Electron Localization in a Mixed-ValenceDiniobium Benzene Complex

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A. X-ray crystallography of 2, 3, 4, and 6

Table S1. Crystallographic parameters

Compound	**2.(DCE)**	**3**	**4.(2DCE)**	**6**
Formula	$C_{98}H_{110}B_1Cl_2F_{20}N_3Nb_1$	$C_{65}H_{66}B_1F_{20}N_3Nb_1O_2$	$C_{95}H_{110}B_1Cl_8F_{20}N_6Nb_2$	$C_{61}H_{59}B_1F_{20}N_3Nb_1$
Formula weight	2019.45	1404.93	2196.12	1331.84
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pn
a (Å)	14.224(3)	18.1669(5)	20.744(2)	15.2666(6)
b (Å)	21.737(3)	17.1279(5)	20.888(2)	16.9177(6)
c (Å)	31.247(2)	19.7092(5)	22.683(3)	25.5770(10)
α (°)	90	90	90	90
β (°)	90.83(4)	90.5590(10)	90.709(2)	97.658(2)
γ (°)	90	90	90	90
V (Å^3)	9660.2(2)	6132.4(3)	9827.6(19)	6547.0(4)
Z	4	4	4	4
ρ_{calcd} (g/cm^3)	1.389	1.522	1.484	1.351
F_{000}	4164	2876	4500	2716
μ (mm^{-1})	0.380	0.305	0.537	0.280
T_{min}/T_{max}	0.8508/0.9453	0.9140 /0.9415	0.8993/0.9892	0.9592 /0.9834
No. rflns measured	79928	57885	157286	66108
No. indep. rflns	17729	11263	17992	23491
R_{int}	0.0364	0.0347	0.0251	0.0483
No. obs. (I> 2.00σ(I))	17729	11263	17992	23491
No. variables	1228	842	1234	1599
R_1, wR_2	0.0562, 0.0929	0.0363, 0.0946	0.0257, 0.0621	0.0418, 0.0847
R_1 (all data)	0.0702	0.0458	0.0288	0.0559
GoF	1.056	1.022	1.058	1.016
Res. peak/hole (e$^-$/Å^3)	1.707/-1.093	0.774/-0.488	1.768/-0.665	0.436/-0.480

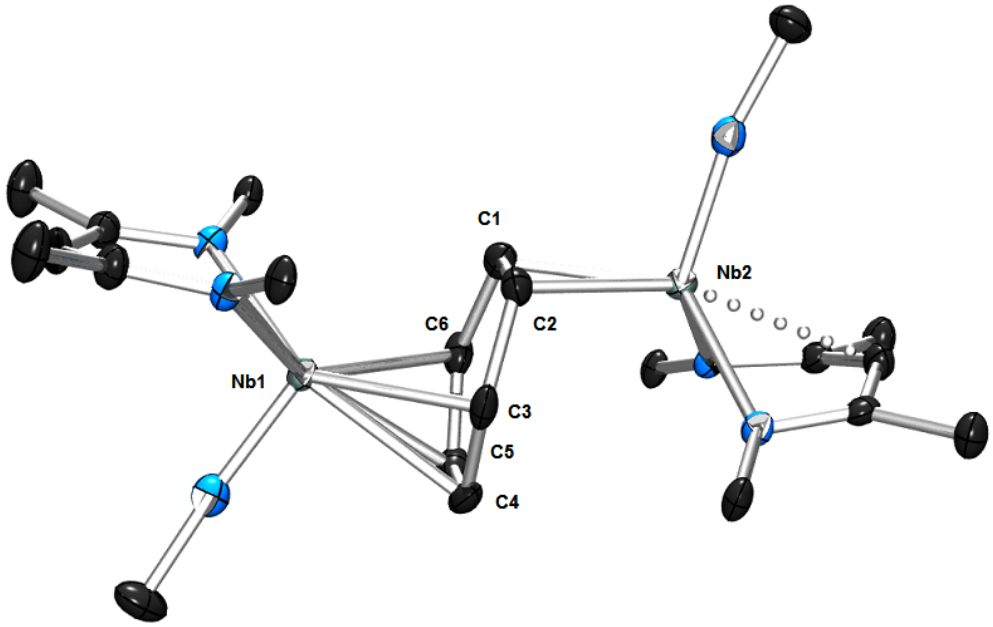

Figure S1. ORTEP diagram of **2**, hydrogens have been removed for clarity. Thermal ellipsoids are represented at 50 %.

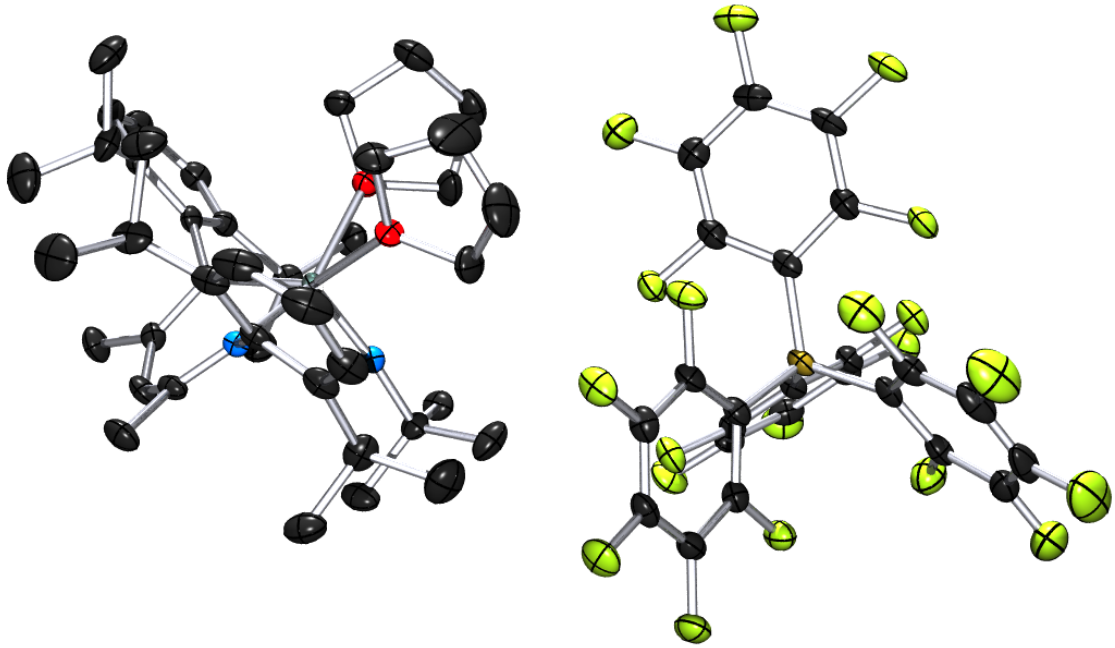

Figure S2. ORTEP diagram of **3**, hydrogens have been removed for clarity. Thermal ellipsoids are represented at 50 %.

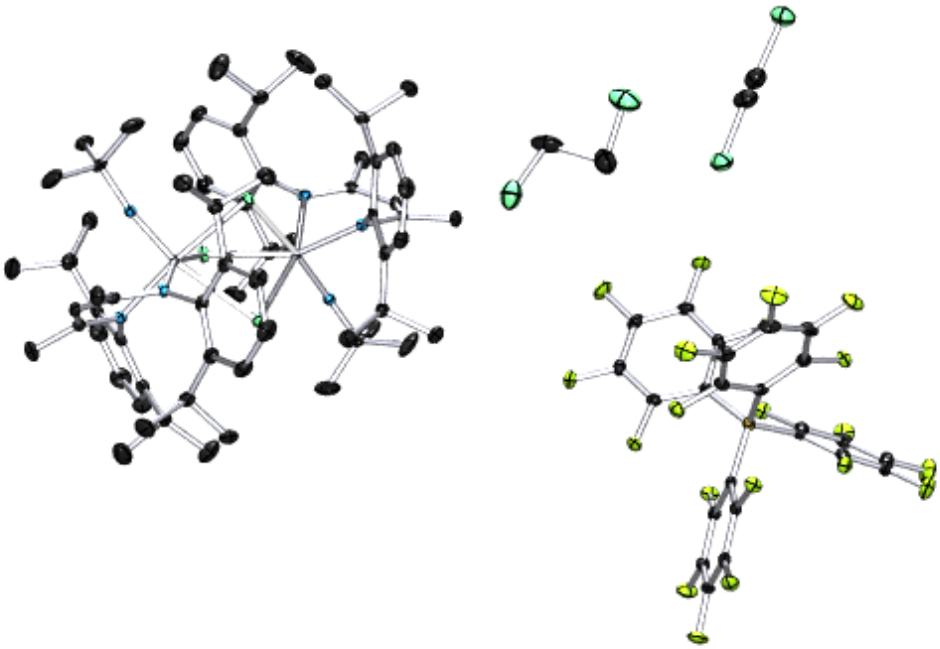

Figure S3. ORTEP diagram of **4**, hydrogens have been removed for clarity. Thermal ellipsoids are represented at 50 %.

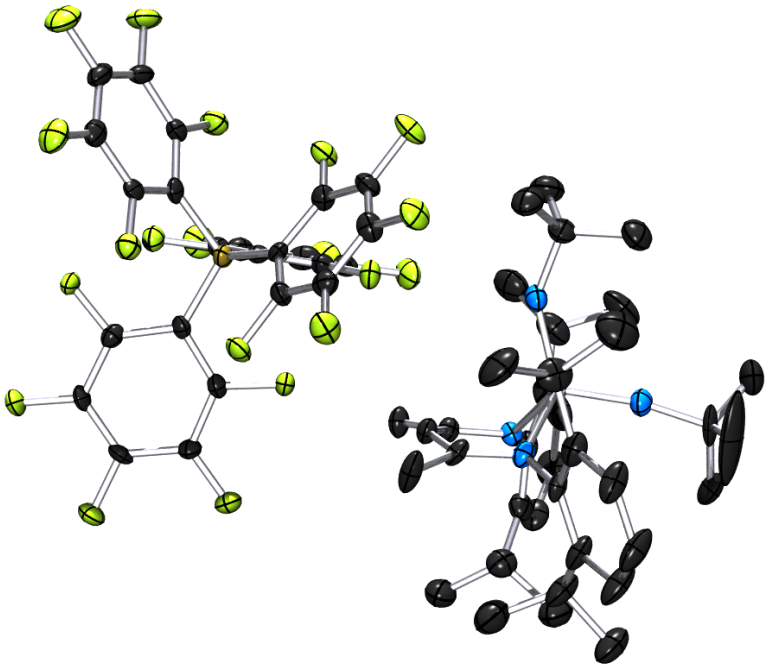

Figure S4. ORTEP diagram of **6**, hydrogens have been removed for clarity. Thermal ellipsoids are represented at 50 %.

B. Cyclic voltammetry

B.1 Complex 1

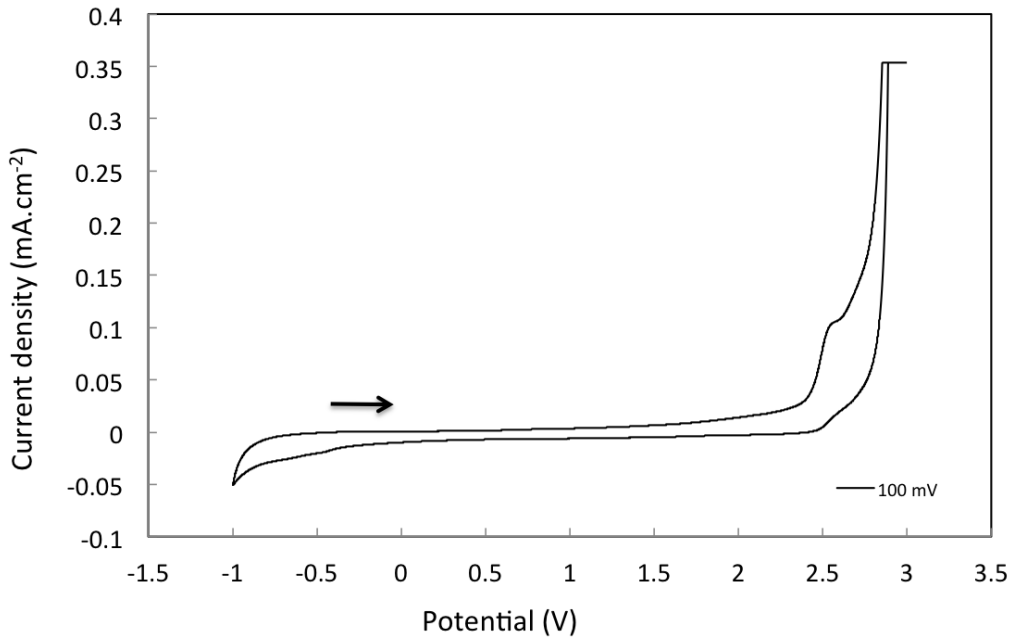

Figure S5 Background scan for the cyclic voltammetry of complex **1**

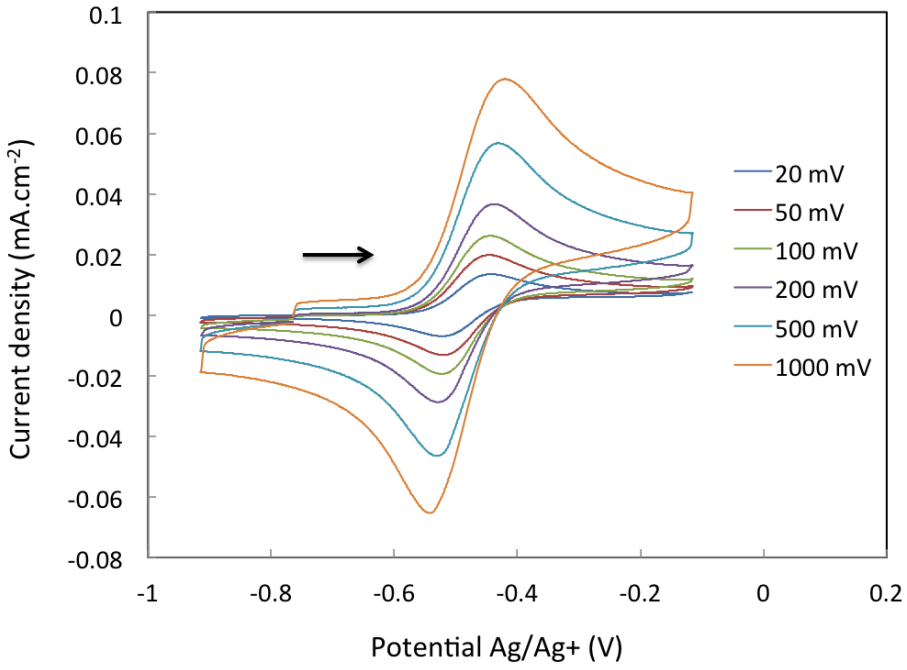

Figure S6 Cyclic voltammetry of complex **1** in α,α,α-trifluorotoluene at different scan-rate.

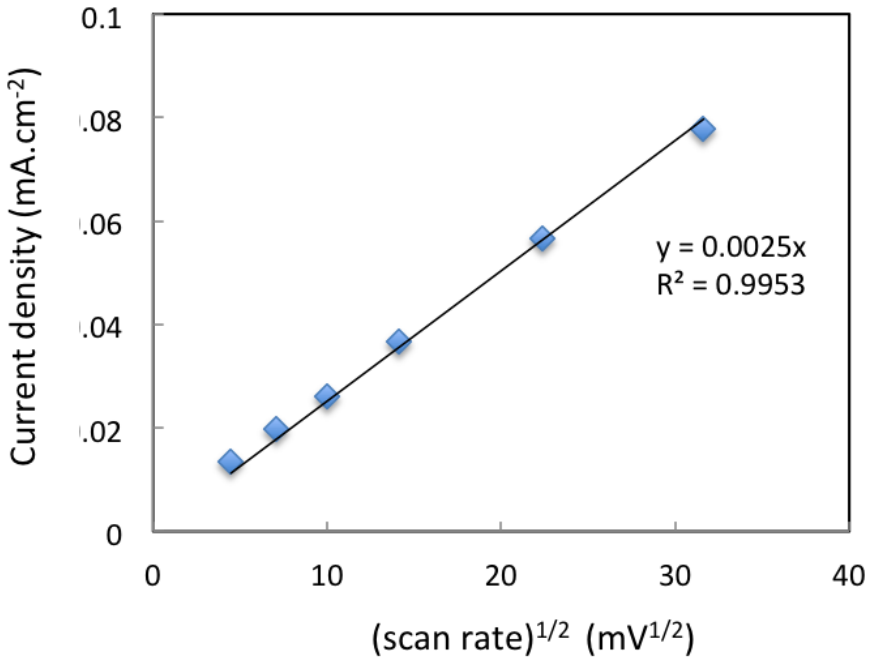

Figure S7 Plot of the peak current versus the square root of the scan rate of complex **1**

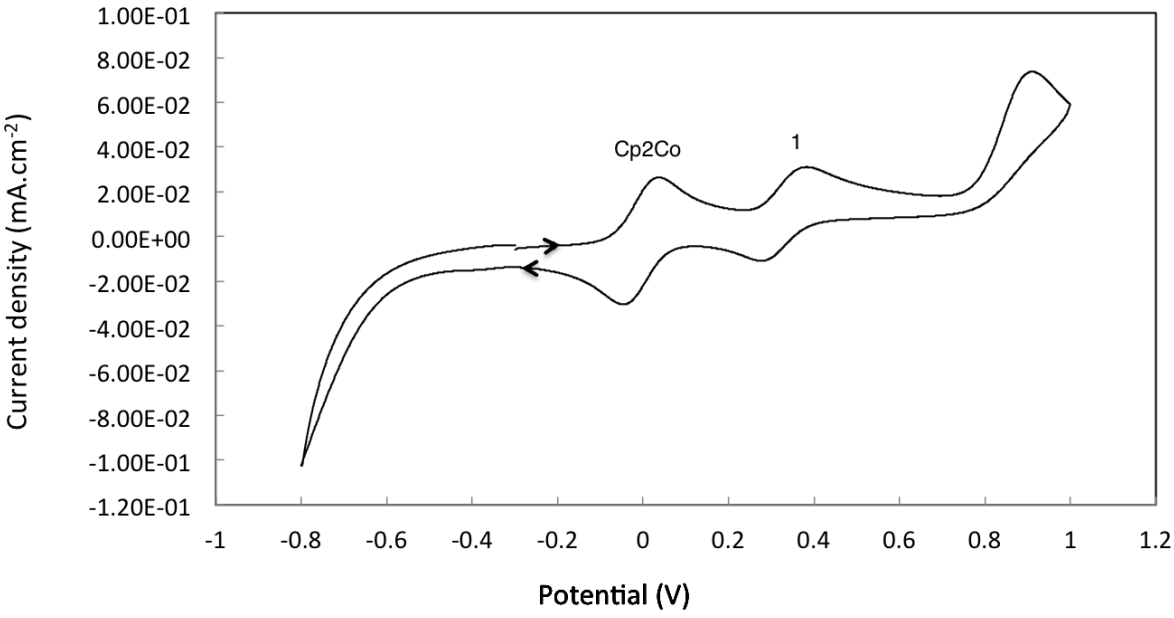

Figure S8 Cyclicvoltametry of complex **1** in α,α,α-trifluorotoluene with a scan rate of 100mV/s referenced to $[Cp_2Co]^{0/+}$ internal standard.

B.2 Complex 2

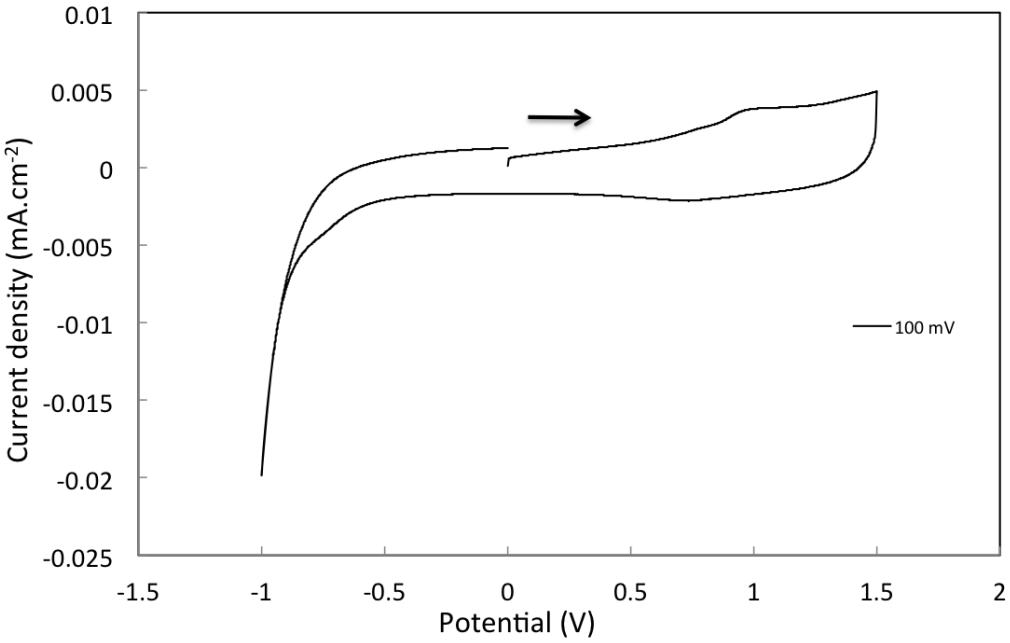

Figure S9 Background scan for the cyclic voltammetry of complex **2**

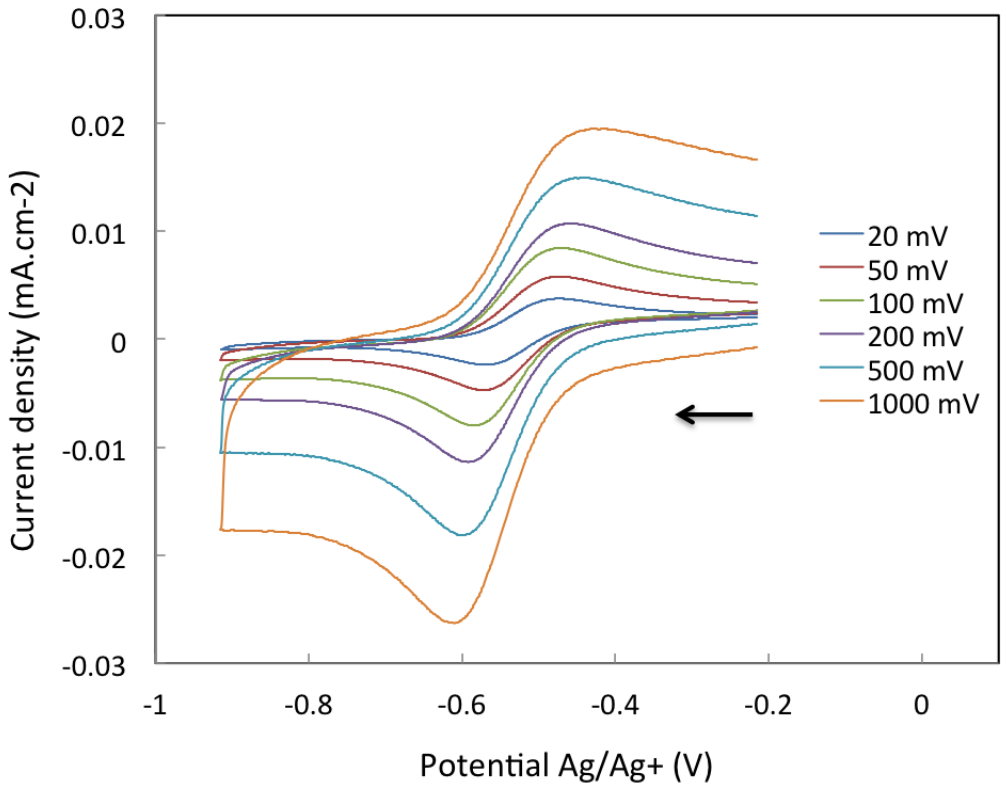

Figure S10 Cyclic voltammetry of complex **2** in α,α,α-trifluorotoluene at different scan-rate.

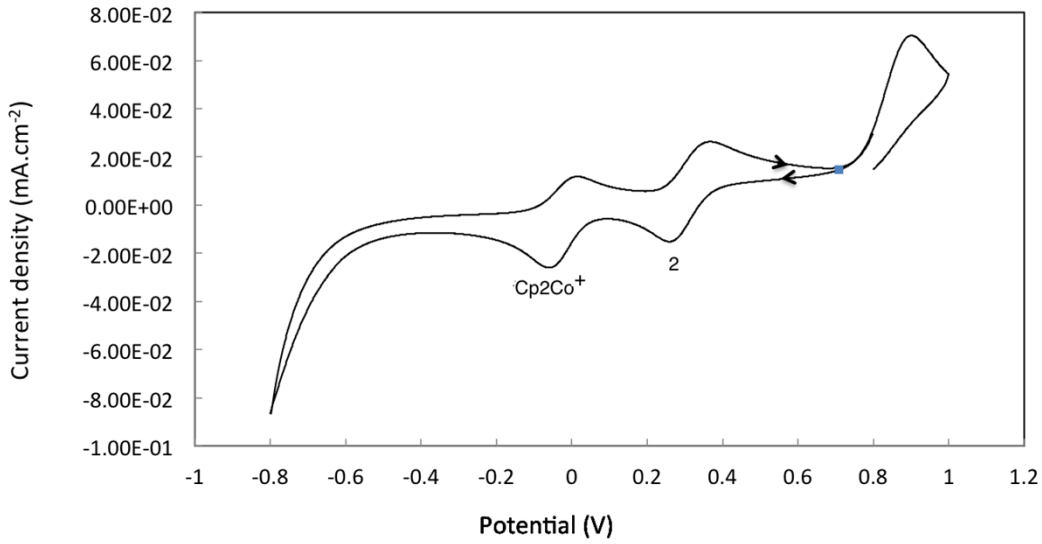

Figure S11 Cyclicvoltametry of complex **2** in α,α,α-trifluorotoluene with a scan rate of 100mV/s referenced to $[Cp_2Co]^{0/+}$ internal standard.

C. Spectroscopic analysis of 2

C.1 NMR spectroscopy

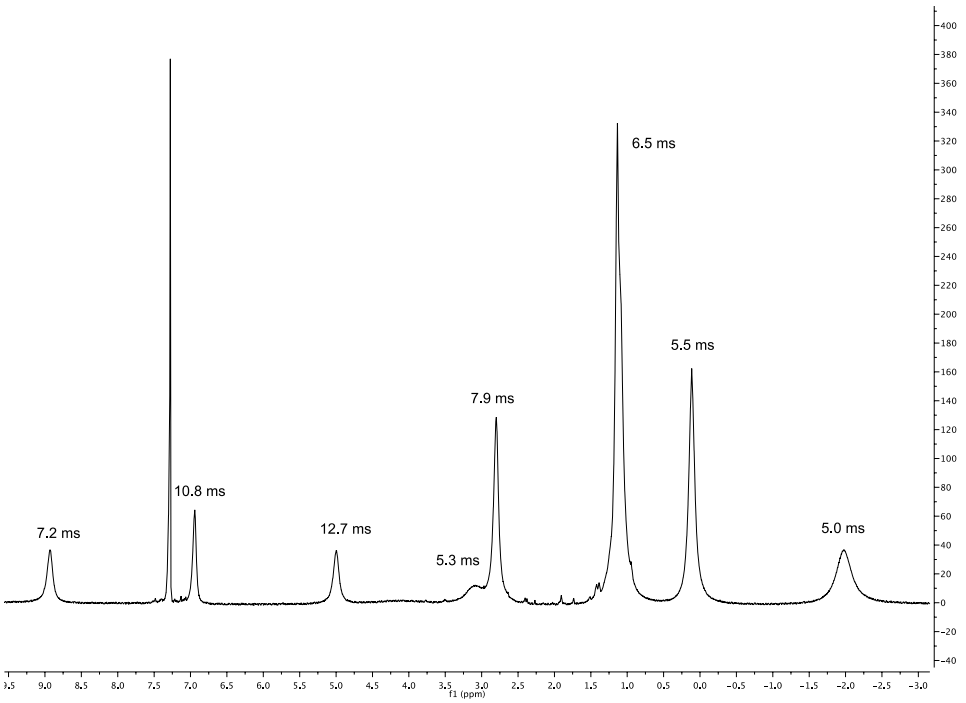

Figure S12. ^{1}H NMR spectrum of **2** and relaxation time of each resonanceat 350 K.

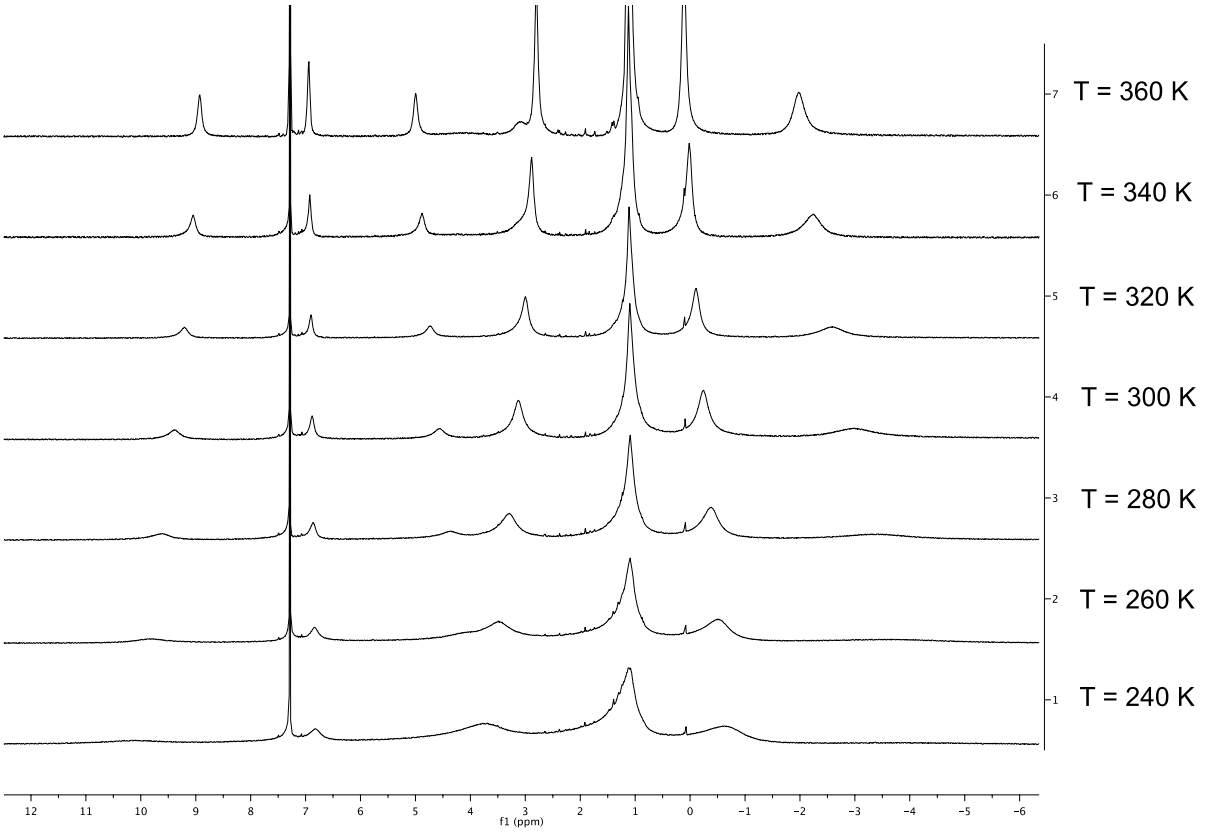

Figure S13. Variable temperature ^{1}H NMR spectroscopy of **2**

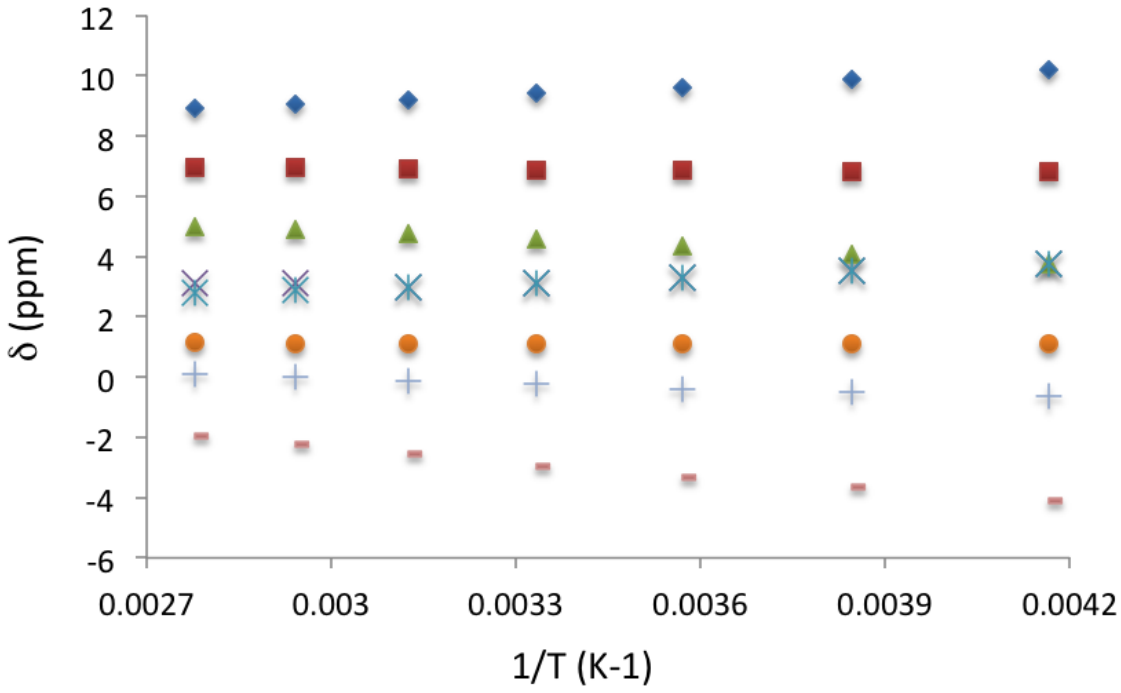

Figure S14. Temperature dependence of the chemical shifts of **2.**

C.2 Magnetism

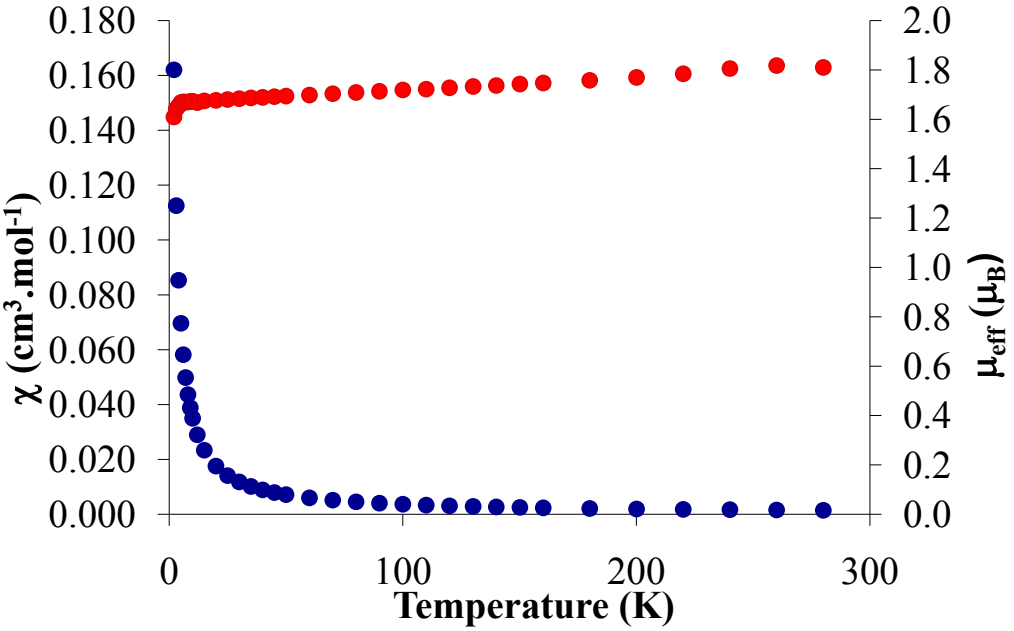

Figure S15. Temperature dependant magnetic data for **2.** Plot of χ vs. T (blue dots) and μ_{eff} vs. T (red dots).

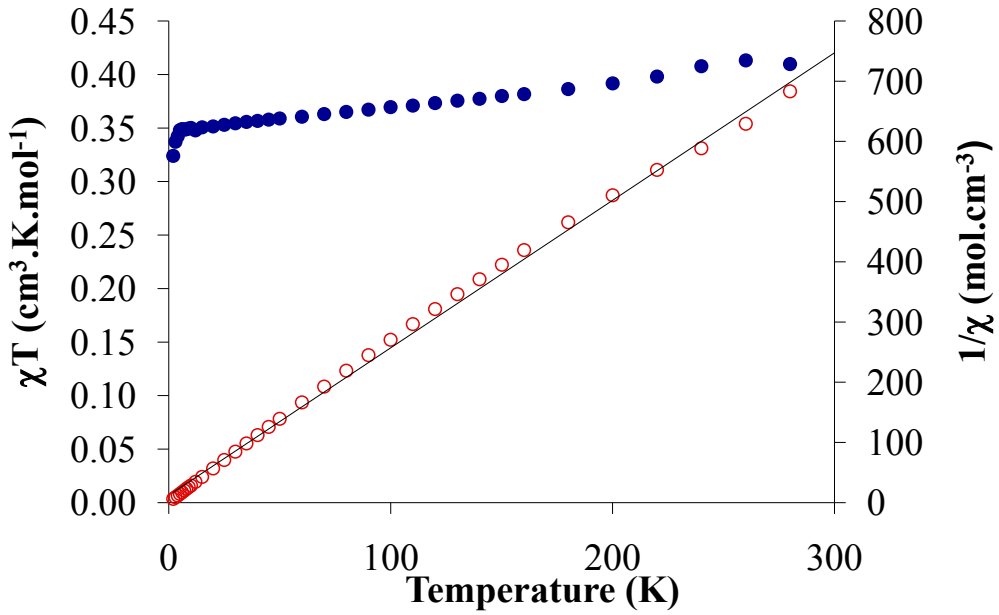

Figure S16. Temperature dependant magnetic data for **2.** Plot of χT vs. T (blue dots) and $1/\chi$ vs. T (red unfilled dots).

C.3. Electron Paramagnetic Resonance (EPR) Spectroscopy

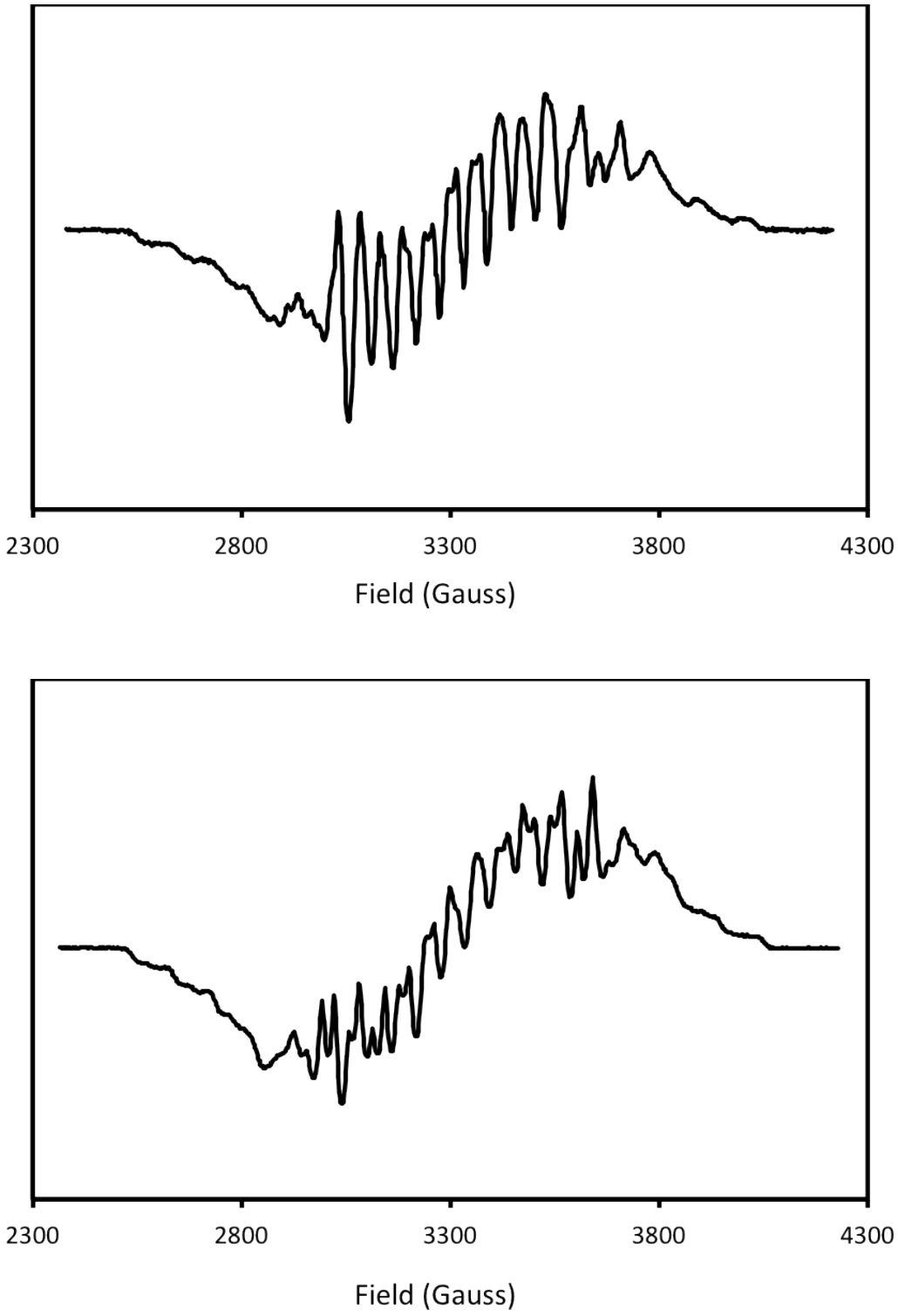

Figure S17. Experimental X-Band EPR of **2** recorded in solid state at 300K (top) and 4K (bottom).

D. DFT calculation

D.1. TD-DFT calculation

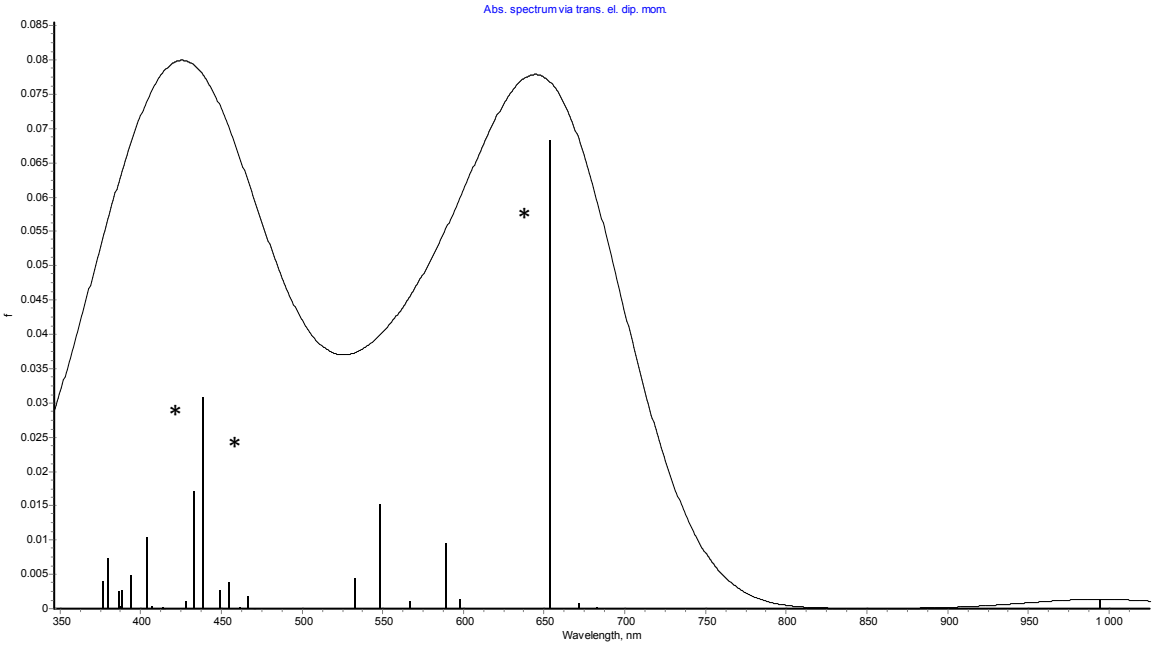

Figure S18. Calculated transition from TD-DFT for **2-I**. The line was obtained using a substantial Doppler broadening and * correspond to the three main transitions discussed in the text.

D.2. DFT optimized Cartesian atomic coordinates of 1 and 2.

Complex1

C	0.989961	0.356613	0.040356
C	0.553186	0.413083	-1.294681
H	-0.196908	1.180579	-1.492151
C	1.059629	-0.215990	-2.440854
C	0.382864	1.413943	0.940825
H	-0.632115	1.084078	1.220994
H	0.279841	2.371233	0.410777
H	0.957288	1.572036	1.862255
C	0.517718	0.314669	-3.751929
H	1.197070	0.138504	-4.595690
H	0.298564	1.388889	-3.681894
H	-0.430755	-0.204713	-3.970455
C	2.425047	-0.315170	1.815699
C	3.621311	0.440698	1.895846
C	4.218809	0.639466	3.143820
H	5.140428	1.218493	3.208583
C	3.665074	0.116061	4.304983
H	4.144616	0.283779	5.270730
C	2.491601	-0.620212	4.219053
H	2.046998	-1.024036	5.130366
C	1.858014	-0.850472	2.994398
C	0.559382	-1.634877	2.997219
H	0.283535	-1.807900	1.948196
C	4.252197	1.074019	0.667904
H	3.955407	0.461447	-0.195962
C	2.563732	-1.603816	-3.662178
C	2.021154	-2.599939	-4.503462
C	2.681361	-2.915486	-5.694818
H	2.254681	-3.676932	-6.350497
C	3.854111	-2.275452	-6.067937
H	4.353223	-2.533598	-7.003291
C	4.385394	-1.300417	-5.234047
H	5.311961	-0.803519	-5.520623
C	3.763291	-0.948855	-4.033544
C	4.376037	0.143073	-3.174068
H	4.098237	-0.081044	-2.133614
C	0.724282	-3.321579	-4.194653
H	0.382126	-2.974424	-3.211328
C	-1.047078	-3.437648	-0.364433
C	-1.098302	-4.519509	0.725754
H	-0.506338	-5.397337	0.424963
H	-2.139156	-4.839891	0.900616
H	-0.684968	-4.134518	1.665715
C	-1.621524	-4.023131	-1.663325
H	-1.647391	-3.261907	-2.455909
H	-2.650678	-4.379916	-1.491908
H	-1.009187	-4.870471	-2.000639
C	-1.899996	-2.227077	0.050474
H	-1.566985	-1.825410	1.017376

H	-2.958442	-2.523383	0.143248
H	-1.814680	-1.429011	-0.702671
C	8.863195	-6.825656	-1.541042
H	8.936058	-6.334559	-2.519563
H	9.043699	-7.902713	-1.663069
H	9.667585	-6.427705	-0.899089
C	7.539739	-6.571127	-0.848971
C	7.208618	-7.504758	0.144071
H	7.966207	-8.270719	0.317098
C	5.989623	-7.728937	0.806021
C	5.928077	-9.022101	1.593797
H	6.392173	-8.851167	2.580021
H	6.499912	-9.815858	1.093503
H	4.900291	-9.368416	1.761791
C	3.686667	-7.358457	1.280819
C	2.781864	-7.957255	0.368940
C	1.521385	-8.354770	0.824327
H	0.819843	-8.811469	0.125797
C	1.139802	-8.180417	2.148762
H	0.149684	-8.493306	2.484176
C	2.038739	-7.611415	3.039769
H	1.751206	-7.488747	4.085716
C	3.311063	-7.198997	2.633052
C	4.249264	-6.631659	3.680258
H	5.172339	-6.335533	3.165225
C	3.163929	-8.217146	-1.077983
H	3.886751	-7.438199	-1.361836
C	7.101403	-4.803951	-2.384759
C	6.526358	-5.263361	-3.595348
C	6.829484	-4.601835	-4.787955
H	6.384346	-4.951211	-5.719463
C	7.681090	-3.506003	-4.812805
H	7.911787	-3.006097	-5.754990
C	8.232678	-3.055565	-3.622348
H	8.909203	-2.199111	-3.637566
C	7.958013	-3.680299	-2.401904
C	8.643142	-3.141067	-1.160132
H	8.238667	-3.690638	-0.299748
C	5.611779	-6.474719	-3.639161
H	5.137711	-6.550020	-2.649832
C	7.573165	-4.031241	2.637623
C	7.784790	-2.509018	2.673770
H	6.844065	-2.001323	2.936945
H	8.115216	-2.145075	1.693425
H	8.547884	-2.245630	3.425311
C	7.080797	-4.483637	4.020090
H	6.960894	-5.575763	4.051539
H	6.117191	-4.009814	4.250018
H	7.810365	-4.192539	4.794052
C	8.897815	-4.746580	2.322836
H	8.728840	-5.831271	2.241352
H	9.631307	-4.555840	3.124269
H	9.322049	-4.391106	1.373761
C	2.932170	-4.665004	-0.652830
H	2.331541	-5.516759	-0.965980
C	3.701368	-3.931678	-1.633641

H	3.792023	-4.304754	-2.654071
C	4.685126	-2.958132	-1.142539
H	5.249447	-2.367881	-1.864836
C	4.552413	-2.510286	0.225800
H	5.139695	-1.663678	0.576713
C	3.561043	-3.081061	1.135999
H	3.590103	-2.772851	2.182110
C	3.053675	-4.402554	0.780984
H	2.375365	-4.924922	1.457489
N	1.841044	-0.552834	0.525397
N	1.929211	-1.234842	-2.424360
N	0.323878	-3.027630	-0.553393
N	4.952486	-6.885790	0.794868
N	6.793866	-5.504763	-1.165455
N	6.595765	-4.346231	1.624358
Nb	2.069661	-2.568570	-0.606533
Nb	5.350003	-4.639306	0.350247
C	10.162384	-3.362592	-1.221468
H	10.608894	-2.776425	-2.041808
H	10.636047	-3.037417	-0.280777
H	10.415948	-4.418293	-1.392296
C	8.350156	-1.650477	-0.950685
H	8.883183	-1.276017	-0.062451
H	8.688303	-1.049337	-1.809825
H	7.275691	-1.469553	-0.811133
C	4.594508	-7.684022	4.745845
H	5.369726	-7.295203	5.426089
H	3.708561	-7.929876	5.354336
H	4.958713	-8.619365	4.297327
C	3.666782	-5.386325	4.358616
H	2.678411	-5.595375	4.798490
H	4.328856	-5.049848	5.171487
H	3.556898	-4.559651	3.644917
C	6.394191	-7.775117	-3.880373
H	7.085356	-7.998610	-3.057389
H	5.697556	-8.623789	-3.976192
H	6.976904	-7.701131	-4.814217
C	4.509347	-6.347073	-4.696470
H	3.753677	-7.132811	-4.545261
H	4.009374	-5.368229	-4.659137
H	4.913371	-6.481437	-5.713398
C	3.862582	-9.576773	-1.239721
H	4.074890	-9.769273	-2.303803
H	4.814494	-9.615250	-0.694381
H	3.213223	-10.385979	-0.864963
C	1.973848	-8.149690	-2.041210
H	1.309524	-9.020838	-1.921186
H	1.368397	-7.241775	-1.901182
H	2.334804	-8.162042	-3.080456
C	3.720342	2.496721	0.432117
H	4.230576	2.954398	-0.430695
H	2.641971	2.501940	0.227933
H	3.908757	3.125504	1.318755
C	5.904881	0.185110	-3.268005
H	6.310789	0.830463	-2.474242
H	6.354310	-0.813848	-3.170299

H	6.234089	0.612344	-4.229584
C	3.811705	1.530787	-3.516905
H	4.335553	2.305792	-2.933979
H	3.959782	1.748069	-4.588326
H	2.740225	1.608107	-3.290626
C	5.783523	1.116996	0.730545
H	6.222208	0.149441	1.016574
H	6.188364	1.400734	-0.252543
H	6.135346	1.871877	1.452377
C	0.709434	-2.998993	3.680427
H	1.045848	-2.892619	4.724056
H	-0.258927	-3.523470	3.701013
H	1.431779	-3.636085	3.154322
C	-0.565101	-0.841343	3.681241
H	-1.521413	-1.382913	3.597101
H	-0.347433	-0.707774	4.754003
H	-0.690213	0.157374	3.240693
C	0.927272	-4.839396	-4.114080
H	-0.031434	-5.343640	-3.916191
H	1.322278	-5.240858	-5.061357
H	1.629763	-5.103766	-3.312491
C	-0.358580	-3.000962	-5.236002
H	-0.087572	-3.411286	-6.222837
H	-1.318907	-3.452760	-4.938688
H	-0.503593	-1.917818	-5.356626

Complex2 :

C	11.945953	4.640686	10.692994
H	11.527975	4.437958	9.699365
H	11.526587	5.595244	11.053912
H	11.616210	3.857059	11.389019
C	13.452737	4.758875	10.686387
C	14.065383	4.584463	11.938702
H	13.363458	4.428205	12.760570
C	15.408561	4.344823	12.280570
C	15.616070	3.779161	13.666140
H	15.077396	2.825247	13.771963
H	15.181945	4.474246	14.403110
H	16.672772	3.616761	13.908287
C	17.726607	4.006282	11.791743
C	17.959166	2.628165	11.575542
C	19.223023	2.106860	11.869937
H	19.407483	1.043160	11.711536
C	20.239871	2.905928	12.369646
H	21.216346	2.477400	12.600302
C	19.993897	4.253490	12.598032
H	20.785461	4.877844	13.013587
C	18.748533	4.824863	12.328336
C	18.514883	6.273161	12.714593
H	17.624164	6.623479	12.175817
C	18.226715	6.382625	14.220814
H	17.330485	5.815895	14.509588
H	18.077192	7.435394	14.508035
H	19.076740	5.987894	14.801630

C	19.683432	7.195790	12.351397
H	20.559715	7.010255	12.992809
H	19.392410	8.246679	12.508355
H	20.006374	7.072274	11.307743
C	16.888189	1.663268	11.094164
H	15.965657	2.232596	10.910794
C	17.286855	0.974211	9.783536
H	17.404099	1.693998	8.960987
H	16.517837	0.241608	9.493343
H	18.236832	0.427250	9.894346
C	16.583577	0.599871	12.162068
H	17.442803	-0.076325	12.298028
H	15.721022	-0.012111	11.854557
H	16.360477	1.051032	13.139020
C	13.412277	4.887374	8.299970
C	12.753503	5.985835	7.703788
C	12.035155	5.775358	6.522523
H	11.509837	6.615434	6.065729
C	11.953470	4.522105	5.934729
H	11.366702	4.375147	5.026637
C	12.628319	3.455840	6.513681
H	12.576657	2.475552	6.040367
C	13.373752	3.612854	7.685119
C	14.089266	2.407628	8.273139
H	14.949244	2.788109	8.846706
C	13.192313	1.624188	9.244005
H	12.906786	2.224928	10.117812
H	13.719122	0.726848	9.607028
H	12.270612	1.296798	8.734755
C	14.618932	1.458478	7.192033
H	13.800833	0.909029	6.699995
H	15.281281	0.707684	7.645611
H	15.182782	1.995035	6.414284
C	12.735892	7.379124	8.305730
H	13.412624	7.374717	9.170416
C	13.232854	8.440779	7.315195
H	14.239956	8.219194	6.934985
H	13.249719	9.430734	7.798201
H	12.562753	8.516573	6.444177
C	11.327422	7.757691	8.790528
H	10.626616	7.812239	7.941719
H	11.340023	8.747335	9.274644
H	10.925500	7.026377	9.504956
C	15.167892	8.639707	11.413239
C	16.043428	8.838474	12.657086
H	15.926770	7.993267	13.349750
H	15.743850	9.761303	13.179133
H	17.102108	8.927632	12.375288
C	13.698272	8.521157	11.844060
H	13.037631	8.425163	10.972564
H	13.401178	9.422254	12.404539
H	13.560799	7.640970	12.489696
C	15.349909	9.828406	10.458096
H	16.406938	9.932233	10.168832
H	15.033305	10.761483	10.951607
H	14.746105	9.690378	9.550377

C	22.941970	5.524167	5.308548
H	23.463486	5.783772	6.238487
H	23.323037	6.145810	4.486312
H	23.171761	4.472434	5.068072
C	21.450519	5.675989	5.449854
C	20.725233	5.727708	4.223031
H	21.355872	5.460186	3.369924
C	19.460070	6.229085	3.807732
C	19.317840	6.491959	2.331515
H	19.152698	5.532173	1.813794
H	20.232621	6.940228	1.919784
H	18.460972	7.144370	2.120689
C	17.240240	7.085395	4.249540
C	16.176213	6.399939	3.628585
C	15.013126	7.117010	3.328346
H	14.182358	6.600498	2.845646
C	14.896250	8.467030	3.623506
H	13.981029	9.007303	3.377150
C	15.958298	9.130265	4.227428
H	15.863092	10.192553	4.451710
C	17.141567	8.463428	4.550619
C	18.304391	9.226334	5.159005
H	18.845174	8.523390	5.812468
C	19.278628	9.701240	4.068745
H	19.731255	8.861289	3.524232
H	20.094202	10.291900	4.514632
H	18.751483	10.337491	3.338642
C	17.872598	10.424800	6.008061
H	17.472269	11.239707	5.384616
H	18.743325	10.832489	6.543253
H	17.107067	10.154800	6.750292
C	16.233593	4.930630	3.250378
H	17.192852	4.518828	3.596509
C	16.158726	4.738066	1.727866
H	15.173540	5.047622	1.343906
H	16.297661	3.675265	1.473638
H	16.919319	5.327108	1.195935
C	15.114533	4.132410	3.928964
H	15.146120	4.233944	5.022415
H	15.197408	3.064676	3.671513
H	14.123310	4.476982	3.594613
C	21.629625	5.785594	7.854771
C	21.791189	7.061098	8.442866
C	22.502526	7.153713	9.640747
H	22.643383	8.128927	10.106252
C	23.034316	6.026173	10.255810
H	23.588587	6.121507	11.190738
C	22.865457	4.783072	9.665443
H	23.292453	3.900026	10.143052
C	22.174318	4.633987	8.458659
C	22.074313	3.246596	7.851614
H	21.508160	3.322579	6.913288
C	23.462645	2.673482	7.527762
H	24.062172	3.358470	6.911285
H	23.364085	1.716516	6.991059
H	24.030332	2.477901	8.451366

C	21.315388	2.281353	8.770063
H	21.855345	2.136726	9.719308
H	21.218011	1.295337	8.288206
H	20.311880	2.656995	9.013072
C	21.252048	8.314839	7.778353
H	20.312251	8.032679	7.277241
C	22.220652	8.835931	6.704875
H	23.210091	9.035198	7.148817
H	21.842478	9.776257	6.273830
H	22.352194	8.119191	5.882518
C	20.939642	9.440655	8.768344
H	20.347056	9.088549	9.625591
H	20.374967	10.236597	8.260026
H	21.860589	9.901130	9.160122
C	19.058033	1.777772	5.030608
C	20.535283	1.476036	4.739248
H	20.946072	2.218519	4.038330
H	20.639070	0.475194	4.289646
H	21.123162	1.501215	5.666993
C	18.512353	0.770546	6.053909
H	19.068083	0.845903	6.999628
H	18.612183	-0.256238	5.665789
H	17.449349	0.964820	6.254728
C	18.246800	1.691481	3.730601
H	17.191526	1.928038	3.926031
H	18.305264	0.676285	3.305813
H	18.637756	2.402534	2.987173
C	16.987225	4.852522	7.240640
C	18.151206	4.640755	8.190664
C	18.520064	5.764562	9.035642
C	18.021989	7.048056	8.801305
C	16.907360	7.242947	7.910066
C	16.326102	6.147447	7.270044
N	16.442757	4.570172	11.457038
N	14.121889	5.025971	9.550075
N	15.569625	7.429817	10.727593
N	20.856878	5.684824	6.646481
N	18.431141	6.387995	4.648250
N	18.941129	3.108025	5.587968
Nb	18.913881	4.823934	6.101694
Nb	16.092186	6.002809	9.794275
H	18.280574	3.648298	8.630276
H	16.352254	3.988971	7.023837
H	18.413481	7.901184	9.356062
H	15.431303	6.290213	6.659513
H	16.474914	8.237705	7.804440
H	19.305335	5.612393	9.779070