

Density functional theoretical study on the preferential selectivity of macrocyclic dicyclohexano-18-crown-6 for Sr^{+2} ion over Th^{+4} ion during extraction from an aqueous phase to organic phases with different dielectric constants

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Abstract The preferential selectivity of dicyclohexano-18-crown-6 (DCH18C6) for bivalent Sr^{+2} ion over tetravalent Th^{+4} ion was investigated using generalized gradient approximated (GGA) BP86 and the hybrid B3LYP density functional, employing split valence plus polarization (SV(P)) and triple-zeta valence plus polarization (TZVP) basis sets in conjunction with the COSMO (conductor-like screening model) solvation approach. The calculated theoretical selectivity of DCH18C6 for Sr^{+2} ion over Th^{+4} ion was found to be in accord with the selectivity for Sr^{+2} ion over Th^{+4} ion observed when performing liquid–liquid extraction experiments in different organic solvents. While 1:1(M:L) stoichiometric complexation reactions can be used to predict the preferential selectivity of Sr^{2+} ion over Th^{4+} ion, the results obtained are not consistent with the experimental results observed upon increasing the dielectric constant of the solvent. The calculated theoretical gas-phase data for the free energy of complexation, ΔG , fail to explain the selectivity for Sr^{+2} ion over Th^{+4} ion. However, when 1:2 (M:L) stoichiometric complexation reactions (reported in previous X-ray crystallography studies) are considered, correct and consistent results for the selectivity for Sr^{+2} ion over a wide range of dielectric constants are predicted. The distribution constant for Sr^{2+} and Th^{4+} ions was found to gradually increase with increasing

dielectric constant of the organic solvent, and was found to be highest in nitrobenzene. The selectivity data calculated from $\Delta\Delta G_{\text{ext}}$ are in excellent agreement with the results obtained from solvent extraction experiments.

Keywords DFT · Dicyclohexano-18-crown-6 ether · Solvent extraction · Strontium · Thorium · Distribution · Selectivity

Introduction

^{90}Sr , along with ^{137}Cs , is one of the major sources of heat generation in aqueous nuclear waste. Hence, it is of the utmost importance to separate ^{90}Sr from nuclear waste prior to vitrification [1]. Sr also has other commercial and research applications, including in certain optical materials, as an oxygen eliminator in electron tubes, and to produce glass for color television tubes. In addition, ^{90}Sr has been used as an isotopic energy source in various research applications. The daughter product of ^{90}Sr decay (^{90}Y) is a useful radioisotope that is employed in nuclear medicine. Also, the heat generated by ^{90}Sr can be beneficial, such as when it is used in thermal electric generators [2]. Classical separation methods such as solvent extraction and ion exchange techniques are commonly used for the separation of Sr from waste solutions. Macrocyclic crown ethers form very stable complexes with alkali and alkaline earth metal ions due to strong ion–dipole interactions [3]. Numerous applications of crown ethers and their derivatives in the nuclear industry for the selective separation of radioactive ^{137}Cs and ^{90}Sr efficiently from nuclear waste [4–6] are reported in the literature. As it is a neutral donor, crown ether can extract both cations and anions from the aqueous phase, leading to the formation of ion pairs in the organic phase. Therefore, the efficiency of extraction strongly depends

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not only upon the target metal ion but also on the anion to which it is associated, the lipophilicity of the anion, and the physical properties of the solvent, among other factors [4, 7]. In addition, the utilization of a solvent with a high dielectric constant and the ability to extract water improves metal ion extraction when compared with nonpolar solvents [4, 8]. Many studies have focused on improving the efficiency of crown ethers by using different solvents and/or additives [4, 9–11]. Thus, the separation of Sr ion is necessary not only for nuclear waste management but also for other useful applications of this metal. During the metal ion–crown ether interaction, the metal ion is transferred from the aqueous phase and is encapsulated in the cavity of the crown ether via weak coordinate covalent bonds. Because Sr^{2+} is mainly present in aqueous phases, knowledge of the coordination numbers and binding enthalpies of $\text{Sr}^{2+}-(\text{H}_2\text{O})_n$ clusters is very useful for extraction studies, as has recently been addressed [12]. Dicyclohexano-18-crown-6 (DCH18C6) has been shown to be a promising extraction agent for Sr metal ion from high-level nuclear waste when employed in solvent extraction technology [1, 4, 7]. It should be noted that, in addition to Sr ion, the waste solution contains other metal ions. To obtain pure radioactive Sr metal ion for various applications [e.g., as mentioned above, the daughter product of ^{90}Sr (^{90}Y) is used in nuclear medicine], it must be separated from other metal ions (i.e., contaminants). Thorium, one of the early members of the actinide family, provides one such metal ion impurity, Th^{4+} ion, which is present in small amounts in the Th-lean raffinate generated during the reprocessing of the irradiated Thoria fuel. These two ions are dissimilar in many ways: the Sr^{2+} ion (diameter: 2.26 Å) is bigger than the Th^{4+} ion (diameter: 1.98 Å), and the charge on the Sr ion is +2, whereas it is +4 on the Th ion, which leads to the very high ionic potential of Th^{4+} compared to that of Sr^{2+} . One of the features of the actinides is the presence of 5*f* electrons (electron distribution in Th: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^6 5f^0 6d^2 7s^2$). The 5*f* orbital is relatively well shielded from the nuclear charge, so electrons in this orbital more readily participate in bond formation. However, although Th is a member of the actinide family, it does not have any electrons in its 5*f* orbital, whereas other actinide members do. In Th, the outer *d* orbital electrons participate in chemical bonding. While there is no electron in the 5*f* orbital for Th, either in its ground state or in the Th^{4+} ion, the additional electron may occupy the 5*f* orbital in Th^{3+} or Th^{2+} , i.e., the valence shell will have $5f^1$ for Th^{3+} and $5f^1 6d^1$ for Th^{2+} , as reported by Dolg et al. [13]. Hence, it is of immense importance (and a significant challenge) to study the selectivity of solvent extraction for the Sr ion in the presence of Th metal ions both experimentally and theoretically.

In order to understand the mechanism for the extraction of a metal ion (M) using a ligand (L), it is of paramount importance to know the stoichiometry of the $\text{ML}_x(\text{NO}_3)_y$ complex.

1:1 (M:L) stoichiometric complexation was observed for Sr ion with the ligand DCH18C6 using the EXAFS technique [14, 15]. The values of *x* and *y* were found to be 1 and 2, respectively. The central Sr metal ion was found to be tenfold coordinated with six O atoms of the DCH18C6 ligand and four O atoms from the two nitrate anions. Each nitrate anion was found to be coordinated to the central metal ion in a bidentate mode. Although extensive experimental research has been carried out on Sr^{2+} ion extraction, experiments focusing on the solvent extraction of Th^{4+} ion using a crown ether are very difficult to find. Only one report of a study of Th ion complexation with crown ethers is available [16]. The authors of that work reported a 1:1 complex of thorium nitrate with 18-crown-6 (18C6) and their IR spectra. In the case of 1:1 complexation for Th ion, the probable stoichiometry was considered to be $\text{ML}_x(\text{NO}_3)_y$ with *x*=1 and *y*=4. Recently, the structure of the complex of Th^{4+} with DCH18C6, as obtained from an X-ray crystallographic study, was reported [17]; in that study, Th^{4+} ion was shown to be sandwiched between two units of hydrated DCH18C6, indicating a 1:2 stoichiometry for the complex, i.e., $\text{ML}_x(\text{NO}_3)_y(\text{H}_3\text{O}^+)_z$ with *x*=2, *y*=6, and *z*=2, respectively. The Th^{4+} ion was at the center of symmetry and did not bind directly to the O atoms of the crown ether. Th^{4+} ion was coordinated to the six nitrate anions in a bidentate mode. Though experimental data on the complexation of Th^{4+} ion with organic cyclic ligands is very scarce, aqueous solvation data for this ion are readily available. Previously published data from experimental studies [18–21] on Th^{4+} ion hydrates indicate that the hydration number of Th^{4+} ion is between 8 and 12, and the length of the Th–O (O of water) bond is between 2.45 and 2.50 Å. These aqueous metal ion coordination numbers and the metal ion–ligand stoichiometry described above were used in the quantum chemical modeling of the metal–ligand complexation reaction reported in the present paper.

The experimental procedure for solvent extraction is lengthy and quite time-consuming. Also, only macroscopic distribution constants for different metal ions can be predicted from solvent extraction experiments. They do not provide any microscopic insights into the ion–ligand interactions. Hence, it is desirable to perform quantum electronic structure-based theoretical calculations, which not only provide these microscopic insights into molecular level interactions, but can also reduce the burden on the experimentalist by predicting a suitable ligand/solvent system for the target metal ion. Therefore, in the work described in the present paper, we investigated the extraction mechanism for the preferential complexation of the DCH18C6 ligand with Sr^{2+} ion over Th^{4+} ion using density functional theory-based calculations.

Computational works addressing systems of Sr^{2+} or Th^{4+} metal ion with DCH18C6 are also very rare in the literature. Most theoretical works have reported the hydration of Sr^{2+} and Th^{4+} ions in the gas as well as in the solvent phase.

Glendening and Feller [22] performed geometry optimizations and single-point energy calculations on $\text{Sr}^{2+}(\text{H}_2\text{O})_n$ complexes with $n=1-6$. Klobukowski [23], Bauschlicher and co-workers [24], as well as Kaupp and Schleyer [25] determined the binding energies of hydrated Sr^{2+} ions with $n=1-4$, $n=1-3$, and $n=1-2$ water molecules using a variety of basis sets. Recently, the binding enthalpies of $\text{Sr}^{2+}(\text{H}_2\text{O})_n$ ($n=1-6$) complexes were reported; these were derived using multiple levels of theory and different basis sets, including two different effective core potentials for Sr [26]. Earlier, Glending et al. [27] presented results on the interaction of Sr^{2+} ion with 18C6 at the restricted Hartree–Fock (RHF) and second-order Møller–Plesset perturbation (MP2) levels of theory using the 6-31 + G* basis set and relativistic effective core potentials. They also reported the gas-phase selectivity of the ligand for various alkaline earth metal ions by including the first solvation shell. The selectivities of crown ethers with different cavities and donor atoms for Sr^{2+} and Cs^+ metal ions were studied recently by Boda et al. [28]. In spite of the great environmental concern over Sr^{2+} ions, only a limited number of computational works have been carried out to determine a suitable and effective ligand/solvent system for the removal of Sr^{2+} from nuclear waste before its safe disposal.

Also, to the best of our knowledge, there is no quantum computational work on the interaction of a crown ether with Th^{4+} ion. Only a few studies have been carried out on the interaction of Th^{4+} ion with water molecules. Tsushima et al. [29] studied the hydration of Th^{4+} ion using ab initio calculations performed with the conductor-like polarizable continuum model (CPCM) at the HF/6-311G** and the HF/6-311 + G* levels. Real et al. [30] investigated the solvation of Th^{4+} ion in aqueous solution using classical molecular dynamics simulations along with ab initio calculations and density functional theory. Our aim in the present work was to find a suitable ligand/solvent system for separating Sr^{2+} ion from a mixture of Sr^{2+} and Th^{4+} ions by analyzing the interaction energy and thermodynamic parameters using quantum electronic structure calculations.

We therefore present our results on the selectivity of the crown ether DCH18C6 for Sr^{2+} ion over Th^{4+} ion using both experimental and theoretical routes. Solvent extraction was used to estimate distribution constants, whereas quantum electronic structure calculations using implicit and explicit solvation models were employed to calculate the free energies of extraction ΔG_{ext} of the metal ions with DCH18C6. The structures and the energetic and thermodynamic parameters for the metal ion–ligand systems were computed using DFT. Solvent effects associated with the water and organic solvent were taken into account using the COSMO approach. An attempt was made to correlate the calculated separation factors with the free energy of extraction ΔG_{ext} . The experimental and theoretical work done is described in the following section.

Experimental and computational studies

Reagents

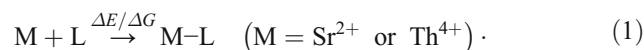
All of the reagents used in the solvent extraction experiments were of AR grade. DCH18C6 ether was procured from Aldrich (St. Louis, MO, USA). A stock solution of 1 M HNO_3 acid was prepared from concentrated HNO_3 acid (S.D. Fine Chemicals, Mumbai, India) using ultrapure deionized water (0.054 $\mu\text{S}/\text{cm}$). Aqueous stock solutions of $\text{Sr}(\text{NO}_3)_2$ and $\text{Th}(\text{NO}_3)_4$ were prepared in 1 M HNO_3 acid from anhydrous $\text{Sr}(\text{NO}_3)_2$ (S.D. Fine Chemicals) and $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ salts (Loba Chemie, Mumbai, India), and these solutions were used as aqueous phases. Stock solutions of 0.05 M DCH18C6 ether were prepared in different organic solvents (toluene, xylene, octanol, and nitrobenzene), and these were used as organic phases.

Distribution studies

Equal volumes (5 ml) of an aqueous phase containing either Sr^{2+} (1.1413×10^{-3} M) or Th^{4+} (4.3096×10^{-4} M) ion and an organic phase were added to a glass bottle for equilibration in a thermostated water bath. The bottles were equilibrated at constant temperature (25 ± 0.1 °C) for 30 min to attain equilibrium. The two phases were then centrifuged and assayed by taking suitable aliquots from both phases. The concentration of Sr^{2+} ion in the feed as well as in the raffinate was estimated using a flame atomic absorption spectrophotometer (Avanta PM3000, GBC, Hampshire, IL, USA). Th^{4+} ion in the aqueous phase (raffinate) and feed samples was analyzed using a UV-visible spectrophotometer (V530, JASCO, Easton, MD, USA), via a previously reported method [31]. Analytical results were typically reproducible within ± 5 %.

Computational methodology

We performed detailed DFT analysis in order to calculate the binding/free energies of complexation $\Delta E/\Delta G$ of Sr^{2+} and Th^{4+} ions towards DCH18C6 (L) as per the following basis complexation reaction, which were then used to compute the selectivity parameter.



The energies of the species M, L, and M–L can be computed in either the gas phase or the solvent phase. Calculations were performed with the generalized gradient approximated (GGA) BP-86 and the hybrid B3LYP functional using def-SV(P) [32], i.e., O (7s4p1d)/[3s2p1d], C (7s4p1d)/[3s2p1d], N (7s4p1d)/[3s2p1d], H (4s)/[2s], Sr (6s6p5d)/[4s3p2d], and Th (14s13p10d8f1g)/[10s9p5d4f1g], and the def2-TZVP [32] basis set, i.e., O (11s6p1d)/[5s3p1d], C (11s6p1d)/[5s3p1d], N (11s6p1d)/[5s3p1d], H (5s1p)/[3s1p],

Sr ($7s\ 7p\ 5d$)/[$6s\ 4p\ 3d$], and Th ($14s\ 13p\ 10d\ 8f\ 1g$)/[$10s\ 9p\ 5d\ 4f\ 1g$] with an effective core potential, as implemented in Turbomole suite of programs [33]. The number of core electrons in the ECP for Sr [34] was considered to be 28, and that for Th [35] to be 60. The BP-86 functional is a combination of the Becke B88 exchange functional [36] and the Perdew P86 correlation functional [37]. The BP86 functional has proven to be quite useful for predicting molecular properties [38]. The BP86 functional does not contain a nonlocal Hartree–Fock (HF) contribution, so it enables geometries and vibrational frequencies to be predicted relatively rapidly. According to reports in the literature, the resulting geometries and frequencies obtained are quite accurate. It is therefore possible to avoid computationally expensive geometry optimizations and frequency computations with a hybrid density functional, since comparable results can be obtained with a GGA functional such as BP86 [39]. Zero-point energy and thermodynamic corrections to the total energy were made by using a scaled vibrational frequency (a scaling factor of 0.9914 was used) to compute the gas-phase free energy, ΔG_{ext} at $T=298.15$ K. The geometries were optimized with the BP-86 functional but the total energies were calculated with the B3LYP functional [40, 41]. The hybrid B3LYP functional was better at predicting the energetics due to the consideration of the nonlocal HF contribution in the exchange functional [39]. Aqueous and organic solvent effects were incorporated into the energetics using the COSMO [42] approach. The dielectric constant ϵ of water was taken as 80. The gas-phase optimized geometries were used to calculate the single-point energy in the COSMO phase. The solvation energies of metal ions in water were computed using the implicit and explicit solvation models within the COSMO formalism. The accuracies of the energies obtained from the BP and B3LYP functionals were further tested by performing an M06-2X calculation using the ADF package [43]. Noncovalent interactions were accounted for by using the M06-2X functional [44] with the TZ2P basis set as implemented in the ADF package. Scalar relativistic effects were incorporated through the use of the zero-order regular approximation (ZORA) [45] approach as implemented in the ADF program. Also, the single-point MP2 energy was calculated using the optimized coordinates obtained at the BP86 level of theory to calibrate the energy obtained from DFT using the TZVP basis set. In addition, the effects of dispersion interactions were evaluated by further performing the B3LYP-D3 calculation as implemented in ADF2012.

Results and discussion

Distribution studies

Liquid–liquid extraction of an acidic solution (1 M nitric acid) of Sr^{2+} and Th^{4+} metal ions using DCH18C6 in organic

diluents was employed for the distribution studies. The distribution ratio of each metal ion in the liquid–liquid distribution, representing the total analytical concentration of the metal ion in the organic phase (extract) with respect to its analytical concentration in the aqueous phase (raffinate), was expressed as $D = [\text{M}]_{\text{org}}/[\text{M}]_{\text{aq}}$ [$\text{M} = \text{Sr}^{2+}$ or Th^{4+}]. (2)

Here, $[\text{M}]_{\text{org}}$ and $[\text{M}]_{\text{aq}}$ are the total metal ion concentrations in the organic and aqueous phases, respectively. The separation factor (α) can be calculated as the ratio of the distribution ratios of the two extractable metal ions measured under the same conditions, as follows:

$$\text{Separation factor}(\text{SF}_{\text{Sr/Th}}) = D_{\text{Sr}}/D_{\text{Th}}, \quad (3)$$

where $D_{\text{Sr}^{2+}}$ and $D_{\text{Th}^{4+}}$ are the distribution ratios of the Sr^{2+} and Th^{4+} ions in various aqueous–organic biphasic systems.

Choice of solvent (diluent)

The amount of metal ion extracted depends on the nature and type of the organic solvent used, i.e., either aliphatic or aromatic. Hence, selecting an appropriate organic solvent is crucial. The solvent should possess low water solubility, and the disengagement of its phase from the mixture should be rapid. In the present study of Sr^{2+} and Th^{4+} ion extraction with DCH18C6, four different types of organic solvent (diluent) were investigated. Draye et al. [46] studied the distribution of Sr in chloroform, but there are practical limitations on the use of chloroform in an actual plant. Hence, we studied organic solvents that could be used in a separation plant. The experimentally observed values of D for Sr ion with four different solvents with different dielectric constants are presented in Table 1. From the table, it is clear that using nitrobenzene (NB) leads to the highest D for DCH18C6 with Sr^{2+} ion. There is moderate extraction of Sr with octanol as the solvent, but very low extraction of Sr was observed when toluene and xylene were used as solvents.

The effect of the organic solvent on the Sr^{2+} ion extraction efficiency and selectivity can be correlated with the dielectric

Table 1 Experimentally measured distribution constants of Sr^{2+} and Th^{4+} ions in different organic solvents (diluents)

Solvents	Dielectric constant	D_{Sr}	D_{Th}	$\text{SF}_{\text{Sr/Th}} (D_{\text{Sr}}/D_{\text{Th}})$
Toluene	2.38	0.0718	0.0316	1.33
Xylene	2.4	0.0763	0.0538	2.41
Octanol	10.3	0.537	0.0753	7.62
Nitrobenzene	34.9	3.029	0.111	27.33

[Sr^{2+}] was 1.1413×10^{-3} M; [Th^{4+}] was 4.3096×10^{-4} M; 0.05 M DCH18C6 was used in the various organic solvents; 1 M HNO_3 was used; organic by aqueous phase volume ration (O/A) 5 ml each; temperature of the water bath was 25 °C; stirring time was 0.5 h

constant of the solvent. The degree of extraction was found to increase with increasing dielectric constant of the diluent. Similarly, the distribution of Th^{4+} ion was found to increase from 0.0316 to 0.111 from toluene to xylene to nitrobenzene (as shown in Table 1). The observed distribution constant for Th^{4+} ion was found to be much lower than that for Sr^{2+} ion. From the table, the distribution constant of Th^{4+} ion in NB ($D=1.0\times 10^{-1}$) indicates negligible extraction at 1 M HNO_3 . The influence of the solvent on the separation factor of $\text{Sr}^{2+}/\text{Th}^{4+}$ is also shown in Table 1. High selectivity for Sr^{2+} and a good separation factor of $\text{Sr}^{2+}/\text{Th}^{4+}$ was observed in NB, as shown in Fig. 1. Therefore, it would be interesting and worthwhile to explore the molecular interactions of Sr^{2+} and Th^{4+} ions using a first-principles quantum chemical DFT approach in order to deduce the reason for the preferential selectivity of DCH18C6 for Sr^{2+} ion over Th^{4+} ion.

In order to model the metal–ligand complexation reaction, it would be useful to know the correct stoichiometry of the metal–ligand (M:L) complex. However, there is a lack of data on the stoichiometry of M:L complexes of Sr^{2+} or Th^{4+} ion with DCH18C6 as the ligand. In order to determine the stoichiometry of these complexes, the distribution constants of the Sr^{2+} and Th^{4+} ions were estimated using different concentrations of ligand. These distribution constants were then plotted against the concentration of the ligand, as shown in Figs. 2 and 3. The slopes of these plots were found to be 1 and 2 for Sr^{2+} and Th^{4+} ion, respectively, indicating that these metal–ligand complexes have stoichiometries of 1:1 and 1:2.

Computational results

The structure of the free crown ether and its complexes with Sr^{2+} and Th^{4+} ions, the complexation energies, and the free

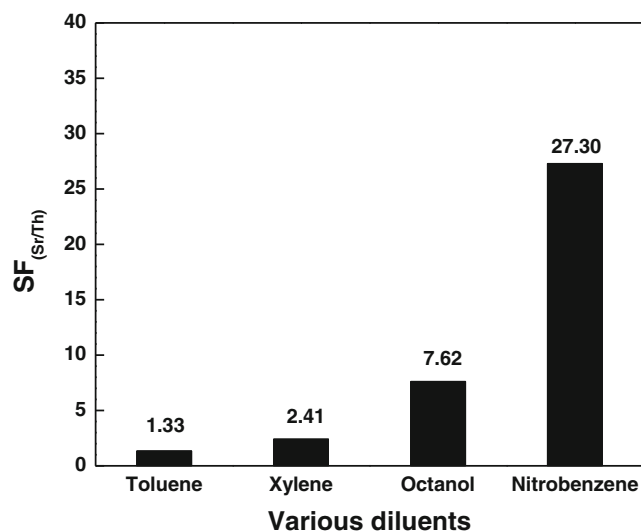


Fig. 1 Plot of separation factor, $\text{SF}_{\text{Sr/Th}}$ ($D_{\text{Sr}}/D_{\text{Th}}$), vs. organic diluents (solvents). [Sr] 1.1413×10^{-3} M; [Th] 4.3096×10^{-4} M; 0.05 M DCH18C6 in the various diluents; 1 M HNO_3 ; O/A 5 ml each; water bath temperature 25 °C; stirring time 0.5 h

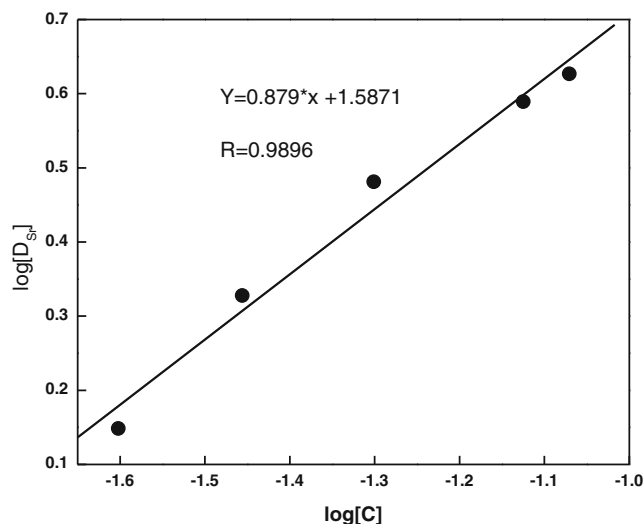


Fig. 2 Plot of the distribution constant D for Sr ion vs the concentration (C) of crown ether in nitrobenzene solvent

energies of extraction for the metal ions were calculated at different levels of DFT employing various basis sets. The detailed calculated results are provided in subsequent sections. The metal ion–ligand complexation reaction was modeled as 1:1 ($\text{Sr}^{2+}:\text{L}$) stoichiometry for Sr^{2+} ion and 1:1 ($\text{Th}^{4+}:\text{L}$) or 1:2 ($\text{Th}^{4+}:\text{2L}$) stoichiometry for Th^{4+} ion. The structures of these 1:1 and 1:2 stoichiometric complexes for Sr^{2+} and Th^{4+} ion were then optimized.

Structures of the ligand and the metal ion–ligand complexes

The optimized minimum-energy structures of the free crown ether and the metal ion–crown ether complexes are displayed in Fig. 4. From the figure, it is clear that in the free crown ether, the O atoms attached to the cyclohexane rings are

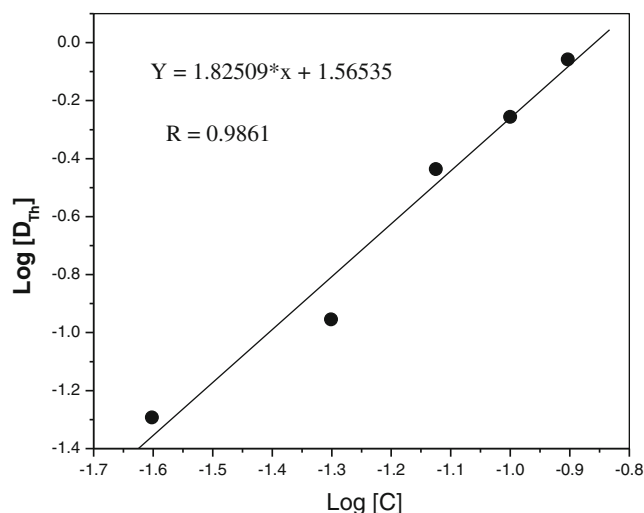
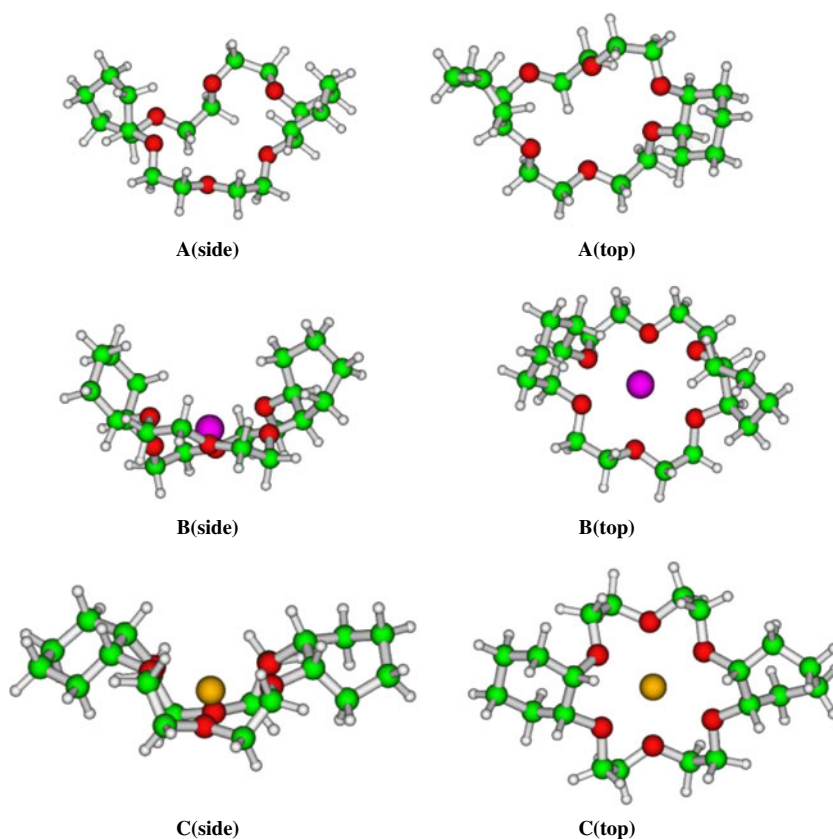


Fig. 3 Plot of the distribution constant D for Th ion vs the concentration (C) of crown ether in nitrobenzene solvent

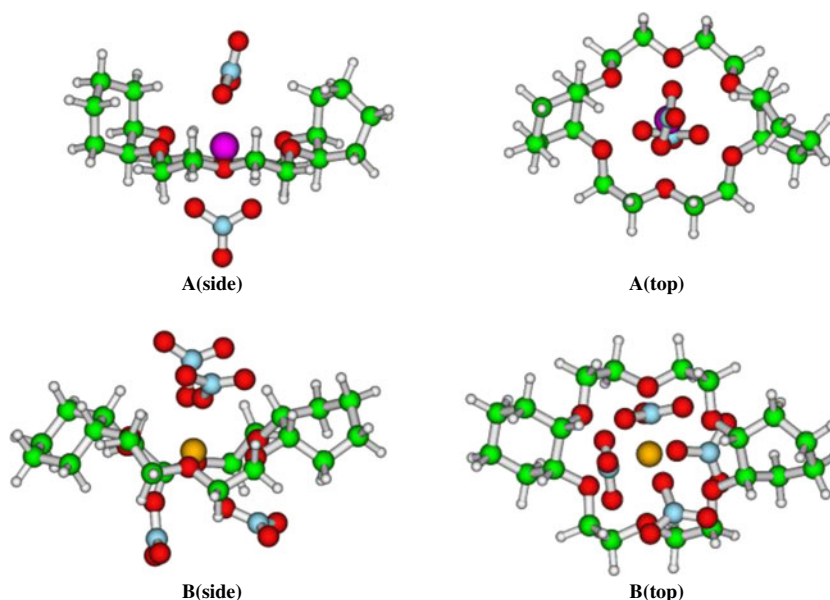
Fig. 4 Optimized structures of the free DCH18C6 crown ether and its complexes with Sr^{2+} and Th^{4+} ions. Side and top views are shown of: **A** free DCH18C6; **B** the Sr^{2+} –DCH18C6 complex; **C** the Th^{4+} –DCH18C6 complex



located in the *trans* position, while the O atom attached to one cyclohexane ring is oriented *syn* with respect to the O atom attached to the other cyclohexane ring. This is known as a *trans-syn-trans* conformation. Since we are interested in the difference in the selectivity of DCH18C6 for the two ions, various possible conformations of DCH18C6 were not considered here. From the subfigures b and c, it is apparent that both Sr^{2+} and Th^{4+} ions (for 1:1 stoichiometry) are encapsulated within the crown ether cavity. The Th^{4+} ion is smaller than the Sr^{2+} ion, meaning that it is better encapsulated than the Sr^{2+} ion, which is reflected in the calculated M–O (M = Sr and Th) bond distances (see Table S1 in the “Electronic supplementary material,” ESM). All of the Sr–O bond distances are found to be almost equidistant (they range from 2.535 to 2.631 Å) in the Sr^{2+} –DCH18C6 complex. A similar situation is observed for the Th^{4+} –DCH18C6 complex, where the Th–O bond distance was found to be in the range 2.376–2.409 Å. The Th–O bond distance was found to be 0.16–0.22 Å shorter than the Sr–O bond distance. In order to study the effect of nitrate anion on the extraction efficiency, the metal ion–ligand complexes with nitrate anions were also optimized. The optimized structures of the Sr^{2+} and Th^{4+} ion complexes with nitrate anions are displayed in Fig. 7. In the complex with Sr^{2+} ion, two nitrate anions are coordinated from opposite sides of the centralized Sr^{2+} ion in a bidentate mode, leading to a total coordination number for the Sr^{2+} ion of 10 (Fig. 5a). The same coordination

was observed in EXAFS experiments [14, 15]. The nitrate anions in the Th^{4+} ion complex were found to coordinate in monodentate mode, with two units binding from the top and two from the bottom, leading to a total coordination number for the Th^{4+} ion of 10. The Sr–O bond length (2.667–2.865 Å) is also increased in the presence of nitrate anions. The length of the Sr–O bond that includes the O atom of the nitrate anion was found to be 2.576–2.624 Å. Similarly, the Th–O bond distance (2.543–2.843 Å) is also increased in the presence of nitrate anions. The length of the Th–O bond that includes the O atom of the nitrate anion was found to be 2.334–2.367 Å, which is smaller than the corresponding Sr–O bond length. Recently, the structure of the Th^{4+} complex with DCH18C6 derived from an X-ray crystallographic study was reported [16]; Th^{4+} ion was shown to be sandwiched between two units of hydrated DCH18C6, indicating a 1:2 complexation stoichiometry. Hence, this metal ion–ligand complex structure with 1:2 stoichiometry was also optimized, and the resulting geometry is presented in Fig. 6. In this structure, the hydronium ion (H_3O^+) is trapped inside the cavity of the crown ether ring by three $\text{OH}\cdots\text{O}$ hydrogen bonds. The distance between the Th^{4+} ion and the O atom from the anchored H_3O^+ is 5.399 Å for one unit of DCH18C6 and 6.398 Å for the other, indicating that the two DCH18C6 units are not positioned symmetrically with respect to the central Th^{4+} ion, thus supporting the validity of the experimental X-ray results. The calculated structural

Fig. 5 Optimized structures of the complexes of Sr^{2+} and Th^{4+} ions with DCH18C6 in the presence of nitrate anion. Side and top views are shown of: **A** the $\text{Sr}(\text{NO}_3)_2$ -DCH18C6 complex; **B** the $\text{Th}(\text{NO}_3)_4$ -DCH18C6 complex



parameters are displayed in Table S1 of the ESM. The Th^{4+} ion is situated at the center of symmetry and does not bind directly to the O atoms of the crown ethers. Th^{4+} is coordinated to the six nitrate anions in a bidentate mode, as also shown by the X-ray crystallographic experiment. All of the Th–O bond distances (where O is from a nitrate anion) are almost equal (range: 2.551 Å–2.597 Å) and correspond well with the experimentally observed bond distances of 2.551–2.587 Å. For the top crown ether, the O–O bond distances where the O atoms

are that of the H_3O^+ trapped in the cavity of the crown ether and that of the crown ether, which are linked through hydrogen bonding, were found to be 2.61, 2.63, and 2.75 Å, which are very close to the experimentally observed values of 2.59, 2.61, and 2.63 Å. Similarly, the other calculated O–O distances (i.e., between the other O atoms of the crown ether and the O of the trapped H_3O^+ , which are not linked through hydrogen bonding) of 2.79, 2.75, and 2.76 Å were found to be close to the corresponding experimentally obtained values of 2.88, 2.84, and 2.86 Å. The calculated N–O distance is 1.28 Å when a coordinated O atom is involved or 1.22 Å when a noncoordinated O atom is involved, which are in close agreement with the reported experimental results of 1.276 Å and 1.209 Å, respectively. Since the BP86/SV (P) level of theory predicts a relatively reliable structure that has calculated crystallographic structural parameters that are very similar to those observed experimentally, no time-consuming higher levels of calculation were attempted.

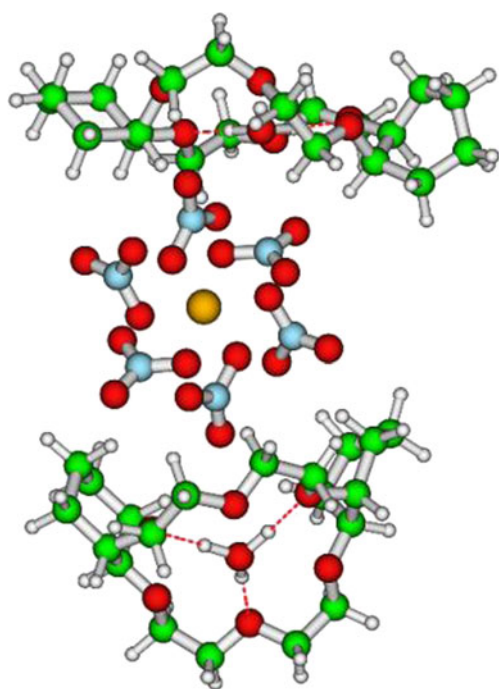


Fig. 6 Optimized structure of the complex of Th^{4+} ion with two units of DCH18C6, six nitrate anions, and two H_3O^+ ions, as calculated at the BP/SV (P) level of theory

Binding energy, extraction energy, free energy of extraction, and selectivity

One of the most important parameters to consider when modeling a metal ion–ligand complexation reaction is the binding energy (BE, ΔE) of the metal ion ($\text{Sr}^{2+}/\text{Th}^{4+}$) with the ligand (L). The metal ion–ligand binding energies, extraction energies, and free energies of extraction for the 1:1 ($\text{Sr}^{2+}:\text{L}$) complex with Sr^{2+} ion and the 1:1 ($\text{Th}^{4+}:\text{L}$) or 1:2 ($\text{Th}^{4+}:2\text{L}$) complex with Th^{4+} ion were calculated in both the gas and solvent phases in order to predict the metal ion selectivity of the ligand in each case. Details are given below.

Binding energy and free energy of complexation in the gas phase The BEs (ΔE) of the bare $\text{Sr}^{2+}/\text{Th}^{4+}$ ions for the 1:1

complexation reaction (Eq. 1) in the gas phase without nitrate anion can be written as

$$\Delta E = E_{M-L} - (E_M + E_L). \quad (4)$$

Here, E_{M-L} , E_M , and E_L refer to the energies of the M–L complex, the M ion, and the free ligand (L) system, respectively. The calculated binding energies in the gas phase for both Sr^{2+} and Th^{4+} ions are presented in Table 2. The binding energy predicted from BP86 was found to be overestimated compared to that obtained at the B3LYP level of theory. The gas-phase binding energy of the Th^{4+} ion with DCH18C6 calculated at the B3LYP level of theory was found to be 566.51 kcal mol⁻¹ higher than that of the Sr^{2+} ion, indicating that this ligand prefers to bind to the Th^{4+} ion over the Sr^{2+} ion. The very high binding energy for the Th^{4+} ion compared to the Sr^{2+} ion is due to the higher ionic potential of the Th^{4+} ion than the Sr^{2+} ion. The theoretical finding of a preference of the ligand for the Th^{4+} ion over the Sr^{2+} ion in the gas phase contradicts what is observed experimentally, as a preference for the Sr^{2+} ion over the Th^{4+} ion was observed with DCH18C6 in different organic solvents. This means that a simple comparison of the gas-phase binding energies cannot explain the experimentally observed selectivity. The higher gas-phase intrinsic binding energy of the Th^{4+} ion over the Sr^{2+} ion is expected due to the higher ionic charge (+4) on the Th^{4+} metal ion than that on the Sr^{2+} metal ion (+2). NBO population analysis was also performed to predict the partial charge on Th and Sr, as shown in Table S2 of the ESM. The partial charge on the Th^{4+} ion is 2.798 a.u., which is much higher than the charge on the Sr^{2+} ion (1.858 a.u.). In addition, there is very small electronic contribution from the *f* orbital in the Th^{4+} ion which is absent in the Sr^{2+} ion. It is also interesting to study the roles of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) frontier orbitals of the water-coordinated Th^{4+} ion complex and the DCH18C6-coordinated Th^{4+} ion complex in the chemical bonding that leads to complex formation. The HOMO–LUMO energy gap in the eight-coordinate water complex of Th^{4+} ion was found to be 7.89 eV, whereas it

was 3.35 eV for the Th^{4+} –DCH18C6 complex. The calculated HOMOs and LUMOs for both the water-coordinated Th^{4+} ion cluster and the Th^{4+} –DCH18C6 complex are presented in Fig. 7. The different HOMO–LUMO characteristics of the water-coordinated and DCH18C6-coordinated Th^{4+} ion complexes are suggestive of different types of complexation.

The accuracy of the BP and B3LYP functionals were further tested by performing single-point energy calculations at the M06-2X/TZ2P level of theory, which takes noncovalent interactions into account. For the 1:1 Sr^{2+} –DCH18C6 complex, the binding energy calculated at the B3LYP/TZVP level of theory was underestimated by only 3.3 % compared to that calculated at the M06-2X/TZ2P level of theory, whereas it was underestimated by only 0.22 % for the 1:1 Th^{4+} –DCH18C6 complex. In the presence of nitrate anion, the binding energy was underestimated by 3.64 % for Sr^{2+} and 2.31 % for Th^{4+} compared to the value predicted from the M06-2X functional. For the 1:2 Th^{4+} –DCH18C6 nitrate complex, the binding energy obtained at the B3LYP/TZVP level of theory was underestimated by 1.9 % compared to the value calculated from the M06-2X functional. The accuracy of the DFT-based binding energy value was further compared with the binding energy value calculated at the second-order Møller–Plesset (MP2) level of theory. In this case, the binding energy was underestimated by 11.54 % at the B3LYP level of theory compared to the value obtained at the MP2 level for the 1:1 Sr^{2+} –DCH18C6 complex, whereas the underestimation was only 1.96 % for the Th^{4+} ion complex. The underestimation is reduced in the presence of nitrate anion (9.15 % for Sr^{2+} ion). Overall, the accuracy of the B3LYP-predicted value was found to be quite reasonable with respect to the values predicted at the M06-2X and MP2 levels of theory.

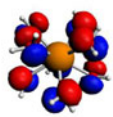
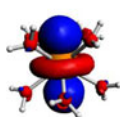
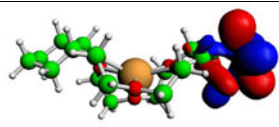
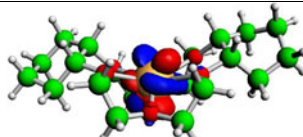
The binding energy was further calculated using the dispersion-corrected B3LYP-D3 functional available in ADF2012. The calculated values for the complexes Sr^{2+} –DCH18C6 and Sr^{2+} –DCH18C6–(NO₃)₂ were found to be –229.02 and –515.54 kcal mol⁻¹, respectively. However, dispersion parameters are only implemented up to Rn in the

Table 2 Binding energies ΔE and free energies of complexation ΔG (in kcal mol⁻¹) of various Th^{4+} and Sr^{2+} complexes with DCH18C6, as calculated at the BP/SV(P) and B3LYP/TZVP levels of theory

Complex	ΔE			ΔG	
	BP/SV(P)	B3LYP/TZVP	M06-2X/TZ2P	BP/SV(P)	B3LYP/TZVP(P)
Sr^{2+} –DCH18C6	–225.92	–211.95 (–239.62)	–219.27	–214.00	–200.03
Th^{4+} –DCH18C6	–818.68	–778.46 (–794.09)	–776.72	–808.42	–768.19
$Sr(NO_3)_2$ –DCH18C6	–582.28	–491.71 (–541.29)	–510.30	–547.00	–456.43
$Th(NO_3)_4$ –DCH18C6	–1782.94	–1668.00	–1707.48	–1715.05	–1600.12
$Th(NO_3)_6$ –(DCH18C6) ₂ (H ₃ O) ₂	–2235.18	–2074.71	–2114.98	–2100.78	–1940.31

Values in parentheses were calculated at the MP2/TZVP level of theory

Fig. 7 Calculated HOMOs and LUMOs of complexes of Th⁴⁺ ion with water and DCH18C6

System	HOMO	LUMO
Th ⁴⁺ -(H ₂ O) ₈		
Th ⁴⁺ -DCH18C6		

ADF2012 version, so calculations of Th⁴⁺-DCH18C6 could not be performed. The binding energies calculated after taking dispersion correction into account are very close to the values calculated without accounting for dispersion.

The free energy of complexation ΔG was also computed using the standard thermodynamical calculation after zero-point energy and thermal correction [47, 48], and the values are presented in Table 2. The free energy of complexation for the Th⁴⁺ ion was found to be 568.116 kcal mol⁻¹ higher than that for the Sr²⁺ ion, indicating that there is selectivity for Th⁴⁺ ion over Sr²⁺ ion, which contradicts the experimentally observed selectivity. A similar contradictory result was observed when selectivity was analyzed using the gas-phase binding energy. Using Tables S1 and S2 in the ESM, the M–O bond distances for Sr²⁺ complexes can be compared to those for Th⁴⁺ complexes. It is apparent that a shorter M–O bond distance implies a higher interaction energy. Also, NBO population analysis indicates that the charge transfer from the metal ion to the ligand is greater in Th⁴⁺ complexes than in Sr²⁺ complexes. In addition, there is a very small electronic contribution from the *f* orbital in Th⁴⁺ ion which is absent in the Sr²⁺ metal ion. The change in the entropy of the complex is negligible for complexation reactions, so electronic energies are the main contributors to the enhanced free energy.

When the metal ion is extracted from the aqueous phase to the organic phase by a neutral ligand, it is accompanied by a co-anion in the organic phase to maintain the neutrality of the system. Therefore, the effect of nitrate anion on the complexation reaction was also considered in the calculation. The binding energy was found to increase for both Sr²⁺ and Th⁴⁺ ion with DCH18C6 when nitrate anion was present (compared to when it was absent). The detailed complexation reaction schemes and the results calculated for the gas phase are presented in the ESM (Section S2).

The binding energies and the free energies of complexation in the gas phase for the bare Sr²⁺ and Th⁴⁺ metal ions in either the absence or the presence of nitrate anion were unable to explain the experimentally observed selectivity for Sr²⁺ ion over Th⁴⁺ ion. During the extraction, the metal ion is transferred from the aqueous phase to the organic phase, so it is useful to consider the hydrated form of the metal ion. Thus, the complexation reaction was modeled using the hydrated cluster of the metal ion. Both Sr²⁺ and Th⁴⁺ were considered to have eight-coordinate first solvation shells. The optimized structures of the hydrated clusters of Sr²⁺ and Th⁴⁺ are displayed in Fig. S1 of the ESM. The calculated Sr–O bond distance (2.65–2.66 Å) and Th–O bond distance (2.48–2.49 Å) were found to be in excellent agreement with the reported experimental results for the Sr–O bond distance (2.60 Å) [49] and Th–O bond distance (2.45–2.49 Å) [50]. The computed binding energy with the hydrated metal ion was found to be much lower than that with the bare metal ion, as shown in Table 3. A similar trend was observed for the free energy of complexation (see Table 3). The detailed reaction scheme and calculated results for the gas phase are also presented in the ESM.

It is interesting to note that, for the bare metal ions, the difference in binding energy between Th⁴⁺ and Sr²⁺ is very high. This difference in binding energy is reduced considerably when hydration is considered. This is due to the higher desolvation energy required for the hydrated Th⁴⁺ ion cluster during transfer from the aqueous phase to the organic phase compared to the hydrated Sr²⁺ ion cluster. When the hydrated metal ion is included, DCH18C6 still shows a preference for Th⁴⁺ ion over Sr²⁺ ion. The gas-phase binding energies and free energies cannot explain the experimental selectivity of DCH18C6 for Sr²⁺ ion over Th⁴⁺ ion. This is due to the lack of consideration of solvent effects in the aqueous and organic

Table 3 Binding energies ΔE and free energies of complexation ΔG (in kcal mol⁻¹) for hydrated metal ion clusters, as calculated at the BP/SV(P) and B3LYP/TZVP levels of theory

Complex (metal–8H ₂ O)	ΔE		ΔG	
	(BP/SV(P))	(B3LYP/TZVP)	(BP/SV(P))	(B3LYP/TZVP)
Sr ²⁺ –DCH18C6	88.76	44.96(–34.96)	9.92	–33.89(–24.11)
Th ⁴⁺ –DCH18C6	57.45	–3.46(–83.88)	–24.61	–85.53(–75.75)
Sr(NO ₃) ₂ –DCH18C6	–267.60	–234.80(–314.71)	–323.08	–290.29(–280.51)
Th(NO ₃) ₄ –DCH18C6	–906.79	–893.01(–972.92)	–931.24	–917.46(–907.68)
Th(NO ₃) ₆ –(DCH18C6) ₂ (H ₃ O) ₂	–1359.03	–1299.71(–1379.63)	–1316.96	–1257.64(–1247.87)

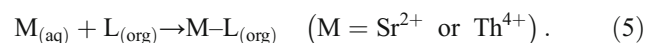
Values in parentheses were calculated using the cluster of water molecules

phases. The metal ions are extracted from the aqueous environment, where they are strongly hydrated. During transfer from the aqueous phase to the organic phase, the metal ion must be dehydrated. Hence, it is essential to compute the solvation energies of the metal ions in the aqueous environment and the ligand and metal ion–ligand complexes in the organic phase if we are to correctly predict selectivity trends by analyzing extraction energies.

Extraction energy and free energy of extraction in the solvent phase Gas-phase calculations could not predict the experimental selectivity for Sr²⁺ ion over Th⁴⁺ ion, so an attempt was made to solve this complex and challenging problem by mimicking the real effects of solvent on the metal ions, the ligand, and the metal ion–ligand complexes through the use of the conductor-like screening model (COSMO) approach. Implicit and explicit solvation models were used to calculate the aqueous solvation energies of the metal ions, which are required to compute the extraction energies and free energies of extraction, ΔG_{ext} .

Extraction energy using the implicit solvation model The extraction energy, ΔE_{ext} , was first evaluated based on the implicit solvation model, where the bare metal ion is directly solvated in the continuum solvent using the COSMO solvation model. The default COSMO radii of Sr, Th, and other atoms available in the Turbomole package were employed.

The solvent-phase complexation reaction for Sr²⁺ and Th⁴⁺ metal ions with the ligand L can be written as



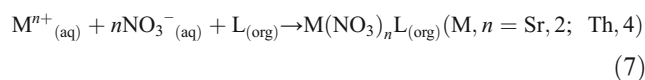
The extraction energy ΔE_{ext} for the above complexation reaction can be expressed as

$$\Delta E_{\text{ext}} = E_{M-L(\text{org})} - (E_{M(\text{aq})} + E_{L(\text{org})}). \quad (6)$$

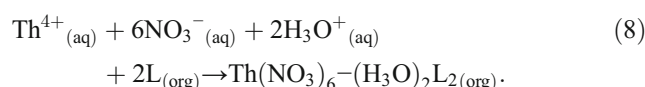
Here, $E_{M-L(\text{org})}$, $E_{L(\text{org})}$, and $E_{M(\text{aq})}$ represent the total energies of the ML complex, the ligand L, and the metal ion M in organic solvent (“org”) and water (“aq”), respectively. The dielectric constants of the organic solvents toluene, xylene, octanol, and nitrobenzene were taken as 2.38, 2.40, 10.30, and 34.90, respectively. The solvation energies of the

Sr²⁺ and Th⁴⁺ ions are presented in Table S3. The difference in free energy of solvation between bare Th⁴⁺ and Sr²⁺ ions was found to be 878.09 kcal mol⁻¹, which decreases to 135.61 kcal mol⁻¹ for the hydrated metal ions. The calculated extraction energies for solvated bare Sr²⁺ and Th⁴⁺ ions without nitrate anion are presented in Table S4 of the ESM. Consideration of the solvent effect leads to interesting results. The value of ΔE_{ext} was found to be lowest in solvents with low dielectric constants such as toluene, and highest in those with high dielectric constants such as nitrobenzene, for both Sr²⁺ and Th⁴⁺ ions. ΔE_{ext} was found to be positive in low dielectric constant solvents such as toluene and xylene but negative in moderate to high dielectric constant solvents such as octanol ($\epsilon = 10.3$) and nitrobenzene ($\epsilon = 34.81$), for both Sr²⁺ and Th⁴⁺ ions.

However, since the metal ion is extracted from nitric acid, it is desirable to consider the nitrate anion in electronic structure calculations for the following 1:1 stoichiometric complexation reaction:



and in calculations for the 1:2 reaction:



The extraction energy ΔE_{ext} for the above 1:1 complexation reaction (Eq. 7) can be expressed as

$$\Delta E_{\text{ext}(Mn+)} = E_{M(\text{NO}_3)_n L_{(\text{org})}} - (E_{Mn+(\text{aq})} + nE_{\text{NO}_3^{-}(\text{aq})} + E_{L(\text{org})}), \quad (9)$$

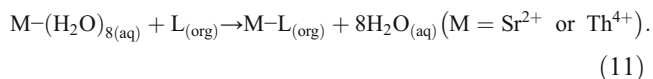
and that for the 1:2 complexation reaction can be expressed as

$$\Delta E_{\text{ext}(\text{Th}4+)} = E_{\text{Th}(\text{NO}_3)_6 - (\text{H}_3\text{O})_2 L_2_{(\text{org})}} - (E_{\text{Th}4+(\text{aq})} + 6E_{\text{NO}_3^{-}(\text{aq})} + 2E_{\text{H}_3\text{O}^+(\text{aq})} + 2E_{L(\text{org})}). \quad (10)$$

The calculated values of ΔE_{ext} for Sr²⁺ and Th⁴⁺ ions with both 1:1 and 1:2 complexation reactions are presented in Table S4. The calculated value of ΔE_{ext} was found to be

negative in all of the organic solvents considered here for both Sr^{2+} and Th^{4+} ions, but the value for the Th^{4+} ion was found to be higher than that for the Sr^{2+} ion, indicating a preference for the Th^{4+} ion over the Sr^{2+} ion, which contradicts the experimental findings. The value of ΔE_{ext} was found to be 38.92–40.8 % higher with 1:2 complexation compared to that with 1:1 complexation. Modeling the complexation reaction using solvated bare metal ions does not yield accurate results, as it does not consider the polarization of the first solvation shell of water molecules.

Extraction energy using the explicit solvation model Bare metal ion solvation in the presence of nitrate anion failed to predict the correct (i.e., experimentally observed) selectivity of DCH18C6 for Sr^{2+} ion over Th^{4+} ion. Hence, an attempt was made to compute the extraction energy ΔE_{ext} while accounting for the explicit solvation of the metal ion by retaining eight water units in the first solvation shell (like gas phase), as per the following complexation reaction:



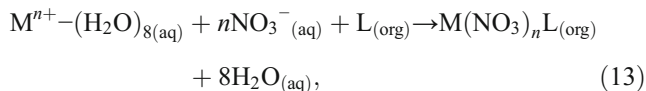
The extraction energy ΔE_{ext} for the above complexation reaction can be expressed as

$$\Delta E_{\text{ext}} = (E_{\text{M}-\text{L}_{(\text{org})}} + 8E_{\text{H}_2\text{O}_{(\text{aq})}}) - (E_{\text{M}-(\text{H}_2\text{O})_{8(\text{aq})}} + E_{\text{L}_{(\text{org})}}). \quad (12)$$

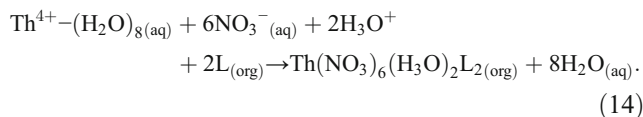
The resulting computed values of ΔE_{ext} are presented in Table 4. It should be noted that the value of ΔE_{ext} is positive for both Sr^{2+} and Th^{4+} ions in all of the organic solvents studied here, which is inconsistent with the experimental results. It is interesting to note that the gas-phase binding energy ΔE_{gas} was higher for the Th^{4+} ion than for the Sr^{2+} ion, but, in the presence of aqueous and organic solvents, this trend is reversed, so that the experimentally observed selectivity is obtained (the values are positive, but they are less positive for the Sr^{2+} ion than the Th^{4+} ion). This selectivity behavior has also been reported for other metal ion systems such as $\text{Am}^{3+}/\text{Eu}^{3+}$

with cyanex301 [38]. The presence of solvent considerably weakens the gas-phase metal–ligand interaction.

Next, ΔE_{ext} was computed in the presence of nitrate anion for the following 1:1 extraction reaction:



and for the 1:2 reaction



The extraction energy ΔE_{ext} for the above 1:1 complexation reaction (Eq. 13) can be expressed as

$$\Delta E_{\text{ext}(\text{Mn}^+)} = (E_{\text{M}(\text{NO}_3)_n\text{L}_{(\text{org})}} + 8E_{\text{H}_2\text{O}_{(\text{aq})}}) - (E_{\text{Mn}^+-(\text{H}_2\text{O})_{8(\text{aq})}} + nE_{\text{NO}_3^-(\text{aq})} + E_{\text{L}_{(\text{org})}}), \quad (15)$$

and that for the 1:2 complexation reaction can be written as

$$\Delta E_{\text{ext}(\text{Th}^{4+})} = (E_{\text{Th}(\text{NO}_3)_6(\text{H}_3\text{O})_2\text{L}_2(\text{org})} + 8E_{\text{H}_2\text{O}_{(\text{aq})}}) - (E_{\text{Th}^{4+}-(\text{H}_2\text{O})_{8(\text{aq})}} + 6E_{\text{NO}_3^-(\text{aq})} + 2\text{H}_3\text{O}^+ + 2E_{\text{L}_{(\text{org})}}). \quad (16)$$

The computed values of ΔE_{ext} are presented in Table S5 of the ESM, and these were found to be negative for both the Sr^{2+} and Th^{4+} ions with DCH18C6 in all of the organic solvents considered here. Note that the values were positive in the absence of nitrate anion. The values of ΔE_{ext} were found to be higher for Th^{4+} ion than for Sr^{2+} ion in all of the organic solvents. The values of ΔE_{ext} were found to be even higher for 1:2 complexation reactions than for 1:1 reactions. When the hydrated metal ions and nitrate anion in the aqueous environment as well as the ligand and metal–ligand complexes in the organic solvents were all considered, it was still found that DCH18C6 prefers Th^{4+} ion over Sr^{2+} ion, in contrast to the experimental findings. It appears that the extraction energy calculated based purely on the electronic energy is not sufficient to accurately predict the selectivity of the ligand for the metal

Table 4 Extraction energies ΔE_{ext} (in kcal mol^{-1}), calculated using the explicit COSMO model at the B3LYP/TZVP level of theory in different organic solvents

Complex	Toluene	Xylene	Octanol	Nitrobenzene
Sr^{2+} -DCH18C6	86.17(53.08)	82.04(48.95)	37.18(4.10)	24.80(-8.27)
Th^{4+} -DCH18C6	336.92(303.84)	319.27(286.18)	125.58(92.50)	71.38(38.30)
$\text{Sr}(\text{NO}_3)_2$ -DCH18C6	-3.07(-36.14)	-3.56(-36.64)	-9.35(-42.42)	-11.09(-44.16)
$\text{Th}(\text{NO}_3)_4$ -DCH18C6	-29.87(-62.94)	-30.50(-63.57)	-37.82(-70.89)	-40.02(-73.09)
$\text{Th}(\text{NO}_3)_6$ -(DCH18C6) $_2$ (H $_3$ O) $_2$	-125.26(-158.33)	-125.86(-158.94)	-132.84(-165.91)	-134.93(-168.01)

Values in parentheses were calculated using the cluster of water molecules

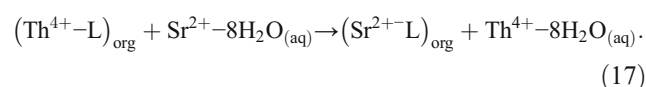
ions. Thermodynamic parameters such as the free energy for this complexation/extraction reaction must therefore be taken into account too. Hence, we then attempted to compute the free energies of extraction ΔG_{ext} for the above complexation reactions in aqueous and organic solvent phases.

Free energy of extraction and selectivity The free energies of extraction for the various complexation reactions described above were calculated using the standard thermodynamic approach [47, 48]. The free energies of extraction (or, actually, the free energies of complexation, as no solvent is involved) for the different complexation reactions in the gas phase are discussed in the ESM (Section S3). The gas-phase binding energies and free energies could not explain the experimental selectivity of DCH18C6 for Sr^{2+} ion over Th^{4+} ion. This is due to a lack of consideration of the effects of the solvent in the aqueous and organic phases. The metal ions are extracted from an aqueous environment, where they are strongly hydrated. During its transfer from the aqueous phase to the organic phase, the metal ion must be dehydrated. Hence, it is essential to compute the solvation energies of the metal ions in the aqueous environment if we are to accurately predict extraction energies. In order to predict the correct selectivity, calculations were also performed for the ions in the solvent phase, using the COSMO solvation approach. First, calculations were performed for each solvated bare metal ion by directly submerging the metal ion in the dielectric continuum of the solvent (implicit solvation). The calculated values of ΔG_{ext} for the bare solvated metal ions in the absence of nitrate anion for the reaction of Eq. 5 are presented in Table S5. The value of ΔG_{ext} was found to be positive for both the Sr^{2+} and Th^{4+} ions with DCH18C6 in toluene and xylene, and negative in octanol and nitrobenzene. From the calculated values of ΔG_{ext} , it is clear that Th^{4+} ion is preferentially extracted over Sr^{2+} ion by DCH18C6, which contrasts with the experimentally observed selectivity. Then, the ΔG_{ext} values were calculated in the presence of nitrate anion for the complexation reactions of Eqs. 7–9, and these values are presented in Table S5. The calculated values of ΔG_{ext} were found to be negative for both the Sr^{2+} and Th^{4+} ions with DCH18C6 in all of the organic solvents. From the calculated values of ΔG_{ext} , it is apparent that Th^{4+} ion is preferentially extracted over Sr^{2+}

ion by DCH18C6, which is again not in agreement with the experimentally observed selectivity. The preferential selectivity of DCH18C6 for Th^{4+} ion over Sr^{2+} ion was found to increase when the 1:2 stoichiometric complexation reaction for Th^{4+} ion was considered.

In view of the failure of the implicit solvation model to predict the correct selectivity, ΔG_{ext} values were computed using the explicit solvation model for the metal ions in the absence of nitrate ion using the model reaction of Eq. 11. These calculated values are presented in Table 5. The calculated values of ΔG_{ext} were found to be positive for both Sr^{2+} and Th^{4+} ions in toluene and xylene but negative for Sr^{2+} ion in octanol and nitrobenzene. In the case of the Th^{4+} ion, the value of ΔG_{ext} was only found to be negative in nitrobenzene. Interestingly, the preferential selection of Sr^{2+} ion over Th^{4+} ion—as observed in the solvent extraction experiment—is observed when explicit solvation is applied. These calculations were further extended by incorporating the nitrate anion when using the 1:1 and 1:2 stoichiometric complexation reactions of Eqs. 13–15. The resulting calculated values of ΔG_{ext} are presented in Table 5 and Fig. S2. From the values of ΔG_{ext} , it is clear that DCH18C6 preferentially binds Sr^{2+} ion over Th^{4+} ion in all of the organic solvents considered here. The calculated value of ΔG_{ext} for the 1:2 stoichiometric complexation reaction was found to be 44 % higher than that for the 1:1 complexation reaction in nitrobenzene.

The preferential extraction of the metal ions (and hence the selectivity of the ligand for the ions) can also be predicted by calculating the difference in extraction energy between the two metal ions, $\Delta\Delta E_{\text{ext}}$ ($\Delta\Delta E_{\text{ext}} = \Delta E_{\text{ext}}(\text{Sr}^{2+}) - \Delta E_{\text{ext}}(\text{Th}^{4+})$), in the solvent phase, employing metal ions that are hydrated up to the first solvation shell and considering the following ion exchange reaction:



The calculated values of $\Delta\Delta E_{\text{ext}}$ are presented in Table 6. It is interesting to note that $\Delta\Delta E_{\text{ext}}$ is positive for all of the organic solvents, with the highest value obtained in the low-dielectric solvent toluene and the lowest value in the

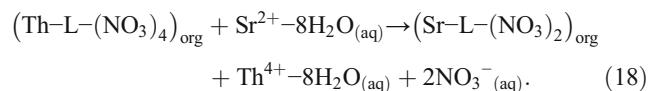
Table 5 ΔG_{ext} values (kcal mol⁻¹) obtained using the explicit COSMO model at the B3LYP/TZVP level of theory in different organic solvents

Complex	Toluene	Xylene	Octanol	Nitrobenzene
Sr^{2+} -DCH18C6	7.32(63.93)	3.19(59.80)	-41.66(14.95)	-54.04(2.57)
Th^{4+} -DCH18C6	254.85(311.46)	237.20(293.81)	43.51(100.12)	-10.69(45.92)
$\text{Sr}(\text{NO}_3)_2$ -DCH18C6	-58.55(-1.93)	-59.05(-2.43)	-64.84(-8.22)	-66.58(-9.96)
$\text{Th}(\text{NO}_3)_4$ -DCH18C6	-54.32(2.29)	-54.95(1.66)	-62.27(-5.65)	-64.47(-7.85)
$\text{Th}(\text{NO}_3)_6$ -(DCH18C6) ₂ (H ₃ O) ₂	-83.19(-26.57)	-83.79(-27.17)	-90.77(-34.15)	-92.86(-36.24)

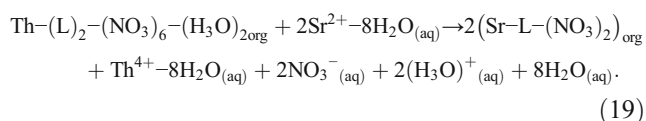
Values in parentheses were calculated using the cluster of water molecules

high-dielectric solvent nitrobenzene. These results are not consistent with the corresponding experimental findings.

The same ion exchange reaction performed in the presence of nitrate anion can be written as



In this case, the values of $\Delta\Delta E_{\text{ext}}$ are found to be positive (Table 6), reflecting the selectivity observed in the experiment. Also, the ion exchange reaction for 1:2 stoichiometric reactions can be written as



The corresponding values of $\Delta\Delta E_{\text{ext}}$ are found to be more positive than those for the 1:1 stoichiometric reaction (Table 6). A detailed discussion of the use of the solvated bare metal ion is presented in the ESM (Section S4).

The analysis of $\Delta\Delta E_{\text{ext}}$ did not produce consistent and accurate selectivity data that could explain the experimental selectivity. In view of these contrasting results, a thermodynamic analysis was performed in an attempt to obtain a consistent and correct selectivity trend for the above ion exchange reaction in the solvent phase. The calculated values of $\Delta\Delta G_{\text{ext}}$ ($\Delta\Delta G_{\text{ext}} = \Delta G_{\text{ext}(\text{Sr}^{2+})} - \Delta G_{\text{ext}(\text{Th}^{4+})}$) for all possible types of ion exchange reaction are presented in Table 6. The computed values of the free energy of extraction $\Delta\Delta G_{\text{ext}}$ for 1:1 complexation reactions are unable to explain the trend seen in the experimental selectivity data. The calculated values of $\Delta\Delta G_{\text{ext}}$ for 1:2 complexation reactions are also presented in Table 6 and Fig. S3. These calculated values of $\Delta\Delta G_{\text{ext}}$ are consistent with the observed experimental results showing the preferential selection of Sr^{2+} ion over Th^{4+} ion with increasing dielectric constant of the solvent.

So far, we have assumed that the first solvation shell of Th^{4+} ion contains eight water units in the calculation of the free energy of extraction. However, some reports [51, 52] suggest that the first solvation shell of the Th^{4+} ion contains nine or ten water units. The optimized hydrated structures of

Th^{4+} ion with $N=9$ and 10 water molecules are presented in Fig. S1 of the ESM. The calculated values of the free energy of hydration ΔG_{hyd} for Th^{4+} ion with CN = 8, 9, and 10 are also presented in Table S3 of the ESM. From this table, it is apparent that the free energy of hydration is highest for CN = 8 and lowest for CN = 10 when n separate monomer water units are considered. With respect to the free energy of hydration, the Th^{4+} ion with eight water molecules in its first solvation shell was found to be the most stable hydrated complex. Different numbers of water molecules in the first solvation shell of the metal ion lead to different hydration energies. Hence, the free energies of extraction for the above ion exchange reactions (Eqs. 17–19) with CN = 9 and 10 were calculated, and the resulting values are presented in Table 7. The table shows that the calculated values of $\Delta\Delta G_{\text{ext}}$ are lower when CN = 9 and 10 than when CN = 8 for both 1:1 and 1:2 stoichiometric complexation reactions with or without nitrate anion. This is expected, as more complexation energy is required to dehydrate more heavily solvated Th^{4+} ions.

Another point to mention here is that the binding/free energies were calculated using Eqs. 11, 13, 14, and 19 by considering the energy of monomeric water units. However, the released water molecules may form clusters during the complexation reaction of the metal ion with the ligand due to strong hydrogen bonding among the water molecules. In view of this, calculations were performed using the energy of a water cluster [53]. The resulting values of binding/free energy are presented in Tables 3, 4, and 5. From Table 3, it is clear that the gas-phase binding energy becomes more negative upon cluster formation via hydrogen bonding, whereas the free energy of the complexation reaction becomes less exothermic, as the favorable positive entropy becomes less positive upon cluster formation from monomeric water units. The same trend was observed in the calculated extraction energies ΔE_{ext} in different organic solvents, as given in Table 4. The free energy of extraction ΔG_{ext} was also calculated using the cluster approach, and the corresponding values are presented in Table 5. The value of ΔG_{ext} was found to decrease upon applying the cluster approach. The value of ΔG_{ext} even became positive for the metal–ligand complexation reaction in the absence of nitrate anion. Since the value of ΔG_{ext} changes, the value of $\Delta\Delta G_{\text{ext}}$ does too. When the first solvation shells

Table 6 $\Delta\Delta E_{\text{ext}}$ and $\Delta\Delta G_{\text{ext}}$ in kcal mol⁻¹ at B3LYP/TZVP level of theory in different organic solvents using different stoichiometric complexation reactions

Reaction	$\Delta\Delta E_{\text{ext}}$				$\Delta\Delta G_{\text{ext}}$			
	Toluene	Xylene	Octanol	Nitrobenzene	Toluene	Xylene	Octanol	Nitrobenzene
Eq. 17	-250.75	-237.23	-88.40	-46.58	-247.53	-234.01	-85.17	-43.35
Eq. 18	26.81	26.94	28.47	28.93	-4.23	-4.10	-2.57	-2.11
Eq. 19	119.13	118.74	114.14	112.75	-33.92	-34.31	-38.91	-40.30

Table 7 $\Delta\Delta G_{\text{ext}}$ values (kcal mol⁻¹) obtained at the B3LYP/TZVP level of theory in different organic solvents for 1:1 and 1:2 (M:L) stoichiometric complexation reactions in which the first solvation shells varied in coordination number (with or without nitrate anion)

CN	Reaction	Toluene	Xylene	Octanol	Nitrobenzene
8w	Eq. 17	-247.53	-234.01	-85.17	-43.35
	Eq. 18	-4.23	-4.10	-2.57	-2.11
	Eq. 19	-33.92(22.69)	-34.31(22.30)	-38.91(17.70)	-40.30(16.31)
9W	Eq. 17	-241.29	-227.77	-78.94	-37.12
	Eq. 18	2.00	2.13	3.67	4.12
	Eq. 19	-27.68	-28.08	-32.68	-34.06
10W	Eq. 17	-234.21(-246.75)	-220.69(-233.23)	-71.86(-84.39)	-30.04(-42.57)
	Eq. 18	9.08(-3.45)	9.21(-3.32)	10.75(-1.79)	11.20(-1.33)
	Eq. 19	-20.60(20.43)	-20.99(20.04)	-25.60(15.44)	-26.98(14.05)

Values in parentheses were calculated using the water cluster formed from the water molecules released during metal ion–ligand complexation

of both Sr²⁺ and Th⁴⁺ ions are taken to contain eight water units, the value of $\Delta\Delta G_{\text{ext}}$ remains the same whether monomeric water units or clusters of water molecules are considered in the presence or absence of nitrate anion for 1:1 stoichiometric complexation reactions (Eqs. 17 and 18), as seen in Table 7. However, as discussed earlier, the 1:1 stoichiometric reaction model failed to predict the correct selectivity trend with respect to solvent dielectric constant. Therefore, the cluster approach was applied in calculations performed for the 1:2 stoichiometric complexation reaction (Eq. 19). The value of $\Delta\Delta G_{\text{ext}}$ was found to be positive, whereas it was found to be negative when monomeric water units were assumed (see Table 7). Next, $\Delta\Delta G_{\text{ext}}$ values were calculated by considering the first solvation shell of Sr²⁺ to contain eight and that of the Th⁴⁺ ion to contain ten water units for both 1:1 and 1:2 stoichiometric complexation in the absence or presence of nitrate anion. The calculated value of $\Delta\Delta G_{\text{ext}}$ gained using the cluster approach (Eq. 17) for 1:1 stoichiometric complexation without nitrate anion was found to be more negative than that obtained when monomeric water was assumed, but the trend in selectivity was found to be the reverse of that observed in the experiment. Next, $\Delta\Delta G_{\text{ext}}$ was evaluated using the cluster approach (Eq. 18) for 1:1 stoichiometric complexation with nitrate anion, and the calculated value of $\Delta\Delta G_{\text{ext}}$ was found to be negative (it was positive when monomeric water was assumed), and the trend in selectivity was again found to be the reverse of that observed in the experiment. Finally, $\Delta\Delta G_{\text{ext}}$ was also calculated for 1:2 stoichiometric complexation (Eq. 19) where the first solvation shell of Sr²⁺ was assumed to contain eight and that of Th⁴⁺ to contain ten water units. The corresponding calculated values of $\Delta\Delta G_{\text{ext}}$ are presented in Table 7. The calculated values of $\Delta\Delta G_{\text{ext}}$ were found to be positive when the cluster approach was applied, whereas they were negative when monomeric water was assumed, leading to the correct trend in selectivity with respect to solvent dielectric constant.

The hydration of the metal ion can be modeled as the successive addition of water molecules up to a full first solvation shell, or the metal ion can be modeled as being encapsulated by a cluster of water units with first solvation shell water molecules, as reported earlier by Dolg et al. [53]. When monomeric water units are assumed, the effect of hydrogen bonding is neglected, leading to a higher hydration energy than that obtained when a cluster of water units is assumed. However, the free energy of hydration is higher with the cluster of water units than with the monomeric water units, due to the smaller negative entropy contribution in the former than the latter model (see Table S3 in the ESM) [54]. We also calculated the effect of the presence of a water cluster during metal ion hydration in the complexation reaction on the free energy of extraction ΔG_{ext} and the difference in free energy between two metal ions $\Delta\Delta G_{\text{ext}}$. The values of ΔG_{ext} and $\Delta\Delta G_{\text{ext}}$ calculated using a thermodynamic cycle by adopting the cluster model of Dolg et al. [53] are presented and discussed in the ESM. The calculated value of $\Delta\Delta G_{\text{ext}}$ was found to increase with increasing dielectric constant, as observed in the solvent extraction experiment, but the negative free energy $\Delta\Delta G$ observed for low dielectric constant solvents such as toluene and xylene was not predicted, which contradicts the experimentally observed selectivity for Sr²⁺ ion over Th⁴⁺ ion. On the other hand, the monomeric water approach yields results that are consistent with the experimental findings.

Conclusions

A DFT methodology was successfully adopted to model the solvent extraction mechanism for Sr²⁺ and Th⁴⁺ ions by calculating various molecular structures, interaction energies, and free energies. The DFT results confirmed the experimentally observed selectivity of the ligand DCH18C6 for Sr²⁺ ion

over Th^{4+} ion during liquid–liquid extraction in nitric acid medium with nitrobenzene as the diluent. The gas- and solvent-phase extraction energies failed to predict the experimentally observed preferential selectivity for Sr^{2+} ion over Th^{4+} ion, as reflected in the value of $\Delta\Delta E_{\text{ext}}$, whether or not the presence of nitrate anion was included, and whether the metal ion was bare or hydrated. The extraction energy calculated based purely on the electronic energy did not predict the correct metal ion selectivity. The gas- and solvent-phase free energies of extraction $\Delta\Delta G_{\text{ext}}$ calculated with or without the inclusion of nitrate anion and with a bare or hydrated metal ion also failed to predict the experimentally observed selectivity for Sr^{2+} ion over Th^{4+} ion when 1:1 complexation reactions were considered. The correct experimental selectivity was, however, replicated when the 1:2 complexation reaction was considered for the Th^{4+} ion. The calculated values of $\Delta\Delta G_{\text{ext}}$ accurately reflected the experimentally observed trend in selectivity for Sr^{2+} ion over Th^{4+} ion when a wide range of organic solvents with different dielectric constants were considered. These results obtained through quantum chemical DFT computations should aid in the design and screening of ligand/solvent (diluent) systems for any metal ion, and should therefore reduce experimental costs and time burdens on experimentalists.

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