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Efficacious selective separation of U(VI) over Mo(VI) using novel 2,9-diamide-1,10-phenanthroline ligands: Liquid-liquid extraction and coordination chemistry

Taoyuan Xiu[a,b,c], Simei Zhang[b,d], Peng Ren[b,d], Siyan Liu[b], Shuai Wang[b], Hamza Shehzad[e], Jingyang Wang[a,b], Meng Zhang[a], Guoan Ye[a,c,*], Caishan Jiao[a,*], Qunyan Wu[b], Liyong Yuan[b,*], Zhifang Chai[b], Weiqun Shi[b,*]

[a] *College of Nuclear Science and Technology, Harbin Engineering University, Harbin 150001, China*
[b] *Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*
[c] *China Institute of Atomic Energy, Beijing 102413, China*
[d] *State Key Laboratory of Nuclear Resources and Environment, School of Nuclear Science and Technology, East China University of Technology, Nanchang 330013, China*
[e] *School of Chemistry, University of the Punjab, Lahore 54590, Pakistan*

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ABSTRACT

Uranium and molybdenum are important strategic elements. The production of ^{99}Mo and the hydrometallurgical process of uranium ore face difficult problems of separation of uranium and molybdenum. In this study, the four phenanthroline diamide ligands were synthesized, and extraction and stripping experiments were performed under different conditions to evaluate the potential application of these ligands for separation of U(VI) over Mo(VI). With the growth of alkyl chain, the solubility of ligands could be greatly improved, and the separation effect of U(VI) over Mo(VI) gradually increased. The $SF_{\mathrm{U/Mo}}$ were around 10,000 at 4 mol/L HNO_3. Three stripping agents were tested with the stripping efficiency of Na_2CO_3 (5%) > H_2O > HNO_3 (0.01 mol/L). The stripping percentages of the three stripping agents were all close to unity, indicating that the ligands had the potential to be recycled. The chemical stoichiometry of U(VI) complexes with ligands was evaluated as 1:1 using electrospray ionization mass spectrometry, ultraviolet visible spectroscopy and single-crystal X-ray diffraction. The consistency between theoretical calculation and experimental results further explains the coordination mechanism.

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With the development of nuclear medicines, medical radioisotopes play a very important role in the diagnosis and treatment of diseases, among which ^{99m}Tc is widely used in nuclear medicine [1–4]. ^{99m}Tc is mainly prepared from its parent nuclide ^{99}Mo by ^{99}Mo/^{99m}Tc generator [5–7]. At present, ^{99}Mo is mainly produced by fission of highly enriched uranium (HEU) and low enriched uranium (LEU) targets in reactors [8,9]. The separation of U(VI) and Mo(VI) in the target element solution is usually achieved by solvent extraction. At the same time, in the process of uranium ore hydrometallurgy, molybdenum is often associated with uranium ore, which makes uranium and molybdenum simultaneously leached [10–15]. This makes the separation of uranium more difficult. Therefore, it is of great significance to study the separation of U(VI) and Mo(VI).

Methods for separation of U(VI) and Mo(VI) from solution include precipitation, extraction, ion exchange and others [16–18]. The first three methods are commonly used at present, while the others have been studied but not applied in industry, such as liquid membrane extraction method and ion flotation method. Solvent extraction is widely used in the front and back ends of the nuclear fuel cycle because of its mild conditions, simple operation and easy industrialization [19–22]. Behera *et al.* [23] studied the separation of U(VI) and Mo(VI) from aqueous phosphoric acid by triisodecylamine (Alamine 310), tributyl phosphate (TBP), di-*n*-pentyl sulfoxide (DPSO) and their mixtures in benzene. It was feasible to separate U(VI) and Mo(VI) with Alamine 310, TBP and DPSO in the low acidity range below 2 mol/L H_3PO_4, and the efficiency order was TBP > DPSO > Alamine 310. Ibrahim *et al.* [13] recovered U(VI) from the enrich leach solution (0.5 g/L Mo,

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* Corresponding authors.
E-mail addresses: yeguoan@ciae.ac.cn (G. Ye), jiaocaishan@hrbeu.edu.cn (C. Jiao), yuanly@ihep.ac.cn (L. Yuan), shiwq@ihep.ac.cn (W. Shi).

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0.05 g/L U) obtained during the leaching of molybdenum-uranium ore materials by solvent extraction *via* LIX 622 N (a salicylaldoxime derivative). The effects of various variables such as concentration of LIX 622 N, phase ratio, pH, different stripping reagents, temperature and diluents were investigated. Lsasheen *et al.* [24] extracted and recovered Mo(VI) from sulfate leaching solution containing U(VI) and Mo(VI) through 5-nonylsalicylaldoxime, and obtained high purity MoO_3 (99.99%). Behera *et al.* [25] extracted U(VI) and Mo(VI) from 0.1 mol/L to 1.0 mol/L HCl solutions by organophosphoric, phosphinic acid and its thiosubstituted derivatives. The extraction efficiencies of PC-88A, Cyanex 272, Cyanex 301 and Cyanex 302 for U(VI) and Mo(VI) extraction were compared. Many ligands have been designed for separation of U(VI) over Mo(VI), and most of them contain phosphorus, which does not comply with the "CHON" principle for secondary waste minimization.

During the nuclear fuel cycle, several amide ligands have been designed for the separation of actinides by liquid-liquid solvent extraction. Among them, phenanthroline amide ligands have the characteristics of fast kinetics, simple synthesis, stability and good selectivity under acidic and under irradiation. At the same time, such ligands meet the "CHON" principle of secondary waste minimization, so it has been widely concerned and studied [26,27]. Many researchers have synthesized a series of phenanthroline amide ligands for separation of actinides and lanthanides, and these ligands have shown good separation effect [28–33]. Recently, we synthesized a series of phenanthroline amide ligands and used them to separate actinides over lanthanides [34,35,37-41]. Among them, *N*,*N*′–diethyl-*N*,*N*′-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen) represents a typical phenanthroline amide ligand [34,35,37,38], shows the best actinide separation performance. Up to now, more and more attention has been paid to the potential of phenanthroline amide ligands in the separation of actinides. Such ligands may have potential application on the separation of U(VI) and Mo(VI), although no date on this topic has been published in the literature.

In this study, we synthesized four phenanthroline diamide ligands (*N*,*N*′-diethylbenzoate-2,9-diamide-1,10-phenanthroline (EB-DAPhen), *N*,*N*′–diethyl-*N*,*N*′-diethylbenzoate-2,9-diamide-1,10-phenanthroline (Et-EB-DAPhen), *N*,*N*′-dibutyl-*N*,*N*′-diethylbenzoate-2,9-diamide-1,10-phenanthroline (But-EB-DAPhen) and *N*,*N*′-dioctyl-*N*,*N*′-diethylbenzoate-2,9-diamide-1,10-phenanthroline (Oct-EB-DAPhen)). Extraction and stripping of U(VI) over Mo(VI) were carried out under different conditions, such as acidity, time, ligand concentration and temperature. The coordination mechanism was studied by fourier transform infrared spectroscopy (FT-IR), ultraviolet visible spectroscopy (UV–vis) titration, electrospray ionization mass spectrometry (ESI-MS), single-crystal X-ray diffraction and theoretical calculation. The details of the experiment were deposited in Supporting information. The findings of this work highlight the vast opportunities of phenanthroline diamide ligands on the separation between U(VI) and Mo(VI).

The choice of diluent has a significant impact on the extraction process. After testing the effects of five different solvents (Fig. S8 in Supporting information), it was found that 3-nitrotrifluorotoluene had the most favorable extraction effect. Therefore, 3-nitrotrifluorotoluene was selected as the solvent for subsequent experiments. The variation in the D_U, D_{Mo} and $SF_{U/Mo}$ as a function of the HNO_3 concentration are shown in Fig. 1. In the experiment, the formation of the third phase was observed in the extraction for L_0 at 4 mol/L HNO_3. This is mainly due to the low solubility of L_0 in 3-nitrotrifluorotoluene. To avoid the formation of three phases, the alkyl chains were introduced to improve the solubility of ligands. The formation of the third phase was not observed during the extraction for the three ligands (L_1, L_2 and L_3) with the alkyl chain. As shown in Fig. S9 (Supporting information), the four ligands have strong separation ability for U(VI) over Mo(VI), and the order is $L_0 < L_1 < L_2 < L_3$. Moreover, the $SF_{U/Mo}$ of L_1, L_2 and L_3 were around 10,000 at 4 mol/L HNO_3. While almost no Mo(VI) extraction occurred for the four ligands at all the test conditions, the *D* value of U(VI) increased with the increase of HNO_3 concentration. It can be attributed to the fact that nitrate ions participate in the formation of complex during the extraction, which is promoted by the increase of nitric acid concentration according to Le Chatelier's principle [36]. Meanwhile the ligands with longer alkyl chain show stronger extraction ability, and the ligand and U(VI) form 1:1 complexes during the extraction (as proved below). The fact that only one ligand coordinates with U(VI) indicates that space resistance occurs mainly between the ligand and U(VI) rather than inter molecules. Therefore, the solubility of the complex in the organic phase plays a significant role in determining the *D* value [26]. For example, the same conclusion was reached for the NTAamide ligands, which form 1:1 complexes with metal ions during the extraction process, and the extraction capacity increases with the increase of substituent alkyl chains [26]. However, DGA forms 3:1 or 4:1 type complexes with metal ions, and the extraction capacity increases with the shortening of the substituent alkyl chain. More DGA molecules involved in the coordination compounds means greater substituent steric hindrance [26]. For L_1, L_2 and L_3 with alkyl chain, the high solubility in 3-nitrotrifluorotoluene makes more complexes distribute in the organic phase, thereby leading to a higher *D* value.

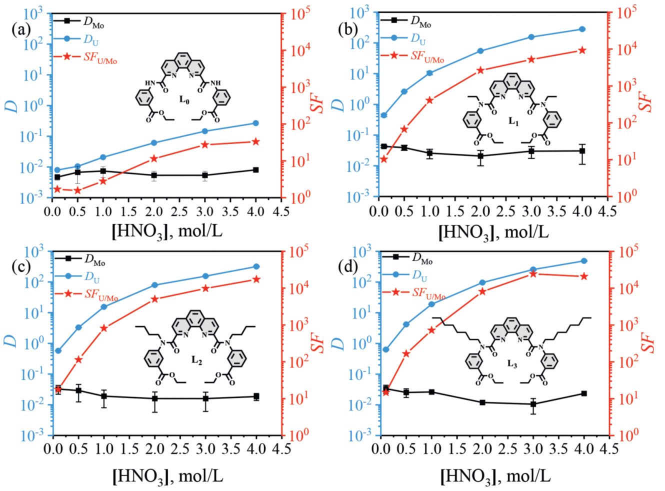


Fig. 1. Influence of HNO_3 concentration on the *D* value and *SF* value of U(VI) and Mo(VI) by L_0, L_1, L_2 and L_3 ligands. Organic phase: $[L_0] = [L_1] = [L_2] = [L_3] = 2$ mmol/L; aqueous phase: $[HNO_3] = 0.1–4.0$ mol/L, $[U(VI)] = 0.5$ mmol/L and $[Mo(VI)] = 0.2$ mmol/L; contact time = 30 min; $T = 298$ K; O/A = 1.

Extraction kinetics is the key parameter for evaluating extraction performance. The influence of contact time on the extraction of U(VI) and Mo(VI) is shown in Fig. S10 (Supporting information). The *D* value of Mo(VI) approached to zero with the increase of contact time where the extraction of U(VI) by L_1 reached equilibrium within 10 min, and the extraction of U(VI) by L_2 and L_3 reached equilibrium within 15 min. That is the U(VI) extraction kinetics for all the three ligands are fast. It can be attributed to the fact that the two coordination nitrogen atoms on the *o*-phenanthroline skeleton are juxtaposed with the same plane, so that the ligand does not need to undergo its own torsion for coordination. Comparing the ligand in this work with Et-Ph-DAPhen [41], the kinetics of Et-Ph-DAPhen is faster. The main reason is that the benzene ring lacking the ester group has less steric hindrance. However, the ester group can improve the solubility of ligand and benefit the extraction performance. With the increase of alkyl chain, the equilibrium time also increased. This results from the increased steric

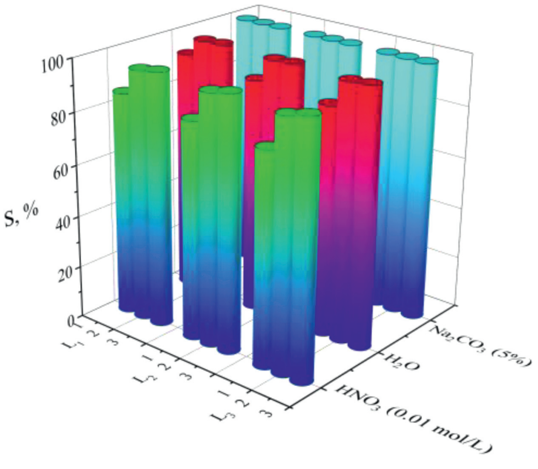


Fig. 2. Stripping of U(VI) from organic phase by ultrapure water, 0.01 mol/L HNO_3 and 5% Na_2CO_3.

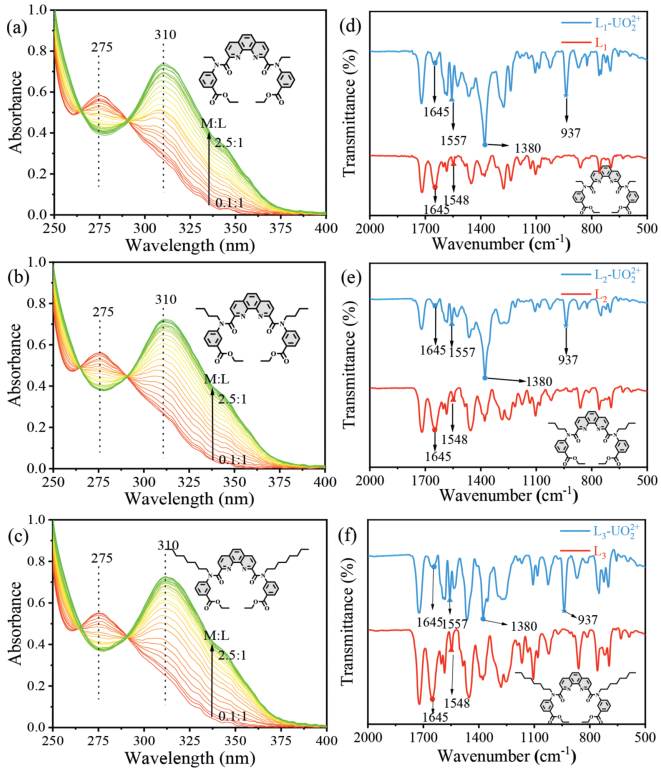


Fig. 3. (a-c) UV–vis titration spectra of L_1, L_2 and L_3 with U(VI) in CH_3CN ($[L] = 1 \times 10^{-5}$ mol/L, $[U(VI)] = 1 \times 10^{-3}$ mol/L, $[Et_4NNO_3] = 0.01$ mol/L). (d-f) The FT-IR spectra of ligands (L_1, L_2 and L_3) and its complex with U(VI).

hindrance of ligands with the increase in alkyl chain. The ligand needs to twist itself during the extraction, thus taking longer time to reach equilibrium.

The *D* value is strongly dependent on the concentration of ligand. To investigate the influence of ligand concentration, HNO_3 concentration was fixed at 0.5 mol/L and the ligands concentration were varied from 1 mmol/L to 10 mmol/L. As shown in Fig. S11 (Supporting information), the *D* value of U(VI) increased rapidly with the increasing ligand concentration, while the *D* value of Mo(VI) kept approaching zero. As well known, slope analysis method is always used to determine the stoichiometric ratio of ligands to metal ions. The slope analysis method can be expressed as Eqs. S4-S7 (Supporting information). As the poor extraction effect of L_1, L_2 and L_3 for Mo(VI), slope analysis method could not analyze the stoichiometric ratio of ligands to Mo(VI). Therefore, only the stoichiometric ratio of ligands to U(VI) were studied. It is noted that the concentration of nitric acid remains 0.5 mol/L throughout the whole extraction process, $\log[NO_3^-]$ can be regarded as a constant. The extraction equilibrium constant (K_{ex}) is constant at constant temperature. Using $\log D_U$ as the ordinate and log[L] as the abscissa, the slope was obtained by linear fitting as the stoichiometric ratio of the ligand to U(VI). As shown in Fig. S11 (Supporting information), the slope of $\log D_U$ and log[L] for L_1, L_2 and L_3 ligands are 0.67, 0.69 and 0.70, respectively. It meant that the stoichiometric ratio is approximately 1:1 between these ligands and U(VI). This is consistent with the results obtained for many phenanthroline diamide ligands [34,41]. As tetracyclic ligands, L_1, L_2, and L_3 all tend to occupy four of the six-coordination sites of the uranyl plane. The two oxygen atoms perpendicular to uranyl itself prevent further coordination of the ligand. Therefore, the metal to ligand ratio of 1:2 complex cannot be formed.

Temperature plays an important role in solvent extraction process. The thermodynamics of extraction at different temperatures have been studied in Supporting information. In addition, the loading capacity of three ligands (L_1, L_2 and L_3) for U(VI) were also studied in Supporting information. The loading capacity of three ligands was found to approach the theoretical value, where each mole of ligand can load one mole of U(VI).

For a promising ligand, it is necessary not only to have good extraction performance, but also to have good stripping performance. The stripping experiment was carried out after the extraction experiment, and the stripping agents for U(VI) were HNO_3 (0.01 mol/L), H_2O and Na_2CO_3 (5%), respectively. The three-stage stripping efficiency of U(VI) are displayed in Fig. 2. The stripping capacity of the three stripping agents is Na_2CO_3 (5%) > H_2O > HNO_3 (0.01 mol/L). The stripping of UO_2^{2+} to achieve close to 100% can be accomplished with just one stage using a 5% Na_2CO_3 solution. This is due to the significantly lower $\log\beta$ value of the ligands and UO_2^{2+} complex compared to carbonate species [37]. Consequently, UO_2^{2+} extracted from the organic phase can be easily stripped by carbonates, resulting in the formation of a more stable $UO_2(CO_3)_n$ [37]. The percentage of triple stripping for all the three agents is close to 100%, which indicated that the ligands have good stripping performance.

The complexation of L_1, L_2 and L_3 with U(VI) was studied by UV–vis spectra titration. As evident from Figs. 3a-c, the UV–vis spectra titration of L_1, L_2 and L_3 exhibited a certain trend of change with the continuous addition of U(VI). It can be observed that the intensity of the peak at 275 nm decreased continuously, and a new peak at 310 nm increased continuously. This may be due to the coordination of U(VI) with the ligands causing the change of molecular orbital. However, obvious peak pattern change and band shift between different ligands were not observed. It is inferred that the complex of ligands and the U(VI) have similar structure and stoichiometric ratio. The HyperSpec software was applied to fit the titration data [42]. The results show that the stoichiometric ratio of the complex is 1:1. The transformation of alkyl chain did not change the stoichiometric ratio of the complex. This result is consistent with that obtained by slope analysis method, which is subsequently confirmed by ESI-MS spectroscopy and single-crystal X-ray diffraction analysis. Meanwhile, the stability constant ($\log\beta$) obtained by the fitting is given in Table S2 (Supporting information). The order of the stability constants of the three ligands is $L_3 > L_2 > L_1$, which proves that the coordination ability of the ligands to U(VI) is $L_3 > L_2 > L_1$. It is consistent with the results of the extraction experiment.

FT-IR spectra can provide characteristic fundamental vibrations of chemical groups, through which molecular structure composi-

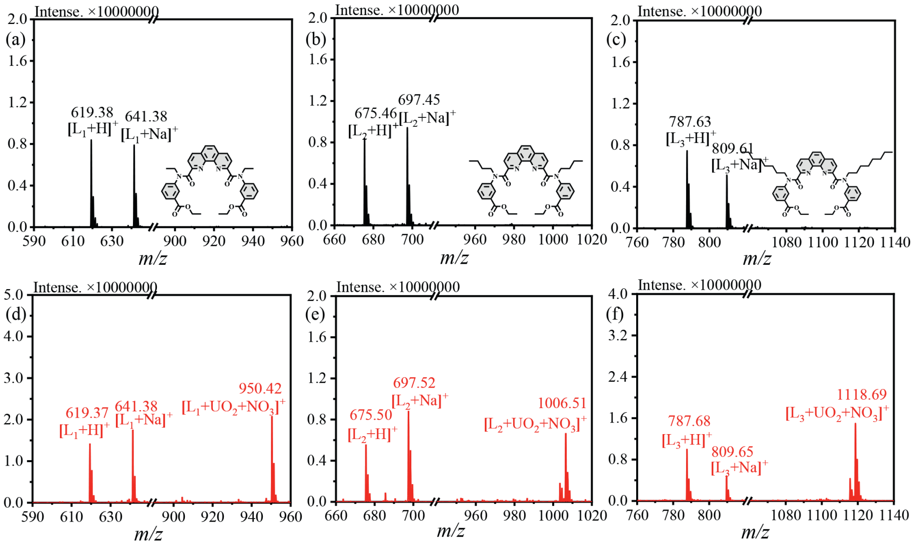


Fig. 4. The ESI-MS spectra of ligands (L_1, L_2 and L_3) before (a-c) and after (d-f) extraction of U(VI).

tion can be elucidated. The FT-IR spectra before and after extraction are shown in Figs. 3d-f. Red curve and blue curve correspond to spectra before and after extraction, respectively. The peaks at 1645 cm^{-1} and 1548 cm^{-1} are considered to be stretching vibration peaks of the C=O bond of the amide group and the C=N bond of the phenanthroline group of the ligands, respectively [41]. After extraction of U(VI), the peak of the C=O bond became weaker, and the peak of the C=N bond moved 9 cm^{-1} to the direction of high wave number, respectively, indicating that the amide and phenanthroline group of the ligands were involved in the coordination of U(VI). The peak at 1380 cm^{-1} was thought to be the peak of nitrate ions [40], which indicated that nitrate ions were also involved in coordination. The peak at 937 cm^{-1} could be attributed to the stretching vibration of the U=O bond. All these results indicate that the ligands coordinate with uranyl ions.

In order to explore the formation of complex species during the extraction process, the positive model of ESI-MS was used to analyze the organic solution before and after the extraction of U(VI) by ligands (L_1, L_2 and L_3). As can be seen from Fig. 4, the peaks of ligands (L_1, L_2 and L_3) binding with H^+ appear at $m/z = 619.38$, 675.46 and 787.63 respectively, while the peaks of ligands binding with Na^+ appear at $m/z = 641.38$, 697.52 and 809.61, respectively. After the extraction, the ESI-MS spectra show that one ligand combine with one uranyl ion, forming nitrate complexes of $[L_1+UO_2+NO_3]^+$ (m/z 950.42), $[L_2+UO_2+NO_3]^+$ (m/z 1006.51) and $[L_3+UO_2+NO_3]^+$ (m/z 1118.69), respectively. According to the above analysis, the stoichiometric ratio of U(VI) to the ligands are 1:1. The results are consistent with the slope analysis method and UV–vis spectra titration.

The complex crystal ($[UO_2L_1NO_3]{\cdot}NO_3$) of UO_2^{2+} and L_1 can be obtained by solvent evaporation. The crystal structure and coordination information of $[UO_2\ L_1NO_3]{\cdot}NO_3$ are shown in Fig. 5, the structural refinement parameters are shown in Table S3 (Supporting information), and the selected bond lengths are listed in Table S4 (Supporting information). As shown in Figs. 5a and b, the side chain of the amide (ethyl benzoate) is close to phenanthroline to reduce steric hindrance which provides the coordination plane for uranyl. The L_1 is coordinated with uranyl by nitrogen atoms on phenanthroline and oxygen atoms on amides. The average bond distances of U-N and U-O are close to those reported in previous literature [35,41]. The uranium atom coordinated with two oxygen atoms on the nitrate anion. As shown in Fig. 5d, another nitrate anion acted as a counter ion to maintain charge balance and did not participate in coordination. The presence of the axial oxygen atom of uranyl prevented the double ligands from participating in the coordination, so that the uranyl and the ligand only form a 1:1 complex. The results are consistent with that of the slope analysis method, ESI-MS spectroscopy and UV–vis spectra titration.

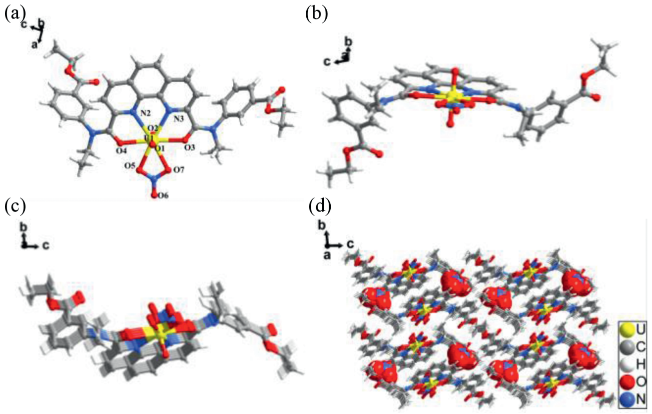
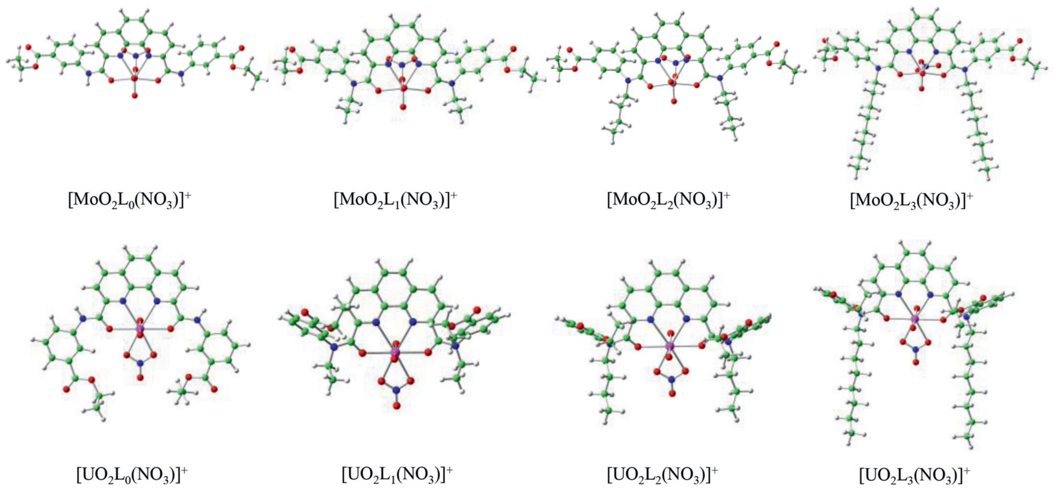


Fig. 5. (a, b) Crystal structure of the $[UO_2L_1NO_3]{\cdot}NO_3$ complex. (c) Three-dimensional stacking mode of the $[UO_2L_1NO_3]{\cdot}NO_3$ complex. (d) NO_3^- counter ions in the $[UO_2L_1NO_3]{\cdot}NO_3$ 3D framework channel. Yellow, gray, white, red and blue represent U, C, H, O and N atoms, respectively.

The structures of the MoO_2^{2+} and UO_2^{2+} complexes with four phenanthroline diamide ligands shown in Fig. 6 were optimized at the B3LYP/6–31G(d)/RECP level of theory [43]. It is clearly seen that four ligands acted as tetra-dentate mode coordinates with both MoO_2^{2+} and UO_2^{2+} ions. MoO_2^{2+} ion coordinates with nitrate ion as mono-dentate mode, while UO_2^{2+} ion coordinates with nitrate ion as bi-dentate one. Moreover, the nitrate ion is out of the plane of MoNN for the MoO_2^{2+} complexes, while it is in the plane of UNN for the UO_2^{2+} complexes. The average M-N and M-O (M = Mo, U atom) bond distances and the OMO bond angles for MoO_2^{2+} and UO_2^{2+} complexes are listed in Table S5 (Supporting information). The Mo=O, Mo-O and Mo-N bond distances for the MoO_2^{2+} complexes are shorter than the corresponding bond distances for UO_2^{2+} ones. Noticeably, the M-N_L and M-O_L bond distances gradually decrease with the increasing carbon atom number in the ligands. The values of the bond distances shows that MoO_2^{2+} and UO_2^{2+} have more interaction with the ligand L_3. In addition, the Mo-O_N bond


$[MoO_2L_0(NO_3)]^+$ $[MoO_2L_1(NO_3)]^+$ $[MoO_2L_2(NO_3)]^+$ $[MoO_2L_3(NO_3)]^+$

$[UO_2L_0(NO_3)]^+$ $[UO_2L_1(NO_3)]^+$ $[UO_2L_2(NO_3)]^+$ $[UO_2L_3(NO_3)]^+$

Fig. 6. Structures of MoO_2^{2+} and UO_2^{2+} complexes with four phenanthroline diamide ligands complexes in the gas phase at the B3LYP/6-31G(d)/RECP level of theory.

distance gradually increases with the increasing carbon chain for the ligands, yet the U-O_N bond distance is converse. It is worthy to note that the OMoO bond angles fall in the range of 104.6–105.7° and the OUO bond angles are close to 180°.

To investigate the extraction of MoO_2^{2+} and UO_2^{2+} with four ligands, the Gibbs free energy (ΔG) for the possible reactions of MoO_2^{2+}/UO_2^{2+} and ligand were calculated at the B3LYP/6-311G(d,p)/RECP level of theory as listed in Table S6 (Supporting information). The extractable species of MoO_2^{2+} and UO_2^{2+} is considered as the $[MoO_2(NO_3)_2(H_2O)]$ and $[UO_2(H_2O)_2(NO_3)_2]$ species. The ΔG values get more negative with the increasing carbon chain which reveals the ligand L_3 has better extraction ability for MoO_2^{2+} and UO_2^{2+}. That is the $[MoO_2(NO_3)_2(H_2O)] + L_3 \rightarrow [MoO_2L_3(NO_3)]^+ + H_2O + NO_3^-$ and $[UO_2(H_2O)_2(NO_3)_2] + L_3 \rightarrow [UO_2L_3(NO_3)]^+ + 2H_2O + NO_3^-$ are energetically favorable. The ΔG for the reaction with UO_2^{2+} complexes are more negative than that with MoO_2^{2+} ones, indicating that four ligands have stronger extraction ability with UO_2^{2+} with MoO_2^{2+}. These results are consistent with the experiment observations.

In summary, four phenanthroline diamide ligands (EB-DAPhen, Et-EB-DAPhen, But-EB-DAPhen and Oct-EB-DAPhen) were synthesized, which can achieve efficient and selective separation of U(VI) over Mo(VI). Extraction experiments showed that the separation effect of U(VI) over Mo(VI) increased gradually with the increase of the alkyl chain of ligands. The ligands and U(VI) form the 1:1 complex during extraction. The fact that only one ligand molecule coordinates with U(VI) indicated that space resistance occurs mainly between the ligand and U(VI) rather than inter molecules. Therefore, the solubility of the complex in the organic phase plays a vital role in the *D* value. The high solubility of L_1, L_2 and L_3 for the introduced alkyl chain in 3-nitrotrifluorotoluene increased the *D* value of U(VI). Stripping experiments showed that the ligands have the potential of recycling. The ligands and U(VI) form a 1:1 complex which was fitted by slope analysis method and UV–vis spectra titration. This conclusion can be supported directly by ESI-MS spectroscopy and single-crystal X-ray diffraction. The single crystal results explained that the presence of the axial oxygen atom in uranyl prevents the double ligands from participating in the coordination, making uranyl and ligand form only 1:1 complex. The theoretical calculation further explains the coordination mechanism. Energy analysis showed that the ΔG of the possible reaction between UO_2^{2+} and the ligands are more negative than that between MoO_2^{2+} and the ligands, which proves that the ability of the ligands to extract UO_2^{2+} is stronger than that of MoO_2^{2+}. The performance of the four ligands provides a scheme for the separation of U(VI) over Mo(VI) in the process of ^{99}Mo production target solution and uranium mine hydrometallurgy.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.108440.

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