Electronic Supplementary Information for:

Vibrational circular dichroism spectroscopy of a spin-triplet *bis*-(biuretato) cobaltate(III) coordination compound with low-lying electronic transitions.

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Contents:

Calculational details: Coordination anion: ([Co(III)-(S,S)-stien(biur)2]-)

Frequency, VCD and geometry calculations were performed at the UB3LYP/TZVP level using Gaussian 03 Rev. B.04 and TD calculations were performed using a Rev. C.02.

A file with the Cartesian coordinates of the anion are provides as a separate file ([Co(III)-S,S-stien(biur)2]-.xyz)

Frequency and VCD data are given in Table S1 below, while TD DFT results are in Table S2:

Table S1: Frequency/VCD output for [Co(III)(*S*,*S*)-stien(biur)$_2$]$^-$ // g03 UB3LYP/TZVP

No.	Frequency / cm^{-1}	Dipole strength / 10^{-40} esu^2 cm^2	Rotational strength / 10^{-44} esu^2 cm^2
1	13,8	4,46E+01	-1,04E+01
2	20,5	6,41E-01	1,88E+00
3	28,6	1,07E+00	-9,28E-01
4	41,1	1,90E+01	1,55E+01
5	43,4	2,15E+01	-4,10E+00
6	51,2	1,13E+02	-6,09E+00
7	56,9	4,78E+00	2,65E+00
8	61,7	2,49E+02	-4,99E-02
9	102,3	7,85E+00	-2,30E+01
10	127,8	4,72E-01	-3,02E-02
11	134,2	1,76E-01	-1,49E+00
12	134,5	6,95E+01	6,97E+00
13	145,1	8,39E-02	-1,35E+00
14	167,6	9,69E+01	1,67E+01
15	211,2	7,89E+00	-2,66E+01
16	215,7	9,45E+00	1,40E+01
17	232,4	6,30E-03	4,14E-01
18	243,7	3,53E+01	8,24E+01
19	248,4	5,64E+00	-1,86E+00
20	291,5	3,40E+01	5,02E+00
21	315,1	8,01E+01	-1,81E+01
22	326,8	3,52E+00	2,85E+01
23	350,0	1,84E+02	9,72E+01
24	385,5	8,34E+02	-6,16E+01
25	394,7	1,03E+02	3,35E+01
26	397,3	7,91E+01	6,87E+01
27	404,8	3,49E+02	-9,61E+01
28	411,8	3,54E-01	2,24E-01
29	412,2	2,40E+00	1,87E+00
30	453,8	2,48E+00	-8,80E+00
31	495,2	9,21E+00	6,08E+00
32	525,8	5,33E+01	-4,11E+01
33	533,0	2,49E+00	-4,18E+00
34	546,7	7,04E+02	1,58E+02
35	564,3	2,05E+00	-5,14E+01
36	570,7	1,24E+02	2,68E+01
37	605,9	3,96E+02	1,11E+02
38	616,5	2,27E+02	-1,22E+02
39	630,7	3,54E+00	-1,08E+02
40	637,1	2,34E+00	3,66E+00
41	638,4	5,36E+00	1,05E+00
42	668,8	7,51E-01	-4,25E+00
43	686,9	3,95E+02	1,92E+01
44	691,4	4,76E+00	3,23E+01
45	693,2	7,79E+02	4,34E+01
46	701,4	2,21E+01	-1,70E+01
47	744,8	1,94E+01	1,07E+02
48	752,6	7,06E+01	7,09E+01
49	762,5	1,62E+00	-3,68E+01
50	766,3	6,95E+02	-4,57E+01

Table S1: Frequency/VCD output for [Co(III)(*S*,*S*)-stien(biur)$_2$]$^-$ // g03 UB3LYP/TZVP

No.	Frequency / cm^{-1}	Dipole strength / 10^{-40} esu^2 cm^2	Rotational strength / 10^{-44} esu^2 cm^2
51	770,0	1,54E+01	-1,50E+01
52	771,9	1,07E+01	-5,70E+01
53	775,1	2,77E+02	-9,90E+01
54	777,1	6,36E+00	7,13E+00
55	806,6	5,77E+01	8,10E+01
56	814,9	1,58E+02	2,68E+01
57	825,4	6,49E+01	5,77E+00
58	848,4	8,55E-02	1,97E+00
59	848,7	3,36E-02	-4,70E-01
60	887,5	5,24E+00	2,80E+01
61	918,0	1,42E+01	7,49E+00
62	928,0	2,46E+00	1,68E+01
63	943,7	1,26E+00	-6,59E-02
64	945,3	7,30E-03	2,71E-02
65	956,7	2,32E-01	-6,05E-01
66	958,3	2,10E+00	3,87E+00
67	999,8	5,00E-04	-7,92E-02
68	1006,5	2,23E+02	9,64E+01
69	1015,8	4,15E-01	-4,23E+00
70	1021,6	3,11E-01	8,44E-01
71	1022,0	6,44E-01	1,62E+00
72	1052,1	5,77E+01	-7,33E+00
73	1053,1	2,59E+01	-3,55E+00
74	1066,7	3,31E+02	-1,33E+02
75	1093,4	1,88E+01	4,01E+01
76	1105,6	3,74E+00	6,50E+00
77	1110,0	3,94E+01	8,42E+01
78	1127,1	5,03E+01	5,66E+01
79	1152,7	2,59E+00	5,71E+00
80	1183,1	2,78E-01	3,30E-01
81	1183,2	8,50E-03	1,17E-01
82	1201,5	5,46E+00	2,47E+01
83	1204,1	1,54E+01	-3,06E+01
84	1207,2	1,63E+01	-4,30E+00
85	1209,4	3,10E+00	-1,27E+00
86	1249,5	1,67E+01	-5,54E+02
87	1271,1	1,08E+03	7,52E+02
88	1280,5	1,42E+00	7,35E+00
89	1301,3	7,40E-02	-4,18E+00
90	1311,2	1,56E+00	1,77E+01
91	1326,5	3,28E+01	2,10E+01
92	1347,2	3,39E+02	2,58E+02
93	1353,3	3,41E+01	-6,63E+01
94	1354,0	8,80E-01	2,27E+00
95	1382,4	1,21E+01	1,84E+01
96	1388,0	6,38E+00	-1,47E+01
97	1399,4	1,95E+01	4,81E+01
98	1413,7	5,70E+01	8,43E+01
99	1413,9	2,34E+01	-8,93E+00
100	1448,5	3,24E+03	5,11E+02

Table S1: Frequency/VCD output for [Co(III)(*S*,*S*)-stien(biur)$_2$]$^-$ // g03 UB3LYP/TZVP

No.	Frequency / cm^{-1}	Dipole strength / 10^{-40} esu^2 cm^2	Rotational strength / 10^{-44} esu^2 cm^2
101	1474,1	4,98E+01	2,03E+01
102	1486,5	5,86E+00	-1,87E+01
103	1487,3	3,94E+01	-2,29E+01
104	1529,1	1,44E+01	-1,81E+00
105	1529,7	6,30E+01	-1,10E+01
106	1624,0	8,74E+00	-1,98E+01
107	1624,2	1,39E+00	5,43E+00
108	1642,4	4,84E+01	-1,18E+01
109	1642,8	7,98E+00	-4,37E+00
110	1675,7	3,31E+03	9,52E+02
111	1690,6	5,30E+02	1,63E+01
112	1707,2	4,22E+02	-2,62E+02
113	1718,0	2,55E+03	3,81E+01
114	3079,5	1,26E+01	2,59E+01
115	3080,0	2,07E+01	-4,14E+01
116	3151,9	7,17E+00	1,04E-01
117	3152,3	6,28E-01	1,28E+00
118	3160,9	9,41E+00	1,57E-01
119	3161,4	4,20E+00	5,34E+00
120	3170,5	4,15E+01	5,94E+01
121	3170,8	4,80E+01	-5,66E+01
122	3182,2	6,79E+01	-3,85E+01
123	3182,4	4,29E+01	2,26E+01
124	3200,2	6,41E+00	9,71E+00
125	3200,3	7,41E+00	-1,56E+01
126	3555,1	1,19E+01	4,64E-01
127	3559,9	1,81E-02	-2,72E-02
128	3634,6	1,35E+02	1,40E+01
129	3634,7	6,01E-01	1,07E+00

Table S2: Excited states for [Co(III)(*S*,*S*)-stien(biur)$_2$]$^-$ // g03 TD-UB3LYP/TZVP

Excited State	Wavelength / nm	Oscillator strength	Rotational strength / 10^{-40} erg-esu-cm/Gauss
1	1607	0.0001	18.46
2	1429	0.0000	-7.79
3	783	0.0000	1.48
4	704	0.0005	6.96
5	517	0.0505	-34.08
6	485	0.0310	6.09
7	451	0.0065	11.07
8	440	0.0003	1.37
9	432	0.0059	1.34
10	425	0.0026	0.58
11	418	0.0005	-2.51
12	413	0.0062	-11.99
13	408	0.0000	0.84
14	398	0.0007	-2.73
15	391	0.0072	1.77
16	391	0.0003	-0.18
17	381	0.0017	0.89
18	375	0.0006	-9.21
19	364	0.0368	12.72
20	361	0.0005	3.76
21	359	0.0119	-0.55
22	354	0.0001	0.20
23	352	0.0106	3.03
24	349	0.0012	-2.48
25	348	0.0007	-4.86
26	341	0.0005	-0.44
27	337	0.0009	0.19
28	334	0.0000	-0.59
29	331	0.0001	0.03
30	330	0.0001	-0.41
31	329	0.0000	0.03
32	322	0.0013	2.18
33	319	0.0002	1.37
34	318	0.0001	-0.20
35	314	0.0001	1.25
36	314	0.0037	-5.19
37	307	0.0006	-3.67
38	303	0.0004	2.65
39	303	0.0000	0.00
40	297	0.0814	-9.08
41	296	0.0000	0.00
42	294	0.0000	0.20
43	293	0.0004	-0.82
44	286	0.0067	1.12
45	281	0.0011	0.59
46	278	0.0062	2.25
47	274	0.0376	-3.81
48	270	0.0000	0.00
49	270	0.0001	0.40
50	269	0.0008	-0.01

Table S2: Excited states for [Co(III)(*S*,*S*)-stien(biur)$_2$]$^-$ // g03 TD-UB3LYP/TZVP

Excited State	Wavelength / nm	Oscillator strength	Rotational strength / 10^{-40} erg-esu-cm/Gauss
51	269	0.0005	0.13
52	267	0.0007	0.19
53	267	0.0011	2.27
54	261	0.0002	1.02
55	260	0.0002	0.66
56	258	0.0004	1.48
57	257	0.0004	-0.19
58	257	0.0004	0.52
59	256	0.0002	0.68
60	254	0.0008	0.48
61	254	0.0002	0.09
62	252	0.0002	-1.98
63	250	0.0031	1.96
64	249	0.0031	-1.49
65	249	0.0140	17.75
66	249	0.0001	-0.35
67	248	0.0038	-0.08
68	246	0.0005	3.01
69	245	0.0011	-1.73
70	244	0.0007	-0.71
71	242	0.0001	0.91
72	240	0.0001	1.65
73	239	0.0003	3.90
74	238	0.0013	3.83
75	238	0.0005	1.80
76	236	0.0290	-1.48
77	235	0.0000	-1.61
78	233	0.0013	2.36
79	233	0.0014	15.50
80	233	0.0040	-3.74
81	232	0.0022	-0.84
82	232	0.0009	-1.93
83	230	0.0075	-0.71
84	227	0.0048	-1.25
85	226	0.0191	-13.14
86	226	0.0023	1.07
87	226	0.0019	1.12
88	225	0.0035	-0.66
89	224	0.0000	-0.05
90	224	0.0020	-4.42
91	223	0.0313	-12.19
92	222	0.0004	0.34
93	222	0.0006	-1.76
94	222	0.0011	-6.72
95	221	0.0032	0.61
96	221	0.0033	-9.05
97	220	0.0009	0.57
98	220	0.0006	-1.62
99	219	0.0131	24.28
100	219	0.0000	0.00

Difference density plots

Difference density plots are surface maps of the difference between the excited state density and the ground state density. The necessary cube files are generated using Gaussian 03 with the keywords cube and density with reference to the checkpoint file of a completed TD DFT calculation, as shown in the example input below:

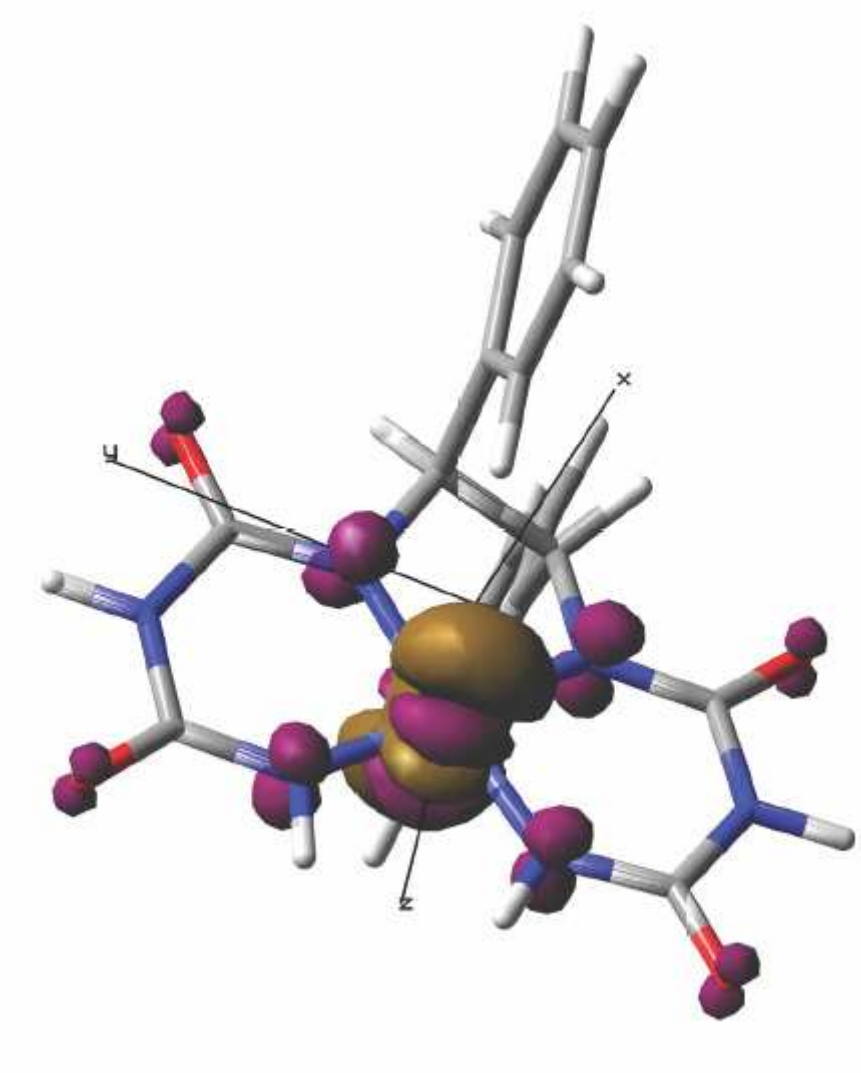
--Start example input--

```
%chk=checkpointfile.chk
# Geom=AllCheck Cube(Density) Guess(Read,Only)
  Density(Checkpoint) Pop=NBO

Density_00.cube

--link1--
%chk=checkpointfile.chk
# Geom=AllCheck Cube(Density) Guess(Read,Only)
  Density(Checkpoint,CIS=1) Pop=NBO

Density_01.cube

--link1--
%chk=checkpointfile.chk
# Geom=AllCheck Cube(Density) Guess(Read,Only)
  Density(Checkpoint,CIS=2) Pop=NBO

Density_02.cube
```

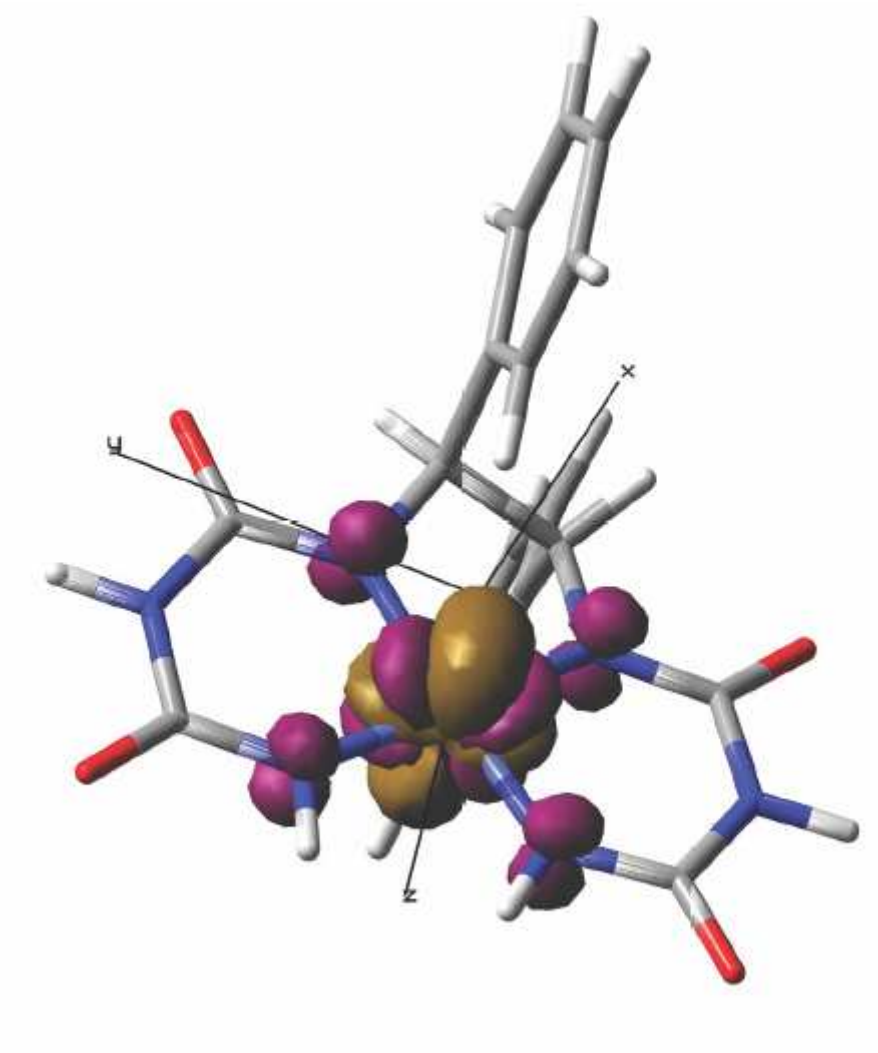
--End example input--

This input file will generate three cube files as output. Subsequently the difference density cube files are obtained using the CubMan utility, requesting to subtract the ground state density (density_00.cube) from each of the excited state densities. Finally the surface plots are generated using GaussView. The plots in this paper were generated at an isovalue of 0.004. The brown color represents negative density (e.g. What is lost from ground state) and the purple color is positive (e.g. excited state) density.

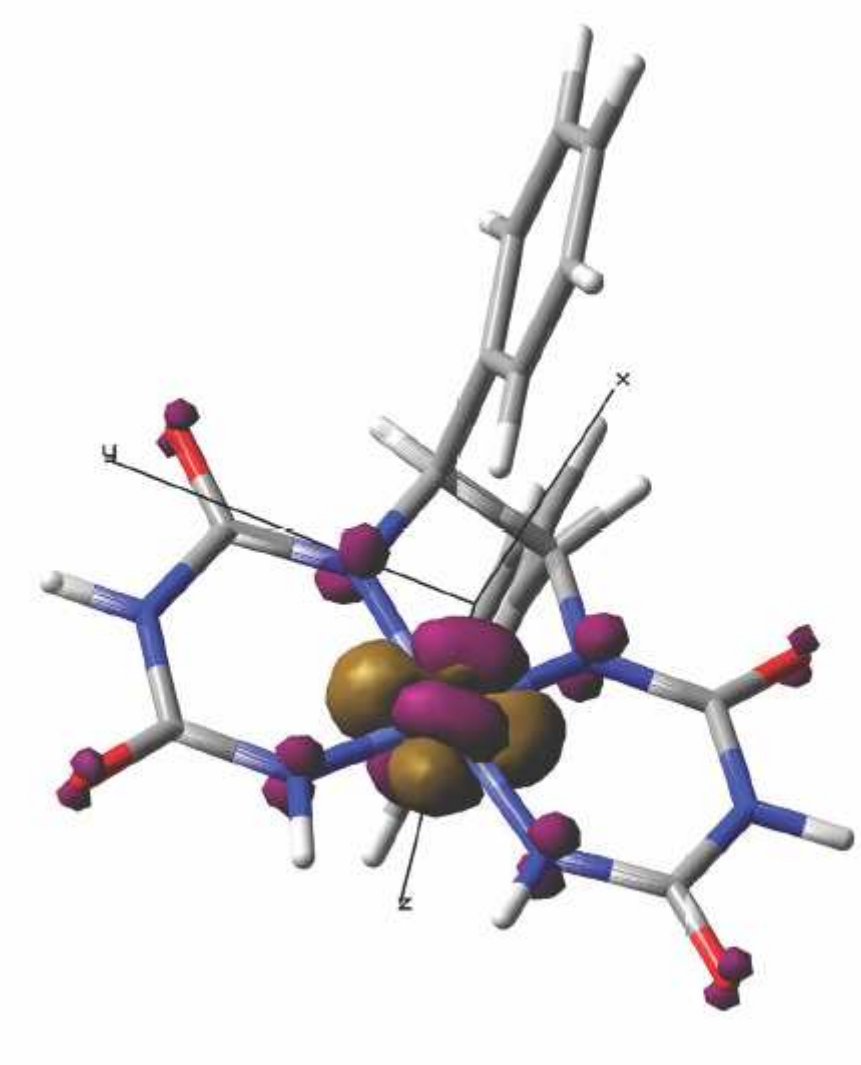
Excited state 1



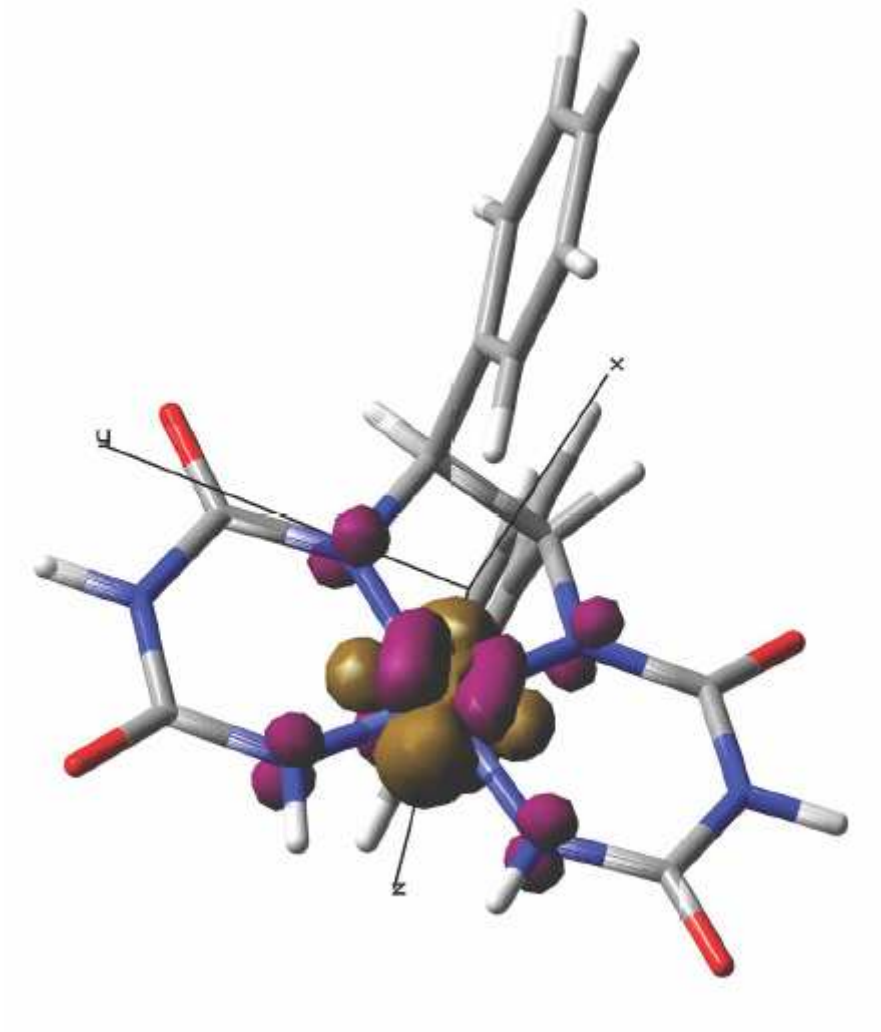
Excited state 2



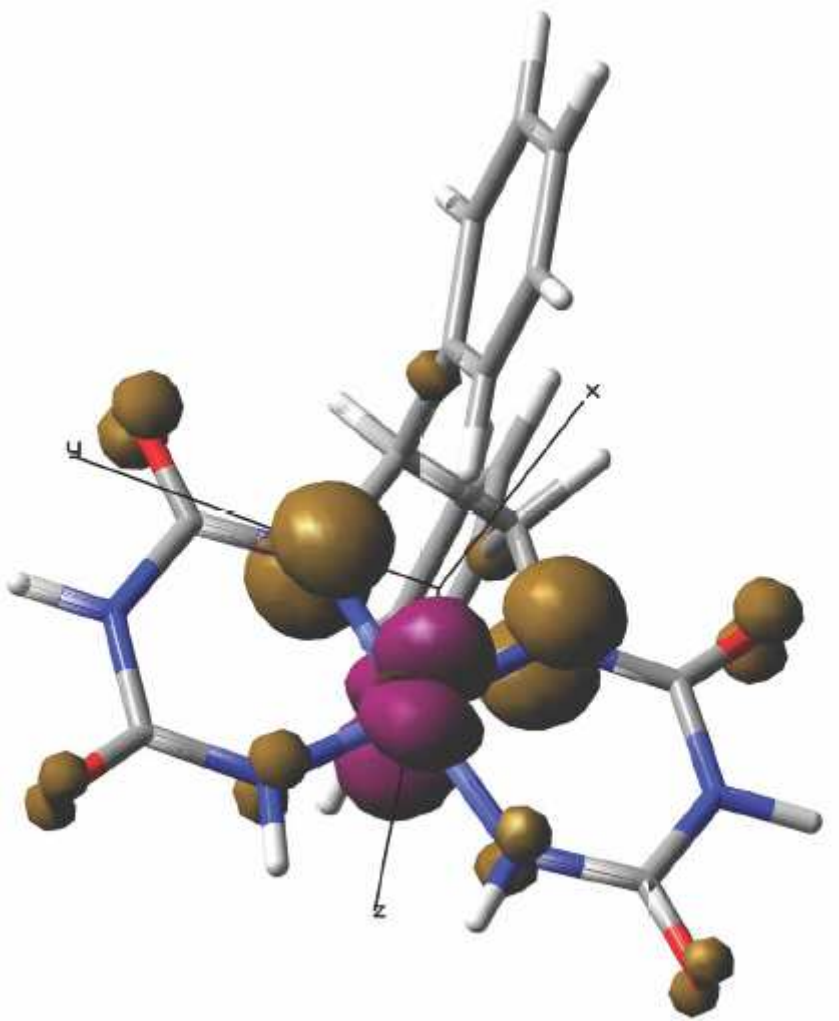
Excited state 3



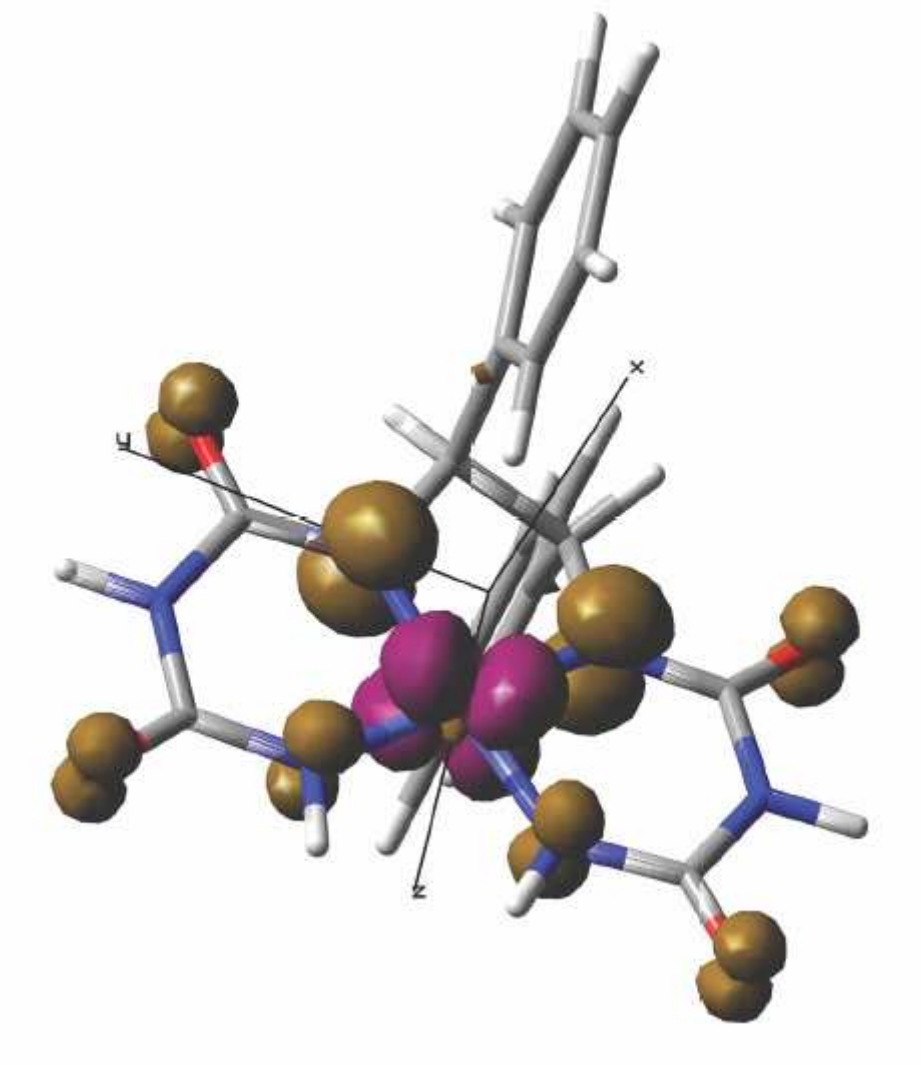
Excited state 4



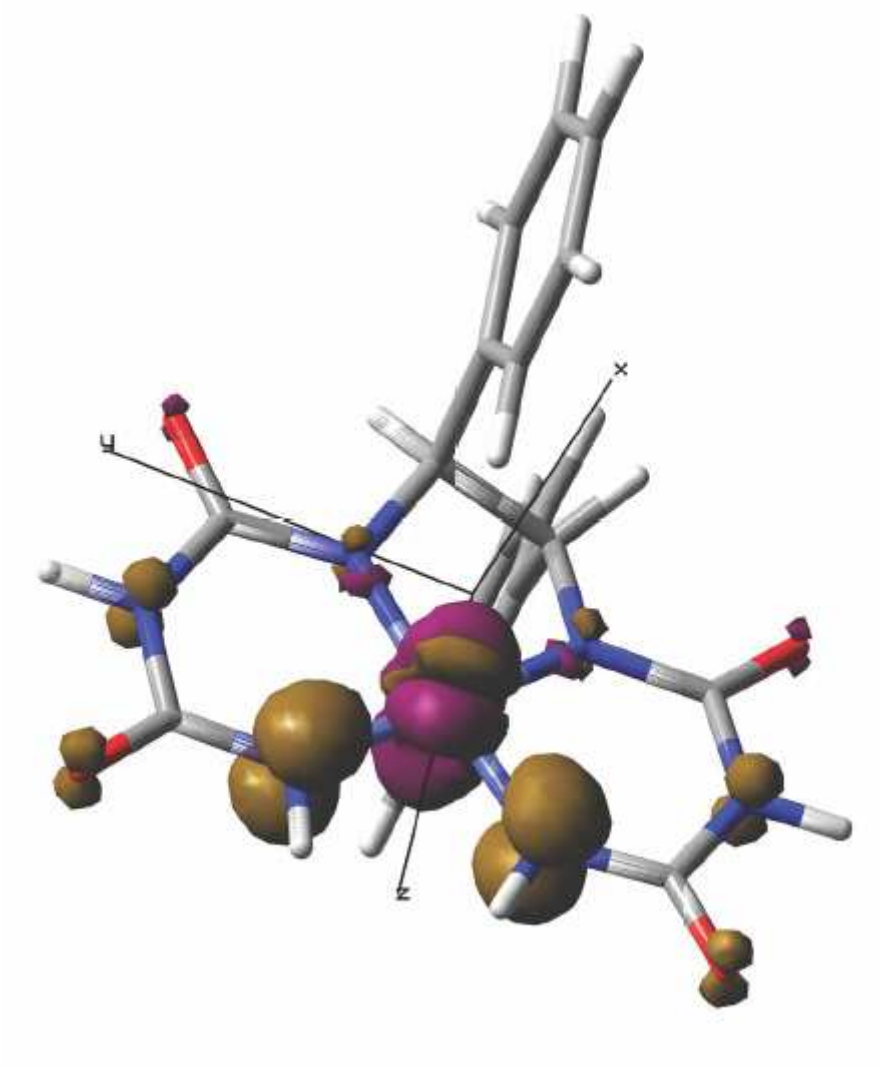
Excited state 5



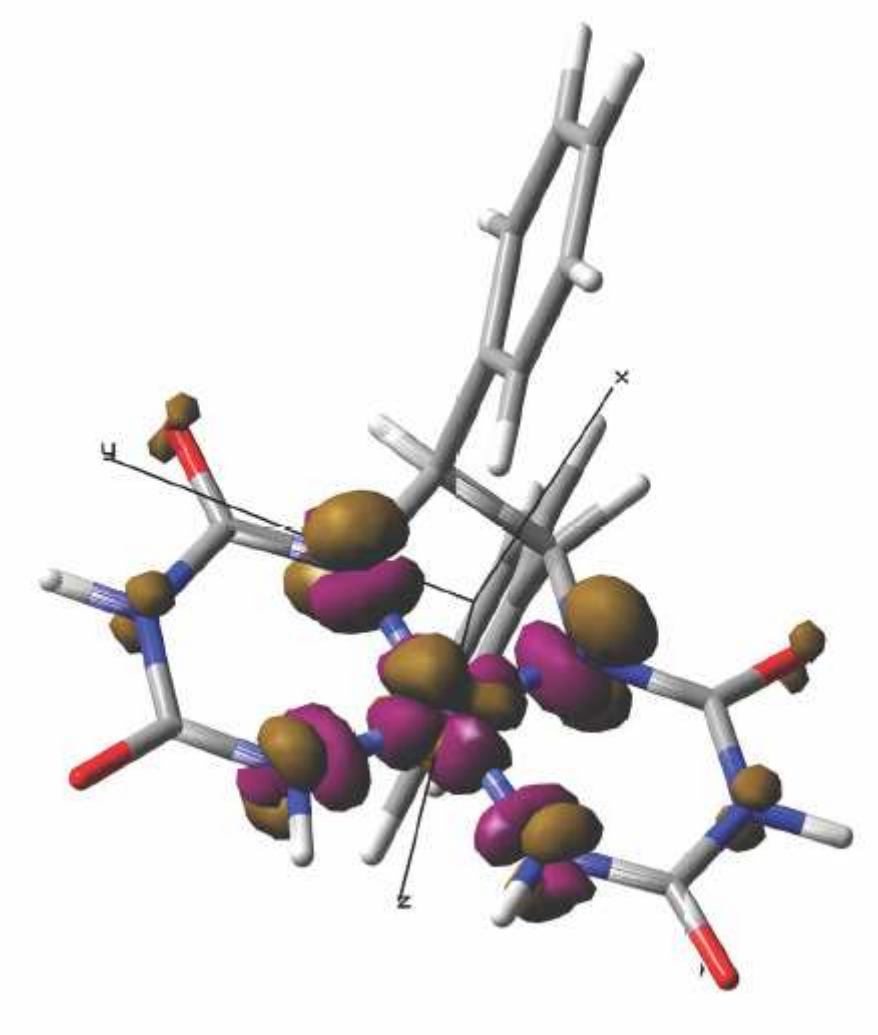
Excited state 6



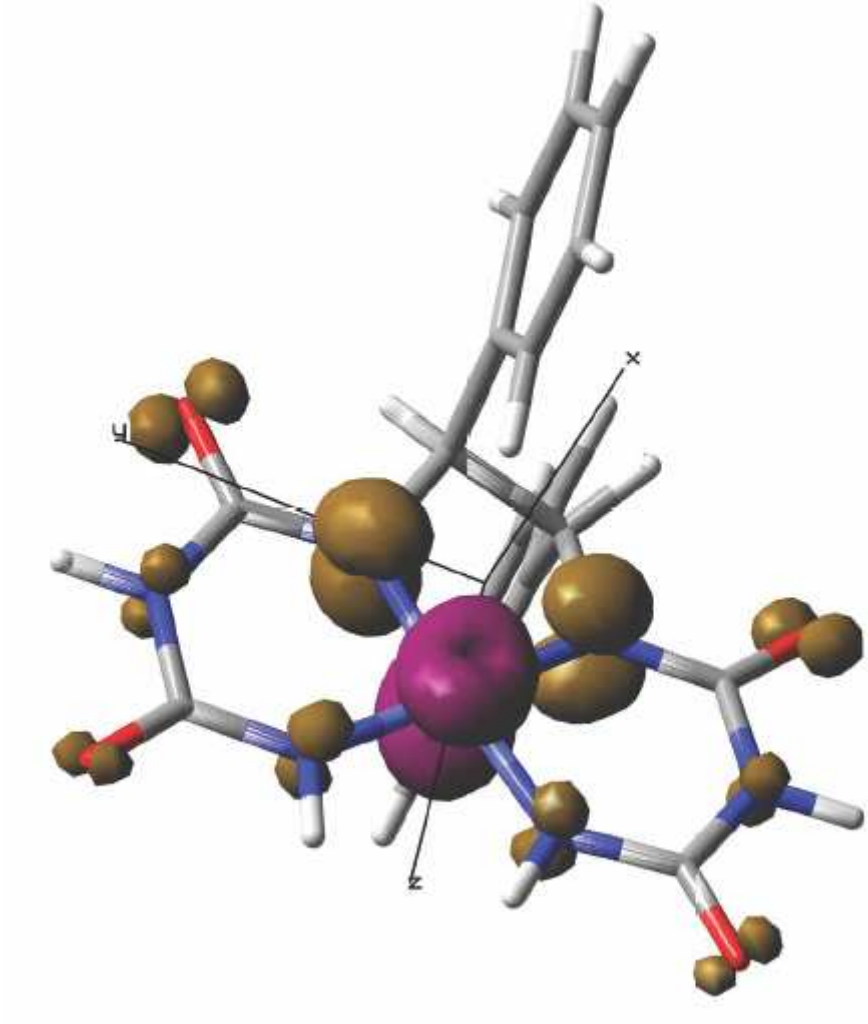
Excited state 7



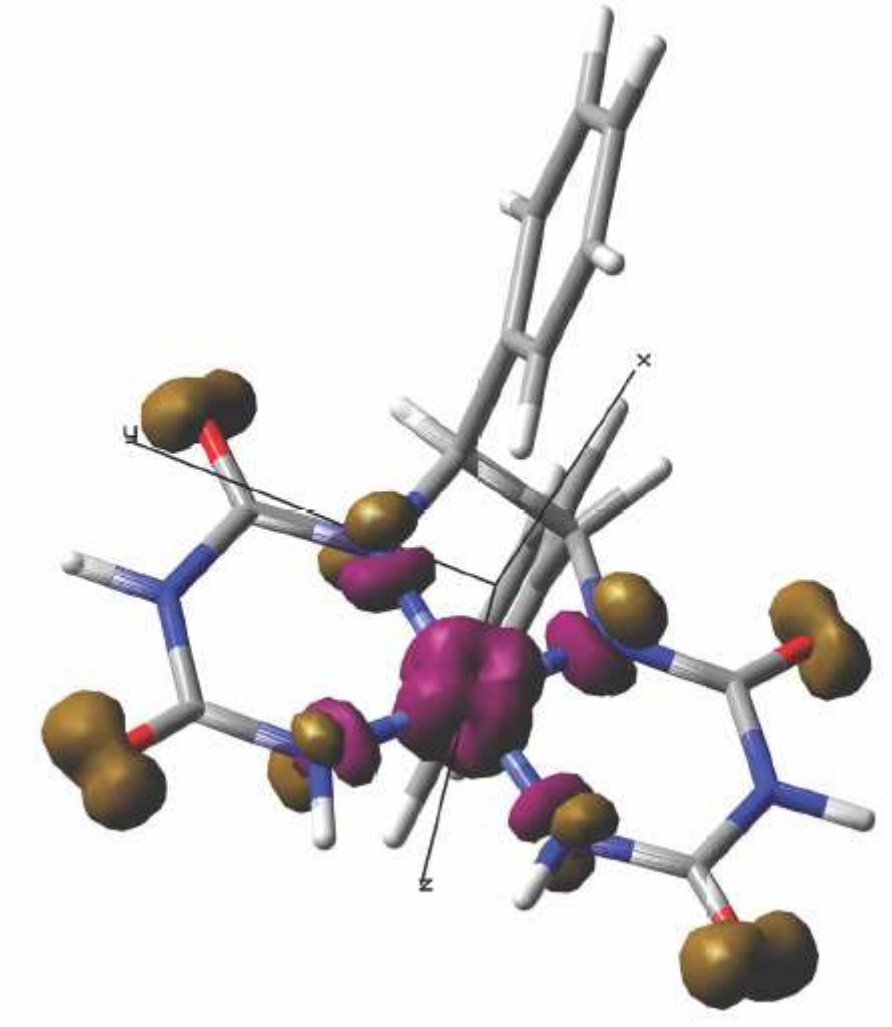
Excited state 8



Excited state 9

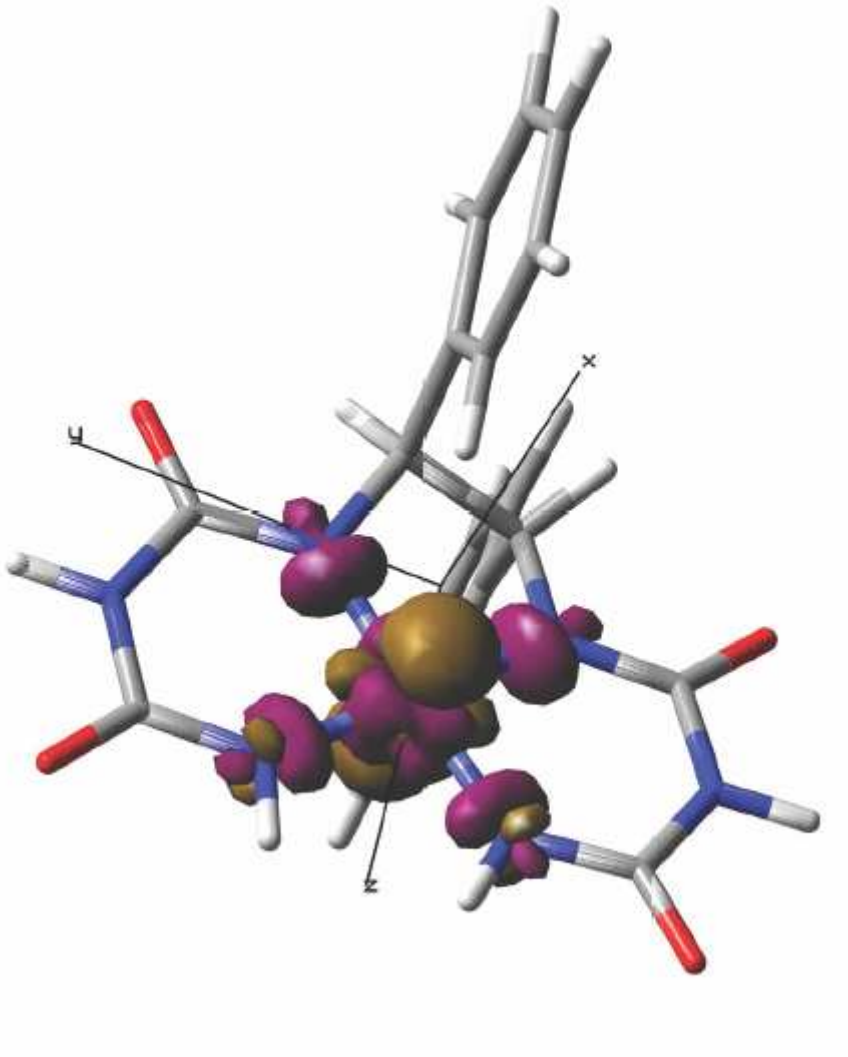


Excited state 10



Excited state

11



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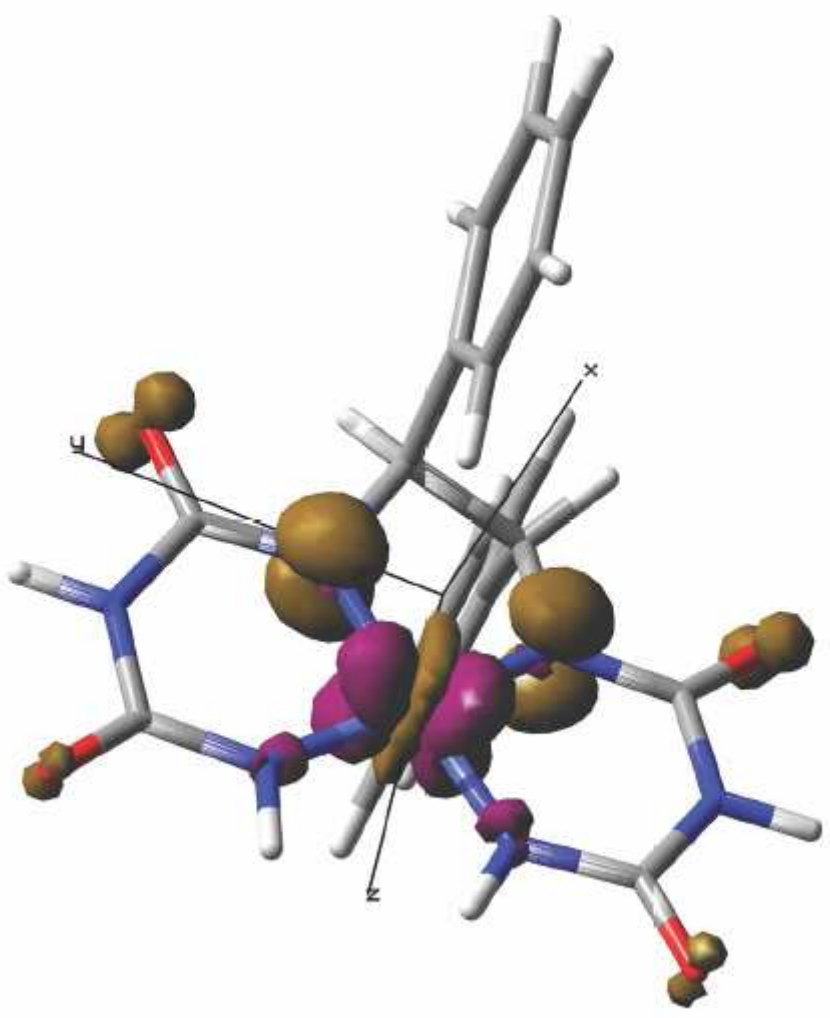
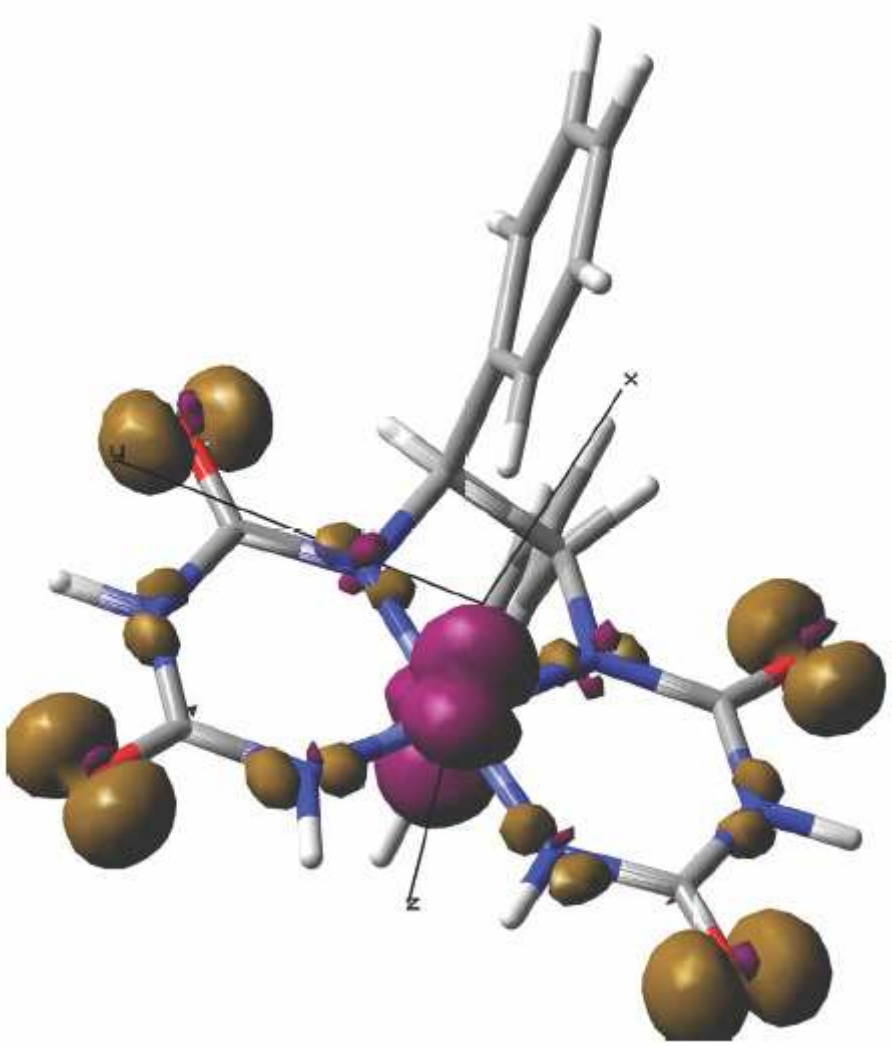
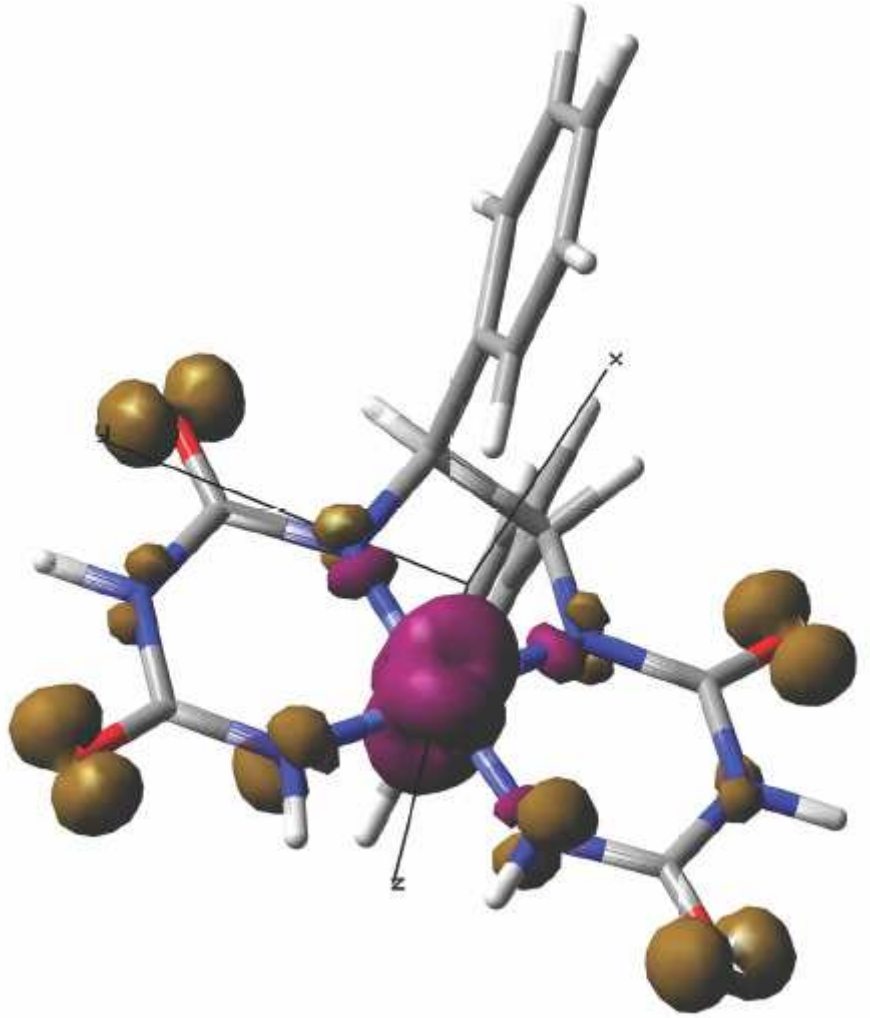


Excited state 13

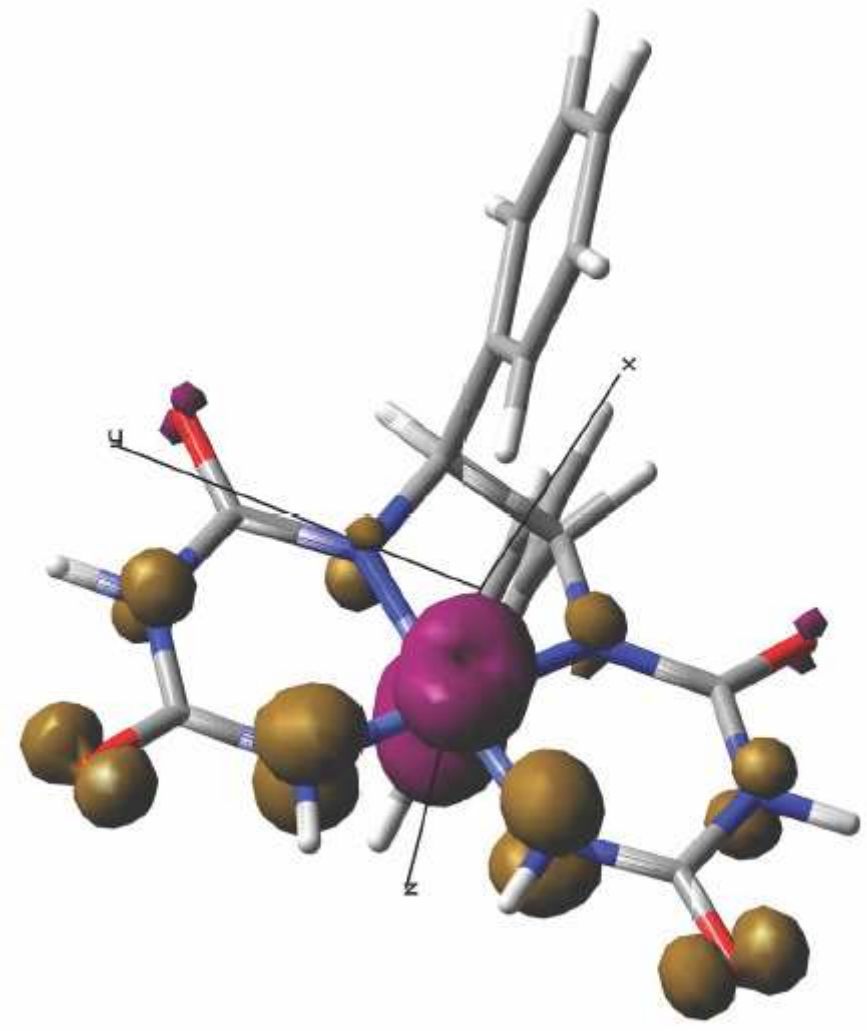


Excited state

14



Excited state 15



Free ligand (S,S-stien(H2biur)2)

The free ligand, having more degrees of freedom than the coordination compound required additional calculational consideration of the possible distribution of conformers. The Conformational Search routine implemented in MacroModel 8.6 was used with the MMFFs force field in gas-phase, employing Torsional Sampling. The five lowest energy conformers were optimized by B3LYP/TZVP.
1.log: SCF Done: E(RB+HF-LYP) = -1327.95908289
2.log: SCF Done: E(RB+HF-LYP) = -1327.95908306
3.log: SCF Done: E(RB+HF-LYP) = -1327.95125431
4.log: SCF Done: E(RB+HF-LYP) = -1327.95549726
5.log: SCF Done: E(RB+HF-LYP) = -1327.95527756

Structures 1 and 2 were found to be identical, yielding the same frequency data. I.e. structure 2 is disregarded. The relative energies based on the SCF energy of the DFT optimized structures reveal that structure 1 is considerably more stable than structures 4, 5 and 3, which are destabilized by ca. 9.4, 10 and 21 kJ mol-1, respectively. The calculated frequency data furthermore shows that structures 4 and 5 each have one significant imaginary frequency, indicating that they are transitions states rather than geometrical minima. A Bolzmann weighing of the contributions of the energies of the four structures (1, 3, 4 and 5) at 298 K reveal that structure 1 has a contribution of 96%, while structures 4 and 5 each contribute ca. 2%. For this reason only the contribution of structure 1 is considered in the discussion of the calculated spectroscopic properties.

The Cartesian coordinates of this conformer is given separately in the xyz file: S,S-stien(H2biur)2.xyz

The frequency and VCD data are given in Table S3 below:

Table S3: Frequency/VCD output for (*S*,*S*)-stien(H_2biur)$_2$ // g03 B3LYP/TZVP

No.	Frequency / cm^{-1}	Dipole strength / 10^{-40} esu^2 cm^2	Rotational strength / 10^{-44} esu^2 cm^2
1	10,8	3,51E+02	1,52E-01
2	18,1	1,60E+02	1,10E+00
3	29,3	1,58E+02	-1,29E+01
4	34,9	6,83E+01	-8,59E+00
5	37,5	2,32E+01	6,07E+00
6	41,4	6,90E-01	-1,19E-01
7	53,6	2,53E+01	4,48E+00
8	57,3	6,05E+01	4,37E+00
9	61,2	4,21E+02	8,94E+00
10	74,8	1,46E+01	1,29E+00
11	81,9	1,44E+02	-1,90E+01
12	107,3	2,34E+01	-2,90E+00
13	118,5	2,19E+02	-2,80E+01
14	138,1	2,10E+01	4,69E-01
15	155,0	2,51E+02	2,10E+01
16	175,3	2,65E+02	4,30E+01
17	202,6	7,81E+00	5,46E+00
18	224,1	4,30E+01	-1,59E+01
19	228,9	1,03E+02	1,73E+01
20	243,3	3,72E+01	-8,42E+00
21	273,5	2,30E+03	1,56E+01
22	294,4	1,77E+02	1,33E+01
23	308,8	1,00E+02	-7,11E+00
24	318,6	2,77E+02	-9,08E+01
25	338,4	1,93E+03	-2,17E+00
26	345,6	2,95E+02	-3,35E+01
27	411,1	9,20E+00	2,14E+00
28	413,2	9,82E+00	5,49E-02
29	415,4	7,03E+01	-6,26E+00
30	436,5	3,28E+01	9,69E+00
31	439,6	1,41E+01	1,37E+01
32	452,2	1,43E+03	8,53E+01
33	476,3	1,08E+02	-1,08E+01
34	512,8	2,93E+01	-1,71E+01
35	520,3	1,06E+02	1,77E+01
36	528,7	1,11E+02	9,44E+00
37	557,0	5,89E+02	-1,33E+02
38	564,4	1,08E+02	-6,17E+01
39	603,6	1,19E+02	-1,37E+02
40	621,2	1,60E+02	1,21E+02
41	635,4	9,97E+02	5,98E+00
42	638,2	1,59E+02	3,70E+01
43	640,0	1,64E+02	-1,46E+01
44	652,6	2,18E+02	-6,87E+00
45	665,5	1,73E+02	1,08E+02
46	671,8	7,56E+00	1,15E+01
47	678,1	2,41E+02	-4,43E+01
48	701,7	3,64E+02	8,28E+01
49	704,7	2,66E+02	2,74E+01
50	745,4	1,33E+02	-1,45E+01

Table S3: Frequency/VCD output for (*S*,*S*)-stien(H_2biur)$_2$ // g03 B3LYP/TZVP

No.	Frequency / cm^{-1}	Dipole strength / 10^{-40} esu^2 cm^2	Rotational strength / 10^{-44} esu^2 cm^2
51	758,5	7,03E+01	6,30E-01
52	764,7	2,13E+02	1,82E+01
53	766,3	1,27E+02	1,76E+01
54	768,3	5,75E+00	1,46E+01
55	774,7	1,15E+01	-3,03E+01
56	780,0	1,27E+02	7,22E+00
57	801,1	3,12E+01	-6,47E+01
58	853,6	4,81E-01	5,32E+00
59	857,7	4,59E+00	-1,92E+00
60	859,4	2,08E+00	4,17E+00
61	880,2	1,94E+01	-1,65E+01
62	924,7	7,10E+00	3,44E+00
63	929,9	2,19E+01	-7,28E+00
64	950,3	6,08E+01	-3,10E+00
65	964,8	2,49E-01	3,43E-01
66	971,0	1,13E-01	5,00E-02
67	972,8	1,22E+01	1,71E+01
68	977,7	2,29E+00	-6,40E-03
69	988,6	1,92E+00	-1,51E-01
70	1022,5	2,13E+01	-3,03E+00
71	1022,8	5,31E+00	-2,32E+00
72	1032,4	7,21E+01	-6,58E+00
73	1051,6	6,20E+01	7,43E+00
74	1055,0	3,32E+01	-1,33E+00
75	1058,1	1,31E+02	-2,23E+00
76	1068,5	9,28E+01	-2,79E+01
77	1103,8	1,04E+01	-4,30E+00
78	1105,4	3,32E+01	3,27E+01
79	1115,9	1,33E+00	-5,93E+00
80	1132,0	3,56E+01	-2,12E+00
81	1135,2	2,69E+00	-5,24E+00
82	1141,7	2,30E+01	1,89E+01
83	1188,5	2,34E-01	1,23E-01
84	1190,1	8,52E-02	3,50E-02
85	1209,8	6,88E+00	3,19E+00
86	1212,3	1,69E+00	-7,98E-01
87	1213,8	2,18E+01	4,52E+01
88	1218,1	1,59E+01	3,22E+01
89	1246,4	7,57E+02	-1,46E+02
90	1262,5	5,64E+02	7,72E+02
91	1268,7	7,31E+02	-6,69E+02
92	1309,5	1,73E+02	-7,92E+00
93	1317,4	6,56E+02	-3,70E+00
94	1329,6	6,60E+01	3,68E+01
95	1352,6	1,19E+01	1,74E+01
96	1358,4	1,44E+01	2,22E+01
97	1378,0	9,85E+02	-1,48E+01
98	1385,4	3,69E+01	1,88E+01
99	1395,8	8,45E+00	4,62E+01
100	1401,3	1,68E+01	3,64E+01

Table S3: Frequency/VCD output for (*S*,*S*)-stien(H_2biur)$_2$ // g03 B3LYP/TZVP

No.	Frequency / cm^{-1}	Dipole strength / 10^{-40} esu^2 cm^2	Rotational strength / 10^{-44} esu^2 cm^2
101	1491,2	3,23E+01	-4,15E+01
102	1492,1	4,06E+01	-3,97E+01
103	1496,4	1,84E+02	6,90E+01
104	1502,1	1,34E+03	-2,55E+01
105	1533,2	2,08E+01	-1,37E+00
106	1534,9	3,35E+01	5,59E+00
107	1566,5	1,25E+03	-1,08E+03
108	1580,0	2,24E+03	1,30E+03
109	1599,7	3,33E+02	-4,82E+01
110	1627,4	1,40E+01	2,94E+00
111	1628,7	1,47E+01	7,74E+00
112	1636,1	2,32E+02	-2,23E+01
113	1646,0	2,94E+00	-1,72E-01
114	1647,9	1,83E+00	7,39E-01
115	1731,4	5,83E+02	3,88E+01
116	1742,6	6,23E+02	1,18E+02
117	1768,2	9,53E+02	-4,34E+01
118	1785,9	1,50E+03	-5,19E+01
119	3071,4	7,36E+00	-4,97E+00
120	3093,2	1,32E+01	1,17E+01
121	3164,3	4,07E+00	2,25E+00
122	3164,3	7,75E+00	-5,31E+00
123	3170,5	1,03E-01	-1,03E+00
124	3171,2	2,88E-01	-1,27E-01
125	3178,2	1,23E+01	2,90E+00
126	3179,1	9,74E+00	2,34E+00
127	3185,9	2,66E+01	-4,26E+00
128	3188,1	2,51E+01	2,57E+00
129	3195,5	1,81E+01	-1,23E+00
130	3197,6	1,61E+01	-1,07E+00
131	3472,3	2,40E+02	1,08E+01
132	3503,6	1,45E+02	2,32E+02
133	3510,1	2,08E+02	-1,50E+02
134	3592,1	7,33E+01	-6,22E+00
135	3608,9	4,64E+01	-3,93E+00
136	3614,5	6,67E+01	-1,18E+01
137	3708,5	1,44E+02	4,59E+00
138	3713,4	5,63E+01	-3,99E+00