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Utilizing electronic effects in the modulation of BTPhen ligands with respect to the partitioning of minor actinides from lanthanides†

Ashfaq Afsar,[a] Dominic M. Laventine,[a] Laurence M. Harwood,*[a] Michael J. Hudson[a] and Andreas Geist[b]

Effects of bromine substitution at the 5 and 5,6-positions of the 1,10-phenanthroline nucleus of BTPhen ligand on their extraction properties for Ln(III) and An(III) cations have been studied. Compared to C5-BTPhen, electronic modulation in BrC5-BTPhen and Br$_2$C5-BTPhen enabled these ligands to be fine-tuned in order to enhance the separation selectivity of Am(III) from Eu(III).

The spent nuclear fuel produced by a typical light water reactor consists mainly (>98.5%) of uranium and short-lived fission products which do not pose a long term hazard.[1–3] However, approximately 1 wt% of the spent fuel is composed of plutonium and minor actinides (Am, Cm, Np), which are highly radiotoxic.[1–3] The PUREX (Plutonium and URanium EXtraction) process is used to remove Pu and U from spent fuel, so that it can be reused as mixed oxide fuel.[4,5] However, the remaining high level liquid waste (PUREX raffinate) still contains the minor actinides that account for the major long-term radiotoxicity of used nuclear fuel despite comprising less than 0.1% by weight.

Separation of the minor actinides from the lanthanides and other fission products is a key step in the partitioning and transmutation scenario for reprocessing of used nuclear fuel, and has been achieved using nitrogen-bearing ligands; for instance the 2,6-di(1,2,4-triazine-3-yl)pyridines (BTPs)[6] and 6,6′-bis(1,2,4-triazin-3-yl)-2,2′-bipyridines (BTBPs)[7–9] (see Fig. 1). In a recent development, the 2,2′-bipyridine moiety was replaced by a 1,10-phenanthroline moiety (BTPhen).[1–3,10,11] The effect of this new modification on the ligand extraction properties was startling. Extractions with solutions of CyMe$_4$–BTPhen ($D_{\mathrm{Am}} \leq 1000$) were about 2 orders of magnitude more efficient than those of CyMe$_4$–BTBP ($D_{\mathrm{Am}} \leq 10$), and the resulting SF were in the range 68–400. More importantly, the kinetics of extraction were significantly faster, such that full equilibrium was reached within 15 min without the need for addition of a phase transfer agent.[1,10,12]

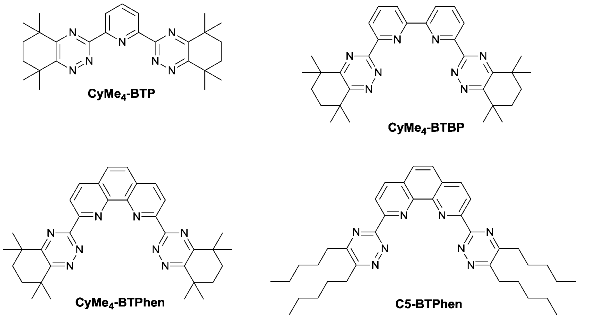

Fig. 1 Structures of CyMe$_4$–BTP, CyMe$_4$–BTBP, CyMe$_4$–BTPhen and C5-BTPhen.

During the development of BTPhens, the aliphatic side chains attached to the traizine units of the ligand were varied to increase the solubility in the organic phase or provide a better resistance towards radiolysis. One such BTPhen ligand was tetra pentyl-BTPhen (Fig. 1), denoted henceforth as C5-BTPhen.[13]

The work described in this communication primarily focuses on the extraction abilities of this ligand and investigates the influence of subtle electronic effects upon ligand selectivity for the minor actinides over the lanthanides. Although both the lanthanides and actinides are f-block elements, the 4f orbitals in the lanthanides do not extend past the 5d orbitals, whereas the 5f orbitals in actinides do extend further than the 6d orbitals.[14,15] This means that, although possessing very similar properties, Ln(III)–ligand interactions are considered to be more ionic and less covalent than An(III)–ligand interactions.[14,15] Thus it is proposed that "softer" ligands bind more effectively to actinides.[14,15]

The 5,6-double bond in phenanthroline can be readily functionalized and we decided to explore the electronic effects of substituents at this position on the ligating selectivity in the BTPhens. 5-Bromo-2,9-dimethyl-1,10-phenonthroline **2** was obtained following the literature procedure (Scheme 1).[16] In addition, when excess bromine was used, bromination of 2,9-dimethyl-1,10-phenanthroline **1** yielded the novel 5,6-dibromo-2,9-dimethyl-1,10-phenanthroline **3**.

The corresponding BTPhen ligands **7b** and **7c** were synthesized from **2** and **3** as previously described[1,13] with the modification that

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[a] *School of Chemistry, University of Reading, Whiteknights, Reading, Berkshire RG6 6AD, UK. E-mail: l.m.harwood@reading.ac.uk*
[b] *Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany*

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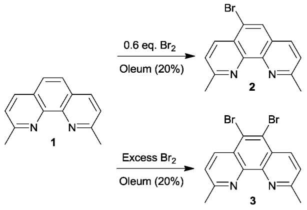
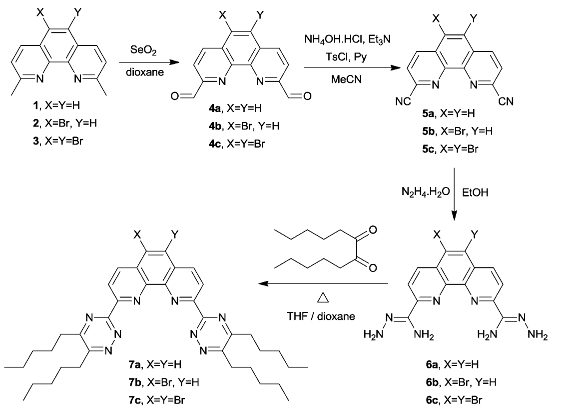


Scheme 1 Bromination of 2,9-dimethyl-1,10-phenanthroline **1**.



Scheme 2 Synthesis of C5-BTPhen ligands.

the final step was performed with dodecane-6,7-dione[17] in dioxane at reflux, rather than in THF at reflux (Scheme 2).

NMR spectroscopic titrations of ligands with diamagnetic metal salts were used to determine the stoichiometries of the complexes in solution.[18–21] NMR titrations of the C5-BTPhen **7a** with a number of trivalent lanthanide (lanthanum and lutetium) salts were thus performed in deuterated acetonitrile (CD_3CN). La(III) (ionic radius = 116 pm)[15] and Lu(III) (ionic radius = 98 pm)[15] were chosen to give the greatest difference in of the Ln(III) radius. The results of the titrations indicated that the ligand initially formed 2 : 1 ligand–metal complexes in solution, since conversion to a new species was complete after addition of 0.5 equivalents of metal salt for all lanthanides tested. Subsequent formation of 1 : 1 complexes was observed upon addition of excess metal salt (Fig. 2–5), although in all cases, the majority of the BTPhen remained bound in 2 : 1 complexes even in the presence of 3 equivalents of Ln(III).

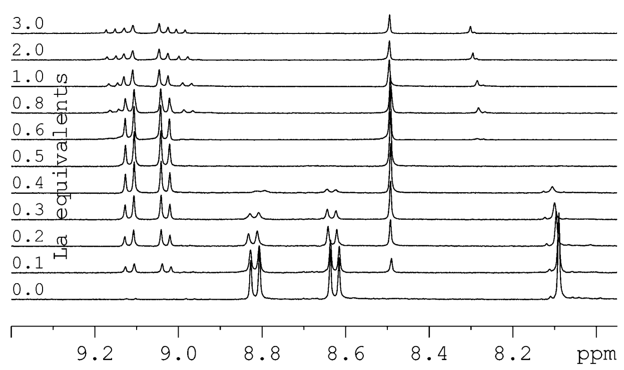


Fig. 2 Stacked ^1H NMR spectra (8.0–9.3 ppm) of C5-BTPhen **7a** (0.01 M) titrated with $La(NO_3)_3 \cdot 6H_2O$ in CD_3CN.

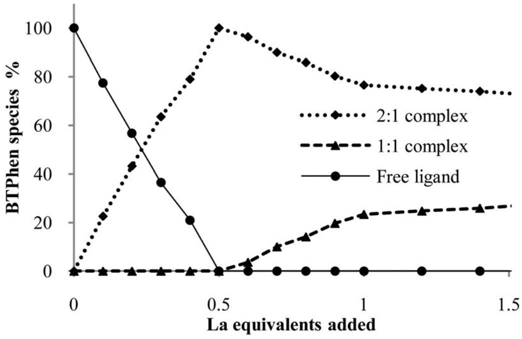


Fig. 3 Graph showing C5-BTPhen **7a** composition at increasing La equivalents.

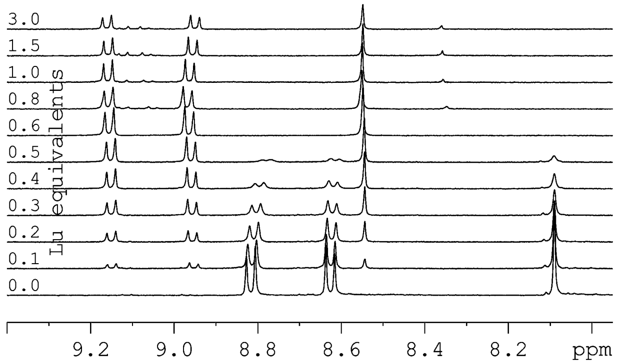


Fig. 4 Stacked ^1H NMR spectra (8.0–9.3 ppm) of C5-BTPhen **7a** (0.01 M) titrated with $Lu(NO_3)_3$ in CD_3CN.

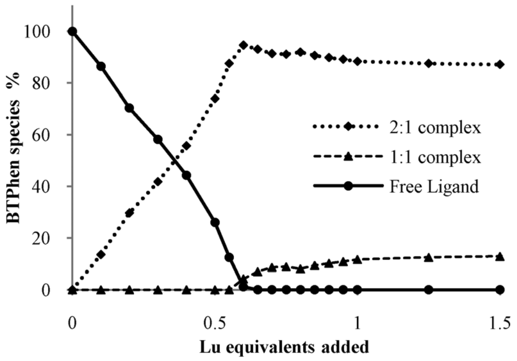


Fig. 5 Graph showing C5-BTPhen **7a** composition at increasing Lu equivalents.

In the case of the lanthanum complexes, formation of the 1 : 1 complex occurred to a greater degree for a given metal concentration, compared to the corresponding lutetium complex. These results suggest that the relative stabilities of 2 : 1 complexes compared to the 1 : 1 complexes are greater for lutetium than for the lanthanum complexes. It has been postulated that the 2 : 1 complex is the extracting species owing to the metal centre being completely enclosed by the hydrophobic shell formed by the two ligands.

Ligands **7a**, **7b** and **7c** were also evaluated for their ability to extract Am(III) selectively in the presence of Eu(III) from aqueous nitric acid solutions into 1-octanol. The distribution factor for Am(III) and Eu(III) (D_{Am} and D_{Eu}) and the separation factor for americium over europium ($SF_{Am/Eu}$) for **7a** in 1-octanol as a

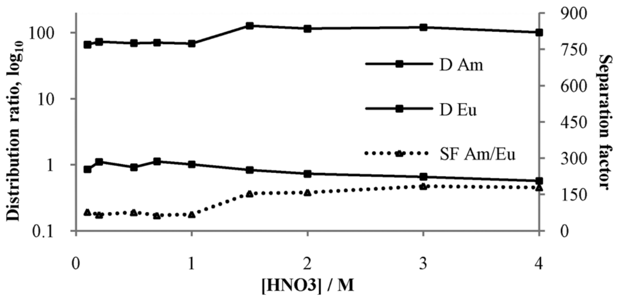


Fig. 6 Extraction of Am(III) and Eu(III) by C5-BTPhen **7a** in 1-octanol as a function of nitric acid concentration.

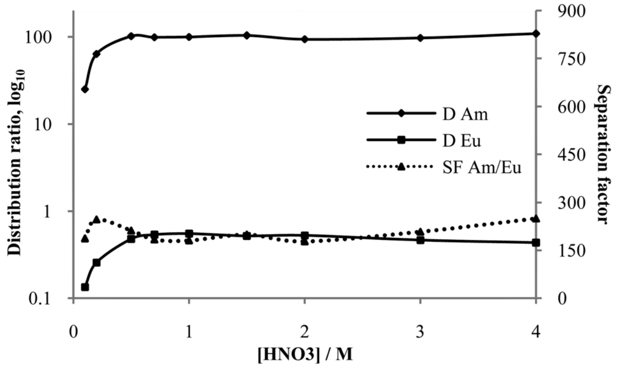


Fig. 7 Extraction of Am(III) and Eu(III) by BrC5-BTPhen **7b** in 1-octanol as a function of nitric acid concentration.

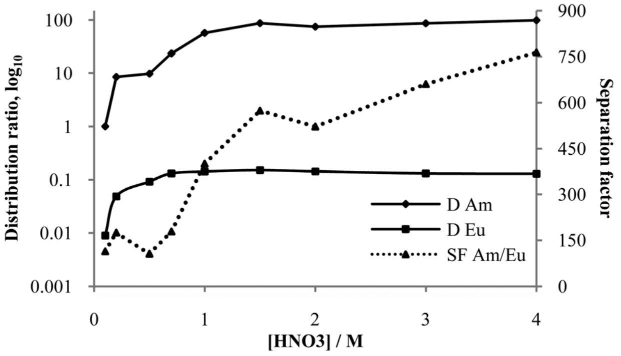


Fig. 8 Extraction of Am(III) and Eu(III) by Br_2C5-BTPhen **7c** in 1-octanol as a function of nitric acid concentration.

function of the nitric acid concentration of the aqueous phase are shown in Fig. 6.

High selectivity was observed for Am(III) over Eu(III) ($SF_{Am/Eu}$ = *ca.* 180 at 4 M HNO_3) and no significant changes in *D* values were observed for both Am(III) and Eu(III) with increasing HNO_3 concentration in the aqueous phase.

Similar results were obtained for BrC5-BTPhen **7b** in 1-octanol (Fig. 7) but a higher separation factor was observed ($SF_{Am/Eu}$ = 250 at 4 M HNO_3). However, while the *D* value for Am(III) remained at 100, the *D* value for Eu(III) was significantly lower for **7b** compared to **7a** over the range of HNO_3 concentrations.

The extraction of Am(III) and Eu(III) from nitric acid solutions by **7c** in 1-octanol were subsequently investigated and compared with the corresponding data for **7a** and **7b**. A similar *D* value for Am(III) was observed (D_{Am} = 100) (Fig. 8) to those found in **7a** and **7b** but, the *D* value for Eu(III) was approximately one order of magnitude lower than that of **7a**, and the resulting separation factor ($SF_{Am/Eu}$ = *ca.* 800 at 4 M HNO_3) was superior to those observed for **7a** and **7b**.

In conclusion, we have reported the synthesis, lanthanide speciation and Am(III)–Eu(III) solvent extraction properties of C5-BTPhen ligands with bromine substitution at the 5 or 5,6-positions of the 1,10-phenanthroline moiety. The presence of bromine did not affect the capacity of the ligands to extract Am(III) but decreased the extraction of Eu(III) from 4 M HNO_3 with the result that the $SF_{Am/Eu}$ ratios were substantially greater than is the case with C5-BTPhen. The Br atoms inductively withdraw electron density from the rings and we conclude that this reduces the electron donating capacity of the phenanthroline nitrogens making the ligand less effective for complexing with lanthanides.

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