NOVEL VERSATILE EUROPIUM AND TERBIUM COMPLEXES AS BIOPROBE AND ANTICANCER AGENTS

Supplemental Information

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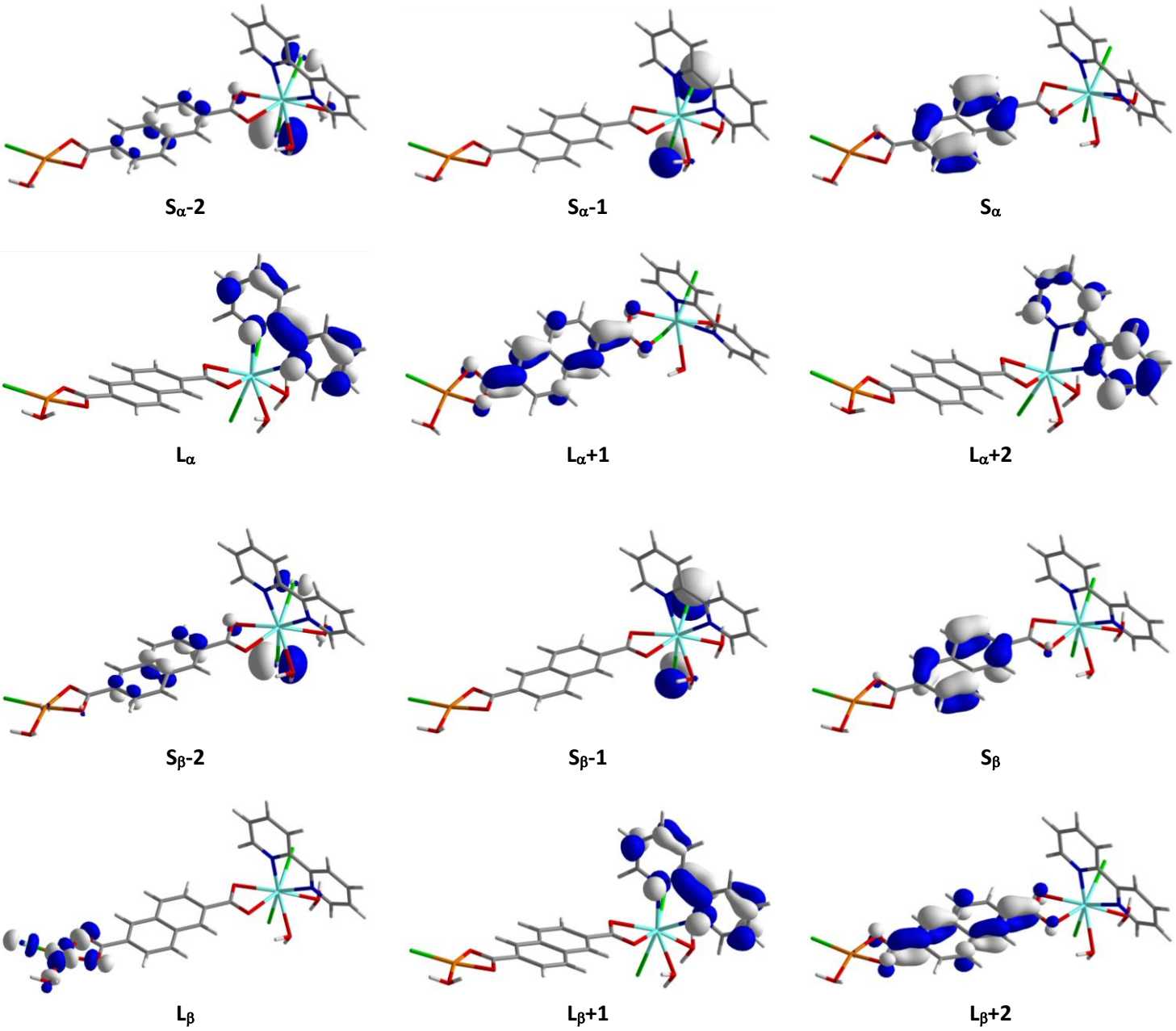

Figure S1. Frontier orbitals of complex **C3** from G09/B3PW91 for both α (top) and β (bottom) densities (S = Single Highest Occupied Molecular Orbital, SOMO; L = Lowest Occupied Molecular Orbital, LUMO).

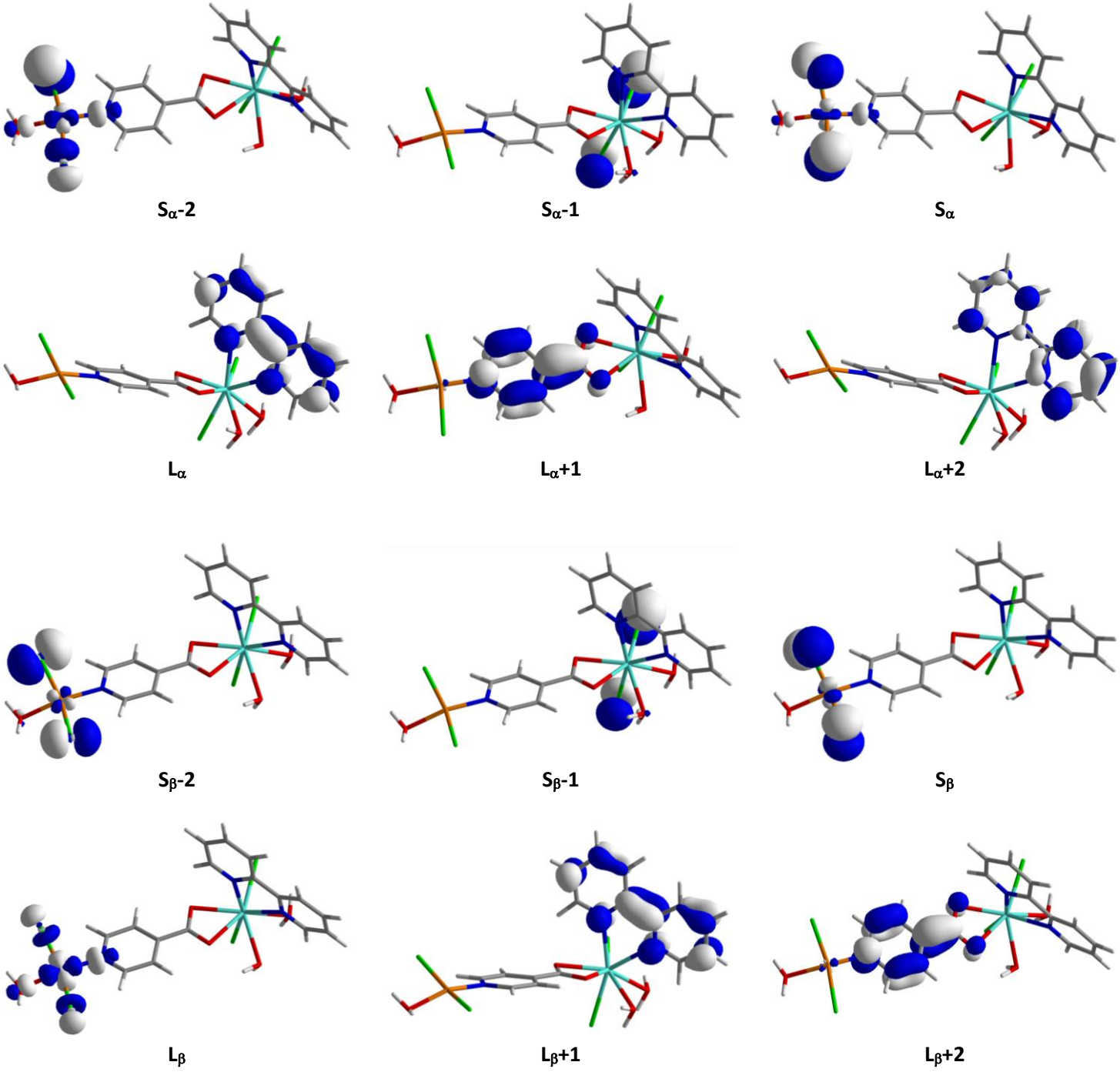

Figure S2. Frontier orbitals of complex **C4** from G09/B3PW91 for both α (top) and β (bottom) densities (S = Single Highest Occupied Molecular Orbital, SOMO; L = Lowest Occupied Molecular Orbital, LUMO).

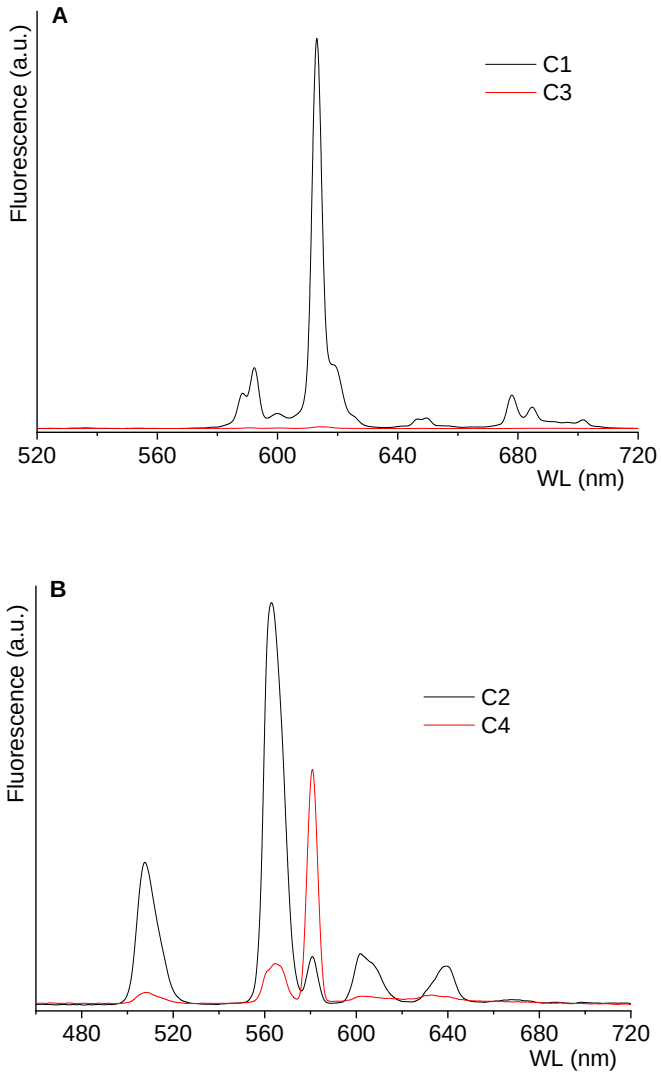

Figure S3. Fluorescence intensity spectra of methanolic solutions of (A) Europium mono- (**C1**) and bimetallic (**C3**) complexes with excitation wavelength of 300 nm. (B) Terbium mono- (**C2**) and bimetallic (**C4**) complexes with excitation wavelength of 282 nm.

ANOVA tests

All ANOVA tests run as single factor considering α = 0.05, assuming "activity of complexes is equal" as the null hypothesis.

HeLa cells

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
C1	9	9.4883	1.054256	0.682541
C3	9	134.701	14.96678	142.1478

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	871.0122	1	871.0122	12.19646	0.003012	4.493998
Within Groups	1142.643	16	71.41517			
Total	2013.655	17				

Null hypothesis rejected: P-value < α ; F > F_{crit}

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
C2	9	13.017	1.446333	0.50074
C4	9	220.537	24.50411	480.8886

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2392.475	1	2392.475	9.939876	0.006159	4.493998478
Within Groups	3851.115	16	240.6947			
Total	6243.59	17				

Null hypothesis rejected: P-value < α ; F > F_{crit}

A549 cells

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
C1	9	289.9975	32.22194	511.0708
C3	9	379.4584	42.16204	835.7729

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	444.6247	1	444.6247	0.660247	0.428398	4.493998
Within Groups	10774.75	16	673.4219			
Total	11219.37	17				

Null hypothesis NOT rejected: P-value > α ; F < F_{crit}

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
C2	9	71.03049	7.892277	39.49269
C4	9	247.089	27.45433	623.8028

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1722.032	1	1722.032	5.192354	0.036753	4.493998
Within Groups	5306.364	16	331.6477			
Total	7028.396	17				

Null hypothesis rejected: P-value < α ; F > F_{crit}

G09 optimized geometries

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---------------------------------------------------------------
#p   b3pw91/gen   pop=regular   opt=(maxcyc=1000)   scfcyc=1000
gfinput gfprint pseudo=read scf=tight
---------------------------------------------------------------


Eu-L1 complex (C1); E(RB3PW91) = -2366.53678900
C       -1.148729000      3.028212000      2.689537000
C       -3.345727000      2.124381000     -0.805124000
C       -4.008648000      3.078287000     -1.578262000
C       -4.734550000      2.674084000     -2.688777000
C       -4.784139000      1.325223000     -3.007259000
C       -4.085664000      0.435257000     -2.203859000
N       -3.380290000      0.820129000     -1.135520000
H       -3.955335000      4.128595000     -1.325529000
H       -5.253529000      3.407685000     -3.296161000
H       -5.342796000      0.960900000     -3.860542000
H       -4.081951000     -0.627364000     -2.411215000
C       -2.579518000      2.486309000      0.412442000
C       -2.629946000      3.765920000      0.966091000
C       -1.904440000      4.039136000      2.116352000
C       -1.156616000      1.777708000      2.086534000
N       -1.849670000      1.509945000      0.977110000
H       -3.240824000      4.540276000      0.521824000
H       -1.939056000      5.027936000      2.560545000
H       -0.570077000      3.190456000      3.590553000
H       -0.589353000      0.949724000      2.496653000
Eu      -2.068051000     -0.983811000      0.178197000
O       -4.236388000     -2.215769000     -0.465307000
H       -4.694086000     -2.086265000      0.381613000
H       -3.870461000     -3.115953000     -0.428610000
O       -1.771538000     -1.608121000     -2.305610000
H       -0.876375000     -1.247686000     -2.391657000
H       -1.636069000     -2.554927000     -2.114517000
Cl      -3.761024000     -0.873338000      2.266316000
Cl      -1.581155000     -3.701603000     -0.116023000
O        0.140829000     -0.354683000     -0.817170000
C        0.735121000     -0.583843000      0.281664000
O        0.079074000     -0.896068000      1.318857000
C        2.216983000     -0.472842000      0.365052000
C        2.937041000     -0.022919000     -0.718393000
C        2.878651000     -0.828225000      1.565936000
C        4.342422000      0.099932000     -0.651515000
H        2.410515000      0.240439000     -1.629296000
C        4.240198000     -0.723457000      1.658271000
H        2.281220000     -1.189458000      2.394328000
C        5.112510000      0.564705000     -1.747730000
C        5.008412000     -0.256206000      0.561011000
H        4.752646000     -1.000670000      2.574077000
C        6.474238000      0.675578000     -1.656648000
H        4.602423000      0.832361000     -2.667774000
C        6.412343000     -0.132526000      0.627535000
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C	7.134534000	0.323324000	-0.453228000
H	7.058920000	1.030311000	-2.496023000
H	6.941875000	-0.397321000	1.536641000
C	8.607753000	0.427460000	-0.304491000
O	9.224779000	0.147318000	0.693882000
O	9.216056000	0.879254000	-1.422252000
H	10.160422000	0.906068000	-1.217472000

Tb-L2 complex (C2); E(RB3PW91) = -2041.57495064

C	0.108437000	3.519544000	1.956786000
C	-2.472177000	1.595680000	-0.779122000
C	-3.455136000	2.252530000	-1.520167000
C	-4.278903000	1.521462000	-2.362906000
C	-4.105120000	0.148387000	-2.450119000
C	-3.095950000	-0.434986000	-1.697624000
N	-2.295034000	0.265656000	-0.887795000
H	-3.575656000	3.325125000	-1.450572000
H	-5.046043000	2.022338000	-2.943449000
H	-4.727663000	-0.465757000	-3.089017000
H	-2.910319000	-1.500625000	-1.734471000
C	-1.580944000	2.313007000	0.164270000
C	-1.789137000	3.648197000	0.511015000
C	-0.932248000	4.258087000	1.415252000
C	0.245395000	2.193145000	1.570976000
N	-0.571989000	1.602729000	0.695279000
H	-2.618930000	4.206436000	0.098740000
H	-1.085200000	5.293996000	1.697568000
H	0.798993000	3.948505000	2.672404000
H	1.036311000	1.568292000	1.969752000
O	-2.327681000	-2.635988000	0.403509000
H	-2.622616000	-2.430576000	1.306138000
H	-1.780243000	-3.435297000	0.487426000
O	-0.485464000	-2.004234000	-1.996814000
H	0.256645000	-1.505016000	-2.367873000
H	-0.091615000	-2.846379000	-1.702034000
Cl	-1.568779000	-0.781548000	2.719604000
Cl	0.596475000	-3.519561000	0.383553000
O	1.340820000	-0.150796000	-1.226731000
C	2.179366000	-0.055707000	-0.279908000
O	1.840537000	-0.287167000	0.914955000
C	3.584973000	0.348391000	-0.577326000
C	3.961120000	0.732579000	-1.861537000
C	4.548725000	0.352898000	0.427441000
C	5.281275000	1.109471000	-2.078432000
H	3.232229000	0.735232000	-2.662918000
C	5.842030000	0.743070000	0.099372000
H	4.284009000	0.049631000	1.433209000
H	6.620555000	0.753391000	0.858325000
N	6.214482000	1.119904000	-1.125173000
H	5.608159000	1.418564000	-3.068506000
Tb	-0.407437000	-0.966573000	0.334351000

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#p   ub3pw91/gen   pop=regular   opt=(maxcyc=1000)   scfcyc=1000
gfinput gfprint pseudo=read scf=tight
---------------------------------------------------------------


Eu-L1-Cu complex (C3); E(UB3PW91) = -3099.99407133
C       -2.780703000      2.934660000      2.785205000
C       -5.017411000      2.238680000     -0.731930000
C       -5.637710000      3.244960000     -1.473373000
C       -6.382621000      2.908664000     -2.593907000
C       -6.493519000      1.573974000     -2.953827000
C       -5.834690000      0.628928000     -2.180378000
N       -5.111231000      0.948142000     -1.102435000
H       -5.537212000      4.283500000     -1.188466000
H       -6.868826000      3.683467000     -3.176757000
H       -7.069327000      1.261753000     -3.816317000
H       -5.879154000     -0.425661000     -2.421384000
C       -4.234470000      2.528067000      0.494403000
C       -4.225221000      3.791517000      1.086069000
C       -3.488059000      3.996428000      2.243075000
C       -2.846379000      1.704585000      2.144899000
N       -3.550454000      1.502411000      1.028481000
H       -4.799472000      4.606204000      0.665785000
H       -3.476760000      4.972112000      2.716477000
H       -2.195781000      3.042683000      3.690296000
H       -2.317942000      0.839695000      2.529933000
Eu      -3.877465000     -0.952522000      0.150825000
O       -6.099694000     -2.063483000     -0.521538000
H       -6.547814000     -1.940394000      0.331559000
H       -5.778858000     -2.981248000     -0.517254000
O       -3.611921000     -1.504446000     -2.353956000
H       -2.703204000     -1.178561000     -2.433508000
H       -3.514383000     -2.461687000     -2.194517000
Cl      -5.555839000     -0.838274000      2.249001000
Cl      -3.507816000     -3.675045000     -0.234688000
O       -1.641486000     -0.389250000     -0.830313000
C       -1.057883000     -0.674168000      0.260614000
O       -1.724207000     -0.991806000      1.288817000
C        0.428104000     -0.621559000      0.346549000
C        1.165964000     -0.179222000     -0.728008000
C        1.073552000     -1.022843000      1.541412000
C        2.574566000     -0.109309000     -0.657604000
H        0.650765000      0.119921000     -1.634270000
C        2.437788000     -0.968091000      1.638279000
H        0.461435000     -1.377144000      2.362009000
C        3.361769000      0.345289000     -1.747192000
C        3.224141000     -0.509169000      0.550643000
H        2.937872000     -1.279165000      2.549971000
C        4.725243000      0.407038000     -1.652001000
H        2.861852000      0.643701000     -2.663248000
C        4.631641000     -0.435105000      0.623801000
C        5.367300000      0.014338000     -0.451566000
H        5.333189000      0.751046000     -2.480086000
H        5.145139000     -0.732869000      1.531693000
C        6.834113000      0.086834000     -0.348104000
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O	7.446502000	-0.254307000	0.709701000
O	7.547483000	0.499402000	-1.323861000
Cu	9.167840000	0.211783000	-0.207954000
O	10.541391000	0.620503000	-1.673437000
H	11.349500000	0.710150000	-1.144254000
H	10.412737000	1.435603000	-2.170061000
Cl	10.826201000	0.048634000	1.218810000

Tb-L2-Cu complex (C4); E(UB3PW91) = -3235.85792727

C	-0.103726000	3.667208000	1.780912000
C	-2.674466000	1.449557000	-0.733758000
C	-3.722913000	2.007080000	-1.466225000
C	-4.544176000	1.182728000	-2.220760000
C	-4.302953000	-0.182927000	-2.229451000
C	-3.229773000	-0.664995000	-1.494173000
N	-2.430151000	0.125932000	-0.770491000
H	-3.896353000	3.074598000	-1.457906000
H	-5.361850000	1.606175000	-2.793840000
H	-4.921579000	-0.867494000	-2.796490000
H	-2.989306000	-1.720156000	-1.475230000
C	-1.786084000	2.268786000	0.125600000
C	-2.056488000	3.608362000	0.406016000
C	-1.203180000	4.315557000	1.240076000
C	0.094930000	2.330942000	1.462540000
N	-0.717510000	1.646820000	0.652250000
H	-2.931735000	4.095571000	-0.002146000
H	-1.404123000	5.356138000	1.470078000
H	0.586342000	4.173286000	2.444711000
H	0.934084000	1.775864000	1.865475000
O	-2.175879000	-2.728147000	0.652534000
H	-2.455391000	-2.517966000	1.558521000
H	-1.576067000	-3.488303000	0.735061000
O	-0.542624000	-2.050880000	-1.873451000
H	0.130610000	-1.529416000	-2.332225000
H	-0.068107000	-2.847337000	-1.568764000
Cl	-1.461850000	-0.701506000	2.835390000
Cl	0.813727000	-3.366704000	0.475107000
O	1.250300000	-0.074389000	-1.257953000
C	2.103274000	0.096964000	-0.341208000
O	1.819941000	-0.078065000	0.874248000
C	3.491408000	0.530727000	-0.703692000
C	3.813408000	0.865880000	-2.014299000
C	4.481955000	0.610782000	0.269824000
C	5.104243000	1.272455000	-2.307420000
H	3.062967000	0.808287000	-2.792280000
C	5.748451000	1.033766000	-0.095990000
H	4.259589000	0.346375000	1.295860000
H	6.547314000	1.140205000	0.627206000
N	6.053031000	1.358843000	-1.362869000
H	5.415681000	1.533251000	-3.311628000
Tb	-0.415038000	-0.919607000	0.411983000
Cu	7.926890000	1.957423000	-1.809212000
Cl	7.797288000	1.853488000	-4.052315000
Cl	8.372004000	2.982299000	0.139526000
O	9.967570000	1.768703000	-2.042167000

H	10.141868000	2.023376000	-2.958624000
H	10.347445000	2.432540000	-1.450344000