Reactions of Lanthanide Atoms with Oxygen Difluoride and the Role of the Ln Oxidation State

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Table. Calculated DFT NBO Analysis for $OTbF_2$ and $OPrF_2$.

Bond	M pop %	M(%6s)	M(%5d)	M(%4f)	F/O pop%	F/O(%2s)	F/O(%2p)
$OTbF_2$ BP86 [a]							
Tb-O σ α	11		96		89	22	78
Tb-F σ β	10	17s	59	22	90	12	88
Tb-O π β	18		44	54	82		100
Tb-O σ β	58	63s	25	11	42		100
Tb-O π β	17		35	63	83	0	100
$OPrF_2$ B3LYP							
Pr-O π α	19		31	67	81		100
Pr-O σ α	37		29	69	63	6	94
Pr-O π α	19		49	50	81		100
Pr-O π β	15		55	44	85		100
Pr-O σ β	25		49	50	75	12	88
Pr-O π β	14		39	59	86		100

[a] The B3LYP analysis is essentially the same.

Table S2. Cartesian coordinates for optimized geometries in Å.

$^{1}CeOF_2$

E = -750.359193 Hartree

CE	-0.097920	0.115440	0.000000
F	-0.097920	-1.076921	1.717868
F	-0.097920	-1.076921	-1.717868
O	0.930241	1.586134	0.000000

$^{5}DyOF_2$

E = -1160.446091 Hartree

DY	-0.108199	0.051932	0.000000
F	-0.108199	-0.969588	1.726581
F	-0.108199	-0.969588	-1.726581
O	1.136085	1.753131	0.000000

$^{5}ErOF_2$

E = -1290.653191 Hartree

ER	-0.000001	0.006603	-0.108178
F	-1.716639	-0.936799	0.279664
F	1.716574	-0.936917	0.279663
O	0.000078	2.051809	0.290272

$^{6}EuOF_2$

E = -985.583940 Hartree

EU	-0.000066	0.078019	0.000000
F	0.000159	-1.212130	1.592047
F	0.000159	-1.212130	-1.592047
O	0.000159	2.112892	0.000000

$^{8}EuOF_2$

E = -985.580481 Hartree

EU	0.000000	0.000000	0.069602
F	0.000000	1.614292	-1.186846
F	0.000000	-1.614292	-1.186846
O	0.000000	0.000000	2.122288

$^{9}GdOF_2$

E = -1040.885833 Hartree

GD	-0.151421	0.102770	0.000000
F	-0.151421	-0.971385	1.716867
F	-0.151421	-0.971385	-1.716867
O	1.552063	1.363457	0.000000

$^{1}HfOF_2$

E = -323.832403 Hartree

HF	-0.103136	0.083344	0.000000

F	-0.103136	-0.912015	1.657531
F	-0.103136	-0.912015	-1.657531
O	1.160279	1.301939	0.000000

$^{6}HoOF_2$
E = -1223.562184 Hartree

HO	-0.121875	0.067333	0.000000
F	-0.121875	-0.970075	1.715289
F	-0.121875	-0.970075	-1.715289
O	1.294917	1.618755	0.000000

$^{2}LuOF_2$
E = -1511.456693 Hartree

LU	-0.021419	0.004672	0.000000
F	-0.021419	-0.929647	1.736388
F	-0.021419	-0.929647	-1.736388
O	0.238289	2.050240	0.000000

$^{5}NdOF_2$
E = -836.604638 Hartree

ND	-0.007763	0.035590	0.000000
F	-0.007763	-1.051540	1.771836
F	-0.007763	-1.051540	-1.771836
O	0.075692	2.099039	0.000000

$^{4}PmOF_2$
E = -883.593882 Hartree

PM	-0.103877	0.054770	0.000000
F	-0.103877	-1.014051	1.766890
F	-0.103877	-1.014051	-1.766890
O	1.025782	1.863997	0.000000

$^{6}PmOF_2$
E = -883.577249 Hartree

PM	-0.000050	0.020996	0.000000
F	-0.000050	-0.992567	1.803797
F	-0.000050	-0.992567	-1.803797
O	0.000498	2.073184	0.000000

$^{2}PrOF_2$
E = -792.226461 Hartree

PR	-0.060790	0.106260	0.000000
F	0.137946	-1.191475	1.615548
F	0.137946	-1.191475	-1.615548
O	0.137946	1.897154	0.000000

$^{5}SmOF_2$
E = -933.215888 Hartree

SM	-0.000130	0.019988	0.000000
F	-0.000130	-0.970617	1.808513
F	-0.000130	-0.970617	-1.808513
O	0.001298	2.028980	0.000000

$^{7}SmOF_2$
E = -933.216931 Hartree

SM	0.000332	-0.008723	0.000000
F	0.000332	-0.925622	1.840996
F	0.000332	-0.925622	-1.840996
O	-0.003316	2.150250	0.000000

$^{8}TbOF_2$
E = -1100.428088 Hartree

TB	-0.132072	0.097432	0.000000
F	-0.132072	-0.914080	1.744810
F	-0.132072	-0.914080	-1.744810
O	1.370252	1.265040	0.000000

$^{4}TmOF_2$
E = -1360.895122 Hartree

TM	-0.047667	0.013054	0.000000
F	-0.047667	-0.954495	1.742110
F	-0.047667	-0.954495	-1.742110
O	0.518379	2.035024	0.000000

$^{3}YbOF_2$
E = -1434.499190 Hartree

YB	-0.021155	0.006447	0.000000
F	-0.021155	-0.942035	1.742788
F	-0.021155	-0.942035	-1.742788
O	0.232709	2.063169	0.000000