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Electronic Supplementary Information (ESI)

Complexation thermodynamics of diglycolamide with f-elements: Solvent Extraction and Density functional theoretical analysis

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Section-S1:

Computational Methodology:

SVP basis set as used in Turbomole:

i.e. O (7s4p1d)/[3s2p1d], N(7s4p1d)/[3s2p1d], C(7s4p1d)/[3s2p1d], H(4s1p)/[2s1p], La(7s6p5d)/[6s3p2d], Eu(14s13p10d8f1g)/[10s8p5d4f1g], Am(14s13p10d8f1g)/[10s9p5d4f1g] and Cm(14s13p10d8f1g)/[10s9p5d4f1g]

TZVPP basis set as used in Turbomole:

i.e. O (11s6p2d1f)/[5s3p2d1f], N(11s6p2d1f)/[5s3p2d1f], C(11s6p2d1f)/[5s3p2d1f], H(5s2p1d)/[3s2p1d], La(7s6p5d1f)/[6s3p3d1f], Eu(14s13p10d8f3g)/[10s8p5d4f3g], Am(14s13p10d8f3g)/[10s9p5d4f3g] and Cm(14s13p10d8f3g)/[10s9p5d4f3g].

Details of the model used for the calculation of free energy of extraction values

One of the key properties to be calculated in the metal ion-ligand complexation is the free energy of extraction (ΔG_{ext}). The metal ion-ligand complexation reaction is modeled as the 1:3 (M:L) stoichiometric reaction as follows:

$$M^{3+}_{(aq)} + 3NO_3^-{}_{(aq)} + 3L_{(org)} \xrightarrow{\Delta G_{ext}} [ML_3(NO_3)_3]_{(org)}), \text{ (M= La, Eu, Eu, Am and Cm)} \quad (1)$$

Here, L corresponds to DGA ligand. The 1:3, M:L stoichiometry has been reported using X-ray study [Kannan, S.; Moody, M.A.; Barnes, C.L.; Duval, P.B. *Inorg. Chem*. 2008, 47, 4691-4695]. The change in Gibbs free energy of extraction, ΔG_{ext}, in Eq.1 can be obtained by the thermodynamic cycle (Born-Haber) as shown in Scheme-1, in terms of the free energy change in gas phase, $\Delta G_{(gp)}$, and the solvation free energies of the products and reactants, $\Delta\Delta G_{(sol)}$. The overall complexation reaction is characterized by the free energy of extraction, ΔG_{ext} as

$$\Delta G_{ext} = \Delta G_{(gp)} + \Delta\Delta G_{(sol)} \quad (2)$$

Where, $\Delta G_{(gp)}$ is expressed as

$$\Delta G_{(gp)} = \Delta E_{(gp)} + \Delta ZPE + \Delta nRT - T\Delta S \quad (3)$$

Here, $\Delta E_{(gp)}$ is change in total electronic energy for the reaction; ΔZPE is the change in zero point energy; Δn is the change in number of molecules; R is the Universal gas constant; T is the temperature in K and ΔS is the change in entropy for the reaction. The solvation free energies of the products and reactants, $\Delta\Delta G_{(sol)}$, is computed as:

$$\Delta\Delta G_{(sol)} = \Delta G_{sol(ML3(NO3)3)} - (\Delta G_{sol(M3+)} + 3\Delta G_{sol(NO3-)} + 3\Delta G_{sol(L)}) \qquad (4)$$

Where, ΔG_{sol} is the solvation free energy of the respective species. In Scheme-1, explicit hydration of metal ion and nitrate ion using monomer and cluster water model was considered. It is interesting to study explicit hydrated ion pair of metal nitrate (monomer and cluster water model) in the solution. Hence, in Scheme-2, hydrated metal nitrate species are considered as:

$$M(NO_3)_{3(aq)} + 3L_{(org)} \longrightarrow [ML_3(NO_3)_3]_{(org)}, \quad (5)$$

The solvation free energies of the products and reactants, $\Delta\Delta G_{(sol)}$, for Scheme-2, is computed as:

$$\Delta\Delta G_{(sol)} = \Delta G_{sol(ML3(NO3)3)} - (\Delta G_{sol(M(NO3)3} + 3\,\Delta G_{sol(L)}) \quad (6)$$

Despite the fact that, GGA based BP86 generates quite reasonable geometries, it has the inbuilt limitation in the accurate energy predictions due to non-consideration of non-covalent interaction. We have further performed single point energy calculation using optimized structures obtained from the BP86 functional with hybrid B3LYP functional as it includes the non-local HF contribution. Hybrid DFT was found to be superior to GGA functional for thermochemistry of actinides as reported earlier [Shamov, G.A.; Schreckenbach, G.; Vo, T.N. *Chemistry A European Journal* 2007, 13, 4932-4947]. The heavier Ln/An element have filled f orbital electrons, which causes a large relativistic effect and hence makes the calculation more difficult. Therefore, scalar relativistic effects were incorporated in the present calculation.

Most of the metal ion extraction takes place from the aqueous solution phase to the organic solvent phase aided by ligand. Hence, the consideration of solvent effect on the complexation of the ligand moiety with metal ion in the QM calculation is thus indispensable. In order to study the aqueous and organic solvent effect, the optimized geometry obtained from BP86 level of theory was used for single point energy calculation using conductor like screening model (COSMO) [Klamt, A. *J. Phys. Chem.* 1995, 99, 2224-2235] as implemented in TURBOMOLE quantum chemistry package [TURBOMOLE V6.0 2009, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH]. COSMO is an improved solvation model, where the polarization charges of the solute is calculated in a continuum solvent using scaled conducting boundary condition.

Thermal corrections to the electronic energy (E_{el}), enthalpy (H) and free energy (G) of the optimized free DGA, metal ion-DGA complexes, hydrated metal ion and metal ion nitrate complexes have been performed following the standard reported procedure [M.A. Scotto, G. Mallet, D. Vasilescu, J. Mol. Struc.: THEOCHEM 2005, 728, 231-242; De, S.; Ali, S.M.; Ali, A.; Gaikar, V.G. *Phys. Chem. Chem. Phys*. 2009, 11, 8285-8294]. The MOLDEN graphical program [Schaftenaar, G.; Noordik, J.H. *J.Comp. Aid. Mol. Des*. 2000, 14, 123–134] was used for the visualization of various molecular geometry, structural parameters and vibrational IR frequencies. Orbital population analysis was performed using natural population analysis (NPA) [Reed, A.E.; Weinstock, R.B.; Weinhold, F. J.Chem.Phys. 1985, 83, 735-746; K. Fukui, *Angew. Chem. Int.Ed. Engl*. 1982, 21, 801-809]. Further, bonding analysis was also done using atom in molecule (AIM) approach [Matta, C.F.; Boyd, R.J. An introduction to the Quantum Theory of Atoms in Molecules Edited by Che´rif F. Matta and Russell J. Boyd, 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; Page 1-34; Biegle-knig, F; Schonbohm, J. An update to the AIM2000, Program for Atoms in Molecules. *J. Comp. Chem.* 2002, 23, 1489-94] whereas second order stabilization energy was calculated using NBO program as implemented in ADF package [Glendening, E.D.; Badenhoop, O.K.; Reed, A.E.; Carpenter, J.E.; Bohmann, J.A. ; Morales, C.M.; Weinhold, F. NBO 5.0, TCI, University of Wisconsin, Madison, WI, 2001; ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com; ADF, te Velde, G.; Bickelhaupt, F.M.; Baerends, E.J.; Fonseca, C.; van Gisbergen, S.J.A.; Snijders, J.G.; Ziegler, T. J. Comp. Chem. 2001, 22, 931-967] using the optimized coordinates of the complexes obtained from Turbomole. In ADF[71-72], the calculation was performed at M06-L [M06-L Zhao Y, Truhlar DG (2008) Accounts Chem. Res. 41:157] level employing scalar relativistic zeroth-order regular approximation (ZORA) approach [Van Lenthe, E.; Baerends, E.J.; Snijders, J.G. J. Chem. Phys. 1993, 99, 4597-4610; Van Lenthe, E.; Baerends, E.J.; Snijders, J.G. J. Chem. Phys. 1994, 101, 9783-9792; Van Lenthe, E.; Ehlers, E.; Baerends, E.J. J. Chem. Phys. 1999, 110, 8943-8953]. The standard all electron ZORA-TZ2P (triple-ζ) Slater type basis sets without frozen cores were utilized for all the atoms.

Structural parameters The optimized structures of M^{3+}-L complexes (1:1) are displayed in Fig.S1. The calculated structural parameters are listed in Table S4. In the complexes of metal ions (La^{3+}, Eu^{3+}, Lu^{3+}, Am^{3+} and Cm^{3+}) with TMDGA, the C=O and C-O bond distance was found to be lengthened whereas the C-N bond distance was found to be shortened substantially compared to free TMDGA. The metal ions were found to be coordinated via three O donor atoms of TMDGA. The M-O (O atom of C=O and O atom of ether link) bond distance was found to be shortest in Lu^{3+} and longest in Eu^{3+} and the bond distance follows the order Eu^{3+}>La^{3+}>Am^{3+}>Cm^{3+}>Lu^{3+}. The M-O (O atom of C=O) bond distance was found to be shorter than the M-O (O atom of ether link) bond distance and plays the dominant role in the coordinated interaction. The optimized structures of M^{3+}-L_2 complexes (1:2) are displayed in Fig.S2 and the calculated structural parameters are tabulated in Table S5. The C=O and C-O bond distance was found to be lengthened whereas the C-N bond distance was found to be shortened substantially. Each TMDGA was found to be coordinated via three O donor atoms to the metal ions leading to hexa coordination. The M-O (O atom of C=O) bond distance was found to be shortest in Cm^{3+} and longest in La^{3+} and the bond distance follows the order La^{3+}>Eu^{3+}>Am^{3+}>Cm^{3+}>Lu^{3+}. The M-O (O atom of ether link) bond distance also follows the same order. The M-O (O atom of ether link) bond distance was found to be higher than the M-O (O atom of C=O) distance as noticed in the case of 1:1 ML complexes indicating the dominant role of the carbonyl O atom in the bonding interaction. In later section, we will see that the binding energy for 1:3 complexes is highest with the metal ion having lowest M-O (O of C=O) bond distance. The Am-O bond distance (2.41-2.46Å) and Eu-O bond distance (2.41-2.43Å) and NPA charge on Am^{3+} (1.93) and Eu^{3+} (1.94) was found to be very close which leads to close value of interaction energy of Eu^{3+} ion (-687.89kcal/mol) and Am^{3+} ion (-664.74kcal/mol).

Section-S2 Binding energy (Gas phase) The stepwise complexation reaction for lanthanides and actinides ion with TMDGA can be written as

$$M^{3+}\text{-}(H_2O)_x + nL = M^{3+}\text{-}L_n + xH_2O \quad (n=1\text{-}3,\ x=0 \text{ or } 9 \text{ and } M= \text{La, Eu, Lu, Am and Cm}) \quad \text{(S1)}$$

The stepwise stabilization energy for different M:L stoichiometry can be written as

$$\Delta E_n = (E_{M3+\text{-}Ln} + nE_{H2O}) - (E_{M3+\text{-}(H2O)x} + nE_L) \qquad \text{(S2)}$$

The calculated value of ΔE_n is listed in Table S6.

Case-1: x=0. The bare metal ion undergoes complexation with TMDGA. The calculated value of ΔE is found to be increased with the successive addition of TMDGA. The ΔE for 1:1 ML complexation was found to be in the following order: Lu^{3+}>Eu^{3+}>Am^{3+}>Cm^{3+}>La^{3+}, whereas for 1:2 and 1:3 complexation, the order was:Lu^{3+}> Eu^{3+}>Cm^{3+}>Am^{3+}>La^{3+}. Point to be noted that though this binding energy is able to capture the experimental selectivity order, this scheme does not represent the real extraction system and hence, in next section hydrated metal ions are considered.

Case-2: x=9 (explicit monomer water model). Here, the metal ion was considered to be nona hydrated in the first solvation shell. Here, also the ΔE was found to be increased with the successive addition of ligands but the value was found to be much lower than that of with bare metal ion. This is due to the large amount of energy required to dehydrate the metal ion prior to complexation. Even for 1:1 complexation, the value of ΔE was found to be positive. The order of ΔE was: Eu^{3+}>Am^{3+}>La^{3+}>Cm^{3+}>Lu^{3+}. For 1:2 and 1:3, the value of ΔE was found to be negative. For 1:2, the ΔE follows the order: Lu^{3+}>Am^{3+}>Eu^{3+}>Cm^{3+}>La^{3+} and for 1:3, Eu^{3+}>Am^{3+}>Cm^{3+}>Lu^{3+}>La^{3+}. This scheme fails to capture the real selectivity trend.

Case-3: x=9 (explicit cluster water model). In this model, the metal ion was considered to be nona hydrated in the first solvation shell, but, the released water molecules form water cluster through hydrogen bonding during complexation with the ligands. Here, also the value of ΔE was found to be much smaller than that of with bare metal ion but greater than that of with monomer units for 1:1 complexes and was found to be positive. The value of ΔE was found to be negative for 1:2 and 1:3 complexes. For 1:2 and 1:3, the value of ΔE was found to be negative. For 1:2, the ΔE follows the order: Lu^{3+}>Am^{3+}>Eu^{3+}>Cm^{3+}>La^{3+} and for 1:3, Eu^{3+}>Am^{3+}>Cm^{3+}>Lu^{3+}>La^{3+}. The cluster based approach also unable to capture the experimental selectivity. The gas phase ΔE though provide intrinsic interaction parameters, it is not adequate to capture the complex metal ion selectivity as in the coordinated complexes with chelating ligands entropy plays a decisive role. Hence, thermodynamic analysis was performed to calculate the entropy and free energy of complexation in the next section.

Section-S3 Thermodynamic analysis (Gas phase) The zero point energy corrected (ZPE) binding energy, ΔU for the metal ion-ligand complexation is listed in Table S7. The ΔE is slightly reduced after zero point correction as revealed from the Table. Though the value was found to be reduced it follows the same trend of ΔE i.e. Lu>Eu>Cm>Am>La. The enthalpy of complexation is found to be increased slightly with keeping the increasing trend. The free energy of complexation, ΔG is found to be decreased substantially due to negative contribution of entropy as the ligand complexation is a structure making process. But, this is true only when bare metal ion was considered. In case of explicit hydrated metal ion, the entropy was found to be positive due to release of water molecules during dehydration of metal ion which make the ΔG more negative compared to enthalpy. But, in case of explicit hydration, when released water molecules form water cluster, the entropy was again found to be negative and hence the ΔG was found to be reduced compared to enthalpy. As expected the gas phase free energy fails to capture the experimental results. Hence, now the thermodynamic parameters are calculated for the listed metal ions in their nitrate form and the gas phase values are listed in Table S8 using the following complexation reaction as

$$\text{M-(NO}_3)_3 + 3\text{L} \longrightarrow \text{M(L)}_3(\text{NO}_3)_3 \qquad \text{(S3)}$$

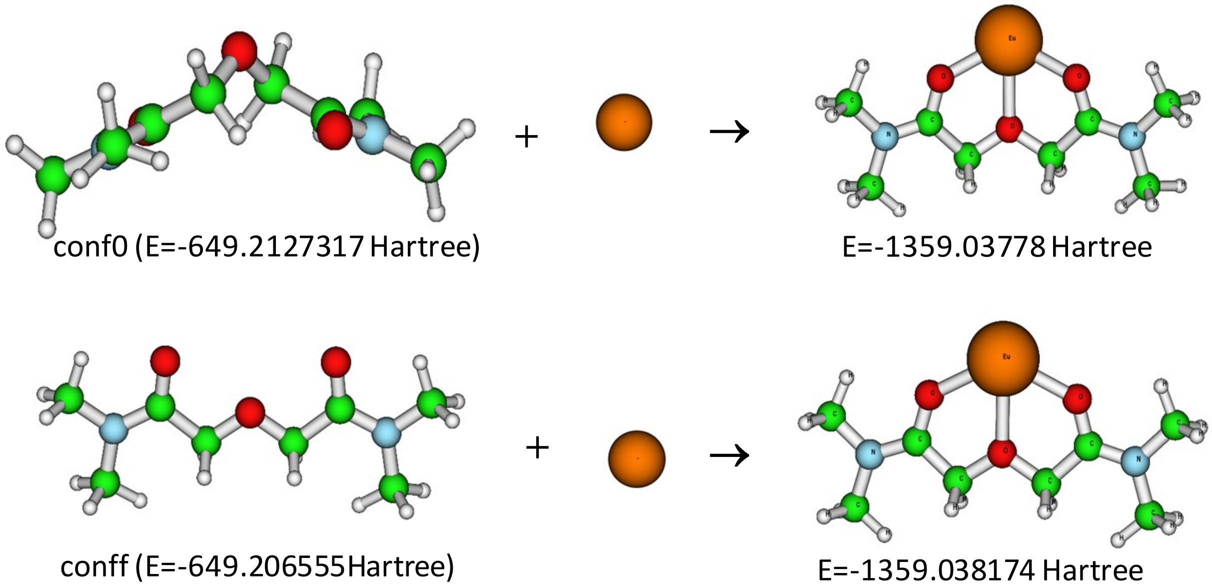
The gas phase values of enthalpy of complexation for all the metal ions are found to be negative. The change in entropy for the complexation reaction was also found to be negative. The negative contribution of entropy outweigh the negative enthalpy value and hence the ΔG was found to be positive except La3+ ion, where it was found to be negative. This gas phase results fails to capture the experimentally observed results. This might be due to non-consideration of aqueous and organic phase in the energy calculation. Next, we have considered the hydrated metal nitrate where five water molecules are coordinated to the metal ion as

$$\text{M-(NO}_3)_3\text{-(H}_2\text{O)}_5 + 3\text{L} \longrightarrow \text{M(L)}_3(\text{NO}_3)_3 + 5\text{H}_2\text{O} \qquad \text{(S4)}$$

The calculated values of ΔU, ΔH, ΔS and ΔG are listed in Table S9. The calculated values of ΔU and ΔH are found to be positive. The value of ΔS is though found to be positive, when it is combined with ΔH fails to make the ΔG negative indicating that the metal ion extraction is thermodynamically unfavourable. So, gas phase value fails to capture the experimental observation. The residual charge using natural population analysis (NPA) and the orbital population for different metal-ligand complexes like $\text{M(L)}_3(\text{NO}_3)_3$ are listed in Table S10. Among, the f orbital containing metal ions, the residual NPA charge was found to be highest on Lu^{3+} ion and lowest on Eu^{3+} ion, whereas, the zero point energy corrected interaction energy was found to be highest with Lu^{3+} ion (-1089.79kcal/mol) and lowest with Am^{3+} ion (-1026.85kcal/mol) indicating the NPA charge cannot be correlated with the interaction energy. Further, there is increased population in s, d and f orbitals indicating covalence in the bonding and the extent of covalence is more in Eu^{3+} ion due to slight more population in f orbitals compared to other metal ions. There is almost zero population in the g orbitals suggesting its non-participation in the bonding.

Conformational analysis of TMDGA and its Eu^{3+} complex

As mentioned earlier, that the initial geometry of TMDGA and its complexes with metal ions were optimized using energy minimization technique (Quasi Newton-Raphson optimization technique) as implemented in Turbomole package. The minimum energy structure in the potential energy is considered to be the stationary point albeit local minima where the energy gradient is zero. It is true that TMDGA molecule is flexible and can adopt several conformations but we believe that the possible conformers will be having close energy spacing and the present structure what we have optimized will not be much differ from the others. Nevertheless, we believe that even a conformer with lower energy is possible; it will not change the selectivity trend between the metal ions and TMDGA. Further, the sampling of the TMDGA was performed for probable conformers using conformational search algorithm, COSMOconf [COSMOconf, COSMOlogicGmbH&Co. KG]. Total 28 conformers were predicted and were found to be more stable (within 2.57-3.87kcal/mol) than that of our reported optimized TMDGA (conff) where all the O donor atoms were in the same plane and projected in the same direction. The optimized structure of most stable conformer (conf0) is displayed in Figure S1 where two carbonyl O atoms are shown be in the same plane but perpendicular to each other whereas the ethereal O atom is found to be perpendicular to the plane containing the carbonyl O atoms. The total energy of the predicted conformers are presented in Table S17.



conf0 (E=-649.2127317 Hartree)

E=-1359.03778 Hartree

conff (E=-649.206555Hartree)

E=-1359.038174 Hartree

Figure S1: Calculated structure and energy of conformers of TMDGA and its complexes with Eu^{3+} ion at the BP/SVP level of theory.

It is worth mentioning that the most stable conformer (conf0) during complexation with Eu^{3+} ion leads to a complex where all the three O donor atoms have come to the same plane and coordinated to the central metal ion as found in the case of least stable conformer (conff). Furthermore, the metal-ligand complex obtained from conf0 is energetically least stable than that of obtained from conff which in turn resulting in the higher binding energy for conff compared to conf0 as shown in Table S17. Therefore from the results, it might be concluded that though there are multiple conformers possible, their energy will be closely spaced after complexation. It is further anticipated that for the larger complexes where more ligands are involved i.e. 1:3 (M:L) stoichiometry, the probable other complexes than that has been reported in the present manuscript will be close in energy.

Table S1: Slope values obtained from the TODGA concentration variation experiments in n-dodecane medium.

M^{3+}	Slope (Ref 26)[a]	Slope (P.W.)[b]
La^{3+}	3.2	2.95
Eu^{3+}	3.9	--
Lu^{3+}	4.2	2.79
Am^{3+}	3.4	--

[a] Experiments were carried out at 3 M HNO_3; [b] Experiments carried out at 1 M HNO_3

Table S2: Calculated structural parameters (in Å) of 1:1 stoichiometric complexes.

System	M-O (O of C=O)	M-O (O of ether)	C=O
La	2.25, 2.25	2.49	1.31, 1.31
Eu	2.28, 2.28	2.49	1.27, 1.27
Lu	2.04, 2.04	2.23	1.31, 1.31
Am	2.19, 2.19	2.43	1.30, 1.30
Cm	2.15, 2.15	2.40	1.31, 1.31

Table S3: Calculated structural parameters (in Å) of 1:2 stoichiometric complexes.

System	M-O (O of C=O)	M-O (O of ether)	C=O
La	2.40, 2.39, 2.40, 2.40	2.63, 2.63	1.28,1.28, 1.28,1.82
Eu	2.31, 2.31, 2.31, 2.31	2.52, 2.54	1.27, 1.27, 1.27, 1.27
Lu	2.16, 2.16, 2.16, 2.16	2.35, 2.35	1.28, 1.28, 1.28, 1.28
Am	2.29, 2.29, 2.30, 2.28	2.51, 2.50	1.28, 1.28, 1.28, 1.28
Cm	2.28, 2.28, 2.28, 2.28	2.52, 2.52	1.28, 1.28, 1.28, 1.28

Table S4: Calculated gas phase binding energy (kcal/mol) of metal ions with TMDGA in different stoichiometric without nitrate anion at B3LYP/TZVPP level of theory.

	1:1			1:2			1:3		
	bare ion	hydrated	cluster	bare ion	Hydrated	cluster	bare ion	hydrated	cluster
La	-354.45	125.20	59.10	-532.55	-52.89	-118.99	-620.31	-140.65	-206.74
Eu	-420.99	116.07	49.97	-599.60	-62.53	-128.63	-687.89	-155.74	-221.84
Lu	-438.42	134.74	68.75	-649.32	-76.15	-142.24	-718.53	-145.36	-211.45
Am	-397.79	120.23	54.13	-580.92	-62.89	-128.99	-664.74	-148.11	-214.21
Cm	-393.38	127.52	61.42	-583.26	-62.35	-128.45	-668.15	-147.41	-213.51

Table S5: Calculated thermodynamic parameters of metal ions with TMDGA in 1:3 complex using explicit and cluster solvation model without nitrate anion at B3LYP/TZVPP level of theory (gas phase).

Metals	ΔU (kcal/mol)	ΔH(kcal/mol)	ΔS (kcal/mol/K)	ΔG(kcal/mol)
bare ion				
La	-613.28	-615.05	-0.12	-579.45
Eu	-680.79	-682.56	-0.12	-646.52
Lu	-710.52	-712.59	-0.13	-672.09
Am	-659.57	-661.34	-0.13	-623.00
Cm	-661.36	-663.13	-0.13	-624.66
explict				
La	-152.51	-148.97	0.16	-197.54
Eu	-162.80	-159.26	0.17	-209.62
Lu	-156.23	-152.69	0.16	-200.74
Am	-160.24	-156.70	0.16	-204.12
Cm	-159.09	-155.55	0.16	-203.10
cluster				
La	-196.27	-197.45	-0.12	-162.83
Eu	-206.56	-207.74	-0.12	-174.91
Lu	-199.99	-201.17	-0.11	-166.03
Am	-204.00	-205.18	-0.12	-169.41
Cm	-202.84	-204.02	-0.12	-168.40

Table S6: Calculated thermodynamic parameters of metal ion nitrates with TMDGA in 1:3 complexes in gas phase at B3LYP/TZVPP level of theory.

Metals	ΔU(kcal/mol)	ΔH(kcal/mol)	ΔS(kcal/mol/K)	ΔG(kcal/mol)
La	-55.30	-57.07	-0.166	-7.30
Eu	-47.28	-49.06	-0.167	0.76
Lu	-51.33	-53.10	-0.184	1.97
Am	-49.66	-51.43	-0.180	2.50
Cm	-49.98	-51.75	-0.178	1.44

Table S7: Calculated thermodynamic parameters of hydrated metal ion nitrates with TMDGA in 1:3 complexes in gas phase at B3LYP/TZVPP level of theory.

Metals	ΔU(kcal/mol)	ΔH(kcal/mol)	ΔS(kcal/mol/K)	ΔG(kcal/mol)
La	5.10	6.28	0.007	4.08
Eu	3.44	4.63	0.014	0.23
Lu	0.67	1.85	-0.0007	2.09
Am	2.79	3.97	0.003	3.01
Cm	3.61	4.79	0.009	1.96

Table S8: Calculated values of NPA charge of metal ions in $M(DGA)_3(NO_3)_3$ complex at B3LYP/TZVPP level of theory.

Metal	Total Charge	n(s)	n(p)	n (d)	n (f)	n(g)
La	2.28	2.12	5.98	0.60	-	-
Eu	1.88	4.14	11.99	10.76	6.21	0
Lu	1.99	4.18	12.00	10.82	13.99	0
Am	1.97	4.16	11.98	10.78	6.12	0.001
Cm	1.98	4.16	11.99	10.77	7.07	0.001

Table S9: Computed values of electron density and Laplacian of electron density and ellipsity of (a) M^{3+}-(TMDGA)$_3$ complexes at the B3LYP/TZ2P level using Bader's AIM calculation as implemented in ADF.

Metal	BCP	ρ	Ave. $\nabla 2\rho$	Ave. ε
La	La-O1	0.0259	0.144	0.0162
	La-O2	0.0425		
	La-O3	0.0426		
	La-O4	0.0263		
	La-O5	0.0426		
	La-O6	0.0424		
	La-O7	0.0260		
	La-O8	0.0429		
	La-O9	0.0423		
Eu	Eu-O1	0.0281	0.182	0.0256
	Eu-O2	0.0524		
	Eu-O3	0.0468		
	Eu-O4	0.0270		
	Eu-O5	0.0470		
	Eu-O6	0.0514		
	Eu-O7	0.0280		
	Eu-O8	0.0519		
	Eu-O9	0.0420		
Lu	Lu-O1	0.0536	0.208	0.0140
	Lu-O2	0.0528		
	Lu-O3	0.0311		
	Lu-O4	0.0537		
	Lu-O5	0.0308		
	Lu-O6	0.0527		
	Lu-O7	0.0308		
	Lu-O8	0.0530		
	Lu-O9	0.0534		
Am	Am-O1	0.0325	0.207	0.0482
	Am-O2	0.0580		
	Am-O3	0.0522		
	Am-O4	0.0365		
	Am-O5	0.0579		
	Am-O6	0.0529		
	Am-O7	0.0340		
	Am-O8	0.0550		
	Am-O9	0.0547		
Cm	Cm-O1	0.0318	0.200	0.0187
	Cm-O2	0.054		
	Cm-O3	0.0531		
	Cm-O4	0.0319		
	Cm-O5	0.0540		
	Cm-O6	0.053		
	Cm-O7	0.0318		
	Cm-O8	0.0547		
	Cm-O9	0.0528		

Table S9: Computed values of electron density and Laplacian of electron density and ellipsity of (b) M^{3+}-$(H_2O)_9$ clusters at the B3LYP/TZ2P level using Bader's AIM calculation as implemented in ADF.

Metal	BCP	ρ	Ave. ∇2ρ	Ave. ε
La	La-O1	0.0341	0.132	0.148
	La-O2	0.0344		
	La-O3	0.0341		
	La-O4	0.0335		
	La-O5	0.0330		
	La-O6	0.0330		
	La-O7	0.0340		
	La-O8	0.0340		
	La-O9	0.0340		
Eu	Eu-O1	0.0366	0.156	0.105
	Eu-O2	0.0368		
	Eu-O3	0.0329		
	Eu-O4	0.0379		
	Eu-O5	0.0361		
	Eu-O6	0.0394		
	Eu-O7	0.0361		
	Eu-O8	0.0393		
	Eu-O9	0.0368		
Lu	Lu-O1	0.0354	0.186	0.148
	Lu-O2	0.0440		
	Lu-O3	0.0438		
	Lu-O4	0.0442		
	Lu-O5	0.0350		
	Lu-O6	0.0348		
	Lu-O7	0.0441		
	Lu-O8	0.0445		
	Lu-O9	0.0443		
Lu*	Lu-O1	0.0470	0.241	0.115
	Lu-O2	0.0484		
	Lu-O3	0.0472		
	Lu-O4	0.0486		
	Lu-O5	0.0470		
	Lu-O6	0.0459		
	Lu-O7	0.0458		
	Lu-O8	0.0470		
	Lu-O9	0.0471		
Am	Am-O1	0.0377	0.167	0.127
	Am-O2	0.0404		
	Am-O3	0.0390		
	Am-O4	0.0416		
	Am-O5	0.0378		
	Am-O6	0.0350		
	Am-O7	0.0400		
	Am-O8	0.0391		
	Am-O9	0.04118		
Cm	Cm-O1	0.0436	0.182	0.12
	Cm-O2	0.0400		
	Cm-O3	0.0429		
	Cm-O4	0.4060		
	Cm-O5	0.0398		
	Cm-O6	0.0431		
	Cm-O7	0.0430		
	Cm-O8	0.0433		
	Cm-O9	0.0427		

*8 water cluster

Table S10: Calculated values of average second order stabilization energies $E_{ij}^{(2)}$ using NBO analysis as implemented in ADF Package at B3LYP/TZ2P level of theory.

Donar nbo (i)	Accepter nbo (j)	E(2) (kcal/mol)
LP(1)O2	LV(7)Eu1	1.94
	LV(8)Eu1	0.06
	LV(9)Eu1	4.29
	LV(10)Eu1	1.33
	LV(11)Eu1	1.87
	LV(12)Eu1	2.57
LP(2)O2	LV(7)Eu1	2.00
	LV(8)Eu1	0.07
	LV(9)Eu1	4.72
	LV(10)Eu1	0.24
	LV(11)Eu1	4.55
	LV(12)Eu1	1.36
	LV(13)Eu1	0.39
LP(1)O3	LV(7)Eu1	3.07
	LV(8)Eu1	7.19
	LV(9)Eu1	6.21
	LV(10)Eu1	0.32
	LV(11)Eu1	4.96
	LV(12)Eu1	1.83
LP(2)O3	LV(7)Eu1	2.24
	LV(8)Eu1	9.74
	LV(9)Eu1	6.90
	LV(10)Eu1	0.27
	LV(11)Eu1	0.28
	LV(13)Eu1	0.53
LP(3)O3	LV(7)Eu1	0.20
	LV(10)Eu1	2.95
	LV(11)Eu1	0.36
	LV(12)Eu1	1.74
	LV(13)Eu1	0.67
LP(1)O4	LV(7)Eu1	2.26
	LV(8)Eu1	3.28
	LV(9)Eu1	5.67
	LV(10)Eu1	0.18
	LV(11)Eu1	6.58
	LV(12)Eu1	1.73
	LV(13)Eu1	0.23
LP(2)O4	LV(7)Eu1	1.63
	LV(8)Eu1	7.85
	LV(9)Eu1	7.87
	LV(11)Eu1	1.54
	LV(12)Eu1	0.28
	LV(13)Eu1	0.04
LP(3)O4	LV(7)Eu1	0.25
	LV(11)Eu1	1.25
	LV(12)Eu1	3.60
	LV(13)Eu1	0.13
LP(1)O5	LV(7)Eu1	0.64
	LV(8)Eu1	2.19
	LV(9)Eu1	5.81
	LV(10)Eu1	0.48
	LV(11)Eu1	4.18
	LV(12)Eu1	2.10
	LV(13)Eu1	0.17
LP(2)O5	LV(7)Eu1	0.29
	LV(8)Eu1	0.95
	LV(9)Eu1	2.65
	LV(10)Eu1	2.59
	LV(11)Eu1	0.08
	LV(12)Eu1	1.87
	LV(13)Eu1	0.07
LP(1)O6	LV(7)Eu1	0.74
	LV(8)Eu1	5.69
	LV(9)Eu1	5.76
	LV(10)Eu1	1.66
	LV(11)Eu1	4.37
	LV(12)Eu1	2.13
	LV(13)Eu1	0.24

LP(2)O6	LV(7)Eu1	2.93
	LV(8)Eu1	7.12
	LV(9)Eu1	7.93
	LV(10)Eu1	0.18
	LV(11)Eu1	1.00
	LV(12)Eu1	0.22
	LV(13)Eu1	0.09
LP(3)O6	LV(7)Eu1	0.03
	LV(8)Eu1	0.12
	LV(10)Eu1	0.13
	LV(11)Eu1	1.75
	LV(12)Eu1	3.26
	LV(13)Eu1	0.17
LP(1)O7	LV(7)Eu1	9.34
	LV(9)Eu1	5.94
	LV(10)Eu1	2.29
	LV(11)Eu1	3.60
	LV(12)Eu1	1.84
LP(2)O7	LV(7)Eu1	11.29
	LV(8)Eu1	0.25
	LV(9)Eu1	6.55
	LV(10)Eu1	0.64
	LV(11)Eu1	0.12
	LV(12)Eu1	0.06
	LV(13)Eu1	0.64
LP(3)O7	LV(7)Eu1	0.14
	LV(8)Eu1	0.15
	LV(10)Eu1	2.70
	LV(11)Eu1	0.04
	LV(12)Eu1	2.12
	LV(13)Eu1	0.54
LP(1)O8	LV(7)Eu1	0.51
	LV(8)Eu1	2.58
	LV(9)Eu1	5.02
	LV(10)Eu1	5.84
	LV(11)Eu1	0.10
	LV(12)Eu1	0.70
	LV(13)Eu1	0.14
LP(2)O8	LV(7)Eu1	0.38
	LV(8)Eu1	1.57
	LV(9)Eu1	3.26
	LV(10)Eu1	2.63
	LV(11)Eu1	2.02
	LV(12)Eu1	0.42
	LV(13)Eu1	0.11
LP(1)O9	LV(7)Eu1	9.02
	LV(8)Eu1	0.27
	LV(9)Eu1	5.62
	LV(10)Eu1	6.92
	LV(11)Eu1	0.25
	LV(12)Eu1	0.38
	LV(13)Eu1	0.29
LP(2)O9	LV(7)Eu1	12.30
	LV(9)Eu1	6.66
	LV(10)Eu1	1.00
	LV(13)Eu1	0.30
LP(3)O9	LV(7)Eu1	6.11
	LV(8)Eu1	0.15
	LV(10)Eu1	0.50
	LV(11)Eu1	0.92
	LV(12)Eu1	3.87
	LV(13)Eu1	0.15

Donar nbo (i)	Accepter nbo (j)	E(2) (kcal/mol)
LP(1)O2	LV(7)Am1	0.68
	LV(8)Am1	2.68
	LV(9)Am1	3.39
	LV(10)Am1	5.08
	LV(11)Am1	3.18
	LV(12)Am1	0.20
	LV(13)Am1	0.31
LP(2)O2	LV(7)Am1	0.38
	LV(8)Am1	1.19
	LV(10)Am1	3.66
	LV(11)Am1	1.44
	LV(12)Am1	1.10
	LV(13)Am1	0.09
LP(1)O3	LV(7)Am1	5.94
	LV(8)Am1	9.85
	LV(9)Am1	2.30
	LV(10)Am1	6.28
	LV(11)Am1	1.26
	LV(13)am1	0.30
LP(2)O3	LV(7)Am1	6.09
	LV(8)Am1	6.61
	LV(9)Am1	1.95
	LV(10)Am1	0.17
	LV(12)Am1	0.78
	LV(13)Am1	0.12
LP(3)O3	LV(8)Am1	0.21
	LV(9)Am1	1.06
	LV(10)Am1	0.19
	LV(11)Am1	3.57
	LV(12)Am1	1.17
	LV(13)Am1	0.11
LP(1)O4	LV(7)Am1	9.18
	LV(8)Am1	1.75
	LV(10)Am1	7.92
	LV(11)Am1	2.52
	LV(12)Am1	0.54
	LV(13)Am1	0.24
LP(2)O4	LV(7)Am1	10.56
	LV(8)Am1	0.39
	LV(9)Am1	0.41
	LV(10)Am1	1.39
	LV(11)Am1	0.07
	LV(12)Am1	0.34
	LV(13)Am1	0.17
LP(3)O4	LV(9)Am1	0.27
	LV(10)Am1	1.38
	LV(11)Am1	2.41
	LV(12)Am1	1.34
	LV(13)Am1	0.12
LP(1)O5	LV(7)Am1	0.32
	LV(8)Am1	1.51
	LV(9)Am1	5.34
	LV(10)Am1	0.38
	LV(11)Am1	1.87
	LV(12)Am1	2.20
	LV(13)Am1	0.10
LP(2)O5	LV(7)Am1	0.72
	LV(8)Am1	1.78
	LV(9)Am1	2.38
	LV(10)Am1	5.79
	LV(11)Am1	3.31
	LV(12)Am1	0.09
	LV(13)Am1	0.17
LP(1)O6	LV(7)Am1	14.67
	LV(8)Am1	0.14
	LV(9)Am1	1.82
	LV(10)Am1	4.74
	LV(11)Am1	0.93
	LV(12)Am1	1.83
	LV(13)Am1	0.28
LP(2)O6	LV(7)Am1	13.87
	LV(8)Am1	1.00
	LV(10)Am1	0.76
	LV(12)Am1	0.04
	LV(13)Am1	0.15

LP(3)O6	LV(7)Am1	0.06
	LV(10)Am1	2.45
	LV(11)Am1	2.87
	LV(12)Am1	0.46
	LV(13)Am1	0.06
LP(1)O7	LV(8)Am1	11.05
	LV(9)Am1	6.63
	LV(10)Am1	3.66
	LV(11)Am1	1.20
	LV(12)Am1	0.77
	LV(13)Am1	0.32
LP(2)O7	LV(7)Am1	0.71
	LV(8)Am1	10.90
	LV(9)Am1	3.42
	LV(10)Am1	0.40
	LV(11)Am1	0.03
	LV(12)Am1	0.32
	LV(13)Am1	0.14
LP(3)O7	LV(8)Am1	0.09
	LV(9)Am1	1.05
	LV(10)Am1	0.04
	LV(11)Am1	3.25
	LV(12)Am1	1.74
	LV(13)Am1	0.06
LP(1)O8	LV(7)Am1	2.81
	LV(8)Am1	0.21
	LV(9)Am1	8.05
	LV(10)Am1	0.13
	LV(11)Am1	4.28
	LV(12)Am1	1.36
	LV(13)Am1	0.25
LP(2)O8	LV(7)Am1	0.92
	LV(8)Am1	0.06
	LV(9)Am1	1.78
	LV(10)Am1	3.19
	LV(11)Am1	1.49
	LV(12)Am1	0.03
	LV(13)Am1	0.07
LP(1)O9	LV(7)Am1	2.80
	LV(8)Am1	10.02
	LV(9)Am1	5.10
	LV(10)Am1	0.52
	LV(11)Am1	2.68
	LV(12)Am1	2.01
	LV(13)Am1	0.31
LP(2)O9	LV(7)Am1	1.19
	LV(8)Am1	13.00
	LV(9)Am1	1.31
	LV(11)Am1	0.04
	LV(12)Am1	0.07
	LV(13)Am1	0.13
LP(3)O9	LV(8)Am1	0.05
	LV(9)Am1	1.24
	LV(10)Am1	0.63
	LV(11)Am1	2.52
	LV(12)Am1	2.20
	LV(13)Am1	0.10
LP(1)O10	LV(7)Am1	8.87
	LV(8)Am1	5.02
	LV(9)Am1	5.27
	LV(10)Am1	1.43
	LV(11)Am1	1.98
	LV(12)Am1	1.41
	LV(13)Am1	0.39
LP(2)O10	LV(7)Am1	6.55
	LV(8)Am1	7.35
	LV(9)Am1	0.93
	LV(10)Am1	0.53
	LV(12)Am1	0.16
	LV(13)Am1	0.12
LP(3)O10	LV(7)Am1	0.25
	LV(9)Am1	0.11
	LV(10)Am1	1.49
	LV(11)Am1	3.01
	LV(12)Am1	0.19
	LV(13)Am1	0.18

Table S11: Calculated values of reaction enthalpy, entropy and free energies in gas phase and solution (kcal/mol).

M^{3+}	$\Delta G_{(gp)}$	$\Delta G_{sol(M(NO3)3}$	$\Delta G_{sol(L)}$	$\Delta G_{sol(ML3(NO3)3}$	ΔG_{ext}	$\Delta\Delta G_{(sol)}$
La	-7.30	-24.82	-6.81	-14.77	23.19	30.49
Lu	1.97	-10.26	-	-15.62	16.64	14.66
Eu	0.76	-10.07	-	-16.05	15.66	14.90
Am	2.50	-11.06	-	-16.43	17.59	15.08
Cm	1.44	-10.81	-	-15.78	16.93	15.48

Table S12: Calculated value of thermodynamic parameters (kcal/mol) for the extraction of different nitrate of Ln-An with TMDGA using B3LYP/TZVPP level of calculation at 298.15K (Scheme-2; monomer water model).

Complexation reaction	ΔH	$T\Delta S$	$\Delta G_{(gp)}$	ΔG_{sol}
La^{3+}-$(H_2O)_9$ + 3 NO_3^- = $La(NO_3)_3$ + 4 H_2O	-522.82	1.35	-524.28	-4.11
Eu^{3+}-$(H_2O)_9$ + 3 NO_3^- = $Eu(NO_3)_3$ + 4 H_2O	-531.90	2.64	-534.53	1.92
Lu^{3+}-$(H_2O)_9$ + 3 NO_3^- = $Lu(NO_3)_3$ + 4 H_2O	-541.25	3.34	-544.60	-7.20
Am^{3+}-$(H_2O)_9$ + 3 NO_3^- = $Am(NO_3)_3$ + 4 H_2O	-529.67	1.83	-531.50	-3.28
Cm^{3+}-$(H_2O)_9$ + 3 NO_3^- = $Cm(NO_3)_3$ + 4 H_2O	-528.21	1.14	-529.33	-0.12

Table S13: Calculated value of thermodynamic parameters (kcal/mol) for the extraction of metal nitrate of Ln-An with TMDGA using B3LYP/TZVPP level of calculation at 298.15K (Scheme-2; cluster water model, DCOSMO-RS).

M^{3+}	$\Delta G_{(gp)}$	$\Delta G_{sol(M(NO3)3}$	$\Delta G_{sol(ML3(NO3)3}$	ΔG_{ext}	$\Delta\Delta G_{(sol)}$
La	-7.30	-47.60	-14.77	33.92	45.98
Lu	1.97	-33.04	-15.62	38.10	39.42
Eu	0.76	-32.85	-16.05	29.70	38.44
Am	2.50	-33.85	-16.43	32.68	40.38
Cm	1.44	-33.59	-15.78	29.68	39.72

Table S14. Calculated values of the thermodynamic parameters (kcal/mol) for the extraction of Ln-An in presence of nitrate anion with TMDGA at the B3LYP/TZVPP level of calculation (T= 298.15K; Scheme-1, monomer water explicit, DCOSMO-RS).

M^{3+}	$\Delta G_{(gp)}$	$\Delta G_{sol(M)}$		$\Delta G_{sol(NO3)}$	$\Delta G_{sol(ML3(NO3)3}$	ΔG_{ext}	$\Delta\Delta G_{sol}$
La	-901.99	-704.06	-17.09	-54.23	-38.26	-22.21	879.78
Eu	-975.20	-767.74		-	-38.72	-32.19	943.00
Lu	-1011.09	-806.02		-	-38.57	-29.64	981.44
Am	-947.43	-747.10		-	-40.19	-26.54	920.89
Cm	-948.51	-749.12		-	-38.81	-24.21	924.30

Table S15: Calculated values of the thermodynamic parameters (kcal/mol) for the extraction of Ln-An in presence of nitrate anion with TMDGA at the B3LYP/TZVPP level of calculation (T= 298.15K; Scheme-1, cluster water, DCOSMO-RS).

M^{3+}	$\Delta G_{(gp)}$	$\Delta G_{sol(M)}$		$\Delta G_{sol(NO3)}$	$\Delta G_{sol(ML3(NO3)3}$	ΔG_{ext}	$\Delta\Delta G_{sol}$
La	-901.99	-770.67	-17.09	-54.23	-38.26	44.40	946.40
Eu	-975.20	-834.35		-	-38.72	34.41	1009.62
Lu	-1011.09	-872.64		-	-38.57	36.97	1048.06
Am	-947.43	-813.71		-	-40.19	40.07	987.51
Cm	-948.51	-815.74		-	-38.81	42.40	990.91

Table S16: Calculated values of the thermodynamic parameters (kcal/mol) for the extraction of Ln-An in presence of nitrate anion with TMDGA at the B3LYP-D3/TZVPP level of calculation (T= 298.15K; Scheme-1, cluster water, DCOSMO-RS).

M^{3+}	$\Delta G_{(gp)}$	$\Delta G_{sol(M)}$	$\Delta G_{sol(L)}$	$\Delta G_{sol(NO3)}$	$\Delta G_{sol(ML3(NO3)3}$	ΔG_{ext}	$\Delta\Delta G_{sol}$
La	-955.13	-779.41	-17.10	-54.23	-38.26	0.01	955.14
Eu	-1028.57	-848.77		-	-36.26	-2.06	1026.50
Lu	-1068.91	--876.71		-	-38.57	-6.77	1062.14

Table S17: Calculated total energy and stabilization energy of the various conformers of TMDGA, total energy of the Eu^{3+}-TMDGA complex with conff (with tridentate donor O atoms)[*] and with most stable conformer, conf0[**] and their corresponding binding energy at the BP/SVP level of theory.

Conformer Of TMDGA	Total energy of TMDGA (Hartree)	Stabilization energy (kcal/mol)	Total energy of TMDGA-Eu^{3+} (Hartree)[*]	Total energy of Eu^{3+} (Hartree)	Binding energy (kcal/mol)[*]	Total energy of TMDGA-Eu^{3+} (Hartree)[**]	Binding energy (kcal/mol)[**]
conff	-649.206555		-1359.038174	-709.095	-461.983		
conf0	-649.2127317	3.87	-1359.038174	-709.095	-458.107	-1359.03778	-457.86
conf1	-649.2126388	3.81	-1359.038174	-709.095	-458.165	-1359.03778	-457.919
conf2	-649.212384	3.65	-1359.038174	-709.095	-458.325	-1359.03778	-458.078
conf3	-649.2119857	3.40	-1359.038174	-709.095	-458.575	-1359.03778	-458.328
conf4	-649.2118999	3.35	-1359.038174	-709.095	-458.629	-1359.03778	-458.382
conf5	-649.2118761	3.33	-1359.038174	-709.095	-458.644	-1359.03778	-458.397
conf6	-649.2118105	3.29	-1359.038174	-709.095	-458.685	-1359.03778	-458.438
conf7	-649.2117558	3.26	-1359.038174	-709.095	-458.719	-1359.03778	-458.473
conf8	-649.2116741	3.21	-1359.038174	-709.095	-458.771	-1359.03778	-458.524
conf9	-649.2116446	3.19	-1359.038174	-709.095	-458.789	-1359.03778	-458.542
conf10	-649.2116153	3.17	-1359.038174	-709.095	-458.808	-1359.03778	-458.561
conf11	-649.2115843	3.15	-1359.038174	-709.095	-458.827	-1359.03778	-458.58
conf12	-649.2115468	3.13	-1359.038174	-709.095	-458.851	-1359.03778	-458.604
conf13	-649.2114602	3.07	-1359.038174	-709.095	-458.905	-1359.03778	-458.658
conf14	-649.2114355	3.06	-1359.038174	-709.095	-458.92	-1359.03778	-458.674
conf15	-649.2113677	3.01	-1359.038174	-709.095	-458.963	-1359.03778	-458.716
conf16	-649.2113261	2.99	-1359.038174	-709.095	-458.989	-1359.03778	-458.742
conf17	-649.2113078	2.98	-1359.038174	-709.095	-459.001	-1359.03778	-458.754
conf18	-649.2112718	2.95	-1359.038174	-709.095	-459.023	-1359.03778	-458.776
conf19	-649.2112136	2.92	-1359.038174	-709.095	-459.06	-1359.03778	-458.813
conf20	-649.211213	2.92	-1359.038174	-709.095	-459.06	-1359.03778	-458.813
conf21	-649.2111318	2.87	-1359.038174	-709.095	-459.111	-1359.03778	-458.864
conf22	-649.2111064	2.85	-1359.038174	-709.095	-459.127	-1359.03778	-458.88
conf23	-649.2111019	2.85	-1359.038174	-709.095	-459.13	-1359.03778	-458.883
conf24	-649.2110476	2.81	-1359.038174	-709.095	-459.164	-1359.03778	-458.917
conf25	-649.2109823	2.77	-1359.038174	-709.095	-459.205	-1359.03778	-458.958
conf26	-649.210931	2.74	-1359.038174	-709.095	-459.237	-1359.03778	-458.99
conf27	-649.2108931	2.72	-1359.038174	-709.095	-459.261	-1359.03778	-459.014
conf28	-649.2106487	2.56	-1359.038174	-709.095	-459.414	-1359.03778	-459.167