ROYAL SOCIETY OF CHEMISTRY

PAPER

Density functional theory investigations of the trivalent lanthanide and actinide extraction complexes with diglycolamides†

Cong-Zhi Wang,[a] Jian-Hui Lan,[a] Qun-Yan Wu,[a] Yu-Liang Zhao,[a] Xiang-Ke Wang,[b] Zhi-Fang Chai*[a,c] and Wei-Qun Shi*[a]

At present, designing novel ligands for efficient actinide extraction in spent nuclear fuel reprocessing is extremely challenging due to the complicated chemical behaviors of actinides, the similar chemical properties of minor actinides (MA) and lanthanides, and the vulnerability of organic ligands in acidic radioactive solutions. In this work, a quantum chemical study on Am(III), Cm(III) and Eu(III) complexes with N,N,-N′,N′-tetraoctyl diglycolamide (TODGA) and N,N′-dimethyl-N,N′-diheptyl-3-oxapentanediamide (DMDHOPDA) has been carried out to explore the extraction behaviors of trivalent actinides (An) and lanthanides (Ln) with diglycolamides from acidic media. It has been found that in the 1 : 1 (ligand : metal) and 2 : 1 stoichiometric complexes, the carbonyl oxygen atoms have stronger coordination ability than the ether oxygen atoms, and the interactions between metal cations and organic ligands are substantially ionic. The neutral $ML(NO_3)_3$ (M = Am, Cm, Eu) complexes seem to be the most favorable species in the extraction process, and the predicted relative selectivities are in agreement with experimental results, i.e., the diglycolamide ligands have slightly higher selectivity for Am(III) over Eu(III). Such a thermodynamical priority is probably caused by the higher stabilities of Eu(III) hydration species and Eu(III)−L complexes in aqueous solution compared to their analogues. In addition, our thermodynamic analysis from water to organic medium confirms that DMDHOPDA has higher extraction ability for the trivalent actinides and lanthanides than TODGA, which may be due to the steric hindrance of the bulky alkyl groups of TODGA ligands. This work might provide an insight into understanding the origin of the actinide selectivity and a theoretical basis for designing highly efficient extractants for actinide separation.

Introduction

Reprocessing of spent nuclear fuels has attracted much attention in recent years. In the traditional PUREX (plutonium uranium extraction) process, although plutonium and uranium can be removed effectively, more than 95% radioactivity still remains in the raffinate, which is called high level liquid waste (HLLW).[1] HLLW contains a host of long-lived fission products and the so-called minor actinides (MA = Am, Cm, Np, etc.) which can result in long term radiotoxicity. In order to reduce the long term risk of HLLW, it is necessary to separate MA from HLLW. Due to the similar chemical properties of trivalent actinides (An) and lanthanides (Ln), co-extraction of An(III) and Ln(III) has

[a]Group of Nuclear Energy Chemistry, Key Laboratory of Nuclear Radiation and Nuclear Energy Technology and Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China. E-mail: shiwq@ihep.ac.cn
[b]Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, China
[c]School of Radiological & Interdisciplinary Sciences, Soochow University, Suzhou 215123, China. E-mail: zfchai@suda.edu.cn

been proposed as the first stage for actinide partitioning at present.[2]

In the past few decades, many extractants have been applied for co-extraction of An(III) and Ln(III),[3] such as the bidentate reagents *n*-octyl(phenyl)-*N*,*N*-diisobutyl-methylcarb-amoyl phosphine oxide (CMPO) used in the TRUEX (Trans Uranium Extraction) process, and the malonamides *N*,*N*'-dimethyl-*N*,*N*'-dibutyltetra-decyl (DMDBTDMA) and *N*,*N*'-dimethyl-*N*,*N*'-dioctyl-2-(2-hexyloxyethyl) (DMDOHEMA) proposed in the DIAMEX (Diamide Extraction) process. In recent years, diglycolamide (DGA) extractants have received particular attention because of their strong affinity for actinides and lanthanides.[4] Normally, these DGA extractants coordinate as tridentate ligands through two carbonyl groups and an ether group.[5–8] Various DGA reagents have been synthesized and their extraction abilities to the metal ions have also been extensively studied.[5–10] It has been found that the alkyl chains on the amidic nitrogen atoms may affect the complexing ability of the DGA derivatives.[9,10] Due to the different solubility and steric hindrance, the DGA reagents with shorter alkyl chains exhibit higher complexation ability.[11] Compared to other extractants, *N*,*N*,*N*',*N*'-tetraoctyl diglycolamide (TODGA) (Fig. 1a) shows much better extraction behaviors for actinides and lanthanides with respect to solubility and stability.[4] It was reported that the stoichiometry of the extraction complexes depends on the nature of diluents.[12] In polar diluents, such as 1,2-dichloroethane and *n*-octanol, the dominant chemical species are the 1:2 (metal:TODGA) type complexes, while in non-polar diluents (*n*-dodecane) and weakly polar diluents (toluene), the 1:3 or 1:4 species are the predominant complexes. Besides, in the mixture of ethanol (60%) and water (40%), all the 1:1, 1:2 and 1:3 type complexes have been found by time resolved luminescence spectroscopy (TRLS).[13] Spectroscopic studies also suggested that the TODGA ligands coordinate to Eu(III) through the carbonyl oxygen atom and no water molecules were observed in the inner sphere.[13,14]

Despite that various DGA extractants have been studied experimentally, the exact coordination modes and the electronic structures for most of these complexes are still unknown. Recently, computational chemistry has become an efficient tool for understanding the structure of the actinide complexes.[15] However, only a few theoretical studies have been reported so far. By molecular dynamics simulations, Hirata *et al.* evaluated the extraction of La³⁺, Eu³⁺ and Lu³⁺ species with the tetramethyl diglycolamide ligand (TMDGA).[16] In this work, we mainly focus on the extraction behaviors of Am(III), Cm(III) and Eu(III) with TODGA and its derivative *N*,*N*'-dimethyl-*N*,*N*'-diheptyl-3-oxapentanediamide (DMDHOPDA)

(Fig. 1b) in nitric acid solution by quantum chemical calculations.

Theoretical methods

All the structures have been optimized using the density functional theory (DFT) method[17] with the B3LYP[18] functional implemented in the Gaussian 09 program.[19] Similar to our previous studies on actinide and lanthanide complexes,[20] the quasi-relativistic effective core potentials (RECP) and the consistent valence basis sets,[21] which replace 60 and 28 electrons as the core for actinides and lanthanides, respectively, were used for americium, curium and europium. The 6-31G(d) basis sets were considered for other atoms. All the optimized structures are confirmed to be local minima structures on the potential energy hypersurface by vibrational frequency analysis at the same level of theory. In addition, the septet state was considered as the ground state of Am(III) and Eu(III), while Cm(III) is considered in the octet spin state. Each species shows negligible spin contamination with $\langle S^2 \rangle$ close to the ideal value $S(S+1)$.

In order to understand the complexation, the C=O stretching frequncies and the extent of charge transfer of the metal cations have been calculated at the B3LYP/6-31G(d)/RECP level of theory. Similar analysis has been carried out by previous studies.[22] It has been found that the COSMO (conductor-like screening model)[23] approach can achieve relatively accurate free energies in solution for actinide complexes containing the first coordination shell.[15] Besides, reoptimizing the structures in the presence of the solvent has little effect on solvation energies.[24] Therefore, in the present study, solvent effects were evaluated on the basis of single-point calculations at the same level of theory using the COSMO model in water and *n*-dodecane (as the organic phase) with atomic radii suggested by Klamt *et al.*[23]

Results and discussion

Am(III), Cm(III) and Eu(III) in nitric acid solution

Since the co-extraction processes of An(III) and Ln(III) usually occur in nitric acid solution, we first investigated the Am(III), Cm(III) and Eu(III) aquo and nitrate complexes. Previous studies[25] found that there are 8 or 9 water molecules in the first hydration shell of Am³⁺, Cm³⁺ and Eu³⁺. We thus considered the octahydrates $[M(H_2O)_8]^{3+}$ (M = Am, Cm and Eu) and nonahydrates $[M(H_2O)_9]^{3+}$ as well as the 9-fold co-ordinated nitrate hydrates with nitrate ions serving as bidentate ligands. Besides, we also optimized their geometries in the gas phase by the exchange correlation functional BP86,[26] which is also a commonly used functional for actinides.[27] As shown in Fig. 2 and Fig. S1 in the ESI,† similar geometrical structures were obtained by the B3LYP and BP86 methods. The optimized structures of $[M(H_2O)_8]^{3+}$ exhibit square antiprism
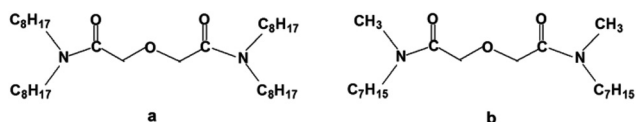

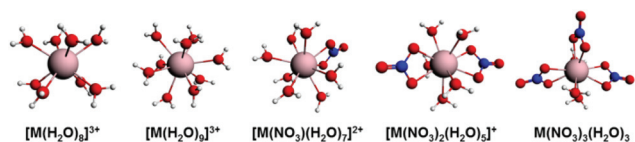Fig. 1 Structures of TODGA (a) and DMDHOPDA (b).

Fig. 2 Optimized structures of Am(ɪɪɪ), Cm(ɪɪɪ) and Eu(ɪɪɪ) complexes by the B3LYP method. White, red, blue and pink spheres represent H, O, N, and M (M = Am, Cm and Eu), respectively.

Table 1 Changes of the Gibbs free energy (kcal mol^{-1}) including zero-point energy (ZPE) corrections and thermal corrections for complexing reactions concerning Am^{3+}, Cm^{3+} and Eu^{3+} in the gas phase and aqueous solution by the B3LYP method

Reactions	ΔG_g	ΔG_{sol}
$[Am(H_2O)_8]^{3+} + H_2O \rightarrow [Am(H_2O)_9]^{3+}$	−14.6	2.5
$[Cm(H_2O)_8]^{3+} + H_2O \rightarrow [Cm(H_2O)_9]^{3+}$	−15.4	−0.6
$[Eu(H_2O)_8]^{3+} + H_2O \rightarrow [Eu(H_2O)_9]^{3+}$	−14.9	−0.3
$[Am(H_2O)_9]^{3+} + NO_3^- \rightarrow [Am(NO_3)(H_2O)_7]^{2+} + 2H_2O$	−243.4	−8.6
$[Cm(H_2O)_9]^{3+} + NO_3^- \rightarrow [Cm(NO_3)(H_2O)_7]^{2+} + 2H_2O$	−250.4	−14.5
$[Eu(H_2O)_9]^{3+} + NO_3^- \rightarrow [Eu(NO_3)(H_2O)_7]^{2+} + 2H_2O$	−257.5	−18.4
$[Am(H_2O)_9]^{3+} + 2NO_3^- \rightarrow [Am(NO_3)_2(H_2O)_5]^+ + 4H_2O$	−435.3	−32.9
$[Cm(H_2O)_9]^{3+} + 2NO_3^- \rightarrow [Cm(NO_3)_2(H_2O)_5]^+ + 4H_2O$	−431.9	−29.5
$[Eu(H_2O)_9]^{3+} + 2NO_3^- \rightarrow [Eu(NO_3)_2(H_2O)_5]^+ + 4H_2O$	−439.8	−32.5
$[Am(H_2O)_9]^{3+} + 3NO_3^- \rightarrow Am(NO_3)_3(H_2O)_3 + 5H_2O$	−542.7	−41.9
$[Cm(H_2O)_9]^{3+} + 3NO_3^- \rightarrow Cm(NO_3)_3(H_2O)_3 + 5H_2O$	−540.9	−37.8
$[Eu(H_2O)_9]^{3+} + 3NO_3^- \rightarrow Eu(NO_3)_3(H_2O)_3 + 5H_2O$	−547.6	−41.2

geometries, while $[M(H_2O)_9]^{3+}$ has distorted tricapped trigonal prism coordination.

According to our calculations by the B3LYP method (Table 1), the changes of Gibbs free energy for $[M(H_2O)_8]^{3+} + H_2O \rightarrow [M(H_2O)_9]^{3+}$ are all negative in the gas phase, indicating that these nonahydrates $[M(H_2O)_9]^{3+}$ are stable in the gas phase. However, for Am^{3+}, Cm^{3+} and Eu^{3+}, the changes of Gibbs free energies decreased obviously in aqueous solution, which are only 2.5, −0.6 and −0.3 kcal mol^{-1}, respectively. Thus, the octahydrate and nonahydrate of Am(ɪɪɪ), Cm(ɪɪɪ) and Eu(ɪɪɪ) species may coexist in aqueous solution. As stronger coordinating ligands, nitrate ions can replace water molecules to form more stable complexes in nitrate-rich environments. Just as expected, for all the reactions of $[M(H_2O)_9]^{3+}$ to nitrate hydrates in the gas phase and aqueous solution, the Gibbs free energy changes are all negative, suggesting that Am^{3+}, Cm^{3+} and Eu^{3+} prefer to form nitrate hydrates in nitric acid solution. Additionally, the neutral $M(NO_3)_3(H_2O)_3$ complexes seem to be the most stable species among all of these nitrate hydrates. Qualitatively, the changes of Gibbs free energy for all the reactions calculated by the BP86 method (Table S1†) are in accordance with those by the B3LYP method. Thus, in the following discussion we only take into account the B3LYP results.

Geometrical and electronic structures of the extraction complexes

The 1:1 (ligand:metal) stoichiometric complexes. The optimized structures of the 1:1 type extraction complexes at the B3LYP/6-31G(d)/RECP level of theory are displayed in Fig. 3
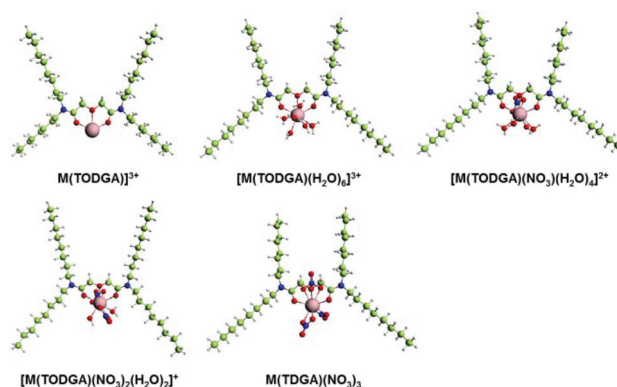

Fig. 3 Optimized structures of the 1:1 type Am(ɪɪɪ), Cm(ɪɪɪ) and Eu(ɪɪɪ) complexes with TODGA by the B3LYP method. Green, white, red, blue, yellow and pink spheres represent C, H, O, N, and M (M = Am, Cm and Eu), respectively. The same arrangement was applied in the subsequent figures.
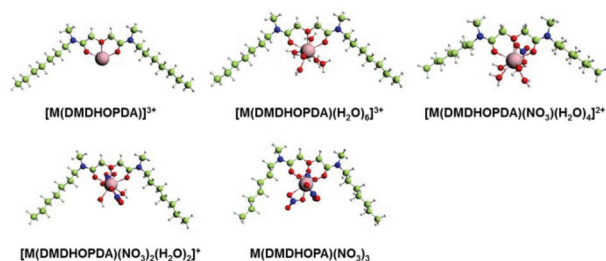

Fig. 4 Optimized structures of Am(ɪɪɪ), Cm(ɪɪɪ) and Eu(ɪɪɪ) complexes with DMDHOPDA (1:1 type) by the B3LYP method.

and 4. We found that the TODGA and DMDHOPDA reagents act as tridentate ligands through the ether oxygen atoms and the carbonyl oxygen atoms, while all the nitrate ions are bidentate ligands. Therefore, all the hydrates, nitrate hydrates and nitrates are 9-coordinated complexes. Additionally, each species with TODGA and DMDHOPDA ligands shows similar geometrical structures. The calculated bond distances between the metal atoms and the ligands of these complexes are listed in Table 2. As expected, the M–O(ether) and M–O(carbonyl) bond lengths in $[ML(H_2O)_6]^{3+}$, $[ML(NO_3)(H_2O)_4]^{2+}$, $[ML(NO_3)_2(H_2O)_2]^+$ and $ML(NO_3)_3$ are longer than those in $[ML]^{3+}$. Besides, for most of these complexes, these M–O bond distances increase gradually with the nitrate ions replacing the inner-sphere water molecules, which may be attributed to the higher electron-donating ability of nitrate ions. Interestingly, the M–O(ether) and M–O(carbonyl) bond lengths in $[ML(H_2O)_6]^{3+}$ seem to be unusual. In these $[ML(H_2O)_6]^{3+}$ species, we found that there exist hydrogen bonds between the water molecules with the O···O bond distances of about 2.7 Å, which may result in the longer M–O bond distances. Moreover, in each species, the M–O(ether) bond lengths are much longer than M–O(carbonyl), indicating that the carbonyl groups of TODGA and DMDHOPDA have higher coordinating ability to the metal cations.

Table 2 The M–O bond lengths (Å) for complexes of Am^{3+}, Cm^{3+}, Eu^{3+} and L (L = TODGA, DMDHOPDA) calculated by the B3LYP method[a]

No.	Species	M–O(ether)	M–O[b](carbonyl)	M–O[b](H$_2$O)	M–O[b](NO$_3^-$)
1	[AmL]$^{3+}$	2.562/2.524	2.325/2.320	—	—
2	[CmL]$^{3+}$	2.429/2.411	2.192/2.190	—	—
3	[EuL]$^{3+}$	2.537/2.520	2.328/2.343	—	—
4	[AmL(H$_2$O)$_6$]$^{3+}$	2.585/2.605	2.376/2.388	2.578/2.575	—
5	[CmL(H$_2$O)$_6$]$^{3+}$	2.588/2.595	2.374/2.383	2.566/2.563	—
6	[EuL(H$_2$O)$_6$]$^{3+}$	2.629/2.601	2.423/2.416	2.589/2.570	—
7	[AmL(NO$_3$)(H$_2$O)$_4$]$^{2+}$	2.558/2.603	2.413/2.427	2.597/2.578	2.444/2.446
8	[CmL(NO$_3$)(H$_2$O)$_4$]$^{2+}$	2.610/2.592	2.404/2.413	2.587/2.573	2.443/2.449
9	[EuL(NO$_3$)(H$_2$O)$_4$]$^{2+}$	2.556/2.565	2.366/2.377	2.555/2.535	2.405/2.414
10	[AmL(NO$_3$)$_2$(H$_2$O)$_2$]$^{+}$	2.630/2.628	2.437/2.441	2.554/2.559	2.485/2.482
11	[CmL(NO$_3$)$_2$(H$_2$O)$_2$]$^{+}$	2.641/2.638	2.421/2.428	2.535/2.532	2.500/2.480
12	[EuL(NO$_3$)$_2$(H$_2$O)$_2$]$^{+}$	2.615/2.592	2.411/2.405	2.492/2.516	2.443/2.450
13	AmL(NO$_3$)$_3$	2.694/2.721	2.495/2.494	—	2.501/2.491
14	CmL(NO$_3$)$_3$	2.663/2.693	2.485/2.488	—	2.499/2.488
15	EuL(NO$_3$)$_3$	2.636/2.653	2.450/2.446	—	2.456/2.457

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

In order to evaluate the binding ability of ligands in these complexes, we monitored the C=O stretching frequencies for all the species and the free ligands (Table S2†). It has been found that for all the 1 : 1 type complexes, the calculated C=O stretching frequencies are all red-shifted compared to those of the free ligands, which indicates that the ligands coordinate strongly to the metal cations. Besides, the stretching frequency changes in [ML]$^{3+}$ are significantly larger than those in other species, implying the stronger interaction between metal atoms and ligands in [ML]$^{3+}$. This may be due to the coordination of water molecules and nitrate anions to the metal ions in the hydrates and nitrate hydrates, which may decrease the binding strength between the metal and ligands.

At the B3LYP/6-31G(d)/RECP level of theory, the bonding nature of these extraction complexes including the bond orders and atomic charges were investigated by the natural bond orbital (NBO) analysis and natural population analysis (NPA).[28]

For all of these complexes, the Wiberg bond indices (WBIs) of the M–O bonds are within the range of 0.10–0.37 (Table S3†), suggesting weak covalent character in the metal–oxygen bonds. In addition, the M–O(carbonyl) WBIs are slightly larger compared to M–O(ether), which indicates the relatively higher covalency of M–O(carbonyl) bonds and stronger coordinating ability of the carbonyl groups to metal cations. Similar results can be obtained by the topological analysis of the electron localization function (ELF)[29] for the model complex AmL(NO$_3$)$_3$ (Fig. S2†), i.e. the M–O(carbonyl) bonds exhibit higher degree of covalent character compared to the M–O(ether) bonds. According to the NPA analysis (Table S4†), the calculated negative charges on the carbonyl oxygen atoms in each species are larger than those on the ether oxygen atoms, giving another evidence of the stronger coordination ability of the carbonyl group. Additionally, we calculated the charge transfer of metal cations in the complexes compared to bare metal cations. For all of these complexes, the charge transfer is more for Eu(III) than for Am(III) and Cm(III), and Cm(III) shows the least charge transfer. This suggests that the

bonding between Eu(III) and the diglycolamide ligands is more favorable. As expected, because nitrate ions have higher electron-donating ability to the studied metal cations, the WBIs of the M–O(NO$_3^-$) bonds are obviously higher than those of the M–O(H$_2$O) bonds. It should be noted that the charge transfer of the metal atoms for [ML]$^{3+}$ is the smallest among species listed in Table S4.† In contrast, the NPA charges on the carbonyl and ether oxygen atoms in [ML]$^{3+}$ become more negative than those in other complexes. This may have resulted from the low coordination numbers of the metal cations in [ML]$^{3+}$.

The 2 : 1 (ligand : metal) stoichiometric complexes. As shown in Fig. 5, we optimized the structures of the charged and neutral 2 : 1 (ligand/metal) type complexes at the B3LYP/6-31G(d) level of theory. For all the [M(TODGA)$_2$]$^{3+}$ and [M(DMDHOPDA)$_2$]$^{3+}$ complexes, TODGA and DMDHOPDA serve as tridentate ligands, which result in 6-coordinated species. In contrast, for neutral M(TODGA)$_2$(NO$_3$)$_3$ complexes, the TODGA ligands act as bidentate ligands through the carbo-
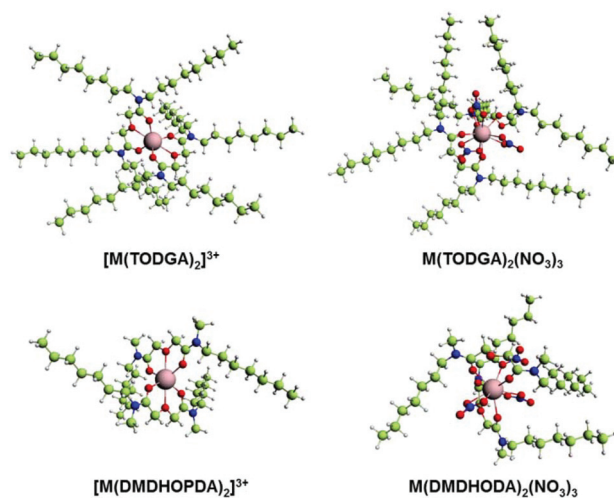

Fig. 5 Optimized structures of Am(III), Cm(III) and Eu(III) complexes with TODGA (2 : 1 type) by the B3LYP method.

Table 3 The M–O average bond lengths (Å) for Am^{3+}, Cm^{3+} and Eu^{3+} complexes with TODGA and DMDHOPDA (2:1 type) calculated by the B3LYP method[a]

No.	Species	M–O(ether)	M–O(carbonyl)
16	$[AmL_2]^{3+}$	2.552/2.520	2.301/2.309
17	$[CmL_2]^{3+}$	2.529/2.536	2.299/2.299
18	$[EuL_2]^{3+}$	2.511/2.505	2.306/2.300
19	$AmL_2(NO_3)_3$	—	2.560/2.504
20	$CmL_2(NO_3)_3$	—	2.535/2.490
21	$EuL_2(NO_3)_3$	—	2.531/2.438

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

Fig. 6 Trends of the binding energies for the 1:1 type Am(III), Cm(III) and Eu(III) complexes with TODGA by the B3LYP method.

nyl groups, and all the nitrate ions are also bidentate ligands. Thus, these species are all 10-fold coordinated complexes. As for neutral $M(DMDHOPDA)_2(NO_3)_3$ complexes, DMDHOPDA is a bidentate ligand. In $Am(DMDHOPDA)_2(NO_3)_3$ and $Cm(DMDHOPDA)_2(NO_3)_3$, two of the nitrate ions are bidentate, while the third one is monodentate. However, $Eu(DMDHOPDA)_2(NO_3)_3$ is a 8-coordinated complex with one bidentate and two monodentate nitrate ions.

From Table 3, the M–O bond lengths in each 2:1 type species with TODGA are very close to those with DMDHOPDA, suggesting a tiny effect of the alkyl chains in the diglycolamides on structure parameters. For the charged 2:1 type complexes, the M–O bond lengths are shorter than those in the corresponding neutral species. Besides, compared to TODGA and DMDHOPDA ligands, the predicted C=O stretching frequencies (Table S2†) in most of the 2:1 type complexes are red-shifted, and $[ML_2]^{3+}$ shows larger frequency changes, which suggests the stronger coordination of the ligands toward the metal cations in the charged 2:1 type species. In addition, the small values of the WBIs (Table S5†) for M–O bonds indicate that electrostatic interactions dominate this bonding. As for $[ML_2]^{3+}$, the metal atoms possess shorter distances to the carbonyl oxygen atoms (M–O(carbonyl)) than the ether oxygen atoms (M–O(ether)). Accordingly, the WBIs of the M–O(carbonyl) bonds are larger than the M–O(ether) bonds. Therefore, in the charged 2:1 type complexes, the carbonyl groups mainly coordinate with the metal cations, and the M–O(carbonyl) bonds show more covalent character. It is worth noting that the WBIs of the M–O(ether) and M–O(carbonyl) bonds in $[EuL_2]^{3+}$ are smaller than those in $[AmL_2]^{3+}$ and $[CmL_2]^{3+}$, while in the neutral $ML_2(NO_3)_3$ complexes, the greater covalency of the An–L bonds has not been observed. In terms of the NPA analysis (Table S5†), the charge transfer of the metal atoms in the $[ML_2]^{3+}$ complexes is between 1.0 and 1.3, which are smaller than the corresponding neutral complexes. Furthermore, the charge transfer of the europium atom for $EuL_2(NO_3)_3$ is the largest in the neutral 2:1 type complexes, which is in accord with the bond length and WBI values of the M–O bonds in the species of $ML_2(NO_3)_3$. As expected, for the 2:1 type extraction complexes, the carbonyl oxygen atoms show larger net charges than the ether oxygen atoms.
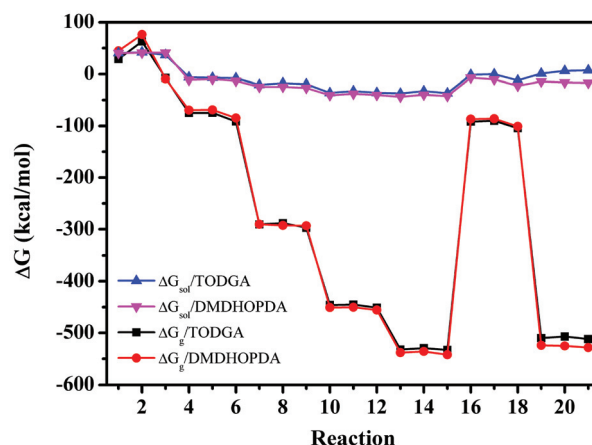
Thermodynamics

In order to further estimate the binding ability of diglycolamide towards metal cations for the 1:1 and 2:1 type extraction complexes, a series of complexation reactions with nonahydrates $[M(H_2O)_9]^{3+}$ as reactants have been considered at the B3LYP/6-31G(d)/RECP level of theory in both the gas phase and aqueous solution (Fig. 6 and Table S6†). As listed in Table S6,† the reaction energies of 1:1 and 2:1 type complexes are within the range of 76.4 to −542.1 kcal mol^{-1} in the gas phase (ΔG_g), while these values decrease significantly to the range of 42.2 to −43.8 kcal mol^{-1} in aqueous solution (ΔG_{sol}). This indicates that the hydration energy has a remarkable negative effect on the stability of these complexes.
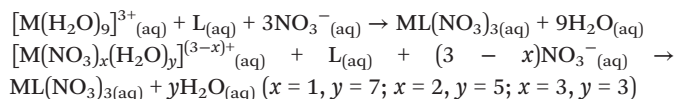
As shown in Fig. 6, for the reactions of $[M(H_2O)_9]^{3+}$ + L → $[ML]^{3+}$ + $9H_2O$, the positive ΔG_{sol} values suggest that formation of $[ML]^{3+}$ is thermodynamically unfavorable in aqueous solution, which may be due to the lower coordination number of $[ML]^{3+}$. For most of the other 1:1 type complexes of DMDHOPDA ligands, the gas phase and hydration reaction energies are more negative than the corresponding complexes of TODGA ligands, indicating that the former are more stable than the latter. For all the hydrates, nitrate hydrates and nitrates, the reaction energies increase with more nitrate ions replacing water molecules, which is mainly due to the stronger electron-donating ability of nitrate ions. In addition, for $[ML(NO_3)_2(H_2O)_2]^+$ and $M(NO_3)_3(H_2O)_3$, the ΔG_{sol} values of Am(III) complexes are found to be more negative than the corresponding Eu(III) complexes, which is consistent with the experimental results[30] that the TODGA ligands exhibit slightly higher affinity for Am(III) than for Eu(III). In the case of the 2:1 type complexes, the absolute values of ΔG_g for charged $[ML_2]^{3+}$ complexes are much smaller than the neutral $ML_2(NO_3)_3$ complexes, confirming that the neutral complexes are more stable than the charged complexes in the gas phase. When taking into account solvent effects, the stabilities of these complexes are found to be associated with the ligands. For example, the reactions for $An(DMDHOPDA)_2(NO_3)_3$ seem to be more avail-

able compared to those of $[An(DMDHOPDA)_2]^{3+}$, while opposite results are observed for the complexes with TODGA. These results may be attributed to the larger steric effect of TODGA compared to DMDHOPDA.

Furthermore, the neutral $ML(NO_3)_3$ complexes exhibit the most negative ΔG values among the 1:1 and 2:1 type species. Thus, $ML(NO_3)_3$ seems to be the most favorable species in thermodynamics. It should be noted that this conclusion was drawn based on quantum chemical calculations with simplified reaction models to explore the complex actual extraction process. Since the extraction of actinides and lanthanides with TODGA ligands is also strongly dependent on organic diluents,[12] we calculated the solvent extraction process including extraction of metal complexes from aqueous solution to organic medium with the predicted most stable complexes $ML(NO_3)_3$ as the model species. Detailed discussions are presented below.

Possible solvent extraction process

(1) The extraction of An(III) and Ln(III) in aqueous solution (ΔG_{sol})

$[M(H_2O)_9]^{3+}_{(aq)} + L_{(aq)} + 3NO_3^-_{(aq)} \rightarrow ML(NO_3)_{3(aq)} + 9H_2O_{(aq)}$
$[M(NO_3)_x(H_2O)_y]^{(3-x)+}_{(aq)} + L_{(aq)} + (3 - x)NO_3^-_{(aq)} \rightarrow ML(NO_3)_{3(aq)} + yH_2O_{(aq)}$ ($x = 1, y = 7; x = 2, y = 5; x = 3, y = 3$)

(2) The extraction of An(III) and Ln(III) from aqueous solution (aq) to n-dodecane (org) (ΔG_{ext})

$[M(H_2O)_9]^{3+}_{(aq)} + L_{(org)} + 3NO_3^-_{(aq)} \rightarrow ML(NO_3)_{3(org)} + 9H_2O_{(aq)}$
$[M(NO_3)_x(H_2O)_y]^{(3-x)+}_{(aq)} + L_{(org)} + (3 - x)NO_3^-_{(aq)} \rightarrow ML(NO_3)_{3(org)} + yH_2O_{(aq)}$
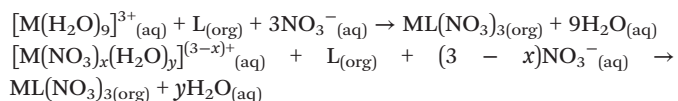
Table 4 lists the Gibbs free energy changes of the probable intermediate reactions during the formation of $ML(NO_3)_3$. It has been found that the ΔG_{sol} values for reactions with $[M(H_2O)_9]^{3+}$ as the reactant are more negative than those for other reactions. In addition, Martin, Hay, and Pratt[31] have pointed out that for calculations of the free energies of reactions in aqueous solution, the correction for the entropy of water should be taken into account, which is about 4.3 kcal mol^{-1} per water molecule of Gibbs free energy. The corrections

to the Gibbs free energies have been applied and the results are tabulated in Table S7.† According to energies including the translation entropy correction, most of the reactions become endothermic because the correction is proportional to the number of water molecules. However, the corrected Gibbs free energies give qualitatively the same result, *i.e.*, $[M(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow ML(NO_3)_3 + 9H_2O$ might be the main reaction in the extraction process.

For all these reactions, ΔG_{ext} for n-dodecane is consistently lower than ΔG_{sol} for aqueous solution, suggesting an exothermic transfer process of complexes from the aqueous to the organic phase. This is in agreement with the experimental finding[30] that the extraction complexes mainly reside in the organic phase. Besides, the ΔG_{ext} values of these reactions indicate that the DMDHOPDA ligand seems to have stronger extractability for actinides and lanthanides. Most of the ΔG_{ext} values for the reactions of Am(III) species are more negative compared to those of Eu(III) species, indicating that the Am(III) complexes are more favorable compared to their Eu(III) analogues. This is also in accordance with the experimental observation.[30] In order to interpret these results, we further analyzed the decomposition energies of the studied M(III) hydration complexes (Table 5) and the hardness of the ligands and metal cations by Hard–Soft Acid–Base (HSAB) theory.[32]

As shown in Table 5, it was found that the Eu(III) hydration complexes require higher energy for dehydration, and the released energies for the formation reactions of Eu(III)–L complexes are also higher than their analogues. In terms of the complexing reactions of $M^{3+} + L + 3NO_3^- \rightarrow ML(NO_3)_3$, $M(DMDHOPDA)(NO_3)_3$ shows much stronger metal–ligand binding ability than $M(TODGA)(NO_3)_3$, which may be attributed to the steric interactions between the bulky alkyl chains in the TODGA ligand. From the above discussions, we can deduce that the hydration behavior of An(III) and Ln(III) plays a crucial role in the extraction process, and the organic medium also plays an important role in the extraction process.

Based on the HSAB theory, species of the same class (soft–soft and hard–hard) prefer to form complexes than those of different classes (hard–soft). The calculations were adopted by the definition of $\eta = (IP - EA)/2$, which was proposed by Parr

Table 4 Calculated reaction energies (kcal mol^{-1}) including ZPE corrections and thermal corrections for $ML(NO_3)_3$ with L by the B3LYP method[a]

Reactions	ΔG_{sol}	ΔG_{ext}
$[Am(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow AmL(NO_3)_3 + 9H_2O$	−37.4/−43.8	−42.4/−48.4
$[Cm(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow CmL(NO_3)_3 + 9H_2O$	−32.8/−39.7	−37.3/−44.0
$[Eu(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow EuL(NO_3)_3 + 9H_2O$	−36.8/−42.4	−42.2/−46.1
$[Am(NO_3)(H_2O)_7]^{2+} + L + 2NO_3^- \rightarrow AmL(NO_3)_3 + 7H_2O$	−28.8/−35.1	−33.7/−39.8
$[Cm(NO_3)(H_2O)_7]^{2+} + L + 2NO_3^- \rightarrow CmL(NO_3)_3 + 7H_2O$	−18.3/−25.2	−22.8/−29.5
$[Eu(NO_3)(H_2O)_7]^{2+} + L + 2NO_3^- \rightarrow EuL(NO_3)_3 + 7H_2O$	−18.4/−24.1	−23.8/−27.7
$[Am(NO_3)_2(H_2O)_5]^+ + L + NO_3^- \rightarrow AmL(NO_3)_3 + 5H_2O$	−4.5/−10.9	−9.5/−15.5
$[Cm(NO_3)_2(H_2O)_5]^+ + L + NO_3^- \rightarrow CmL(NO_3)_3 + 5H_2O$	−3.3/−10.2	−7.8/−14.5
$[Eu(NO_3)_2(H_2O)_5]^+ + L + NO_3^- \rightarrow EuL(NO_3)_3 + 5H_2O$	−4.3/−9.9	−9.7/−13.6
$Am(NO_3)_3(H_2O)_3 + L \rightarrow AmL(NO_3)_3 + 3H_2O$	4.5/−1.8	−0.5/−6.5
$Cm(NO_3)_3(H_2O)_3 + L \rightarrow CmL(NO_3)_3 + 3H_2O$	5.0/−1.9	0.5/−6.2
$Eu(NO_3)_3(H_2O)_3 + L \rightarrow EuL(NO_3)_3 + 3H_2O$	4.4/−1.2	−1.0/−4.9

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

Table 5 Calculated decomposition energies and the metal–ligand complexation reaction energies (kcal mol^{-1}) including ZPE corrections and thermal corrections for the Am^{3+}, Cm^{3+} and Eu^{3+} complexes by the B3LYP method

Reactions	Am	Cm	Eu
$[M(H_2O)_9]^{3+} \rightarrow M^{3+} + 9H_2O$ ^{a}	480.1/158.6	480.3/163.3	486.2/172.1
$[M(NO_3)(H_2O)_7]^{2+} \rightarrow M^{3+} + NO_3^- + 7H_2O$ ^{a}	723.5/167.3	730.8/177.9	743.7/190.4
$[M(NO_3)_2(H_2O)_5]^+ \rightarrow M^{3+} + 2NO_3^- + 5H_2O$ ^{a}	915.5/191.5	912.2/192.9	926.0/204.6
$M(NO_3)_3(H_2O)_3 \rightarrow M^{3+} + 3NO_3^- + 3H_2O$ ^{a}	1022.8/200.5	1021.3/201.2	1033.8/213.3
$M^{3+} + TODGA + 3NO_3^- \rightarrow M(TODGA)(NO_3)_3$ ^{b}	−196.1/−201.0	−196.2/−200.7	−208.9/−214.3
$M^{3+} + DMDHOPDA + 3NO_3^- \rightarrow M(DMDHOPDA)(NO_3)_3$ ^{b}	−202.4/−207.0	−203.1/−207.4	−214.5/−218.2

^{a} .../... refers to the results for ΔG_g and ΔG_{sol}, respectively. ^{b} .../... refers to the results for ΔG_{sol} and ΔG_{ext}, respectively.

and Pearson,[33] where η is the hardness, while IP and EA denote the first vertical ionization potential and electron affinity, respectively. For the TODGA and DMDHOPDA ligands in *n*-dodecane, the calculated hardness values are 95.2 and 95.6 kcal mol^{-1}, respectively, indicating the comparable hardness of these diglycolamide ligands. As for the metal cations, the predicted polarizabilities are in the order of Am^{3+} > Cm^{3+} > Eu^{3+}. Since species with high hardness have low polarizability,[34] trivalent actinides seem to be softer compared to trivalent lanthanides. Thus, the Am(III) species with TODGA and DMDHOPDA are more stable than the corresponding Eu(III) species according to the HSAB theory. However, ΔG_{ext} for most of the reactions of the Cm(III) species is higher than the corresponding Eu(III) species, which is not in agreement with our expectations. Note that these theoretical results are obtained with simple reaction models and only the 1:1 and 2:1 type extraction complexes have been taken into account. Therefore, to obtain more reliable data, calculations on accurate reaction models for actual extraction processes as well as the 3:1 and 4:1 type extraction complexes should be done in the future, even though these large complexes are computationally challenging for quantum chemical calculations.

Conclusions

In this work, the geometrical and the electronic structures as well as the stabilities of Am(III), Cm(III) and Eu(III) complexes with TODGA and DMDHOPDA ligands in nitric acid solution have been systematically investigated using quasi-relativistic DFT methods. Our calculations reveal that in the 1:1 and charged 2:1 type complexes, TODGA and DMDHOPDA are always coordinated as tridentate ligands, whereas these reagents act as bidentate ligands through the carbonyl groups in the neutral 2:1 type complexes. NBO analysis suggests that the metal–ligand bonds are mainly of ionic character for all the 1:1 and 2:1 type species, and the carbonyl oxygen atoms have stronger coordinating ability to actinides and lanthanides compared to the ether oxygen atoms. For the 1:1 type complexes, the reaction energies in aqueous solution predicted by the COSMO model are found to be much lower than those in the gas phase. Even so, the stabilities of the 1:1 species in the gas phase and aqueous solution follow the order $[ML]^{3+}$ < $[ML(H_2O)_6]^{3+}$ < $[ML(NO_3)(H_2O)_4]^{2+}$ < $[ML(NO_3)_2(H_2O)_2]^+$ <

$ML(NO_3)_3$. The neutral 2:1 type $ML_2(NO_3)_3$ complexes are less stable than $ML(NO_3)_3$ in aqueous solution. According to the reaction energies from water to *n*-dodecane, $AmL(NO_3)_3$ is predicted to be more stable than $EuL(NO_3)_3$, which is in accordance with the experimental results. Besides, M(DMDHOPDA)-$(NO_3)_3$ is more favorable energetically than M(TODGA)(NO$_3$)$_3$, confirming the stronger complexing ability of the DGA ligands with shorter alkyl chains. We hope that this work could shed light on the extraction mechanism of trivalent actinide and lanthanide separation using diglycolamides, and future studies should be carried out on the 3:1 and 4:1 stoichiometric extraction complexes.

Notes and references

1 P. A. Baisden and G. R. Choppin, Nuclear waste management and the nuclear fuel cycle, in *Radiochemistry and Nuclear Chemistry*, ed. S. Nagyl, Encyclopedia of Life Support Systems (EOLSS), Oxford, UK, 2007.
2 M. Arisaka and T. Kimura, *Solvent Extr. Ion Exch.*, 2011, **29**, 72.
3 K. L. Nash, C. Madic, J. N. Mathur and J. Lacquement, Actinide Separation Science and Technology, in *The Chemistry of the Actinide and Transactinide Elements*, ed. L. R. Morss, N. M. Edelstein, J. Fuger and J. J. Katz, Springer, The Netherlands, 3rd edn, 2006, vol. 4, pp. 2622.
4 Y. Sasaki, Y. Sugo, S. Suzuki and S. Tachimori, *Solv. Extr. Ion Exch.*, 2001, **19**, 91.

5 Y. Sasaki and G. R. Choppin, *Anal. Sci.*, 1996, **12**, 225.

6 Y. Sasaki and G. R. Choppin, *J. Radioanal. Nucl. Chem.*, 1996, **207**, 383.

7 H. Narita, T. Yaita, K. Tamura and S. Tachimori, *Radiochim. Acta*, 1998, **81**, 223.

8 H. Narita, T. Yaita, K. Tamura and S. Tachimori, *J. Radioanal. Nucl. Chem.*, 1999, **239**, 381.

9 Y. Sasaki, H. Suzuki, Y. Sugo, T. Kimura and G. R. Choppin, *Chem. Lett.*, 2006, **35**, 256.

10 Y. Sasaki, Y. Sugo, Y. Kitatsuji, A. Kirishima, T. Kimura and G. R. Choppin, *Anal. Sci.*, 2007, **23**, 727.

11 S. A. Ansari, P. Pathak, P. K. Mohapatra and V. K. Manchanda, *Chem. Rev.*, 2012, **112**, 1751.

12 S. A. Ansari, P. N. Pathak, M. Husain, A. K. Prasad, V. S. Parmar and V. K. Manchanda, *Radiochim. Acta*, 2006, **94**, 307; Y. Sasaki, P. Rapold, M. Arisaka, M. Hirata, T. Kimura, C. Hill and G. Cote, *Solvent Extr. Ion Exch.*, 2007, **25**, 187.

13 P. N. Pathak, S. A. Ansari, S. V. Godbole, A. R. Dhobale and V. K. Manchanda, *Spectrochim. Acta, Part A*, 2009, **73**, 348.

14 M. Arisak and T. Kimura, *Solvent Extr. Ion Exch.*, 2011, **29**, 72.

15 G. Schreckenbach and G. A. Shamov, *Acc. Chem. Res.*, 2010, **43**, 19.

16 M. Hirata, P. Guilbaud, M. Dobler and S. Tachimori, *Phys. Chem. Chem. Phys.*, 2003, **5**, 691.

17 A. W. Ehlers and G. Frenking, *J. Am. Chem. Soc.*, 1994, **116**, 1514; B. Delly, M. Wrinn and H. P. Lüthi, *J. Chem. Phys.*, 1994, **100**, 5785; J. Li, G. Schreckenbach and T. Ziegler, *J. Am. Chem. Soc.*, 1995, **117**, 486; V. Jonas and W. J. Thiel, *Chem. Phys.*, 1995, **102**, 8474.

18 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785.

19 M. J. Frisch, *et al.*, *GAUSSIAN 09 (Revision A.02)*, Gaussian, Inc., Wallingford CT, 2009, (see ESI† for the full reference).

20 J. H. Lan, W. Q. Shi, L. Y. Yuan, Y. L. Zhao, J. Li and Z. F. Chai, *Inorg. Chem.*, 2011, **50**, 9230; J. H. Lan, W. Q. Shi, L. Y. Yuan, Y. X. Feng, Y. L. Zhao and Z. F. Chai, *J. Phys. Chem. A*, 2012, **116**, 504; J. H. Lan, W. Q. Shi, L. Y. Yuan, J. Li, Y. L. Zhao and Z. F. Chai, *Coord. Chem. Rev.*, 2012, **256**, 1406; C. Z. Wang, J. H. Lan, Y. L. Zhao, Z. F. Chai, Y.-Z. Wei and W. Q. Shi, *Inorg. Chem.*, 2013, **52**, 196; C. Z. Wang, W. Q. Shi, J. H. Lan, Y. L. Zhao, Y.-Z. Wei and Z. F. Chai, *Inorg. Chem.*, 2013, **52**, 10904.

21 W. Kuchle, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1994, **100**, 7535; X. Cao and M. Dolg, *J. Mol. Struct. (THEOCHEM)*, 2004, **673**, 203; X. Cao and M. Dolg, *J. Mol. Struct. (THEOCHEM)*, 2002, **581**, 139.

22 N. K. Jena, M. Sundararajan and S. K. Ghosh, *RSC Adv.*, 2012, **2**, 2994; M. Sundararajan, V. Sinha, T. Bandyopadhyay and S. K. Ghos, *J. Phys. Chem. A*, 2012, **116**, 4388; M. Sundararajan and S. K. Ghosh, *J. Phys. Chem. A*, 2011, **115**, 6732.

23 A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799.

24 G. A. Shamov and G. Schreckenbach, *J. Phys. Chem. A*, 2005, **109**, 10961; G. A. Shamov, G. Schreckenbach, R. L. Martin and P. J. Hay, *Inorg. Chem.*, 2008, **47**, 1465.

25 P. G. Allen, J. J. Bucher, D. K. Shuh, N. M. Edelstein and I. Craig, *Inorg. Chem.*, 2000, **39**, 595; T. Stumpf, C. Hennig, A. Bauer, M. A. Denecke and T. Fanghaenel, *Radiochim. Acta*, 2004, **92**, 133; J. Ciupka, X. Cao-Dolg, J. Wiebke and M. Dolg, *Phys. Chem. Chem. Phys.*, 2010, **12**, 13215; C. Beuchat, D. Hagberg, R. Spezia and L. Gagliardi, *J. Phys. Chem. B*, 2010, **114**, 15590; P. D'Angelo and R. Spezia, *Chem. – Eur. J.*, 2012, **18**, 11162; J. Wiebke, A. Moritz, X. Cao and M. Dolg, *Phys. Chem. Chem. Phys.*, 2007, **9**, 459.

26 A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098; J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8822.

27 V. Vetere, B. O. Roos, P. Maldivi and C. Adamo, *Chem. Phys. Lett.*, 2004, **396**, 452; V. Vetere, P. Maldivi and C. Adamo, *J. Comput. Chem.*, 2003, **24**, 850; J. P. Austin, M. Sundararajan, M. A. Vincent and I. H. Hillier, *Dalton Trans.*, 2009, 5902.

28 J. E. Carpenter and F. Weinhold, *J. Mol. Struct. (THEOCHEM)*, 1988, **169**, 41; J. P. Foster and F. J. Weinhold, *J. Am. Chem. Soc.*, 1980, **102**, 7211; A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735; A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1986, **6**, 899.

29 A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.*, 1990, **92**, 5397.

30 S. A. Ansari, P. N. Pathak, M. Husain, A. K. Prasad, V. S. Parmar and V. K. Manchanda, *Solvent Extr. Ion Exch.*, 2005, **23**, 463.

31 R. L. Martin, P. J. Hay and L. R. Pratt, *J. Phys. Chem. A*, 1998, **102**, 3565.

32 R. G. Pearson, *Chemical Hardness*, VCH, Weinheim, 1997.

33 R. Parr and R. G. Pearson, *J. Am. Chem. Soc.*, 1983, **105**, 7512.

34 T. K. Ghanty and S. K. Ghosh, *J. Phys. Chem.*, 1993, **97**, 4951; P. Politzer, *J. Chem. Phys.*, 1987, **86**, 1072.