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N-Alkyl calix[4]azacrowns for the selective extraction of uranium

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The selective extraction of uranium by N-octylcalix[4]azacrown (NOCAC) and N-ethylhexylcalix[4]azacrown (NEHCAC) was investigated. The ligands were synthesised in three steps through the functionalisation of t-butyl calix[4]arene at the distal-1,3-positions of the lower rim with ethyl acetate groups followed by cyclisation with (imino)bis(ethane-2,1-diyl))diamide. A detailed investigation on the effect of various parameters, such as the aqueous phase acidity (sulfuric acid), the ionic strength, and ligand concentration, on the extraction of uranium(VI) has been conducted. The effect of the H_2SO_4 concentration has been studied from 0.02 to 3 M. Preliminary studies carried out on NOCAC in dodecane/octanol diluents showed that the uranium extraction from sulfuric acid is more efficient at a low H_2SO_4 concentrations. The stoichiometry of complexation was estimated from the slope method, NMR titration, and electrospray ionisation-mass spectrometry analysis. Both ligands were found to be highly selective for uranium(VI) over other competitive cations present in a simulated leach solution containing seven competitive cations. The successful recovery of the uranium from the organic phase has been performed thanks to stripping steps involving ammonium oxalate, ammonium carbonate, and sodium carbonate as stripping agents.

Introduction

Uranium is one of the more common elements in the Earth's crust. It can be found, in association with many other elements, in rocks, soil, rivers, and ocean water.[1-4] Uranium can be mined as a primary product, co-product, or important by-product. The extraction of uranium from ores or its recycling from spent nuclear fuel has been the subject of a considerable amount of research effort since the inception of nuclear power generation.

At the start of the fuel cycle, conventional ores are leached by acid or carbonate reactants; subsequently, a liquid-liquid extraction process can be performed to recover uranium with high purity. Among many leaching reactants, sulfuric acid typically combines high leaching performance and relatively low cost.

Liquid-liquid extraction is one of the most widely employed and useful techniques for the extraction and separation of uranium from impurities present in natural resources, as well as in nuclear wastes. Many different extractants have been developed for the extraction of uranium such as trialkyl phosphine,[5] carbamoylalkyl-phosphonates,[6] carbamoylalkyl-phosphonic acid ligands,[7] dialkyl phosphonic acid,[8] diamides,[9] and trialkyl amines.[10]

Calixarenes as chelating systems are well known in the field of separation science,[11] and, over the past three decades, have been used as preorganised structures for the extraction and complexation of uranium and others through host-guest recognition.[12-15] This chelating systems can been also can be immobilized by impregnation on solid supports.[16, 17] More generally, interest in these structures has arisen because of their unique molecular architectures, which makes them suitable platforms for constructing host molecules that can selectively bind a variety of guest substrates, ranging from cations and anions to fullerenes. The special feature of these ligands is the conformational rigidity gained from the organisation of the chelating systems on both rims of the calixarene platform, in which the coordinated atoms are placed in positions that ensure the appropriate orientation of the donor groups for complexation.

The coordinating ability of calixarenes could be extended by the introduction of O-donor and N-donor atoms, such as in the calix[4]azacrowns, where azacrown bridges are attached to the calixarene platform.[18-20] These modified compounds show attractive properties based on their structures, especially when the azacrown bridges are fixed at the distal 1,3-positions.[21-24] The azacrown bridges can be designed to have amides and amine functionalities, which are both known for their capability to bind lanthanide and actinide ions via interactions with the carbonyl oxygen atoms of the amide groups,[25-28] and the nitrogen atom of the amino groups.[29-31] However, these compounds have been studied in regards to their complexation behaviour with lanthanide ions.[32-34]

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On the basis of these findings, it appeared interesting to evaluate such calix[4]azacrowns containing both amine and diamides groups for uranium extraction.

Here, we report the synthesis of two N-substituted calix[4]azacrowns, N-octylcalix[4]azacrown (NOCAC) and N-ethylhexylcalix[4]azacrown (NEHCAC), cyclised at distal 1,3-positions as efficient ligands for the extraction of uranium. Indeed, these ligands contain two different chelating sites: alkylamine with soft nitrogen donor atom, which should induce uranium selectivity, and two amide groups with hard oxygen donor atoms, which should enhance the complex stability and ligand solubility in the diluents. The synthesis, characterisation, and preliminary evaluations of the ligands for uranium extraction from sulfuric acid media in comparison to competitive ions have been carried out. Mechanistic investigations (slope method and NMR titration) indicate a 1:1 complexing species. The ligands showed the ability to extract uranium preferentially over other metal cations present in an equimolar leaching mixture. Also, the recovery of uranium has been established.

Results and discussion

Synthesis

N-Substituted calix[4]azacrowns were synthesised via a well-known synthetic route in three steps, as shown in Figure 1. 4-*tert*-Butyl-25,27-ethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene (**2**) was prepared by reacting the 4-*tert*-butylcalixarene with ethylbromoacetate in the presence of potassium carbonate, as described in the literature[35]. Then, the calixazacrown (**3**) was quantitatively obtained by amide coupling of the diester groups of calix[4]arene (**2**) with diethylenetriamine. The success of the cyclisation/amide formation on the calixarene lower rim was confirmed by NMR. The spectra exhibit a signal at 8.2 ppm, which corresponds to the resonance signals of the amide protons. Moreover, C=O amide group is characterised by a ^{13}C-NMR resonance signal located at 168.5 ppm, as well as a broad signal in the Fourier transform (FT)-IR spectrum at 1685 cm^{-1}. Finally, in order to increase the lipophilicity of the ligand, fatty alkyl chains (octyl and ethylhexyl) were introduced to the central amino group through the reaction of calix[4]arene (**3**) with the corresponding alkyl iodide/bromide in the presence of K$_2$CO$_3$ to afford the targeted N-substituted calix[4]azacrowns (**4a** NOCAC and **4b** NEHCAC).

Solvent extrac
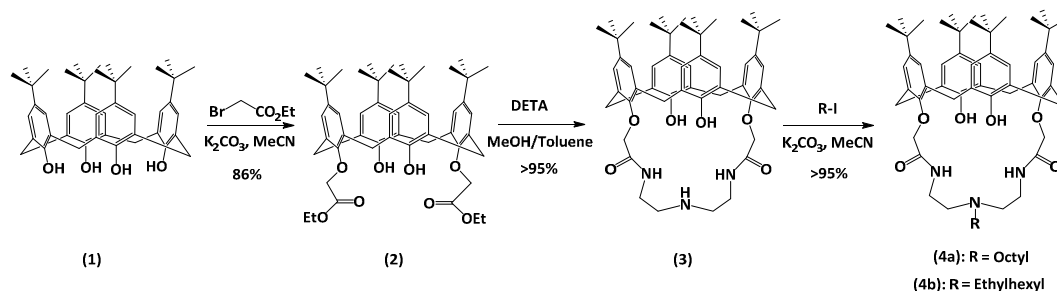
tion studies

The extraction profile of NOCAC and NEHCAC was established for U (VI), Mo(VI), Zr(IV), Ti(IV), La(III), Ce(III), and Fe(III), which are metals potentially present in uranium deposits. Equimolar concentrations of the target metals were chosen arbitrarily. Different solutions of NOCAC were prepared in dodecane/octanol (8.5/1.5, v/v). Octanol was used to avoid the formation of a third phase and to enhance the solubility of the ligand in the diluent. The effect of the ligand was studied from a metal/ligand ratio of 1:10 up to 1:50. The stoichiometry of the complex was estimated from the slope method, NMR titration, and mass analysis. Recovery of the extracted metals from the organic phase was successfully performed by stripping with ammonium carbonate, ammonium oxalate, and sodium carbonate.
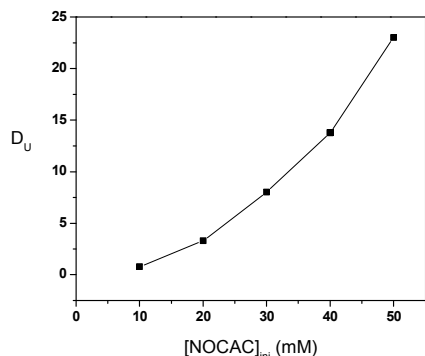
Effect of the feed acidity

The effect of varying the sulfuric acid concentration in the range 0.02–5 M on the extraction of U(VI) cations was investigated with NOCAC. Figure 2 shows the distribution coefficient values obtained for the extraction of uranium by 0.02 M of NOCAC from different feed acidity. The results show the clear dependence of the extraction efficiency of NOCAC on the feed sulfuric acid concentration. The distribution values decreased sharply with a slight increase in the sulfuric acid concentration from 0.02 M (D = 3.8) to 1 M (D = 0.23), which is in good agreement with the liquid-liquid extraction study reported for the extraction of uranium with tertiary amine ligands.[31, 36, 37] The reduced extraction capacity of the ligand with increasing sulfuric acid concentration is mainly due to the increase in competition from HSO$_4^-$ and SO$_4^{2-}$ anions. These ions, when present at high sulfuric acid concentrations, inhibit the uranyl sulfate complexes from interacting with the protonated amino calix[4]arene, resulting in a decrease in extraction.

Effect of the ligand concentration

The extraction of U(VI) with varying NOCAC concentrations was also investigated, and the results are shown in Figure 3. Increasing the concentration of the ligand from 10 to 50 mM, at 0.1 M H$_2$SO$_4$ aqueous feed solution, resulted in a progressive improvement in the distribution coefficient from 0.8 to 23, respectively.

The data presented in Figure 3 indicates that, at a first approximation, the ligand at 30mM extracts uranium efficiently from the aqueous solution, where about 90% of the uranium was extracted.

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Figure 1: Synthetic scheme for NOCAC (4a) and NEHCAC (4b).
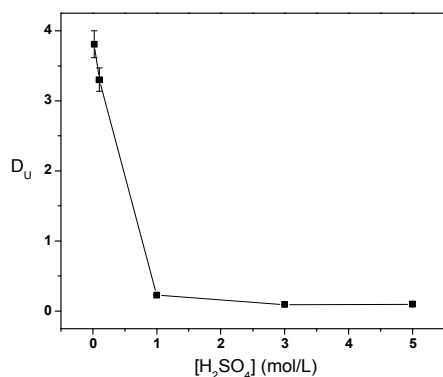
Figure 2: Effect of feed sulfuric acid concentration (0.02–5 M) on the distribution ratio of UO_2^{2+}. Organic phase: 0.02 M NOCAC in dodecane/octanol (83/17 v/v); aq. phase: 1 mM $UO_2(NO_3)_2$ in H_2SO_4. Aqueous to organic ratio (A/O) = 1.

spectra of uranyl nitrate, the free ligand (**LI**), and the metal/ligand complex (**LI-U**) complex (1:1).

Figure 4: Effect of the extractant concentration on the distribution ratios of U(VI). Organic phase: NOCAC 10–50 mM in dodecane/octanol (83/17 v/v). Aqueous phase: 1 mM $UO_2(NO_3)_3$ in 0.1 M H_2SO_4. A/O = 1. $LogD_U = f$(log [NOCAC]): $y = 0.968(\pm0.004)x - 0.025(\pm0.006)$, $R^2 = 0.999$.

Figure 3 : Effect of the extractant concentration on the distribution ratios of U(VI). Organic phase: NOCAC 10–50 mM in dodecane/octanol (83/17 v/v); aqueous phase: 1 mM $UO_2(NO_3)_3$ in 0.1 M H_2SO_4. A/O = 1.
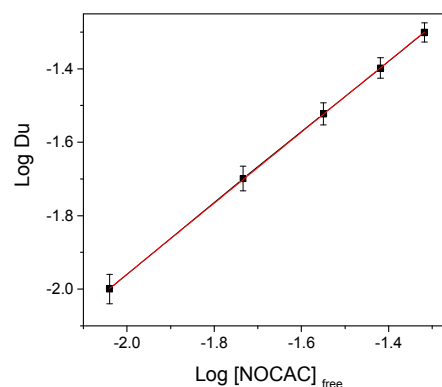
Slope method analysis

The plot of $logD_U$ versus the concentration of extractant should result in a straight line with a slope corresponding to the number of NOCAC molecules associated with the complex formed during the extraction. The fundamental stoichiometry of the U-NOCAC complex formed at 0.1 M H_2SO_4 feed was determined from the $logD_U$ value with the NOCAC free concentration (Figure 4). A straight line with a slope of 0.968 ± 0.004 was obtained, suggesting that the stoichiometry of complexation between the extractant and uranium is 1:1, which is consistent with the NMR and electrospray ionisation-mass spectrometry (ESI-MS) studies.

Determination of the complex structure

To determine the structure of the complex, NOCAC was reacted with uranium nitrate $(UO_2)(NO_3)\cdot5H_2O$ in a mixture of $CHCl_3/MeOH$ (1:1) and analysed spectroscopically.

IR spectroscopic study

The complexation of the uranyl cation via the amide carbonyl groups was confirmed by FT-IR analysis. Figure 5 shows the IR

The C=O stretching band of neat **LI** was observed at 1685 cm^{-1}, while the corresponding band after complexation was shifted to 1628 cm^{-1}. This redshift supports the results obtained in the ^{1}H- and ^{13}C-NMR analyses that the amidic carbonyl oxygen atoms of **LI** molecules contribute to the coordination of **LI** to U(VI). However, the asymmetric uranyl stretch, assigned to the stretching band (υ_3) of UO_2 (O=U=O),[38-40] found at 940 cm^{-1} did not shift on complexation. The fact that the $\upsilon3$ band is not affected by complexation suggests the uranyl is not totally dehydrated during its coordination with the amidic oxygens.[41]

Mass spectroscopy study

Electrospray ionisation mass spectrometry (ESI-MS) was used to confirm the stoichiometry of the complexes formed between (**LI**) and uranium. Species were identified by comparison to the calculated isotopic patterns, as shown. The spectrum in Figure 6 shows different peaks corresponding to $[(LIH)(UO_2)(NO_3)(OH)]^+$, $[(LIH)(UO_2)(OH)_2\cdot3H_2O]^+$, $[(LIH)(UO_2)(NO_3)(OH)\cdot H_2O]^+$, $[(LIH)(UO_2)(OH)_2\cdot4H_2O]^+$, $[(LIH)(UO_2)(NO_3)\cdot2H_2O]^+$, and $[(LIH)(UO_2)(NO_3)_2]^+$ located at m/z 1294.6, 1304.7, 1311.6, 1321.7, 1330.0, and 1338.7, respectively. These obtained peaks indicate a 1:1 stoichiometry in the gas phase.
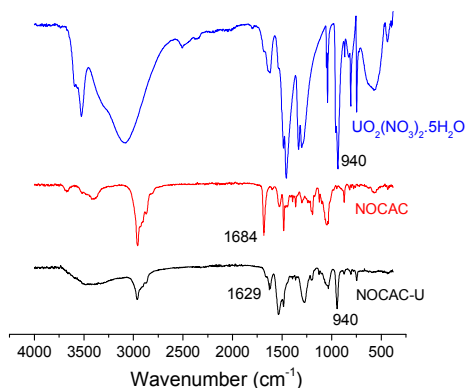
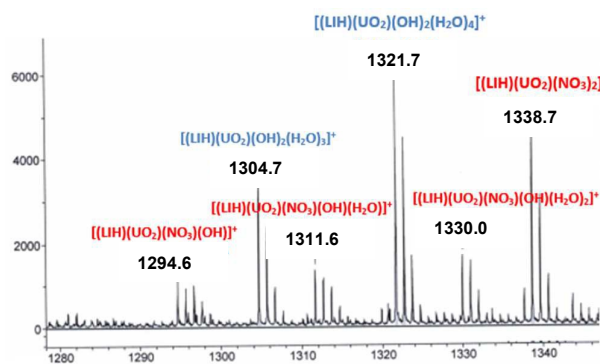Figure 5 : IR spectra of uranyl nitrate, free LI, and the LI-U complex.

Figure 6: Mass spectrum of LI complexes with UO_2^{2+} cations.

NMR studies

Figure 7 shows the NMR titration spectra of NOCAC with variable amounts of uranyl nitrate. Significant shifts and splittings of the resonance signals were observed with increasing uranyl concentration until a 1:1 metal-ligand ratio.

The characteristic signals of the chelating sites of the free ligand, including the phenolic OH groups initially present at 6.42 ppm, the amide NH groups at 8.19 ppm, and the methylene groups linked to the amine nitrogen atom at 2.75 and 2.43 ppm, disappeared completely in the 1H-NMR spectrum when [NOCAC]/[$UO2^{2+}$] = 1:1.

This observation from the 1H-NMR titration is in good agreement
with the
stoichiometr
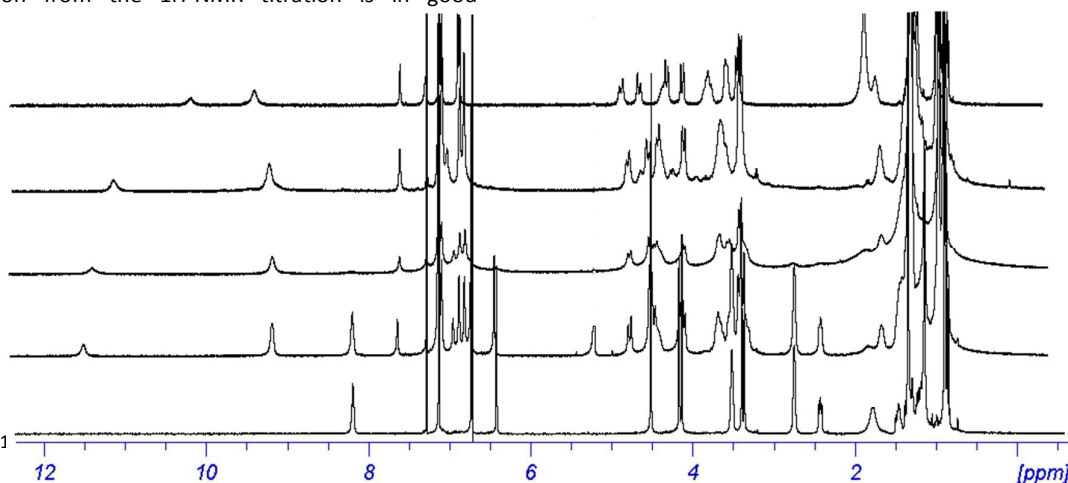
y of the complexation between the ligand NOCAC and uranium estimated by the slope method. The result from ^{1}H-NMR analysis of the free ligand and the complex suggests a dissymmetric structure of the calixarene[42], which is indicated by the shifts in the resonance signals (two singlets) corresponding to the Ar-H protons into four singlets, in addition to the splitting of the methylene bridging Ar-CH$_2$-Ar, which is observed in 2 AB systems, (Figure 7 and Table SI-1 see supporting information).

The analysis of the ^{1}H- and ^{13}C-NMR spectra suggests a complex in a partially flattened cone conformation, in which two amidic oxygens and one phenolic OH are involved in the complexation (Figure 8).

The contribution of the carbonyl groups appears from the downfield shift of the amide NH proton from 8.19 ppm in the ^{1}H-NMR spectrum of the free ligand to 9.42 ppm in the ^{1}H-NMR spectrum of the complex. The signal of the phenolic -OH groups initially located at 6.42 ppm was split into two resonance signals, located at 7.3 and 7.61 ppm, respectively. Thus, the appearance of two different signals corresponding to the two phenolic -OH suggests that one of the OHs is involving in a strong interaction with the uranium nucleus, which explains the dissymmetry of the complex structure and the resulting partial flattened cone conformation. Indeed, the OH displaced at 7.61 ppm was not affected by increasing the concentration of uranium, whereas the other OH shifts gradually from 6.42 to 7.3 ppm in the ^{1}H-NMR spectra during complexation.

The appearance of two pairs of axial/equatorial AB patterns of the characteristic bridging methylene groups (Ar-CH$_2$-Ar) at 3.43, 3.46, 4.13, and 4.32 ppm in the ^{1}H-NMR spectra during complexation confirms this hypothesis, which is in agreement with the data obtained from the ^{13}C-NMR spectrum, which showed only one signal located at 31 ppm corresponding to the Ar-CH$_2$-Ar in a cone conformation (Figure SI-1 see supporting information).[43] Moreover, the AB system located at 4.88–4.68 ppm, which corresponds to the resonance signal of the Ar-O-CH$_2$-C(O) moiety, indicates the high rigidity of the complex. These observations have been confirmed by 2D analyses (Figure SI-2, SI-3 and SI-4 see supporting Information).

The dissymmetry, as well as the flattened cone conformation of the structure, was finally confirmed using density functional theory (DFT) calculations, as shown in Figure 9.

Figure 7: NMR titration spectra of the ligand NOCAC with $UO_2(NO_3)_2$ at different ratios varied from ([NOCAC]/[UO_2^{2+}] = 1:0 to 1:2), [NOCAC] = 30 mM in $CDCl_3$.
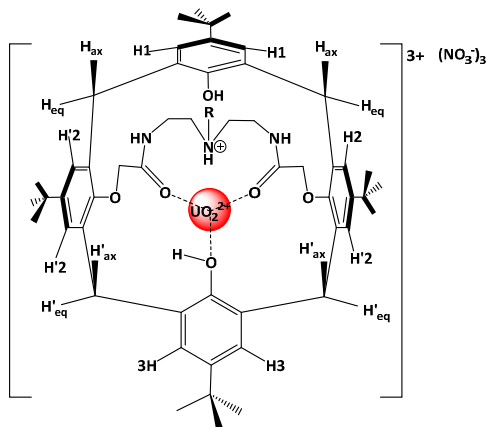

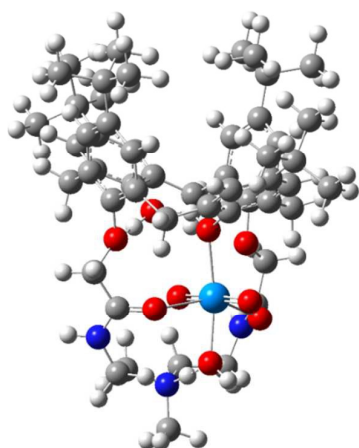Figure 8: The proposed structure of the U-NOCAC complex, UO_2^{2+}= red ball.

Figure 9: Structure obtained by DFT calculations on the U-NOCAC complex.

The chelating behaviour of the macrocycle was also evaluated through molecular modelling of its uranyl complexes (DFT calculations) with the B3LYP functional and 6-31G basis set for H, C, N, and O and the Stuttgart RSC 1997 effective core potential (ECP) for U. The modelling is based on the structure of the ligand that has been obtained by single X-ray diffraction (Figure SI-5 see supporting information). The proposed

structure by DFT allow to highlight the proton position and movement observed by the NMR study.

The [UO_2-NOCAC] structure was also obtained in a partially flattened cone conformation, where one of the phenol groups, as well as the amide carbonyls, interact with the uranyl cation. The structure also shows the presence of a water molecule bridged between the nitrogen atom of the amine and uranium nucleus.

Proposed mechanism

Based on the preliminary study focused on the determination of the structure of the uranyl-ligand complex, a mechanism can be suggested for the steps following a preliminary protonation of the amine site by sulfuric acid (whatever the acid concentration), as represented by the following equation:

$$\overline{2L} + H_2SO_4 \leftrightarrow \overline{(LH)_2SO_4}. \qquad eq\ (1)$$
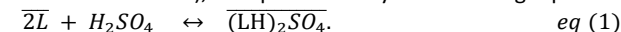
Here, $\overline{(LH)_2SO_4}$ represents the dimer form of the protonated extractant, and the overbar refers to species in the organic phase. The absence of t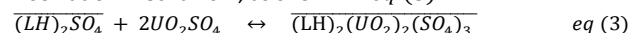he overbar denotes aqueous species. Uranyl sulfate species can exist as UO_2SO_4, $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$, depending on the concentration of sulfuric acid. Referring to the literature,[44, 45] at pH 1, the major species of the aqueous uranyl sulfate is UO_2SO_4, with a minor quantity of $UO_2(SO_4)_2^{2-}$. At a high concentration of H_2SO_4, bisulfate and trisulfate anions exist as major species.

At low acidity, two possibilities can drive the extraction of uranium based on:

A combination of solvation and anion exchange mechanism involving water molecules, as represented by $eq\ (2)$.

$$\overline{(LH)_2SO_4} + 2UO_2SO_4 + 2H_2O$$
$$\leftrightarrow \overline{2[(LH)(UO_2)(SO_4)(OH)_2]} + H_2SO_4\ \ eq\ (2)$$
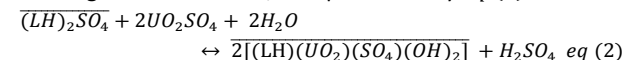
A solvation mechanism, as shown in $eq\ (3)$.

$$\overline{(LH)_2SO_4} + 2UO_2SO_4 \leftrightarrow \overline{(LH)_2(UO_2)_2(SO_4)_3} \qquad eq\ (3)$$

At high sulfuric acid concentrations, an anionic exchange mechanism takes place according to $eq\ (4)$.

$$\overline{(LH)_2SO_4} + 2UO_2(SO_4)_2^{2-}$$
$$\leftrightarrow \overline{(LH)_2(UO_2)_2(SO_4)_3} + 2SO_4^{2-}\ \ eq\ (4)$$
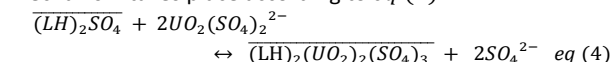
Finally, whatever the acid concentration, if we consider that no water molecules are involved in the extraction mechanism, only one complex system can be suggested, as shown in Figure 10 below.

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Figure 10: Suggested ligand-uranyl extracted species.

Ligand selectivity study

For comparison purposes, the performance of 0.05 M NEHCAC toward the extraction of uranium from 0.1 M H$_2$SO$_4$ was evaluated, and the distribution coefficient was found to be about 56 (Table SI2, see supporting Information). The performance is nearly three times higher a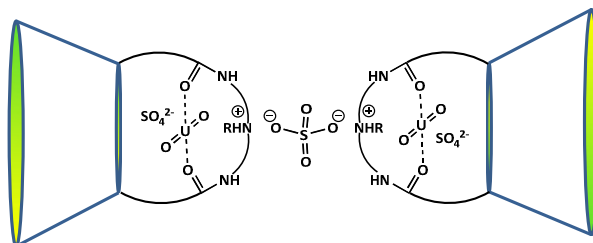fter replacing the linear alkyl chains of the amine by branched alkyl ones. The extraction is enhanced by the presence of the 2-ethylhexyl chains, as reported in the literature.[46, 47] In addition, the positive influence on the efficiency arising from the 2-ethylhexyl chain at the central amino chelating site in NEHCAC could be due to a different conformation of the ligands around the guest atom. Solvent extraction studies of several other cations were carried out to evaluate the selectivity of the ligand toward uranium.

Extraction experiments

The potential (efficiency and selectivity) of NOCAC and NEHCAC was studied with respect to the preferential extraction of U over Mo, Zr, Ti, Ce, Fe, and La in a simulated leaching solution. The ligands (20 mM) in dodecane/octanol (8.3/1.7 v/v) were mixed with a mixture of the metal cations, each having a concentration of 25 ppm. As for the extraction with U(VI) alone, the extraction data presented in Table 1 and Table SI4 show clearly that NEHCAC is more efficient than NOCAC, in which the D_U of NEHCAC is about three times higher than that of NOCAC.

Table 1: Distribution values and selectivity factors of NOCAC and NEHCAC toward U, Mo, Zr, Ti, Ce, Fe, and La cations from 0.1 M H$_2$SO$_4$ aqueous solution at 25 °C.

|		U	Mo	Zr	Ti	La	Fe	Ce
NOCAC	Du	6.8	2.9	0.2	0.05	0.03	0.03	0.03
	$S_{(U/M)}$		2.4	31	137	>200	>200	>200
NEHCAC	Du	17	5.3	0.6	0.05	0.01	0.02	0.01
	$S_{(U/M)}$		3	30	332	>1600	830	>1600

Organic phase: 20 mM NOCAC or NEHCACin 83% dodecane/17% octanol (v/v); aqueous phase: 25 ppm of each metal in 0.1 M H$_2$SO$_4$.

For both ligands, similar behaviour was observed with respect to the extraction of the cations. The ligands are selective for U(VI) with respect to other cations with separation factors higher than 10, except for molybdenum.

Mo and U have a similar behaviour in regards to their extraction, this is due to an ionic radii very close and to their coordination number.[48, 49] As for U, the extraction of Mo may

result from the chemical complexation of Mo with N inside N-alkyl calix[4]azacrowns which takes place outside the cavity. For both Mo and U the chemical complexation is relatively similar as proposed in the literature which describe the extraction of Mo by diamide or trialkyl amine.[50, 51]

The effect of the concentration of the ligand on the extractability and the selectivity of uranium from the same leaching solution was studied by varying the concentration of NOCAC from 0.01 to 0.05 M. The results presented in Figure 11 show that, at a low ligand concentration (6.6 mM), a significant amount of U and Mo were extracted without any remarkable extraction for other elements.
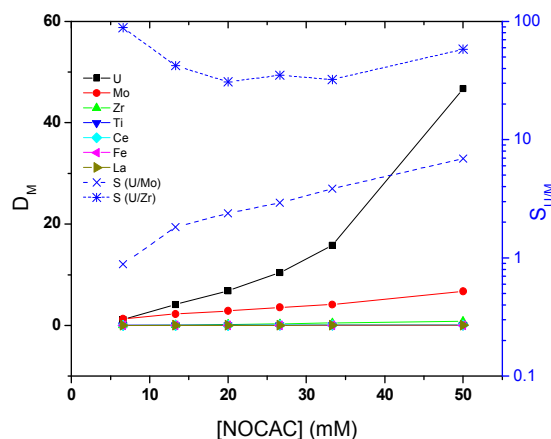
Figure 11: Effect of the concentration of NOCAC on the distribution values and selectivities, $S_{(U/M)}$. Organic phase: NOCAC 0.01–0.05 M in dodecane/octanol (83/17 v/v). Aqueous phase: 25 ppm of each metal in 0.1 M H$_2$SO$_4$.

The extraction of metal cations increased gradually on increasing the concentration of NOCAC, and, at 50 mM, the ligand extracts mostly U (D$_U$ = 46.75), a significant amount of Mo (D$_{Mo}$ = 6.76), and a small amount of Zr (D$_{Zr}$ = 0.8). However, no real extraction was observed for Ti, Ce, Fe, and La at any concentration (D < 0.05). The selectivity of U over Mo, $S_{(U/Mo)}$, increased on increasing the ligand concentration from 1 to 7, while the selectivity of U over Zr, $S_{(U/Zr)}$ showed a slight decrease on increasing the ligand concentration, having a value around 60 over the concentration range of the ligand.

These results are encouraging and can be applied for the selective extraction of U(VI), even though a significant extraction of molybdenum is observed. Indeed, the concentration of molybdenum in uranium ores is smaller than that of uranium by about 31 times.[31]

Stripping and recovery of U

After the extraction steps with NOCAC and NEHCAC systems, the loaded organic solutions contain, respectively, about 85% and 92%of the U(VI) initially present in the feed sulfuric acid.. Stripping or back-extraction experiments were implemented to strip uranium quantitatively from the organic phases using aqueous bases such as ammonium carbonate and ammonium

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oxalate with an aqueous to organic (A/O) ratio of 1 or 5. Both basic solutions showed promising results which allow to recover the uranium in its carbonate or oxalate form. As shown in Table 2, uranium can be totally recovered after stripping the organic phases with the basic solutions with an A/O ratio of about 5. In this condition, the molybdenum is also mainly stripped from the organic phase.

Actually, other stripping solutions, washing steps, or methods, such as precipitation, are still under investigation to selectively recover the uranium. Indeed, usually, the molybdenum dose is not co-precipitated with uranium but can be removed by bleeding after the uranium precipitation.[52]

Table 2: Recovery of the extracted U from an extracting phase (20 mM ligand in dodecane/octanol (8.3/1.7)) by an aqueous solution (A/O = 1 or 5).

	Stripping solution	A/O	Metal recovery (%)			
			U	Ti	Mo	Zr
NOCAC	$[(NH4)_2C_2O_4]$	1	82	11	77	68
	(sat)	5	95	-	87	90
	$[(NH4)_2CO_3]$	1	76	-	76	52
	(1 mol/L)	5	100	92	100	93
	$[M]_{org}$ ppm		**22**	**1.3**	**18.3**	**4.2**

	Stripping solution	A/O	Metal recovery (%)			
			U	Ti	Mo	Zr
NEHCAC	$[(NH4)_2C_2O_4]$	1	85	33	86	83
	(sat)	5	89	2	91	89
	$[(NH4)_2CO_3]$	1	80	13	82	65
	(1 mol/L)	5	91	5	97	74
	$[M]_{org}$ ppm		**23.8**	**1.2**	**20.8**	**8.4**

Experimental

Chemicals and analysis

Chemicals (analytically pure) were purchased from Sigma-Aldrich, Eburon Organics, or Alfa Aesar and were used without further purification. Anhydrous solvents were purchased from Acros (AcroSeal®).

Reactions were monitored by thin-layer chromatography (Merck TLC Silica Gel 60 F254). Flash chromatography was performed using a Combiflash Agilent Intelliflash 971-FP.

NMR analyses were performed on a Bruker 400 Ultrashield VS spectrometer. Displacements are reported in parts-per-million using the solvent ($CDCl_3$: 7.26 ppm for ^1H; 77.16 ppm for ^{13}C) as an internal reference.

Metal concentrations were determined using a Spectro ARCOS ICPAES spectrometer. Background acquisition was made before measurement. ESI-MS was performed on a Flexar SQ 300 MS instrument. DFT calculations were carried out using the B3LYP functional and 6-31G basis set for H, C, N, and O. For U, the Stuttgart RSC 1997 ECP was used.

Synthesis

Preparation of 25,27-ethoxycarbonylmethoxy-26, 28-dihydroxycalix[4]arene (2)

A solution of the starting *tert*-butylcalixarene (4 g, 6.17 mmol) and K_2CO_3 (0.93 g, 6.78 mmol) in dry acetonitrile was stirred under nitrogen for 1 h; subsequently, bromoethylacetate (2.11 g, 12.64 mmol) was introduced. The reaction mixture was stirred for 16 h, and the crude product was concentrated under reduced pressure, followed by the addition of cold methanol. The obtained precipitate was filtered and washed with cold methanol and dried to obtain the afforded compound **2** as a white powder in 86% yield.

^1H-NMR (400 MHz, $CDCl_3$) δ [ppm]: 1.0 (s, 18 H, CC**H₃**), 1.29 (s, 18 H, CC**H₃**), 1.36 (t, J = 7.2 Hz, 6H, -CH₂-C**H₃**), 3.35 (d, 4 H, J = 14.2 Hz, inner of Ar-C**H₂**-Ar), 4.32 (q, J = 7.2 Hz, 4H, O-C**H₂**-CH₃), 4.47 (d, 4 H, J = 14.2 Hz, outer of Ar-C**H₂**-Ar), 4.74 (s, 4 H, Ar-*O*-C**H₂**-*CO*), 6.84 (s, 4H, Ar-**H**), 7.05 (s, 4H, Ar-**H**), 7.08 (s, 2H, Ar-O**H**).

^{13}C-NMR (100 MHz, $CDCl_3$) δ [ppm]: 14.2, 31.1, 31.7, 31.8, 33.8, 34.0, 61.3, 72.4, 125.1, 125.8, 128.0, 132.5, 141.6, 147.2, 150.2, 150.7, 169.3.

Preparation of calix[4]azacrown (3)

Cavitand **3** was prepared by mixing calixarene **2** (3.3 g, 4.02 mmol) with an equivalent amount of diethylene triamine (0.414 g, 4.02 mmol) in 50 mL of a mixture of methanol/toluene (1:1) and refluxed overnight at 80 °C. The solvent was evaporated under reduced pressure, and the resulting white product was then dried under vacuum to give the pure compound quantitatively, 3.34 g.

^1H-NMR (400 MHz, $CDCl_3$) δ [ppm]: 0.9 (s, 18 H, CC**H₃**), 1.35 (s, 18 H, CC**H₃**), 1.36 (t, J = 7.2 Hz, 6H, -CH₂-C**H₃**), 2.97 (t, J = 5.2 Hz, 4H, NH-CH₂-C**H₂**-CO), 3.38 (d, 4 H, J = 13.2 Hz, inner of Ar-C**H₂**-Ar), 3.56 (t, J = 5.2 Hz, 4H, NH-C**H₂**-CH₂-CO), 4.19 (d, 4 H, J = 13.2 Hz, outer of Ar-C**H₂**-Ar), 4.74 (s, 4 H, Ar-*O*-C**H₂**-*CO*), 6.373 (s, 2H, Ar-O**H**), 6.74 (s, 4H, Ar-**H**), 7.15 (s, 4H, Ar-**H**),

^{13}C-NMR (100 MHz, $CDCl_3$) δ [ppm]: 30.9, 31.3, 31.7, 33.9, 34.0, 40.1, 49.0, 74.8, 125.3, 128.3, 129.0, 131.6, 143.0, 148.0, 148.9, 149.8, 168.5.

General procedure for the preparation of *N*-alkyl calixazacrown (4a,b)

A mixture of the calixazacrown (**3**) (1 g, 1.2 mmol) and K_2CO_3 (0.116 g, 0.84 mmol) in dry acetonitrile (20 mL) was stirred under nitrogen for 1 h; subsequently, iodooctane or 2-ethylhexyl iodide (0.317 g, 1.32 mmol) were introduced. The resulting mixture was refluxed overnight; then, the solvent was evaporated under vacuum. Then, 30 mL of CH_2Cl_2 was added to the crude product, and the resulting salts were isolated by filtration. Finally, the dichloromethane was evaporated to afford the desired product in quantitative yield for both *N*-octyl calixazacrown (**4a**) and *N*-ethylhexyl calixazacrown (**4b**).

N-Octyl calixazacrown (4a)

^1H-NMR (400 MHz, $CDCl_3$) δ [ppm]: 0.87 (t, J = 7.2 Hz, 3 H, CH₂C**H₃**), 0.89 (s, 18 H, CC**H₃**), 1.14 (m, 10H, C**H₂**), 1.34 (s, 18 H, CC**H₃**), 1.45 (m, 2 H, N-CH₂-C**H₂**-hexyl), 2.43 (t, 2H, J=7.6Hz, N-C**H₂**-heptyl), 2.75 (m, 4H, NH-C**H₂**-CH₂-NH), 3.36 (d, 4 H, J = 14.2 Hz, inner of Ar-C**H₂**-Ar), 3.52 (m, 4H, NH-CH₂-C**H₂**-NH), 4.15 (d, 4 H, J = 14.2 Hz, outer of Ar-C**H₂**-Ar), 4.52 (s, 4 H, Ar-O-

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C**H₂**-CO). 6.42 (s, 2H, Ar-O**H**), 6.73 (s, 4H, Ar-**H**), 7.13 (s, 4H, Ar-**H**). 8.2 (t, 2H, J = 5.2 Hz, N**H**-CO).

^{13}C-NMR (100 MHz, CDCl₃) δ [ppm]: 14.15, 22.63, 27.30, 27.42, 29.39, 29.65, 30.86, 31.33, 31.68, 31.89, 33.95, 38.51, 54.98, 74.62, 125.31, 125.89, 127.79, 131.59, 142.83, 148.00, 148.69, 149.87, 168.47.

ESI-MS *m/z*: 944.5 [(M+H)⁺].

N-Ethylhexyl calixazacrown (4b)

^{1}H-NMR (400 MHz, CDCl₃) δ [ppm]: 0.81 (t, 6 H, CH₂C**H₃**), 0.84 (s, 18 H, CC**H₃**), 1.23 (m, 6H, C**H₂**), 1.34 (s, 18 H, CC**H₃**), 1.49 (m, 3 H, C**H** and C**H₂**), 2.18 (dd, 1H, J = 4.4 Hz, N-C**H₂**), 2.34 (dd, 1H, J = 4.4 Hz, N-C**H₂**), 2.56 (dd, 2 H, J = 3.6 Hz, N-CH₂-C**H₂**-NH), 2.86 (m, 2H, N-CH₂-C**H₂**-NH), 3.35 (d, 2 H, J = 14.2 Hz, inner of Ar-C**H₂**-Ar), 3.41 (d, 2 H, J = 14.2 Hz, inner of Ar-C**H₂**-Ar), 3.6 (s, 2 H, m, 2H, N-C**H₂**-CH₂-NH). 4.12 (d, 2 H, J = 14.2 Hz, outer of Ar-C**H₂**-Ar), 4.17 (d, 2 H, J = 14.2 Hz, outer of Ar-C**H₂**-Ar), 4.45 (d, 2 H, J = 7.4 , Ar-O-C**H₂**-CO), 4.57 (d, 2 H, J=7.4 , Ar-O-C**H₂**-CO), 6.47 (s, 2H, Ar-O**H**), 6.71 (s, 1H, Ar-**H**), 6.74 (s, 1H, Ar-**H**), 7.12 (s, 1H, Ar-**H**), 7.14 (s, 1H, Ar-**H**), 8.19 (t, 2H, J = 5.2 Hz, N**H**-CO).

^{13}C-NMR (100 MHz, CDCl₃) δ [ppm]: 10.16, 14.15, 23.24, 23.79, 28.86, 30.93, 31.23, 31.38, 33.93, 33.96, 36.92, 38.45, 55.4, 58.53, 74.68, 125.21, 125.42, 126.14, 127.55, 128.04, 131.33, 131.81, 142.88, 148.01, 148.75, 149.87, 168.54.

ESI-MS *m/z*: 944.5 [(M+H)⁺].

Preparation of the LI-U complex

Solutions of uranyl nitrate in methanol (0.5 mL) and NOCAC in chloroform (0.5 mL) were mixed in an open 2-mL vial at various UO₂²⁺/NOCAC ratios, ranging from 0.25:1 to 2:1.

The obtained solutions were heated for 1 h at 60 °C and then left to stand overnight at room temperature; subsequently, they were dried under vacuum to obtain the complex as brown powder.

^{1}H-NMR (400 MHz, CDCl₃) δ [ppm]: 0.87 (t, J =7.0 , 3 H, CH₂C**H₃**), 0.89 (s, 18 H, CC**H₃**), 1.23 (m, 10H, C**H₂**), 1.34 (s, 18 H, CC**H₃**), 1.75 (m, 2 H, N-CH₂-C**H₂**-hexyl), 3.43 (d, 2H, J = 8 Hz, inner of Ar-C**H₂**-Ar), 3.47 (d, 2H, J = 8 Hz, inner of Ar-C**H₂**-Ar), 3.59 (m, 4H, N-C**H₂**-CH₂-NH and N-C**H₂**-heptyl), 3.81 (m, 4H, N-C**H₂**-CH₂-NH and N-CH₂-C**H₂**-NH), 4.14 (d, 2 H, J = 16 Hz, outer Ar-C**H₂**-Ar), 4.32 (d, 2 H, J = 13.2 Hz, outer Ar-C**H₂**-Ar), 4.37 (m, 2H, N-CH₂-C**H₂**-NH), 4.66 (d, 2H, J = 15.2 Hz, Ar-O-C**H₂**-CO), 4.88 (d, 2H, J = 15.2 Hz, Ar-O-C**H₂**-CO), 6.87 (s, 2H, Ar-**H**), 6.90 (s, 2H, Ar-**H**), 7.09 (s, 2H, Ar-**H**), 7.13, (s, 2H, Ar-**H**), 7.30 (s, 2H, Ar-O**H**-U), 7.16 (s, 2H, Ar-O**H**), 9.40 (m, 2H, N**H**-CO).

ESI-MS *m/z*: 1338.66 [(M+H+UO₂(NO₃)₂⁺].

Extraction experiments

The metal stock solutions were prepared at the desired acidity from 10000 mg L⁻¹ ICP standards (in 1% HNO₃). The desired concentrations were prepared by dilution using ultrapure water (MilliQ, Millipore, >18 MΩ cm⁻¹) and the acidity was adjusted with sulfuric acid or nitric acid.

Different organic solutions were prepared from NOCAC or NEHCAC at different specific concentrations in a mixture of dodecane/octanol (83/17 v/v). Octanol was used as a phase modifier. Turbid solutions were obtained when solutions

without the phase modifier were mixed with the sulfuric acid aqueous phase.

Organic phases were pre-equilibrated with an aqueous phase at the same acidity as the extraction step without metal cations. The pre-equilibrated organic phases were then mixed with an equal volume of an aqueous acidic stock solution of the cations in a thermostated shaker (Infor-ht® Ecotron) at 25 °C for 1 h at 400 rpm. The phases were separated after centrifugation at 4000 rpm for 30 min (Sigma 3-16 PK).

The metal distribution ratios were measured under batch conditions. Equal volumes of aqueous and organic solutions were vigorously shaken at 25 °C to obtain a good emulsion by means of an automatic vortex shaker equipped with a thermostated cell for 30 min for equilibrium distribution measurements. After phase separation by centrifugation, the aqueous phase was analysed by ICP-AES (Spectro ARCOS) to measure the concentrations of cations. From the results obtained by ICP-AES, the distribution ratios (D_M = [Mⁿ⁺]org /[Mⁿ⁺]aq) were determined at equilibrium. The experiments were carried out in duplicate measurements with a precision of ± 5%.

Back-extraction experiments

The loaded organic phase was stripped with solutions of ammonium carbonate, ammonium oxalate (typically 0.5 M), and sodium carbonate. Back-extraction was performed at room temperature (22–25 °C) by mixing equal volumes of organic and aqueous phases for 1 h (A/O ratio of 1). After separation by centrifugation (4000 rpm for 10 min), the metal concentrations were measured in the aqueous phase by ICP/OES.

Conclusions

Two *N*-substituted calix[4]azacrown extractants in 1,3-alternate conformation were synthesised in yield (>80%) and characterised using ^{1}H, ^{13}C, DEPT, COSY, and HSQC-NMR, as well as ESI-MS and DFT studies. The two ligands were investigated for the extraction of uranium from sulfuric acid solution. Preliminary extraction studies and mechanistic investigations have been performed for the *N*-octylcalix[4]azacrown (NOCAC) ligand. The effect of various parameters such as the feed acidity and NOCAC concentration were studied. The variation of the concentration of NOCAC at a constant uranium concentration and specific acidity has been studied to determine the stoichiometry of the extracted complex. The slope analysis method indicates a 1:1 molar ratio for U:NOCAC in the extracted complex. This was also supported by NMR titration experiments. Selectivity studies using NOCAC and NEHCAC have been performed on a leaching solution containing seven metals representative of uranium ores. The results highlight that the NOCAC and NEHCAC molecules are selective extractants for uranium over other metal ions present in the simulated leach solution. The extraction of uranium was enhanced on replacing the linear alkyl chains of the amine by branched alkyl chains. Successful stripping and recovery of the extracted metals by both ligands

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have been recovered from the organic phase using ammonium carbonate and ammonium oxalate.

Conflicts of interest

There are no conflicts to declare.

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