Inorganic Chemistry

Complexation Behavior of Eu(III) and Am(III) with CMPO and Ph_2CMPO Ligands: Insights from Density Functional Theory

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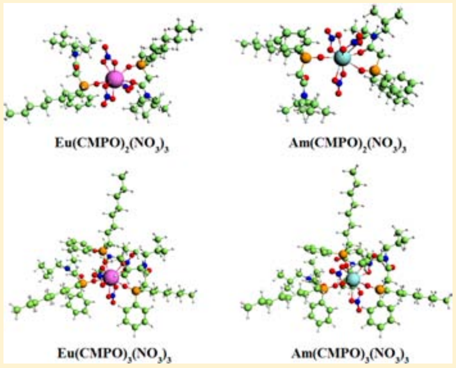
S *Supporting Information*



ABSTRACT: A series of extraction complexes of Eu(III) and Am(III) with CMPO (*n*-octyl(phenyl)-*N*,*N*-diisobutyl-methylcarbamoyl phosphine oxide) and its derivative Ph_2CMPO (diphenyl-*N*,*N*-diisobutyl carbamoyl phosphine oxide) have been studied using density functional theory (DFT). It has been found that for the neutral complexes of 2:1 and 3:1 (ligand/metal) stoichiometry, CMPO and Ph_2CMPO predominantly coordinate with metal cations through the phosphoric oxygen atoms. Eu(III) and Am(III) prefer to form the neutral 2:1 and 3:1 type complexes in nitrate-rich acid solutions, and in the extraction process the reactions of $[M(NO_3)(H_2O)_7]^{2+} + 2NO_3^- + nL \rightarrow ML_n(NO_3)_3 + 7H_2O$ (M = Eu, Am; $n = 2, 3$) are the dominant complexation reactions. In addition, CMPO and Ph_2CMPO show similar extractability properties. Taking into account the solvation effects, the metal−ligand binding energies are obviously decreased, i.e., the presence of solvent may have an significant effect on the extraction behavior of Eu(III) and Am(III) with CMPOs. Moreover, these CMPOs reagents have comparable extractability for Eu(III) and Am(III), confirming that these extractants have little lanthanide/actinide selectivity in acidic media.

1. INTRODUCTION

With the development of nuclear energy, safe disposal of the spent nuclear fuel especially high level liquid waste (HLLW) generated from the plutonium uranium extraction (PUREX) process has drawn extensive attention around the world. Liquid−liquid extraction is a very efficient separation method, which has proven to be applicable for the recovery and purification of minor actinides (MA) and other long-lived fission products. Nowadays, the co-extraction of MA and lanthanides is considered to be the precondition for MA separation from HLLW.[1]

Various extractants for co-extraction of actinides and lanthanides have been developed in the past few decades.[2] In particular, neutral bidentate organophosphorous reagents have gained much research attention for the recovery of actinides and lanthanides from HLLW.[3−5] Normally, these reagents coordinate in a bidentate pattern to the metal atoms with the carbonyl and phosphoric oxygen atoms. It has been found that the phosphoric oxygen is the predominant coordinating group due to its higher electron-donating ability.[6] Among these organophosphorous extractants, CMPO (*n*-octyl(phenyl)-*N*,*N*-diisobutyl-methylcarbamoyl phosphine oxide) (Figure 1a), which was selected for the so-called TRUEX (transuranium extraction) process, has been found to possess a strong extracting ability for trivalent actinides and lanthanides from highly acidic solutions.[7,8] Another alternative extractant, Ph_2CMPO (diphenyl-*N*,*N*-diisobutyl carbamoyl phosphine oxide) (Figure 1b), in which the alkyl groups on the phosphine moiety of CMPO are replaced by the phenyl groups, has also been deeply studied by Russian scientists and found to be efficient for actinide extraction.[9−11]

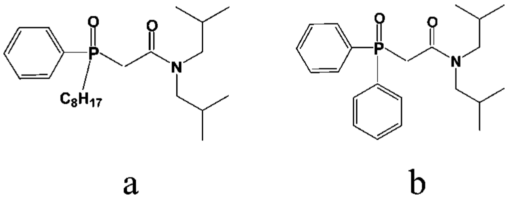


Figure 1. The CMPO (a) and Ph_2CMPO (b) extractants.

Received: April 10, 2013
Published: September 18, 2013

Table 1. Changes of the Gibbs Free Energy (kcal/mol) with Zero-Point Energy (ZPE) Corrections and Thermal Corrections for Complexing Reactions of Eu^{3+} and Am^{3+} in the Gas Phase and Aqueous Solution

reactions	ΔG_g	ΔG_{sol}
$[Eu(H_2O)_8]^{3+} + H_2O \rightarrow [Eu(H_2O)_9]^{3+}$	−12.2	1.0
$[Am(H_2O)_8]^{3+} + H_2O \rightarrow [Am(H_2O)_9]^{3+}$	−12.1	−0.6
$[Eu(H_2O)_9]^{3+} + NO_3^- \rightarrow [Eu(NO_3)(H_2O)_7]^{2+} + 2H_2O$	−253.2	−4.7
$[Am(H_2O)_9]^{3+} + NO_3^- \rightarrow [Am(NO_3)(H_2O)_7]^{2+} + 2H_2O$	−251.5	−7.0
$[Eu(H_2O)_9]^{3+} + 2NO_3^- \rightarrow [Eu(NO_3)_2(H_2O)_5]^{+} + 4H_2O$	−434.9	−21.1
$[Am(H_2O)_9]^{3+} + 2NO_3^- \rightarrow [Am(NO_3)_2(H_2O)_5]^{+} + 4H_2O$	−434.2	−19.4
$[Eu(H_2O)_9]^{3+} + 3NO_3^- \rightarrow Eu(NO_3)_3(H_2O)_3 + 6H_2O$	−541.6	−23.3
$[Am(H_2O)_9]^{3+} + 3NO_3^- \rightarrow Am(NO_3)_3(H_2O)_3 + 6H_2O$	−541.1	−24.6

There are numerous experimental investigations on the extraction behaviors of lanthanides and actinides from nitric acid solutions with CMPOs. For instance, Martin et al.[12] studied the efficiency of CMPO for separating Am(III) and Eu(III) in 1,2-dichloroethane and found that CMPO shows synergistic effects in combination with HTTA (thenoyltrifluoroacetone). Nagar et al.[13] isolated some lanthanide and actinide nitrate complexes of Nd(III), Pu(IV), U(VI), and Th(IV) with CMPO and suggested that these extractants serve as bidentate ligands in these complexes. Belair et al.[14] reported the extraction of some trivalent lanthanide nitrates with CMPO diluted in nitrophenylhexyl ether and demonstrated that $Ln(CMPO)_2(NO_3)_3$ and $Ln(CMPO)_3(NO_3)_3$ are the predominant species. Mathur et al.[15] investigated the extraction complexes of Eu(III) and Am(III) from NH_4NO_3 by CMPO in *n*-dodecane and found that $M(CMPO)_3(NO_3)_3$ is the dominant extracted complex between the temperatures of 15.0 and 45.0 °C. In addition, the effect of other anions, such as SCN^-, ClO_4^-, and a mixture of NO_3^- + ClO_4^-, on the extraction of Eu^{3+} and Am^{3+} with CMPO in xylene has also been evaluated.[16]

Though some experimental studies on the extraction complexes of lanthanides and actinides with CMPOs ligands have been carried out, the scarcity and radioactivity of the actinides are still the major hindrance to experimental investigations.[17] In contrast, theoretical studies can offer another alternative approach for studying these complexes. As far as we know, there is only one theoretical work published previously, which mainly focuses on the stoichiometry of the europium nitrate complexes with CMPO by molecular dynamics simulations.[18] In this study, the extraction of Eu(III) and Am(III) by CMPO and Ph_2CMPO in nitric acid solutions was explored via quantum mechanical (QM) calculations. The equilibrium geometries, electronic structures, and the stabilities of the Eu(III) and Am(III) extraction complexes will be systematically discussed.

2. THEORETICAL METHODS

The complexes were studied using density functional theory (DFT) methods[19−22] with the hybrid B3LYP[23,24] functional. Similar to our previous studies,[25−27] for geometry optimizations, the quasi-relativistic effective core potentials (RECP) and the corresponding valence basis sets[28−30] are used for the Eu and Am atom, including 28 and 60 electrons in the core, respectively, while the 6-31G(d) basis sets were adopted for the other atoms H, C, N, O and P. At the B3LYP/6-311G(d,p)/RECP level of theory, the harmonic vibrational frequencies were calculated on the basis of the optimized structures. All the computations were performed using the Gaussian 03 code.[31]

As for the f electrons in each Am(III) and Eu(III) complex, the ground state is considered to be the $5f^6$ and $4f^6$ configuration, respectively, and the electronic states are all ^7A. The default fine grid was (75, 302) for evaluating integrals numerically.[32] In order to reevaluate the small imaginary vibrational frequencies, a finer grid of (120, 974) was used. At the B3LYP/6-311G(d,p)/RECP level of theory, all the extraction complexes studied here show real vibrational frequencies, confirming the minima on the potential energy surfaces of these structures. Additionally, all the structures in the unrestricted DFT ground states exhibit negligible spin contamination, i.e., the $\langle S^2 \rangle$ values are very close to the $S(S + 1)$ ideal values.

At the B3LYP/6-311G(d,p)/RECP level of theory, the gas-phase Gibbs free energies (G_g) were gained, including the zero-point energy (ZPE) and thermal corrections. At the same level of theory, for the 1:1 (ligand/metal) stoichiometric complexes, the solvation Gibbs free energies (G_{sol}) were calculated in water by the conductor-like screening model (COSMO)[33] with the default atomic radii based on the optimized structures in the gas phase. Previous studies[33,34] referring to actinide species indicated that COSMO could get more accurate free energies in solvation. Besides, since reoptimizing the structures in solvent has little effect on energetics, single-point calculations based on the gas-phase geometries are thus sufficient for solvation energies.[35,36] We only calculated the electronic energies (E) for the large molecular systems of the 2:1 and 3:1 type complexes.

3. RESULTS AND DISCUSSION

3.1. Eu(III) and Am(III) Aquo and Nitrate Complexes.

Some experimental and theoretical studies[37−41] on the structures of the Eu(III) and Am(III) aquo complexes found that Eu^{3+} and Am^{3+} ions prefer an eight- or nine-coordinate in aqueous solution. For Eu^{3+} and Am^{3+} in the gas phase, our calculations (Table 1) show that the changes of the Gibbs free energy (ΔG_g) for the reaction of octahydrate to nonahydrate are all negative. Thus, nonahydrate seem to more stable for Eu^{3+} and Am^{3+}. Nevertheless, taking into account the solvent effect, the predicted changes of the Gibbs free energy is only 1.0 and −0.6 kcal/mol for the two reactions, respectively. These low energies suggest that, for Eu^{3+} and Am^{3+} in aqueous solution, a thermal equilibrium may exist between octahydrate and nonahydrate, which is consistent with the experimental results.[38]

As shown in Table 1, for the reactions of nonahydrate to the nine-coordinated nitrate hydrates, the ΔG_g values are in the range from −253.2 to −541.6 kcal/mol. In contrast, the ΔG_{sol} values are much lower, which are between −4.7 and −24.6 kcal/mol. These negative values demonstrate that the europium

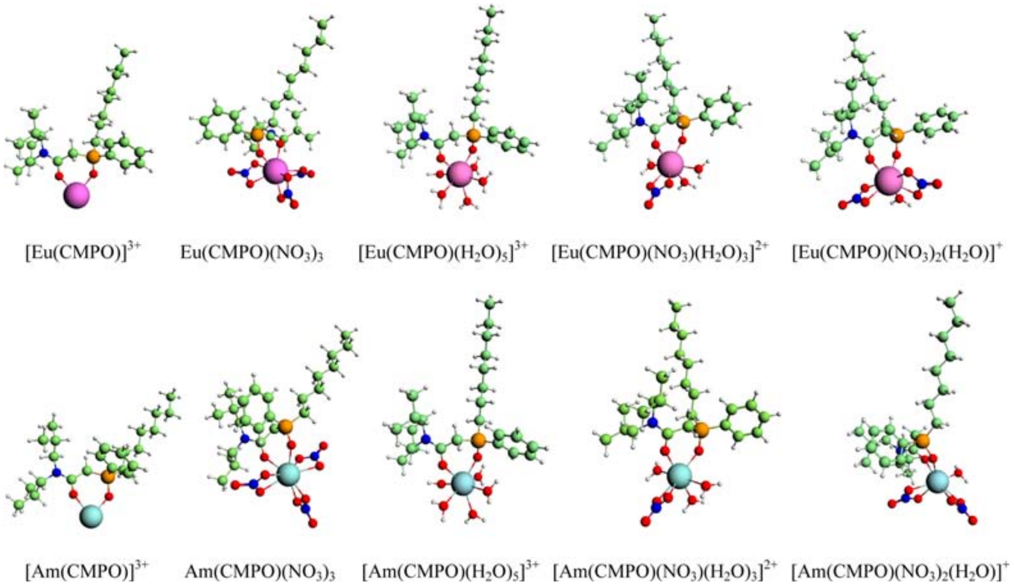


Figure 2. Optimized structures of the 1:1 type Eu(III) and Am(III) complexes with CMPO. Green, white, red, blue, orange, pink, and light blue spheres represent C, H, O, N, P, Eu, and Am, respectively.

Table 2. Calculated M−O Bond Lengths (Å) for the 1:1 Type Eu^{3+} and Am^{3+} Complexes with L (L = CMPO, Ph_2CMPO) by the B3LYP Method[a]

species	$M-O_C$	$M-O_P$	$M-O(NO_3^-)$[b]	$M-O(H_2O)$[b]
$[EuL]^{3+}$	2.265/2.269	2.269/2.320	–	–
$EuL(NO_3)_3$	2.488/2.420	2.371/2.403	2.438/2.437	–
$[EuL(H_2O)_5]^{3+}$	2.336/2.296	2.326/2.289	–	2.506/2.480
$[EuL(NO_3)(H_2O)_3]^{2+}$	2.289/2.288	2.281/2.287	2.374/2.377	2.467/2.459
$[EuL(NO_3)_2(H_2O)]^+$	2.341/2.336	2.294/2.300	2.404/2.402	2.453/2.462
$[AmL]^{3+}$	2.238/2.165	2.213/2.173	–	–
$AmL(NO_3)_3$	2.462/2.462	2.412/2.455	2.483/2.476	–
$[AmL(H_2O)_5]^{3+}$	2.297/2.297	2.280/2.265	–	2.519/2.527
$[AmL(NO_3)(H_2O)_3]^{2+}$	2.330/2.392	2.311/2.319	2.422/2.419	2.514/2.491
$[AmL(NO_3)_2(H_2O)]^+$	2.430/2.428	2.323/2.330	2.431/2.430	2.504/2.508

[a] .../... refers to the results of the complexes with CMPO and Ph_2CMPO, respectively. [b] Average bond lengths of An-O.

Table 3. Calculated Wiberg Bond Indices (WBIs) of the M−O Bonds for the 1:1 Type Eu^{3+} and Am^{3+} Complexes with L (L = CMPO, Ph_2CMPO) by the B3LYP Method[a]

species	$M-O_C$	$M-O_P$	$M-O(NO_3^-)$[b]	$M-O(H_2O)$[b]
$[EuL]^{3+}$	0.123/0.123	0.122/0.098	–	–
$EuL(NO_3)_3$	0.064/0.075	0.088/0.076	0.120/0.112	–
$[EuL(H_2O)_5]^{3+}$	0.115/0.142	0.113/0.133	–	0.069/0.076
$[EuL(NO_3)(H_2O)_3]^{2+}$	0.136/0.098	0.147/0.113	0.142/0.130	0.075/0.068
$[EuL(NO_3)_2(H_2O)]^+$	0.104/0.098	0.119/0.121	0.127/0.134	0.078/0.069
$[AmL]^{3+}$	0.176/0.268	0.202/0.296	–	–
$AmL(NO_3)_3$	0.106/0.090	0.108/0.096	0.121/0.132	–
$[AmL(H_2O)_5]^{3+}$	0.171/0.149	0.176/0.181	–	0.098/0.088
$[AmL(NO_3)(H_2O)_3]^{2+}$	0.148/0.142	0.169/0.150	0.156/0.175	0.100/0.100
$[AmL(NO_3)_2(H_2O)]^{2+}$	0.102/0.097	0.135/0.132	0.143/0.144	0.090/0.088

[a] .../... refers to the results of the complexes with CMPO and Ph_2CMPO, respectively. [b] Average WBIs of the M−O bonds.

and americium nitrate hydrates are more energetically favorable than the hydrates in both the gas phase and aqueous solution. Therefore, nitrate ions have a larger affinity for Eu^{3+} and Am^{3+} than water molecules. This result can be expected since nitrate ion is a negatively charged species and it has stronger electron-donating ability compared to water molecule. Moreover, for these nitrate hydrates, the neutral $Eu(NO_3)_3(H_2O)_3$ and $Am(NO_3)_3(H_2O)_3$ complexes are more stable than the charged nitrate hydrates.

3.2. 1:1 (Ligand/Metal) Type Extraction Complexes.

3.2.1. Geometrical Structures. Figures 2 and S1 (Supporting Information) show the optimized geometrical structures of the extraction complexes with 1:1 CMPO/Ph_2CMPO to metal stoichiometry. At the B3LYP/6-31G(d)/RECP level of theory, CMPO and Ph_2CMPO in all of the species act as bidentate

Table 4. Calculated Mulliken Orbital Populations (s, p, d, and f) and Natural Charges on the Metal and O Atoms for the 1:1 Type Eu^{3+} and Am^{3+} Complexes with L (L = CMPO, Ph_2CMPO) by the B3LYP Method[a]

	Mulliken orbital populations				Q		
species	s	p	d	f	O_C	O_P	M
$[EuL]^{3+}$	4.089/4.084	12.077/12.074	10.417/10.377	6.995/6.996	−0.904/−0.913	−1.265/−1.232	1.871/1.885
$EuL(NO_3)_3$	4.216/4.210	12.229/12.225	10.805/10.764	6.152/6.103	−0.793/−0.768	−1.194/−1.190	2.454/2.507
$[EuL(H_2O)_5]^{3+}$	4.191/4.191	12.260/12.272	10.646/10.718	6.347/6.362	−0.867/−0.887	−1.241/−1.250	2.394/2.343
$[EuL(NO_3)(H_2O)_3]^{2+}$	4.187/4.147	12.256/12.166	10.757/10.610	6.131/6.124	−0.858/−0.882	−1.232/−1.230	2.537/2.608
$[EuL(NO_3)_2(H_2O)]^{+}$	4.193/4.170	12.232/12.164	10.798/10.728	6.122/6.165	−0.826/−0.843	−1.227/−1.212	2.514/2.502
$[AmL]^{3+}$	4.134/4.205	12.073/12.115	10.523/10.729	6.691/6.382	−0.924/−0.936	−1.257/−1.211	2.088/2.284
$AmL(NO_3)_3$	4.241/4.261	12.303/12.295	10.776/10.813	6.106/6.107	−0.769/−0.767	−1.181/−1.182	2.444/2.410
$[AmL(H_2O)_5]^{3+}$	4.231/4.226	12.303/12.298	10.840/10.831	6.091/6.049	−0.895/−0.893	−1.251/−1.254	2.512/2.576
$[AmL(NO_3)(H_2O)_3]^{2+}$	4.229/4.228	12.304/12.292	10.834/10.813	6.106/6.120	−0.860/−0.852	−1.236/−1.229	2.461/2.458
$[AmL(NO_3)_2(H_2O)]^{+}$	4.250/4.219	12.278/12.209	10.847/10.761	6.078/6.103	−0.830/−0.834	−1.220/−1.216	2.473/2.481

[a] .../... refers to the results of the complexes with CMPO and Ph_2CMPO, respectively.

Table 5. Metal-Ligand Binding Energies (kcal/mol) for the 1:1 Type Eu^{3+} and Am^{3+} Complexes with L (L = CMPO, Ph_2CMPO) Calculated by the B3LYP Method[a]

reactions	ΔG_g	ΔG_{sol}
$Eu^{3+} + L \rightarrow [EuL]^{3+}$	−462.5/−443.1	−100.8/−111.4
$Eu^{3+} + L + 5H_2O \rightarrow [EuL(H_2O)_5]^{3+}$	−559.4/−554.6	−165.3/−169.0
$Eu^{3+} + L + 3NO_3^- \rightarrow EuL(NO_3)_3$	−1025.2/−1027.6	−197.5/−193.6
$Eu^{3+} + L + NO_3^- + 3H_2O \rightarrow [EuL(NO_3)(H_2O)_3]^{2+}$	−771.0/−771.0	−175.1/−174.8
$Eu^{3+} + L + 2NO_3^- + H_2O \rightarrow [EuL(NO_3)_2(H_2O)]^{+}$	−926.8/−929.6	−185.5/−185.6
$Am^{3+} + L \rightarrow [AmL]^{3+}$	−420.1/−398.1	−92.9/−91.9
$Am^{3+} + L + 5H_2O \rightarrow [AmL(H_2O)_5]^{3+}$	−534.4/−535.4	−147.1/−146.9
$Am^{3+} + L + 3NO_3^- \rightarrow AmL(NO_3)_3$	−1007.7/−1011.1	−167.6/−178.4
$Am^{3+} + L + NO_3^- + 3H_2O \rightarrow [AmL(NO_3)(H_2O)_3]^{+}$	−754.2/−751.5	−162.0/−157.9
$Am^{3+} + L + 2NO_3^- + H_2O \rightarrow [AmL(NO_3)_2(H_2O)]^{+}$	−905.8/−907.3	−164.9/−169.1

[a] .../... refers to the results of the complexes with CMPO and Ph_2CMPO, respectively.

ligands via the carbonyl and phosphoryl groups, and most of the species with CMPO and Ph_2CMPO ligand have similar geometrical structures. As shown in Table 2, the M−O_C and M−O_P bond lengths for most of the hydrates, nitrates, and nitrate hydrates are longer than those for the $[ML]^{3+}$ species. Besides, for most complexes these bond lengths increased with the nitrate ions replacing the water molecules and $ML(NO_3)_3$ exhibit the longest M−O bonds. These results indicate the strong affinity of nitrate ions to the metal centers. Interestingly, $[EuL(H_2O)_5]^{3+}$ and $[EuL(NO_3)(H_2O)_3]^{2+}$ seem to buck the trend, which may be due to the steric effect of the water molecules compared to the nitrate ions and the weak intramolecular hydrogen bonding between the water molecules and the nitrate ions with O···O distances of about 2.7 Å. In addition, since for each species with CMPO and Ph_2CMPO ligand, the M−O bond lengths are very close to each other, the substituents of these CMPOs ligands have little influence on the geometrical structures of these complexes.

3.2.2. Electronic Structures.

At the B3LYP/6-31G(d)/RECP level of theory, the natural bond orbital (NBO) analysis[42−45] was carried out in order to analyze the nature of the bonding for these Eu(III) and Am(III) extraction complexes.

As listed in Table 3, for all the M−O bonds in these extraction complexes, the Wiberg bond indices (WBIs) are between 0.1 and 0.3. This indicates that these bonds are mainly ionic, that is, electrostatic interactions dominate the M−O bondings. For each species with CMPO and Ph_2CMPO ligands, the WBIs of the M−O bonds are nearly equal to each other, which is consistent with the M−O bond lengths for these complexes. For the $[EuL]^{3+}$ and $[AmL]^{3+}$ species, the M−O WBIs are larger than most of the corresponding hydrates and nitrate hydrates, suggesting the more ionic character of the metal−ligand bonds in the hydrates and nitrate hydrates relative to those in $[ML]^{3+}$. The M−O_C WBIs for most of these species are smaller than the M−O_P bonds, implying a higher degree of covalence in the M−O_P bond. It should be noted that, in most cases, the M−O WBIs of the Am(III) extraction complexes are slightly larger than those for the corresponding Eu(III) extraction complexes. This result seems to be in accordance with the higher covalent character of the actinide bonding compared to the lanthanide bonding.[46]

To gain more insight into the nature of the metal−ligand bonding in these extraction complexes, the Mulliken orbital population occupancy of the valence s, p, d, f shells and natural population analysis (NPA) for these species are calculated at the same level of theory (Table 4). The small-core RECPs applied in this work attribute $4s^24p^64d^{10}4f^65s^25p^6$ and $5s^25p^65d^{10}5f^66s^26p^6$ as the ground-state valence subconfigurations for Eu^{3+} and Am^{3+}, respectively. Compared with the free trivalent europium and americium cations, Mulliken orbital populations show that additional electrons occupied the s, p, d and f shells in these complexes. Although $[EuL]^{3+}$ and $[AmL]^{3+}$ show relatively high populations in the valence f shells, the s, p, and d shells are significantly less occupied than for other species. Moreover, the additional f populations for the Eu^{3+} species are higher than for the corresponding Am^{3+} species, while the Eu^{3+} species have lower s, p, and d orbital populations. In terms of NPA analysis, the natural charges on the Eu and Am atoms are in the range from 1.871 to 2.608, indicating significant electronic charge transfer from the ligands to the metal atoms. As for $[EuL(H_2O)_5]^{3+}$, the oxygen atoms of the phosphoryl and the carbonyl groups show more negative natural charges, which result in smaller natural charges on the europium atoms. Additionally, the natural charge on the phosphoric oxygen atom for each complexes is more negative compared to the carbonyl oxygen atom, indicating the stronger electron-donating ability of the P=O group to the metal atoms.

3.2.3. Metal–Ligand Binding Energy. At the B3LYP/6-311G(d,p) level of theory, the stabilities of these extraction complexes have been estimated by the metal–ligand complexation reactions (Table 5). For all these species, the gas-phase binding energies (ΔG_g) are in the range from −398.1 to −1027.6 kcal/mol, which are much higher than the hydration binding energies (ΔG_{sol}). Thus, solvation energy may be one of the major factors influencing the extraction process. It can be seen that both the gas-phase and hydration binding energies of the Eu(III) complexes are slightly higher than those of the corresponding Am(III) complexes, implying that the Eu(III) complexes are more stable than the Am(III) complexes. For all these extraction complexes, the gas-phase and hydration binding energies of the neutral $EuL(NO_3)_3$ and $AmL(NO_3)_3$ complexes are found to be much higher than those of the charged species. This suggests that Eu^{3+} and Am^{3+} prefer to form neutral nitrate complexes in the gas phase and aqueous solution, which may be due to the stronger electron-donating ability of the nitrate ions. It is noteworthy that $EuL(NO_3)_3$ and $AmL(NO_3)_3$ exhibit higher coordination number than other species. Moreover, for the complexes with CMPO ligands and the corresponding complexes with Ph_2CMPO ligands, there is a very small difference in the metal–ligand binding energies. Therefore, CMPO and Ph_2CMPO show similar coordinating ability to Eu(III) and Am(III).

3.3. 2:1 and 3:1 Type Extraction Complexes. *3.3.1. Molecular Structures and Electronic Structures.* As shown in Figures 3 and 4 and S2 and S3 (in the Supporting Information), at the B3LYP/6-31G(d)/RECP level of theory, the CMPO and Ph_2CMPO ligands serve as bidentate ligands in the charged 2:1 and 3:1 type complexes. For each of the neutral 2:1 type complexes with CMPO ligand, one CMPO ligand is coordinated as a bidentate ligand, while the other ligand is a monodentate ligand with its phosphoric oxygen atom bound to europium and americium. Nevertheless, the Ph_2CMPO ligands act as bidentate ligands for the neutral 2:1 type complexes. In addition, for all the neutral 2:1 type complexes, the nitrate anions coordinate in bidentate fashion to the metal centers. Thus, the neutral 2:1 type complexes $M(CMPO)_2(NO_3)_3$ and $M(Ph_2CMPO)_2(NO_3)_3$ exhibit 9- and 10-fold metal coordination, respectively. As for the neutral 3:1 type complexes $M(CMPO)_2(NO_3)_3$, the CMPO ligands and the nitrate anions serve as monodentate and bidentate ligands, respectively, which results in 9-fold-coordinated complexes. In $Am(Ph_2CMPO)_2(NO_3)_3$, the Ph_2CMPO ligands are in monodentate and bidentate coordination at the same time, while all the nitrate anions are coordinated as bidentate ligands. In contrast, the Ph_2CMPO ligands and two nitrate anions in $Eu(Ph_2CMPO)_2(NO_3)_3$ act as monodentate and bidentate ligands, respectively. Additionally, for the other nitrate anion in $Eu(Ph_2CMPO)_2(NO_3)_3$, the $Eu-O(NO_3^-)$ bond distances are 2.477 and 2.738 Å.

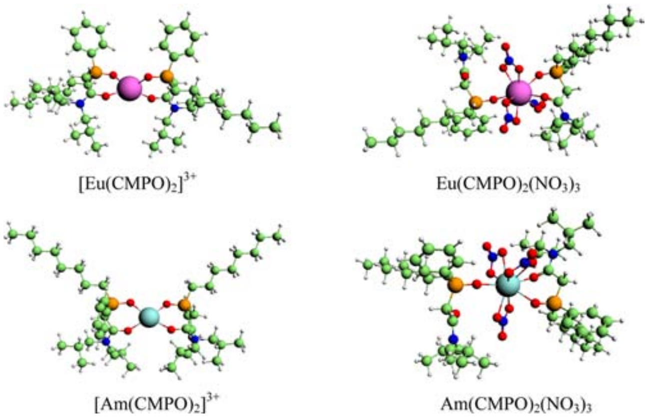


Figure 3. Optimized structures of 2:1 type Eu(III) and Am(III) complexes with CMPO. Green, white, red, blue, orange, pink, and light blue spheres represent C, H, O, N, P, Eu, and Am, respectively.

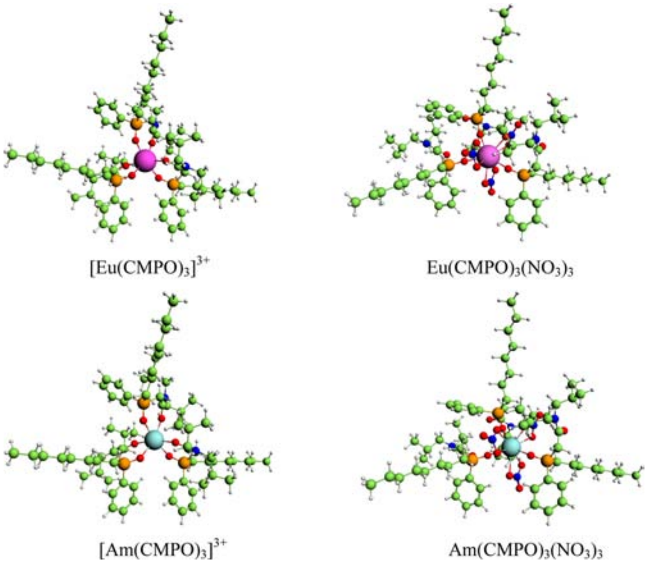


Figure 4. Optimized structures of the 3:1 type Eu(III) and Am(III) complexes with CMPO. Green, white, red, blue, orange, pink, and light blue spheres represent C, H, O, N, P, Eu, and Am, respectively.

As listed in Table 6, similar to the 1:1 type complexes, the M–O bond lengths with different ligands (CMPO and Ph_2CMPO) are nearly equal for the 2:1 and 3:1 type species. However, due to the steric effect of the CMPOs ligands, most of these 2:1 and 3:1 type complexes show larger M–O bond lengths compared with the corresponding 1:1 type complexes. Moreover, the M–O bond lengths for all the charged complexes are shorter than those for the corresponding neutral complexes, implying that the degree of covalence in the metal–ligand bonds decreases when M^{3+} coordinates with the nitrate ions. According to the NBO analysis, the M–O WBIs are in the range from 0.05 to 0.40 for the 2:1 and 3:1 type extraction complexes, indicating ionic interactions between the centered metal atoms and the ligands. As expected, the M–O WBIs of the neutral complexes are all smaller than those of the corresponding charged complexes, confirming that the M–O bonds of $ML_n(NO_3)_3$ (n = 2, 3) exhibit more ionic character than those of $[ML_n]^{3+}$. It should be mentioned that the calculated M–O WBIs for the 3:1 type complexes are much large than the corresponding 2:1 type complexes, which suggests that the M–O bonds in the 3:1 type complexes

Table 6. M−O Average Bond Lengths (Å) and the M−O WBIs for the 2:1 and 3:1 Type Eu^{3+} and Am^{3+} Complexes with CMPO and Ph_2CMPO Obtained by the B3LYP Method[a]

	bond lengths		WBI	
species	M−O_C	M−O_P	M−O_C	M−O_P
$[EuL_2]^{3+}$	2.297/2.243	2.252/2.198	0.110/0.179	0.125/0.179
$EuL_2(NO_3)_3$	2.523/2.572	2.385/2.481	0.056/0.060	0.080/0.074
$[AmL_2]^{3+}$	2.285/2.266	2.216/2.221	0.174/0.197	0.216/0.209
$AmL_2(NO_3)_3$	2.554/2.605	2.431/2.527	0.081/0.068	0.104/0.081
$[EuL_3]^{3+}$	2.340/2.344	2.298/2.299	0.357/0.353	0.390/0.384
$EuL_3(NO_3)_3$	–	2.399/2.404	–	0.347/0.337
$[AmL_3]^{3+}$	2.384/2.383	2.341/2.342	0.310/0.303	0.348/0.336
$AmL_3(NO_3)_3$	–/2.617	2.448/2.505	–/0.255	0.326/0.306

[a] .../... refers to the results of the complexes with CMPO and Ph_2CMPO, respectively.

Table 7. Mulliken Orbital Populations (s, p, d, and f), and Natural Charges on the Metal Atom and the O Atom for the 2:1 and 3:1 Type Eu^{3+}, Am^{3+} Complexes with L (L = CMPO, Ph_2CMPO) Calculated by the B3LYP Method[a]

	Mulliken orbital populations				Q		
species	s	p	d	f	O_C	O_P	M
$[EuL_2]^{3+}$	4.153/4.153	12.187/12.186	10.751/10.871	6.435/6.192	−0.904/−0.903	−1.262/−1.265	2.363/2.534
$EuL_2(NO_3)_3$	4.239/4.244	12.233/12.221	10.796/10.765	6.186/6.123	−0.779/−0.736	−1.195/−1.156	2.570/2.481
$[AmL_2]^{3+}$	4.188/4.194	12.204/12.196	10.893/10.887	6.109/6.099	−0.900/−0.893	−1.250/−1.251	2.541/2.537
$AmL_2(NO_3)_3$	4.280/4.284	12.356/12.350	10.833/10.782	6.094/6.107	−0.763/−0.736	−1.192/−1.148	2.434/2.422
$[EuL_3]^{3+}$	4.207/4.209	12.288/12.285	10.820/10.825	6.116/6.094	−0.722/−0.724	−1.093/−1.094	1.714/1.729
$EuL_3(NO_3)_3$	4.241/4.243	12.226/12.214	10.764/10.756	6.115/6.089	−0.655/−0.643	−1.053/−1.045	1.383/1.380
$[AmL_3]^{3+}$	4.237/4.235	12.342/12.348	10.868/10.862	6.104/6.107	−0.748/−0.752	−1.118/−1.121	1.822/1.844
$AmL_3(NO_3)_3$	4.280/4.277	12.387/12.381	10.783/10.748	6.104/6.099	−0.655/−0.622	−1.063/−1.046	1.454/1.345

[a] .../... refers to the results of the complexes with CMPO and Ph_2CMPO, respectively.

have much covalent character compared to the 2:1 type complexes.

In order to further investigate the nature of the metal−ligand bonding for the 2:1 and 3:1 type complexes, the Mulliken orbital populations and the NPA analysis were also investigated at the B3LYP/6-31G(d)/RECP level of theory (Table 7). In general, for all these 2:1 and 3:1 type complexes, the metal cations show lower f-occupancy numbers than the corresponding 1:1 type species. Compared to the charged complexes, the metal cations for most of the neutral complexes have lower d- and f-occupancy numbers, while they have higher s- and p-occupancy numbers. Although europium in $[EuL_2]^{3+}$ exhibits the highest f populations, the s- and p-occupancy numbers for europium are significantly lower than for other species. Similar to the 1:1 type complexes, for most of the 2:1 and 3:1 type complexes, Eu^{3+} possesses higher f- but lower s-, p-, and d-occupancy numbers than Am^{3+}. On the basis of natural population analysis, for the 3:1 type species, the natural charges on the metal atoms are significantly smaller than those in the corresponding 2:1 type species, suggesting a larger ligand-to-metal donation for each of the 3:1 type complexes. Alternatively, the calculated negative charges on the oxygen atoms for the 3:1 type complexes are smaller as compared to the 2:1 type complexes. These results confirm the higher degree of covalence in the M−O bonds for the 3:1 type complexes. Additionally, for most species the Eu ion shows more positive charges than the Am ion, proving its stronger electron affinity. Moreover, compared with the carbonyl oxygen atoms, the natural charges on the phosphoric oxygen atoms for all these complexes are more negative, which confirms that the phosphoric oxygen atoms exhibit stronger coordinating ability to Eu(III) and Am(III).

3.3.2. Stability. To study the stability of the 2:1 and 3:1 stoichiometric complexes, the metal ligand gas-phase binding energies are calculated at the B3LYP/6-311G(d,p)/RECP level of theory (Table 8). Since it is difficult to evaluate the solvent effects by using the QM method for these large molecular systems, only the gas-phase electronic energies (E_g) are calculated here.

Table 8. Binding Energies (kcal/mol) with ZPE Corrections for the 2:1 and 3:1 Type Eu^{3+} and Am^{3+} Complexes with L (L = CMPO, Ph_2CMPO) in the Gas Phase Calculated by the B3LYP Method[a]

reactions	ΔE_g
$Eu^{3+} + 2L \rightarrow [EuL_2]^{3+}$	−594.6/−589.7
$Eu^{3+} + 2L + 3NO_3^- \rightarrow EuL_2(NO_3)_3$	−1091.0/−1088.3
$Am^{3+} + 2L \rightarrow [AmL_2]^{3+}$	−567.3/−571.2
$Am^{3+} + 2L + 3NO_3^- \rightarrow AmL_2(NO_3)_3$	−1076.4/−1073.7
$Eu^{3+} + 3L \rightarrow [EuL_3]^{3+}$	−679.5/−681.4
$Eu^{3+} + 3L + 3NO_3^- \rightarrow EuL_3(NO_3)_3$	−1099.3/−1095.3
$Am^{3+} + 3L \rightarrow [AmL_3]^{3+}$	−661.1/−665.2
$Am^{3+} + 3L + 3NO_3^- \rightarrow AmL_3(NO_3)_3$	−1083.7/−1081.7

[a] .../... refers to the results of the complexes with CMPO and Ph_2CMPO, respectively.

As shown in Table 8, for all of these 2:1 and 3:1 type complexes, the calculated gas-phase binding energies are between −567.3 and −1094.2 kcal/mol, indicating that these complexes are very stable. The binding energies for the complexes with CMPO ligands are close to those with Ph_2CMPO ligands. For the neutral complexes, the binding energies are much more negative than those for the corresponding charged complexes, suggesting that

Table 9. Calculated Reaction Energies (kcal/mol) with ZPE Corrections for Complexing Reactions of the 2:1 and 3:1 Type Eu^{3+} and Am^{3+} Complexes with L (L = CMPO, Ph_2CMPO) in the Gas Phase by the B3LYP Method[a]

reactions	ΔE_g
$[Eu(H_2O)_9]^{3+} + 2L \rightarrow [EuL_2]^{3+} + 9H_2O$	−31.7/−26.9
$[Eu(NO_3)(H_2O)_7]^{2+} + 2NO_3^- + 2L \rightarrow EuL_2(NO_3)_3 + 7H_2O$	−283.1/−280.5
$[Am(H_2O)_9]^{3+} + 2L \rightarrow [AmL_2]^{3+} + 9H_2O$	−19.4/−23.3
$[Am(NO_3)(H_2O)_7]^{2+} + 2NO_3^- + 2L \rightarrow AmL_2(NO_3)_3 + 7H_2O$	−291.4/−288.7
$[Eu(H_2O)_9]^{3+} + 3L \rightarrow [EuL_3]^{3+} + 9H_2O$	−116.6/−118.6
$[Eu(NO_3)(H_2O)_7]^{2+} + 2NO_3^- + 3L \rightarrow EuL_3(NO_3)_3 + 7H_2O$	−291.5/−287.4
$[Am(H_2O)_9]^{3+} + 3L \rightarrow [AmL_3]^{3+} + 9H_2O$	−113.2/−117.3
$[Am(NO_3)(H_2O)_7]^{2+} + 3NO_3^- + 3L \rightarrow AmL_3(NO_3)_3 + 7H_2O$	−298.6/−296.7
$EuL(NO_3)_3 + L \rightarrow EuL_2(NO_3)_3$	−22.9/−18.0
$AmL(NO_3)_3 + L \rightarrow AmL_2(NO_3)_3$	−25.4/−19.9
$EuL(NO_3)_3 + 2L \rightarrow EuL_3(NO_3)_3$	−31.2/−24.9
$AmL(NO_3)_3 + 2L \rightarrow AmL_3(NO_3)_3$	−32.7/−27.8

[a] .../... refers to the results of the complexes with CMPO and Ph_2CMPO, respectively.

$ML_2(NO_3)_3$ and $ML_3(NO_3)_3$ are more stable than $[ML_2]^{3+}$ and $[ML_3]^{3+}$. For all the neutral complexes, the binding energies of the 3:1 type complexes are slightly higher than the corresponding 2:1 type complexes, and the predicted differences are about 8.0 kcal/mol. These small differences suggest that the neutral 2:1 and 3:1 type Am(III) and Eu(III) complexes may coexist in nitrate-rich acid solutions, which is consistent with the previous results.[14] Although the metal−ligand bonds of the 3:1 type Am(III) complexes show a higher degree of covalent character, our calculations indicate that the 2:1 and 3:1 type complexes of Am(III) have comparable binding strength. Thus, we speculate that covalence is only a minor component in the metal−ligand bonding of these complexes. Furthermore, the difference of the predicted binding energies between the Eu(III) and the Am(III) complexes are smaller than 20 kcal/mol, which confirms the experimental observation[47] that the CMPOs reagents have comparable extracting ability for Eu(III) and Am(III) in acidic media.

Moreover, the thermodynamic stability of these 2:1 and 3:1 type complexes have also been estimated at the same level of theory by a series of other possible complexing reactions, including the hydrates, nitrate hydrates, and the 1:1 type complexes. The results of the reaction energies are summarized in Table 9.

In general, for all the complexes with CMPO ligands, the reaction energies are close to those with Ph_2CMPO ligands. As for the reactions of americium and europium hydrates forming the charged 2:1 and 3:1 type complexes, the reaction energies are all negative, proving that these reactions are favorable in the gas phase. For the reactions with $M(NO_3)(H_2O)_7$ as the reactants, the reaction energies are between −280.4 and −292.8 kcal/mol, which are more negative than other reactions. Thus, these reactions of $[M(NO_3)(H_2O)_7]^{2+} + 2NO_3^- + nL \rightarrow ML_n(NO_3)_3 + 7H_2O$ (n = 2, 3) are probably the dominant complexing reactions. As expected, the reactions with the neutral 1:1 type complexes $ML(NO_3)_3$ as the reactants are all exothermic, suggesting that $ML_2(NO_3)_3$ and $ML_3(NO_3)_3$ are more favorable energetically than $ML(NO_3)_3$. Though the reaction energies of forming the neutral 3:1 type complexes are higher than those of the corresponding 2:1 type complexes, there is no significant difference in these energies. This also indicates that $ML_2(NO_3)_3$ and $ML_3(NO_3)_3$ seem to be the predominant species in nitrate-rich acid solutions. In addition, all of the reactions forming the Eu(III) and Am(III) complexes have comparable reaction energies. Therefore, as reported in the literature,[47] though CMPOs is efficient for lanthanide and actinide extraction, these extractants exhibit little lanthanide/actinide selectivity. It is noteworthy that for all of these reactions, since the reactants and products possess different coordination numbers, e.g., for $[Eu(H_2O)_9]^{3+} + 2L \rightarrow [EuL_2]^{3+} + 9H_2O$, which goes from a 9-fold coordinated complex to a 4-fold coordinated complex, steric effects may play an important role in the process of complexing reaction.

4. CONCLUSIONS

In the present work, the equilibrium geometries, electronic structures, and the stability of the Eu(III) and Am(III) extraction complexes with the CMPO and Ph_2CMPO ligands have been studied by the B3LYP method.

Our results show that Eu(III) and Am(III) prefer to form 8- to 9-fold coordinated species in aqueous solution, while the 9-coordinated neutral complexes $M(NO_3)_3(H_2O)_3$ are the most stable species in the presence of nitrate ions. For the 1:1 type extraction complexes and the charged 2:1 and 3:1 type complexes, CMPO and Ph_2CMPO act as bidentate ligands, which bind to the metal ions through the carbonyl and phosphoric oxygen atoms, whereas the neutral 2:1 and 3:1 type complexes are mainly coordinated to the metal cations via the phosphoric oxygen atoms. NBO analysis indicates that in the 3:1 type complexes the electrostatic interaction for the M−O bonding is weaker than those in the 1:1 and 2:1 type complexes. It has been found that the 1:1 type complexes are much weaker than the 2:1 and 3:1 type complexes, and the neutral $ML_2(NO_3)_3$ and $ML_3(NO_3)_3$ complexes are more favorable than $[ML_2]^{3+}$ and $[ML_3]^{3+}$ in the extraction process. In addition, hydration energies might play an important role in the extractability of CMPO and Ph_2CMPO for Eu(III) and Am(III). On the basis of our calculations, these reagents have comparable extracting ability for Eu(III) and Am(III). Moreover, the molecular structures, electronic structures, and stability of the species with CMPO ligands are qualitatively similar to those with Ph_2CMPO ligands. Thus, we deduce that the replacement of alkyl groups at the phosphorus atom of the CMPO and Ph_2CMPO ligands has no obvious effect on the extractability for Eu(III) and Am(III).

Overall, this study might prove useful in exploring the origin of selectivity in extracting Eu(III) and Am(III) with CMPO and Ph_2CMPO, and the extraction complexes as well as reactions in aqueous solution should be further investigated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1, showing optimized structures of the 1:1 type Eu(III) and Am(III) complexes with Ph_2CMPO using the B3LYP method; Figure S2, showing optimized structures of the 2:1 type Eu(III) and Am(III) complexes with Ph_2CMPO using the B3LYP method; and Figure S3, showing optimized structures of the 3:1 type Eu(III) and Am(III) complexes with Ph_2CMPO using the B3LYP method; and the complete Gaussian 03 reference (ref 31). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21201166, 21101157, 11105162, 21261140335), the Major Research Plan “Breeding and Transmutation of Nuclear Fuel in Advanced Nuclear Fission Energy System” of Natural Science Foundation of China (Grant Nos. 91026007, 91126006), and the “Strategic Priority Research Program” of the Chinese Academy of Sciences (Grant Nos. XDA03010401 and XDA03010403). The results described in this work were obtained on the ScGrid of Supercomputing Center, Computer Network Information Center of Chinese Academy of Sciences.

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