Supporting Information

Computational Thermodynamic Study on the Complexes of Am(III) with Tridentate N-donor Ligands

Yan-Ni Liang[ab], Xia Yang,[c] Songdong Ding,[b] Shoujian Li,[b] Fan Wang,*[b] Zhifang Chai[cd] and Dongqi Wang *[c]

[a]Shaanxi Collaborative Innovation Center of Chinese Medicinal Resources Industrialization, Shaanxi University of Chinese Medicine, Xianyang, 712046

[b]Institute of Atomic and Molecular Physics, College of Chemistry, Sichuan University, Chengdu, 610065

[c]Multidisciplinary Initiative Center, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049

[d]School of Radiation Medicine and Interdisciplinary Sciences (RAD-X), Soochow University, Suzhou, 215123, China

Table S1. Calculated atomic q_M and group charges Q_c, Q_{taz}, and Q_{Lpy} of the free ligand L and the corresponding $[AmL]^{3+}$ complexes and the 5*f* occupancy of Am, Occ.(5*f*),of the complexes in the aqueous solution.

L (water)	Free ligand charges			$[AmL]^{3+}$ charges				
	Q_c	Q_{taz}	Q_{Lpy}	Q_c	Q_{taz}	Q_{Lpy}	q(M)	Occ.(5*f*)
BTP	0.054	-0.027	-	0.133	0.041	-	2.786	6.02
hemi-BTP	0.025	-0.034	0.009	0.110	0.052	0.099	2.738	6.06
TPY	-0.006	-	0.003	0.079	-	0.099	2.723	6.07
C2-BTP	0.033	-0.017	--	0.123	0.075	-	2.726	6.07
C2-hemi-BTP	0.013	-0.019	0.006	0.085	0.055	0.092	2.767	6.02
C2-TPY	-0.019	-	0.010	0.062	-	0.113	2.712	6.07
MeOPh-BTP	0.029	-0.015	-	0.107	0.096	-	2.700	6.09
MeOPh-hemi-BTP	0.012	-0.018	0.006	0.090	0.093	0.105	2.712	6.08
MeOPh-TPY	-0.008	-	0.004	0.062	-	0.114	2.710	6.07
CyMe4-BTP	0.031	-0.015	-	0.107	0.066	-	2.761	6.04
CyMe4-hemi-BTP	0.013	-0.019	0.006	0.097	0.078	0.098	2.727	6.07
CyMe4-TPY	-0.019	-	0.0098	0.045	-	0.107	2.741	6.03
CF3-BTP	0.117	-0.059	-	0.197	0.013	-	2.777	6.05
CF3-hemi-BTP	0.059	-0.075	0.016	0.136	-0.009	0.117	2.757	6.05
CF3-TPY	0.052	-	-0.026	0.135	-	0.055	2.756	6.05

Table S2. Calculated Am-N distances ($d_{Am\text{-}N}$, in Å), Mayer bond order(MBO) and bond overlap populations (BOPs) in $[AmL]^{3+}$ complexes in the aqueous solution.

L	$d_{Am\text{-}N}$			MBO			BOPs		
	N_1	N_2	N_4	N_1	N_2	N_4	N_1	N_2	N_4
BTP	2.66	2.59	2.59	0.27	0.27	0.27	0.18	0.18	0.18
hemi-BTP	2.62	2.56	2.59	0.31	0.29	0.33	0.19	0.18	0.19
TPY	2.57	2.55	2.55	0.34	0.34	0.34	0.21	0.21	0.21
C2-BTP	2.66	2.56	2.56	0.29	0.30	0.30	0.18	0.19	0.19
C2-hemi-BTP	2.61	2.54	2.59	0.30	0.29	0.32	0.20	0.20	0.20
C2-TPY	2.55	2.52	2.52	0.35	0.36	0.36	0.22	0.21	0.21
MeOPh-BTP	2.65	2.55	2.55	0.30	0.32	0.32	0.20	0.20	0.20
MeOPh-hemi-BTP	2.62	2.52	2.54	0.31	0.32	0.36	0.20	0.21	0.21
MeOPh-TPY	2.59	2.52	2.52	0.33	0.36	0.36	0.21	0.21	0.21
CyMe4-BTP	2.65	2.57	2.57	0.27	0.30	0.30	0.18	0.18	0.18
CyMe4-hemi-BTP	2.62	2.53	2.59	0.31	0.31	0.33	0.19	0.19	0.19
CyMe4-TPY	2.57	2.54	2.54	0.32	0.36	0.36	0.21	0.21	0.21
CF3-BTP	2.70	2.60	2.60	0.27	0.25	0.25	0.17	0.165	0.165
CF3-hemi-BTP	2.62	2.62	2.56	0.31	0.24	0.35	0.19	0.17	0.19
CF3-TPY	2.60	2.59	2.59	0.32	0.30	0.30	0.19	0.17	0.17

Table S3. Calculated binding energies (kcal mol^{-1}) of the complexes $[AmL]^{3+}$ in the gas phase and aqueous solution.

L	Gas/BS1		Water/BS1		Gas/BS2		Water/BS2	
	ΔE_{cf}	ΔG_{cf}	ΔE_{cf}	ΔG_{cf}	ΔE_{cf}	ΔG_{cf}	ΔE_{cf}	ΔG_{cf}
BTP	-397.3	-387.9	-23.8	-12.8	-390.3	-380.9	-19.3	-8.3
hemi-BTP	-402.1	-392.1	-30.9	-21.1	-394.2	-384.2	-25.8	-15.9
TPY	-408.1	-399.5	-34.2	-25.1	-399.2	-390.5	-28.5	-19.4
C2-BTP	-444.0	-432.7	-32.3	-22.1	-436.1	-424.8	-26.9	-16.7
C2-hemi-BTP	-426.8	-416.4	-33.4	-22.8	-418.5	-408.0	-27.9	-17.2
C2-TPY	-444.5	-435.9	-37.7	-27.4	-436.0	-427.4	-31.8	-21.5
MeOPh-BTP	-530.1	-520.5	-33.7	-23.4	-519.3	-509.7	-27.8	-17.4
MeOPh-hemi-BTP	-495.6	-486.3	-33.5	-22.6	-485.3	-476.0	-27.7	-16.7
MeOPh-TPY	-526.0	-516.7	-35.5	-24.8	-514.9	-505.6	-29.5	-18.7
CyMe4-BTP	-448.0	-438.2	-26.7	-16.8	-439.7	-429.9	-21.4	-11.5
CyMe4-hemi-BTP	-434.8	-425.4	-33.2	-23.0	-426.4	-416.9	-27.7	-17.5
CyMe4-TPY	-455.3	-447.1	-33.5	-23.0	-446.4	-438.3	-27.6	-17.0
CF3-BTP	-366.5	-356.5	-16.0	-5.6	-352.5	-342.6	-10.7	-0.2
CF3-hemi-BTP	-386.1	-376.3	-25.4	-15.3	-374.8	-364.9	-20.0	-9.9
CF3-TPY	-372.4	-364.0	-22.4	-12.6	-357.7	-349.4	-16.1	-6.6

Table S4. Calculated Am-N distances ($d_{Am\text{-}N}$, in Å), averaged Am-O bond lengths ($d_{Am\text{-}O}$, in Å), Mayer bond order (MBO) of [$AmL(NO_3)_3$] complexes in the aqueous solution.

L	$d_{Am\text{-}N}$					MBO				
	N_1	N_2	N_4	O_i[a]	O_o[a]	N_1	N_2	N_4	O_i[a]	O_o[a]
BTP	2.69	2.62	2.65	2.52	2.52	0.22	0.21	0.20	0.32	0.32
hemi-BTP	2.64	2.58	2.61	2.55	2.53	0.23	0.22	0.27	0.30	0.32
TPY	2.61	2.59	2.62	2.53	2.53	0.27	0.28	0.27	0.30	0.31
C2-BTP	2.66	2.59	2.62	2.52	2.53	0.23	0.23	0.22	0.32	0.32
C2-hemi-BTP	2.63	2.57	2.63	2.53	2.53	0.24	0.23	0.27	0.30	0.31
C2-TPY	2.61	2.62	2.57	2.55	2.55	0.24	0.26	0.29	0.29	0.30
MeOPh-BTP	2.67	2.60	2.59	2.53	2.53	0.22	0.22	0.24	0.31	0.31
MeOPh-hemi-BTP	2.65	2.55	2.64	2.55	2.53	0.24	0.25	0.27	0.30	0.31
MeOPh-TPY	2.63	2.58	2.59	2.55	2.54	0.25	0.29	0.28	0.30	0.31
CyMe4-BTP	2.65	2.59	2.62	2.52	2.53	0.23	0.23	0.22	0.32	0.32
CyMe4-hemi-BTP	2.65	2.56	2.61	2.53	2.54	0.23	0.24	0.27	0.30	0.31
CyMe4-TPY	2.61	2.58	2.61	2.54	2.53	0.27	0.29	0.28	0.30	0.31
CF3-BTP	2.71	2.63	2.62	2.52	2.52	0.20	0.18	0.19	0.32	0.33
CF3-hemi-BTP	2.67	2.63	2.61	2.55	2.52	0.23	0.19	0.27	0.30	0.32
CF3-TPY	2.64	2.63	2.63	2.53	2.52	0.25	0.25	0.24	0.30	0.32

[a] O_i and O_o denote the coordinating oxygen atoms of the in- and out-of-plane molecules, respectively.

Table S5. Calculated binding energies (kcal mol^{-1}) of the complexes [$AmL(NO_3)_3$] in the gas phase and aqueous solution.

L	Gas/BS1		Water/BS1		Gas/BS2		Water/BS2	
	ΔE_{cf}	ΔG_{cf}	ΔE_{cf}	ΔG_{cf}	ΔE_{cf}	ΔG_{cf}	ΔE_{cf}	ΔG_{cf}
BTP	-1080.7	-1036.8	-111.5	-65.2	-1056.6	-1012.7	-88.7	-42.3
hemi-BTP	-1084.7	-1039.3	-116.6	-70.4	-1060.7	-1015.1	-94.1	-47.9
TPY	-1088.6	-1043.0	-118.3	-73.3	-1064.2	-1018.4	-95.2	-50.1
C2-BTP	-1086.2	-1040.6	-115.3	-67.8	-1061.8	-1016.1	-92.2	-44.5
C2-hemi-BTP	-1087.7	-1042.0	-117.1	-72.4	-1063.4	-1017.6	-94.3	-49.4
C2-TPY	-1092.2	-1046.7	-119.1	-72.3	-1068.0	-1022.4	-96.9	-50.0
MeOPh-BTP	-1087.3	-1042.5	-117.6	-70.5	-1062.7	-1017.8	-94.7	-47.4
MeOPh-hemi-BTP	-1087.4	-1042.4	-113.5	-66.9	-1062.9	-1017.8	-90.6	-43.9
MeOPh-TPY	-1091.9	-1046.1	-119.8	-72.7	-1067.6	-1021.6	-97.4	-50.1
CyMe4-BTP	-1087.2	-1042.8	-115.9	-70.1	-1063.0	-1018.5	-93.1	-47.1
CyMe4-hemi-BTP	-1088.2	-1043.3	-118.4	-73.2	-1064.0	-1019.0	-95.7	-50.4
CyMe4-TPY	-1093.5	-1048.7	-120.9	-75.6	-1069.5	-1024.6	-97.9	-52.5
CF3-BTP	-1072.6	-1027.6	-106.1	-58.6	-1047.3	-1002.3	-83.1	-35.5
CF3-hemi-BTP	-1080.4	-1034.8	-111.7	-65.5	-1055.7	-1010.0	-88.9	-42.6
CF3-TPY	-1079.7	-1034.1	-110.7	-64.1	-1054.4	-1008.7	-87.5	-40.7

Table S6. Calculated changes of the Gibbs free energies (kcal mol^{-1}) for the complexing reactions $Am(NO_3)_3(H_2O)_3 + L \rightarrow AmL(NO_3)_3 + 3(H_2O)$.

L	ΔG_g/BS1	ΔG_s/BS1	ΔG_g/BS2	ΔG_s/BS2
BTP	-1.6	-6.6	-3.3	-7.2
hemi-BTP	-4.1	-11.8	-5.7	-12.8
TPY	-7.8	-14.7	-9.1	-15.0
C2-BTP	-5.5	-9.2	-6.7	-9.4
C2-hemi-BTP	-6.8	-13.8	-8.2	-14.3
C2-TPY	-11.6	-13.7	-13.1	-14.9
MeOPh-BTP	-7.4	-11.9	-8.4	-12.3
MeOPh-hemi-BTP	-7.3	-8.3	-8.4	-8.8
MeOPh-TPY	-10.9	-14.1	-12.2	-15.0
CyMe4-BTP	-7.7	-11.5	-9.1	-12.0
CyMe4-hemi-BTP	-8.2	-14.6	-9.6	-15.2
CyMe4-TPY	-13.5	-17.0	-15.2	-17.4
CF3-BTP	7.5	-0.02	7.1	-0.4
CF3-hemi-BTP	0.3	-6.9	-0.6	-7.4
CF3-TPY	1.0	-5.5	0.7	-5.6

Table S7. Characteristics of Am-N Bond Critical Points (BCP) for the various complexes. $\rho(r)$ – density of all electrons. $\nabla^2\rho(r)$ - Laplacian of electron density. H_b - total energy density. ELF- Electron localization function. LOL - Localized orbital locator.

L	$[AmL]^{3+}$	r_N/r_M (Å)	$\rho(r)$ $e^-/bohr^3$	$\nabla^2\rho(r)$ $e^-/bohr^5$	H_b(au)	ELF	LOL
BTP	M-N_1	1.22/1.37	0.049	0.137	-0.37E-02	0.197	0.330
	M-N_2	1.08/1.24	0.085	0.233	-0.17E-01	0.286	0.386
hemi-BTP	M-N_1	1.17/1.32	0.060	0.164	-0.69E-02	0.236	0.356
	M-N_2	1.07/1.24	0.089	0.237	-0.19E-01	0.300	0.395
	M-N_4	1.10/1.27	0.078	0.213	-0.14E-01	0.273	0.379
TPY	M-N_1	1.14/1.30	0.065	0.188	-0.81E-02	0.232	0.354
	M-N_2	1.13/1.29	0.069	0.202	-0.97E-02	0.233	0.354
$CyMe_4$-BTP	M-N_1	1.14/1.30	0.064	0.195	-0.80E-02	0.217	0.344
	M-N_2	1.12/1.29	0.071	0.207	-0.11E-01	0.244	0.361
$CyMe_4$-hemi-BTP	M-N_1	1.17/1.33	0.057	0.166	-0.58E-02	0.214	0.342
	M-N_2	1.08/1.25	0.085	0.233	-0.17E-01	0.287	0.386
	M-N_4	1.13/1.29	0.069	0.203	-0.10E-01	0.236	0.356
$CyMe_4$-TPY	M-N_1	1.14/1.31	0.062	0.196	-0.71E-02	0.204	0.335
	M-N_2	1.14/1.31	0.062	0.198	-0.72E-02	0.201	0.333

CF_3-BTP	M-N_1	1.22/1.37	0.048	0.134	-0.35E-02	0.194	0.328
	M-N_2	1.08/1.24	0.084	0.233	-0.17 E-01	0.284	0.385
CF_3-hemi-BTP	M-N_1	1.17/1.32	0.060	0.163	-0.67 E-02	0.235	0.356
	M-N_2	1.07/1.24	0.089	0.238	-0.19E-01	0.298	0.393
	M-N_4	1.10/1.26	0.079	0.213	-0.14 E-01	0.275	0.380
CF_3-TPY	M-N_1	1.15/1.30	0.064	0.185	-0.79E-02	0.231	0.354
	M-N_2	1.13/1.29	0.068	0.200	-0.94E-02	0.231	0.353

L	AmL(NO_3)$_3$	r_N/r_M (Å)	ρ(r) e^-/bohr^3	∇^2 ρ(r) e^-/bohr^5	H_b(au)	ELF	LOL
BTP	M-N_1	1.28/1.45	0.033	0.113	-0.20E-03	0.111	0.260
	M-N_2	1.24/1.41	0.038	0.133	-0.11E-03	0.120	0.269
hemi-BTP	M-N_1	1.27/1.43	0.035	0.119	-0.24E-05	0.117	0.266
	M-N_2	1.23/1.39	0.041	0.144	-0.38E-03	0.128	0.276
	M-N_4	1.24/1.41	0.039	0.131	-0.66E-03	0.129	0.277
TPY	M-N_1	1.24/1.41	0.030	0.140	-0.31E-03	0.058	0.198
	M-N_2	1.25/1.40	0.031	0.143	-0.33E-04	0.058	0.198
$CyMe_4$-BTP	M-N_1	1.27/1.44	0.034	0.115	-0.12E-03	0.114	0.263
	M-N_2	1.24/1.39	0.040	0.138	-0.40E-03	0.129	0.278
$CyMe_4$-hemi-BTP	M-N_1	1.26/1.42	0.036	0.124	-0.14E-03	0.120	0.269
	M-N_2	1.23/1.38	0.042	0.145	-0.65E-03	0.133	0.281
	M-N_4	1.24/1.40	0.040	0.134	-0.75E-03	0.131	0.279
$CyMe_4$-TPY	M-N_1	1.24/1.41	0.039	0.131	-0.45E-03	0.127	0.275
	M-N_2	1.24/1.39	0.040	0.135	-0.86E-03	0.137	0.284
CF_3-BTP	M-N_1	1.28/1.45	0.032	0.109	-0.33E-03	0.107	0.256
	M-N_2	1.26/1.42	0.035	0.125	-0.34E-03	0.112	0.262
CF_3-hemi-BTP	M-N_1	1.26/1.43	0.035	0.121	-0.19E-04	0.117	0.266
	M-N_2	1.25/1.41	0.036	0.128	-0.30E-03	0.113	0.263
	M-N_4	1.24/1.40	0.040	0.134	-0.84E-03	0.133	0.281
CF_3-TPY	M-N_1	1.25/1.42	0.036	0.125	-0.12E-03	0.120	0.269
	M-N_2	1.26/1.42	0.036	0.122	-0.15E-03	0.121	0.271

Table S8. Gibbs Free Energy changes (kcal mol^{-1}) of the nitration reactions of $[Am(NO_3)_n(H_2O)_m]^{3-n}$ (m=3,5,7,9 and n=0-3) in the gas phase (ΔG_g) with B3LYP and MP2 both based on BS1 level.

Complexation reactions	ΔG_g/B3LYP	ΔG_g/MP2
$[M(H_2O)_9]^{3+} + NO_3^- \rightarrow [M(NO_3)(H_2O)_7]^{2+} + 2H_2O$	-248.4	-250.7
$[M(NO_3)(H_2O)_7]^{2+} + NO_3^- \rightarrow [M(NO_3)_2(H_2O)_5]^+ + 2H_2O$	-176.5	-179.7
$[M(NO_3)_2(H_2O)_5]^+ + NO_3^- \rightarrow M(NO_3)_3(H_2O)_3 + 2H_2O$	-109.6	-114.7
$[M(NO_3)_3(H_2O)_3] + NO_3^- \rightarrow [M(NO_3)_4(H_2O)]^- + 2H_2O$	-39.7	-43.0
$[M(NO_3)_2(H_2O)_5]^+ + H_2O \rightarrow [M(NO_3)_2(H_2O)_6]^+$	-8.8	-13.4
$[M(NO_3)_3(H_2O)_3] + H_2O \rightarrow [M(NO_3)_3(H_2O)_4]$	-3.8	-7.0
$M(NO_3)_3(H_2O)_3 + L \rightarrow ML(NO_3)_3 + 3(H_2O)$		
L=BTP	-3.3	-15.6
L=hemi-BTP	-5.7	-17.9
L=TPY	-9.1	-22.5

Table S9. Calculated binding energies (kcal mol^{-1}) of the complexes $[AmL]^{3+}$ with B3LYP and MP2 both based on BS2 level.

	L	B3LYP/BS2		MP2/BS2	
		ΔE_{cf}	ΔG_{cf}	ΔE_{cf}	ΔG_{cf}
$[ML]^{3+}$	BTP	-390.3	-380.9	-379.8	-370.4
	hemi-BTP	-394.2	-384.2	-388.9	-378.8
	TPY	-399.2	-390.5	-392.5	-383.8
$ML(NO_3)_3$	BTP	-1056.6	-1012.7	-1090.4	-1046.4
	hemi-BTP	-1060.7	-1015.1	-1094.3	-1048.7
	TPY	-1064.2	-1018.4	-1099.1	-1053.3