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Recent Progress in Trivalent Actinide and Lanthanide Solvent Extraction and Coordination Chemistry with Triazinylpyridine N-Donor Ligands

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Abstract

A follow up to an earlier review on the coordination and extraction of trivalent actinide and lanthanide ions with triazinylpyridine N-donor ligands is presented. It reviews the recent development in the fields of ligand modifications and improvements, considering both hydrophobic compounds (to be used as extracting agents) and hydrophilic compounds (to be used as stripping agents), with a focus on fundamental studies.

Introduction

For more than 50 years, Renato Chiarizia had inspired the Solvent Extraction and Actinide Separations community, both as a scientist and as a long-time Editor of *Solvent Extraction & Ion Exchange.* The separation of trivalent "minor" actinides is one of the numerous fields he was interested in.[1-6] Working in this field, too (albeit using different chemistry), we feel honoured for having been invited to contributing to this special issue of *Solvent Extraction and Ion Exchange* in memory of Renato. We hope he would have enjoyed reading our contribution.

In 2012 we reviewed the complexation and extraction of trivalent actinides, An(III), and lanthanides, Ln(III) by bis-triazinyl-(bi)pyridine N-donor ligands.[7] Such ligands play a central role in the development of solvent extraction processes aimed at separating An(III) from irradiated nuclear fuels.[8] Ligand design ultimately must keep applicability in mind. With this, among the major constraints are *compatibility* (i. e. sufficient solubility of both the ligand and the formed complexes in appropriate media), *selectivity* (more is better; however, even a separation factor of ≈ 2 is sufficient to design a separation process), *affinity* (equilibria must be easily reversible — too high distribution ratios impede stripping), *kinetics* (obviously, faster is better), chemical and radiolytic *stability*.

Indeed, alkylated bis-triazinyl pyridines (known as BTP, Figure 1 left) were the first extracting agents to extract Am(III) and Cm(III) selectively over Ln(III) out of solutions containing approximately molar nitric acid.[9-10]

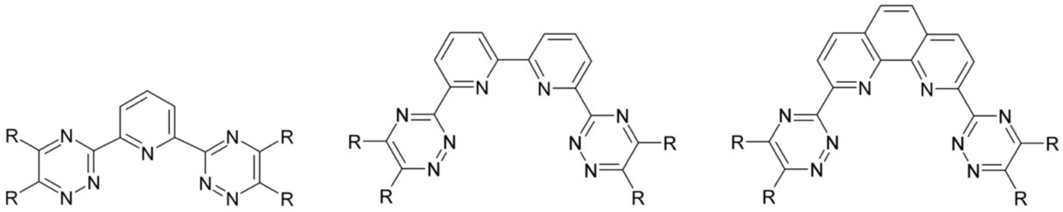

Figure 1. Generic BTP (left), BTBP (centre), and BTPhen (right) structures.

The first BTP compounds unfortunately were easily degraded by nitric acid and by radiation. The development leading to 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-2,2'-bipyridine (CyMe$_4$-BTBP, Figure 2),[11-12] the European reference compound for An(III)/Ln(III) separations to date, is reviewed in the literature in due detail.[7, 13-16]

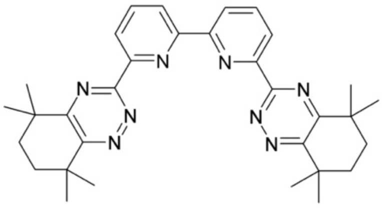

Figure 2. Molecular structure of CyMe$_4$-BTBP.

Covering the period from 2013 onwards, the present review gives an update on BTP, BTBP, and BTPhen (Figure 1) compounds (including some promising modifications to the backbone) relating to An(III)/Ln(III) separations. We explicitly do not review the literature on solid-state structures,[17-18] solvent extraction process development,[19-30] solid-liquid applications,[31-40] radiolysis and stability studies,[41-50] non-An(III)-Ln(III) chemistry, [51-56] and theory studies.[57-66]

A sound knowledge of their coordination chemistry is instrumental to designing improved extracting and complexing agents. Thus, this article reviews the recent literature on An(III)/Ln(III) solvent extraction and coordination chemistry with the above-mentioned ligands, highlights current trends, and proposes directions to proceed. Finally, this article also reflects the authors' views.

Systematic modifications to hydrophobic BTP and BTBP ligands

To optimize their properties as extracting agents, structural modifications were carried out on BTP and BTBP ligands. Recent modifications include variations to the substituents at the triazines[67] or the substituents on the pyridine ring.[68-69] 2,6-bis(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8-methano-1,2,4-benzotriazin- 3-yl)pyridine (CA-BTP, Figure 3 top left)[70] was further studied, extending to further diluents.[71] CA-BTP however is not further studied in Europe due to problems with scale-up of the synthesis, i. e. the production of larger batches with reproducible properties.

So far, ligands foregoing the basic triazine-(bi)pyridine-triazine structure (e.g., 2,6-bis(1,2,4-triazol-3-yl)pyridines (Figure 3 bottom left),[9] 2,6-bis(pyrazol-3-yl)pyridines (Figure 3 bottom right),[72] and others[73-74]) did not extract An(III) nitrates, requiring addition of a lipophilic anion source such as 2-bromohexanoic acid.

Based on the favourable complexing properties of the water-soluble ligand PyTri-Diol (see section *PyTri-Diol* below and references[75-76]), several lipophilic derivatives were synthesised and tested. Of these, 2,6-bis[1-(2-ethylhexyl)-1,2,3-triazol-4-yl]pyridine (PTEH, Figure 3 top right) dissolved in kerosene/1-octanol mixtures extracts Am(III) directly (i. e., without requiring the addition of 2-bromohexanoic acid) from 1–4 mol/L HNO_3, separating it from Eu(III) ($SF_{\mathrm{Am(III)/Eu(III)}}$ = 70–100).[77]

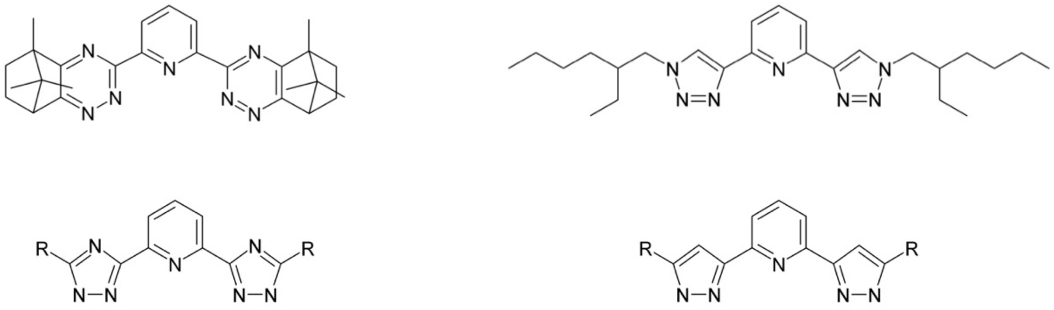

Figure 3. Molecular structures of CA-BTP (top left), PTEH (top right), 2,6-bis(1,2,4-triazol-3-yl)pyridines (bottom left), and 2,6-bis(pyrazol-3-yl)pyridines (bottom right).

Furthermore, the influence of the number of aromatic nitrogen atoms in the lateral rings on complexation properties was studied. In this context, two remarkable studies have to be mentioned. These show that theoretical predictions[78] are not necessarily confirmed by experiment.[79]

Density functional theory was used to evaluate fundamental properties (intrinsic binding affinity for Ln(III), basicity, and hardness) for prototype azine donors pyridine, pyridazine, pyrimidine, pyrazine, 1,2,3-triazine, 1,2,4-triazine, and 1,3,5-triazine.[78] The calculations showed pyridazine having the strongest intrinsic affinity for metal ions and being the second softest donor. Based on this information, three new prototype compositions of different azines were proposed which should exhibit improved metal ion affinity and An(III)/Ln(III) selectivity: pyridazine-pyridine-pyridazine, pyridazine-pyrazine-pyridazine, and pyridazine-1,3,5-triazine-pyridazine.

To obtain experimental evidence of these predictions two BTP-type N-donor ligands with different numbers of aromatic nitrogen atoms were synthesized and studied: 2,6-bis(4-ethyl-pyridazin-1-yl)pyridine (Et-BDP, a pyridazine-pyridine-pyridazine) and 2,6-bis(4-propyl-2,3,5,6-tetrazin-1-yl)pyridine (nPr-tetrazine), see Figure 4. Their complexation properties towards Cm(III) in 2-propanol–water (1:1, vol.) were compared to that of nPr-BTP (Figure 1 left, R = propyl) in the same solvent.[79]

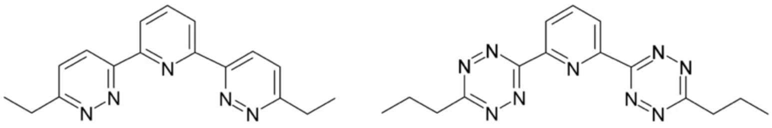

Figure 4. Molecular structures of Et-BDP (left) and nPr-tetrazine (right).

Speciation studies using time-resolved fluorescence spectroscopy (TRLFS) showed both Et-BDP and nPr-tetrazine to form 1:1, 1:2, and 1:3 complexes with Cm(III), whereas in case of nPr-BTP the 1:3 complex is formed exclusively. The conditional stability constants of the 1:3 complexes in 2-propanol/water (1:1, vol.) increase in the order lg β_3 [Cm(Et-BDP)$_3$] = 7.7 ± 0.3, lg β_3 [Cm(nPr-Tetrazine)$_3$] = 9.1 ± 0.4 and lg β_3 [Cm(nPr-BTP)$_3$] = 12.9 ± 0.3. Hence, the complexation of Cm(III) with both ligands is thermodynamically less favoured than the formation of [Cm(nPr-BTP)$_3$]. A similar trend was observed in solvent extraction tests:[73] Both Et-BDP and nPr-Tetrazine hardly extract any Am(III) and Eu(III) from solutions containing > 0.1 mol/L HNO_3. In contrast to the theoretical predictions,[78] the 1,2,4-triazine substituent was found to represent a structural optimum regarding complexation and solvent extraction performance.

Stability constants of An(III)-BTP and An(III)-BTBP complexes

A wealth of conditional stability constants for the complexation of Ln(III) with BTP and BTBP ligands is summarized in our previous review article,[7] together with few constants for An(III).

New stability constants were determined for [Am(BTP)$_3$]$^{3+}$ [80] and [Am(BTBP)$_2$]$^{3+}$ complexes[81] in acetonitrile + 0.01 mol/L tetramethylammonium nitrate. The values are in good agreement with stability constants for the respective Cm(III) complexes,[82-85] considering that different solvents (alcohol-water mixtures) were used.

To better understand the effect of solvent composition on stability constant values, a systematic investigation on the complexation of Cm(III) and Eu(III) with nPr-BTP in methanol/water mixtures (5–50 vol% water) using TRLFS was performed.[84] The stability constant of the $[\text{Cm(nPr-BTP)}_3]^{3+}$ complex was shown to increase by three orders of magnitude when the water content was reduced from 50 vol% ($\lg \beta_3 = 14.3 \pm 0.1$) to 5 vol% ($\lg \beta_3 = 17.4 \pm 0.4$). Only a slight increase was observed between 50 vol% and 20 vol% due to the preferential solvation of Cm(III) by water;[86] the increase was more pronounced for water contents between 20 vol% and 5 vol%. A similar trend was observed for the stability constant of the $[\text{Eu(nPr-BTP)}_3]^{3+}$ complex ($\lg \beta_3 = 12.0 \pm 0.1$ at 50 vol% water content; $\lg \beta_3 = 14.7 \pm 0.4$ at 5 vol% water content), resulting in a constant difference between the stability constants of the Cm(III) and Eu(III) 1:3 complexes ($\Delta\lg \beta_3 \approx 2.3$, see Figure 5).

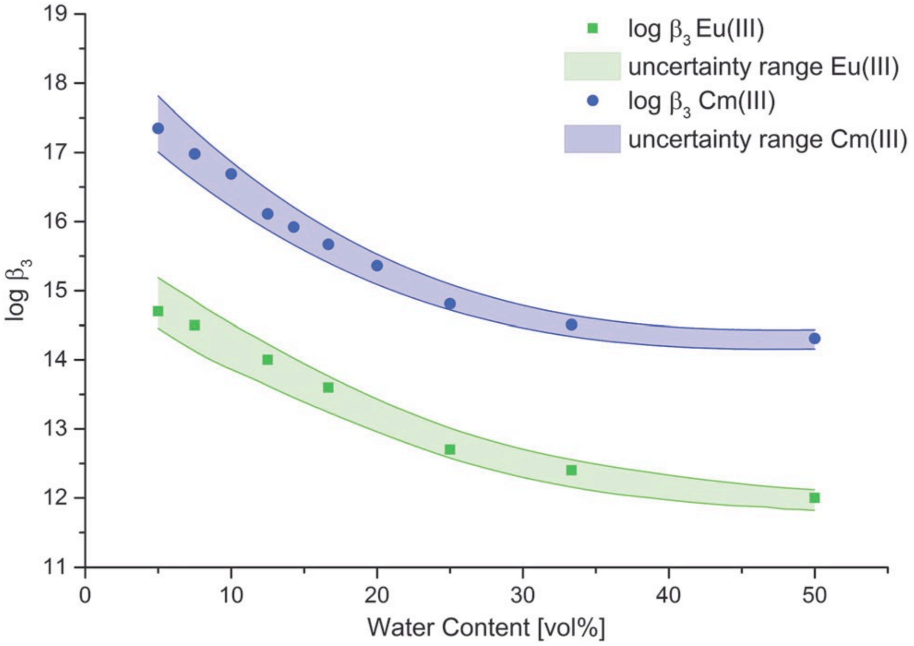

Figure 5. Stability constants of $[\text{Cm(nPr-BTP)}_3]^{3+}$ and $[\text{Eu(nPr-BTP)}_3]^{3+}$ as a function of the water content in methanol-water mixtures (water content, 5–50 vol%, $c(\text{Cm(III)})_{\text{ini}} = 10^{-7}$ mol/L, $c(\text{Eu(III)})_{\text{ini}} = 10^{-5}$ mol/L, $c(\text{H}^+)$ =10 mmol/L). Reproduced from reference[84] by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

These results demonstrate the strong impact of the solvent on a ligand's complexation strength as evident from the changes of the stability constants, whereas the selectivity remained constant for all solvent mixtures investigated.

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Update on NMR investigations

Speciation studies by NMR including ^{1}H-NMR titrations and relaxation titrations have been performed to determine the species distribution and complex stoichiometry of An(III) and Ln(III) with BTP, BTBP and BTPhen[11, 87-95] in solution.

In addition, comparative NMR studies on Am(III) and Ln(III) with BTP and similar ligands were performed to obtain further information on the molecular origin of the selectivity of N-donor ligands. In particular, ^{15}N NMR spectroscopy using ^{15}N-enriched ligands gave detailed insight into the bonding of N-donor ligands with Am(III) and Ln(III). ^{15}N signals from coordinating N-atoms in the Am(III) complexes were shifted upfield by ≈ 300 ppm in comparison both to Ln(III) complexes and to the free ligand (see Figure 6).[96-97] Furthermore, a slight temperature dependence of the chemical shifts of NMR resonance signals of the Am(III) complexes was observed, indicating a weak paramagnetism of Am(III). This shows that metal-ligand bonding in $[Am(BTP)_3]^{3+}$ has a larger share of covalence than in the respective Ln(III) complexes. Comparable upfield shifts of the ^{15}N signals of the coordinating N atoms were also observed for the $[Am(C5\text{-}BPP)_3]^{3+}$ complex (C5-BPP = 2,6-bis(5-(2,2-dimethylpropyl)-pyrazol-3-yl)pyridine, Figure 3 bottom right, R = 2,2-dimethylpropyl),[98] confirming significant differences in the bonding of Am(III) and Ln(III) complexes with N-donor ligands in general.

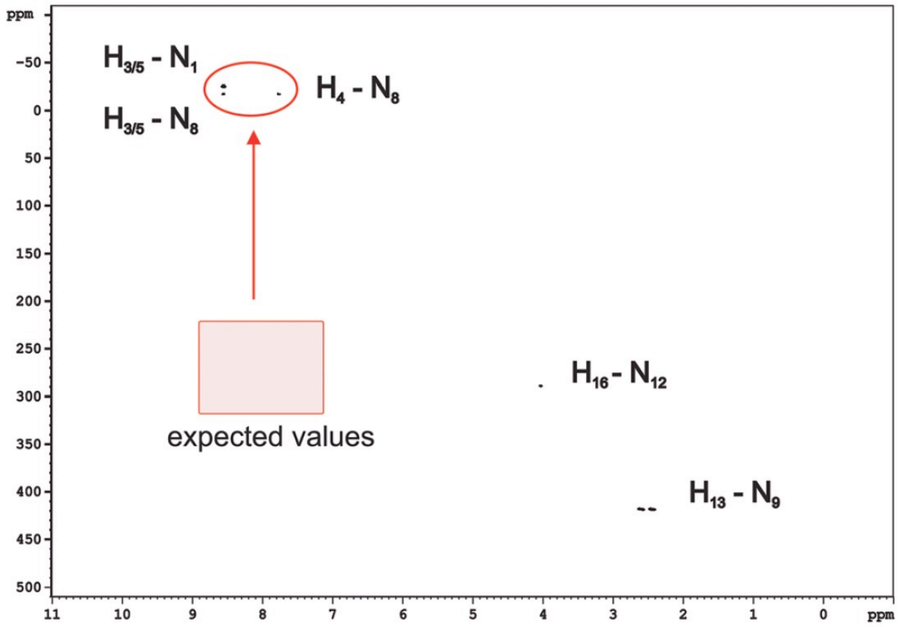

Figure 6. Overlay of two $^{1}H,^{15}N$-HMQC spectra of $^{243}Am(III)$ complexed with unlabelled and 10% labelled nPr-BTP (MeOD-d_4 and D_2O 3:1) with $^{n}J_{HN}$ of 5 and 2 Hz, respectively. The "expected values" range is taken from similar experiments with pure ligand and Lu(III) and Sm(III) complexes. Reproduced from reference[96] by permission of The Royal Society of Chemistry.

BTPhen compounds

As an alternative to CyMe$_4$-BTBP, CyMe$_4$-BTPhen had been introduced.[99] The BTPhen backbone is pre-organized in the *cis* conformation required for complexation and extraction while BTBP must overcome a rotational energy barrier prior to complexation. This was expected to result in improved properties as an extracting agent.

Indeed, this modification resulted in drastically changed properties: CyMe$_4$-BTPhen actually is a too strong extracting agent, showing significant co-extraction of Ln(III) and impeding back-extraction. Consequently, numerous studies were performed to understand and improve its performance.[58, 85, 92-93, 95, 100-111] The following conclusions are drawn:

- The fact that BTPhen are stronger extracting agents for An(III) and Ln(III) is caused by differences in complex stability as evident from displacement experiments performed by NMR[93] and stability constants determined by TRLFS.[85]
- Distribution ratios are repressed by electronically modifying the BTPhen,[92, 101, 103-104] by adding TEDGA (a competing water soluble ligand),[106] by changing the diluent[99] or using ionic liquids as diluents,[107, 111] or by tuning the aliphatic ring size.[95]
- Increased Am(III)/Cm(III) selectivity and different intra-Ln(III) selectivity patterns for BTPhen[99] compared to BTBP[12, 112-113] are due to a kinetic effect. Upon extended contacting times, BTPhen show a selectivity similar to BTBP.[104, 108]

Concluding, BTPhen fulfil the expectation of being stronger ligands compared to BTBP. However, bigger is not always better, and their performance as extracting agents to separate An(III) from Ln(III) indeed is inferior to that of the corresponding BTBP.

Water soluble compounds

SO$_3$-Ph-BTP

A water soluble BTP, (2,6-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)pyridine tetra-sodium salt, SO$_3$-Ph-BTP, Figure 7 top left)[114-116] was introduced to selectively strip An(III) from a solvent loaded with An(III) and Ln(III). This compound is an alternative to polyaminocarboxylates used in TALSPEAK-like processes.[117]

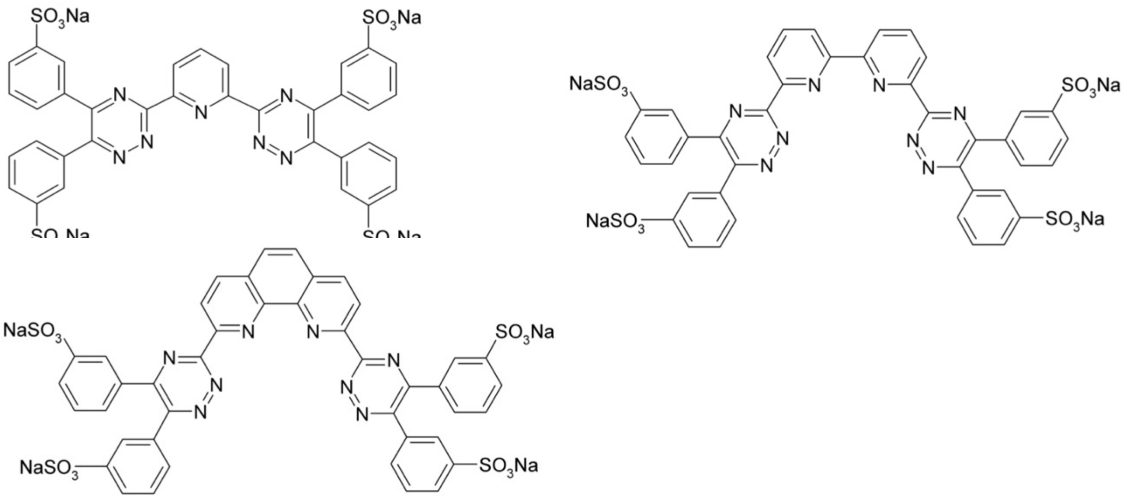

Figure 7. Molecular structures of SO_3-Ph-BTP (top left), SO_3-Ph-BTBP (top right), and SO_3-Ph-BTPhen (bottom).

A couple of recent publications illustrate this compound's impact on the development of An(III)/Ln(III) separation processes. Indeed, processes applying SO_3-Ph-BTP to generate an Am(III) + Cm(III) product solution[26] or a product solution containing Np, Pu, Am and Cm[25] were demonstrated using laboratory scale centrifugal contactor equipment. The latter process (known as EURO-GANEX) was finally demonstrated successfully using a genuine high level feed solution.[30] A product solution containing Np, Pu, Am and Cm with high purity was obtained, with recoveries of ≈ 99.9%. A variation to the EURO-GANEX process, generating separate Np, Pu and Am, Cm product solutions, was also demonstrated.[27]

SO_3-Ph-BTBP

Owing to the success achieved with SO_3-Ph-BTP, sulphonated BTBP and BTPhen (only mentioned briefly in our previous review[7]) were further studied in more detail.[118] A BTBP carrying two sulphophenyl moieties proved to be rather inefficient. However, BTBP and BTPhen with four sulphophenyl moieties had promising properties and were thus studied more deeply.

The solvent extraction properties of a system containing 6,6'-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)-2,2'-bipyridine tetra-sodium salt (SO_3-Ph-BTBP, Figure 7 top right) in the aqueous phase and *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA)[119-121] in the organic phase were studied in detail.[122] Distribution ratios of Am(III), Cm(III) and Ln(III) were determined as a function of time and of nitric acid and SO_3-Ph-BTBP concentrations. It was expected that a TODGA/ SO_3-Ph-BTBP solvent extraction system would separate Am(III) from Cm(III) and Ln(III), enabling the development of improved Am-only separation processes.[123] As evident from Figure 8, $D_{\mathrm{Am(III)}} < 1$ and $D_{\mathrm{Cm(III),\,Ln(III)}} > 1$ for $[HNO_3] \approx 0.8$ mol/L, with $SF_{\mathrm{Cm(III)/Am(III)}}$

≈ 2.5.[122] This separation factor results from TODGA's selectivity for Cm(III) over Am(III),[115] $SF_{\mathrm{Cm(III)/Am(III)}}$ ≈ 1.6, and a preferential affinity of BTBP for Am(III) over Cm(III), as observed e.g. for CyMe$_4$-BTBP,[12] $SF_{\mathrm{Am(III)/Cm(III)}}$ ≈ 1.6.

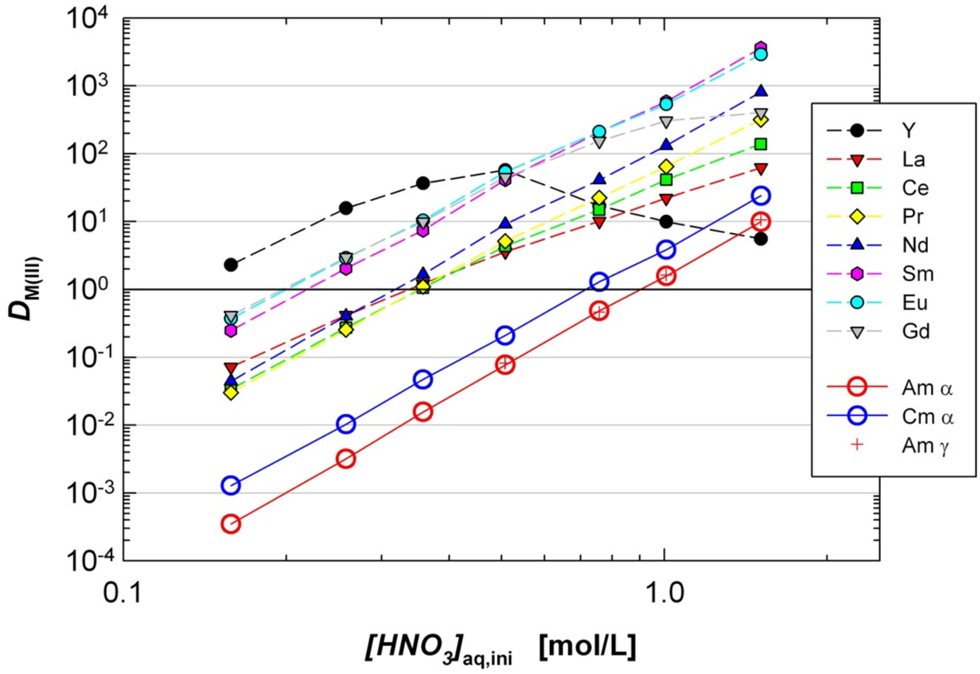

Figure 8. Distribution ratios of Am(III), Cm(III), Y(III), and light Ln(III) as a function of nitric acid concentration. Organic phase, 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80. Aqueous phase, ^{241}Am(III), ^{244}Cm(III), and ^{152}Eu(III) (1 kBq/mL each) + Ln(III) (6 mg/L each) and 20 mmol/L SO$_3$-Ph-BTBP in HNO$_3$. Data are from reference.[122]

The complexation of Cm(III) and Eu(III) with SO$_3$-Ph-BTBP in various aqueous solutions (10^{-3} mol/L and 0.5 mol/L HClO$_4$, 0.5 mol/L HNO$_3$, NaNO$_3$, and NaClO$_4$) was studied using TRLFS.[124] SO$_3$-Ph-BTBP was shown to form 1:2 complexes [M(SO$_3$-Ph-BTBP)$_2$]$^{5-}$ (M = Cm, Eu), as observed for hydrophobic BTBP.[12, 125] The conditional stability constants show a systematic variation in dependence of acidity and ionic strength. The conditional stability constants in 10^{-3} mol/L HClO$_4$ were determined to lg $\beta_{2,\,\mathrm{Cm(III)}} = 10.4 \pm 0.4$ and lg $\beta_{2,\,\mathrm{Eu(III)}} = 8.4 \pm 0.4$. The difference, Δlg β_{02} = 2 was in good agreement with the respective difference observed for a lipophilic BTBP[83] and with the Cm(III)/Eu(III) selectivity of CyMe$_4$-BTBP,[12] $SF_{\mathrm{Cm(III)/Eu(III)}}$ ≈ 90.

SO$_3$-Ph-BTPhen

2,9-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)-1,10-phenanthroline tetra-sodium salt (SO$_3$-Ph-BTPhen, Figure 7 bottom) was studied under similar conditions.[126] A SO$_3$-Ph-BTPhen/TODGA solvent extraction system performed slightly better than the respective system containing SO$_3$-Ph-BTBP: $D_{\mathrm{Am(III)}} < 1$ and $D_{\mathrm{Cm(III),\,Ln(III)}} > 1$ for [HNO_3] ≈ 0.6 mol/L with $SF_{\mathrm{Cm(III)/Am(III)}} = 3.6$ (compared to $SF_{\mathrm{Cm(III)/Am(III)}} \approx 2.5$[122]). With a stability constant of $\lg \beta_{2,\mathrm{Cm(III)}} = 10.7$, SO_3-Ph-BTPhen forms slightly more stable complexes with Cm(III) compared to SO_3-Ph-BTBP ($\lg \beta_{2,\mathrm{Cm(III)}} = 10.4$[124]). This trend, however more pronounced, was also observed for lipophilic BTBP and BTPhen.[85]

Heteroleptic complexes

The systems combining TODGA and hydrophilic ligands such as SO_3-Ph-BTP, SO_3-Ph-BTBP or SO_3-Ph-BTPhen show an unexpected dependence of Am(III) and Cm(III) distribution ratios on ligand concentration: With SO_3-Ph-BTP forming 1:3 complexes[116] and SO_3-Ph-BTBP and SO_3-Ph-BTPhen forming 1:2 complexes,[124, 126] plots of $\lg D_{\mathrm{Am(III)}}$ versus $\lg [ligand]$ should have slopes of −3 (SO_3-Ph-BTP) or −2 (SO_3-Ph-BTBP, SO_3-Ph-BTPhen), respectively. However, slopes closer to −2[115, 127] and −1,[122, 126] respectively, were found.

A study was carried out to verify whether this behaviour is caused by the formation of heteroleptic complexes in the organic phase, i.e. the replacement of a TODGA molecule by the hydrophilic ligand.[128] Samples of both organic and aqueous phases from solvent extraction experiments with Cm(III) were studied by TRLFS. Only the respective complexes, $[\mathrm{Cm(SO_3\text{-}Ph\text{-}BTP)_3}]^{9-}$ and $[\mathrm{Cm(SO_3\text{-}Ph\text{-}BTBP)_2}]^{5-}$ were detected in the aqueous phases. Organic phases only contained the TODGA complex, $[\mathrm{Cm(TODGA)_3}]^{3+}$, without any proof of a heteroleptic complex (see also reference[124]). However, 5.5×10^{-5} mol/L SO_3-Ph-BTP was detected in the organic phase from a solvent extraction experiment involving elevated concentrations (0.03 mol/L) of Eu(III).[128] Eu(III) is not expected to partition to the organic phase as a homoleptic SO_3-Ph-BTP complex. Hence, the finding that SO_3-Ph-BTP measurably partitions to the organic phase when higher concentrations of Eu(III) are extracted was seen as a clear indication for the formation of heteroleptic complexes. The heteroleptic complexes' concentration was estimated to 0.2% relative to the $[\mathrm{Eu(TODGA)_3}]^{3+}$ complex, which was used as an explanation for why they could not be detected spectroscopically. Finally, the formation of such heteroleptic complexes was forced by preparing monophasic samples containing Cm(III), SO_3-Ph-BTP or SO_3-Ph-BTBP, and TEDGA, a water soluble DGA. Indeed, emission spectra from heteroleptic complexes were identified (see Figure 9 for the TEDGA/SO_3-Ph-BTP system).[128]

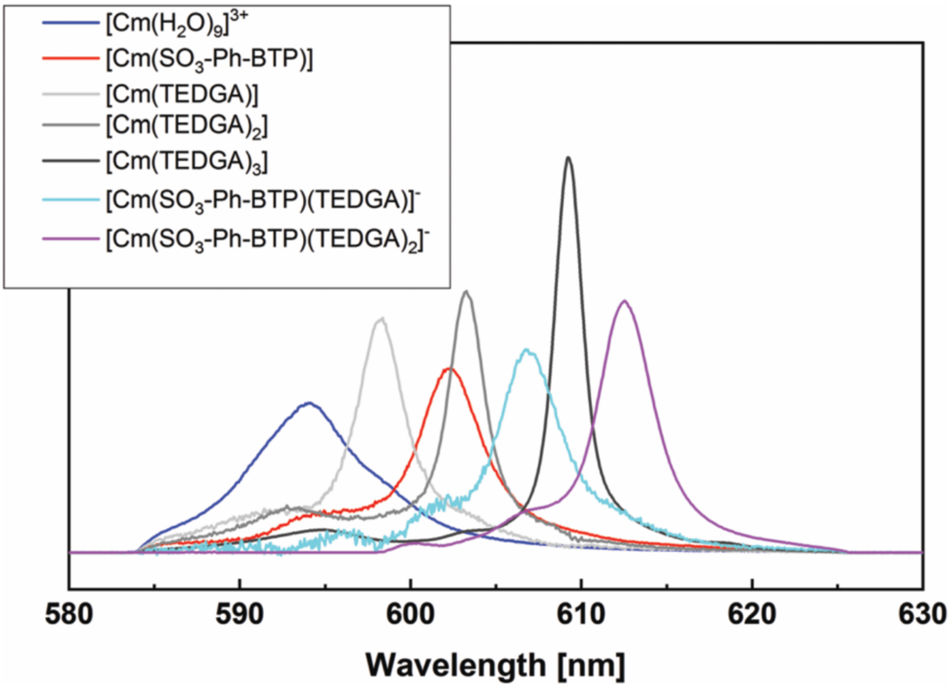

Figure 9. Pure component spectra of the Cm(III) complexes with SO_3-Ph-BTP and with TEDGA, and the heteroleptic complexes. Reproduced from reference[128] by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

Further hydrophilic ligands

Since such stripping agents are not intended to be recycled, the sulphur content of SO_3-Ph-BTP and SO_3-Ph-BTBP results in the generation of large volumes of solid secondary waste. This is a serious problem in a potential industrial application. Compounds containing only C, H, O, or N atoms (known as *CHON* compounds) are combustible to gaseous products.[129] Consequently, work focused on developing *CHON* compounds with properties similar to those of SO_3-Ph-BTP and SO_3-Ph-BTBP. Unfortunately, compounds hydrophilised by carboxylate groups[130] or quaternary ammonium functions[58] turned out to be rather inefficient for the intended applications.

PyTri-Diol

A considerable breakthrough was achieved with the development of 2,6-bis(1,2,3-triazol-4-yl)pyridine ligands hydrophilised with two, four, or six hydroxyl functions.[75] These compounds allowed stripping Am(III) from a TODGA solvent containing Am(III) and Eu(III) with a selectivity up to $SF_{\mathrm{Eu(III)/Am(III)}} = 240$. 2,6-bis[1-(3-hydroxypropyl)-1,2,3-triazol-4-yl]pyridine (PyTri-Diol, Figure 10), containing two hydroxyl functions, was selected for further studies.

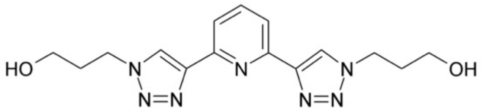

Figure 10. Molecular structure of PyTri-Diol.

A study of the PyTri-Diol/TODGA system's applicability reports Am(III) and Ln(III) distribution data in dependence of PyTri-Diol (Figure 11) and nitric acid concentrations.[131] Nitric acid and PyTri-Diol concentrations of ≈ 0.4 mol/L and 0.08 mol/L, respectively, were identified as optimum conditions to selectively strip An(III), i. e. $D_{\mathrm{An(III)}} < 1$ and $D_{\mathrm{Ln(III)}} > 1$.

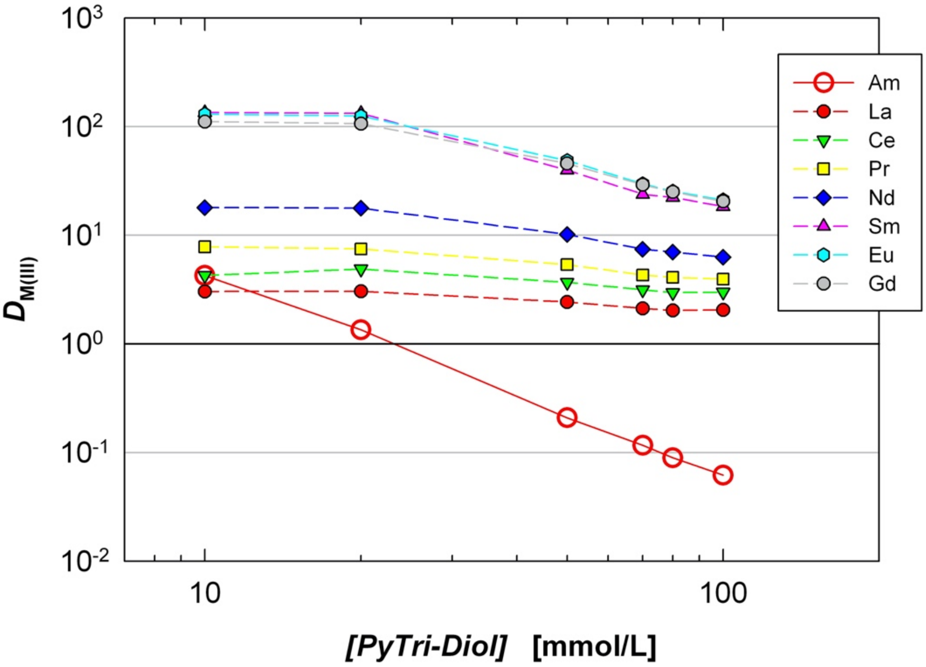

Figure 11. Am(III) and lighter Ln(III) distribution ratios as a function of PyTri-Diol concentration. Organic phase, 0.2 mol/L TODGA + 5 vol.% 1-octanol in kerosene. Aqueous phase, PyTri-Diol, Am(III) and Ln(III) in 0.4 mol/L HNO_3. Data are from reference.[131]

To better understand the behaviour of the PyTri-Diol/TODGA solvent extraction system, the complexation of Cm(III) and Eu(III) with PyTri-Diol was studied in different solutions (10^{-3} mol/L $HClO_4$, 0.44 mol/L HNO_3; the latter to reflect conditions relevant to solvent extraction) and in aqueous phases from solvent extraction experiments using TRLFS.[76] Conditional stability constants for the 1:3 Cm(III) complexes were $\log \beta_{3,\,\mathrm{Cm(III)}} = 9.7 \pm 0.3$ (10^{-3} mol/L $HClO_4$) and $\log \beta_{3,\,\mathrm{Cm(III)}} = 5.7 \pm 0.3$ (0.44 mol/L HNO_3). This pronounced decrease was found to be due to ligand protonation ($pK_a = 2.1$[75]). The respective Eu(III) stability constants were lower by approximately two orders of magnitude (similar differences between Cm(III) and Eu(III) stability constants were reported for BTP,[82, 84, 116] BTBP,[83, 124] and BTPhen[85]). The aqueous phases from a Cm(III) solvent extraction experiment contained 22%

1:2 complex and 78% 1:3 complex. An equivalent experiment with SO_3-Ph-BTP revealed the formation of only the 1:3 complex.[128] This difference explains the lower An(III)/Ln(III) selectivity of the PyTri-Diol/TODGA solvent extraction system[75, 131] compared to SO_3-Ph-BTP/TODGA.[115]

To increase the affinity of PyTri-Diol for An(III), an electron donating methoxy moiety was attached to the para position of the pyridine.[132] This indeed resulted in an increased stability constant of the Cm(III) 1:3 complex from $\log \beta_{3,\,\mathrm{Cm(III)}} = 9.9 \pm 0.5$ (PyTri-Diol) to $\log \beta_{3,\,\mathrm{Cm(III)}} = 10.8 \pm 0.4$ (PTD-OMe[76]). Unfortunately, this came along with a greater pK_a value (2.54 vs. 2.1 for PyTri-Diol[75]), overcompensating the increased affinity for An(III) and resulting in inferior performance in solvent extraction experiments.

A *CHON* BTPhen

Based on the PyTri-Diol and PyTri-Tetraol compounds, the first *CHON* BTPhen ligands were synthesized and screened for Am(III)/Eu(III) and Am(III)/Cm(III) separation in combination with TODGA.[133] Although Am(III)/Eu(III) selectivity was inferior to that of PyTriDiol, the new BTPhen/TODGA systems showed an appreciable selectivity for Cm(III) over Am(III), $SF_{\mathrm{Cm(III)/Am(III)}} \approx 2.5$. This value is comparable to that of the non-*CHON* SO_3-Ph-BTBP/TODGA system.[122] Unfortunately, the system had not been studied towards its selectivity between Am(III) and the lightest Ln(III), which is usually the bottleneck of such systems.

Conclusions and outlook

Our previous review[7] on BTP and BTBP coordination and solvent extraction chemistry recapitulated the development and evolution of these ligands, from the first BTP up to water soluble SO_3-Ph-BTP and SO_3-Ph-BTBP. We pointed out the link between fundamental complexation properties and solvent extraction behaviour. Compiling the structures, stoichiometry and stability of An(III) and Ln(III) complexes made evident a wealth of data on Ln(III) but a striking lack of data on An(III).

A traditional cook-and look approach to ligand development had largely been followed in early European research programmes. This resulted in a multitude of ligands, most of them without useful properties as extracting agents. More systematic approaches have been followed lately, focussing on the most promising backbones and considering insight from fundamental and theory studies.

For many years, finding experimental evidence for a larger covalent share in the An(III)-N bond compared to the Ln(III)-N bond was an important goal. The first few NMR studies on Am(III)-BTP complexes finally provided such evidence.

Although application and process development were not covered in this review, the advent of hydrophilic BTBP and BTPhen ligands have promoted the development of processes for separating only Am(III) from Cm(III) and Ln(III). *CHON* alternatives to SO_3-Ph-BTBP has to be the next step.

The development of efficient processes for separating actinides should always be supported by fundamental studies. Such studies are not only of scientific value but also help closing gaps in process understanding.

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