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New route to amide-functionalized N-donor ligands enables improved selective solvent extraction of trivalent actinides†

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A new general synthetic route to selective actinide extracting ligands for spent nuclear fuel reprocessing has been established. The amide-functionalized ligands separate Am(III) and Cm(III) from the lanthanides with high selectivities and show rapid rates of metal extraction. The ligands retain the advantages of the analogous unfunctionalized ligands derived from camphorquinone, whilst also negating their main drawback; precipitate formation when in contact with nitric acid. These studies could enable the design of improved solvent extraction processes for closing the nuclear fuel cycle.

Some of the main contributors to the long-term radiotoxicity of spent fuel arising from nuclear electricity production are the minor actinides americium, curium and neptunium. After reprocessing to remove uranium and plutonium in the PUREX process,[1] the remaining spent fuel remains radiotoxic for *ca.* 10^4 years.[2] If the minor actinides are also removed, the remaining material would take only a few hundred years to decay to the levels of natural uranium and its heat load would decrease significantly. As nuclear energy expands worldwide,[3] it becomes imperative to develop viable options for future reprocessing to remove these elements prior to geological disposal of the remaining waste.[4]

To accomplish this, a solvent extraction process is required that can extract the minor actinides from nitric acid solution and separate them from the chemically similar, less-radiotoxic lanthanide fission products prior to their burn-up in advanced

reactors or accelerator-driven systems.[5] Many soft N- and S-donor ligands that can discriminate between the more extended 5f orbitals of the actinides and the more contracted 4f orbitals of the lanthanides have been evaluated for this separation.[6,7] Bis-1,2,4-triazine ligands such as **1–3** (Fig. 1) fulfil many of the challenging criteria for use in such a separation process, and are among the current N-donor ligands of choice for further development.[8]

More recently, ligand **4** derived from camphor (Fig. 1) was disclosed as a highly promising actinide selective extracting agent.[9] In particular, **4** showed significantly higher solubilities than ligands **1–3** in diluents compatible with nuclear reprocessing, and the rates of metal extraction for ligand **4** were significantly faster than for ligands **2** and **3**. However, in contrast to ligands **1–3**, solutions of **4** formed precipitates in contact with nitric acid solutions of high concentrations, which renders **4** unsuitable for further process development. The precipitate formation observed is thought to be due to competing protonation of **4** and precipitation of the protonated ligand.

We proposed that more lipophilic derivatives of **4** and related ligands would be less likely to form precipitates in contact with nitric acid, whilst also retaining the advantages
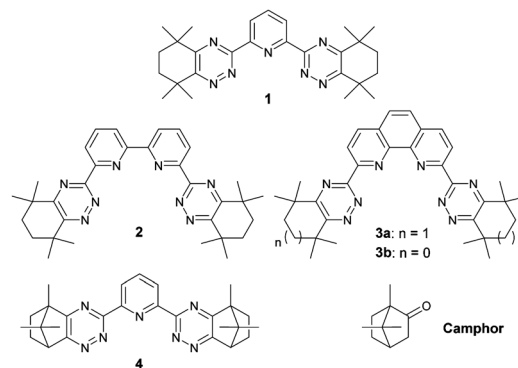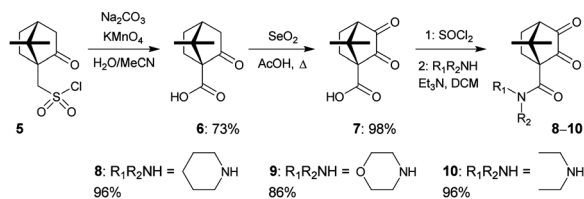
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Fig. 1 Structures of bis-1,2,4-triazine N-donor ligands **1–4** and camphor.

Scheme 1 Synthesis of diketones **8–10** from (+)-10-camphorsulfonyl chloride **5**.

of **4**. Since derivatives of camphor (Fig. 1) can be readily functionalized at each of its three methyl groups,[10] we decided to explore functionalized derivatives of camphor as synthetic precursors to new, more lipophilic bis-1,2,4-triazine ligands. In this communication, we present our preliminary results on novel, amide-functionalized ligands derived from a functionalized camphor derivative.

We chose enantiomerically pure and inexpensive (+)-10-camphorsulfonyl chloride **5** as the starting material for the synthesis of the novel diketones to avoid the possibility of diastereomer formation during ligand synthesis, and to maximize the extraction of metal ions.[11] Compound **6** was synthesized in 73% yield from **5** following the literature procedure,[12] and converted into the known diketone **7** in 98% yield.[13] The novel diketones **8–10** were then obtained from **7** and three representative secondary amines in 86–96% yields (Scheme 1).

We next explored the synthesis of novel ligands by condensation reactions of diketones **8–10** with the known bis-amidrazone **11**.[8c] Condensation reactions of **11** with diketones **8–10** in acetic acid cleanly gave the novel ligands **12–14** in moderate yields (Scheme 2). Use of ethanol or 1,4-dioxane as solvents resulted in incomplete conversion to the products.

We also decided to synthesize ligands **17** and **18** in order to determine what effect, if any, the addition of an amide functionality onto the aliphatic part would have on the minor actinide extraction properties of these ligands. The synthesis of **18** was previously reported[14] but its minor actinide extraction properties have not been determined. Thus, condensation reaction of enantiomerically pure (+)-camphorquinone **16** with each of **15** and **11** in acetic acid afforded the novel ligands **17** and **18** in 53% and 59% yields, respectively (ESI†).

The measured solubilities of ligands **12–14** in 1-octanol ranged from 40.9–50.4 mM (ESI†). These are significantly higher than the maximum solubilities of **2** and **3a** in the same diluent (10 mM[15] and 15 mM,[8c] respectively), but significantly
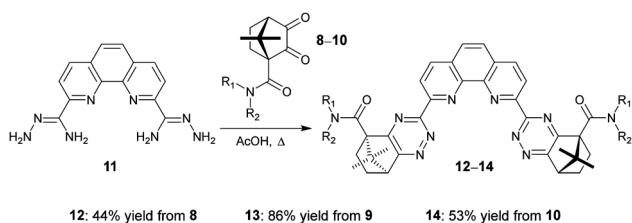
lower than the solubility of **4** (200 mM).[9] The measured solubility of **17** in 1-octanol was 58.1 mM.

With ligands **12–14**, **17** and **18** in hand, we next studied their ability to extract and separate Am(III) and Cm(III) from Eu(III) and the lanthanides in the SANEX process. Nitric acid solutions spiked with ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) radionuclides containing all the lanthanides (except Pm) were contacted with 10 mM solutions of the ligands **12–14**, **17** and **18** in 1-octanol for 1 hour, and distribution ratios (D) for metal ions were measured by α- and γ-spectroscopy or ICP-MS. For ligand **12**, an effective separation of Am(III) and Cm(III) from Eu(III) and other lanthanides was observed (Fig. 2). The maximum D values for Am(III) and Cm(III) were 55 and 17, respectively, at ≥ 1 M HNO$_3$, while the D values for Eu(III) were less than 1 across the range of nitric acid concentrations. The separation factor for Am(III) over Eu(III) (SF$_{Am/Eu}$) increased with increasing nitric acid concentration to a maximum value of 231. The maximum distribution ratios for Am(III) and Cm(III) for **12** were significantly lower than those of **3a** ($D_{Am} \leq 1000$)[8c] and about half as high as those of **3b** ($D_{Am} \leq 100$).[16] The extraction results for ligand **14** were broadly comparable to those of **12**, although this ligand was somewhat less selective than **12** (SF$_{Am/Eu} \leq 112$, ESI†).

Interestingly, no precipitate formation was observed for ligands **12** and **14** in any of the extraction experiments, in contrast to **4**.[9] However, extensive precipitate formation was observed for **13** in the extraction experiments at all nitric acid concentrations, and this ligand did not extract Am(III) or Cm(III) from nitric acid into 1-octanol ($D_{Am} < 1$, ESI†).

We next probed the rates of extraction of Am(III), Cm(III) and Eu(III) by ligands **12–14** into 1-octanol. Rapid rates of metal extraction are desirable in a solvent extraction process so that equilibrium can be reached within short contact times. The D values for the extraction of Am(III), Cm(III) and Eu(III) from 1.0 M HNO$_3$ by ligands **12** and **14** as a function of contact time are presented in the ESI.† Both ligands **12** and **14** showed rapid

Scheme 2 Synthesis of ligands **12–14** from diketones **8–10**.
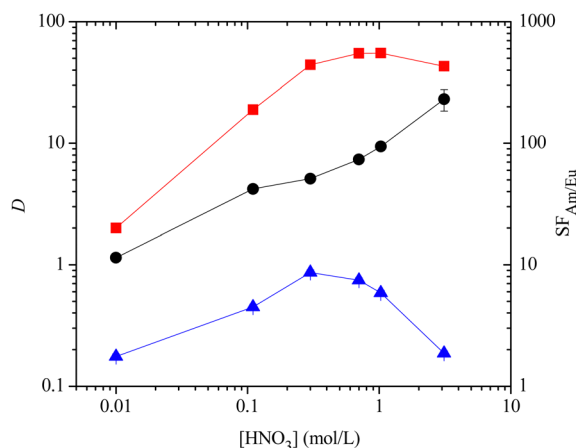

Fig. 2 Extraction of Am(III) and Eu(III) by ligand **12** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (D = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = SF$_{Am/Eu}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

rates of metal extraction and equilibrium D values were already reached for all metal ions within 5 minutes of phase mixing in the absence of a phase-modifier. These rates of metal extraction are significantly faster than those of ligands **2**[15] and **3a**[8c] (which require 60 minutes and 15 minutes of phase mixing, respectively, to reach equilibrium), and are comparable to those of ligand **4**.[9]

We also measured the D values for Am(III), Cm(III) and Eu(III) for the parent ligands **17** and **18** derived from (+)-camphorquinone **16** (ESI†). For **17**, an effective separation of Am(III) and Cm(III) from Eu(III) and other lanthanides was observed at nitric acid concentrations between 0.8–1.0 M HNO_3 ($D_{Am} \geq 3$, $D_{Eu} \leq 0.06$, $SF_{Am/Eu} = 133$–153). The D values for **18** were significantly higher than those of **17**, and **18** showed an effective and highly selective separation of Am(III) and Cm(III) from Eu(III) and other lanthanides across the range of nitric acid concentrations ($D_{Am} \geq 46$, $D_{Eu} \leq 0.23$, $SF_{Am/Eu} \leq 265$). For both ligands **17** and **18** however, there was a significant drop in the D values for all metal ions at 3 M HNO_3 and there was significant precipitate formation in the extraction experiments at all nitric acid concentrations. This was presumably due to precipitation of the protonated ligand, as observed previously with ligand **4**. Thus, it appears all three parent ligands **4**, **17** and **18** derived from (+)-camphorquinone **16** are susceptible to precipitate formation in contact with nitric acid, in contrast to the amide-functionalized ligands **12** and **14**.

We then carried out NMR titrations with La(III), Lu(III) and Y(III) (as nitrate salts) to probe for differences in metal speciation between the camphor-derived ligands **12**, **14** and **18**, and the analogous ligands **3a** and **3b** reported previously.[16,17] A single complex species was observed initially during the titrations of **12** and **14** with each metal, and the complete disappearance of the free ligand resonances at a metal : ligand ratio of *ca.* 0.5 in each case indicates this was the expected 1 : 2 complexes $[M(L)_2(NO_3)]^{2+}$ (L = ligand), in agreement with previous results for ligands **3a**[17] and **3b**.[16] However, in contrast to these ligands, the 1 : 1 complexes of **12** and **14** predominated at higher metal : ligand ratios and, in the case of La(III), the 1 : 2 complexes of **12** and **14** disappeared completely at the end of the titrations. One exception was the titration of **14** with Y(III), where 50% of the 1 : 2 complex was present at a metal : ligand ratio of 1.2. However, when the titration was resumed after one week, all of the 1 : 2 complex had completely dissociated. We attribute this to the relative kinetic inertness of Y(III) toward ligand substitution[18] compared to La(III) and Lu(III), which was observed previously in NMR titrations of **3a** and **3b**.[16,17]

Interestingly, examination of the aromatic region of the ^{1}H NMR spectra at the end of the titrations of **12** and **14** with each metal revealed the presence of three additional complex species, instead of the one additional species expected for the neutral 1 : 1 complex $[M(L)(NO_3)_3]$ previously observed with ligands **3a** and **3b**.[16,17] Since only 1 : 1 metal : ligand complexes are formed at higher metal : ligand ratios by dissociation of the 1 : 2 complexes,[16,17] these species were assigned to the three 1 : 1 complexes of **12** and **14** that are theoretically possible; the symmetrical 1 : 1 complex involving tetradentate coordination of the ligand (species A; formed by initial dissociation of the 1 : 2 complex), the unsymmetrical 1 : 1 complex involving
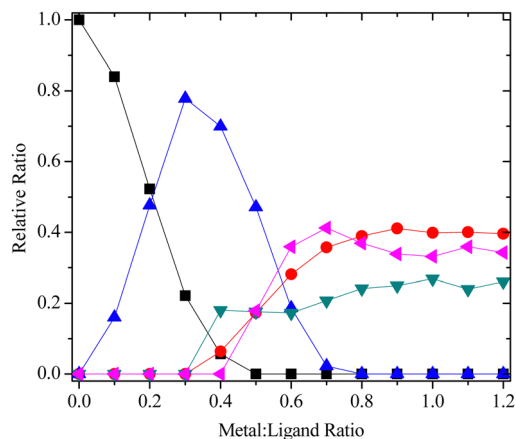

Fig. 3 Species distribution for the ^{1}H NMR titration of **14** with $La(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1 : 2 complex, ● = species A, ▼ = species B, ◄ = species C).

pentadentate coordination of the ligand (species B) and the symmetrical 1 : 1 complex involving hexadentate coordination of the ligand (species C). The speciation of ligand **14** with La(III) is shown in Fig. 3, and the structures of the different 1 : 1 complex species are shown in the ESI.†

Species B and C are formed when the N4 nitrogen of the triazine ring and amide carbonyl O atom both coordinate to the metal instead of the N2 nitrogen of the triazine ring. Complexation *via* N4 is highly unusual in metal complexes of bis-1,2,4-triazine ligands, and previous structural evidence shows it is always the N2 nitrogen of the triazine ring that coordinates to the metal.[19] To our knowledge, there is only one isolated report in the literature describing coordination of bis-1,2,4-triazine ligands with lanthanides *via* the N4 atom.[20] Although species B and C are presumably less stable than species A, this is offset by the increase in ligand denticity that results when the amide carbonyl O atom also coordinates to the metal.

In the ^{1}H NMR titrations of ligand **18** with La(III), Lu(III) and Y(III), only the expected 1 : 2 and 1 : 1 complexes were observed initially, in agreement with previous results.[16,17] However, close examination of the ^{1}H NMR spectra showed minor amounts ($\leq 10\%$) of a third complex species, which was tentatively assigned as the unsymmetrical 1 : 1 complex where the N4 atom of one of the two triazine rings coordinates to the metal. This 1 : 1 complex species was not as prominent as the analogous 1 : 1 complex species B and C observed with ligands **12** and **14**, presumably due to the absence of the additional ligating O atom in **18** that is present in **12** and **14**.

On comparing the species distribution of metal complexes of ligands **12**, **14** and **18** with those of the related ligands **3a** and **3b** with the same metals (ESI†), it is evident that the hydrophobic 1 : 2 complexes $[M(L)_2(NO_3)]^{2+}$ are significantly less favoured for the camphor-derived ligands **12**, **14** and **18** than for ligands **3a** and **3b**. Since it is these 1 : 2 complexes that are extracted into the organic phase, this could explain why the D values observed for Am(III), Cm(III) and Eu(III) in the extraction

experiments were consistently lower with the camphor-derived ligands **12**, **14** and **18** than with **3a** and **3b**.[8c,16]

To uncover the reasons for the rapid rates of metal extraction observed for ligands **12** and **14**, we measured the interfacial tensions between aqueous 1 M nitric acid solutions and solutions of **12** in 1-octanol using the du Noüy ring method, and compared them to the previous results for **3a**.[8c] The decrease in interfacial tension as the ligand concentration increases clearly shows that ligand **12** is surface active at the interface, in agreement with the rapid rates of metal extraction observed and previous measurements with **3a** (ESI†). We then compared the extraction kinetics of Eu(III) and Am(III) of ligands **12** and **3a** dissolved in 1-octanol using the rotating membrane cell method (ESI†).[8c] The Eu(III) extraction and back-extraction rate constants for **12** are significantly larger than the Eu(III) extraction rate constant for **3a**, both in the absence and presence of *N,N,N′,N′*-tetraoctyldiglycolamide (TODGA) as phase modifier (ESI†). In addition, the Am(III) extraction rate constant for ligand **12** is significantly larger than that for Eu(III). These results suggest that, although both **12** and **3a** are surface active, **12** extracts metal ions at the interface more rapidly than **3a** does, in agreement with the extraction results.

Finally, to explain why precipitate formation was observed in the extraction experiments with **13** and not with **12** and **14**, we compared the calculated log *P* values of the three ligands (ESI†). Ligand **13** is predicted to be significantly less lipophilic than ligands **12** and **14**, due to the presence of the ether oxygen atoms in ligand **13** that are absent in ligands **12** and **14**.

In summary, we present a new route to amide-functionalized, camphor-derived ligands for selective actinide extraction. The ligands show high solubilities in 1-octanol, are able to extract and separate Am(III) and Cm(III) from the lanthanides with good selectivity, and exhibit rapid rates of metal extraction. However, the ligands are unable to separate Am(III) from Cm(III). In contrast to the unfunctionalized ligands **4**, **17** and **18**, two of the ligands do not form precipitates in contact with nitric acid solutions. We conclude that precipitate formation by camphor-derived ligands is influenced by the interplay between ligand hydrophobicity and ligand basicity, and precipitate formation can be avoided by optimizing ligand design. Further studies are underway on the evaluation of a broader library of these ligands.

Conflicts of interest

There are no conflicts to declare.

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