Perrhenate and pertechnetate complexation by an azacryptand in nitric acid medium†

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Technetium is present as the pertechnetate anion in spent nuclear fuel solutions, and its extraction by several extractant systems is a major problem for the liquid–liquid extraction processes used to separate uranium and plutonium. To prevent technetium extraction into the organic phase, a complexing agent may be added to the aqueous nitric acid phase to selectively bind the pertechnetate anion. In the present study, liquid–liquid extraction experiments reveal that technetium distribution ratios are considerably lowered with addition of an azacryptand, which is a good receptor for pertechnetate anion recognition. This ligand is able to overcome the Hofmeister bias and selectively bind techetium in nitric acid solution. Coordination studies using infrared and Raman spectoscopies and DFT calculations show the formation of an inclusion complex with hydrogen bonds stabilizing the oxo-anion within the cavity. For the first time, the cage molecules are studied for an extraction process.

Introduction

The design of anion receptors with high affinity and selectivity in water remains a key challenge in supramolecular chemistry.1-2 Among these anions, the recognition of TcO_4^- and ReO_4^- (used as an inactive surrogate of technetium) is difficult due to their relatively large size and low charge density.3 Technetium can be found in nuclear medicine for both diagnostic and therapeuthic applications, but its main production source is as fission product in nuclear reactors. Indeed, technetium is produced artificially in nuclear reactors by fission of 235U, with a relatively high fission yield (6.06%).4,5 Among the forty-five isotopes of Tc reported, 99Tc is the most abundant in spent nuclear fuel reprocessing solutions. 6 Due to its high mobility and long half-life (2.1×10^5 years), 99Tc is considered as one of the most problematic radionuclides in the spent nuclear fuel management.7,8 In solutions of spent nuclear fuel in nitric acid, and in absence of reducing agent, the technetium oxidation state is +VII, which is the most stable oxidation state in nitric acid, and forms pertechnetic acid (strong acid). This acid is easily dissociated9–11 to form H+ and the oxo-anion TcO_4^-. Without special care, Tc is found in all process steps and in all end products of the nuclear fuel cycle. It may be responsible for hydrazine destruction12,13 and lower decontamination factors of uranium and plutonium. In the PUREX process (plutonium and uranium refining by extraction), Tc is co-extracted with zirconium, uranium and plutonium8,14–17 as mixed complexes with TBP (TriButyl phosphate) in the organic phase. Hence, to decrease organic phase Tc concentration, the solvent undergoes a further scrubbing operation, known as “technetium scrubbing”, where it comes into contact with a highly concentrated nitric acid solution.18 Similarly, technetium could also be a major problem in the UREX19,20 process (uranium extraction) studied in the United States, or any other process aiming at recovering uranium from spent nuclear fuel solutions. For reprocessing used nuclear fuel with higher plutonium content, new extractants are studied as alternatives to the TBP molecule to selectively extract uranium(VI) and plutonium(IV) from spent nuclear fuel solutions.21–24 The N,N-dialkylamide MOEHA (N-methyl-N-octyl-(2-ethyl)hexanamide)25 is one of these alternative extractants. However, as observed with TBP, the pertechnetate anion is co-extracted with uranium as a mixed complex with the monoamide1 in the organic phase.

To prevent the extraction of technetium into the organic phase, several approaches have been considered in the literature. In the UREX process, the nitrosylation of technetium during its reduction by acetohydroxamic acid (AHA), used as reductive agent of Np and Pu to avoid their extraction, results in the formation of technetium species that are not extracted. However, further studies are needed to determine whether the presence of actinides in the solution will affect the formation of theses complexes.26Other methods27 which have been largely studied for the U–Tc partition are the solid phase separation or its precipitation. Anion exchange resins26,28–31 based on tertiary amine provide a good selectivity for the pertechnetate anion towards uranyl cation depending on the elution conditions. In their work, Poineau et al.28 obtained the Tc metal after precipitation of TcO4- as (n-Bu4)NTcO4 by pyrolysis and steam reforming under argon. The recovery of Tc demonstrated that a reasonable yield of Tc metal was achievable directly from the eluent. However, this does not constitute a likely industrial-scale process. Another alternative to improve uranium and plutonium decontamination factors versus Tc consists of the addition of a ligand in the aqueous phase, which selectively binds the per- technetate anion in nitric acid medium, decreasing its extraction into the organic phase, whereas uranium and plutonium are still extracted into the organic phase. The objective here is to find ligands that are selective for TcO4− over NO3−, knowing that the latter is the main anionic constituent of the aqueous phase in such processes (with [NO3−] 1300 times higher than [TcO4−]). The recognition of the pertechnetate anion in nitrate medium is then a very challenging task because the ligand has to overcome the Hofmeister bias,32 in a solution where the concentration of nitrate ions is far much higher. The Hofmeister bias states that nitrate anions with a higher charge density and smaller size than ReO4−/TcO4− anions have a higher affinity with organic hosts.27 In order to overcome the Hofmeister bias, one of the key strategy is to bind the oxo- anion inside an artificial cavity that presents complementary hydrogen bonding possibilities: for maximal binding interaction and selectivity, the cavity must match the size and the shape3 of ReO4−/TcO4−. In addition, the ligand requires a degree of rigidity33 to reduce the loss of entropy and conformational strain associated with the rearrangement of the receptor to the binding conformation. Thus, if the fit and the rigidity prevent nitrate anions from being accommodated, selective complexation of the pertechnetate and perrhenate anions can be achieved.34For the removal of Tc from high-level radioactive waste, Sasaki35,36 et al. studied several masking agents for technetium or rhenium (used as a surrogate of Tc)37 in 0.2 M HNO3. Several water miscible reagents with soft N- and S-donor atoms have been tested: diaminopropane (DAP), ethylenediamine (ED), diethylenediamine (DT) and cysteamine (CA). In their extraction systems, N,N',N',N",N"-hexaoctylnitrilotriacetamide (NTAamide) or N,N,N',N'-tetraoctymethyliminodiacetamide (MIDOA) were used at 0.1 M in n-dodecane. They succeeded in drastically reducing the rhenium distribution ratio from 89.2 (without any ligand in the aqueous phase) to 0.13 and 0.12 for DT and CA, respectively, with MIDOA as the extracting agent, and from 201 to 0.06 with NTAamide(C8) for the same extrac- tants. However, these experiments were performed without any uranium in the aqueous phase, despite the fact that technetium is mainly co-extracted with uranium to the organic phase (as mixed U–Tc complexes).Several ligands were studied for the recognition of ReO4−and TcO4− anions. Positively charged macrocyclic receptors proved to be very efficient.38–41 P. D. Beer42,43 et al. worked on halogen bonding bis-iodotriazolium acyclic receptor for the perrhenate anion recognition in water. Neutral receptors39 con- taining NH groups that are capable of binding the oxo-anions via hydrogen bonding interactions were developed by E. A. Kataev et al.44 and Sessler et al.45,46 Another study demonstrates the high affinity of an azacryptand,3,47–49 containing two tripodal tetra-amine subunits covalently linked by p-xylyl spacers, for ReO4− and TcO4−. This ligand was studied for new solid-phase separation processes50 and as an extractant for liquid–liquid extraction in chloroform for the removal of tech- netium from aqueous solutions.51,52 However, this azacryptand is not soluble enough in the organic phase under these conditions leading to very low distribution ratios (DTc = 0.01). Indeed, there is still a high proportion of the charged species LH55+, LH44+ and LH33+ present at the pH range between 7 and 8. More recently, Amendola and co-workers53,54 have studied in more details the complexation of this azacryptand with perrhenate and pertechnetate anions in a triflate medium. They revealed that this receptor has a suitable cavity for the incorporation of these oxoanions,55 forming stable 1 : 1 adducts. The selectivity of LH6 for TcO4- over nitrate was also demonstrated by measuring the affinity constant53 by ITC (isothermal titration calorimetry) and 1H NMR spectroscopy. The formation of an inclusion complex was confirmed by X-ray diffraction studies of the adduct [LH6(TcO4)](TcO4)-(CF3SO3)4·8H2O. However, the studied triflate medium is significantly different from the spent nuclear fuel dissolution solutions, composed of 3–5 M nitric acid, where the competition between the complexation of the pertechnetate and nitrate anions is predominant. In this paper, the behaviour of technetium was studied in the presence of this azacryptand as a complexing agent in the aqueous phase to avoid its co-extraction with uranium to the organic phase. Due to costs and limited access to TcO4−, ReO4− was first used as an inactive surrogate, as it shows close chemical properties and similar coordination.37 In the present work, the experiments were performed with MOEHA (N-methyl-N-octyl-(2-ethyl)hexanamide)25 as an organic phase extractant, because as mentioned above, it is a good candidate for uranium and plutonium extraction like TBP and it has also the tendancy to form mixed U–Tc complexes in the organic phase.1 The cryptates formed were characterized in the solid state using X-Ray diffraction, infrared (IR) and Raman spectroscopies, and density functional theory (DFT) theoretical calculations in order to characterize and understand the inter- actions between the azacryptand and the two oxo-anions.

Results and discussion

Liquid–liquid extraction studies

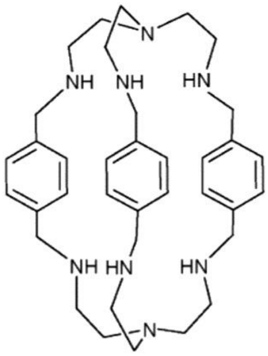


Fig. 1 Structure of the azacryptand LH66+.

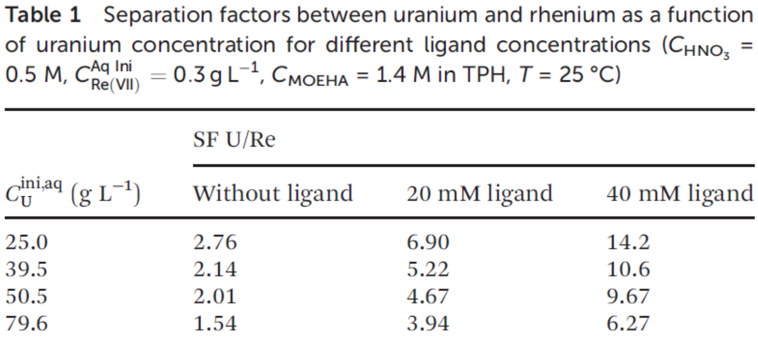


Table 1 Separation factors between uranium and rhenium as a function of uranium concentration for different ligand concentrations (C_{HNO_3} = 0.5 M, $C_{Re(VII)}^{Aq\ Ini}$ = 0.3 g L^{-1}, C_{MOEHA} = 1.4 M in TPH, T = 25 °C)

	SF U/Re		
$C_U^{ini,aq}$ (g L^{-1})	Without ligand	20 mM ligand	40 mM ligand
25.0	2.76	6.90	14.2
39.5	2.14	5.22	10.6
50.5	2.01	4.67	9.67
79.6	1.54	3.94	6.27

The maximum solubility of the azacryptand LH66+ (Fig. 1) was obtained in 0.5 M HNO3, as determined by total organic carbon (TOC) measurement (164 mM). Thus, liquid–liquid extraction experiments were performed at this acidity using 1.4 M MOEHA in TPH (hydrogenated tetrapropylene) as the extractant system. The metal concentration (Tc or Re) was held constant at 0.3 g L–1 to be representative of spent nuclear fuel solutions. Preliminary experiments were performed with rhenium, as a surrogate of technetium, to evaluate the efficiency of the azacryptand LH6 to maintain ReO4– in the aqueous phase. Fig. 2 shows the distribution ratio values of rhenium as a function of the initial uranium concentration in the aqueous phase for various ligand concentrations. An increase of DRe with the increase of the uranium concentration from 0 to 80 g L–1 is observed. This is in agreement with the previously observed formation of mixed complexes between uranium, rhenium and MOEHA in the organic phase.1 Moreover, DRe values decrease with increasing concentration of the masking agent (LH66+) from 0 to 40 mM in the aqueous phase. No influence on the uranium extraction was observed with the addition of the masking agent in the aqueous phase. The separation factor (SF) between uranium and rhenium increases in the presence of the masking agent LH66+ (Table 1) indicating a good selectivity of this azacryptand for perrhenate over nitrates and uranium. Considering the good masking properties of this ligand toward Re, the experiments were extended to the study of technetium extraction under the same experimental conditions (Fig. 3). The same behavior is observed for technetium: the Tc distribution ratio increases with uranium concentration. The DTc values decrease by a factor of around two when 20 mM of the masking agent LH66+ is added to the aqueous phase. To the best of our knowledge, this is the first time that a ligand is able to reduce the extraction of technetium from a nitric acid solution in presence of uranium. In all cases, TcO4– is significantly better extracted than ReO4– (Table 2). This behavior is well-known for various extractant types, and is due to the higher lipophilicity of the pertechnetate anion3,40,51 compared to perrhenate (in agreement with their classification in the Hofmeister series).33,56 Charge density calculations confirm this finding.

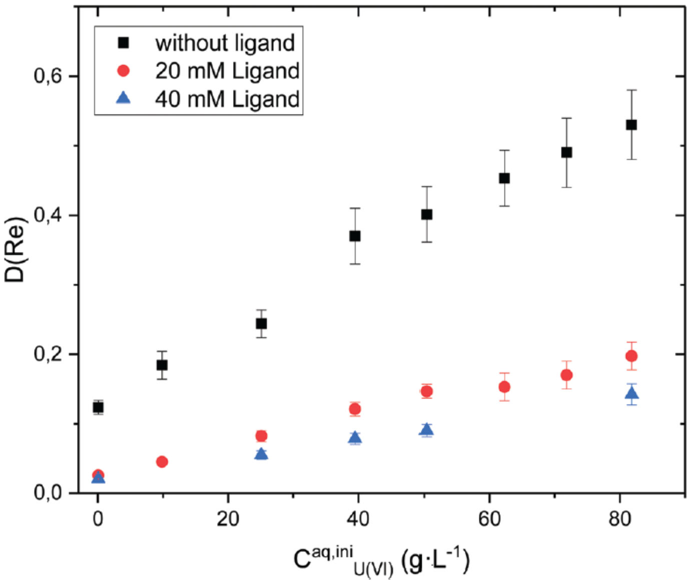


Fig. 2 Influence of uranium concentration on D_{Re} for different ligand concentrations (C_{HNO_3} = 0.5 M, $C^{Aq\ Ini}_{Re(VII)} = 0.3\,g\,L^{-1}$, C_{MOEHA} = 1.4 M in TPH, T = 25 °C).

The partial negative charge of the oxygen atoms of perrhenate (–0.755) is clearly increased compared to those of the pertechnetate anion (–0.739),51 leading to a significantly stronger hydration of the perrhenate ions, and consequently to a more difficult transfer of perrhenate to the organic solvent. For the complexation, this preorganized ligand is able to overcome the Hofmeister bias and shows an excellent affinity toward ReO4– and TcO4– in concentrated nitric acid solution. Another experiment was performed with an increasing azacryptand concentration from 0 to 100 mM in the aqueous phase to study the solubility limit of this azacryptand in the presence of uranium and technetium. In this case, uranium concentration was fixed at 30 g L–1, while nitric acid and pertechnetate concentrations were fixed at 0.5 M and 0.3 g L–1, respectively. As seen in Fig. 4, addition of the azacryptand to the aqueous phase results in a decrease of the technetium distribution coefficient: DTc decreases 5-fold with 40 mM of ligand compared to the solution without the ligand. As the ligand concentration increases, DTc reaches a plateau because a precipitate appears at concentrations exceeding 60 mM (open labels on the graph). The mass balance for Tc in this extraction test is close to 100%. Based on these promising results, this azacryptand LH6 6+ is able to maintain the pertechnetate anion in the aqueous phase, decreasing the distribution ratio 5-fold with a ligand concentration of 40 mM in 0.5 M HNO3. The azacryptand shows slightly better affinity for the perrhenate anion than the pertechnetate anion. Compared to the reference without any azacryptand in the aqueous phase, perrhenate distribution ratios are indeed lower than pertechnetate distribution ratios.

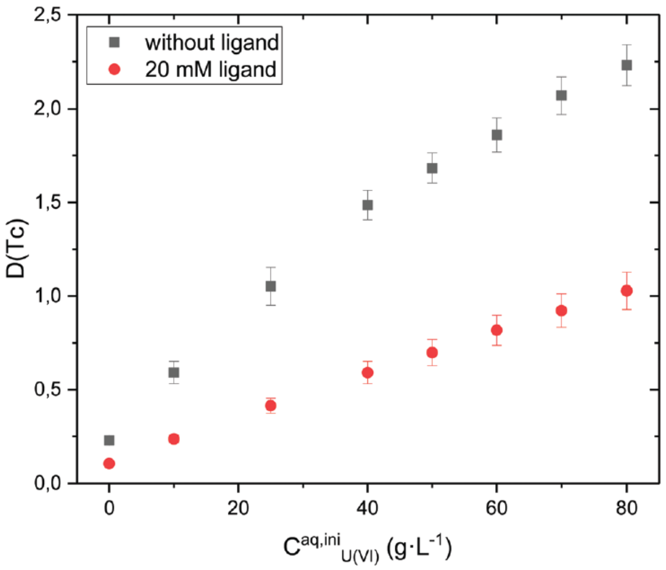


Fig. 3 Influence of uranium concentration on D_{Tc} with and without the addition of the azacryptand in the aqueous phase (C_{HNO_3} = 0.5 M, $C^{Aq\ Ini}_{Tc(VII)} = 0.3\,g\,L^{-1}$, $A_{^{99}Tc}$ = 10 kBq mL^{-1}, C_{MOEHA} = 1.4 M in TPH, T = 25 °C).

Table 2 Distribution ratios for rhenium and technetium (C_{HNO_3} = 0.5 M, $C^{Aq\ Ini}_{Tc(VII)\ and\ Re(VII)} = 0.3\,g\,L^{-1}$, C_{MOEHA} = 1.4 M in TPH, T = 25 °C)

	Without ligand		20 mM ligand	
$C_{U^{ini}_{aq}}$ (g L^{-1})	D(Re)	D(Tc)	D(Re)	D(Tc)
0	0.12	0.23	0.03	0.10
25.0	0.24	1.1	0.08	0.42
50.5	0.40	1.7	0.15	0.70
79.6	0.53	2.2	0.20	1.0

Thermodynamic studies

Calorimetric experiments were carried out for the inactive surrogate of the pertechnetate anion, ReO4– , to determine the complexation thermodynamic data in nitric acid medium. The complexation constants of the pertechnetate and perrhenate anions with this azacryptand, determined previously in triflate medium, were similar.53,54 The complexation of the perrhenate anion in nitric acid solution was performed in chemical conditions similar to the liquid–liquid extraction experiments, i.e.at 0.5 M nitric acid concentration and at 25 °C. Hence, the ionic strength is fixed by the nitric acid concentration. In large excess of nitric acid compared to the azacryptand, the formation of a 1 : 1 complex between the ligand and one nitrate anion within the cage was assumed. Therefore, the complexation equilibrium is described as:

$$\left[\mathrm{LH_6}^{6+},\mathrm{NO_3}^{-}\right] + \mathrm{ReO_4}^{-} \overset{\beta}{\longleftrightarrow} \left[\mathrm{LH_6}^{6+},\mathrm{ReO_4}^{-}\right] + \mathrm{NO_3}^{-}$$

The complexation constant β between $\mathrm{ReO_4^-}$ and the azacryptand in nitric acid medium was followed by microcalorimetric titrations. The resulting $\mathrm{kcal\ mol^{-1}}$ vs. molar ratio titration graph is given in Fig. 5. The resulting isotherms were then fitted with the Gibbs– Helmholtz equation, allowing determination of the complexation constant (log β), the stoichiometry of the complex and the enthalpy of complexation (ΔH). The corresponding entropy (ΔS) was then calculated, knowing the free energy of complexation ($\Delta G = -RT \ln \beta = \Delta H - T\Delta S$). The resulting data, given in Table 3, are consistent with a 1 : 1 complex with the perrhenate anion. It was impossible to fit the titration isotherms using higher complex stoichiometry. The binding affinity is driven by the exothermic enthalpy contribution, as expected for H-bond interactions. Moreover, the negative sign of the entropic term, −1.2 $\mathrm{kcal\ mol^{-1}}$, can be related to the highly pre-organized structure and the formation of an inclusion complex, as seen in triflate medium.53,54 Amendola et al.53,54 previously obtained a complexation constant log β = 5.2 in triflate medium for the perrhenate anion. In this work, the complexation constant is lower (log β = 2.1), because of the strong competition between perrhenate and nitrate anions for complexation, the latter being in large molar excess in the experimental conditions.

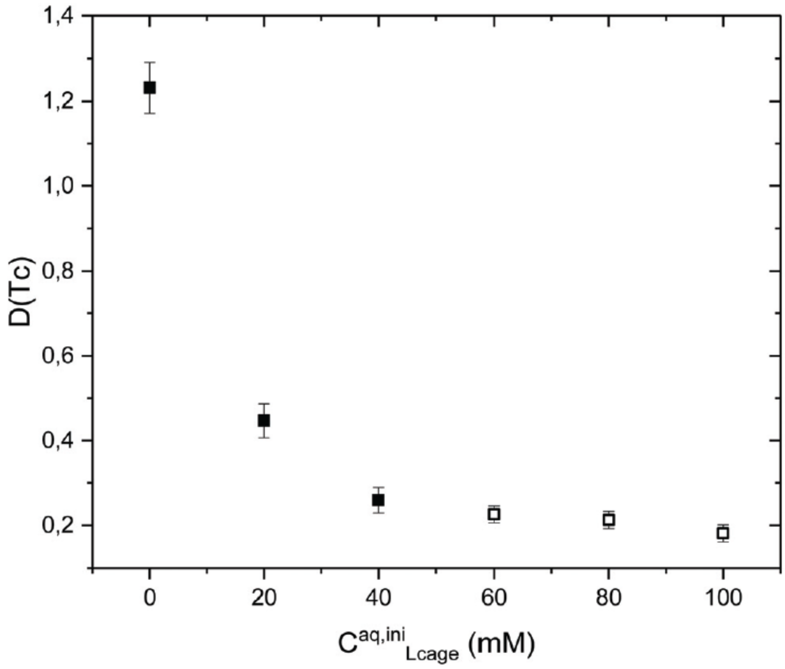


Fig. 4 Influence of ligand concentration in aqueous phase on D_{Tc}. Open labels correspond to ligand precipitation ($C_{\mathrm{HNO_3}}$ = 0.5 M, $C^{\mathrm{Aq\ Ini}}_{\mathrm{Tc(VII)}} = 0.3\ \mathrm{g\ L^{-1}}$, $A_{^{99}\mathrm{Tc}}$ = 10 kBq $\mathrm{mL^{-1}}$, C_{MOEHA} = 1.4 M in TPH, T = 25 °C).

Structural studies

Because of the low solubility of the azacryptand in nitric acid,it was possible to form single crystals of the azacryptand-perrhenate anion complex by slow evaporation in a 0.5 M nitric acid solution. The formation of an inclusion complex was confirmed (Fig. 6) by single crystal X-Ray diffraction (XRD).

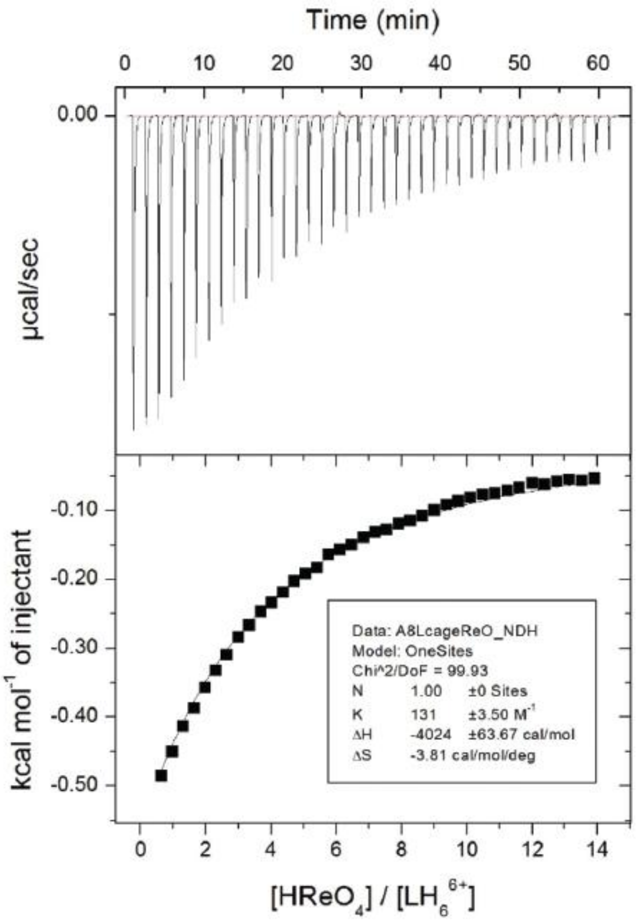
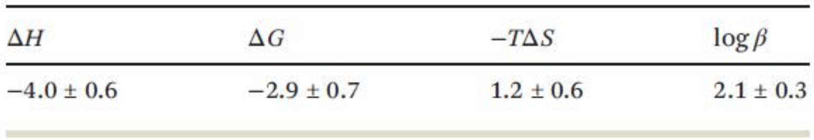


Fig. 5 Thermogram and fit of the titration curve obtained for 39 × 1 µL injections of 40.03 mM ReO_4^- in 0.5 M HNO_3 into a solution containing azacryptand concentration of 1.18 mM in 0.5 M HNO_3.

There are three cristallographically different perrhenate ions in this structure. One is located inside the cavity (Re1) of the ligand, whereas the two others are outside the cavity (Re2 and Re3). Re3 presents a partial occupational rate and shares the crystallographic site with a nitrate molecule. The refinement of the occupational rate gives an optimal of 0.48 that was averaged to 0.5 in the final refinement. This configuration has already been observed in a Tc structure with TcO4– located in the same site as a triflate ion with an occupational rate of 0.08.53 The interspace of the structure is completed with two water molecules and three nitrate groups. The proton atoms could be located from the electron density maps, but to obtain a higher accuracy, particularly on the distances, their positions were calculated. The charge compensation consideration implies a ligand protonation state of six. The global formula of the compound is thus: [(LH6)(ReO4)]·(ReO4)1.5(NO3)3.5·(H2O)3. Both internal (Re1) and external (Re3) rhenium anions form H-bond interactions with water molecules and some of the protonated amino groups of the ligand (see Fig. 6). The oxygen atoms of the internal rhenium anion are coordinated to the ligand through two strong hydrogen bonds with two water molecules, with d(O–H) = 1.99 and 2.01 Å, and two weaker hydrogen bonds with two protonated amine groups NH2R2+, d(O–H) = 2.17 and 2.25 Å. Thus, it seems that the water molecules play an important role in the coordination of rhenium in the cage.

However, the hydrogen bonds are likely sufficient to stabilize the ReO4− anion inside the cage. One of the external rhenium anions, Re3, also undergoes hydrogen bonds with water molecules, d(O–H) = 1.78 Å, and with one protonated amine group NH2R2+, d(O–H) = 2.3 Å. It is interesting to note that one oxygen atom of the "on-the-same-site"-nitrate is superimposed with the oxygen of the ReO4− group that is involved in the hydrogen bonds network. The last perrhenate (Re2) does not exhibit strong hydrogen bonds and is likely to interact with the other elements of the structure through dipolar interactions or very weak hydrogen bonds with O···H > 2.4 Å. The same behaviour is described for one of the perrhenate in the triflate structure.54

Table 3 Thermodynamic data (kcal mol^{-1}) and complexation constant (log β) obtained at 0.5 M HNO_3 from microcalorimetry for the 1 : 1 ReO_4^-/azacryptand complex (T = 25 °C)



ΔH	ΔG	$-T\Delta S$	$\log\beta$
-4.0 ± 0.6	-2.9 ± 0.7	1.2 ± 0.6	2.1 ± 0.3

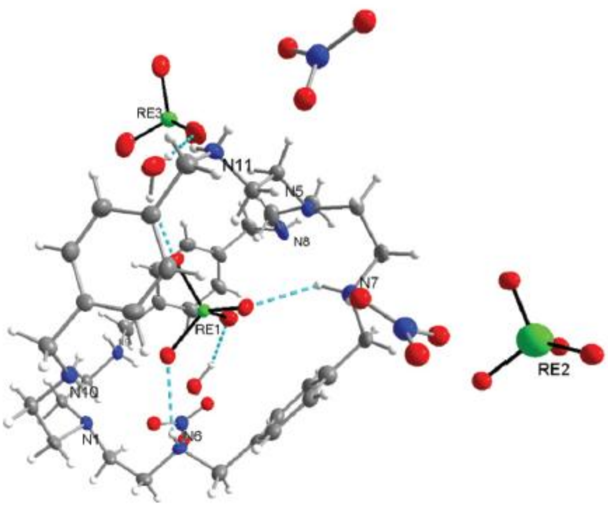


Fig. 6 Crystal structure of $[(LH_6)(ReO_4)]\cdot(ReO_4)_{1.5}(NO_3)_{3.5}\cdot(H_2O)_3$ and illustration of H-bonding interactions (blue dashed lines).

Single crystals were also obtained for the fully protonated azacryptand (i.e., free ligand, H6L6+(NO3 −)6) from a 0.7 M nitric acid solution. It was difficult to obtain correct refinement parameters, probably due to the presence of twin structures.

Nevertheless, even if the structural resolution is incomplete, the global conformation of the molecule can be observed and roughly discussed (see ESI, Fig. 1†). Without perrhenate or pertechnetate, the four hydrogen atoms of the protonated amines, which in the metal complex were directed toward the anion to take part to hydrogen bonds, point outside the cage. The ligand conformation is largely modified with anion complexation, with the rotation of the amine groups. During the complexation, the ligand structure adapts itself to let one perrhenate anion enter the cage. The single crystals for the free ligand and the rhenium complex were analyzed by Raman (Fig. 7) and infrared spectroscopy (see ESI, Fig. 2†). A precipitate of the technetium complex was also analyzed. It was obtained by adding pertechnetic acid into an azacryptand solution (15 mM) in 0.5 M HNO3. A white precipitate was obtained, and then dried for structural studies. Table 4 summarizes the main vibrational frequencies of the three species.

For both perrhenate and pertechnetate, complex formation was evidenced by the significant shift of several Raman vibrational bands. First, the “free” (hydrated) perrhenate or pertechnetate molecular anions have specific vibrations bands at 333 and 972 cm−1, and at 325 and 912 cm−1, respectively.57,58 In presence of the azacryptand, these vibrational bands are shifted to 330 and 965 cm−1 for ReO4 −, and to 320 and 909 cm−1 for TcO4 −. The free azacryptand ligand has awaiting vibrational bands at 1622 cm−1 (vCvC) and 2978 cm−1 (vC–Har). These bands are shifted in the presence of ReO4− or TcO4−: the first one to 1618 cm−1 and 1620 cm−1 with ReO4− and TcO4−, respectively, and the second band to 2976 cm−1 and 2972 cm−1 with ReO4− and TcO4, respectively (see ESI, Fig. 3,† for the full spectra). Moreover, the narrow band at 900 cm−1 in the free ligand (vC–N) is broadened in the rhenium complex. This band broadening is due to two additional asymmetric deformation bands of the perrhenate anion in the same range.59 In the technetium complex, the vC–N band is also superimposed with the bound pertechnetate signal. The analysis of the infrared spectra leads to similar observations. The main IR vibrational bands are reported in Table 5. The bands at 322 and 885 cm−1 are assigned to the bound perrhenate (333 and 918 cm−1 for the free perrhenate)57,58 and confirm the complex formation. For the technetium complex, the band at 875 cm−1 corresponds to the bound pertechnetate (903 cm−1 for the free pertechnetate).57 A shift of vNH2 is observed from 1605 (ref. 60) for the free ligand to 1594 cm−1 for the oxo-anion complex. This bathochromic effect is due to hydrogen bond formation, which weakens the N–H bond strength. An attempt was made to confirm the speciation of the perrhenate anion with the azacryptand in solution in 0.5 M HNO3. A solution containing the perrhenate complex was analyzed by Raman spectroscopy. However, the complex solubility is too low to observe any peaks in the spectrum; only the free nitrate band is observed. From the microcalorimetric studies, the complex formed in nitric acid solution is a 1 : 1 adduct, i.e., an encapsulation in liquid state of the perrhenate anion. This 1 : 1 complex formation with ReO4− and TcO4− was also observed in previous work in a triflate medium.53,54-

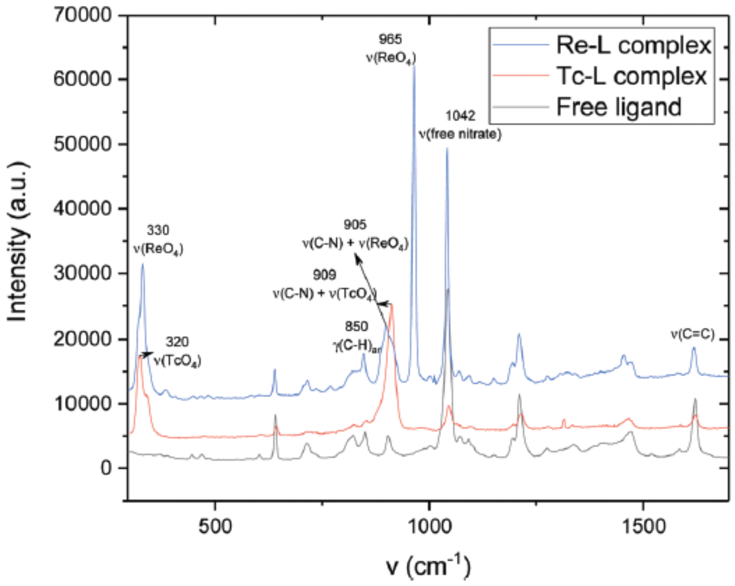


Fig. 7 Raman spectra of the free ligand single crystals (black line), the rhenium complex (blue line) and the technetium precipitate (red line).

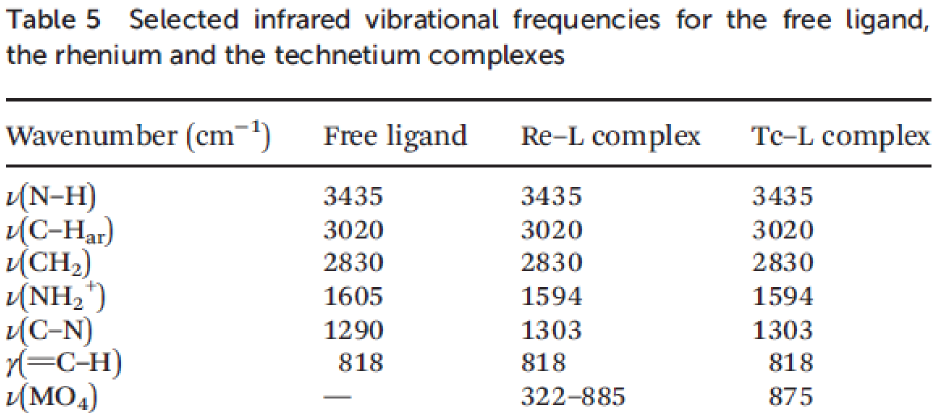


Table 5 Selected infrared vibrational frequencies for the free ligand, the rhenium and the technetium complexes

Wavenumber (cm^{-1})	Free ligand	Re–L complex	Tc–L complex
ν(N–H)	3435	3435	3435
ν(C–H_{ar})	3020	3020	3020
ν(CH_2)	2830	2830	2830
ν(NH_2^+)	1605	1594	1594
ν(C–N)	1290	1303	1303
γ(=C–H)	818	818	818
ν(MO_4)	—	322–885	875

DFT calculations

Binding strength being largely driven by the H-bond interactions, DFT calculations were conducted in order to investigate H-bonding interactions in the azacryptand and to compare binding affinities for perrhenate and pertechnetate anions. The geometry of (LH6)(ReO4)(H2O)2(NO3)5 inclusion complex was first calculated by using the XRD structure as a starting point for the geometry optimization. Calculated H-bond distances involving ReO4 are reported in Table 6. Like in the crystal structure, a total of five H-bonding interactions are found with ReO4 −: three direct bonds with NH groups and two water-mediated H-bonds. The geometry of the inclusion complex was further optimized by successively removing the nitrate ions and water molecules in an attempt to maximize the number of hydrogen bonds toward the perrhenate and to enhance the complexation strength (Fig. 8). In the absence of nitrate ions, in [(LH6)(ReO4)(H2O)2]5+, the number of H-bonding interactions increases from 5 to 7. In [(LH6)(ReO4)]5+ without water molecules, the two water-mediated H-bonds are replaced by two direct bonds with NH group, but the total number of H bonds remains equal to 7. Several conformations of the azacryptand were considered in the calculation. As the lowest energy conformation, shown in Fig. 8,

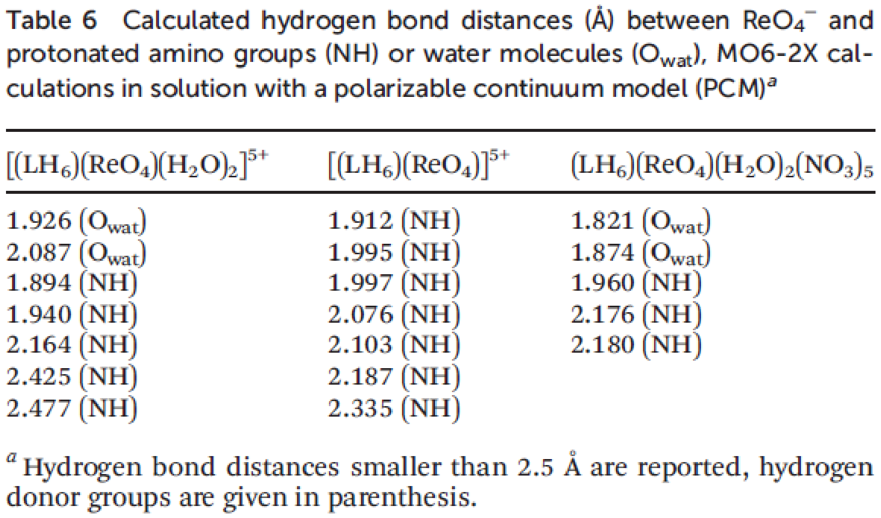


Table 6 Calculated hydrogen bond distances (Å) between ReO_4^- and protonated amino groups (NH) or water molecules (O_{wat}), MO6-2X calculations in solution with a polarizable continuum model (PCM)[a]

$[(LH_6)(ReO_4)(H_2O)_2]^{5+}$	$[(LH_6)(ReO_4)]^{5+}$	$(LH_6)(ReO_4)(H_2O)_2(NO_3)_5$
1.926 (O_{wat})	1.912 (NH)	1.821 (O_{wat})
2.087 (O_{wat})	1.995 (NH)	1.874 (O_{wat})
1.894 (NH)	1.997 (NH)	1.960 (NH)
1.940 (NH)	2.076 (NH)	2.176 (NH)
2.164 (NH)	2.103 (NH)	2.180 (NH)
2.425 (NH)	2.187 (NH)	
2.477 (NH)	2.335 (NH)	

[a] Hydrogen bond distances smaller than 2.5 Å are reported, hydrogen donor groups are given in parenthesis.

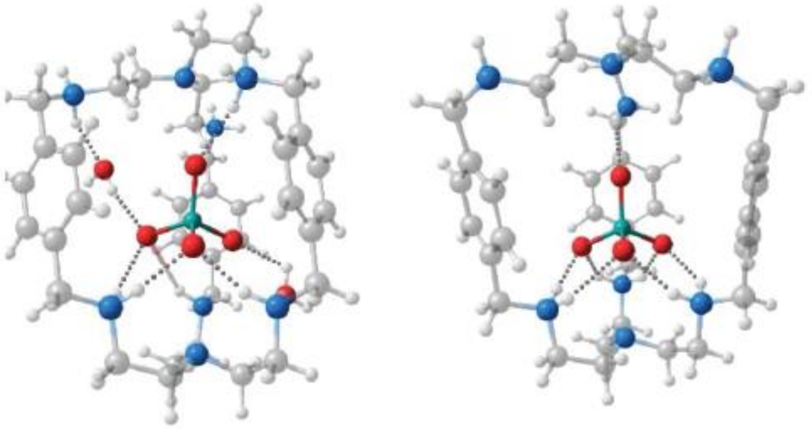


Fig. 8 Schematic representation of $[(LH_6)(ReO_4)(H_2O)_2]^{5+}$ (left) and $[(LH_6)(ReO_4)]^{5+}$ (right).

Table 7 Binding energies (ΔE in kJ mol^{-1}) calculated for ReO_4^- and TcO_4^- encapsulation in $[(LH_6)(MO_4)]^{5+}$ and $[(LH_6)(MO_4)(H_2O)_2]^{5+}$ structures, MO6-2X calculations in solution with a PCM solvent model

	ΔE_{gas}	ΔE_{sol}
$ReO_4^- + LH^{6+} \rightarrow [(LH_6)(MO_4)]^{5+}$	−1658	−216
$ReO_4^- + LH(H_2O)_2^{6+} = [(LH_6)(ReO_4)(H_2O)_2]^{5+}$	−1609	−229
$TcO_4^- + LH^{6+} = [(LH_6)(TcO_4)]^{5+}$	−1652	−208
$TcO_4^- + LH(H_2O)_2^{6+} = [(LH_6)(TcO_4)(H_2O)_2]^{5}$	−1602	−219

corresponds to the XRD structure, it was not possible to increase the number of H-bonds, and thus the complexation strength, by changing the conformation of the ligand. Binding energies were computed for the two [(LH6)(ReO4)]5+ and [(LH6)(ReO4)(H2O)2]5+ structures and are reported in Table 7. In the gas phase, binding strength is stronger in the absence of water molecules in the cavity by about 50 kJ mol−1. It is the opposite in aqueous phase calculations: the binding strength is 13 kJ mol−1 weaker without water molecules in the cavity. This suggests that, in solution, the anion is encapsulated with coordinated water molecules, as in the XRD solid state structure. The binding energies were also computed for TcO4−. Differences between the anions are small: for each structure (i.e., with or without water molecules in the cavity) binding energies differ by less than 10 kJ mol−1. However, binding strength is in all cases slightly stronger for perrhenate than for pertechnetate anions both in the gas phase and in solution. This is consistent with the observations of the distribution ratio study which indicate a slightly stronger effect of the masking agent for ReO4– over TcO4–.

Conclusions

In conclusion, an azacryptand was studied to prevent technetium extraction to the organic phase during a spent nuclear fuel separation process. Liquid–liquid extraction studies show that addition of the azacryptand to the aqueous phase leads to a significant decrease in the technetium distribution ratio (DTc is diminished by a factor of 5 with 40 mM ligand in the aqueous phase). For the first time, this preorganized molecule was studied in nitric acid medium for its use in an extraction process. Structural studies by XRD, infrared, and Raman spectroscopies performed with the perrhenate anion reveal that one oxo-anion is located within the cage of the ligand, stabilized by hydrogen bonds. The existence of H-bonds was confirmed by DFT calculations. The affinity of the azacryptand was calculated for the two oxo-anions. The binding energies are close for both anions, but are slightly stronger for ReO_4^- over TcO_4^-. Further work will involve thermodynamic studies to measure the complexation constant with the pertechnetate anion in nitric acid medium.

Experimental

Materials and methods

MOEHA was synthesized by Pharmasynthese (purity higher than 99% verified by gas chromatography-mass spectrum) and diluted to 1.4 M in TPH (Novasep). The azacryptand was synthesized at the Department of Chemistry, University of Pavia. The uranium stock solution used for the liquid–liquid extraction experiments was prepared from uranyl nitrate purchased from Prolabo and titrated using ICP-AES (ICP-AES Optima 8300 from PerkinElmer). An aqueous stock solution of pertechnic acid was prepared starting with pure $NH_4{}^{99}TcO_4$ following the procedure described by Boyd and Moeyaert et al.[61,62] Initial aqueous solutions of $HTcO_4$ spiked with ^{99m}Tc (produced from ^{99}Mo generator provided by Curium Pharma) were prepared at 0.5 M HNO_3 for the extraction experiments. The perrhenic acid $HReO_4$ was obtained from Alfa Chemistry and used without any further purification. All other high purity grade chemical reagents (HNO_3, NaOH...) were purchased from Prolabo and used without any further purification.

Liquid–liquid extraction

The liquid–liquid extraction experiments were performed at T = 25 °C ± 1 °C, T being controlled by a thermostated cell. Before the extraction, the organic phase was contacted with 0.5 M nitric acid ($V_{aq}/V_{org} = 3$) twice for 10 minutes by Vortex horizontal mechanical shaking. Equal volumes of the organic and aqueous phases (0.8 mL) were contacted for 15 minutes in microcentrifuge tubes (2 mL) The extraction equilibrium was reached during this period. After extraction, all samples were centrifuged and the phases separated. Uranium and rhenium were analyzed by ICP-AES (inductively coupled plasma-atomic emission spectroscopy). For the experiments with rhenium, uranium and rhenium were back-extracted from the organic phase using 0.01 M HNO_3 and 10 M HNO_3, respectively, ($V_{aq}/V_{org} = 5$) before analysis. This step is required because the direct analysis of the elements in the organic phases is not feasible by ICP-AES. The distribution ratios of rhenium and uranium were defined as the ratio of their concentrations in the organic phase at equilibrium $C_{org;eq}$ M versus their concentrations in the aqueous phase at equilibrium $C_{aq;eq}$ M :

$$D_{\mathrm{M}} = C_{\mathrm{M}}^{\mathrm{org,eq}} / C_{\mathrm{M}}^{\mathrm{aq,eq}}$$

^{99}Tc is a weak β-emitter. Although radiation from a small amount of material is completely shielded by the glass walls of standard laboratory vessels, all the experiments were performed in glove boxes to avoid any contamination. The initial aqueous phases containing ^{99}Tc were spiked with ^{99m}Tc, which is a strong gamma emitter. This technetium metastable state is obtained from elution of a molybdenum-99 source. Technetium concentration in the organic and aqueous phases was directly analyzed by gamma spectrometry (Hyper pure Ge detector, CANBERRA). The distribution ratio of technetium (D_{Tc}) is defined as:

$$D_{\mathrm{Tc}} = \overline{A_{\mathrm{Tc}}}/A_{\mathrm{Tc}}$$

where ā and A are the γ activities of 99mTc in the organic and the aqueous phase respectively (expressed in terms of decays per volume unit). It was assumed that D-values between 1 and 10 exhibit a maximum error of about 5% and 10% outside of these values.

From the distribution coefficients, the separation factors were calculated:

$$\mathrm{SF}_{\mathrm{U/M}} = D_{\mathrm{U}}/D_{\mathrm{M}}$$

where DM is the distribution ratio of technetium or rhenium. Nitric acid concentration in the aqueous phases were determined by acid–base titration with 0.1 M NaOH solution, by diluting the sample aliquot in saturated ammonium oxalate in the presence of uranium. Oxalates allow the complexation of uranyl cation to avoid its hydrolysis by hydroxo anions. Then, only the protons are titrated in the solution during titration.

TOC measurement

TOC measurements were performed with a Sievers M5310C Laboratory TOC analyzer. Samples were diluted in water to obtain a concentration of around 20 ppm. Pure water was also analyzed to determine the carbon concentration of water (around 0.4 ppm).

Microcalorimetry

The isothermal microcalorimetric titrations were performed at 25 °C using an isothermal titration calorimetry ITC 200 instrument (Malvern). ITC monitors the heat changes by measuring the differential power, applied to the cell heaters, required to maintain zero temperature difference between the reference and sample cells as the ligand and the metal are titrated. The aqueous phase, containing an azacryptand concentration of 1.18 mM at HNO3 0.5 M, was introduced into a sample cell (206 µL). The perrhenic acid solution (40.03 mM in HNO3 0.5 M) was injected by 1 µL addition by syringe (39 µL total injection volume), and was stirred upon addition. Each injection of metal results in a heat pulse that is integrated with respect to time and normalized for concentration to generate a kcal mol−1 vs. molar ratio (ligand/sample) titration curve. The resulting isotherms were fitted to a binding model with Origin 7 to generate the affinity constant (K), stoichiometry (n), and enthalpy of interaction (ΔH). ΔG and ΔS were subsequently obtained by difference. At the end of the calorimetric run, the rhenium concentration was measured by ICP-AES. The measured heat is the sum of multiple reactions occurring simultaneously (reaction, mixing, dilution). In this case, a common medium (0.5 M HNO3) was used for the ligand and the metal solutions; it was therefore not necessary to measure the heat of mixing. Only the azacryptand dilution in media was first measured: the azacryptand in 0.5 M HNO3 was introduced in a sample cell and 0.5 M HNO3 was injected in 1 µL additions with the same parameters as complexation (39 injections). The heat of dilution was found to be negligible. Experimental uncertainties are based on multiple (at least two) replicate titrations.

[(LH6)(ReO4)]·(ReO4)1.5(NO3)3.5·(H2O)3 single crystal synthesis

Single crystals of the perrhenate complex were made by dissolving 10.14 mg of the azacryptand in 1 M HNO3 (30.5 mM). A perrhenic acid solution (1.05 eq., 0.1 M) was added to the mixture. The crystals were obtained in two days at low temperature (6 °C). Another procedure was developed by slow evaporation of the solution containing the azacryptand (7 mM in 1 M HNO3) and perrhenic acid (3 eq.). In both cases, the same unit cell parameters were observed.

Technetium precipitate synthesis

A technetium precipitate was obtained by dissolving the azacryptand in 1 M HNO3 (15 mM). An aqueous solution of pertechnic acid was added to the solution (3 eq.). A white precipitate was obtained immediately. The solution was centrifuged and the liquid removed. Before the analysis, the precipitate was dried on a filter.

X-Ray diffraction

Each crystal was mounted on MicroMount patented by MiTeGen and inserted into a goniometer base. A MicroRT capillary was then drawn over the sample and onto the base, where it was sealed by adhesive. The single crystal XRD intensities were measured on a Nonius four-circle diffractometer equipped with an Apex II detector. The crystals were cooled to 150 K using a 600 series cryostreamcooler device (Oxford Cryosystem). The instrument is equipped with a fine-focus Motarget X-ray tube (λ = 0.71073 Å) operated at 1500 W. Data were collected using phi and omega scans, with 10 s and 30 s frame exposures and 0.5° frame widths. Intensities were extracted from the collected frames using the program SAINTPlus.63 The unit cell parameters were refined from the complete data set, and an empirical absorption correction was performed using SADABS procedure.64 The structure determination and refinements were performed with SHELX-97 software.65 The heavy atoms were located by direct methods, while the remaining atoms were found from successive Fourier map analyses. The hydrogen atoms were calculated and isotropically refined. The crystal data and details of the final refinement for the rhenium are reported in Table 1 and in the ESI.† CCDC 1950939† contains the supplementary crystallographic data for this paper.

Raman spectroscopy

A HORIBA Jobin-Yvon LabRamHR evolution spectrometer was used mounted on a support with an objective turret (10×, 20×, and 50×). An AG laser (532 nm) with adjustable output power (from 20 to 120 mW) with a variable filter was used to provide low-excitation-beam power levels. The Raman spectrometer and laser were set with a fiber-optic signal transmission line. The analyses were carried out on an average of five selected single crystals by using 20× objective.

IR spectroscopy

The single crystals were analysed with a dual channel FTIR spectrophotometer from Bruker optics (Vertex 70) equipped with an ATR module, which enables solid samples to be examined directly without further preparation.

DFT calculations

The geometries were optimized at the density functional theory (DFT) level with the Gaussian 16 software using M06-2X functional.66 For Re and Tc, a relativistic effective core potential (RECP) was employed with associated (8s7p6d2f1g)/[6s5p3d2f1g] basis set.67 For other atoms, the 6-31+g(d) basis set was used. Calculations were done in the presence of a IEFPCM solvent model. Binding energies were computed from gas phase optimized structures and single point calculations in water.

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