Uncovering the impact of 'capsule' shaped amine-type ligands on Am(III)/Eu(III) separation

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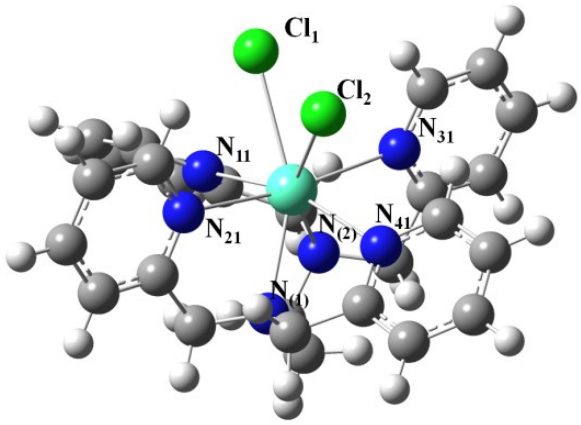

Fig. S1 Optimized structure of $[Eu(TPEN)Cl_2]^+$

Table S1 Bond lengths of $[Eu(TPEN)Cl_2]^+$ obtained through different theoretical methods.

Bonds	Bond Lengths(Å)							
	BP86	B3LYP	PBE0	B3PW9	M06-2x	M06	M06-L	Exptl.[a]
Eu-$N_{(1)}$	2.720	2.597	2.675	2.689	2.649	2.690	2.672	2.603
Eu-$N_{(2)}$	2.722	2.598	2.675	2.689	2.649	2.692	2.672	2.621
Eu-N_{11}	2.763	2.785	2.736	2.580	2.706	2.568	2.581	2.628
Eu-N_{21}	2.758	2.786	2.737	2.581	2.709	2.566	2.578	2.602
Eu-N_{31}	2.616	2.720	2.566	2.758	2.545	2.737	2.744	2.593
Eu-N_{41}	2.614	2.720	2.564	2.759	2.544	2.731	2.742	2.546
Eu-Cl_1	2.635	2.600	2.577	2.584	2.592	2.594	2.625	2.653
Eu-Cl_2	2.636	2.600	2.577	2.584	2.593	2.594	2.623	2.672

[a]R. Hazama, K. Umakoshi, C. Kabuto, K. Kabuto, Y. A. Sasaki, *Chem. Commun.* 1996, 15-16

Table S2 Comparison of bond lengths of some Eu(III), Sm(III),Tb(III), and Am(III) complexes obtained by M06-2X, B3LYP and experimental measurements.

Complexes and Bonds	Bond Length (Å)		
	Expt.	M06-2X	B3LYP
$[Eu(H_2O)_9]^{3+}$			
Eu-O	2.457[b]	2.464(0.3%)	2.504(0.8%)
$[Am(H_2O)_9]^{3+}$			
Am-O	2.503[c]	2.512(0.4%)	2.549(1.8%)
$[Tb(TPEN)(NO_3)_2]^{+}$			
Tb-N	2.624[d]	2.704(3.0%)	2.907(10.8%)
Tb-O_n	2.492	2.419(-2.9%)	2.389(-4.1%)
$[Sm(TPEN)Cl_2]^{+}$			
Sm-N	2.637[e]	2.651(0.5%)	2.707(2.7%)
Sm-Cl	2.659	2.597(-2.3%)	2.606(-2.0%)

[a]Relative deviation of calculated bond lengths are listed in the bracket.

[b]R. Gerkin, W. Reppart, *Acta. Crystallogr. Sect. C: Cryst. Struct. Commun.*1984, **40**, 781.

[c]P. Lindqvist-Reis, C. Apostolidis, J. Rebizant, A. Morgenstern, R. Klenze, O. Walter, T. Fanghänel, R. Haire, *Angew. Chem. Int. Ed*., 2007, **46**, 919.

[d]L. R. Morss, R. D. Rogers, *Inorg. Chim. Acta*, 1997, **255**, 193.

[e]H. Jin, M. Akiba, K. Umakoshi, Y. Sasaki, K. Kabuto, *Acta Crystallogr. Sect. C,* 1997, **53**, 60.

Table S3 Contribution (%) of metal atom and the nitrogen atoms(N_{Amine}, $N_{Pyridine}$) and oxygen atoms of nitrate anion (O_N) to the delocalized canonical MOs for complexes [Eu(TPEN) - $(NO_3)_2]^+$ and $[Am(TPEN)(NO_3)_2]^+$

	182	**171**	**164**	**161**	**158**
Eu	4f: 2.23	5d: 1.27	5d: 1.65	5d: 1.47	5d: 1.12
N_{Amine}	—	5.4	—	—	—
$N_{Pyridine}$	21.47	—	—	28.46	3.69
$O_{Nitrate}$	—	1.9	22.01	20.45	34.15
	188	**181**	**178**	**172**	**166**
Am	5f: 9.84	5f: 1.23	5f: 1.18	6d:1.71	6d: 4.67
N_{Amine}	—	17.16	—	—	—
$N_{Pyridine}$	—	12.61	15.47	27.35	—
$O_{Nitrate}$	61.03	11.91	17.25	17.69	70.92

Table S4 QTAIM parameters of M-N and M-O bonds BCPs in M-TPEN(L_a) and M-TBPEN(L_b) complexes at the M06-2X/6-31g(d)//RECP Level of Theory[a]

Complex and Bonds	ρ	$\nabla^2\rho$	H	|V|/G
$[ML_a(NO_3)]^{2+}$				
$M\text{-}N_{Amine}$	0.0420/0.042	0.138/0.145	-0.00110/-0.00210	1.031/1.055
$M\text{-}N_{Pyridine}$	0.0444/0.046	0.152/0.164	-0.00138/-0.00202	1.034/1.047
$M\text{-}O_{Nitrate}$	0.0583/0.057	0.236/0.241	-0.00293/-0.00230	1.048/1.037
$[ML_b(NO_3)]^{2+}$				
$M\text{-}N_{Amine}$	0.0408/0.042	0.137/0.145	-0.000903/-0.00197	1.029/1.052
$M\text{-}N_{Pyridine}$	0.0460/0.048	0.159/0.172	-0.00169/-0.00228	1.043/1.052
$M\text{-}O_{Nitrate}$	0.0549/0.055	0.228/0.235	-0.00191/-0.00200	1.030/1.033
$[ML_a(NO_3)(H_2O)]^{2+}$				
$M\text{-}N_{Amine}$	0.0369/0.039	0.124/0.132	-0.0000359/-	1.002/1.045
$M\text{-}N_{Pyridine}$	0.0401/0.041	0.140/0.145	0.00043/-0.00115	0.995/1.037
$M\text{-}O_{Nitrate}$	0.0497/0.050	0.211/0.214	-0.00008/-0.00286	1.000/1.027
$M\text{-}O_{Water}$	0.0266/0.034	0.142/0.148	0.00223/0.000703	0.934/0.081
$[ML_b(NO_3)(H_2O)]^{2+}$				
$M\text{-}N_{Amine}$	0.0369/0.038	0.121/0.131	-0.000383/-0.00150	1.011/1.044
$M\text{-}N_{Pyridine}$	0.0422/0.042	0.142/0.150	-0.00105/-0.00132	1.028/1.033
$M\text{-}O_{Nitrate}$	0.0488/0.048	0.203/0.204	-0.000734/-0.00111	1.012/1.021
$M\text{-}O_{Water}$	0.0324/0.034	0.139/0.147	0.00208/0.000666	0.939/0.981
$[ML_a(NO_3)(H_2O)_2]^{2+}$				
$M\text{-}N_{Amine}$	0.0355/0.038	0.118/0.128	0.000160/-0.00139	0.995/1.042
$M\text{-}N_{Pyridine}$	0.0328/0.035	0.111/0.124	0.0000784/-	0.971/1.014
$M\text{-}O_{Nitrate}$	0.0464/0.046	0.195/0.198	0.000420/-0.000826	0.991/1.016
$M\text{-}O_{Water}$	0.0324/0.034	0.140/0.144	0.00224/0.000603	0.933/0.982
$[ML_b(NO_3)(H_2O)_2]^{2+}$				
$M\text{-}N_{Amine}$	0.0357/0.038	0.117/0.129	-0.000180/-0.00136	1.003/1.024
$M\text{-}N_{Pyridine}$	0.0341/0.037	0.113/0.128	-0.000140/-	1.004/1.018
$M\text{-}O_{Nitrate}$	0.0462/0.045	0.188/0.188	-0.000310/-	1.003/1.013
$M\text{-}O_{Water}$	0.0328/0.034	0.140/0.144	0.00209/0.000596	0.935/0.983

[a]…/… represents results for Eu and Am complexes respectively.

Table S5 Changes of Gibbs free energies (kcal/mol) for complexation reactions of Am^{3+} and Eu^{3+} complexes with TPEN and TBPEN ligands in the gas Phase, aqueous, 1-Octanol and nitrobenzene at the M06-2X/6-311G(d,p)/RECP Level of Theory.[a]

Reactions	ΔG_{gas}	$\Delta G_{n\text{-}oct}$	ΔG_{nitro}	ΔG_{aq}
$[M(NO_3)(H_2O)_7]^{2+}+L_a \rightarrow [ML_a(H_2O)_2]^{3+}+NO_3^-+5H_2O$	157.7/155.4	-12.8/-10.5	-32.3/-30.0	-32.8/-31.6
$[M(NO_3)(H_2O)_7]^{2+}+L_b \rightarrow [ML_b(H_2O)_2]^{3+}+ NO_3^-+5H_2O$	136.8/134.0	-14.5/-12.4	-33.0/-30.9	-32.8/-31.7
$[M(NO_3)(H_2O)_7]^{2+}+L_a \rightarrow [ML_a(NO_3)]^{2+}+7H_2O$	-55.7/-57.4	-33.0/-30.6	-41.2/-38.5	-39.8/-38.1
$[M(NO_3)(H_2O)_7]^{2+}+L_b \rightarrow [ML_b(NO_3)]^{2+}+7H_2O$	-65.4/-66.6	-37.5/-32.9	-45.4/-43.2	-43.5/-41.1
$[M(NO_3)(H_2O)_7]^{2+}+L_a \rightarrow [ML_a(NO_3)(H_2O)]^{2+}+6H_2O$	-67.8/-69.0	-39.2/-34.7	-47.3/-40.6	-46.4/-40.5
$[M(NO_3)(H_2O)_7]^{2+}+L_b \rightarrow [ML_b(NO_3)(H_2O)]^{2+}+6H_2O$	-72.8/-75.7	-40.3/-37.1	-48.3/-45.0	-46.6/-43.9
$[M(NO_3)(H_2O)_7]^{2+}+L_a \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+}+5H_2O$	-77.6/-76.8	-44.1/-36.7	-52.1/-44.7	-51.1/-44.2
$[M(NO_3)(H_2O)_7]^{2+}+L_b \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+}+5H_2O$	-80.5/-79.7	-43.7/-38.0	-50.4/-43.5	-50.3/-42.4
$[M(NO_3)(H_2O)_7]^{2+}+ NO_3^-+L_a \rightarrow [ML_a(NO_3)_2]^{+}+7H_2O$	-214.2/-213.0	-51.3/-43.1	-53.4/-45.2	-50.8/-43.4
$[M(NO_3)(H_2O)_7]^{2+}+ NO_3^-+L_b \rightarrow [ML_b(NO_3)_2]^{+}+7H_2O$	-208.8/-209.1	-52.3/-44.9	-55.0/-47.6	-52.0/-44.5
$[M(NO_3)_2(H_2O)_3]^{+}+L_a \rightarrow [ML_a(H_2O)_2]^{3+}+2NO_3^-+H_2O$	297.6/300.2	-26.9/-24.5	-46.4/-44.0	-46.9/-45.6
$[M(NO_3)_2(H_2O)_3]^{+}+L_b \rightarrow [ML_b(H_2O)_2]^{3+}+2 NO_3^-+H_2O$	276.7/278.8	-28.6/-26.4	-47.1/-44.9	-46.9/-45.7
$[M(NO_3)_2(H_2O)_3]^{+}+L_a \rightarrow [ML_a(NO_3)]^{2+}+NO_3^-+3H_2O$	84.3/87.4	-47.1/-44.6	-55.3/-52.5	-53.9/-52.1
$[M(NO_3)_2(H_2O)_3]^{+}+L_b \rightarrow [ML_b(NO_3)]^{2+}+NO_3^-+3H_2O$	74.5/78.1	-51.6/-46.9	-59.6/-57.2	-57.6/-55.1
$[M(NO_3)_2(H_2O)_3]^{+}+L_a \rightarrow [ML_a(NO_3)(H_2O)]^{2+}+2H_2O+NO_3^-$	72.2/75.7	-53.3/-48.7	-61.4/-54.6	-60.5/-54.5
$[M(NO_3)_2(H_2O)_3]^{+}+L_b \rightarrow [ML_b(NO_3)(H_2O)]^{2+}+2H_2O+ NO_3^-$	67.1/69.1	-54.4/-51.1	-62.4/-59.0	-60.7/-57.9
$[M(NO_3)_2(H_2O)_3]^{+}+L_a \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+}+H_2O+NO_3^-$	62.4/68.0	-58.2/-50.7	-66.2/-58.7	-65.2/-58.2
$[M(NO_3)_2(H_2O)_3]^{+}+L_b \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+}+H_2O+NO_3^-$	59.4/65.1	-66.7/-59.7	-64.5/-57.5	-64.4/-56.4
$[M(NO_3)_2(H_2O)_3]^{+}+ L_a \rightarrow [ML_a(NO_3)_2]^{+}+3H_2O$	-74.2/-68.2	-65.4/-57.1	-67.5/-59.2	-64.9/-57.4
$[M(NO_3)_2(H_2O)_3]^{+}+ L_b \rightarrow [ML_b(NO_3)_2]^{+}+3H_2O$	-68.8/-64.3	-66.5/-58.9	-69.2/-61.6	-66.1/-58.5
$[M(NO_3)_2(H_2O)_4]^{+}+L_a \rightarrow [ML_a(H_2O)_2]^{3+}+2NO_3^-+2H_2O$	320.2/323.3	-13.2/-11.0	-32.6/-30.6	-33.2/-32.1
$[M(NO_3)_2(H_2O)_4]^{+}+L_b \rightarrow [ML_b(H_2O)_2]^{3+}+2NO_3^-+2H_2O$	299.3/301.9	-14.9/-12.9	-33.4/-31.5	-33.1/-32.3
$[M(NO_3)_2(H_2O)_4]^{+}+L_a \rightarrow [ML_a(NO_3)]^{2+}+NO_3^-+4H_2O$	106.8/110.5	-33.4/-31.1	-41.5/-39.1	-40.2/-38.7
$[M(NO_3)_2(H_2O)_4]^{+}+L_b \rightarrow [ML_b(NO_3)]^{2+}+NO_3^-+4H_2O$	97.1/101.2	-37.9/-33.4	-45.8/-43.8	-43.9/-41.7

$[M(NO_3)_2(H_2O)_4]^+ + L_a \rightarrow [ML_a(NO_3)(H_2O)]^{2+} + 3H_2O + NO_3^-$	94.7/98.8	-39.6/-35.3	-47.6/-41.2	-46.7/-41.0
$[M(NO_3)_2(H_2O)_4]^+ + L_b \rightarrow [ML_b(NO_3)(H_2O)]^{2+} + 3H_2O + NO_3^-$	89.6/92.2	-40.7/-37.7	-48.6/-45.6	-46.9/-44.5
$[M(NO_3)_2(H_2O)_4]^+ + L_a \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+} + 2H_2O + NO_3^-$	84.9/91.1	-44.5/-37.3	-52.5/-45.3	-51.5/-44.8
$[M(NO_3)_2(H_2O)_4]^+ + L_b \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+} + 2H_2O + NO_3^-$	82.0/88.2	-53.0/-46.3	-50.8/44.1	-50.6/-43.0
$[M(NO_3)_2(H_2O)_4]^+ + L_a \rightarrow [ML_a(NO_3)_2]^+ + 4H_2O$	-51.7/-45.1	-51.6/-43.7	-53.8/-45.7	-51.1/-43.9
$[M(NO_3)_2(H_2O)_4]^+ + L_b \rightarrow [ML_b(NO_3)_2]^+ + 4H_2O$	-46.3/-41.2	-52.7/-45.4	-55.4/-48.1	-52.3/-45.1
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(H_2O)_2]^{3+} + 3NO_3^- + 2H_2O$	448.9/450.0	4.3/4.3	-15.1/-15.8	-15.7/-16.8
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(H_2O)_2]^{3+} + 3NO_3^- + 2H_2O$	428.0/428.7	2.6/2.4	-15.9/-16.1	-15.6/-16.9
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(NO_3)]^{2+} + 2NO_3^- + 4H_2O$	235.5/237.3	-15.9/-15.8	-24.0/-23.7	-22.7/-23.3
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(NO_3)]^{2+} + 2NO_3^- + 4H_2O$	225.8/228.0	-20.4/-18.1	-28.3/-28.4	-26.4/-26.3
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(NO_3)(H_2O)]^{2+} + 3H_2O + 2NO_3^-$	223.4/225.6	-22.1/-19.9	-30.1/-25.8	-29.2/-25.7
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(NO_3)(H_2O)]^{2+} + 3H_2O + 2NO_3^-$	218.3/218.9	-23.2/-22.3	-31.1/-30.2	-29.4/-29.1
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+} + 2H_2O + 2NO_3^-$	213.8/217.8	-27.0/-21.9	-35.0/-29.9	-33.9/-29.4
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+} + 2H_2O + 2NO_3^-$	210.7/214.9	-35.5/-30.9	-33.3/-28.7	-33.1/-27.6
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(NO_3)_2]^+ + 4H_2O + NO_3^-$	77.0/81.6	-34.1/-28.3	-36.3/-30.4	-33.6/-28.6
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(NO_3)_2]^+ + 4H_2O + NO_3^-$	82.4/85.5	-35.2/-30.1	-37.9/-32.8	-34.8/-29.7
$[M(H_2O)_9]^{3+} + L_a \rightarrow [ML_a(H_2O)_2]^{3+} + 7H_2O$	-88.1/-86.6	-19.7/-19.7	-39.2/-39.2	-39.7/-40.8
$[M(H_2O)_9]^{3+} + L_b \rightarrow [ML_b(H_2O)_2]^{3+} + 7H_2O$	-109.0/-108.0	-21.4/-21.6	-39.9/-40.2	-39.7/-40.9
$[M(H_2O)_9]^{3+} + NO_3^- + L_a \rightarrow [ML_a(NO_3)]^{2+} + 9H_2O$	-301.5/-299.4	-39.9/-39.8	-48.1/-47.8	-46.7/-47.3
$[M(H_2O)_9]^{3+} + NO_3^- + L_b \rightarrow [ML_b(NO_3)]^{2+} + 9H_2O$	-311.2/-308.7	-44.4/-42.1	-52.3/-52.5	-50.4/-50.3
$[M(H_2O)_9]^{3+} + L_a + NO_3^- \rightarrow [ML_a(NO_3)(H_2O)]^{2+} + 8H_2O$	-313.6/-311.1	-46.1/-43.9	-54.2/-49.8	-53.3/-49.7
$[M(H_2O)_9]^{3+} + L_b + NO_3^- \rightarrow [ML_b(NO_3)(H_2O)]^{2+} + 8H_2O$	-318.6/-317.7	-47.2/-46.3	-55.2/-54.2	-53.5/-53.2
$[M(H_2O)_9]^{3+} + L_a + NO_3^- \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+} + 7H_2O$	-323.4/-318.8	-51.0/-45.9	-59.0/-54.0	-58.0/-53.5
$[M(H_2O)_9]^{3+} + L_b + NO_3^- \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+} + 7H_2O$	-326.3/-321.7	-59.5/-55.0	-57.3/-52.8	-57.2/-51.6
$[M(H_2O)_9]^{3+} + L_a + 2NO_3^- \rightarrow [ML_a(NO_3)_2]^+ + 9H_2O$	-460.0/-455.0	-58.2/-52.3	-60.3/-54.4	-57.7/-52.6
$[M(H_2O)_9]^{3+} + L_b + 2NO_3^- \rightarrow [ML_b(NO_3)_2]^+ + 9H_2O$	-454.6/-451.1	-59.2/-54.1	-61.9/-56.8	-58.9/-53.7

[a] …/… represents results for Am and Eu complexes respectively.

Table S6 Differences in the Gibbs free energies (kcal/mol) of formation and extraction of the TPEN and TBPEN complexes with Am^{3+} and Eu^{3+} in the gas phase, aqueous, 1-Octanol, and nitrobenzene at the M06-2x/6-311G(d,p)/RECP level of theory.

Reactions	$\Delta\Delta G_{gas}$	$\Delta\Delta G_{1\text{-}oct}$	$\Delta\Delta G_{nitro}$	$\Delta\Delta G_{aq}$
$[M(NO_3)(H_2O)_7]^{2+}+L_a \rightarrow [ML_a(H_2O)_2]^{3+}+ NO_3^-+5H_2O$	2.3	-2.3	-2.3	-1.3
$[M(NO_3)(H_2O)_7]^{2+}+L_b \rightarrow [ML_b(H_2O)_2]^{3+}+ NO_3^-+5H_2O$	2.8	-2.1	-2.1	-1.1
$[M(NO_3)(H_2O)_7]^{2+}+L_a \rightarrow [ML_a(NO_3)]^{2+}+7H_2O$	1.7	-2.4	-2.6	-1.7
$[M(NO_3)(H_2O)_7]^{2+}+L_b \rightarrow [ML_b(NO_3)]^{2+}+7H_2O$	1.3	-4.6	-2.2	-2.4
$[M(NO_3)(H_2O)_7]^{2+}+L_a \rightarrow [ML_a(NO_3)(H_2O)]^{2+}+6H_2O$	1.3	-4.5	-6.7	-5.9
$[M(NO_3)(H_2O)_7]^{2+}+L_b \rightarrow [ML_b(NO_3)(H_2O)]^{2+}+6H_2O$	2.8	-3.2	-3.3	-2.6
$[M(NO_3)(H_2O)_7]^{2+}+L_a \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+}+5H_2O$	-0.8	-7.4	-7.3	-6.9
$[M(NO_3)(H_2O)_7]^{2+}+L_b \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+}+5H_2O$	-0.8	-5.6	-6.9	-7.8
$[M(NO_3)(H_2O)_7]^{2+}+ NO_3^-+L_a \rightarrow [ML_a(NO_3)_2]^{+}+7H_2O$	-1.2	-8.2	-8.2	-7.4
$[M(NO_3)(H_2O)_7]^{2+}+ NO_3^-+L_b \rightarrow [ML_b(NO_3)_2]^{+}+7H_2O$	0.3	-7.4	-7.4	-7.5
$[M(NO_3)_2(H_2O)_3]^{+}+L_a \rightarrow [ML_a(H_2O)_2]^{3+}+2NO_3^-+H_2O$	-2.6	-2.4	-2.4	-1.3
$[M(NO_3)_2(H_2O)_3]^{+}+L_b \rightarrow [ML_b(H_2O)_2]^{3+}+2NO_3^-+H_2O$	-2.1	-2.2	-2.2	-1.2
$[M(NO_3)_2(H_2O)_3]^{+}+L_a \rightarrow [ML_a(NO_3)]^{2+}+ NO_3^-+3H_2O$	-3.1	-2.5	-2.8	-1.8
$[M(NO_3)_2(H_2O)_3]^{+}+L_b \rightarrow [ML_b(NO_3)]^{2+}+ NO_3^-+3H_2O$	-3.6	-4.7	-2.4	-2.5
$[M(NO_3)_2(H_2O)_3]^{+}+L_a \rightarrow [ML_a(NO_3)(H_2O)]^{2+}+2H_2O+NO_3^-$	-3.5	-4.6	-6.8	-6.0
$[M(NO_3)_2(H_2O)_3]^{+}+L_b \rightarrow [ML_b(NO_3)(H_2O)]^{2+}+2H_2O+ NO_3^-$	-2.0	-3.3	-3.4	-2.8
$[M(NO_3)_2(H_2O)_3]^{+}+L_a \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+}+H_2O+ NO_3^-$	-5.6	-7.5	-7.5	-7.0
$[M(NO_3)_2(H_2O)_3]^{+}+L_b \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+}+H_2O+ NO_3^-$	-5.7	-7.0	-7.0	-8.0
$[M(NO_3)_2(H_2O)_3]^{+}+ L_a \rightarrow [ML_a(NO_3)_2]^{+}+3H_2O$	-6.0	-8.3	-8.3	-7.5
$[M(NO_3)_2(H_2O)_3]^{+}+ L_b \rightarrow [ML_b(NO_3)_2]^{+}+3H_2O$	-4.5	-7.6	-7.6	-7.6
$[M(NO_3)_2(H_2O)_4]^{+}+L_a \rightarrow [ML_a(H_2O)_2]^{3+}+2NO_3^-+2H_2O$	-3.1	-2.2	-2.0	-1.1
$[M(NO_3)_2(H_2O)_4]^{+}+L_b \rightarrow [ML_b(H_2O)_2]^{3+}+2NO_3^-+2H_2O$	-2.6	-2.0	-1.9	-0.8
$[M(NO_3)_2(H_2O)_4]^{+}+L_a \rightarrow [ML_a(NO_3)]^{2+}+ NO_3^-+4H_2O$	-3.7	-2.3	-2.4	-1.5
$[M(NO_3)_2(H_2O)_4]^{+}+L_b \rightarrow [ML_b(NO_3)]^{2+}+ NO_3^-+4H_2O$	-4.1	-4.5	-2.0	-2.2

$[M(NO_3)_2(H_2O)_4]^+ + L_a \rightarrow [ML_a(NO_3)(H_2O)]^{2+} + 3H_2O + NO_3^-$	-4.1	-4.3	-6.4	-5.7
$[M(NO_3)_2(H_2O)_4]^+ + L_b \rightarrow [ML_b(NO_3)(H_2O)]^{2+} + 3H_2O + NO_3^-$	-2.6	-3.0	-3.0	-2.4
$[M(NO_3)_2(H_2O)_4]^+ + L_a \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+} + 2H_2O + NO_3^-$	-6.2	-7.2	-7.2	-6.7
$[M(NO_3)_2(H_2O)_4]^+ + L_b \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+} + 2H_2O + NO_3^-$	-6.2	-6.7	-6.7	-7.6
$[M(NO_3)_2(H_2O)_4]^+ + L_a \rightarrow [ML_a(NO_3)_2]^+ + 4H_2O$	-6.6	-7.9	-8.1	-7.2
$[M(NO_3)_2(H_2O)_4]^+ + L_b \rightarrow [ML_b(NO_3)_2]^+ + 4H_2O$	-5.1	-7.3	-7.3	-7.2
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(H_2O)_2]^{3+} + 3NO_3^- + 2H_2O$	-1.1	0	-0.7	-1.1
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(H_2O)_2]^{3+} + 3NO_3^- + 2H_2O$	-0.7	0.2	-0.2	-1.3
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(NO_3)]^{2+} + 2NO_3^- + 4H_2O$	-1.8	-0.1	-0.3	-0.6
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(NO_3)]^{2+} + 2NO_3^- + 4H_2O$	-2.2	-2.3	0.1	-0.1
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(NO_3)(H_2O)]^{2+} + 3H_2O + 2NO_3^-$	-2.2	-2.2	-4.3	-3.5
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(NO_3)(H_2O)]^{2+} + 3H_2O + 2NO_3^-$	-0.6	-0.9	-0.9	-0.3
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+} + 2H_2O + 2NO_3^-$	-4.0	-5.1	-5.1	-4.5
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+} + 2H_2O + 2NO_3^-$	-4.2	-4.6	-4.6	-5.5
$M(NO_3)_3(H_2O)_4 + L_a \rightarrow [ML_a(NO_3)_2]^+ + 4H_2O + NO_3^-$	-4.6	-5.8	-5.9	-4.6
$M(NO_3)_3(H_2O)_4 + L_b \rightarrow [ML_b(NO_3)_2]^+ + 4H_2O + NO_3^-$	-3.1	-5.1	-5.1	-5.1
$[M(H_2O)_9]^{3+} + L_a \rightarrow [ML_a(H_2O)_2]^{3+} + 7H_2O$	-1.5	0	0	1.1
$[M(H_2O)_9]^{3+} + L_b \rightarrow [ML_b(H_2O)_2]^{3+} + 7H_2O$	-1.0	0.2	0.3	1.2
$[M(H_2O)_9]^{3+} + NO_3^- + L_a \rightarrow [ML_a(NO_3)]^{2+} + 9H_2O$	-2.1	-0.1	-0.3	-0.6
$[M(H_2O)_9]^{3+} + NO_3^- + L_b \rightarrow [ML_b(NO_3)]^{2+} + 9H_2O$	-2.5	-2.1	-0.2	-0.1
$[M(H_2O)_9]^{3+} + L_a + NO_3^- \rightarrow [ML_a(NO_3)(H_2O)]^{2+} + 8H_2O$	-2.5	-2.2	-4.4	-3.6
$[M(H_2O)_9]^{3+} + L_b + NO_3^- \rightarrow [ML_b(NO_3)(H_2O)]^{2+} + 8H_2O$	-0.9	-0.9	-1.0	-0.3
$[M(H_2O)_9]^{3+} + L_a + NO_3^- \rightarrow [ML_a(NO_3)(H_2O)_2]^{2+} + 7H_2O$	-4.6	-5.1	-5.0	-4.5
$[M(H_2O)_9]^{3+} + L_b + NO_3^- \rightarrow [ML_b(NO_3)(H_2O)_2]^{2+} + 7H_2O$	-4.6	-4.5	-4.5	-5.6
$[M(H_2O)_9]^{3+} + L_a + 2NO_3^- \rightarrow [ML_a(NO_3)_2]^+ + 9H_2O$	-5.0	-5.9	-5.9	-5.1
$[M(H_2O)_9]^{3+} + L_b + 2NO_3^- \rightarrow [ML_b(NO_3)_2]^+ + 9H_2O$	-3.5	-5.1	-5.1	-5.2