Electronic Supplementary Material (ESI) for Dalton Transactions.

Computational chemical analysis of Eu(III) and Am(III) complexes with pnictogen-donor ligands using DFT calculations

Taiki Kimura,[a,b] Masashi Kaneko,[b] Masayuki Watanabe,[b] Sunao Miyashita,[a] and Satoru Nakashima*[a,c]

[a]Graduate School of Science, Hiroshima University, Japan
[b]Nuclear Science and Engineering Center, Japan Atomic Energy Agency, Japan
[c]Natural Science Center for Basic Research and Development, Japan

E-mail: snaka@hiroshima-u.ac.jp

Table S1 Data of total energy (E^{tot}) and Gibbs correction energy (G^{corr}) of each compound

Compounds	E^{tot} / kJ mol^{-1}	G^{corr} / kJ mol^{-1}	$G = E^{tot} + G^{corr}$ / kJ mol^{-1}
H_2O	-200851.6379	8.49	-200843.15
DMNE	-913063.6974	479.77	-912583.93
DMPE	-2424284.4593	431.41	-2423853.05
DMAsE	-12569220.1422	415.95	-12568804.19
DMSbE	-35136753.1158	395.12	-35136358.00
$Eu(H_2O)_8$	-30691142.4517	382.43	-30690760.02
$Eu(H_2O)_9$	-30892016.0811	437.94	-30891578.14
$Eu(DMNE)(H_2O)_6$	-31202480.2656	812.86	-31201667.40
$Eu(DMPE)(H_2O)_6$	-32713670.7291	760.28	-32712910.45
$Eu(DMAsE)(H_2O)_6$	-42858572.7519	739.88	-42857832.87
$Eu(DMSbE)(H_2O)_6$	-65426077.0168	722.01	-65425355.00
$Am(H_2O)_8$	-85840791.0149	377.49	-85840413.53
$Am(H_2O)_9$	-86041671.2177	432.85	-86041238.37
$Am(DMNE)(H_2O)_6$	-86352134.9875	806.29	-86351328.69
$Am(DMPE)(H_2O)_6$	-87863326.8582	753.34	-87862573.52
$Am(DMAsE)(H_2O)_6$	-98008226.8547	733.57	-98007493.28
$Am(DMSbE)(H_2O)_6$	-120575724.5638	713.45	-120575011.11

Table S2 Calculated ΔG values in the complexation reaction,

$[M(H_2O)_8]^{3+} + DMXE \rightarrow [M(DMXE)(H_2O)_6]^{3+} + 2H_2O$

Reactions	ΔG(M) / kJ mol^{-1}		ΔG(Am)-ΔG(Eu) / kJ mol^{-1}
	M = Eu	M = Am	
X = N	-9.75	-17.54	-7.79
X = P	16.32	6.76	-9.56
X = As	45.05	38.14	-6.91
X = Sb	76.72	74.11	-2.61

Table S3 Calculated ΔG values in the complexation reaction,

$[M(H_2O)_9]^{3+} + DMXE \rightarrow [M(DMXE)(H_2O)_6]^{3+} + 3H_2O$

($[M(DMXE)(H_2O)_6]^{3+}$ is optimized from X = N geometry)

Reactions	ΔG(M) / kJ mol^{-1}		ΔG(Am)-ΔG(Eu) / kJ mol^{-1}
	M = Eu	M = Am	
X = N	-35.50	-36.56	-1.06
X = P	-7.58	-13.02	-5.44
X = As	24.88	23.84	-1.04
X = Sb	58.04	66.92	8.88

Table S4 α-Orbital energies in valence region with PDOS and OP for $[Eu(DMNE)(H_2O)_6]^{3+}$

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-N] (x10^2)	OP [M(f)-N] (x10^2)
54	-18.8804	0.3	1.2	0.1823	0.0406
55	-18.7141	0	96.9	-0.0040	-0.0207
56	-18.3225	0.7	0.6	-0.0131	-0.0078
57	-18.1636	0.4	1.1	-0.0041	0.0065
58	-18.0825	0.6	0.5	0.0248	-0.0048
59	-18.0357	0.5	1	0.0174	-0.0042
60	-17.8126	0.5	1.7	-0.0014	-0.0027
61	-17.7473	0.3	0.6	-0.0090	-0.0018
62	-17.2648	0	97.5	0.0007	0.0206
63	-17.0379	0	94.3	-0.0064	-0.0496
64	-16.5206	0.1	93.1	0.0115	0.0288
65	-16.4893	0	94	-0.0072	0.0290
66	-16.4482	0	96.1	-0.0014	0.0116
67	-16.2953	0	0.4	-0.1139	-0.0428
68	-16.2006	0.1	1.4	0.0625	-0.0382
69	-15.8822	0.3	1.8	0.1030	0.0318
70	-15.6030	2.2	2.1	0.1740	-0.0882
71	-15.3124	1.7	0.7	-0.0179	-0.0756
72	-15.2631	1	0.5	0.0705	-0.1162
73	-15.0933	0.4	1.7	-0.0989	-0.0194
74	-14.9878	0.1	0.2	-0.0203	-0.1388
75	-14.9750	0.9	5.4	0.0055	0.0129
76	-14.8158	2.3	2.8	-0.0469	-0.0162
77	-14.7290	2.9	3.8	0.0109	0.0155
78	-14.4343	0.1	0.4	0.0388	-0.0914
79	-13.7431	0.3	0.2	-0.1052	-0.0119
80	-13.3300	0	0.1	0.0219	0.0179
81	-13.2530	0.6	0.1	0.0516	0.0190
82	-12.8598	0.8	0	-0.0915	-0.0017
83	-12.8125	0.4	0.1	-0.0959	-0.0116
84	-12.6862	0.9	0.1	-0.1130	-0.0154
85	-12.6111	0.4	0	0.1090	-0.0104
86	-12.5649	0.5	0.1	-0.0911	-0.0023

Table S4 cont.

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-N] (x10^2)	OP [M(f)-N] (x10^2)
87	-12.4620	1	0	0.0626	-0.0045
88	-12.3945	0.9	0	-0.0429	-0.0285
89	-12.3385	0.7	0	-0.0621	-0.0079
90	-12.2024	0.5	0	0.2009	0.0295
91	-12.1450	0.6	0	0.0061	0.0051
92	-11.8487	-0.1	0	0.1713	0.0949
93	-11.6383	0	0	0.2949	0.1073
94	-10.0337	2.6	0.3	2.2871	0.2122
95	-9.9316	5.7	1.4	4.2355	0.6988

Table S5 α-Orbital energies in valence region with PDOS and OP for $[Eu(DMPE)(H_2O)_6]^{3+}$

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-P] (x10^2)	OP [M(f)-P] (x10^2)
61	-18.2746	0	89.6	-0.0026	-0.0011
62	-18.2338	0.4	5.2	0.0305	-0.0017
63	-18.1941	0.6	0.9	-0.0083	-0.0006
64	-18.0754	0.5	4	0.0292	0.0047
65	-18.0520	0.3	1.3	-0.0025	-0.0048
66	-17.9005	0.8	0.7	0.3486	0.0125
67	-17.8746	0.4	0.9	0.3414	0.1388
68	-17.7840	0.5	1.3	0.0277	-0.0019
69	-17.2790	0	96.6	0.0010	-0.0207
70	-17.0640	0.7	2	0.7278	0.3454
71	-16.9864	0	94.4	0.0020	-0.0436
72	-16.4030	0	92.3	-0.0028	-0.0059
73	-16.3521	0.1	91.2	-0.0016	-0.0124
74	-16.3070	0	96.7	-0.0029	-0.0133
75	-15.8955	0.9	2.9	-0.0129	0.0014
76	-15.1853	3.9	6.4	-0.0016	0.0023
77	-15.1075	2.2	2.4	0.0102	0.0010
78	-15.0142	1.1	1.1	-0.0087	0.0011
79	-14.9780	0.7	6.1	0.0030	0.0107
80	-14.8520	0.3	0.2	0.0404	0.0339
81	-14.7940	2.7	4.4	0.0448	0.0187
82	-14.5769	-0.1	0.3	-0.0565	-0.0115
83	-14.0626	-0.1	0	-0.0744	-0.0665
84	-13.9235	0	0	-0.0112	-0.0247
85	-13.6416	0	0	-0.0154	-0.0309
86	-13.5736	-0.1	0	0.0151	-0.0292
87	-13.3306	0	0	0.0016	-0.0215
88	-13.1213	0.1	0	0.0268	-0.0111
89	-13.1107	0	0	-0.0126	-0.0037
90	-12.9885	0	0	-0.0201	-0.0171
91	-12.6968	1.7	0.1	-0.1117	-0.0057
92	-12.6519	1.1	0.2	-0.0238	-0.0001
93	-12.5869	0.9	0.1	-0.0806	-0.0056

Table S5 cont.

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-P] (x10^2)	OP [M(f)-P] (x10^2)
94	-12.5532	0.2	0	-0.0170	-0.0020
95	-12.5336	0.8	0	-0.0416	0.0011
96	-12.4473	1.3	0	-0.0366	0.0003
97	-12.2391	1	0	-0.0315	-0.0004
98	-11.4242	0	0	0.0409	0.0429
99	-11.1912	0.1	0	0.1324	0.0486
100	-10.8739	0	0	0.0199	0.1585
101	-10.8255	0	0	0.0710	0.0631
102	-9.4317	4.6	0.5	2.9756	0.3322
103	-8.5708	11.1	2.5	6.4443	1.5926

Table S6 α-Orbital energies in valence region with PDOS and OP for $[Eu(DMAsE)(H_2O)_6]^{3+}$

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-As] (x10^2)	OP [M(f)-Sb] (x10^2)
79	-18.4292	0	96.9	-0.0032	-0.0064
80	-18.2825	0.5	1.5	0.0793	-0.0068
81	-18.2523	0.7	0.5	-0.0156	0.0002
82	-18.1225	0.4	2.1	0.0183	0.0249
83	-18.0869	0.5	1.4	-0.0005	-0.0039
84	-18.0237	0.6	0.8	0.3634	0.0964
85	-17.9522	0.4	1.6	-0.0638	0.0125
86	-17.8406	0.6	0.9	0.0251	-0.0022
87	-17.4822	0.1	95.7	-0.0037	-0.0110
88	-17.2267	0	91.3	0.0354	0.0296
89	-17.1851	0.5	5.1	0.4975	0.2957
90	-16.5995	0	93.4	-0.0055	-0.0137
91	-16.5394	0.1	92.9	-0.0007	-0.0104
92	-16.5092	0	97	-0.0020	-0.0206
93	-15.9628	0.9	2.3	-0.0096	-0.0001
94	-15.2923	4.1	5.1	0.0019	0.0012
95	-15.1812	2	2	0.0052	0.0007
96	-15.0789	1	0.8	-0.0065	-0.0002
97	-15.0354	0.8	5.5	0.0019	0.0034
98	-14.8471	3.1	3.8	0.0133	0.0058
99	-14.6340	0	0	0.0112	0.0502
100	-14.2218	-0.1	0	-0.0420	-0.0025
101	-13.7837	-0.1	0	-0.0671	-0.0114
102	-13.6903	0	0	0.0067	0.0062
103	-13.4691	0	0	0.0099	-0.0152
104	-13.4457	0	0	0.0067	-0.0183
105	-13.2313	0	0	-0.0010	-0.0002
106	-13.0726	0.1	0	0.0270	-0.0198
107	-13.0617	0	0	-0.0246	-0.0143
108	-13.0370	0	0	-0.0171	-0.0054
109	-12.7711	1.7	0	-0.0643	-0.0025
110	-12.7260	1.2	0.2	-0.0179	-0.0008
111	-12.6509	0.9	0.1	-0.0649	-0.0034

Table S6 cont.

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-As] (x10^2)	OP [M(f)-Sb] (x10^2)
112	-12.5926	1	0.1	-0.0322	0.0015
113	-12.4947	0.3	0	-0.0586	-0.0008
114	-12.4821	1.1	0	-0.0121	-0.0034
115	-12.2955	0.9	0	-0.0164	-0.0002
116	-10.8244	0	0	-0.0943	0.0703
117	-10.6995	0.1	0	0.0731	0.0882
118	-10.4644	0	0	-0.3491	0.1833
119	-10.1357	0.1	0	0.0534	0.0721
120	-9.3479	3.9	0.4	2.3553	0.2513
121	-8.4110	9.7	2.2	5.3400	1.3188

Table S7 α-Orbital energies in valence region with PDOS and OP for $[Eu(DMSbE)(H_2O)_6]^{3+}$

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-Sb] (x10^2)	OP [M(f)-Sb] (x10^2)
96	-19.6613	0.1	0	0.0495	0.0342
97	-18.4725	0	96.3	-0.0032	-0.0155
98	-18.2994	0.7	1.2	0.0015	-0.0027
99	-18.2588	0.5	1.8	0.0057	0.0014
100	-18.1612	0.6	2.9	0.0168	0.0007
101	-18.1244	0.4	3.7	-0.0030	0.0004
102	-17.9979	0.5	1	-0.0001	0.0002
103	-17.8618	0.4	1.5	-0.0031	0.0001
104	-17.6635	0.1	93.7	-0.0009	-0.0084
105	-17.3437	0	96.1	0.0005	-0.0052
106	-16.7219	0.1	76.8	0.1199	0.1253
107	-16.6828	0.5	42.7	0.3809	0.1316
108	-16.6596	0.1	93.7	-0.0032	-0.0031
109	-16.6093	0	72.8	0.1072	-0.1353
110	-15.9891	1.1	0.8	0.9023	0.3078
111	-15.9657	1.2	1.5	0.0251	0.0017
112	-15.2993	4	4	-0.0070	0.0012
113	-15.2000	2.1	1.7	-0.0039	-0.0012
114	-15.1053	1.2	1.2	-0.0059	-0.0006
115	-15.0533	1	4.4	-0.0020	0.0003
116	-14.8708	3	4.3	0.0035	0.0008
117	-14.2435	0.1	0	0.1256	0.0650
118	-13.7469	-0.1	0	-0.0055	-0.0065
119	-13.4193	-0.2	0	-0.0564	0.0123
120	-13.3964	0	0	0.0283	0.0242
121	-13.2533	0	0	0.0152	-0.0056
122	-13.2250	0	0	0.0022	-0.0069
123	-13.0822	0	0	0.0173	0.0019
124	-13.0109	0	0	0.0067	-0.0100
125	-12.9741	0	0	0.0054	-0.0024
126	-12.9578	-0.1	0	-0.0351	-0.0155
127	-12.8302	1.7	0.2	-0.0974	-0.0011
128	-12.7385	1.5	0.1	-0.0416	-0.0031

Table S7 cont.

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-Sb] (x10^2)	OP [M(f)-Sb] (x10^2)
129	-12.6566	0.7	0.3	-0.0310	-0.0008
130	-12.6095	0.9	0.1	-0.0482	0.0019
131	-12.5385	1.3	0.2	-0.0866	0.0009
132	-12.3398	0.7	0	-0.1277	0.0020
133	-12.3202	0.3	0	0.0284	-0.0042
134	-10.1014	0	0	-0.1229	0.1613
135	-10.0500	0	0	0.0102	0.0858
136	-9.8941	0	0	-0.1282	0.0611
137	-9.2785	0.2	0	0.1390	0.1298
138	-8.9583	3.9	0.3	2.1423	0.2115
139	-7.9177	9.6	1.9	5.0560	1.0018

Table S8 α-Orbital energies in valence region with PDOS and OP for $[Am(DMNE)(H_2O)_6]^{3+}$

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-N] (x10^2)	OP [M(f)-N] (x10^2)
70	-18.7750	0.3	0	0.1774	0.0711
71	-18.1919	0.6	0.2	-0.0093	-0.0032
72	-18.1622	0.6	0	0.0038	0.0038
73	-18.0436	0.7	0	0.0216	-0.0023
74	-17.9870	0.7	0.2	0.0134	-0.0063
75	-17.8896	0.7	0.1	0.0001	-0.0017
76	-17.7900	0.3	0	-0.0187	-0.0025
77	-16.3388	0	0	-0.0832	-0.0127
78	-16.1976	0.1	0	0.0449	-0.0072
79	-15.9119	0.5	0	0.1126	-0.0235
80	-15.6270	1.6	0.7	0.2228	0.0269
81	-15.2993	2.4	2.7	0.0831	0.0136
82	-15.2825	1.4	1.8	0.1099	-0.0014
83	-15.1075	0.8	6.2	0.0111	0.0015
84	-15.0849	0.9	3.5	-0.1505	0.0345
85	-15.0623	0.2	0.7	0.0811	0.0260
86	-14.9867	0.9	1.4	-0.0367	-0.0390
87	-14.9361	1.9	1.8	-0.0108	-0.0043
88	-14.5154	0.2	0.5	0.1505	0.0533
89	-13.6979	0.4	2.8	-0.0728	0.0186
90	-13.3447	0.1	4.3	0.0395	0.0935
91	-13.2914	0.4	28.3	0.0067	0.0758
92	-13.1717	0.3	46.1	-0.0056	-0.0500
93	-12.9540	0.7	1.7	-0.1280	0.0236
94	-12.8707	0.8	6.2	-0.1256	-0.0065
95	-12.7001	0.6	20.7	-0.0294	0.0544
96	-12.6672	0.7	5.6	-0.1081	-0.0248
97	-12.5926	0.5	6.6	0.0421	-0.0877
98	-12.5581	0.6	5.5	0.2581	0.0509
99	-12.4220	0.8	9.1	-0.1030	0.0063
100	-12.3649	0.5	12	-0.0146	0.0625
101	-12.2225	0.6	8.2	-0.0621	0.0081
102	-12.2149	0.5	2.5	0.1534	0.0479

Table S8 cont.

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-N] (x10^2)	OP [M(f)-N] (x10^2)
103	-12.0536	0.2	64.1	0.0344	0.1322
104	-11.9083	0	8.7	0.1136	-0.0846
105	-11.7697	0.2	76.5	0.0145	0.0902
106	-11.6503	0.1	11.5	0.2903	0.3414
107	-11.5507	0	88.3	0.0067	0.0109
108	-11.4663	0.1	88.6	0.0054	0.0094
109	-11.4155	0.2	79.3	0.0123	-0.1676
110	-9.8279	2.6	2.7	2.4748	-0.1809
111	-9.6369	5.3	4.8	4.3525	0.3487

Table S9 α-Orbital energies in valence region with PDOS and OP for $[Am(DMPE)(H_2O)_6]^{3+}$

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-P] (x10^2)	OP [M(f)-P] (x10^2)
77	-18.1655	0.6	0.3	0.0248	0.0008
78	-18.0991	0.7	0.1	-0.0100	-0.0003
79	-18.0120	0.5	0.1	0.0013	-0.0024
80	-18.0069	0.4	0.2	0.0184	-0.0010
81	-17.9244	0.3	0.2	0.0250	-0.0024
82	-17.8324	0.4	0.2	0.4770	0.1056
83	-17.8183	0.7	0.1	0.2762	0.0082
84	-16.9946	0.6	0.4	0.5983	0.2613
85	-15.9026	0.7	0.3	-0.0276	-0.0004
86	-15.3434	3.4	2.9	0.0028	-0.0005
87	-15.2509	2.5	5.8	0.0134	-0.0037
88	-15.1143	2.4	4.5	0.0465	-0.0055
89	-14.9883	0.3	3.4	0.0083	-0.0005
90	-14.9320	0.7	1.9	0.0017	0.0014
91	-14.8240	-0.1	0.1	-0.0249	0.0463
92	-14.5527	-0.2	0.1	-0.0610	0.0191
93	-14.0373	0	0.2	-0.0588	-0.0090
94	-13.8860	0	0	-0.0071	-0.0021
95	-13.6228	0	0.8	-0.0131	-0.0036
96	-13.5418	-0.2	0	-0.0001	-0.0146
97	-13.3039	0	6.6	-0.0341	0.0157
98	-13.1627	0.4	50.9	0.0019	0.0152
99	-13.0596	0	1.2	0.0047	0.0085
100	-13.0307	0	13.1	0.0000	-0.0110
101	-12.9562	0	6.7	-0.0142	-0.0289
102	-12.7126	1.5	8.3	-0.0498	0.0114
103	-12.6840	1.1	6.7	-0.0218	-0.0057
104	-12.6027	0.7	11.7	-0.0658	0.0213
105	-12.5649	0.6	7.4	-0.0982	0.0244
106	-12.5287	0.2	2.2	0.0665	0.0003
107	-12.4805	1.7	9.1	-0.0705	-0.0102
108	-12.3249	0.8	8	-0.0250	0.0013
109	-11.8710	0.2	87.3	0.0183	0.0817

Table S9 cont.

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-P] (x10^2)	OP [M(f)-P] (x10^2)
110	-11.5512	0.2	67.5	0.1053	0.3061
111	-11.4193	0.1	87.2	0.0671	0.1887
112	-11.3907	0	25.3	-0.0415	-0.1835
113	-11.2808	0.3	78.5	0.0069	0.0118
114	-11.2495	0.3	86.8	-0.0037	0.0130
115	-11.1765	0	12.2	0.1088	-0.0832
116	-10.8748	0	0.2	0.0283	0.0931
117	-10.7901	0	0.6	0.0538	-0.0124
118	-9.3166	4.4	2.4	3.0797	-0.0145
119	-8.3925	10.2	3.4	6.2697	1.5512

Table S10 α-Orbital energies in valence region with PDOS and OP for $[Am(DMAsE)(H_2O)_6]^{3+}$

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-As] (x10^2)	OP [M(f)-As] (x10^2)
95	-18.2150	0.5	0.3	0.0712	0.0003
96	-18.1797	0.7	0.1	-0.0055	-0.0007
97	-18.0689	0.8	0	0.0479	0.0008
98	-18.0608	0.2	0.3	-0.0558	0.0077
99	-18.0082	0.4	0	0.1567	-0.0011
100	-17.9641	0.2	0.2	0.1593	0.0774
101	-17.8869	0.5	0.1	0.0498	-0.0025
102	-17.1157	0.4	0.4	0.3673	0.2510
103	-15.9834	0.7	0.4	-0.0247	0.0003
104	-15.4436	3.7	2.9	0.0033	-0.0005
105	-15.3448	2.6	6.4	0.0083	-0.0024
106	-15.1848	2.5	4.2	0.0244	-0.0018
107	-15.0686	0.3	3.6	0.0026	0.0000
108	-15.0144	0.6	2.5	0.0012	0.0009
109	-14.6163	0	0	-0.0257	0.0500
110	-14.2065	-0.2	0.1	-0.0684	0.0143
111	-13.7834	0	0.7	-0.0454	0.0215
112	-13.6710	0	0.3	0.0022	0.0204
113	-13.4555	0	11.8	0.0055	0.0277
114	-13.4280	0	5	0.0228	-0.0067
115	-13.3494	0.2	57.4	-0.0413	0.0122
116	-13.2016	0	4.6	0.0008	-0.0235
117	-13.0373	0.1	0.2	0.0111	-0.0068
118	-13.0226	0	0.3	-0.0056	-0.0044
119	-12.9801	0	2.9	-0.0125	-0.0056
120	-12.7994	1.4	8.4	-0.0378	0.0070
121	-12.7700	0.9	8.9	-0.0176	0.0020
122	-12.7061	0.6	15.7	-0.0309	0.0188
123	-12.6642	1	8.9	-0.0402	0.0087
124	-12.5602	1.5	10.7	-0.0411	0.0013
125	-12.4802	0	0	-0.0250	0.0002
126	-12.4040	0.7	8.8	-0.0081	0.0009
127	-12.0623	0.2	84.1	0.0076	0.0568

Table S10 cont.

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-As] (x10^2)	OP [M(f)-As] (x10^2)
128	-11.7319	0.3	86.7	0.0260	0.0935
129	-11.6122	0.2	87.6	0.0340	0.1163
130	-11.4745	0.3	87.1	-0.0011	0.0206
131	-11.4367	0.3	86.6	-0.0024	0.0083
132	-10.8244	0	1	-0.1225	-0.0129
133	-10.6905	0	0.5	-0.0249	-0.0012
134	-10.4794	-0.1	0	-0.2943	0.0847
135	-10.0960	0	0.1	0.0333	0.0275
136	-9.2527	3.8	1.7	2.3771	0.0019
137	-8.2442	8.4	2.9	5.0464	1.2716

Table S11 α-Orbital energies in valence region with PDOS and OP for $[Am(DMSbE)(H_2O)_6]^{3+}$

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-Sb] (x10^2)	OP [M(f)-Sb] (x10^2)
112	-19.5734	0	0	0.0294	0.0175
113	-18.2080	0.8	0.1	-0.0006	-0.0009
114	-18.1484	0.4	0.4	0.0072	0.0012
115	-18.0937	0.5	0.2	0.0062	-0.0001
116	-18.0461	0.5	0.2	-0.0035	0.0007
117	-18.0017	0.2	0.1	0.0024	-0.0003
118	-17.9277	0.5	0.2	-0.0069	0.0000
119	-16.5717	0.6	0	0.5814	0.0713
120	-15.9638	0.9	0.4	-0.0103	0.0091
121	-15.8814	0.8	0.5	0.7022	0.2311
122	-15.4422	3.6	3.2	0.0020	0.0003
123	-15.3742	2.6	6.8	0.0015	-0.0029
124	-15.2256	2.5	4.4	-0.0062	-0.0010
125	-15.0887	0.3	4	0.0009	-0.0016
126	-15.0283	0.4	3	-0.0056	-0.0008
127	-14.2011	0.1	0	0.1216	0.0592
128	-13.6596	0	0.6	-0.0105	0.0101
129	-13.5491	0.4	82.1	-0.0009	0.0335
130	-13.3358	-0.1	0.8	-0.0343	-0.0012
131	-13.3077	0	0	0.0168	0.0179
132	-13.1695	0	0.1	0.0081	0.0049
133	-13.1382	0	0.5	0.0182	-0.0042
134	-13.0041	0	0.4	0.0076	-0.0007
135	-12.9390	0.1	0.3	0.0022	-0.0012
136	-12.8805	0.3	0.6	0.0130	0.0006
137	-12.8691	0.1	3.9	-0.0411	0.0022
138	-12.8362	0.9	8.7	-0.0373	0.0047
139	-12.7665	0.7	18.7	-0.0395	0.0163
140	-12.7453	0.5	15.6	-0.0288	0.0084
141	-12.7009	1.3	10.2	-0.0199	0.0029
142	-12.5926	1.7	11.9	-0.0757	-0.0006
143	-12.4511	0.7	11	-0.0345	0.0043
144	-12.2729	0	5.5	-0.0116	0.0084

Table S11 cont.

MO(α)	Orbital energy / eV	PDOS(d) [%]	PDOS(f) [%]	OP [M(d)-Sb] (x10^2)	OP [M(f)-Sb] (x10^2)
145	-12.2141	0.4	71	-0.0136	0.0148
146	-11.9151	0.3	82.4	0.0012	0.0252
147	-11.7828	0.1	85.6	0.0034	0.0375
148	-11.6495	0.3	84.1	-0.0030	0.0061
149	-11.6152	0.3	83.6	-0.0074	0.0034
150	-10.0791	-0.1	0.1	-0.1689	0.0609
151	-10.0037	0	0	-0.0175	0.0319
152	-9.8649	0	0	-0.0629	0.0197
153	-9.1640	0.1	0	0.0744	0.0666
154	-8.7934	3.7	0.9	2.1531	0.0756
155	-7.6472	8	2.6	4.6445	1.0498

Figure S1 Ball-and-stick illustrations of optimized complexes from X = N geometry, $[Eu(DMPE)(H_2O)_6]^{3+}$

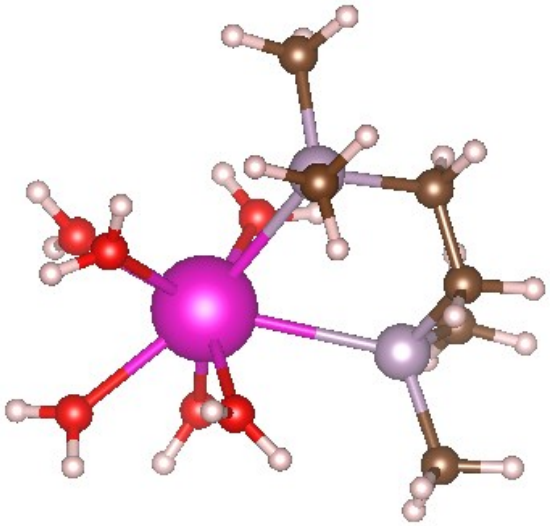

Figure S2 Ball-and-stick illustrations of optimized complexes from X = N geometry, $[Eu(DMAsE)(H_2O)_6]^{3+}$

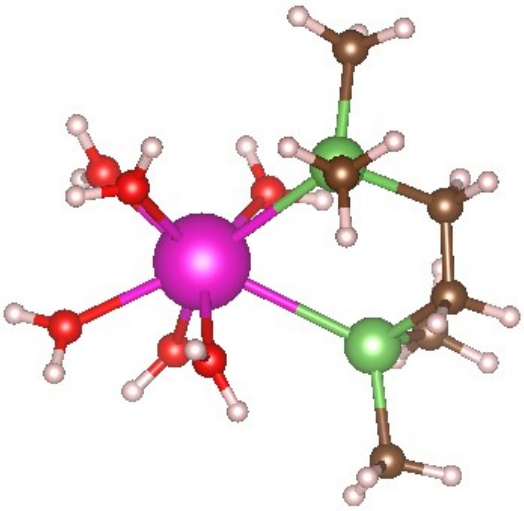

Figure S3 Ball-and-stick illustrations of optimized complexes from X = N geometry, $[Eu(DMSbE)(H_2O)_6]^{3+}$

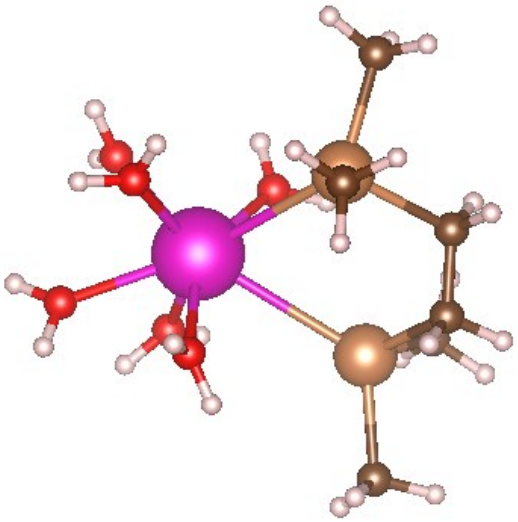

Figure S4 Ball-and-stick illustrations of optimized complexes from X = N geometry, $[Am(DMPE)(H_2O)_6]^{3+}$

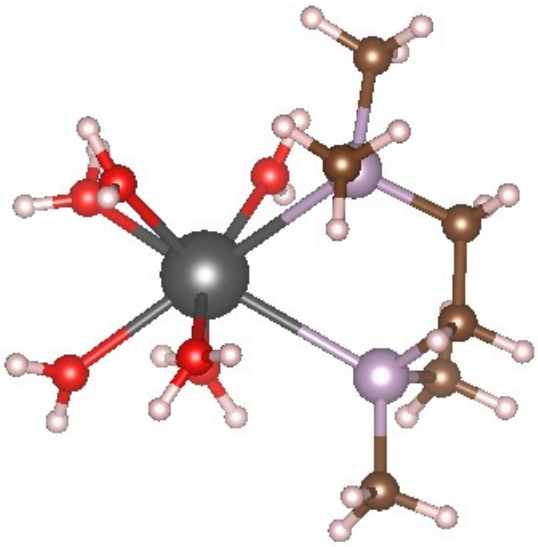

Figure S5 Ball-and-stick illustrations of optimized complexes from X = N geometry, $[Am(DMAsE)(H_2O)_6]^{3+}$

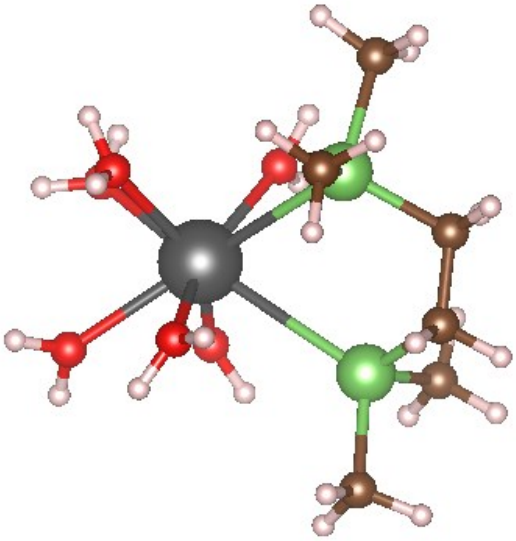

Figure S6 Ball-and-stick illustrations of optimized complexes from X = N geometry, $[Am(DMSbE)(H_2O)_6]^{3+}$