

Mononuclear [tris(2-mercaptop-1-*tert*-butylimidazol-yl- κ S²)hydroborato]bismuth(I) dichlorido complex: soft scorpionate ligand can be coordinated to *p*-block elements

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Supporting information

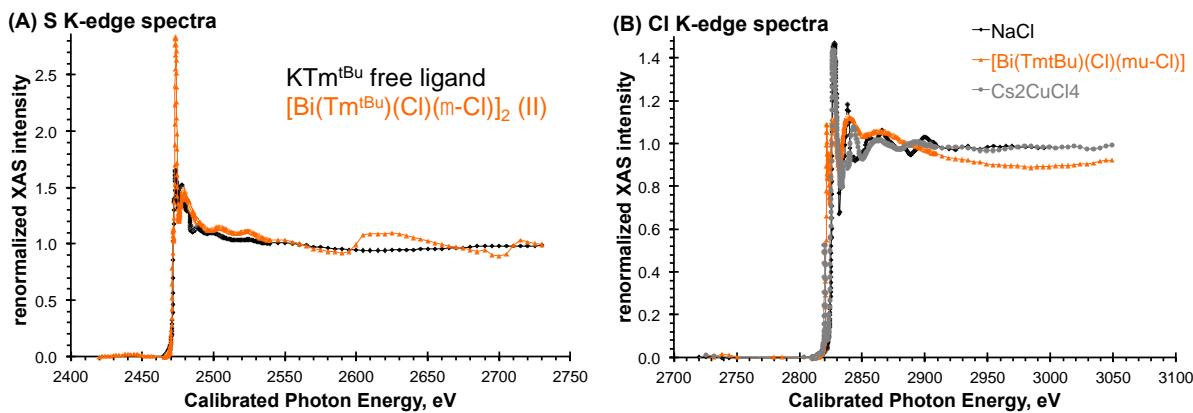


Figure S1 Comparison of background subtracted and normalized spectra for the full energy range at (A) S K-edge and (B) Cl K-edge.

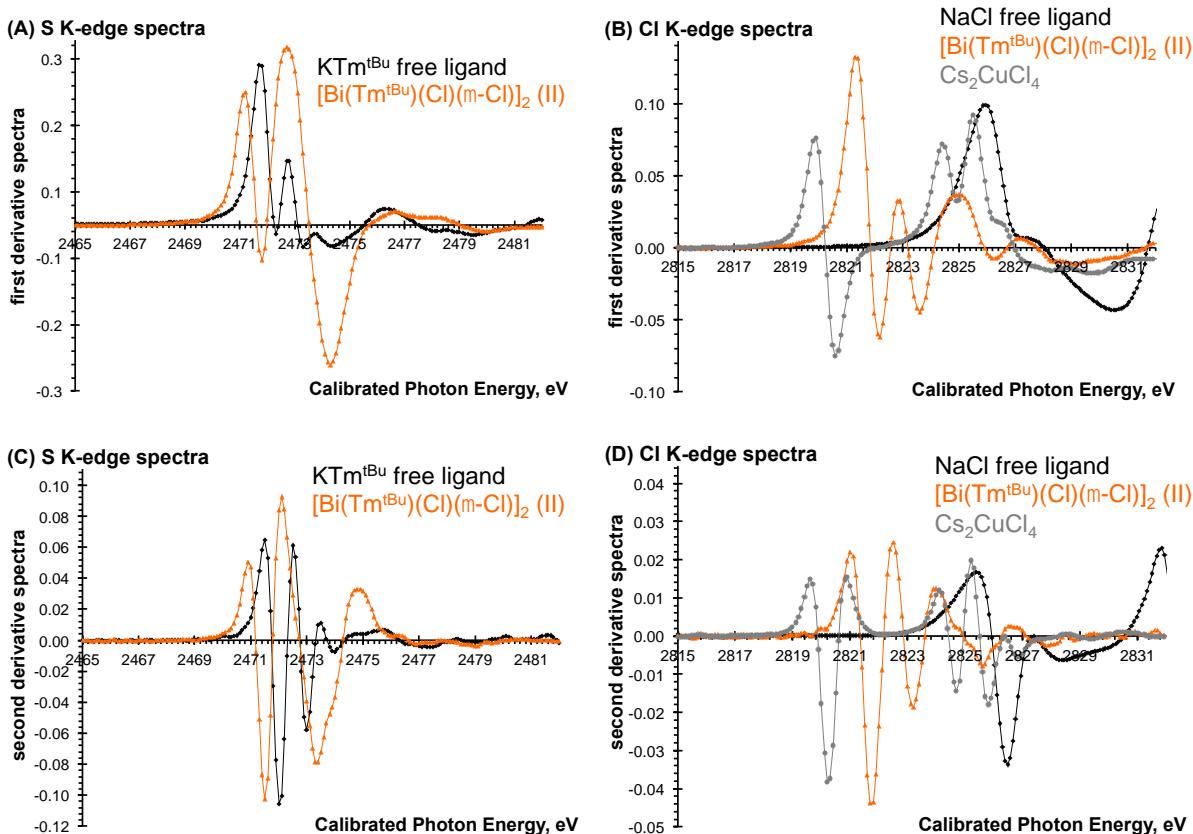


Figure S2 First (A and B) and second derivative (C and D) S K- and Cl K-edge spectra, respectively.

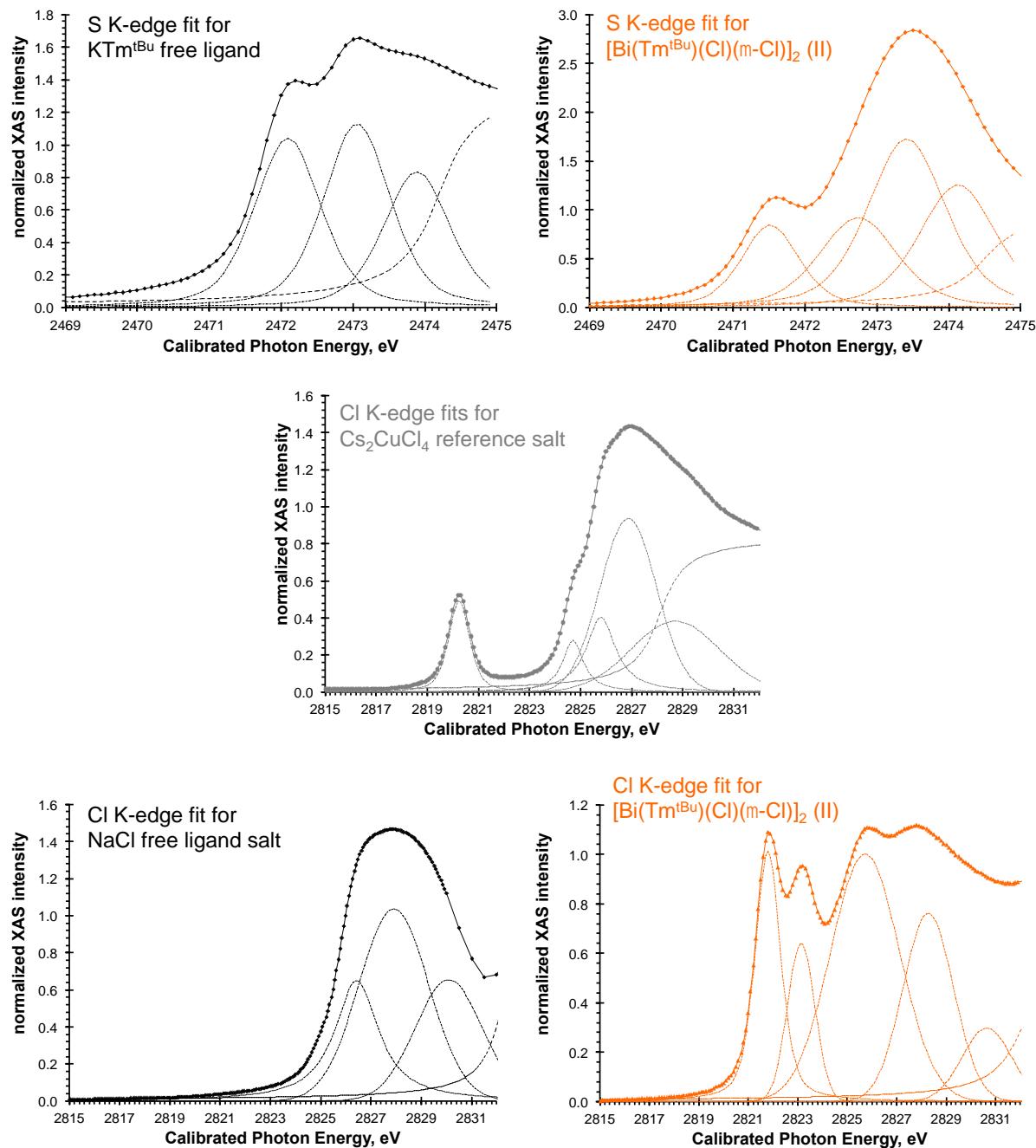


Figure S3 First to individual spectra for pre-edge and rising-edge intensity analysis at the S K- and Cl K-edges.

Table S1 Details of spectral fits shown in Figure S3. Pre-edge features used in Bi-Cl/Bi-S covalency analysis are highlighted in bold.

Sample	Fit Function ^a	Amplitude, -	Energy position, eV	Line width, eV	G/L mixing	Area, -
KTm ^{tBu} (S K)	G+L Area	1.45	2472.1	1.09	0.50	1.44
	G+L Area	1.57	2473.1	1.09	0.50	1.57
	G+L Area	1.16	2473.9	1.09	0.50	1.15
	Lor. C.A.	1.40	2474.2	0.40	n/a	n/a
	G+L Area	1.01	2471.5	0.95	0.50	1.01
[Bi(Tm ^{tBu})(Cl)(μ-Cl)] ₂ (S K)	G+L Area	1.50	2472.7	1.28	0.50	1.50
	G+L Area	2.81	2473.4	1.28	0.50	2.81
	G+L Area	2.04	2474.1	1.28	0.50	2.04
	Lor.C.A.	1.00	2474.5	0.40	n/a	n/a
	G+L Area	0.49	2820.2	0.97	0.50	0.64
NaCl (Cl K)	G+L Area	0.65	2826.4	2.10	0.03	2.11
	G+L Area	1.04	2827.9	3.37	1.00	3.61
	G+L Area	0.65	2830.1	3.13	1.00	2.18
	Lor. C.A.	0.99	2832.2	0.61	n/a	n/a
	G+L Area	1.01	2821.8	1.21	0.50	1.60
Cs ₂ [CuCl ₄] (Cl K)	G+L Area	0.64	2823.1	1.30	0.50	0.89
	G+L Area	1.00	2825.7	3.29	1.00	3.51
	G+L Area	0.76	2828.3	2.40	1.00	1.95
	G+L Area	0.30	2830.6	2.36	1.00	0.75
	Lor. C.A.	0.50	2829.0	0.47	n/a	n/a
[Bi(Tm ^{tBu})(Cl)(μ-Cl)] ₂ (Cl K)	Lor. C.A.	0.57	2831.3	0.90	n/a	n/a

^a Fit functions: G+L Area = Gaussian+Lorentzian Area, Lor. C.A. = Lorentzian Cumulative Ascending function (from built in PeakFit fit functions) used for pre-edge/rising-edge features and edge jumps, respectively.

Table S2 Conversion of Cl and S K-edge pre-edge intensities to orbital compositions.

$$\text{Transition dipole expression: } D_0 = \frac{1}{3} \frac{\text{holes}}{\text{absorbers}} \alpha^2 I$$

Cl K-edge - following procedures outlined in (Barton *et al.*, 2015)

Reference spectrum Cs_2CuCl_4 pre-edge intensity: 0.64 units corresponds to 0.29e Cl donation,
thus terminal $\text{Cl}(1s \rightarrow 3p)$ transition dipole is $I(\text{Cl}^t) = 26.4$ units with 4 absorbers

Bridging Cl dipole integral is approximately 13% larger than terminal Cl

thus bridging $\text{Cl}(1s \rightarrow 3p)$ transition dipole is $I(\text{Cl}^b) = 29.7$ units

Pre-edge feature for $[\text{Bi}(\text{Tm}^{t\text{Bu}})(\text{Cl})(\mu\text{-Cl})]_2$ at 2821.8 eV of 1.60 unit intensity is due to $\text{Cl}^t(1s \rightarrow 3p)$
thus total terminal Cl donation is 0.36 e for 4 absorbers

Pre-edge feature for $[\text{Bi}(\text{Tm}^{t\text{Bu}})(\text{Cl})(\mu\text{-Cl})]_2$ at 2823.1 eV of 0.89 unit intensity is due to $\text{Cl}^b(1s \rightarrow 3p)$
thus total terminal Cl donation is 0.18 e for 4 absorbers

S K-edge - following procedures outlined in (Queen *et al.*, 2014)

Step 1: free ligand-based transition dipole integral (I^L)

Inflection point after the last resolved/assigned rising-edge feature: 2474.4 eV

Chemical shift relative to the sulphide ligand: $\Delta E^L = 2.7$ eV

$$I^L = 0.36 (\Delta E^L)^2 + 4.5 = 7.12 \text{ units}$$

Step 2: coordinated ligand-based transition dipole integral (I^C)

Chemical shift between the free and coordinated $\text{Tm}^{t\text{Bu}}$ ligand: $\Delta E^{L \rightarrow C} = 0.2$ eV

$$\text{A 'slope' parameter} = 3.2 (\Delta E^L) + 2.3 = 10.9$$

$$I^C = I^L + \text{slope} (\Delta E^{L \rightarrow C}) = 9.3 \text{ units}$$

Step 3: correction for the presence of extensive N-based conjugation ($I^{C(N)}$)

$$I^{C(N)} = 19.3 \text{ units}$$

Pre-edge feature for $[\text{Bi}(\text{Tm}^{t\text{Bu}})(\text{Cl})(\mu\text{-Cl})]_2$ at 2471.5 eV of 1.01 unit intensity is due to $\text{S}(1s \rightarrow 3p)$
thus total S donation is 0.95e for 6 absorbers

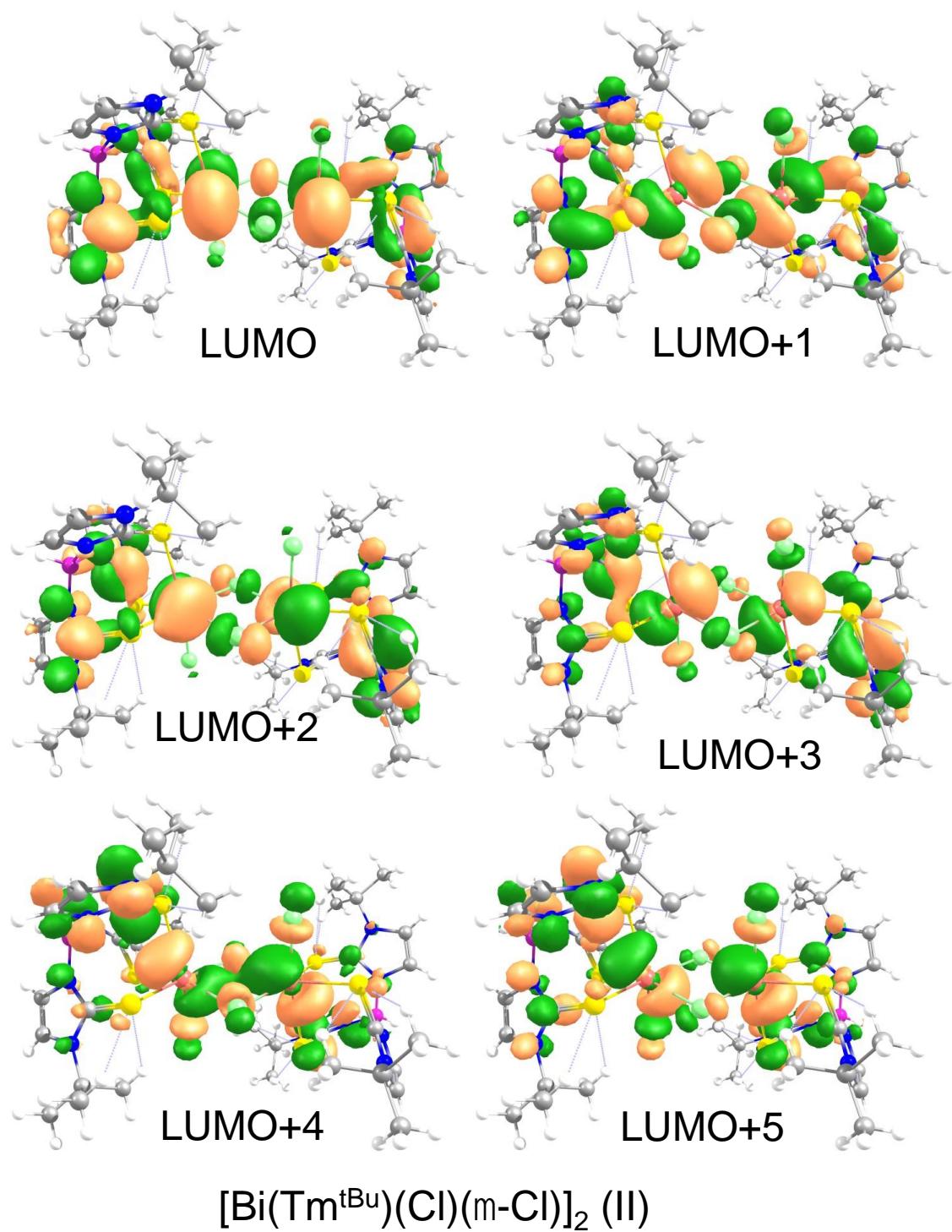


Figure S4 Frontier unoccupied orbitals probed by ligand K-edge XAS for the binuclear complex (II)

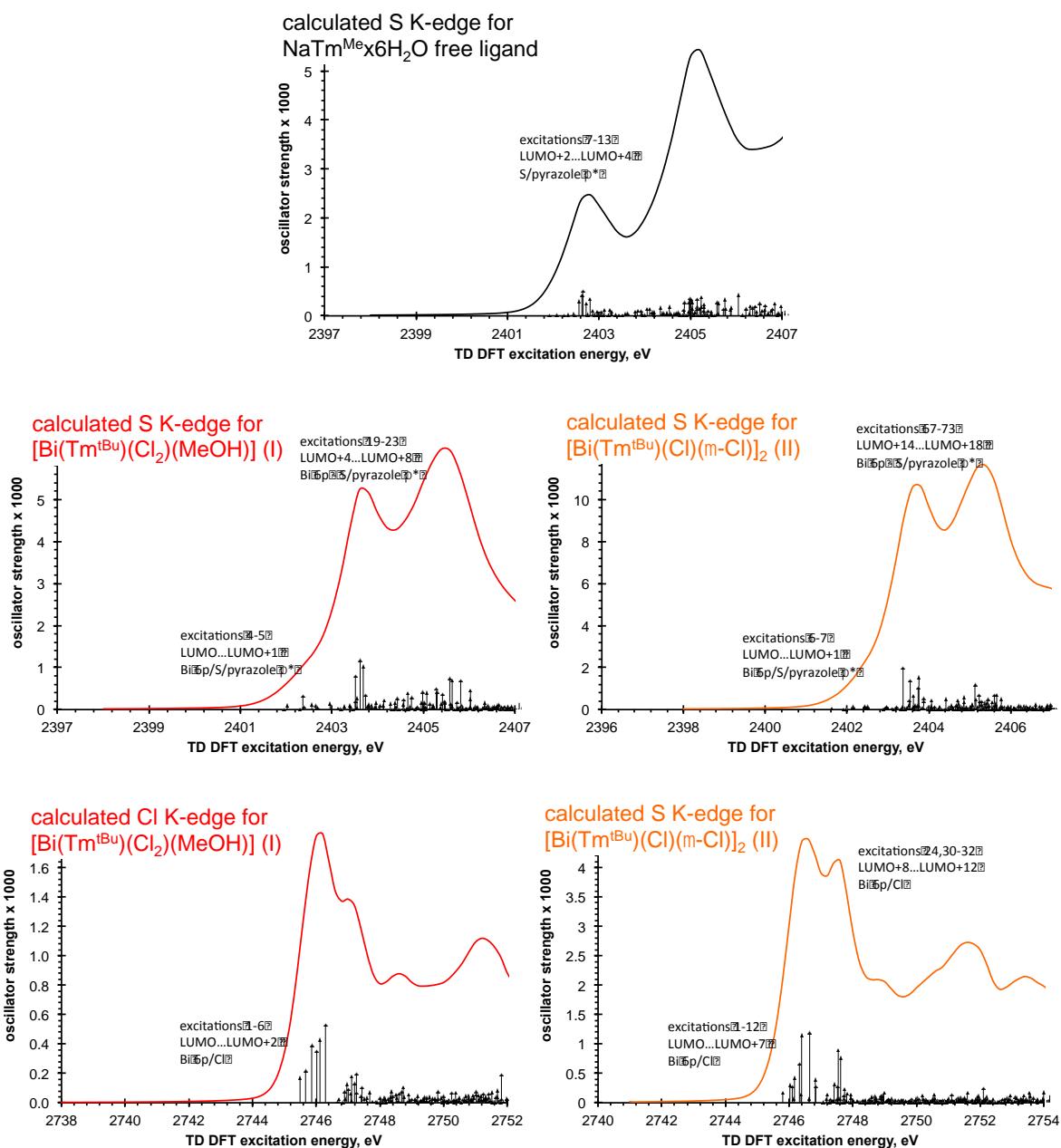
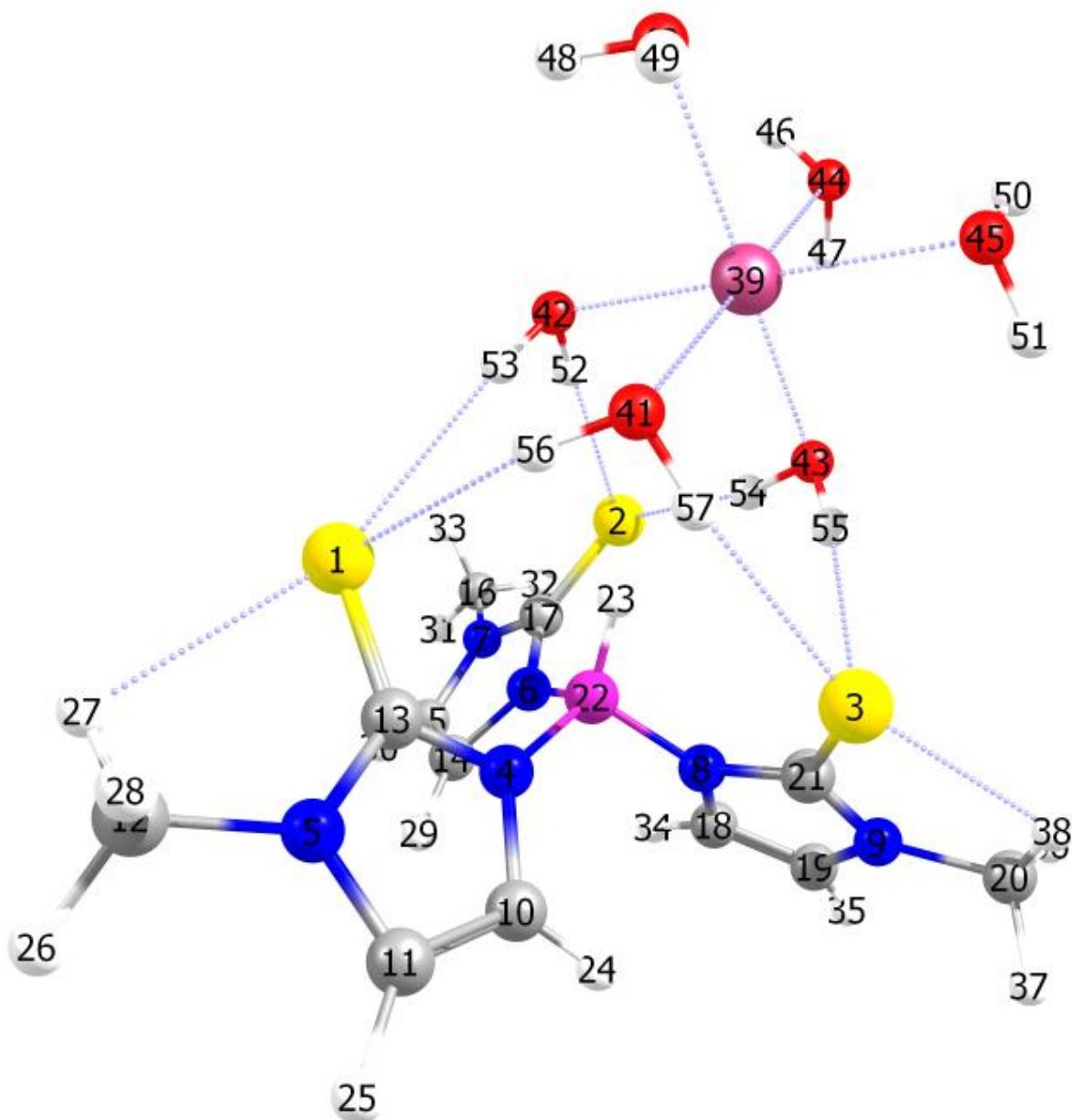


Figure S5 Calculated core level excited state spectra using the TD-DFT formalism at BP86/def2TZVP level for the S K- and Cl K-edge excitations of the mononuclear complex (I) and binuclear complex (II)

Atomic positional coordinates for the $\text{NaTm}^{\text{tBu}} \times 6\text{H}_2\text{O}$ ligand with optimized H positions at BP86/def2TZVP level.

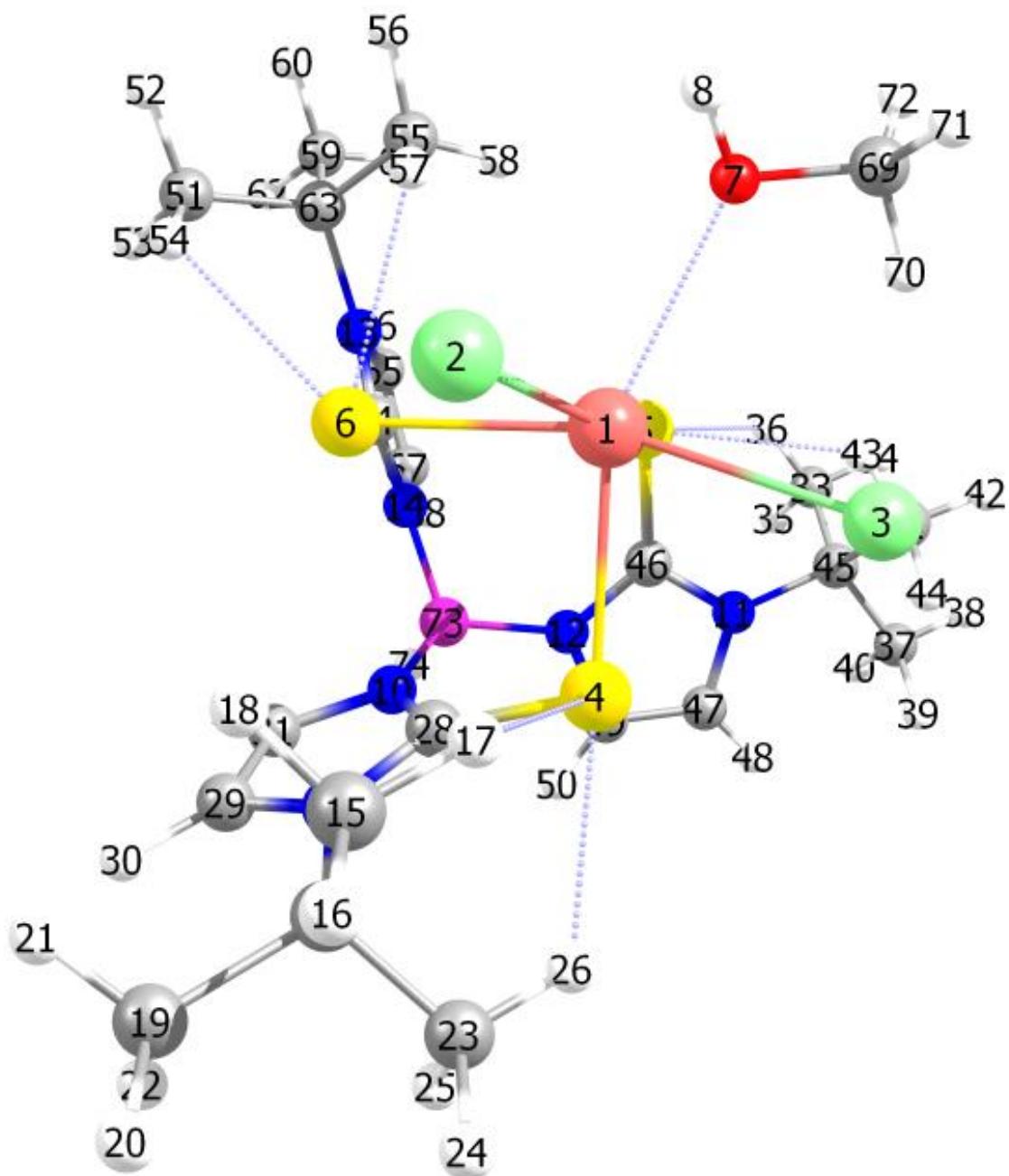


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free ligand salt - NaTmMex6H2O

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S	-0.119174000	-1.655019000	-2.527583000
S	-0.694068000	2.816269000	0.486684000
N	1.720279000	0.283906000	1.358404000
N	2.116770000	-0.169250000	3.450733000
N	1.911633000	-0.918652000	-0.832245000
N	2.402462000	-2.558088000	-2.191715000
N	1.344903000	1.526058000	-0.797402000
N	1.069445000	3.577018000	-1.462672000
C	2.523711000	1.276981000	1.869625000
C	2.738026000	1.015730000	3.167766000
C	2.062383000	-0.851007000	4.778526000
C	1.472331000	-0.608052000	2.344919000
C	3.227579000	-1.327622000	-0.602637000
C	3.522240000	-2.333623000	-1.424508000
C	2.298424000	-3.566299000	-3.236321000
C	1.429261000	-1.712665000	-1.836326000
C	2.292203000	1.797317000	-1.755885000
C	2.111303000	3.071383000	-2.153684000
C	0.533201000	4.932445000	-1.559154000
C	0.587559000	2.628894000	-0.608167000
B	1.137083000	0.169718000	-0.075097000
H	-0.028824000	-0.107839000	-0.026718000
H	2.839442000	2.124492000	1.273278000
H	3.309271000	1.560162000	3.911449000
H	3.037313000	-0.742839000	5.269868000
H	1.826733000	-1.904869000	4.589417000
H	1.272569000	-0.405935000	5.399584000
H	3.830472000	-0.869921000	0.173513000
H	4.427027000	-2.918702000	-1.540401000
H	3.293713000	-3.993231000	-3.407179000
H	1.918597000	-3.105741000	-4.158228000
H	1.598529000	-4.360185000	-2.938818000
H	3.006246000	1.054763000	-2.088614000
H	2.645134000	3.653366000	-2.897416000
H	0.273529000	5.161268000	-2.602234000
H	1.268083000	5.665106000	-1.194528000
H	-0.365067000	4.967581000	-0.929517000
Na	-3.704523000	-0.433694000	0.124715000
O	-5.129092000	-1.532872000	1.710292000
O	-2.244205000	0.070324000	2.014940000
O	-2.390323000	-2.437389000	-0.029446000
O	-2.279721000	0.665202000	-1.460990000
O	-5.164590000	-0.937986000	-1.765690000
O	-5.018532000	1.569838000	0.278823000
H	-5.425449000	-1.871847000	-1.835181000
H	-4.511254000	-0.796149000	-2.475048000
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H	-4.463623000	2.321139000	0.003147000
H	-1.827703000	-2.405158000	-0.841566000
H	-1.702084000	-2.324153000	0.663516000
H	-1.536306000	0.069457000	-1.736253000
H	-1.822585000	1.372965000	-0.939100000
H	-1.515006000	-0.570455000	2.204987000
H	-1.745928000	0.852117000	1.678299000

Atomic positional coordinates for mononuclear $[\text{Bi}(\text{Tm}^{\text{tBu}})\text{Cl}_2(\text{MeOH})]$ complex (I) with optimized H positions at BP86/def2TZVP level.



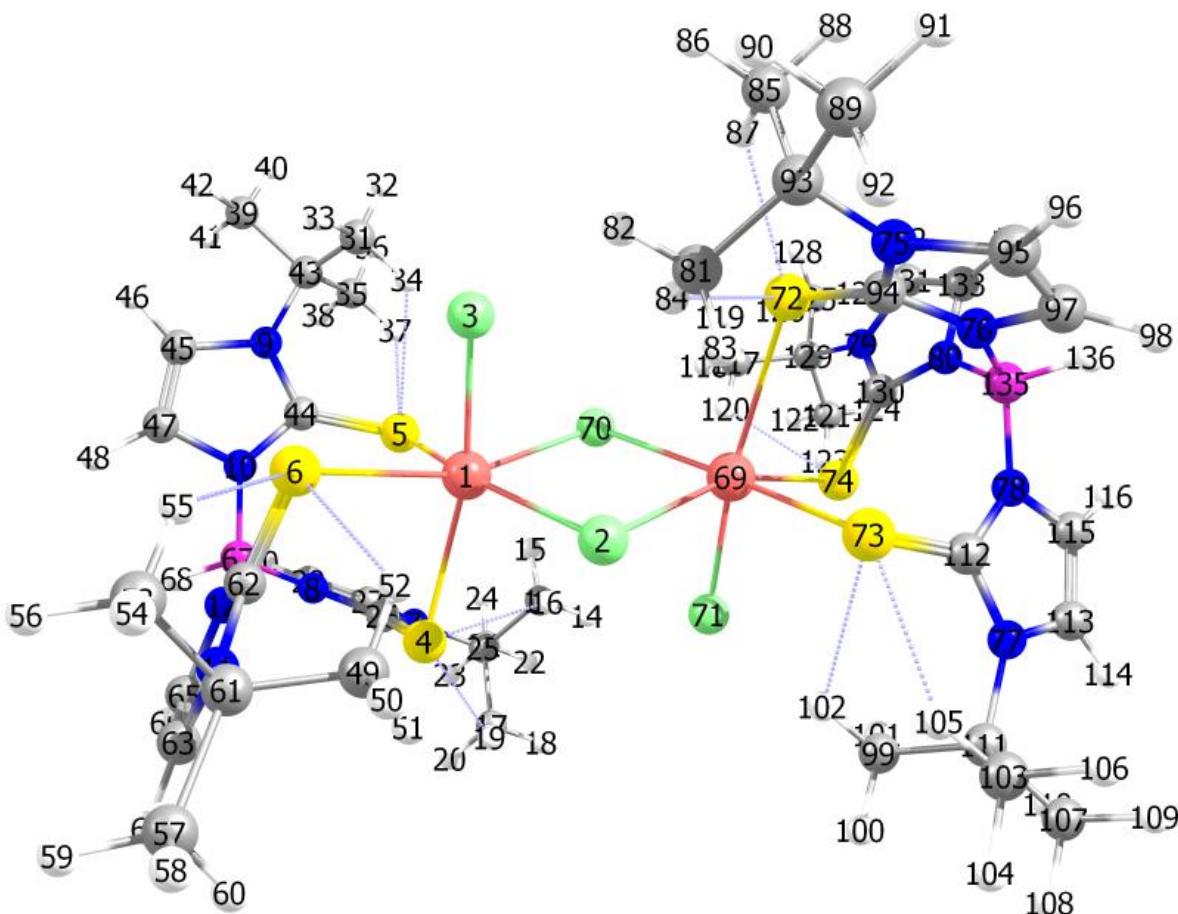
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mononuclear - $[\text{Bi}(\text{TmtBu})(\text{Cl})_2(\text{MeOH})]$			
Bi	-0.014896000	0.014943000	1.466343000
Cl	-2.041037000	1.004574000	2.938988000
Cl	0.124942000	-2.373817000	2.821307000
S	-1.336852000	-1.710794000	-0.042875000
S	2.182546000	-0.087922000	-0.315198000
S	-0.991335000	2.036580000	-0.076713000
O	2.218696000	0.825120000	2.952496000
H	1.924302000	1.500002000	3.589819000

N	-3.553297000	-0.584112000	-1.250637000
N	-1.663334000	-0.105297000	-2.264545000
N	2.224487000	-2.512220000	-1.616847000
N	0.718422000	-1.112505000	-2.403210000
N	1.090857000	3.288113000	-1.383537000
N	0.387444000	1.455695000	-2.382267000
C	-4.425645000	-0.750452000	1.072295000
H	-5.240904000	-1.158368000	1.688829000
H	-3.475302000	-1.086727000	1.499165000
H	-4.453875000	0.345172000	1.145895000
C	-5.990543000	-0.766967000	-0.855577000
H	-6.744030000	-1.243544000	-0.214039000
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H	-6.195864000	-1.078368000	-1.890744000
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H	-5.300137000	-3.206253000	0.096507000
H	-4.642529000	-3.046001000	-1.551586000
H	-3.542000000	-3.106969000	-0.142058000
C	-4.612978000	-1.216202000	-0.366329000
C	-2.205305000	-0.769445000	-1.218056000
C	-3.845800000	0.243210000	-2.322523000
H	-4.852760000	0.548581000	-2.565977000
C	-2.690944000	0.529974000	-2.938675000
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H	2.496970000	3.214870000	0.903194000
C	2.394853000	5.330070000	-0.913680000
H	2.502347000	6.164712000	-0.207152000
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C	0.206001000	2.259667000	-1.302883000
C	1.848217000	3.121003000	-2.535805000
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C	1.408102000	2.007088000	-3.140896000
H	1.741964000	1.534393000	-4.057545000
C	3.015903000	-0.125123000	3.642703000

H	3.042680000	-1.027739000	3.016636000
H	2.575385000	-0.407166000	4.611817000
H	4.044196000	0.249769000	3.792732000
B	-0.207233000	0.087120000	-2.782654000
H	-0.280535000	0.084557000	-3.996377000

Atomic positional coordinates for the binuclear $[\text{Bi}(\text{Tm}^{\text{tBu}})(\text{Cl})(\mu\text{-Cl})]_2$ complex (II) with optimized H positions at BP86/def2TZVP level.



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binuclear - $[\text{Bi}(\text{TmtBu})(\text{Cl})(\mu\text{-Cl})]_2$		
Bi	-0.860488000	-0.808138000
Cl	-1.533625000	1.317183000
Cl	0.508216000	0.979915000
S	-2.979848000	-2.553618000
S	0.127594000	-2.994683000
S	-2.473311000	-0.249286000
N	-2.106496000	-5.171203000
N	-2.716452000	-4.411833000
N	0.078601000	-2.749303000
N	-1.892881000	-3.192237000
N	-5.137161000	-0.606582000
N	-4.101656000	-2.460589000
C	-0.680963000	-4.291475000
H	-0.372129000	-4.443928000
H	0.199208000	-4.435654000
H	-1.014451000	-3.253019000
C	-3.057885000	-5.055063000

H	-2.823795000	-5.155518000	2.557283000
H	-3.461201000	-4.049347000	1.318019000
H	-3.828275000	-5.798836000	1.230925000
C	-1.289166000	-6.708376000	0.950577000
H	-1.072674000	-6.784690000	2.024768000
H	-2.044740000	-7.472037000	0.711389000
H	-0.357444000	-6.938993000	0.412697000
C	-1.785193000	-5.288033000	0.672878000
C	-2.583234000	-4.071695000	-1.457450000
C	-1.938149000	-6.186536000	-1.715904000
H	-1.572689000	-7.165977000	-1.442017000
C	-2.314109000	-5.724796000	-2.911359000
H	-2.332465000	-6.215941000	-3.877293000
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H	1.303345000	-0.353900000	-5.862791000
H	1.745054000	-1.095159000	-4.316087000
C	2.378899000	-3.630872000	-5.327769000
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H	2.255014000	-3.652833000	-4.239391000
H	2.095118000	-4.612203000	-5.738251000
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H	2.943037000	-2.392123000	-7.604283000
H	1.583024000	-3.481149000	-7.947961000
H	1.367690000	-1.700897000	-8.013626000
C	1.561889000	-2.508666000	-5.971366000
C	-0.586363000	-2.981032000	-4.595631000
C	-0.851099000	-2.771136000	-6.792780000
H	-0.581314000	-2.610095000	-7.826593000
C	-2.050378000	-3.048172000	-6.253197000
H	-3.018901000	-3.166125000	-6.724532000
C	-4.638473000	1.313013000	-1.667234000
H	-4.942228000	2.335321000	-1.396017000
H	-4.797051000	0.667322000	-0.791919000
H	-3.567057000	1.331905000	-1.890250000
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H	-5.498513000	2.711593000	-3.919114000
H	-4.166784000	1.638512000	-4.410738000
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H	-7.604247000	0.595632000	-3.319348000
H	-7.200110000	0.369226000	-1.585205000
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C	-3.939649000	-1.129216000	-3.533458000
C	-6.049100000	-1.644774000	-3.046792000
H	-7.076888000	-1.496910000	-2.750105000
C	-5.412117000	-2.771801000	-3.400390000
H	-5.773380000	-3.792365000	-3.449990000
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Bi	0.860488000	0.808138000	1.728075000
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S	-0.127594000	2.994683000	3.013942000
S	2.473311000	0.249286000	3.811312000
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N	1.892881000	3.192237000	4.886544000

N	5.137161000	0.606582000	3.143399000
N	4.101656000	2.460589000	3.705713000
C	0.680963000	4.291475000	-1.024841000
H	0.372129000	4.443928000	-2.069355000
H	-0.199208000	4.435654000	-0.382190000
H	1.014451000	3.253019000	-0.933140000
C	3.057885000	5.055063000	-1.487324000
H	2.823795000	5.155518000	-2.557283000
H	3.461201000	4.049347000	-1.318019000
H	3.828275000	5.798836000	-1.230925000
C	1.289166000	6.708376000	-0.950577000
H	1.072674000	6.784690000	-2.024768000
H	2.044740000	7.472037000	-0.711389000
H	0.357444000	6.938993000	-0.412697000
C	1.785193000	5.288033000	-0.672878000
C	2.583234000	4.071695000	1.457450000
C	1.938149000	6.186536000	1.715904000
H	1.572689000	7.165977000	1.442017000
C	2.314109000	5.724796000	2.911359000
H	2.332465000	6.215941000	3.877293000
C	-1.908876000	1.144469000	5.398140000
H	-2.969951000	0.924919000	5.593676000
H	-1.303345000	0.353900000	5.862791000
H	-1.745054000	1.095159000	4.316087000
C	-2.378899000	3.630872000	5.327769000
H	-3.442336000	3.462098000	5.551966000
H	-2.255014000	3.652833000	4.239391000
H	-2.095118000	4.612203000	5.738251000
C	-1.860425000	2.525618000	7.478053000
H	-2.943037000	2.392123000	7.604283000
H	-1.583024000	3.481149000	7.947961000
H	-1.367690000	1.700897000	8.013626000
C	-1.561889000	2.508666000	5.971366000
C	0.586363000	2.981032000	4.595631000
C	0.851099000	2.771136000	6.792780000
H	0.581314000	2.610095000	7.826593000
C	2.050378000	3.048172000	6.253197000
H	3.018901000	3.166125000	6.724532000
C	4.638473000	-1.313013000	1.667234000
H	4.942228000	-2.335321000	1.396017000
H	4.797051000	-0.667322000	0.791919000
H	3.567057000	-1.331905000	1.890250000
C	5.222412000	-1.664538000	4.113537000
H	5.498513000	-2.711593000	3.919114000
H	4.166784000	-1.638512000	4.410738000
H	5.837404000	-1.298129000	4.949738000
C	6.952776000	-0.930289000	2.498343000
H	7.185934000	-1.985930000	2.303183000
H	7.604247000	-0.595632000	3.319348000
H	7.200110000	-0.369226000	1.585205000
C	5.470195000	-0.837578000	2.853544000
C	3.939649000	1.129216000	3.533458000
C	6.049100000	1.644774000	3.046792000
H	7.076888000	1.496910000	2.750105000
C	5.412117000	2.771801000	3.400390000
H	5.773380000	3.792365000	3.449990000
B	3.125377000	3.617794000	4.034683000
H	3.751002000	4.393701000	4.733668000