Density Functional Theory Investigations of the Trivalent Lanthanides and Actinides Extraction Complexes with Diglycolamides

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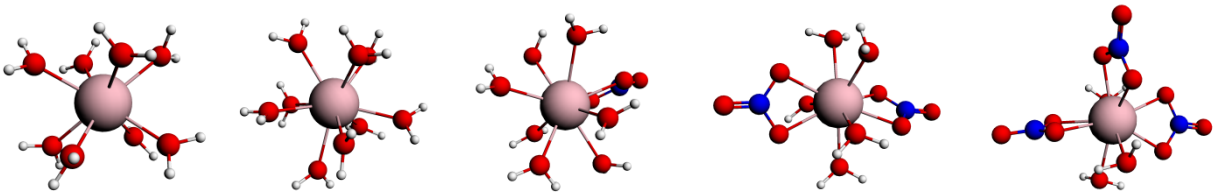
Complete Gaussian 09 reference (Reference 19)



$[M(H_2O)_8]^{3+}$ $[M(H_2O)_9]^{3+}$ $[M(NO_3)(H_2O)_7]^{2+}$ $[M(NO_3)_2(H_2O)_5]^{+}$ $M(NO_3)_3(H_2O)_3$

Figure S1. Optimized structures of Am(III), Cm(III) and Eu(III) complexes by the BP86 method. White, red, blue and pink spheres represent H, O, N, M (M=Am, Cm and Eu), respectively.

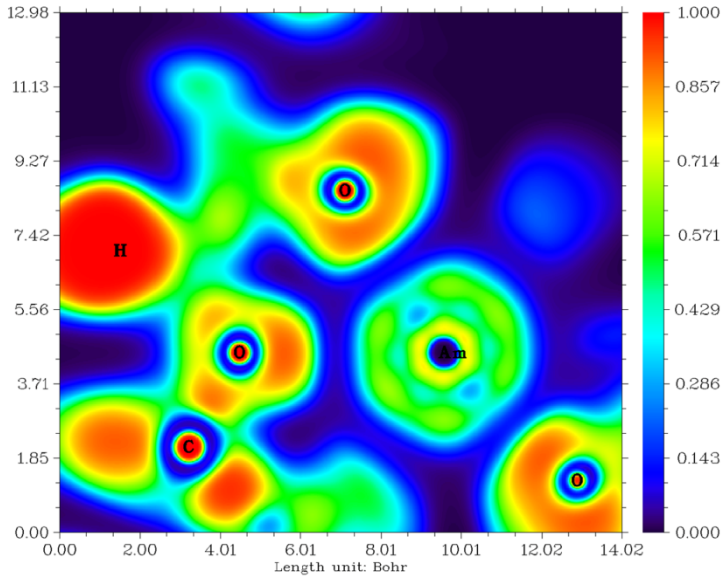


Figure S2. The two-dimensional (2D) color-filled map of ELF for $AmL(NO_3)_3$.[1-4]

Table S1 Changes of the Gibbs free energy (kcal/mol) including zero-point energy (ZPE) corrections and thermal corrections for complexing reactions concerning Am^{3+}, Cm^{3+} and Eu^{3+} in the gas phase and aqueous solution by the BP86 method.

Reactions	ΔG_g	ΔG_{sol}
$[Am(H_2O)_8]^{3+} + H_2O \rightarrow [Am(H_2O)_9]^{3+}$	-13.3	1.8
$[Cm(H_2O)_8]^{3+} + H_2O \rightarrow [Cm(H_2O)_9]^{3+}$	-14.1	0.3
$[Eu(H_2O)_8]^{3+} + H_2O \rightarrow [Eu(H_2O)_9]^{3+}$	-13.4	-2.4
$[Am(H_2O)_9]^{3+} + NO_3^- \rightarrow [Am(NO_3)(H_2O)_7]^{2+} + 2H_2O$	-256.8	-38.6
$[Cm(H_2O)_9]^{3+} + NO_3^- \rightarrow [Cm(NO_3)(H_2O)_7]^{2+} + 2H_2O$	-253.5	-35.9
$[Eu(H_2O)_9]^{3+} + NO_3^- \rightarrow [Eu(NO_3)(H_2O)_7]^{2+} + 2H_2O$	-264.0	-42.2
$[Am(H_2O)_9]^{3+} + 2NO_3^- \rightarrow [Am(NO_3)_2(H_2O)_5]^{+} + 4H_2O$	-444.1	-76.9
$[Cm(H_2O)_9]^{3+} + 2NO_3^- \rightarrow [Cm(NO_3)_2(H_2O)_5]^{+} + 4H_2O$	-437.9	-73.2
$[Eu(H_2O)_9]^{3+} + 2NO_3^- \rightarrow [Eu(NO_3)_2(H_2O)_5]^{+} + 4H_2O$	-449.3	-80.0
$[Am(H_2O)_9]^{3+} + 3NO_3^- \rightarrow Am(NO_3)_3(H_2O)_3 + 5H_2O$	-554.0	-107.1
$[Cm(H_2O)_9]^{3+} + 3NO_3^- \rightarrow Cm(NO_3)_3(H_2O)_3 + 5H_2O$	-549.8	-102.2
$[Eu(H_2O)_9]^{3+} + 3NO_3^- \rightarrow Eu(NO_3)_3(H_2O)_3 + 5H_2O$	-558.2	-108.9

Table S2 Calculated C=O stretching vibrational frequencies (cm^{-1}) for the Am^{3+}, Cm^{3+} and Eu^{3+} complexes with L (L= TODGA, DMDHOPDA) and the free ligands by the B3LYP method

No.	Species	C=O	
		TODGA	DMDHOPDA
	L	1741.8, 1761.1	1752.5, 1774.3
1	$[AmL]^{3+}$	1473.1, 1481.8	1462.0, 1472.9
2	$[CmL]^{3+}$	1413.6, 1420.1	1401.8, 1413.7
3	$[EuL]^{3+}$	1484.9, 1499.0	1472.1, 1493.2
4	$[AmL(H_2O)_6]^{3+}$	1682.0, 1691.6	1688.6, 1698.8
5	$[CmL(H_2O)_6]^{3+}$	1682.8, 1692.8	1690.1, 1700.2
6	$[EuL(H_2O)_6]^{3+}$	1677.0, 1681.9	1680.4, 1685.2
7	$[AmL(NO_3)(H_2O)_4]^{2+}$	1672.1, 1699.2	1696.4, 1707.8
8	$[CmL(NO_3)(H_2O)_4]^{2+}$	1670.7, 1675.8	1689.3, 1705.3
9	$[EuL(NO_3)(H_2O)_4]^{2+}$	1680.6, 1698.2	1694.5, 1705.0
10	$[AmL(NO_3)_2(H_2O)_2]^{+}$	1681.4, 1703.2	1690.8, 1710.7
11	$[CmL(NO_3)_2(H_2O)_2]^{+}$	1680.5, 1702.6	1691.0, 1710.4

12	$[EuL(NO_3)_2(H_2O)_2]^+$	1688.3, 1709.0	1696.3, 1714.1
13	$AmL(NO_3)_3$	1684.6, 1706.0	1694.8, 1712.9
14	$CmL(NO_3)_3$	1687.0, 1706.7	1697.4, 1716.8
15	$EuL(NO_3)_3$	1697.6, 1716.6	1699.1, 1716.5
16	$[AmL_2]^{3+}$	1678.0, 1680.0, 1680.2, 1704.8	1688.4, 1690.6, 1691.1, 1712.8
17	$[CmL_2]^{3+}$	1680.2, 1682.0, 1682.1, 1705.8	1689.6, 1691.2, 1691.3, 1713.2
18	$[EuL_2]^{3+}$	1668.5, 1671.3, 1674.5, 1676.3	1680.2, 1683.3, 1684.6, 1684.8
19	$AmL_2(NO_3)_3$	1687.0, 1693.5, 1721.7, 1740.8	1692.0, 1700.7, 1711.8, 1735.2
20	$CmL_2(NO_3)_3$	1685.8, 1692.2, 1719.8, 1740.0	1692.5, 1705.0, 1712.2, 1736.4
21	$EuL_2(NO_3)_3$	1691.7, 1698.5, 1724.4, 1742.3	1694.0, 1695.7, 1707.2, 1731.8

Table S3 The Wiberg bond indices (WBIs) of M-O bonds for complexes of Am^{3+}, Cm^{3+}, Eu^{3+} and L by the B3LYP method[a]

No.	Species	M-O (ether)	M-O[b] (carbonyl)	M-O[b] (H_2O)	M-O[b] (NO_3^-)
1	$[AmL]^{3+}$	0.106/0.117	0.217/0.225	—	—
2	$[CmL]^{3+}$	0.175/0.183	0.355/0.359	—	—
3	$[EuL]^{3+}$	0.100/0.100	0.189/0.182	—	—
4	$[AmL(H_2O)_6]^{3+}$	0.230/0.222	0.371/0.365	0.266/0.267	—
5	$[CmL(H_2O)_6]^{3+}$	0.218/0.216	0.352/0.346	0.262/0.264	—
6	$[EuL(H_2O)_6]^{3+}$	0.198/0.208	0.313/0.323	0.238/0.247	—
7	$[AmL(NO_3)(H_2O)_4]^{2+}$	0.225/0.213	0.342/0.333	0.257/0.266	0.339/0.339
8	$[CmL(NO_3)(H_2O)_4]^{2+}$	0.200/0.199	0.328/0.329	0.253/0.264	0.317/0.308
9	$[EuL(NO_3)(H_2O)_4]^{2+}$	0.218/0.216	0.354/0.340	0.260/0.268	0.354/0.365
10	$[AmL(NO_3)_2(H_2O)_2]^+$	0.195/0.193	0.310/0.308	0.269/0.267	0.324/0.327
11	$[CmL(NO_3)_2(H_2O)_2]^+$	0.187/0.188	0.312/0.308	0.264/0.265	0.300/0.302
12	$[EuL(NO_3)_2(H_2O)_2]^+$	0.206/0.199	0.318/0.313	0.273/0.268	0.332/0.330
13	$AmL(NO_3)_3$	0.167/0.159	0.282/0.279	—	0.305/0.307
14	$CmL(NO_3)_3$	0.168/0.161	0.273/0.270	—	0.287/0.290
15	$EuL(NO_3)_3$	0.178/0.173	0.285/0.288	—	0.309/0.314

[a].../... refers to the results for TODGA and DMDHOPDA complexes, respectively. [b]M-O denotes average WBIs.

Table S4 The charge transfer of the metal atoms (ΔQ) and NPA charges (Q) on the O atoms in complexes of Am^{3+}, Cm^{3+}, Eu^{3+} and L by the B3LYP method[a]

No.	Species	ΔQ	Q	
		M	O(ether)	O(carbonyl)[b]
1	$[AmL]^{3+}$	1.234/1.156	-0.640/-0.648	-0.826/-0.825
2	$[CmL]^{3+}$	1.020/0.889	-0.652/-0.660	-0.842/-0.845
3	$[EuL]^{3+}$	1.278/1.270	-0.637/-0.640	-0.817/-0.809
4	$[AmL(H_2O)_6]^{3+}$	1.443/1.431	-0.567-0.566	-0.734/-0.727
5	$[CmL(H_2O)_6]^{3+}$	1.415/1.410	-0.568/-0.567	-0.740/-0.732
6	$[EuL(H_2O)_6]^{3+}$	1.633/1.597	-0.555/-0.557	-0.713/-0.708
7	$[AmL(NO_3)(H_2O)_4]^{2+}$	1.499/1.502	-0.558/-0.554	-0.705/-0.702
8	$[CmL(NO_3)(H_2O)_4]^{2+}$	1.455/1.466	-0.559/-0.557	-0.719/-0.706
9	$[EuL(NO_3)(H_2O)_4]^{2+}$	1.554/1.572	-0.552/-0.548	-0.700/-0.697
10	$[AmL(NO_3)_2(H_2O)_2]^{+}$	1.540/1.540	-0.543/-0.542	-0.664/-0.659
11	$[CmL(NO_3)_2(H_2O)_2]^{+}$	1.497/1.497	-0.544/-0.543	-0.669/-0.664
12	$[EuL(NO_3)_2(H_2O)_2]^{+}$	1.599/1.590	-0.540/-0.537	-0.651/-0.653
13	$AmL(NO_3)_3$	1.511/1.513	-0.547/-0.544	-0.645/-0.640
14	$CmL(NO_3)_3$	1.462/1.466	-0.548/-0.544	-0.648/-0.640
15	$EuL(NO_3)_3$	1.548/1.577	-0.538/-0.539	-0.629/-0.630

[a].../... refers to the results for TODGA and DMDHOPDA complexes, respectively. [b]average NPA charges.

Table S5 The average WBIs of M-O bonds, the charge transfer of the metal atoms and natural charges on the O atoms for the complexes of Am^{3+}, Eu^{3+} and L (2:1 type) by the B3LYP method[a]

No.	Species	WBI		ΔQ	Q		
		M-O (ether)	M-O (carbonyl)	M	O(ether)[b]	O(carbonyl)[b]	$O(NO_3^-)$[b]
16	$[AmL_2]^{3+}$	0.192/0.208	0.367/0.362	1.070/1.074	-0.595/-0.596	-0.758/-0.751	—
17	$[CmL_2]^{3+}$	0.190/0.189	0.354/0.351	1.054/1.045	-0.598/-0.597	-0.760/-0.758	—
18	$[EuL_2]^{3+}$	0.188/0.193	0.333/0.336	1.215/1.202	-0.591/-0.591	-0.742/-0.740	—
19	$AmL_2(NO_3)_3$	—	0.281/0.288	1.692/1.635	—	-0.624/-0.627	-0.493/-0.516
20	$CmL_2(NO_3)_3$	—	0.281/0.290	1.635/1.597	—	-0.630/-0.633	-0.501/-0.523
21	$EuL_2(NO_3)_3$	—	0.293/0.312	1.764/1.711	—	-0.615/-0.622	-0.482/-0.507

[a].../... refers to the results for TODGA and DMDHOPDA complexes, respectively. [b]average NPA charges.

Table S6 Calculated reaction energies (kcal/mol) including ZPE corrections and thermal corrections for the Am^{3+}, Cm^{3+} and Eu^{3+} complexes with L by the B3LYP method[a]

No.	Reactions	ΔG_g	ΔG_{sol}
1	$[Am(H_2O)_9]^{3+} + L \rightarrow [AmL]^{3+} + 9H_2O$	28.7/44.7	40.5/40.5
2	$[Cm(H_2O)_9]^{3+} + L \rightarrow [CmL]^{3+} + 9H_2O$	62.9/76.4	42.2/41.1
3	$[Eu(H_2O)_9]^{3+} + L \rightarrow [EuL]^{3+} + 9H_2O$	-7.3/9.3	37.0/41.2
4	$[Am(H_2O)_9]^{3+} + L \rightarrow [AmL(H_2O)_6]^{3+} + 3H_2O$	-74.9/-69.5	-6.2/-11.3
5	$[Cm(H_2O)_9]^{3+} + L \rightarrow [CmL(H_2O)_6]^{3+} + 3H_2O$	-74.7/-68.9	-7.0/-9.6
6	$[Eu(H_2O)_9]^{3+} + L \rightarrow [EuL(H_2O)_6]^{3+} + 3H_2O$	-91.5/-84.7	-7.8/-13.1
7	$[Am(H_2O)_9]^{3+} + L + NO_3^- \rightarrow [AmL(NO_3)(H_2O)_4]^{2+} + 5H_2O$	-290.5/-290.3	-20.8/-24.8
8	$[Cm(H_2O)_9]^{3+} + L + NO_3^- \rightarrow [CmL(NO_3)(H_2O)_4]^{2+} + 5H_2O$	-288.3/-292.6	-17.4/-24.5
9	$[Eu(H_2O)_9]^{3+} + L + NO_3^- \rightarrow [EuL(NO_3)(H_2O)_4]^{2+} + 5H_2O$	-296.8/-293.3	-19.4/-26.8
10	$[Am(H_2O)_9]^{3+} + L + 2NO_3^- \rightarrow [AmL(NO_3)_2(H_2O)_2]^{+} + 7H_2O$	-446.1/-451.0	-36.1/-40.9
11	$[Cm(H_2O)_9]^{3+} + L + 2NO_3^- \rightarrow [CmL(NO_3)_2(H_2O)_2]^{+} + 7H_2O$	-445.2/-450.3	-32.7/-38.1
12	$[Eu(H_2O)_9]^{3+} + L + 2NO_3^- \rightarrow [EuL(NO_3)_2(H_2O)_2]^{+} + 7H_2O$	-451.2/-455.7	-36.0/-40.2
13	$[Am(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow AmL(NO_3)_3 + 9H_2O$	-532.2/-538.1	-37.4/-43.8
14	$[Cm(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow CmL(NO_3)_3 + 9H_2O$	-529.4/-535.7	-32.8/-39.7
15	$[Eu(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow EuL(NO_3)_3 + 9H_2O$	-532.9/-542.1	-36.8/-42.4
16	$[Am(H_2O)_9]^{3+} + 2L \rightarrow [AmL_2]^{3+} + 9H_2O$	-91.8/-86.7	-1.3/-7.1

17	$[Cm(H_2O)_9]^{3+} + 2L \rightarrow [CmL_2]^{3+} + 9H_2O$	-90.1/-86.2	-0.2/-10.3
18	$[Eu(H_2O)_9]^{3+} + 2L \rightarrow [EuL_2]^{3+} + 9H_2O$	-104.4/-100.9	-12.1/-22.7
19	$[Am(H_2O)_9]^{3+} + 2L + 3NO_3^- \rightarrow AmL_2(NO_3)_3 + 9H_2O$	-510.0/-523.9	1.2/-14.3
20	$[Cm(H_2O)_9]^{3+} + 2L + 3NO_3^- \rightarrow CmL_2(NO_3)_3 + 9H_2O$	-507.0/-525.2	6.2/-16.1
21	$[Eu(H_2O)_9]^{3+} + 2L + 3NO_3^- \rightarrow EuL_2(NO_3)_3 + 9H_2O$	-511.9/-528.3	7.2/-17.0

[a] .../... refers to the results for TODGA and DMDHOPDA complexes, respectively.

Table S7 Calculated reaction energies (kcal/mol) including the correction for entropy of water for $ML(NO_3)_3$ with L in aqueous solution by the B3LYP method[a]

Reactions	ΔG_{corr}
$[Am(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow AmL(NO_3)_3 + 9H_2O$	1.3/-5.1
$[Cm(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow CmL(NO_3)_3 + 9H_2O$	5.9/-1.0
$[Eu(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow EuL(NO_3)_3 + 9H_2O$	1.9/-3.7
$[Am(NO_3)(H_2O)_7]^{2+} + L + 2NO_3^- \rightarrow AmL(NO_3)_3 + 7H_2O$	1.3/-5.0
$[Cm(NO_3)(H_2O)_7]^{2+} + L + 2NO_3^- \rightarrow CmL(NO_3)_3 + 7H_2O$	11.8/4.9
$[Eu(NO_3)(H_2O)_7]^{2+} + L + 2NO_3^- \rightarrow EuL(NO_3)_3 + 7H_2O$	11.7/6.0
$[Am(NO_3)_2(H_2O)_5]^{+} + L + NO_3^- \rightarrow AmL(NO_3)_3 + 5H_2O$	17.0/10.6
$[Cm(NO_3)_2(H_2O)_5]^{+} + L + NO_3^- \rightarrow CmL(NO_3)_3 + 5H_2O$	18.2/11.3
$[Eu(NO_3)_2(H_2O)_5]^{+} + L + NO_3^- \rightarrow EuL(NO_3)_3 + 5H_2O$	17.2/11.6
$Am(NO_3)_3(H_2O)_3 + L \rightarrow AmL(NO_3)_3 + 3H_2O$	17.4/11.1
$Cm(NO_3)_3(H_2O)_3 + L \rightarrow CmL(NO_3)_3 + 3H_2O$	17.9/11.0
$Eu(NO_3)_3(H_2O)_3 + L \rightarrow EuL(NO_3)_3 + 3H_2O$	17.3/11.7

[a] .../... refers to the results for TODGA and DMDHOPDA complexes.

References

1. T. Lu and F. Chen, *J. Comput. Chem.,* 2012, **33**, 580.

2. A. Savin, O. Jepsen and J. Flad, *Angew. Chem., Int. Ed. Engl.,* 1992, **31**, 187.

3. E. D. Santo, M. C. Michelini and N. Russo, *Organometallics,* 2009, **28**, 3716.

4. L. Petit, L. Joubert and P. Maldivi, *J. Am. Chem. Soc.,* 2006, **128**, 2190.

Complete Gaussian 09 reference (Reference 19)

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr. , J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.