A comparative study on the coordination of diglycolamide isomers with Nd(III): extraction, third phase formation, structure, and computational studies†

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A novel asymmetric diglycolamide N,N-dimethyl-N',N'-dioctyl diglycolamide (LII) was synthesized. The Nd(III) extraction behavior from HNO₃ and loading capability of the solution of LII in 4D/60 (v/v)% n-octanol/kerosene were studied. Analyses by the slope method, ESI-MS, and FT-IR indicated that, similar to the previously studied isomer ligand N,N'-dimethyl-N,N'-dioctyl diglycolamide (LI), 1 : 3 Nd(III)/LII complexes formed. Under the same experimental conditions, the distribution ratio and limiting organic concentration of LII towards Nd(III) were smaller than those of LI, but the critical aqueous concentration of LII was larger, which implies that LII exhibited poorer extraction and loading capabilities towards Nd(III) than LI, and LII has a tendency to be less likely to form the third phase. The quasi-relativistic density functional theory (DFT) calculation was performed to provide some explanations for the differences in their extraction behaviors. The electrostatic potential of the ligands indicated that the electron-donating ability of the amide O atoms in LII displayed certain differences compared with LI. This inhomogeneity in LII affected the interaction between LII and Nd(III), as supported by QTAIM and bonding nature analysis, and it seemed to reflect in the extraction performance towards Nd(III).

Introduction

In order to meet the growing demand for energy and combat climate change, many countries have put forward the strategy of developing nuclear power. However, the treatment and disposal of radioactive waste, especially high-level liquid waste (HLLW) generated from spent fuel reprocessing, has always been a challenging and controversial issue associated with the sustainable use of nuclear fuels. Minor actinides (MAs) and long-lived radionuclides are separated from HLLW and then incinerated into short-lived nuclides in nuclear reactors or accelerators, and this process is called partitioning & transmutation (P&T).

Thus, the radiotoxicity and volume of HLLW can be decreased significantly. In the past few decades, diglycolamides (DGAs, Fig. 1) have been identified as one of the most up-and-coming extractants in the field of HLLW separation due to their strong affinity towards actinides (An) and lanthanides (Ln), which results in tridentate chelates with CHON compositions that are benign to the environment.²

DGAs can be divided into two categories, namely symmetric DGAs (R₁ = R₂ = R₃ = R₄) and asymmetric DGAs (structure A: R₁ = R₂, R₃ = R₄ or structure B: R₁ = R₂, R₃ = R₄) on the basis of the alkyl substituent attached to the N atom of amide, N,N,N',N'-Tetraoctyl diglycolamide (TODGA)³⁻⁵ and N,N,N',N'-tetra(2-ethylhexyl) diglycolamide (TEHDGA) are the most extensively studied DGAs and have been applied in several HLLW separation processes.⁶⁻⁷ However, they suffer the problem of third phase formation in the extraction process. Although adding phase modifiers, such as tributyl phosphate (TBP), N,N-diethyl

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† Electronic supplementary information (ESI) available: Characterization data of LII by ¹H NMR, ¹³C NMR and FT-IR; effect of NO₃⁻ and H⁺ concentration on Dₒₒ; effect of temperature on the K; LOC of Nd(III) as a function of aqueous phase acidity and ligand concentration; stripping behavior; Mulliken charge population analysis; average Nd-O bond lengths of complexes. See DOI: 10.1039/d1ra04222j

Fig. 1 The structure of DGA (R₁–R₄ are alkyl groups).
octyl amide (DHOA), and n-octanol, can increase the metal loading capacity of the extractant, this adjustment complicates the solvents and causes more fission products like Zr\textsuperscript{IV} and Mo\textsuperscript{VI} to proceed to the organic phase.\textsuperscript{8} It was found that some asymmetric DGAs, such as \(N_2N\text{-di(2-ethylhexyl)\text{-}}N',N'\text{-dioctyl diglycolamide}\) and \(N_2N\text{-didecyl\text{-}}N',N'\text{-dioctyl diglycolamide}\),\textsuperscript{9,10} improved the performance to a certain extent by inhibiting third phase formation, as well as extraction performance, and selectivity for An\textsuperscript{III} and Ln\textsuperscript{III}. For example, \(N_2N\text{-didecyl\text{-}}N',N'\text{-dioctyl diglycolamide}\) displayed the advantages of a high distribution ratio of Nd\textsuperscript{III} and no third phase formation with Nd\textsuperscript{III} even at the initial concentration of 600 mM in 3 to 4 M nitric acid medium.\textsuperscript{11} \(N_2N\text{-Dihexyl\text{-}}N',N'\text{-didecyl diglycolamide}\) could separate Ln\textsuperscript{III} from Fe\textsuperscript{III}, Ni\textsuperscript{II}, Co\textsuperscript{II} and Cs\textsuperscript{I} effectively.\textsuperscript{32} \(N_2N\text{-Dimethyl\text{-}}N',N'\text{-dioctyl diglycolamide}\) exhibited the high LOC (the limiting organic concentration) and CAC (the critical aqueous concentration) of Nd\textsuperscript{III} in nitric acid and considerably good extraction ability towards actinide and lanthanide ions with various oxidation states, such as Nd\textsuperscript{III}, Pu\textsuperscript{IV}, Np\textsuperscript{V}, and U\textsuperscript{VI}.\textsuperscript{13-17} These asymmetric DGAs are supposedly superior ligands for the separation of An\textsuperscript{III}/Ln\textsuperscript{III} from HLLW.

Although asymmetric DGAs have obtained extensive attention, most studies have focused on one type of asymmetric DGAs, either the A or B structure, while a few studies involve the comparison of the two types of asymmetric DGAs in terms of the loading capacity of acid and metal ions, and extraction behaviors, as well as separation performances. The two types of asymmetric DGAs differ in many characteristics, such as electron donor ability, space steric hindrance and coordination ability, which probably affect the interaction strength between metal ions and the ligands. Both theoretical and experimental studies on DGA-type or DAPhen-type soft ligands have shown that the subtle steric and electronic charge variations markedly affect the structure–activity relationship of the ligands,\textsuperscript{18-20} which is ultimately reflected in the metal-ion extraction performance. In this study, neodymium, a typical member of the lanthanide series, was selected as the target element because, on the one hand, high-level radioactive waste contains a large proportion of lanthanides (~45%), and on the other hand, it has often been used as the research object in the formation of the third phase.\textsuperscript{22} Two types of DGAs (Fig. 2), \(N_2N\text{-dimethyl\text{-}}N',N'\text{-dioctyl diglycolamide}\) (L\textsuperscript{I}) and \(N_2N\text{-dimethyl\text{-}}N',N'\text{-dioctyl diglycolamide}\) (L\textsuperscript{II}), were used as the extractants, and the differences in their extraction performance, extraction thermodynamics, and loading capabilities towards Nd\textsuperscript{III} were investigated through extraction experiments, in conjunction with the scalar-relativistic theoretical method.

### Experimental methods

#### Materials

Diglycolic anhydride (98%), diocytamine (95%), dimethylamine in tetrahydrofuran (THF) (2 M), isobutyl chloroformate (IBCF, 98%), 4-methylmorpholine (NMM, 98%), neodymium nitrate hexahydrate (99.9%) were supplied by Aladdin Industrial Corporation. The other chemicals (analytical grade) were supplied by Sinopharm Reagent Co., Ltd.

#### Synthesis

The ligand L\textsuperscript{I} was synthesized by two-step method.\textsuperscript{21} The ligand L\textsuperscript{II} was synthesized by a mixed anhydride method.\textsuperscript{24} The synthetic route of L\textsuperscript{II} is depicted in Fig. 3. A brief description of the synthesis steps is given below:

Diglycolic anhydride (3, DODGAA) was first synthesized by the reaction between diglycolic anhydride (1) and dialkyldimethylamine (2).\textsuperscript{9} A mixture of 0.03 mol DODGAA dissolved in 150 mL THF and 0.03 mol N-methylmorpholine was stirred in an ice brine bath. When the temperature dropped to ~10 °C, a mixture of 3.8 mL (0.03 mol) isobutyl chloroformate and THF (volume ratio 1 : 1) was slowly added. Then, 15 mL dimethylamine in THF (4, 2 M) was added dropwise at ~2 °C. Excess THF was evaporated under reduced pressure. After washing, filtering, rotary evaporation and separation on a silica gel column, the target product L\textsuperscript{II} ligand (5) was obtained with a yield of 80%. Characterization data from \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and FT-IR spectroscopy are presented in the ESI.\textsuperscript{†}

#### Solvent extraction and third phase formation

The aqueous solution containing Nd\textsuperscript{III} and the organic phase were mixed in equal volumes for 30 min at 25 ± 0.2 °C (s100 oscillator, Dianshan Lake Instrument Company, Kunshan, Jiangsu, China). The equilibrium time experiments demonstrated that 30 min was enough for the two phases to reach equilibrium. The two phases were then separated by centrifugation (LG16B high-speed centrifuge, Leiboer Medical Devices Co., Ltd., Beijing, China) at 2500 rpm for 10 min. The Nd\textsuperscript{III} concentration in the raffinate was assayed by inductively coupled plasma mass spectroscopy (X-H ICP-MS, Thermo Fisher Scientific, Waltham, MA, USA). The Nd\textsuperscript{III} concentration in the organic phase was determined by subtracting the Nd\textsuperscript{III} concentration in the raffinate from the Nd\textsuperscript{III} concentration in the aqueous solution.

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**Fig. 2** The structures of the isomeric extractants studied in this paper.
concentration in the raffinate from the initial aqueous Nd(III) concentration.

The distribution ratio, $D_{Nd}$, was derived from:

$$D_{Nd} = \frac{C_o}{C_a} = \frac{C - C_a}{C_a}$$

1. The IR spectra of the extracted species were recorded on a Fourier Transform Infrared Spectrometer (Spectrum 100 FT-IR, Perkin Elmer, Waltham, MA, USA), and the detailed procedure has been described in a previous study.  

**ESI-MS methods**

Mass spectrometric measurements were recorded in the positive-ion mode using a Bruker microOTOF Q II (Bruker Daltonics, Bremen, Germany), and an electrospray interface was used as the ionization source. The solutions for ESI-MS measurements were prepared by adding a certain volume of the metal stock solution ($2 \times 10^{-2}$ M) to 5 mL of the ligand solution ($5 \times 10^{-4}$ M), and the ESI-MS spectra were obtained in the presence of excess extractant.

**Infrared spectroscopy**

The IR spectra of the extracted species were recorded on a Fourier Transform Infrared Spectrometer (Spectrum 100 FT-IR, Perkin Elmer, Waltham, MA, USA), and the detailed procedure has been described in a previous study.  

**Theoretical calculations**

The Gaussian 16 program package was used for structural optimization by DFT. The three-parameter hybrid functional common formulation, B3LYP, which has been demonstrated to produce reliable structural results for actinide and lanthanide complexes, was employed. The 28 electron core pseudopotentials (ECPs) and the corresponding ECP28MWB-SEG valence basis sets were applied for Nd, and the polarized 6-311G(d) basis set was used for the lighter atoms (H, C, N, and O).

All the geometrical parameters were optimized at the B3LYP/6-311G(d)/RECP level of theory in the gas phase. M052X/6-31G(d)/RECP was chosen for the thermodynamics analysis based on the optimized molecular geometries to gain more accurate energies. Solvation effects were evaluated by the Solvation Model Based on Density (SMD) with the custom SMD mixing solvent parameters.

The electrostatic potentials (ESP) and Mulliken charge population analysis of the two ligands were investigated. In order to understand the metal–ligand bonding properties, the Mayer bond order (MBO) was calculated at the same theory level, and the quantum theory of atoms in molecules (QTAIM) parameters were explored at the bond critical points (BCPs) using the Multiwfn software version 3.7.

**Results and discussion**

**Solvent extraction**

**Effect of nitric acid concentration.** Fig. 4 illustrates the trend of $D_{Nd}$ at the concentrations of 0.5 M to 6.0 M HNO₃, and the results show that $D_{Nd}$ first increased and then decreased slightly and that the maximum values of $D_{Nd}$ appear at about 3.0 M HNO₃. The upward trend of the distribution ratio can be explained by the mass action law and the salting-out effect of NO₃⁻ with increasing HNO₃ concentration. The competitive effect of H⁺ suppresses the extraction of Nd(III). The effects of nitrate concentration and H⁺ concentration on $D_{Nd}$ are shown in Fig. S1 and S2.†

**Effect of ligand concentration.** The ligands L¹ and L² are neutral extractants, and the equation for the extraction of Nd(III) by L² can be expressed as:
The extraction equilibrium constant $K$ can be expressed as:

$$K = \frac{[\text{Nd(NO}_3\text{)}_3 \cdot n\text{L}^\text{II}]}{[\text{Nd}^{3+}]_{\text{aq}} [\text{NO}_3^-]_{\text{aq}}^3}$$

The subscripts ‘aq’ and ‘o’ represent the aqueous phase and the organic phase, respectively. $[\text{L}^\text{I}]_{\text{org}}$ and $[\text{Nd(NO}_3\text{)}_3 \cdot n\text{L}^\text{II}]_{\text{org}}$ are the concentrations of the free extractant and the complex in the organic phase, respectively. $[\text{Nd}^{3+}]_{\text{aq}}$ and $[\text{NO}_3^-]_{\text{aq}}$ are the concentrations of Nd(III) and NO$_3^-$ in the aqueous phase, respectively. $g_{\text{Nd(NO}_3\text{)}_3}$ is the average ionic activity coefficient of Nd(NO$_3$)$_3$. The average activity coefficient $\gamma_{\text{Nd(NO}_3\text{)}_3}$ has been addressed using a simplified Pitzer model in mixed electrolyte solutions, and the equations, related parameters, and the average activity coefficients at various temperatures for some lanthanides have been solved in our previous studies.$^{16}$

The term $D_{\text{Nd}}$ can be calculated as:

$$D_{\text{Nd}} = \gamma_{\text{Nd(NO}_3\text{)}_3} g_{\text{Nd(NO}_3\text{)}_3} 4[N\text{O}_3^-]_{\text{aq}} [\text{L}^\text{I}]_{\text{org}}^3$$

Adjusting eqn (3) in the logarithmic form gives:

$$\log D_{\text{Nd}} = n \log [\text{L}^\text{I}]_{\text{org}} + \log K \gamma_{\text{Nd(NO}_3\text{)}_3} g_{\text{Nd(NO}_3\text{)}_3} 4[N\text{O}_3^-]_{\text{aq}}$$

The ‘$n$’ values obtained by slope analysis are shown in Fig. 5. As seen, the slopes are all around 3, indicating that the stoichiometric ratio of Nd(III) to L$^\text{II}$ in the extracted species was 1 : 3. This result is similar to the previously published results.$^{53-56}$

Fig. 6 displays the ESI-MS of L$^\text{I}$ and L$^\text{II}$ ligands and their complexes with Nd(III). The characteristic peaks in the mass spectra of the two ligands are almost identical ([L$^\text{I}$ + H$^+$, m/z 385.5; L$^\text{II}$ + H$^+$, m/z 385.5]). When the ligands complexed with Nd(III) a peak appeared at m/z 681.6 corresponding to [Nd + 3L$^\text{I}$ + NO$_3^-$]/[Nd + 3L$^\text{II}$ + NO$_3^-$]. The structures of the complexes of L$^\text{I}$ and L$^\text{II}$ with Nd(III) could be identified as [NdL$^\text{I}_3$]$^{3+}$ and [NdL$^\text{II}_3$]$^{3+}$, respectively. Therefore, the compositions of the complexes formed by the two ligands and Nd(III) are the same.

Table 1 compares the Nd(III) extraction performances of the L$^\text{I}$ and L$^\text{II}$ ligands and lists the distribution ratios at different
concentrations of nitric acid and ligands. Under the same experimental conditions, the $D_{\text{Nd}}$ of L$^I$ is higher than that of L$^{II}$.

**Thermodynamics of extraction.** The thermodynamic data of the extraction process was obtained over the range of 298–333 K. According to the Vant'Hoff equation, the relationship between $\Delta G$, $\Delta H$, $\Delta S$, $K$ and $T$ can be expressed as presented in eqn (6).

$$\Delta G = \Delta H - T \Delta S = -2.303RT \lg K$$

$$\lg K = \lg \frac{D_{\text{Nd}}}{\gamma_{\text{Nd(NO}_3)_3}} \frac{[\text{NO}_3\text{-}]_{\text{aq}}^2}{[\text{L}]_{\text{org}}} = - \frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R}$$ (7)

where $T$ and $R$ denote the absolute temperature and gas constant, respectively.

Table 2 lists the thermodynamic data of Nd(III) extraction with the L$^{II}$ ligand, and the data of the L$^I$ ligand is also included for comparison. The $\Delta G$ values of the two ligands are negative, implying that the two extraction processes are exothermic. The absolute value of $\lg K$ of L$^I$ is larger than that of L$^{II}$, which means that Nd(III) is more prone to complexation with L$^I$ ligand than with L$^{II}$ ligand at 298 K. The negative values of $\Delta S$ is because the degree of disorder in the extraction systems is reduced by the formation of the extracted species. The thermodynamic data on the extraction reaction combined with the results of the $D_{\text{Nd}}$ demonstrates that the L$^I$ ligand has better Nd(III) extraction capability.

**Stripping studies of Nd(III).** Dilute nitric acid is considered as a better stripping agent for DGA extractants. In our previous studies, 0.001 M nitric acid is highly effective in stripping and is more effective in light lanthanides. The effect of nitric acid concentration on the stripping efficiency of the organic phase of the L$^{II}$ ligand loaded with Nd(III) is shown in Table S1.† It is evident that 0.001 M HNO$_3$ also exhibits the best stripping efficiency.

**Infrared spectroscopy studies.** The FT-IR spectra of pure L$^{II}$ ligand and the organic phase loaded with Nd(III) were analyzed, as shown in Fig. 7. For the organic phase containing Nd(NO$_3$)$_3$·3L$^{II}$, the coordinated C–O absorption band is blueshifted from its position in the pure L$^{II}$ ligand spectrum at 1649 cm$^{-1}$ to 1638 cm$^{-1}$. The asymmetric stretching vibration band of the ether bond is located at 1117 cm$^{-1}$. After complexing with the metal ions, the absorption band of the ether bond is red-shifted to 1121 cm$^{-1}$. This suggests that the L$^{II}$ molecule might form a tridentate complex with Nd(III) through two carbonyl groups and one ether group.

**Third phase formation**

Fig. 8 exhibits the LOC and CAC of nitric acid depending on the concentration of n-octanol. LOC and CAC increase with an increase in the n-octanol concentration, which is consistent with previous results. The variation in the LOC and CAC of...
Ndx(III) in LII with n-octanol concentration at 298 K for two different concentrations are shown in Fig. 9. It was found that n-octanol, as a phase modifier, effectively inhibited the third phase formation; moreover, at the same n-octanol concentration, the LOC and CAC of Nd(III) in the 0.24 M LII system are larger than those in the 0.12 M LII system. Generally, the formation of the third phase is owing to the increased polarity of the complexes after the Nd ions be extracted, which decreases their solubility in the non-polar diluent.† Therefore, the degree of solvation of the complexes increase with the increasing of the n-octanol concentration.

Fig. S4 and S5† show the trends of the LOC of Nd(III) with the initial HNO3 acidity and LII concentration, respectively. The LOC values decrease with an increasing of the nitric acid concentration on account of the competition between nitric acid and Nd(III) and increase with an increasing of the concentration of the extractant. When HNO3 or Nd(III) is transferred from the aqueous phase to the organic phase, acid-solvates, such as DGA·(HNO3)3½, and metal-solvates, such as DGA·(Nd(NO3)3)½, are formed.63,64 The solvent molecules have strong polarity and tend to interact with each other automatically and undergo self-aggregation, thus forming spherical reverse micelles at mesoscopic scales.65 The tendency of aggregation depends on the polarity of the functional groups and the van der Waals interaction between the alkyl groups of the ligand and diluent.66,67 Typically, these reverse micelles have a structure with the metal ion as the core surrounded by long-chain alkyl groups. Table 3 presents the LOC and CAC of Nd in the L1 and LII solvent systems. In general, compared with the LII ligand, the L1 ligand have lower CAC values and higher LOC values. The higher LOC of L1 means that the extraction capability of L1 was better than LII, and the lower CAC value means that it is easier to form the third phase in L1 than LII.

**Theory Calculations**

**Geometrical and electronic structures of the ligands.** The electrostatic potential (ESP) diagrams for the L1 and LII ligands are presented in Fig. 10. The molecular geometries of the two ligands were optimized at the theoretical level B3LYP/6-311G(d) in the gas phase. The red and blue regions indicate the local maximum/minimum and positive/negative potentials, respectively. The negative electrostatic potential corresponds to the enrichment of electrons, and electron-rich positions are the preferred sites for Nd(III) coordination.68,69

As shown in Fig. 10, there are minimum electrostatic potential points close to the ether O atom denoted as Oether and the two amide O atoms denoted as Oamide1 and Oamide2. For the L1 ligand, the ESP values of Oamide1 and Oamide2 atoms are −40.30 and −40.11 kcal mol⁻¹, respectively. For the LII ligand, Oamide1 is connected with two octyl groups, and its ESP value is −41.47 kcal mol⁻¹, and Oamide2 is connected with two methyl groups, and the corresponding ESP value is −37.59 kcal mol⁻¹. It is clear that for both L1 and LII ligands, Oamide1 and Oamide2 have more negative electrostatic potentials than Oether; thus, the two amide O atoms are more likely to coordinate with the metal ions than the ether O atom. In addition, the difference between the ESP values of Oamide1 and Oamide2 in L1 is larger than that in LII. In general, long-chain alkyl groups have a stronger electron-donating inductive effect than short alkyl chains, leading to a larger electron density on the amide O atom adjacent to the long alkyl chains. Therefore, the ESP value of Oamide1 is more negative than that of Oamide2 in L1, and the ESP values of Oamide1 and Oamide2 are approximately identical in LII.

The Mulliken charges on the Oether and Oamide of L1 and LII are shown in Table S2.† The Mulliken charges on Oether of the two ligands are the same and less than those on the two amide O atoms. For L1, the Mulliken charges on Oamide1 and Oamide2 are the same, whereas, for LII, the Mulliken charge on Oamide1 is larger than that on Oamide2, which would affect the interaction of solvation of the complexes after the Nd ions be extracted, which decreases their solubility in the non-polar diluent.† Therefore, the degree of solvation of the complexes increase with the increasing of the n-octanol concentration.

| Ligand | L1 | LII |
|--------|----|----|
| [L] (M) | n-octanol (M) | CAC (mM) | LOC (mM) | CAC (mM) | LOC (mM) |
| 0.024  | 0.14 | 0.30 | 3.73 | 0.42 | 2.81 |
| 0.22   | 0.46 | 7.05 | 0.60 | 5.27 |
| 0.27   | 1.06 | 12.09 | 1.23 | 9.02 |

![ESP plots of the optimized L1 and LII ligands.](image)
between these ligands and metal ions, and further affect the stability of the complexes.

**Optimized structures of the [NdL₃]⁺⁺ complexes.** It has been reported that when DGA ligands complex with Ln(III) from the nitric acid medium, the nitrate ions do not directly bond to the Ln(III) centers in the solvent extraction system but rather act as counterions in the form of ion pairs to balance the positive charge of the 1:3 complexes. The geometries of the two complexes were optimized at the B3LYB/6-311G(d)/RECP level of theory, and the structures are shown in Fig. 11. They indicated that both ligands coordinate with the Nd(III) ion acting as the tridentate type. Table S3 lists the bond lengths between Nd(III) and the ether O atom and the two amide O atoms of L¹ and L¹. In both L¹ and L¹, the O ether-Nd bond lengths are longer than the Oamide₁-Nd and Oamide₂-Nd bond lengths. The bond length of Oamide₁-Nd is almost identical to that of Oamide₂-Nd in L¹, and the bond length of Oamide₂-Nd is shorter than that of Oamide₂-Nd in the L¹ ligand; therefore, there are some differences in the complexation strength between the two amide O atoms and Nd(III) in the L¹ ligand.

**Bonding nature and topological analysis of the complexes.** Mayer bond orders (MBOs) of the Nd-O bonds were calculated and are presented in Table 4. MBOs were within the 0.113–0.325 range, indicating that the interactions between the ligands and the metal ions display weak covalency. MBOs between Oamide₁-Nd and Oamide₂-Nd in L¹ are almost the same, while the MBOs of Oamide₁-Nd and Oamide₂-Nd in L¹ are different. Besides, the average value of the MBOs of Oamide₁-Nd and Oamide₂-Nd in L¹ is slightly larger than that in L¹, which mean that the coordination bond between L¹ and Nd(III) was more stable.

Topological analysis based on the electronic wave function information was also performed as part of QTAIM using Multiwfn 3.7, which has already been widely applied in the analysis of the Ln(III)/An(III) complexes. The topological analysis of electron density ρ(r) and its Laplacian (V²ρ(r)) provides information about the bond properties. The (3,−1) saddle point on the electron density curvature is the bond critical point (BCP), and the electron curvature is positive in the direction of the atomic interaction line and negative in the direction of its orthogonality, and the electron density ρ(r) and potential energy density V(r) at the BCP position are closely related to the strength of the chemical bond. Generally, BCP ρ(r) > 0.20 a.u. and a negative V²ρ(r) value represent a covalent (open-shell) interaction, while ρ(r) < 0.10 a.u. with a positive V²ρ(r) value corresponds to a closed-shell interaction, which can be considered as ionic, hydrogen or van der Waals interaction. As shown in Table 5, the ρ(r) values at the Oamide₁-Nd and Oether-Nd BCPs are <0.1 a.u., and all the V²ρ(r) values are positive. Therefore, the interactions between the two ligands and Nd(III) show the mainly ionic characteristics.

In addition, the ρ(r) values at the Oamide₁-Nd BCP for the two complexes are larger than those at Nd-Oether, demonstrating that Oamide has a stronger capacity for complexation. The slightly larger difference between the ρ(r) values at the Oamide₁-Nd and Oamide₂-Nd of the L¹ ligand combined with the results on MBOs and electrostatic potential prove that the interactions between the two Oamide of L¹ and Nd(III) are in a state of imbalance. The average ρ(r) value at the Nd-Oamide BCP of [NdL₃]⁺⁺ is larger than that of [NdL₃]⁺⁺, further showing that there is a stronger interaction between Nd(III) and the L¹ ligand.

**Thermodynamic analysis.** The theoretically calculated Gibbs free energy (∆G) at the M05-2X/6-31G(d)/SMD level for the reactions between L¹/L¹ and Nd(III) are shown in Table 6. The values of ∆G for the two reactions are both negative, which
prove that the coordination reaction proceeded spontaneously. The calculated free energy for the formation of the 1 : 3 Nd(III)/LI complex (−211.35 kJ mol⁻¹) is more negative than that of 1 : 3 Nd(III)/LII complex (−181.87 kJ mol⁻¹), which is in good agreement with the order of the experimentally determined distribution ratio values. This further verify that LII possesses outstanding complexing ability with Nd(III) than LII.

## Conclusions

In the present study, N,N-dimethyl-N’,N’-dioctyl diglycolamide (LII) was synthesized, and its extraction and loading capabilities towards Nd(III) from the nitric acid medium were studied by employing 40/60 (v/v)% n-octanol/kerosene as the diluent. \( D_{Nd} \) increases with nitric acidity and the concentration of the extractant and decreases with increasing temperature. The stoichiometry of the extracted species is \( \text{Nd(NO}_3)_3\cdot3\text{LII} \), as verified by the results of ESI-MS and FT-IR. The LOC and CAC of Nd increase with the increasing in the concentrations of n-octanol and extractant and decrease with the increase in the initial acidity of the aqueous medium. In comparison with its isomeric ligand N,N’-dimethyl-N,N’-dioctyl diglycolamide (LIII), LII shows a lower distribution ratio of Nd(III) but is more advantageous in terms of preventing the formation of the third phase, which is reflected in its higher CAC value under similar experimental conditions.

The electrostatic potential and Mulliken charge analysis of the two ligands indicate that the difference in the electron-donating ability of the two amide O atoms in LII is larger than that in LII. The complexation between LII/LII and Nd(III) is predominantly through ionic interactions. The MBOs and QTAIM show that the complexation interaction strength of Nd–Oamide1 and Nd–Oamide2 are almost identical in LII, while those in LII display certain differences, and this inhomogeneity in LII seem to influence its extraction performance towards metal ions, such as Nd(III), which is in accordance with the thermodynamic results. These results may shed light on the design of DGA class ligands for separating HLLW and help us better understand the structure–activity relationship in DGAs.

## Conflicts of interest

There are no conflicts to declare.

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