4 Energy diagrams and view of isosurfaces of frontier MO participating in the formation of EAS bands of nickel complex **2a**.

Table S2 Calculated wave lengths λ, energy E of electron transitions between appropriate MO, contributions of distinct electron transitions and oscillator strength (f) for nickel complex **2a** obtained from TDDFT calculations.

λ, nm	E, eV	Electron transitions, (contributions[a], %)	f
835.77	1.4835	HOMO→LUMO+2 (21)	0.00
775.05	1.5997	HOMO-4→LUMO+2 (32) HOMO-2→LUMO+2 (14)	0.00
678.59	1.8271	HOMO-13→LUMO+2 (16)	0.00
572.59	2.1653	HOMO-17→LUMO+2 (25) HOMO-16→LUMO+2 (18) HOMO-15→LUMO+2 (23)	0.00
442.27	2.8034	HOMO→LUMO (85)	0.18

382.74 (389)[b]	3.2394	HOMO-1→LUMO+1 (73) HOMO-1→LUMO+2 (14)	0.14
371.26	3.3396	HOMO-6→LUMO (19) HOMO-4→LUMO (29) HOMO-2→LUMO (38)	0.10
352.68	3.5155	HOMO-6→LUMO (17) HOMO-1→LUMO+2 (47)	0.14
342.39	3.6211	HOMO-13→LUMO (10) HOMO-7→LUMO (13) HOMO-6→LUMO (27) HOMO-1→LUMO+2 (22)	0.09
338.39	3.6639	HOMO-7→LUMO (32) HOMO-5→LUMO+1 (18) HOMO-3→LUMO+1 (29)	0.10
331.98	3.7347	HOMO-7→LUMO (37) HOMO-3→LUMO+1 (18)	0.08
329.29	3.7652	HOMO-13→LUMO (10) HOMO-6→LUMO (23) HOMO-5→LUMO+2 (16) HOMO-3→LUMO+2 (26)	0.07
290.96	4.2612	HOMO-13→LUMO (12) HOMO-12→LUMO+1 (13) HOMO-10→LUMO+1 (18) HOMO-9→LUMO+2 (12)	0.26

[a]Contributions were indicated if only the value was ≥ 10%, [b]experimental values.

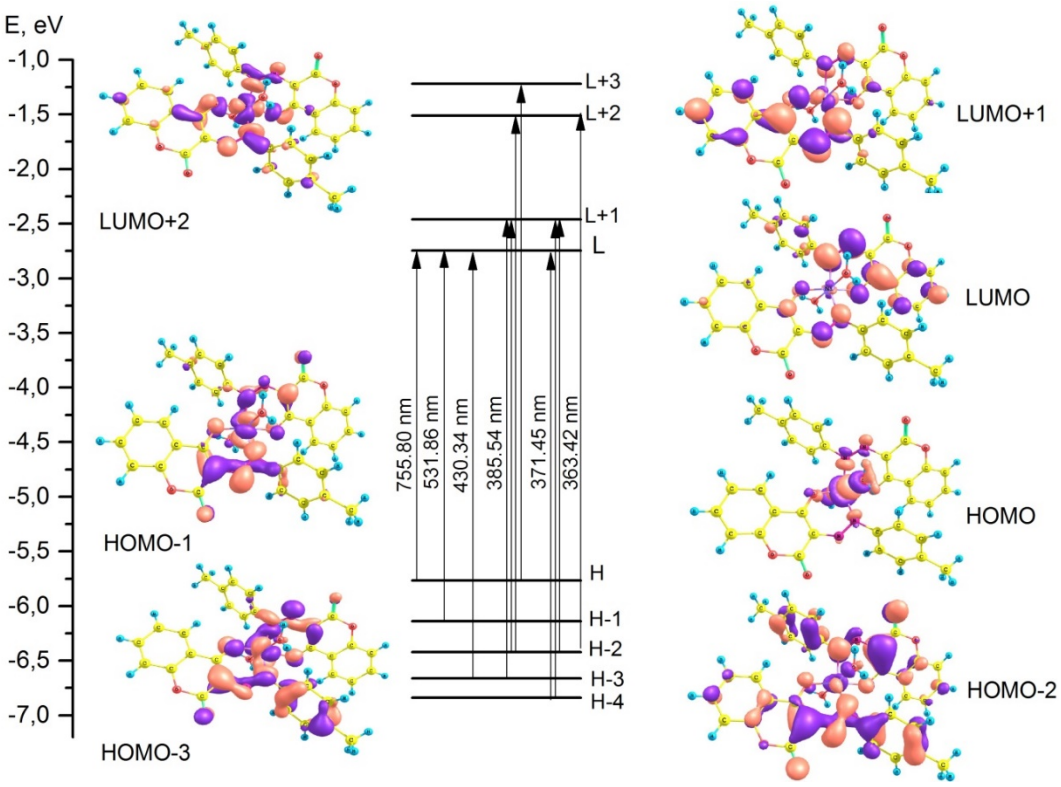


Figure S5 Energy diagrams and view of isosurfaces of frontier MO participating in the formation of EAS bands of nickel complex **4**.

Table S3 Calculated wave lengths λ, energy E of electron transitions between appropriate MO, contributions of distinct electron transitions and oscillator strengths (f) for nickel complex **4** obtained from TDDFT calculations.

λ, nm	E, eV	Electron transitions, (contributions,[a] %)	f
854.77	1.4505	HOMO→LUMO (77 %)	0.0001
755.80	1.6404	HOMO→LUMO (19 %)	0.0012
531.86	2.3311	HOMO-1→LUMO (85 %)	0.06
430.34	2.8811	HOMO-3→LUMO (75 %)	0.02
385.54 (389)[b]	3.2158	HOMO-3→LUMO+1 (19 %) HOMO-2→LUMO+1 (32 %) HOMO-2→LUMO+2 (13 %) HOMO→LUMO+3 (10 %)	0.07
371.45	3.3378	HOMO-4→LUMO (10 %) HOMO-4→LUMO+1 (23 %)	0.11

		HOMO-2→LUMO+1 (12 %)	
363.42	3.4116	HOMO-2→LUMO+2 (38 %)	0.07

[a]Contributions were indicated if only the value was ≥ 10 %, [b]experimental values.

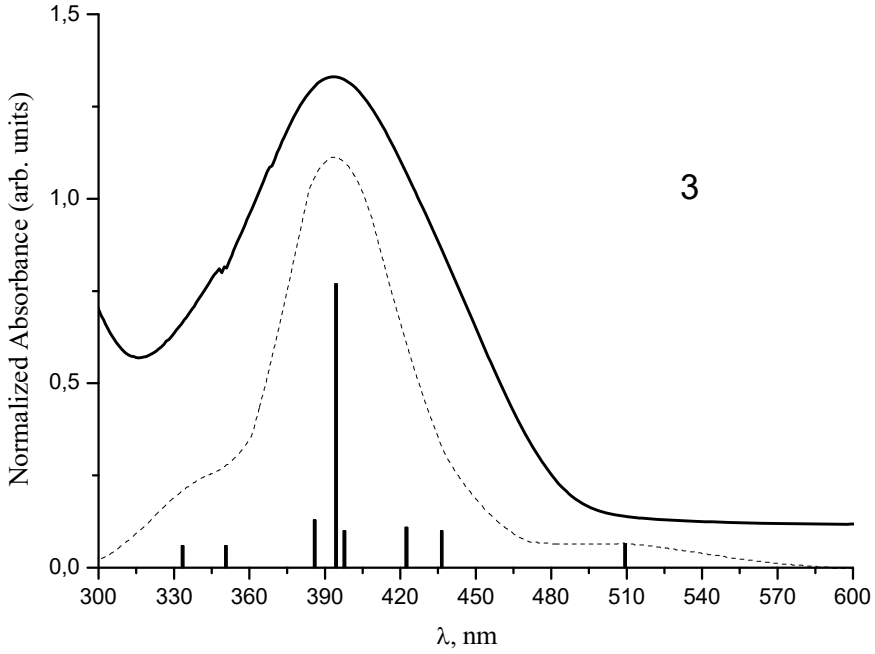


Figure S6 EAS of copper complex **3** solution in DMSO, experimental data is presented as solid line, theoretical data is shown by dotted one. The wave lengths of electron transitions are shown by vertical lines, the values of oscillator strengths corresponding to electron transitions are ordinates of lines. The energy shift of theoretical EAS is - 17 nm.

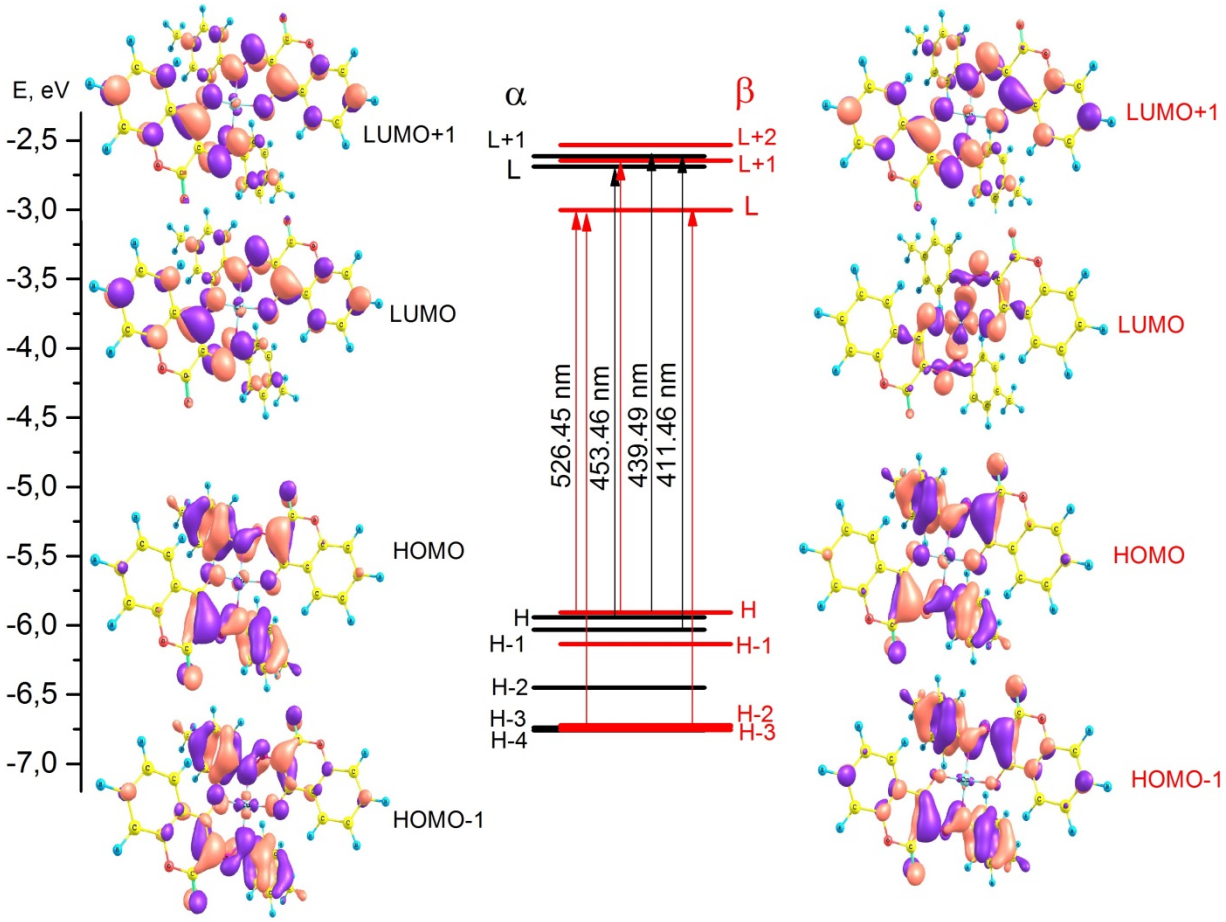


Figure S7 Energy diagram and view of isosurfaces of frontier MO participating in the formation of EAS bands of copper complex **3**.

Table S4 Calculated wave lengths λ, energy E of electron transitions between appropriate MO, contributions of distinct electron transitions and oscillator strengths (f) for copper complex **3** obtained from TDDFT calculations.

λ, nm	E, eV	Electron transitions, (contributions,[a] %)	f
526.45	2.3551	HOMO(β)→LUMO(β) (45 %) HOMO-2(β)→LUMO(β) (20 %)	0.065
453.46	2.7342	HOMO(α)→LUMO(α) (45 %) HOMO(β)→LUMO+1(β) (39 %)	0.10
439.49	2.8211	HOMO(α)→LUMO+1(α) (44 %)	0.11
414.78	2.9892	HOMO-2(α)→LUMO(α) (20 %) HOMO-2(β)→LUMO+2(β) (33 %) HOMO(β)→LUMO+2(β) (10 %)	0.10

411.46 (395)[b]	3.0133	HOMO-1(α)→LUMO(α) (24 %) HOMO-1(β)→LUMO+1(β) (43 %)	0.77
402.90	3.0773	HOMO-2(α)→LUMO+1(α) (11 %) HOMO-1(α)→LUMO+1(α) (21 %) HOMO-1(β)→LUMO+2(β) (36 %)	0.13
350.39	3.5384	HOMO-4(α)→LUMO(α) (15 %) HOMO-4(β)→LUMO+1(β) (24 %)	0.06

[a]Contributions were indicated if only the value was ≥ 10%, [b]experimental values

The specific magnetic susceptibility in a solid phase was found on a magnetometer from Southern Federal University[1] by the relative Faraday method within temperature range of 77.4–300 K using Hg[Co(CNS)4] as reference compound for calibration.

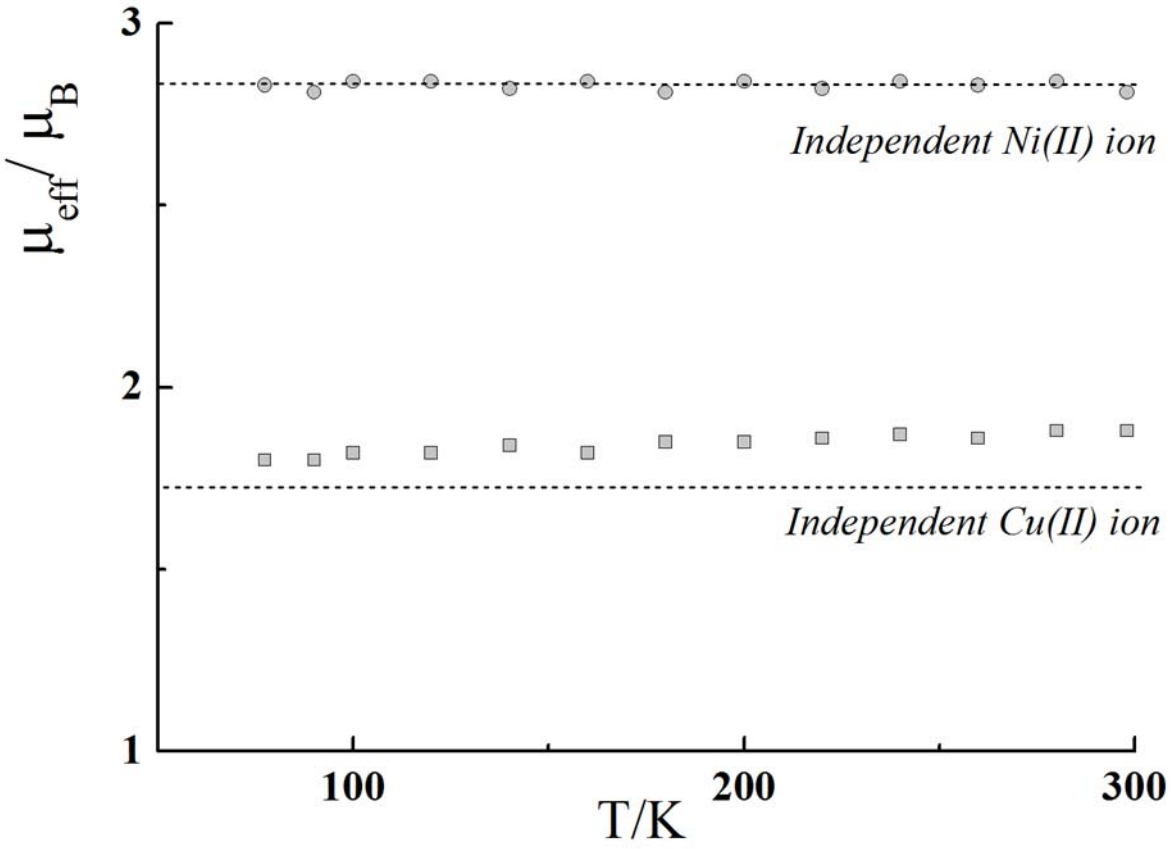
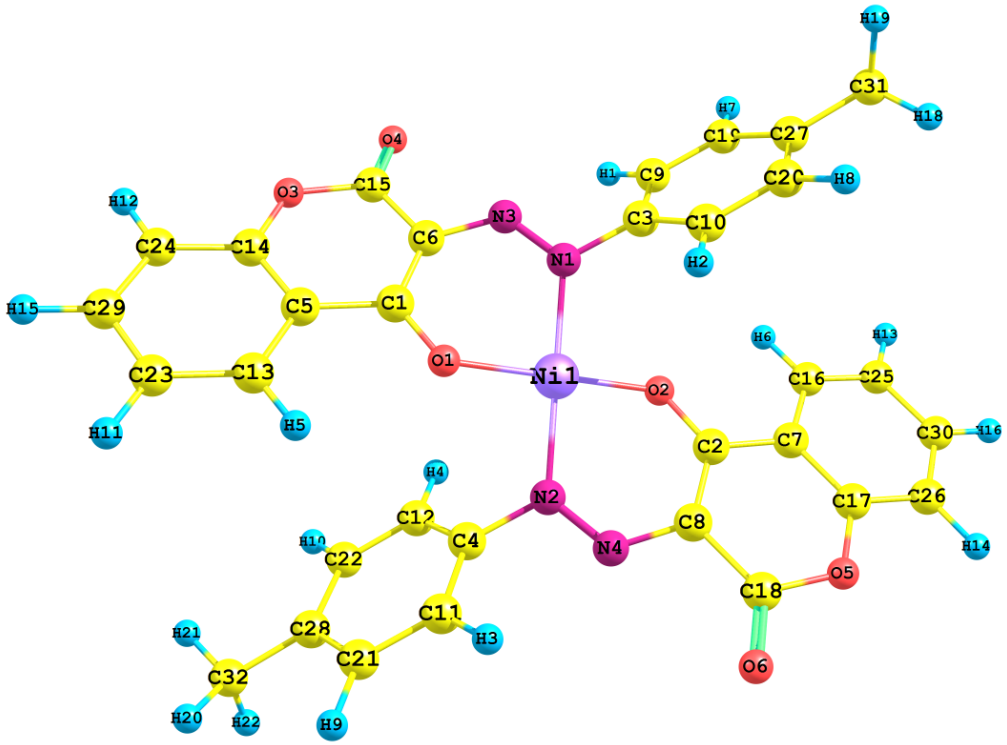


Figure S8 Temperature dependence of the effective magnetic moment of complex **3** (squares) and complex **4** (circles).

Coordinates for complex 2a and **2b, standard orientation, total energies (a.u.)**



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Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	8	0	-1.762882	-0.143492	-0.583023
3	8	0	1.762882	0.143492	0.583023
4	7	0	0.076545	-1.920362	0.208085
5	7	0	-0.076545	1.920362	-0.208085
6	6	0	-2.580833	-1.045367	-0.209412
7	6	0	2.580833	1.045367	0.209412
8	7	0	-0.907578	-2.656137	0.515941
9	6	0	1.316934	-2.644551	0.144332
10	7	0	0.907578	2.656137	-0.515941
11	6	0	-1.316934	2.644551	-0.144332
12	6	0	-3.989115	-0.896458	-0.543813
13	6	0	-2.186309	-2.227645	0.458933
14	6	0	3.989115	0.896458	0.543813
15	6	0	2.186309	2.227645	-0.458933
16	6	0	1.628131	-3.616858	1.091883
17	6	0	2.193917	-2.395723	-0.907113
18	6	0	-1.628131	3.616858	-1.091883
19	6	0	-2.193917	2.395723	0.907113
20	6	0	-4.472670	0.184660	-1.297100
21	6	0	-4.893214	-1.859271	-0.078267
22	6	0	-3.164393	-3.196408	0.967636

23	6	0	4.472670	-0.184660	1.297100
24	6	0	4.893214	1.859271	0.078267
25	6	0	3.164393	3.196408	-0.967636
26	1	0	0.935557	-3.814057	1.898740
27	6	0	2.814548	-4.328444	0.980518
28	6	0	3.369940	-3.124958	-1.014036
29	1	0	1.945404	-1.648571	-1.649742
30	1	0	-0.935557	3.814057	-1.898740
31	6	0	-2.814548	4.328444	-0.980518
32	6	0	-3.369940	3.124958	1.014036
33	1	0	-1.945404	1.648571	1.649742
34	1	0	-3.767050	0.927193	-1.642871
35	6	0	-5.819415	0.286204	-1.587019
36	8	0	-4.501785	-2.928522	0.670106
37	6	0	-6.252707	-1.757137	-0.363856
38	8	0	-2.930543	-4.173757	1.618936
39	1	0	3.767050	-0.927193	1.642871
40	6	0	5.819415	-0.286204	1.587019
41	8	0	4.501785	2.928522	-0.670106
42	6	0	6.252707	1.757137	0.363856
43	8	0	2.930543	4.173757	-1.618936
44	1	0	3.051273	-5.077962	1.727100
45	6	0	3.704156	-4.102374	-0.073393
46	1	0	4.039186	-2.929971	-1.844049
47	1	0	-3.051273	5.077962	-1.727100
48	6	0	-3.704156	4.102374	0.073393
49	1	0	-4.039186	2.929971	1.844049
50	1	0	-6.187143	1.117861	-2.173602
51	6	0	-6.707688	-0.687212	-1.116213
52	1	0	-6.923440	-2.519213	0.009470
53	1	0	6.187143	-1.117861	2.173602
54	6	0	6.707688	0.687212	1.116213
55	1	0	6.923440	2.519213	-0.009470
56	6	0	4.968040	-4.910914	-0.211587
57	6	0	-4.968040	4.910914	0.211587
58	1	0	-7.763976	-0.608344	-1.342002
59	1	0	7.763976	0.608344	1.342002
60	1	0	5.307719	-5.287704	0.754269
61	1	0	5.774431	-4.320232	-0.649501
62	1	0	4.808012	-5.776542	-0.861637
63	1	0	-5.307719	5.287704	-0.754269
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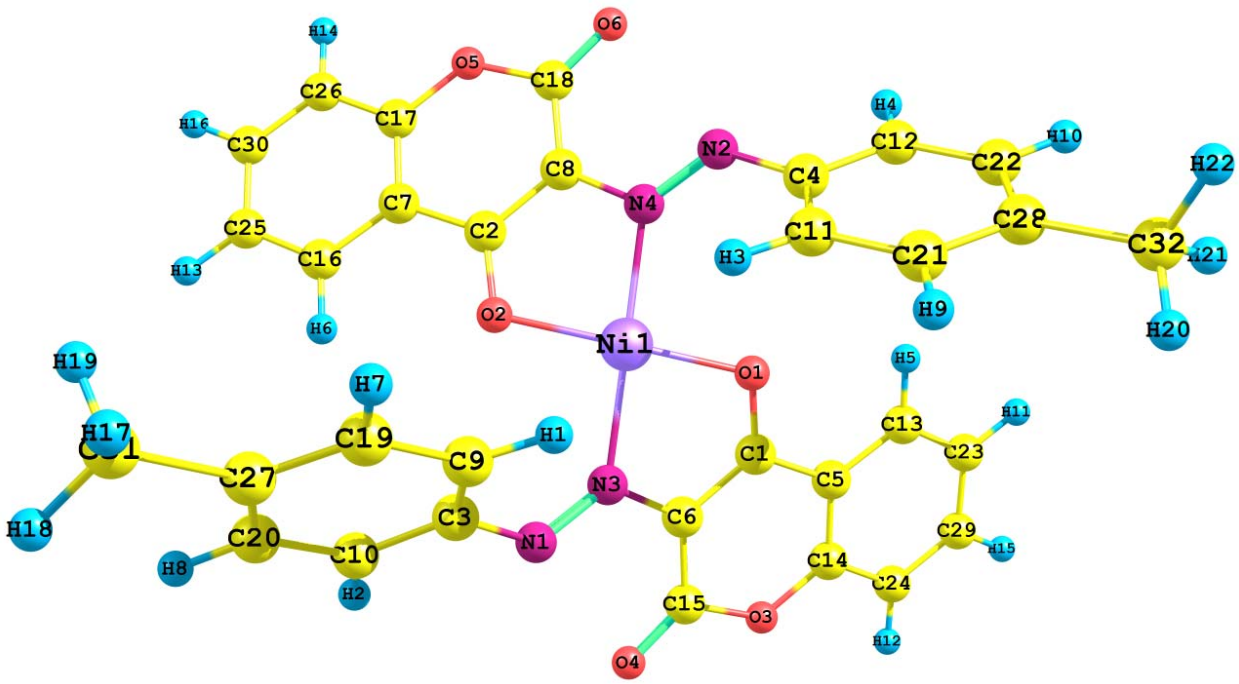
65	1	0	-4.808012	5.776542	0.861637



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4	7	0	-0.364756	-2.927507	0.219733
5	7	0	0.367199	2.925268	0.195257
6	6	0	2.350259	-0.940662	-0.687484
7	6	0	-2.348121	0.930797	-0.693995
8	7	0	0.352240	-1.932210	-0.045973
9	6	0	-1.486545	-2.776999	1.039671
10	7	0	-0.349704	1.927558	-0.061528
11	6	0	1.488297	2.783971	1.017553
12	6	0	3.698610	-0.984983	-1.208339
13	6	0	1.597261	-2.121180	-0.650393
14	6	0	-3.697050	0.970887	-1.213828
15	6	0	-1.595221	2.111614	-0.666627
16	6	0	-1.536003	-1.917947	2.143916
17	6	0	-2.553532	-3.652672	0.807335
18	6	0	1.539868	1.932056	2.127307
19	6	0	2.555431	3.657000	0.776256
20	6	0	4.527569	0.144466	-1.280006
21	6	0	4.177980	-2.221195	-1.660844
22	6	0	2.112289	-3.400563	-1.102084
23	6	0	-4.525642	-0.159379	-1.276574
24	6	0	-4.177402	2.203668	-1.674495
25	6	0	-2.111105	3.387495	-1.127166
26	1	0	-0.679550	-1.301370	2.384472
27	6	0	-2.653812	-1.907605	2.962638
28	6	0	-3.676544	-3.608937	1.615979

29	1	0	-2.481018	-4.350690	-0.016590
30	1	0	0.687168	1.310542	2.368536
31	6	0	2.658023	1.929045	2.945386
32	6	0	3.678836	3.620577	1.584723
33	1	0	2.485318	4.342771	-0.058139
34	1	0	4.141449	1.089874	-0.922981
35	6	0	5.804745	0.035204	-1.794397
36	8	0	3.425185	-3.352434	-1.617008
37	6	0	5.466443	-2.333006	-2.181189
38	8	0	1.570863	-4.469050	-1.109995
39	1	0	-4.138515	-1.102232	-0.913837
40	6	0	-5.803481	-0.054267	-1.790271
41	8	0	-3.424877	3.335331	-1.639782
42	6	0	-5.466592	2.311327	-2.193980
43	8	0	-1.570100	4.456075	-1.143672
44	1	0	-2.672117	-1.251735	3.825642
45	6	0	-3.752068	-2.733644	2.705720
46	1	0	-4.502716	-4.280998	1.413684
47	1	0	2.680817	1.273986	3.809028
48	6	0	3.752935	2.758401	2.684923
49	1	0	4.508051	4.285598	1.371599
50	1	0	6.444987	0.905825	-1.851447
51	6	0	6.269338	-1.206602	-2.245075
52	1	0	5.810501	-3.299243	-2.524753
53	1	0	-6.443305	-0.925609	-1.840822
54	6	0	-6.269143	1.184217	-2.248987
55	1	0	-5.811412	3.274980	-2.543983
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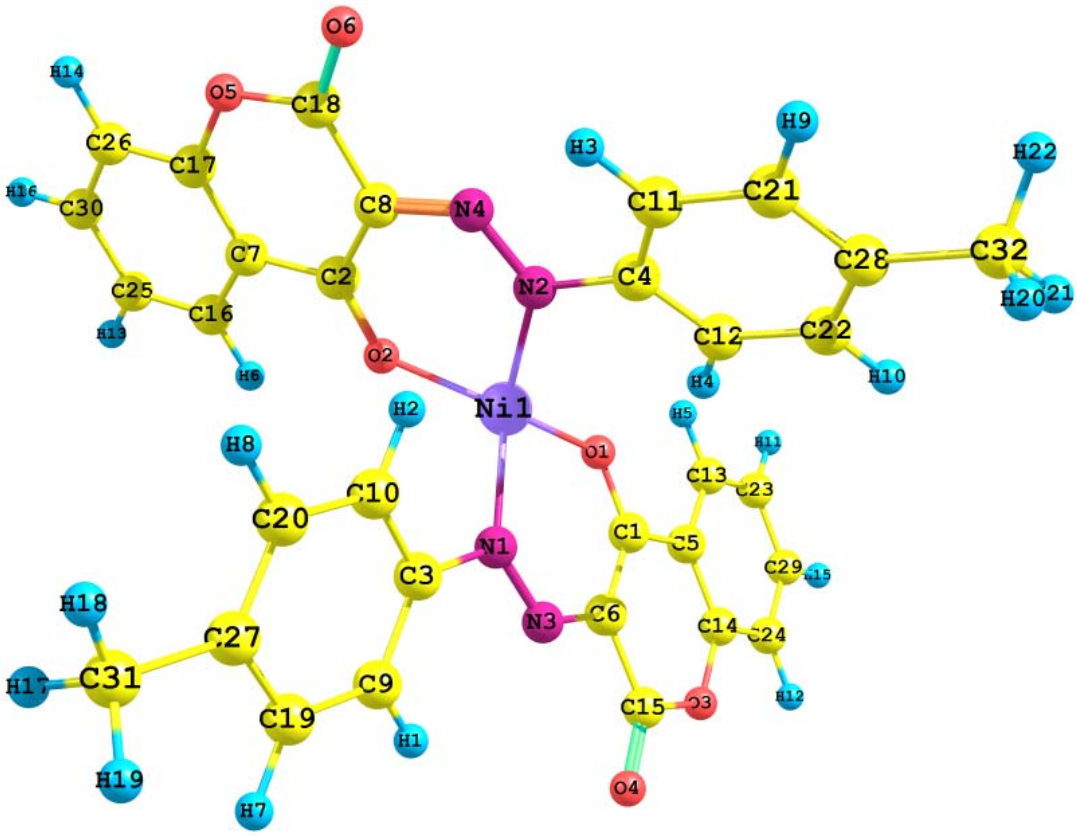
62	1	0	-5.723462	-1.998333	3.163443
63	1	0	5.073989	1.810357	4.103988
64	1	0	5.869293	2.978349	3.042361
65	1	0	4.852756	3.538361	4.365817



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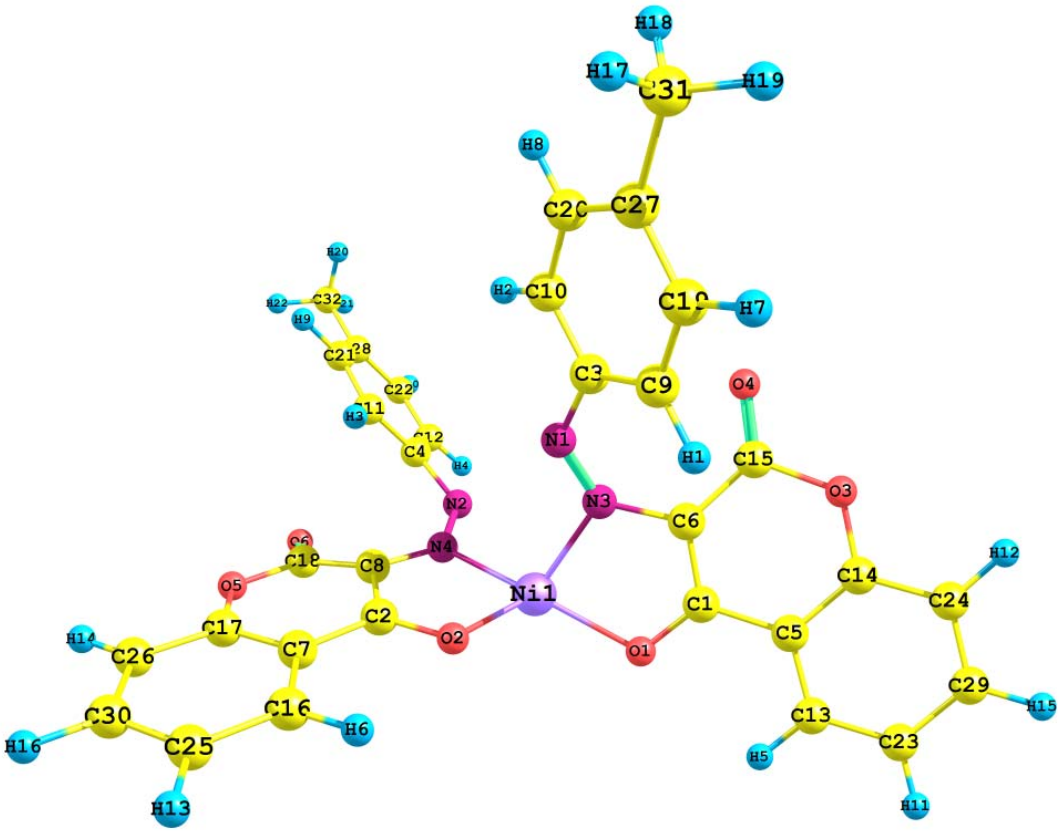
3	8	0	-1.540470	-1.049770	-0.988712
4	7	0	0.738805	-0.749960	1.356747
5	7	0	-0.766254	1.618397	-0.594002
6	6	0	2.898635	-0.924861	-0.619372
7	6	0	-2.669553	-0.515567	-1.219419
8	7	0	1.902076	-1.182823	1.631622
9	6	0	-0.175673	-0.841025	2.455855
10	7	0	-1.991488	1.839606	-0.863818
11	6	0	-0.025731	2.805327	-0.285759
12	6	0	4.113307	-1.118885	-1.399128
13	6	0	2.928438	-1.261192	0.758091
14	6	0	-3.786109	-1.372418	-1.595982
15	6	0	-2.901966	0.885798	-1.143044
16	6	0	0.067723	-1.684892	3.546143
17	6	0	-1.339168	-0.075050	2.434640
18	6	0	-0.660597	3.989106	0.107479
19	6	0	1.364617	2.770756	-0.370104
20	6	0	4.174597	-0.816084	-2.768678
21	6	0	5.258311	-1.607629	-0.761617
22	6	0	4.152931	-1.797575	1.387194

23	6	0	-3.647688	-2.764622	-1.710651
24	6	0	-5.033472	-0.792629	-1.847678
25	6	0	-4.244201	1.452465	-1.389554
26	1	0	0.974009	-2.273175	3.566611
27	6	0	-0.844521	-1.748247	4.584535
28	6	0	-2.242833	-0.145586	3.488086
29	1	0	-1.530148	0.599611	1.613028
30	1	0	-1.739673	4.017580	0.162013
31	6	0	0.097058	5.107278	0.408928
32	6	0	2.110075	3.904260	-0.068440
33	1	0	1.863773	1.871609	-0.703749
34	1	0	3.282751	-0.438848	-3.250304
35	6	0	5.347139	-1.001540	-3.474453
36	8	0	5.272229	-1.924247	0.561398
37	6	0	6.443978	-1.797132	-1.468424
38	8	0	4.282586	-2.131957	2.529042
39	1	0	-2.678527	-3.200741	-1.510382
40	6	0	-4.726686	-3.547504	-2.071334
41	8	0	-5.245258	0.548295	-1.746742
42	6	0	-6.125353	-1.576819	-2.213518
43	8	0	-4.558320	2.604994	-1.310102
44	1	0	-0.642715	-2.408283	5.420879
45	6	0	-2.018479	-0.984011	4.578957
46	1	0	-3.134793	0.469099	3.458323
47	1	0	-0.407769	6.016827	0.715011
48	6	0	1.495567	5.089916	0.331988
49	1	0	3.189980	3.861797	-0.149473
50	1	0	5.389452	-0.767740	-4.530220
51	6	0	6.482275	-1.492317	-2.818605
52	1	0	7.309896	-2.178396	-0.944127
53	1	0	-4.615505	-4.620415	-2.158375
54	6	0	-5.966357	-2.948018	-2.322671
55	1	0	-7.075350	-1.095138	-2.402054
56	6	0	-3.010304	-1.085162	5.707380
57	6	0	2.302406	6.309829	0.690052
58	1	0	7.402850	-1.638377	-3.370041
59	1	0	-6.813890	-3.559906	-2.605868
60	1	0	-3.573864	-2.021290	5.650954
61	1	0	-3.729043	-0.265508	5.680424
62	1	0	-2.510477	-1.067061	6.678173
63	1	0	2.311059	6.470062	1.772250
64	1	0	3.338031	6.212253	0.362757
65	1	0	1.885393	7.210094	0.233451



#P B3LYP/TZVP opt Pop=Full

Charge = 0 Multiplicity = 3

SCF Done: E(UB+HF-LYP) = -3412.03486244 A.U. after 19 cycles

Convg = 0.3130D-08 -V/T = 2.0032 S**2 = 2.0098

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	0.301284	-1.246331	-0.936639
2	8	0	2.091552	-1.931326	-1.334174
3	8	0	-0.602764	-2.211888	0.526470
4	7	0	0.712800	1.028511	0.690079
5	7	0	-1.617898	0.400937	-2.096539
6	6	0	3.004404	-1.086027	-1.033719
7	6	0	-1.866365	-2.030670	0.499779
8	7	0	1.344636	0.255458	-0.074488
9	6	0	1.263543	1.786730	1.734718
10	7	0	-1.542239	-0.567557	-1.289584
11	6	0	-2.630731	1.369190	-2.123247
12	6	0	4.387991	-1.342933	-1.388141
13	6	0	2.711268	0.110228	-0.335282
14	6	0	-2.729530	-2.723515	1.440126
15	6	0	-2.474358	-1.147628	-0.428044
16	6	0	2.326311	1.369615	2.546405
17	6	0	0.551011	2.938806	2.087218
18	6	0	-3.291931	1.859883	-0.987637
19	6	0	-2.823213	2.012233	-3.350699
20	6	0	4.805410	-2.549796	-1.969145
21	6	0	5.339035	-0.352903	-1.115297

22	6	0	3.675193	1.186753	-0.254154
23	6	0	-2.225698	-3.522094	2.477440
24	6	0	-4.114103	-2.563347	1.313977
25	6	0	-3.901516	-1.170527	-0.659432
26	1	0	2.863345	0.459206	2.317553
27	6	0	2.663932	2.102418	3.671593
28	6	0	0.934334	3.689954	3.184608
29	1	0	-0.289882	3.235456	1.473754
30	1	0	-3.115413	1.412077	-0.019451
31	6	0	-4.130734	2.953944	-1.097419
32	6	0	-3.707234	3.073618	-3.454595
33	1	0	-2.275633	1.656278	-4.213740
34	1	0	4.057971	-3.304373	-2.174294
35	6	0	6.139245	-2.756997	-2.262507
36	8	0	4.994563	0.851582	-0.581058
37	6	0	6.685855	-0.557470	-1.407806
38	8	0	3.461188	2.333034	0.042647
39	1	0	-1.153155	-3.635911	2.560326
40	6	0	-3.087721	-4.137047	3.364694
41	8	0	-4.668229	-1.828611	0.309520
42	6	0	-4.987858	-3.179629	2.207422
43	8	0	-4.492891	-0.706140	-1.599650
44	1	0	3.479234	1.759369	4.298417
45	6	0	1.991758	3.282695	4.004080
46	1	0	0.393001	4.598350	3.422928
47	1	0	-4.621746	3.333030	-0.207996
48	6	0	-4.373977	3.568909	-2.331311
49	1	0	-3.867146	3.540672	-4.419368
50	1	0	6.459928	-3.689232	-2.708906
51	6	0	7.077385	-1.757513	-1.977683
52	1	0	7.395821	0.228588	-1.188211
53	1	0	-2.697497	-4.751188	4.165822
54	6	0	-4.469730	-3.960787	3.226992
55	1	0	-6.052970	-3.038886	2.081243
56	6	0	2.369714	4.068309	5.231369
57	6	0	-5.317256	4.737850	-2.432007
58	1	0	8.123337	-1.919238	-2.207402
59	1	0	-5.146169	-4.442138	3.922495
60	1	0	1.824648	3.708593	6.109911
61	1	0	2.135460	5.127225	5.113160
62	1	0	3.434930	3.977566	5.449710
63	1	0	-4.976411	5.575851	-1.817819
64	1	0	-5.405515	5.090368	-3.459873
65	1	0	-6.317135	4.467440	-2.082448

References

1 V. P. Kurbatov, A. V. Khokhlov, A. D. Garnovskii, O. A. Osipov and L. A. Khulhachieva, *Koord. Khim.*, 1979, **5**, 351 (in Russian).