A mixed valence diruthenium (II,III) complex endowed with high stability: from experimental evidences to theoretical interpretation

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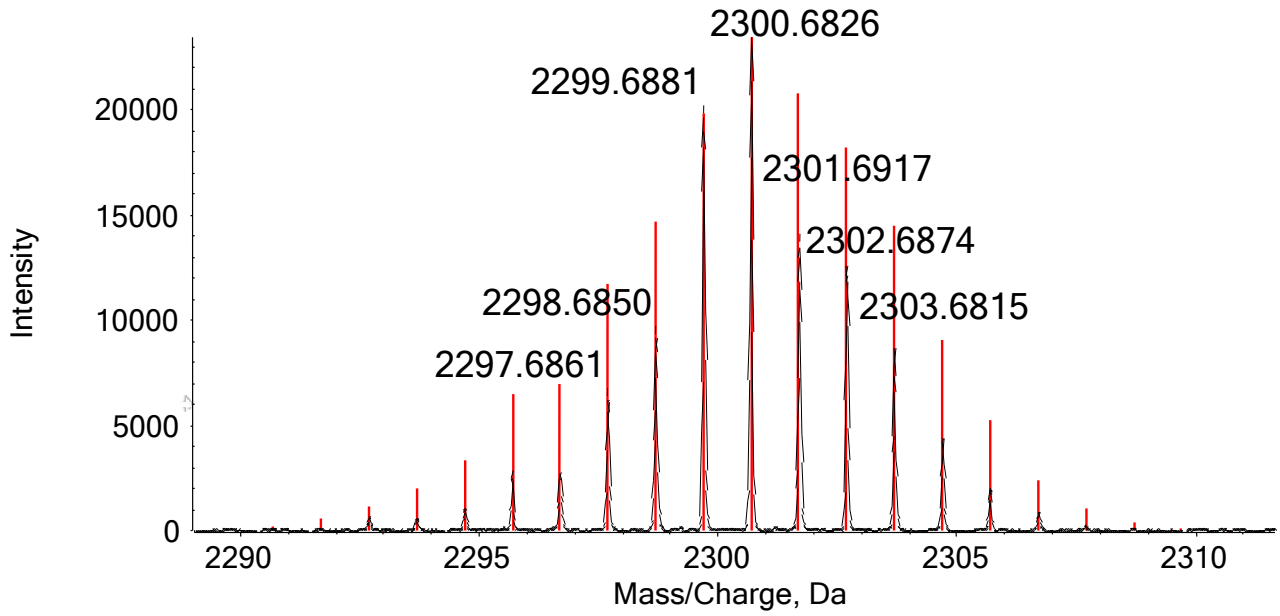
HR-ESI-MS characterization

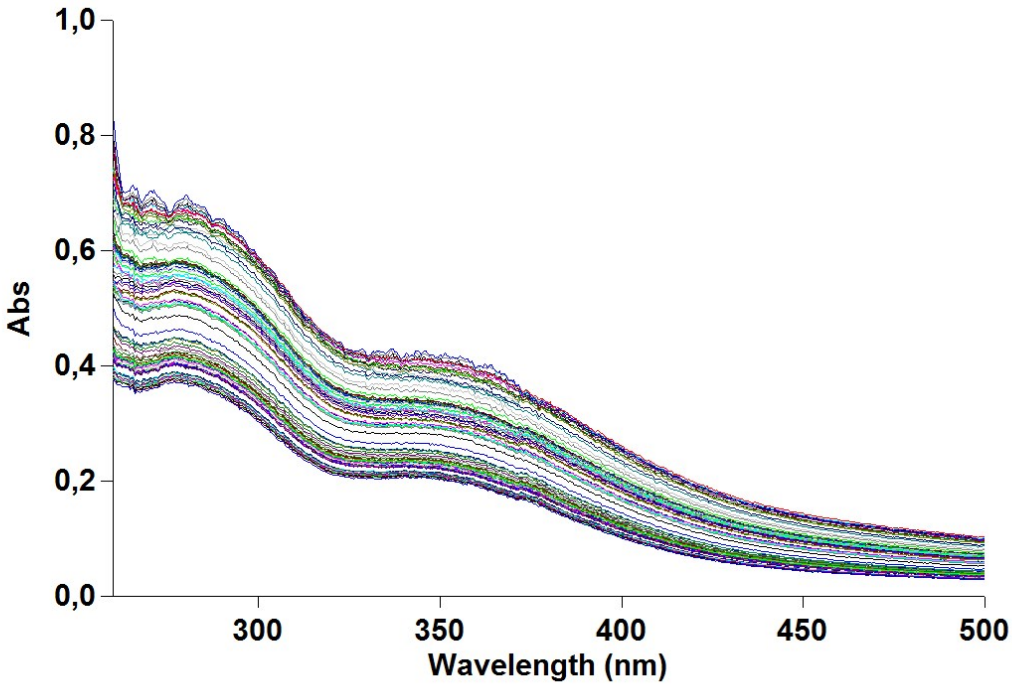


High-resolution ESI mass spectrum of $[Ru_2(EB106)_4Cl]$, 10^{-5} M in EtOH. Experimental isotopic distribution for $C_{124}H_{120}N_{12}O_{20}Ru_2^+$ (black line) vs the theoretical one (red lines). Measured *m/z* = 2300.68256; theoretical *m/z* = 2300.68233; mass error = 0.1 ppm.

UV-Vis Spectra

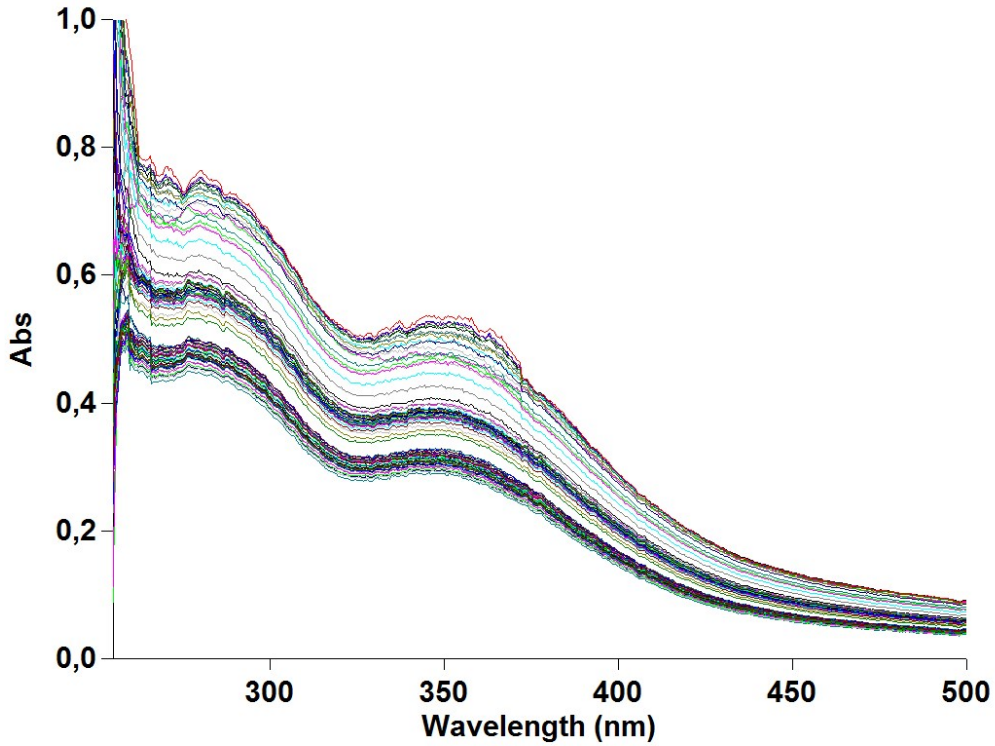
3:1 = complex to protein ratio.

$[Ru_2(EB106)_4Cl]$ 10^{-5} M + HUHf (Human H Ferritin) (3 : 1) 15 % DMSO PB 10 mM pH 7.4

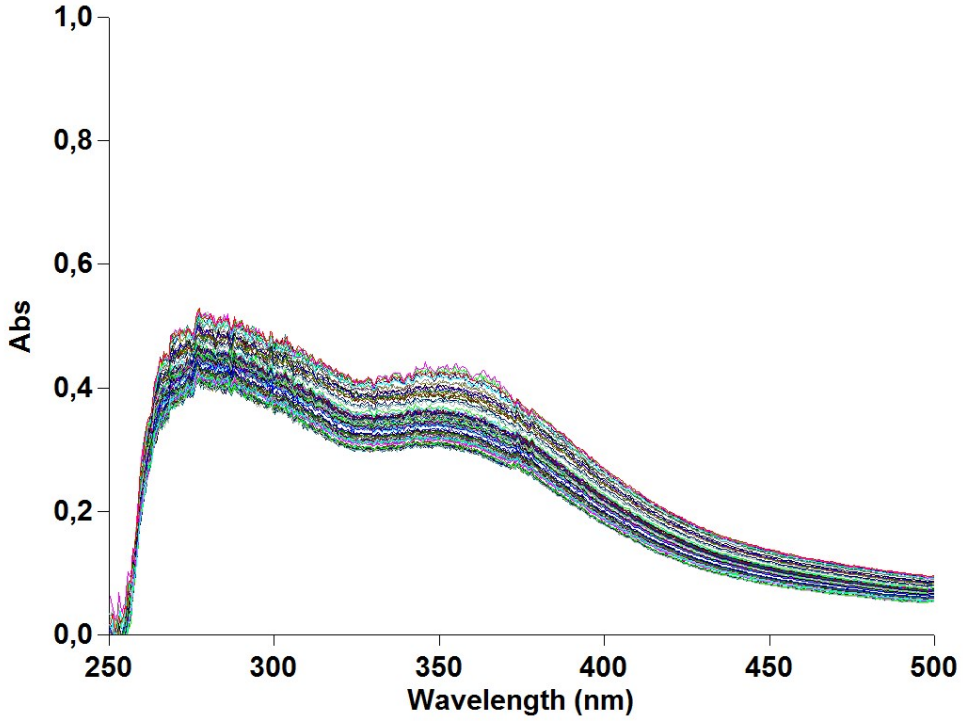


mM

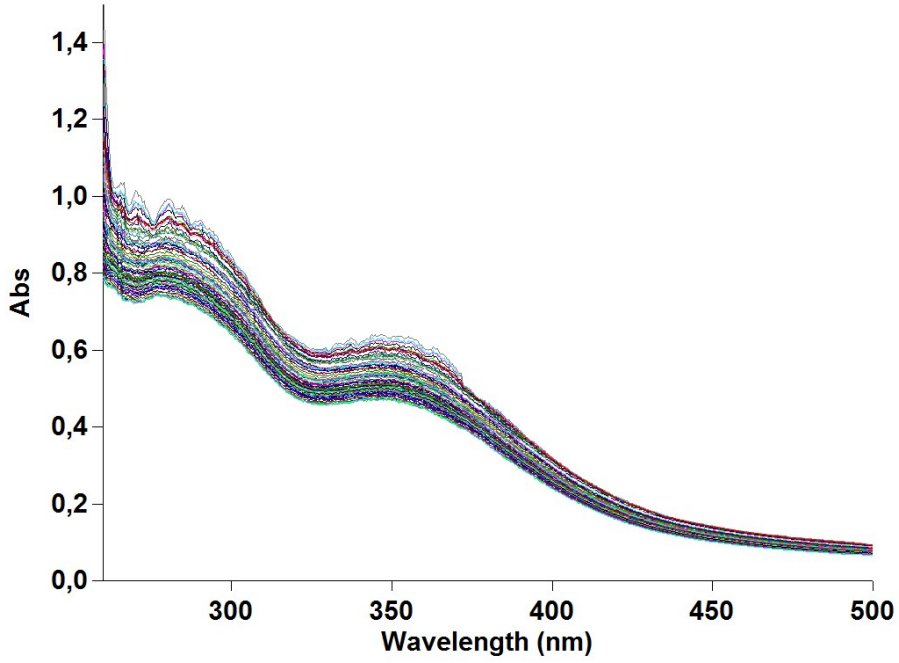
$[Ru_2(EB106)_4Cl]$ 10^{-5} M + Ubi (Ubiquitin)(3:1) 15 % DMSO PB 10 mM pH 7.4



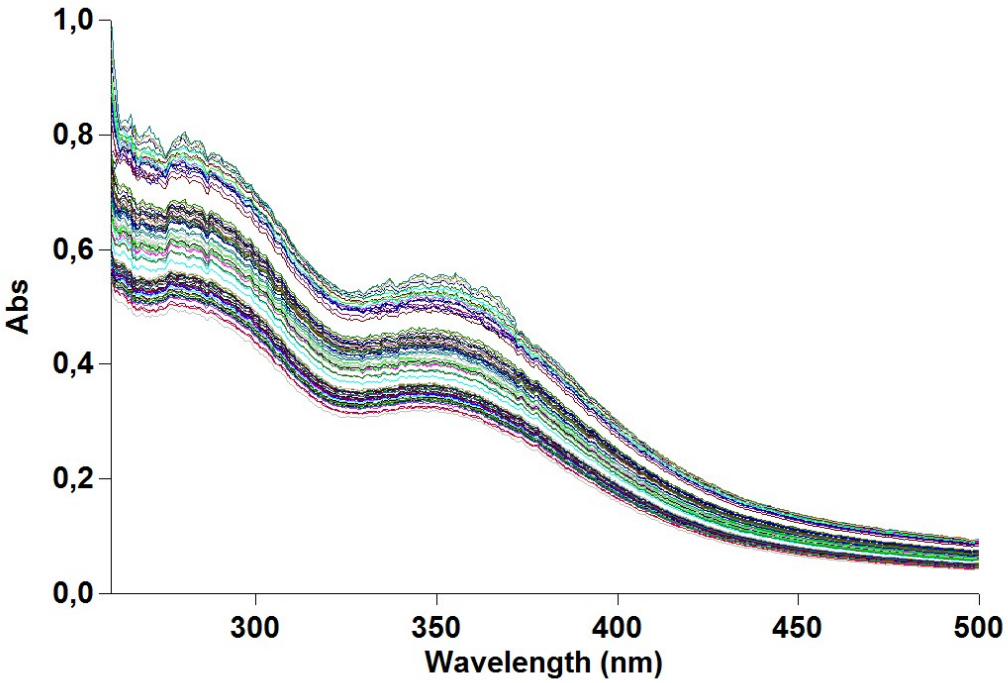
$[Ru_2(EB106)_4Cl]$ 10^{-5} M + CA1 (carbonic anhydrase) (3:1) 15 % DMSO PB 10 mM pH 7.4



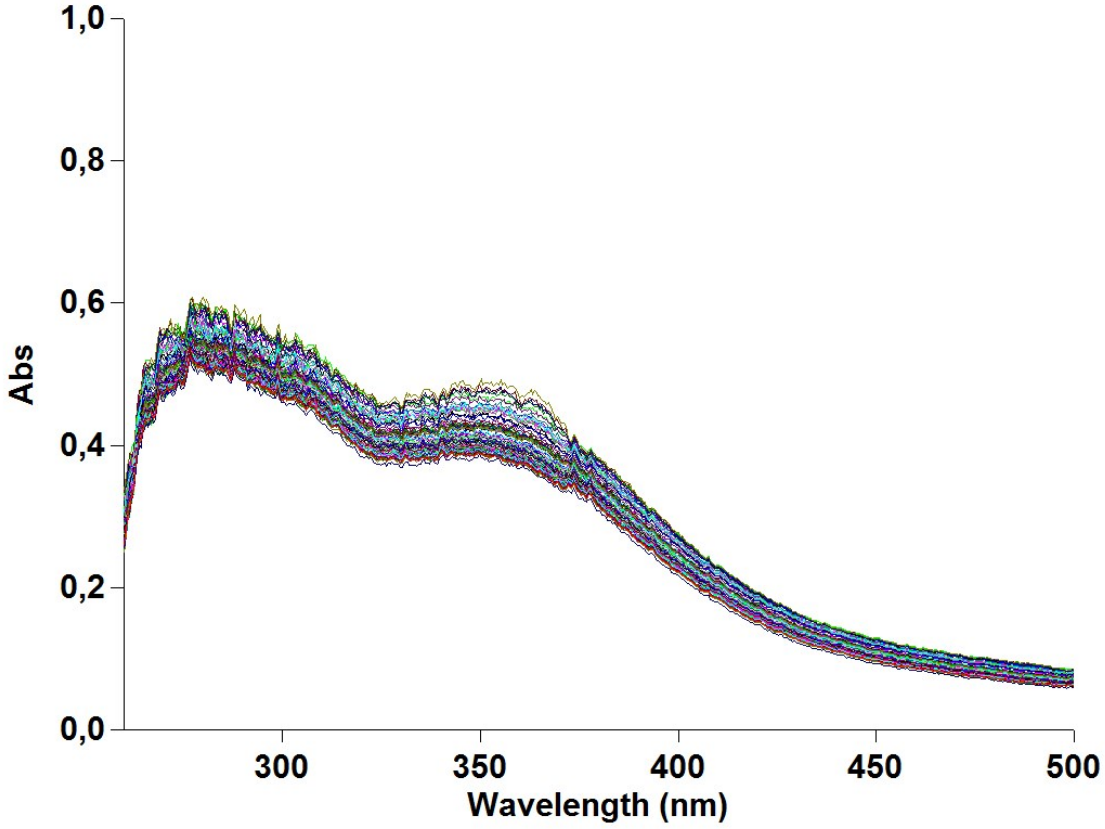
$[Ru_2(EB106)_4Cl]$ 10^{-5} M + holoTf (Transferrin) (3:1) 15 % DMSO PB 10 mM pH 7.4



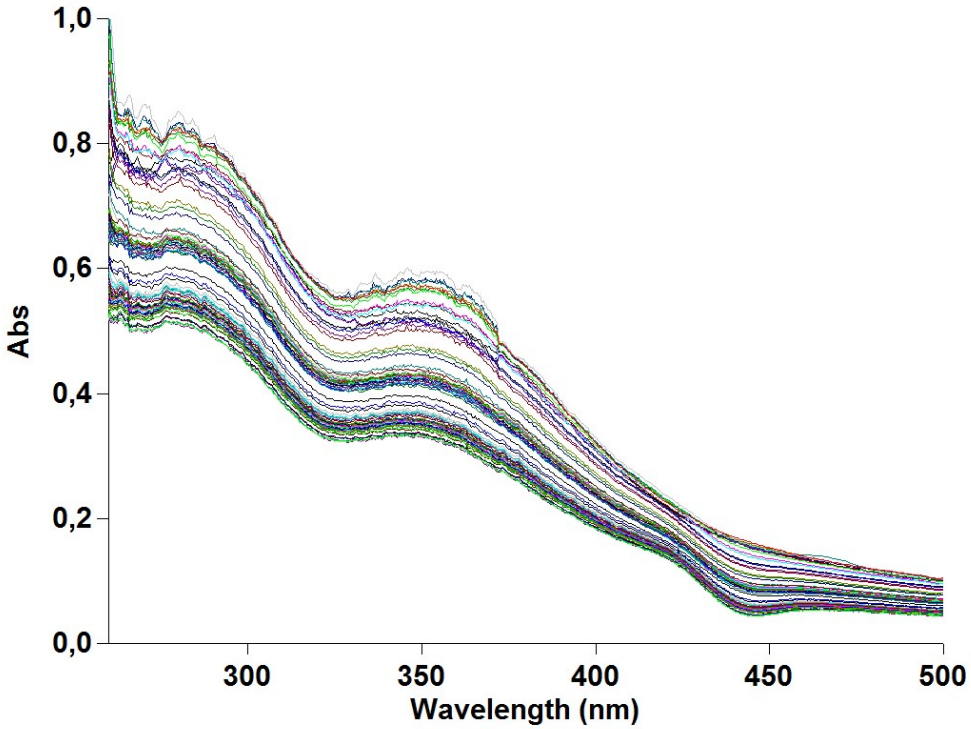
$[Ru_2(EB106)_4Cl]$ 10^{-5} M + SOD (superoxide dismutase)(3:1) 15 % DMSO PB 10 mM pH 7.4



$[Ru_2(EB106)_4Cl]$ 10^{-5} M + HAS (Human serum Albumin) (3:1) 15 % DMSO PB 10 mM pH 7.4



$[Ru_2(EB106)_4Cl]$ 10^{-5} M + HB (Hemoglobin) (3:1) 15 % DMSO PB 10 mM pH 7.4



Protein interaction studies through ESI-MS

Stock solution of $[Ru_2(EB106)_4Cl]$ was freshly prepared in DMSO to a final concentration of $3x10^{-2}$ M. Stock solutions of the proteins were prepared in 2 mM ammonium acetate solution, pH 6.8, at 10^{-3} M. For each $[Ru_2(EB106)_4Cl]$/protein pair, appropriate aliquots of these stock solutions were mixed and diluted with 2 mM ammonium acetate solution (pH 6.8) to a final protein concentration of 10^{-4} M and a protein-to-metal molar ratio of 1 : 3. The solutions were incubated up to 72 h at 37 °C. Aliquots of the various solutions were sampled after 24 and 72 h of incubation and were further diluted
with 2 mM ammonium acetate solution (pH 6.8) at 5×10^{-7} M protein final concentration.
Spectra were acquired through direct infusion at 5 µL/min flow rate in a TripleTOF® 5600^+ mass spectrometer (Sciex, Framingham, MA, U.S.A.), equipped with a DuoSpray® interface operating with an ESI probe in positive polarity. The ESI source parameters were optimized and were as follows: positive polarity, Ionspray Voltage Floating 5500 V, Temperature 30 °C, Ion source Gas 1 (GS1) 45 L/min; Ion source Gas 2 (GS2) 0 L/min; Curtain Gas (CUR) 15 L/min, Declustering Potential (DP) 100 V, Collision Energy (CE) 10 V. For acquisition, Analyst TF software 1.7.1 (Sciex) was used and deconvoluted spectra were obtained by using the Bio Tool Kit micro-application v.2.2 embedded in PeakView™ software v.2.2 (Sciex).

Table S1. Comparison between calculated bond distances for $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl_2]^-$ and the corresponding experimental X-ray values for analogous dimeric, $Cs[Ru_2(\mu\text{-}O_2CCH_3)_4Cl_2]$, and polymeric , $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl_2]$ ans $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl_2]$, complexes. All bond distances are in ångströms, angles in degrees, the slash separates the minimum and the maximum values for the parameter.

	$[Ru_2(\mu\text{-}O_2CMe)_4Cl_2]^-$ [a]	$Cs[Ru_2(\mu\text{-}O_2CMe)_4Cl_2]$ [b]	$Ru_2(\mu\text{-}O_2CMe)_4Cl_2$ [c]	$Ru_2(\mu\text{-}O_2CMe)_4Cl_2$ [d]
Ru-Cl	2.54	2.52	2.58	2.57
Ru-Ru	2.38	2.29	2.29	2.28
Ru-O	2.06/2.08	2.02	2.02/2.01	2.01/2.04
O-C	1.27	1.27	1.27	1.29/2.04
C-C	1.51	1.49	1.50	1.47
Ru-Ru-O	87.3/89.3	88.7/89.4	88.7/89.1	88.8/89.7
Ru-O-C	118.6/119.9	118.0/119.0	119.6/120.4	120.0/121.0
O-C-O	124.9	119.0/123.0	121.6/122.6	120.0/122.0
Ru-Ru-Cl	179.0	176.2	(not reported)	177.0

[a] theoretical values

[b] A. Bino, F.A. Cotton, T.R. Felthouse, Inorg. Chem. 18 (1979) 2599.

[c] T. Togano, M. Mukaida, T. Nomura, Bull. Chem. Soc. Jpn. 53 (1980) 2085.

[d] D.S. Martin, R.A. Newman, L.M. Vlasnik, Inorg. Chem. 19 (1980) 3404.

Table S2 Cartesian coordinates

Complex [$Ru_2(\mu\text{-}O_2CCH_3)_4Cl$]

Ru	5.05230	2.50750	6.36820
O	7.09500	2.43420	6.37460
O	5.12210	4.55010	6.35180
O	3.00910	2.57900	6.37060
O	4.98020	0.46460	6.39440
Ru	5.05210	2.48090	4.02450
O	2.97200	2.55180	4.11980
Cl	5.05880	2.46300	1.64020
O	7.13300	2.40830	4.12380
O	4.98120	0.40190	4.14400
O	5.11910	4.56280	4.10050
C	5.14000	5.15580	5.21680
C	5.20820	6.65950	5.23780
H	4.99960	7.06420	4.24770
H	4.50140	7.05090	5.97320
H	6.21260	6.96430	5.54980
C	7.71330	2.39640	5.24670
C	9.21730	2.33950	5.28760
H	9.62410	2.25200	4.28060
H	9.59860	3.24650	5.76680
H	9.53180	1.48970	5.89990
C	4.95860	-0.16620	5.27310
C	4.90030	-1.66960	5.32970
H	4.91440	-2.09080	4.32500
H	5.74940	-2.04360	5.90890
H	3.98860	-1.97500	5.85190
C	2.39110	2.58720	5.24210
C	0.88730	2.64970	5.28050
H	0.47570	2.57410	4.27450
H	0.50510	1.84180	5.91050
H	0.57960	3.59510	5.73820

Complex [$Ru_2(EB106)_4Cl$]

C	-3.11680	-2.58750	-0.50120
N	-3.46970	-3.04930	-1.83360
C	-4.31100	-1.81010	0.11940
H	-2.91610	-3.48050	0.10000
H	-4.50410	-0.94050	-0.51400
C	-4.29560	-1.36550	1.58390
H	-5.17620	-2.47100	-0.00220
C	-4.30540	-0.56820	4.29090
C	-4.63770	-2.28720	2.59400
C	-3.96350	-0.04110	1.93260
C	-3.96780	0.35550	3.28380
C	-4.64220	-1.89090	3.94540
H	-4.90600	-3.30120	2.33410
H	-3.69120	0.67540	1.17140
H	-3.70430	1.36990	3.54590
H	-4.90240	-2.60200	4.71600
H	-4.30000	-0.26170	5.32740
H	-3.82680	-3.99790	-1.90140
C	-3.85850	-2.20340	-2.84790
C	-4.43110	-2.93650	-4.05140
O	-3.77180	-0.98340	-2.77420
C	-4.40830	-2.09110	-5.32990
N	-5.81330	-3.18110	-3.74860

H	-3.99320	-3.91960	-4.23020
H	-4.97110	-2.61410	-6.10860
C	-3.01110	-1.74610	-5.90490
H	-4.95860	-1.15840	-5.16550
C	-2.21620	-2.98970	-6.33940
H	-2.42260	-1.22990	-5.14500
C	-3.14980	-0.76540	-7.07900
H	-3.71420	-1.20520	-7.90200
H	-2.17320	-0.47130	-7.46480
H	-3.66480	0.14540	-6.77150
H	-1.97350	-3.63120	-5.49230
H	-1.26790	-2.70730	-6.79790
H	-2.77080	-3.58570	-7.06480
C	-6.36370	-4.03650	-2.86750
H	-6.48380	-2.52690	-4.14440
O	-5.75560	-4.93120	-2.27050
C	-7.82790	-3.66370	-2.57880
C	-7.96120	-2.75610	-1.45110
O	-8.74340	-4.04480	-3.30910
C	-7.92060	-1.38400	-1.55440
N	-8.00720	-0.83750	-0.28620
C	-7.76530	-0.50780	-2.71060
C	-8.05900	-3.06140	-0.04880
C	-8.21250	-2.98120	2.80190
C	-8.09160	-1.82800	0.66830
C	-8.09840	-4.25210	0.71620
C	-8.17430	-4.21440	2.12370
C	-8.16920	-1.78050	2.07050
H	-8.06740	-5.20690	0.21120
H	-8.20650	-5.13800	2.68570
H	-8.18610	-0.83270	2.58740
H	-8.27080	-2.95740	3.88150
H	-8.01300	0.15790	-0.11950
C	-7.40130	1.15690	-4.97130
C	-6.78090	0.50380	-2.70590
C	-8.57490	-0.66750	-3.85560
C	-8.39380	0.15870	-4.98190
C	-6.59520	1.33030	-3.83080
H	-6.13820	0.63010	-1.84670
H	-9.34250	-1.42890	-3.87340
H	-9.01810	0.02540	-5.85390
H	-5.82750	2.09020	-3.82000
H	-7.25850	1.78890	-5.83600
C	-1.38100	3.20600	-0.43920
N	-1.22120	3.87640	0.83430
C	-2.82070	3.24510	-1.03860
H	-0.69950	3.73030	-1.12090
H	-3.30910	2.27120	-0.95550
C	-2.82540	3.70320	-2.49390
H	-3.43080	3.93600	-0.45810
C	-2.83830	4.54970	-5.18470
C	-2.67960	5.06990	-2.80570
C	-2.98000	2.76160	-3.53270
C	-2.98630	3.18340	-4.87620
C	-2.68320	5.49180	-4.14910
H	-2.55840	5.79860	-2.01580
H	-3.08500	1.70930	-3.30270
H	-3.09970	2.45550	-5.66690
H	-2.56580	6.54100	-4.38120

H	-2.83930	4.87570	-6.21530
H	-0.47230	4.55400	0.87060
C	-2.18200	4.02120	1.79310
C	-1.87720	5.14040	2.77960
O	-3.22520	3.37760	1.80950
C	-2.22010	4.73330	4.22040
N	-2.79490	6.16080	2.35410
H	-0.87860	5.57510	2.72860
H	-2.45980	5.64970	4.76800
C	-1.07560	4.04330	5.00450
H	-3.13250	4.13310	4.28610
C	-1.40430	4.01610	6.50540
H	-0.17260	4.64550	4.89130
C	-0.74600	2.61780	4.52360
H	-1.62590	1.97480	4.53150
H	0.00340	2.14830	5.16170
H	-0.33380	2.60370	3.51500
H	-1.57020	5.02060	6.89620
H	-0.58800	3.57740	7.08040
H	-2.30140	3.42870	6.70480
C	-2.75700	6.94140	1.25630
H	-3.64440	6.29170	2.90050
O	-1.80880	7.00590	0.46710
C	-4.10370	7.67200	1.05200
C	-4.61200	7.65060	-0.31310
O	-4.71380	8.12280	2.02490
C	-5.76660	7.00530	-0.69690
N	-5.96600	7.21270	-2.05020
C	-6.71610	6.17810	0.04130
C	-4.06830	8.25950	-1.50200
C	-3.57430	9.22340	-4.14880
C	-4.95560	7.98080	-2.58380
C	-2.91950	9.03240	-1.80120
C	-2.67280	9.50690	-3.10580
C	-4.72130	8.45230	-3.88740
H	-2.21490	9.25940	-1.01400
H	-1.78800	10.09660	-3.30430
H	-5.41480	8.22750	-4.68340
H	-3.38350	9.59560	-5.14600
H	-6.75070	6.82340	-2.55000
C	-8.56380	4.54580	1.43600
C	-6.26720	5.11520	0.85400
C	-8.10390	6.41120	-0.06880
C	-9.02440	5.60130	0.62590
C	-7.18210	4.30270	1.54960
H	-5.21240	4.91220	0.94680
H	-8.46650	7.22550	-0.67910
H	-10.08410	5.79410	0.54150
H	-6.81760	3.49670	2.17080
H	-9.26870	3.92760	1.97320
C	2.74490	0.90500	-0.64260
C	3.97290	1.81540	-0.59790
N	4.34320	2.25900	-1.92540
C	5.15720	1.26150	0.23590
H	3.58480	2.71890	-0.10680
H	5.17520	0.16850	0.21630
C	5.16290	1.75720	1.68150
H	6.07830	1.60480	-0.24240
C	5.20140	2.68620	4.34700

C	5.74280	3.00490	1.98960
C	4.61220	0.97170	2.71530
C	4.62460	1.43760	4.04410
C	5.76360	3.46820	3.31930
H	6.18520	3.60730	1.20830
H	4.16310	0.01310	2.49270
H	4.18620	0.83470	4.82690
H	6.21670	4.42190	3.54890
H	5.21290	3.04230	5.36750
H	4.66120	3.22040	-2.00010
C	4.80740	1.40980	-2.90050
C	5.37500	2.15530	-4.10370
O	4.77130	0.19270	-2.78530
C	5.34910	1.33700	-5.39980
N	6.74730	2.41840	-3.77210
H	4.92680	3.13660	-4.27170
H	6.17680	1.67530	-6.03050
C	4.06700	1.50200	-6.25290
H	5.55740	0.27650	-5.22940
C	4.25900	0.84870	-7.63040
H	3.91680	2.56790	-6.43320
C	2.78760	0.96830	-5.58220
H	2.91130	-0.05670	-5.23550
H	1.94070	0.98750	-6.26850
H	2.50180	1.57180	-4.72060
H	5.10130	1.29150	-8.16330
H	3.37680	0.97950	-8.25790
H	4.45080	-0.22040	-7.54380
C	7.26440	3.28310	-2.87940
H	7.43960	1.78270	-4.15970
O	6.62790	4.16350	-2.29000
C	8.73350	2.95010	-2.57260
C	8.91160	2.32990	-1.27100
O	9.61540	3.12160	-3.41570
C	8.86730	0.97200	-1.04380
N	9.01090	0.74510	0.31410
C	8.65640	-0.15830	-1.94460
C	9.07200	2.95970	0.01230
C	9.37430	3.56020	2.78780
C	9.13960	1.93310	1.00020
C	9.15080	4.29810	0.46770
C	9.30070	4.59660	1.83760
C	9.29090	2.22040	2.36740
H	9.09500	5.10490	-0.24880
H	9.36360	5.62700	2.16020
H	9.33650	1.42240	3.09320
H	9.49040	3.79350	3.83730
H	9.01820	-0.18200	0.71320
C	8.18250	-2.32900	-3.70290
C	7.74300	-1.17830	-1.59870
C	9.34630	-0.25190	-3.17330
C	9.10790	-1.32750	-4.05110
C	7.50680	-2.25700	-2.47080
H	7.19480	-1.13190	-0.66870
H	10.06820	0.50380	-3.44870
H	9.63880	-1.38430	-4.99050
H	6.80140	-3.02380	-2.18750
H	7.99760	-3.15450	-4.37480
O	-0.68070	1.24720	-1.58710

Ru	0.43930	-0.44570	-1.72100
O	1.56720	-2.11770	-1.88420
O	2.11300	0.73750	-1.73990
O	-1.24400	-1.58610	-1.67140
Ru	0.57150	-0.57040	0.61860
Cl	0.73120	-0.66880	2.99940
O	2.37050	0.43610	0.47140
O	-1.26020	-1.54750	0.57450
O	-0.44720	1.25790	0.65330
C	1.93590	-2.71880	-0.81080
O	1.63900	-2.34490	0.35390
C	2.70160	-4.02220	-1.03270
N	3.20920	-4.56420	0.21350
C	3.78600	-3.92230	-2.14640
H	1.91660	-4.72310	-1.34500
H	4.40820	-3.04670	-1.95630
C	3.31060	-3.91410	-3.60280
H	4.43270	-4.80030	-2.03200
C	2.45210	-3.91600	-6.29600
C	2.53670	-4.98180	-4.10430
C	3.66730	-2.85600	-4.46390
C	3.23940	-2.85730	-5.80600
C	2.10200	-4.97960	-5.44370
H	2.27360	-5.81350	-3.46630
H	4.26510	-2.03400	-4.09700
H	3.51130	-2.04080	-6.45750
H	1.50400	-5.79940	-5.81510
H	2.11900	-3.91280	-7.32440
H	2.79560	-5.44870	0.49580
C	4.46260	-4.33460	0.72890
C	4.82970	-5.37480	1.78960
O	5.18510	-3.41450	0.36700
C	6.06660	-4.98350	2.60620
N	5.14150	-6.58050	1.06990
H	4.00290	-5.64550	2.44910
H	6.39280	-5.84760	3.19220
C	5.89310	-3.79050	3.58020
H	6.90130	-4.77110	1.93060
C	4.89310	-4.08190	4.71240
H	5.52240	-2.92320	3.03210
C	7.25230	-3.38170	4.16740
H	7.69520	-4.19040	4.74960
H	7.15390	-2.51550	4.82270
H	7.95690	-3.11320	3.37950
H	3.87990	-4.21950	4.33470
H	4.84970	-3.25230	5.41890
H	5.16860	-4.97720	5.27060
C	4.34030	-7.48520	0.47870
H	6.12820	-6.78930	0.94140
O	3.10570	-7.48420	0.53000
C	5.16080	-8.47450	-0.36410
C	5.00420	-8.28560	-1.79790
O	5.95780	-9.24570	0.17350
C	6.00240	-7.81780	-2.61930
N	5.52130	-7.73530	-3.91290
C	7.36550	-7.39600	-2.33010
C	3.84170	-8.46730	-2.62930
C	1.97920	-8.66350	-4.78850
C	4.20570	-8.14020	-3.97000

C	2.50440	-8.87910	-2.41070
C	1.58330	-8.97380	-3.47390
C	3.29780	-8.24160	-5.03820
H	2.18380	-9.12890	-1.40880
H	0.56950	-9.29700	-3.27900
H	3.60540	-7.99330	-6.04270
H	1.27070	-8.74780	-5.60120
H	6.09450	-7.44130	-4.68940
C	9.99760	-6.55020	-1.73650
C	7.75690	-6.06170	-2.56740
C	8.30440	-8.30400	-1.79810
C	9.61580	-7.88460	-1.50180
C	9.06700	-5.63810	-2.26900
H	7.04390	-5.35450	-2.96540
H	8.01480	-9.32830	-1.60850
H	10.32600	-8.58720	-1.09010
H	9.35880	-4.61210	-2.44160
H	11.00210	-6.22560	-1.50540
C	-1.78100	-1.83860	-0.53960
C	-0.81380	1.78610	-0.42910

Complex $[Ru_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]^+$

Ru	5.04890	2.50470	6.36690
O	7.09440	2.42130	6.34620
O	5.11150	4.54790	6.30900
O	3.00030	2.57000	6.34970
O	4.97440	0.45380	6.36250
O	4.93390	2.42280	8.72050
Ru	5.04090	2.46720	4.07170
O	2.99290	2.54660	4.10920
O	5.14710	2.57320	1.72450
O	7.09550	2.39720	4.10540
O	4.97580	0.41820	4.12190
O	5.11470	4.52090	4.06830
C	5.13240	5.14990	5.18080
C	5.19950	6.64840	5.17240
H	4.96090	7.03820	4.18310
H	4.51690	7.05380	5.92240
H	6.21330	6.95890	5.44750
C	7.71000	2.38490	5.22530
C	9.20950	2.33230	5.23740
H	9.60040	2.23790	4.22480
H	9.59720	3.24400	5.70230
H	9.53960	1.48910	5.85050
C	4.95230	-0.17910	5.24910
C	4.89280	-1.67810	5.28140
H	4.90530	-2.08440	4.27060
H	5.74110	-2.06420	5.85380
H	3.98040	-1.99190	5.79770
C	2.38090	2.58100	5.22750
C	0.88190	2.64240	5.23990
H	0.48710	2.56780	4.22730
H	0.48810	1.83290	5.86070
H	0.56420	3.58660	5.69350
H	5.14790	3.48200	1.39110
H	5.92050	2.13870	1.33780
H	4.02650	2.49150	9.05060
H	5.30450	1.61690	9.10740