SUPPORTING INFORMATION

Covalent Bonding and the Trans Influence in Lanthanide Compounds

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1. Complete Reference 47

Gaussian 03, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

2. Optimized geometries of 1 and 2 using PBE exchange-correlation functionals and ECP's/BasisII as described in the text.

(THF)3Yb(SC6F5)3 , molecule **1,** PBE/BasisII optimized

Charge = 0 Multiplicity = 1

Yb,0,-0.133857246,-0.4741043024,0.1744969447
S,0,-1.8598494881,-2.5613049386,0.1768965732
S,0,-2.036527926,1.3342908731,-0.2019335994
S,0,1.9625375831,1.2518329366,0.158025861
F,0,-2.8519819784,-1.4078437574,-2.4727255104
F,0,-5.2544526909,-0.2718139761,-2.9874104088
F,0,-7.1531693623,-0.0576119706,-0.9987410268
F,0,-6.5956189621,-1.0127079622,1.5250068715
F,0,-4.1937008766,-2.1467587916,2.0654421723
F,0,-1.099151177,3.1692063749,-2.4296878891
F,0,0.3622926144,5.4402673739,-2.2215074259
F,0,1.1955954384,6.3428438406,0.243975487
F,0,0.5177690917,4.9296746509,2.5139199172
F,0,-0.9475096845,2.6614919198,2.3283805002
F,0,3.7915092222,0.0605408162,2.2807425065
F,0,6.1329819932,-1.2419068417,1.9189902378
F,0,7.106235498,-1.6926264944,-0.6226384775
F,0,3.3332180765,0.5094643865,-2.4682390756
C,0,-3.4124882609,-1.8064575524,-0.1755182073
C,0,-3.7512005062,-1.3245704719,-1.4605021188
C,0,-4.991799688,-0.7389900468,-1.7501694139
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C,0,3.4449670054,0.3373673498,-0.0762613941
C,0,4.2220199456,-0.1300825031,1.0112758748
C,0,5.4409047383,-0.8057721547,0.8448510304
C,0,5.9402769141,-1.0409524419,-0.4485472539
C,0,5.2041732144,-0.5860180619,-1.5569847828
C,0,3.9902284666,0.0916088525,-1.3598588733
O,0,0.2730268029,-0.899985563,-2.0915109121
O,0,1.302098724,-2.3281784116,0.8476684734
O,0,-0.3321472626,-0.3216598065,2.5005862082
C,0,0.2239969323,0.2409318443,-3.0316748765
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H,0,1.7164272486,-0.4363012969,-4.4605729631
C,0,-0.0401492933,-1.7443148403,-4.3100591938
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C,0,0.199785386,-2.1544439867,-2.8547419198
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H,0,1.2764788138,-4.6027521052,-0.952279545
H,0,2.7453815433,-5.1326303882,-0.0864204816
C,0,1.0077555058,-4.6615114416,1.2310816717
H,0,-0.0155981011,-4.9634758006,0.9555559935
H,0,1.4273972029,-5.4260028554,1.9059489991
C,0,0.9886466699,-3.2795280846,1.907727266
H,0,0.0100711355,-2.9953881254,2.32232532
H,0,1.7728256252,-3.1903873325,2.6859744655
C,0,0.7304877532,0.0274217437,3.4504176833
H,0,1.0230467311,1.0765259251,3.2691777029
H,0,1.5935865344,-0.6217977992,3.2368663333
C,0,-1.3549875881,0.2488645906,4.585123871
H,0,-1.4396665788,1.3492511279,4.5897212015
H,0,-2.0539878007,-0.1596481788,5.3340000239
C,0,0.1056795879,-0.1773052656,4.8277967838
H,0,0.1571437869,-1.2407086717,5.1269984899
H,0,0.6099532338,0.4273043096,5.600186502
C,0,-1.6381670653,-0.3056452364,3.1882119772
H,0,-2.3182708786,0.3181369426,2.5850726445
H,0,-2.0111030564,-1.3446031635,3.2045006411
F,0,5.6706097064,-0.802601143,-2.8047839064

(THF)3Er(SeC6F5)3, molecule **2,** PBE/BasisII optimized

Charge = 0 Multiplicity = 1
F,0,-2.8299423048,-1.9780439935,-2.5398603727
F,0,-5.2595517546,-0.9120462768,-3.0808194336
F,0,-7.0401132682,-0.3933209914,-1.0418696653
F,0,-6.3392985867,-0.9617370683,1.5607712025
F,0,-3.9121962955,-2.0268093771,2.1261383138
F,0,-1.6798238934,3.2900571315,-2.2527293591
F,0,-0.2859732118,5.6103025231,-2.1870500118
F,0,0.8722450858,6.4771644347,0.1550818287
F,0,0.5898997905,4.9798393845,2.4541432195
F,0,-0.8116004638,2.6654801361,2.4156399485
F,0,4.1061317293,-0.0105709936,2.0842976871
F,0,6.2556998242,-1.535083223,1.4832026245
F,0,6.9605255798,-1.9853502007,-1.144715737
F,0,3.3099906641,0.6710195425,-2.5921499209
C,0,-3.265574186,-2.0304174938,-0.182245644
C,0,-3.6692948322,-1.7412064889,-1.5016262571
C,0,-4.9258250951,-1.1951594414,-1.8051162977
C,0,-5.8362792812,-0.9282300009,-0.7679680588
C,0,-5.4744384129,-1.2197135716,0.5589550192
C,0,-4.2095945714,-1.7649160601,0.8317182208
C,0,-1.2584666275,2.8515133843,0.0663948126
C,0,-1.1197270187,3.6639453625,-1.0797577421
C,0,-0.411544196,4.8759319497,-1.0637620974
C,0,0.1784768382,5.3252017377,0.1314133428
C,0,0.0347112884,4.5582070155,1.2997719745
C,0,-0.6823960395,3.3522315697,1.2523632706
C,0,3.5990436995,0.3853168034,-0.227589889
C,0,4.4053282833,-0.1940466352,0.7754322705
C,0,5.5287485521,-0.9857642467,0.4865226889
C,0,5.8908361868,-1.2212913849,-0.8520618779
C,0,5.1177867449,-0.6530818188,-1.8802018161
C,0,4.0035858852,0.140025156,-1.5575947949
O,0,0.3049122032,-0.5952176563,-2.1129439031
O,0,1.5827335965,-2.246250022,0.8065856056
O,0,-0.0327352689,-0.2845805849,2.6068544959
C,0,0.1086278621,0.6138736138,-2.9465072763
H,0,0.7993615523,1.3817967314,-2.5626672319
H,0,-0.936035995,0.9392815324,-2.8029370249
C,0,0.3845832239,0.1636176042,-4.3781801481
H,0,-0.1597732148,0.7854245932,-5.1083643254
H,0,1.4644955311,0.2167132455,-4.6038344891
C,0,-0.0987965758,-1.2984145436,-4.3560007949
H,0,0.3242952598,-1.9080284083,-5.1721742934
H,0,-1.199769401,-1.347049735,-4.410154787
C,0,0.3871542391,-1.7704508847,-2.9874085692
H,0,-0.2240849867,-2.5667402836,-2.5303110366

H,0,1.449206595,-2.0829626984,-3.0376865405
C,0,2.3679368597,-3.0415598354,-0.1230260881
H,0,3.4378702313,-2.9274643661,0.1393406222
H,0,2.2041751515,-2.6398864895,-1.1339827541
C,0,1.878079474,-4.4794313715,0.0843507868
H,0,1.0057834484,-4.6809904575,-0.5596960264
H,0,2.6656116422,-5.2137638396,-0.1536541126
C,0,1.4579365011,-4.5073474046,1.5838143719
H,0,0.4248909584,-4.8755471761,1.6906449818
H,0,2.1195362683,-5.1484746364,2.1900015626
C,0,1.563381809,-3.0356024311,2.0331285066
H,0,0.7110242747,-2.6827374887,2.631680014
H,0,2.5091001419,-2.8387096097,2.5757350526
C,0,1.0430933458,0.1975446401,3.4862201054
H,0,1.1733354224,1.2781479823,3.3032506449
H,0,1.9687661223,-0.3221923645,3.196001875
C,0,-0.962512229,0.1282334494,4.7685934984
H,0,-1.1927251463,1.2079600512,4.7747437339
H,0,-1.5463576942,-0.3599774458,5.5667003124
C,0,0.5552705054,-0.096528468,4.9021598568
H,0,0.7707796015,-1.1439781173,5.184707834
H,0,1.0290348451,0.568794485,5.643224497
C,0,-1.2653195583,-0.4742743993,3.3971958767
H,0,-2.0883919531,0.0213076872,2.8573837571
H,0,-1.4663172921,-1.5605078455,3.4419330157
F,0,5.4537035548,-0.8715810501,-3.1690152136
Er,0,0.0144819726,-0.4139007993,0.2353958198
Se,0,-2.2627209778,1.2124676654,0.0158637553
Se,0,2.1263066922,1.5353869024,0.1927265015
Se,0,-1.5554684745,-2.8016748479,0.2130485633

Table S-1. Comparison of Computed (DFT) Metal-Ligand Bond Lengths [Å] for $(THF)_3Yb(SC_6F_5)_3$ and $(THF)_3Er(SeC_6F_5)_3$ Using Different Functionals and the Large Basis Set (BasisII) Described in the Text.

	PBE	TPSS	B3LYP	M05	X-Ray[a]
Yb(1)-O(1)	2.339	2.329	2.342	2.353	2.271
Yb(1)-O(2)	2.440	2.406	2.418	2.475	2.308
Yb(1)-O(3)	2.341	2.334	2.344	2.370	2.280
Yb(1)-S(1)	2.708	2.716	2.728	2.713	2.678
Yb(1)-S(2)	2.652	2.667	2.665	2.654	2.642
Yb(1)-S(3)	2.716	2.719	2.729	2.718	2.680
$\Delta_{Yb\text{-}O}$[b]	0.100	0.075	0.075	0.114	0.033
$\Delta_{Yb\text{-}S}$[c]	-0.060	-0.051	-0.063	-0.062	-0.037
Er(4)-O(12)	2.373	2.364	2.375	2.398	2.304
Er(4)-O(11)	2.478	2.445	2.451	2.515	2.337
Er(4)-O(10)	2.375	2.364	2.377	2.406	2.310
Er(4)-Se(12)	2.858	2.868	2.883	2.881	2.828
Er(4)-Se(11)	2.807	2.823	2.824	2.825	2.802
Er(4)-Se(10)	2.874	2.889	2.893	2.888	2.833
$\Delta_{Er\text{-}O}$[b]	0.104	0.081	0.075	0.113	0.030
$\Delta_{Er\text{-}Se}$[c]	-0.059	-0.056	-0.064	-0.060	-0.029

[a] Comparison is made to Molecule 4 in the unit cell of **2**, because the conformation of this molecule shows the strongest similarity to the conformation of **1.** [b] $\Delta_{Ln\text{-}O}$ = (Ln-O bond length when trans to anionic E) - (average Ln-O bond length when trans to THF). [c] $\Delta_{Ln\text{-}E}$ = (Ln-E bond length when trans to THF) - (average Ln-E bond length when trans to anionic E).

Table S-2. Comparison of Computed (DFT) Metal-Ligand Bond Lengths [Å] for $(THF)_3Yb(SC_6F_5)_3$ and $(THF)_3Er(SeC_6F_5)_3$ Using Different Functionals and Smaller Basis Set (BasisI) Described in the Text.

	PBE	TPSS	B3LYP	M05	X-Ray[a]
Yb(1)-O(1)	2.331	2.319	2.332	2.344	2.271
Yb(1)-O(2)	2.410	2.380	2.394	2.443	2.308
Yb(1)-O(3)	2.344	2.334	2.346	2.363	2.280
Yb(1)-S(1)	2.728	2.736	2.736	2.740	2.678
Yb(1)-S(2)	2.680	2.692	2.693	2.689	2.642
Yb(1)-S(3)	2.728	2.737	2.744	2.741	2.680
$\Delta_{Yb\text{-}O}$[b]	0.073	0.054	0.055	0.090	0.033
$\Delta_{Yb\text{-}S}$[c]	-0.048	-0.044	-0.047	-0.052	-0.037
Er(4)-O(12)	2.369	2.356	2.368	2.382	2.304
Er(4)-O(11)	2.444	2.411	2.427	2.473	2.337
Er(4)-O(10)	2.370	2.364	2.381	2.399	2.310
Er(4)-Se(12)	2.877	2.887	2.897	2.898	2.828
Er(4)-Se(11)	2.842	2.856	2.859	2.852	2.802
Er(4)-Se(10)	2.896	2.908	2.910	2.911	2.833
$\Delta_{Er\text{-}O}$[b]	0.073	0.051	0.053	0.083	0.030
$\Delta_{Er\text{-}Se}$[c]	-0.045	-0.042	-0.045	-0.053	-0.029

[a]Comparison is made to molecule 4 in the unit cell of **2** (see text). [b]$\Delta_{Ln\text{-}O}$ = (Ln-O bond length when trans to anionic E) - (average Ln-O bond length when trans to THF). [c]$\Delta_{Ln\text{-}E}$ = (Ln-E bond length when trans to THF) - (average Ln-E bond length when trans to anionic E).

Table S-3. Comparison of Computed (PBE/BasisI) Metal-Ligand Bond Lengths [Å] for $(THF)_3Yb(SC_6F_5)_3$ and $(THF)_3Er(SeC_6F_5)_3$ with Modified Yb or Er Basis Sets.

Removal of d-type basis functions from Yb

Yb basis set	[5s4p3d]	[5s4p2d]	[5s4p1d]	[5s4p]	[5s4p2d][c]
Yb(1)-O(1)	2.331	2.331	2.303	2.399	2.389
Yb(1)-O(2)	2.410	2.410	2.373	2.410	2.429
Yb(1)-O(3)	2.344	2.343	2.321	2.383	2.400
Yb(1)-S(1)	2.728	2.728	2.735	2.877	2.806
Yb(1)-S(2)	2.680	2.681	2.691	2.867	2.780
Yb(1)-S(3)	2.728	2.729	2.737	2.874	2.797
$\Delta_{Yb\text{-}O}$[a]	0.073	0.073	0.061	0.019	0.035
$\Delta_{Yb\text{-}S}$[b]	-0.048	-0.047	-0.045	-0.008	-0.021

Removal of p-type basis functions from Yb

Yb basis set	[5s4p3d]	[5s3p3d]	[5s2p3d]	[5s1p3d]
Yb(1)-O(1)	2.331	2.331	2.327	2.322
Yb(1)-O(2)	2.410	2.410	2.393	2.388
Yb(1)-O(3)	2.344	2.344	2.341	2.337
Yb(1)-S(1)	2.728	2.727	2.723	2.717
Yb(1)-S(2)	2.680	2.680	2.681	2.675
Yb(1)-S(3)	2.728	2.727	2.727	2.720
$\Delta_{Yb\text{-}O}$[a]	0.073	0.072	0.059	0.059
$\Delta_{Yb\text{-}S}$[b]	-0.048	-0.047	-0.044	-0.044

Removal of s-type basis functions from Yb

Yb basis set	[5s4p3d]	[4s4p3d]	[3s4p3d]	[2s4p3d]
Yb(1)-O(1)	2.331	2.329	2.323	2.288
Yb(1)-O(2)	2.410	2.409	2.404	2.391
Yb(1)-O(3)	2.344	2.343	2.337	2.318
Yb(1)-S(1)	2.728	2.728	2.728	2.727
Yb(1)-S(2)	2.680	2.680	2.680	2.677
Yb(1)-S(3)	2.728	2.729	2.728	2.732
$\Delta_{Yb\text{-}O}$[a]	0.074	0.073	0.074	0.088
$\Delta_{Yb\text{-}S}$[b]	-0.048	-0.048	-0.048	-0.052

Addition of f-type basis functions on Yb

Yb basis set	[5s4p3d]	[5s4p3d1f]	[5s4p3d3f]	[5s4p3f]
Yb(1)-O(1)	2.331	2.319	2.322	2.372
Yb(1)-O(2)	2.410	2.398	2.405	2.397
Yb(1)-O(3)	2.344	2.332	2.335	2.374
Yb(1)-S(1)	2.728	2.722	2.719	2.864
Yb(1)-S(2)	2.680	2.677	2.674	2.850
Yb(1)-S(3)	2.728	2.724	2.719	2.860
$\Delta_{Yb\text{-}O}$[a]	0.073	0.072	0.077	0.024
$\Delta_{Yb\text{-}S}$[b]	-0.048	-0.046	-0.045	-0.012

Removal of s, p or d-type basis functions from Er

Er basis set	[5s4p3d]	[5s4p]	[5s1p3d]	[2s4p3d]
Er(4)-O(12)	2.368	2.416	2.362	2.336
Er(4)-O(11)	2.443	2.440	2.419	2.414
Er(4)-O(10)	2.370	2.430	2.363 .	2.351
Er(4)-Se(12)	2.876	3.035	2.871	2.878
Er(4)-Se(11)	2.843	3.034	2.845	2.834.
Er(4)-Se(10)	2.892	3.041	2.891	2.896
$\Delta_{Er\text{-}O}$[a]	0.074	0.017	0.057	0.071
$\Delta_{Er\text{-}Se}$[b]	-0.041	-0.004	-0.036	-0.053

[a] $\Delta_{Ln\text{-}O}$ = (Ln-O bond length when trans to anionic E) - (average Ln-O bond length when trans to THF). [b] $\Delta_{Ln\text{-}E}$ = (Ln-E bond length when trans to THF) - (average Ln-E bond length when trans to anionic E). [c] Innermost d-type basis function deleted.

Table 1. **Summary of Crystallographic Details for 1 and 2.**

Compound	**1**	**2**
Empirical formula	$C_{30}H_{24}F_{15}O_3S_3Yb$	$C_{30}H_{24}ErF_{15}O_3Se_3$
fw	986.71	1121.63
space group	$P2_1/c$	$P2_1$
a (Å)	9.581(2)	19.481(2)
b (Å)	15.885(2)	15.625(2)
c (Å)	25.035(3)	23.555(2)
β (°)	100.03(1)	105.766(2)
V ($Å^3$)	3452.3(9)	6900(1)
Z	4	8
D(calcd) (g/cm^{-3})	1.898	2.159
Temperature (K)	233(5)	100(2)
λ (Å)	0.71073	0.71073
abs coeff (mm^{-1})	3.004	5.711
R(F)[a] [I > 2 σ(I)]	0.0384	0.0433
$R_W(F^2)$[b] [I > 2 σ(I)]	0.0856	0.0966

Definitions: [a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$