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Direct nano ESI time-of-flight mass spectrometric investigations on lanthanide BTP complexes in the extraction-relevant diluent 1-octanol

Michael Steppert,*[a] Clemens Walther,[a] Andreas Geist[a] and Thomas Fanghänel[b]

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The present work focuses on investigations of a highly selective ligand for Am(III)/Ln(III) separation: bis-triazinyl-pyridine (BTP). By means of nano-electrospray mass spectrometry, complex formation of BTP with selected elements of the lanthanide series is investigated. We show that the diluent drastically influences complex speciation. Measurements obtained in the extraction-relevant diluent 1-octanol show the occurrence of $Ln(BTP)_i$ (i = 1–3) species in different relative abundances, depending on the lanthanide used. Here, the relative abundances of the $Ln(BTP)_3$ complexes correlate with the distribution ratios for extraction to the organic phase of the respective lanthanide.

1. Introduction

The concept of partitioning and transmutation (P&T) aims at reducing the long term radiotoxicity of spent nuclear fuels *via* the separation of the long-lived actinides, converting them into short lived or stable nuclides with the help of fission reactions. One of the key steps in this P&T strategy is the separation of the trivalent actinides Am(III) and Cm(III), which have similar chemical properties, from the lanthanides. Some lanthanide nuclides have large neutron capture cross-sections and could lower the transmutation efficiency drastically.[1] Alkylated bis-triazinyl-pyridines (BTPs, *e.g.* see Fig. 1) have been developed for this important separation step.[2,3] These molecules are able to extract the trivalent actinides Am(III) and Cm(III) selectively over fission lanthanides from 1 M nitric acid into an organic phase containing 1-octanol and 40 mM *n*-Pr-BTP in kerosene/1-octanol.[4–6] Fig. 2 shows the different distribution ratios of the trivalent actinides Am(III) and Cm(III), and the lanthanides for extraction. Besides good extracting properties, BTPs have the advantage of only consisting of carbon, hydrogen, oxygen and nitrogen atoms ("CHON" principle), making them combustible into gaseous products.[7] The high selectivity of tridentate BTP ligands towards the extraction of the trivalent actinides is not yet understood completely. Meanwhile, a different ligand, BTBP (alkylated bis-triazinyl-bipyridine), is considered the reference molecule for Ln/An separation.[8–10] Nevertheless, BTPs are still useful for gaining a fundamental understanding of extraction selectivity. The developing of distribution ratio values through the lanthanide series (Fig. 2) is comparable to those of the newer BTBP ligands.[11] The pyridine and triazinyl nitrogen atoms in the 2-position act as donor atoms.[12] Slope analysis of the extraction experiments showed that at high BTP concentrations, trivalent actinides and lanthanides are complexed by three BTPs.[3] The complexation of Cm(III) and Eu(III) by *n*-propyl-BTP was compared by EXAFS, time-resolved laser fluorescence spectroscopy (TRLFS) and quantum chemical methods.[13] The EXAFS results indicated similar Cm–N and Eu–N bond lengths in these complexes. Quantum chemical calculations on this system agreed with this finding. The $Cm/Eu(BTP)_3$ complexes have a tri-capped trigonal prismatic structure with planar BTP ligands. These results show that the origin of the selective extraction of trivalent actinides Am(III) and Cm(III) over Ln(III) does not lie in differences in coordination number or bond length. The TRLFS investigations showed that the formation of the $Cm(BTP)_3$ complex begins at a lower BTP concentration than for the respective Eu complex. This points to the different thermodynamic stabilities of these complexes. Iveson *et al.* obtained similar results for the complexation of U(III) and Ce(III) with methyl-BTP in ref. 14. NMR titrations showed that $U(BTP)_3$ complexes formed even with sub-stoichiometric amounts of BTP; in contrast, Ce formed $Ce(BTP)_2$ complexes under these conditions. X-Ray crystallography results[14,15] revealed similar structures for the U- and Ce-BTP complexes, but with shorter U–N than Ce–N bond lengths. The shorter U–N bond length was discussed in terms of the higher degree of covalency of the U–N bond and the π-donor ability of U(III).[16,17]

The interaction of different BTP ligands with trivalent lanthanides has been studied before by ESI mass spectrometry, but in contrast to the present work, a nitric acid/methanol mixture was used as the solvent.[18,19] The exclusive formation of 3 : 1 complexes ($[Ln(BTP)_3(NO_3)_n]^{(3-n)+}$ (n = 0, 1)) was detected. The occurrence of $Ln(BTP)_2$ complexes in these spectra was traced back to fragmentation reactions within the ESI process. The calculated stability constants for the 3 : 1 complexes of La and the lanthanides increased by about

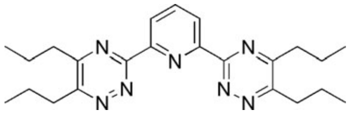

Fig. 1 2,6-Di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (*n*-propyl-BTP).

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[a] *Institute for Nuclear Waste Disposal, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany. E-mail: michael.steppert@ine.fzk.de*
[b] *Institute for Transuranium Elements, European Commission, Joint Research Center, 76125 Karlsruhe, Germany*

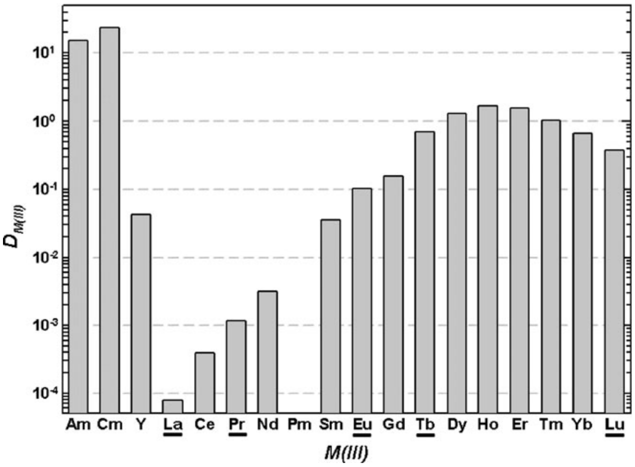

Fig. 2 Distribution ratios for lanthanide extraction to the organic phase with a BTP ligand (aqueous phase: 1 M HNO_3, organic phase: 40 mM *n*-Pr-BTP in kerosene/1-octanol). The highlighted lanthanides are the subject of the presented investigations.

four orders of magnitude from La to Lu. The investigations were corroborated by TRLFS measurements to confirm the stability constant of the Eu(*i*-Pr-BTP)$_3$ complex.[20]

In extraction experiments, different diluents showed an effect on complex speciation.[10,21,22] While Colette *et al.*[18,19] restricted their investigations to the solvent nitric acid/methanol, the present work aims at determining whether the interaction of BTPs with lanthanides could be studied directly in organic solution (*i.e.* in the extraction relevant diluent 1-octanol) by means of nano-electrospray mass spectrometry. Furthermore, these measurements should provide a better understanding of the different extraction behaviour of the lanthanides depicted in Fig. 2. We have found that it is not only possible to perform ESI measurements in 1-octanol, but that, as expected, the diluent strongly influences the complexes detected by ESI-MS.

2. Experimental

2.1 Sample preparation

n-Propyl-BTP was synthesised as described in ref. 2. All BTP solutions were freshly prepared before measurements since BTP is stable in solution for only a few days.

2.1.1 Investigations on the influence of the solvent on complex speciation. For the nitric acid/methanol and nitric acid/propanol measurements, $Eu(NO_3)_3{\cdot}6H_2O$ (Sigma-Aldrich) stock solutions with [Eu] = 10^{-4} M were prepared in nitric acid at pH 4.3. *n*-Propyl-BTP stock solutions (2×10^{-4} M) were prepared by dissolution of appropriate amounts of the ligand in methanol (Sigma-Aldrich) and 1-propanol (Sigma-Aldrich), respectively. For the nano-ESI measurements 1 : 1 v/v stock solutions were prepared, resulting in [Eu] = 5×10^{-5} M and [BTP] = 10^{-4} M. The investigations in the 1-hexanol and 1-octanol systems were carried out using the same concentrations as for Eu and the extraction ligand by following the aforementioned procedure, except for diluting the $Eu(NO_3)_3{\cdot}6H_2O$ directly in the respective alcohol.

2.1.2 Investigations on the complex speciation of selected lanthanides. BTP stock solutions (10^{-3} M) were prepared by dissolving appropriate amounts of *n*-propyl-BTP in 1-octanol (Sigma-Aldrich, ≥ 99,5%). Ln(III) (Ln = La, Pr, Eu, Tb and Lu) stock solutions (10^{-4} M) were produced by dissolving a weighed amount of $Ln(NO_3)_3{\cdot}nH_2O$ (n = 5 or 6) in 1-octanol (Sigma-Aldrich).

Solutions for the nano-ESI TOF MS measurements (0.25 ml) were prepared by mixing appropriate volumes of the stock solutions and 1-octanol, resulting in [Ln] = 5×10^{-5} M. Measurements were performed on samples of two different ligand-to-metal ratios. A ligand-to-metal ratio of 2 : 1 was applied to check if the exclusive formation of 3 : 1 complexes, found in the water/methanol system (even with sub-stoichiometric BTP concentrations),[18] also occurs in 1-octanol. A higher BTP concentration (ligand-to-metal ratio 10 : 1) was used to approach the conditions of the extraction process.

2.2 Electrospray mass-spectrometer

The electrospray ionisation method was developed by Dole *et al.*[23] and is coupled to mass spectrometry, which is broadly applied to investigate macromolecules.[24–26] Being a very soft ionisation method, it is also used to analyse the hydrolysis products of metal salts, for instance of Fe^{3+} and Al^{3+} ions,[27–30] and of Zr(IV),[31] Th(IV)[32] and Pu(IV).[33]

The ALBATROS ESI-TOF mass spectrometer was built by Bergmann *et al.*[34–37] The home made nanospray ion source was equipped with spray capillaries with an inner tip diameter of 1 μm from Proxeon (Odense, Denmark). These were filled with a 10 μl sample solution. A voltage of 2100 V was connected to the spray capillaries to generate the electrospray, and a static nitrogen pressure of $<$0.5 bar was applied to the end of the capillary. The sample flow rate was approximately 15 nl min^{-1}. The voltage between the orifice and skimmer was kept at 42 V. Nitrogen at flow rates of *ca.* 0.5 l min^{-1} was used as the gas curtain. The charged droplets were injected orthogonally into the TOF mass spectrometer after they had passed through differential pumping stages. The device was operated in positive ion mode.

Mass resolutions of up to $m/\Delta m$ = 26 000 are possible. In the present studies, the typical settings allowed $m/\Delta m$ = 12 000.

3. Results

TOF spectra are plotted on a logarithmic scale to facilitate the visualisation of minor species and of the isotopic patterns. Due to the natural isotope distributions of Eu (^{151}Eu, 47.82%, ^{153}Eu, 52.18%), C (^{12}C, 98.89%, ^{13}C, 1.11%), N (^{14}N, 99.63%, ^{15}N, 0.37%) and O (^{16}O, 99.76%, ^{18}O, 0.20%), the peaks of the respective complexes are split into so-called isotopic patterns. These patterns act as a fingerprint for the particular detected species. The natural abundances of some of the mentioned isotopes are relatively small, but nevertheless the abundance of ^{13}C (1.11%) gives rise to a significant pattern, since one BTP molecule consists of 27 carbon atoms, which increases the probability of finding one ^{13}C to about 30%.

In order to prove the low-invasiveness of the nano-ESI approach, the previous measurements in the water/methanol

Table 1 Nano-ESI TOF MS measurements of [Eu] = 5 × 10^{-5} M with the ligand-to-metal ratios of 2 : 1 in nitric acid/methanol, nitric acid/propanol (both pH 4.6), 1-hexanol and 1-octanol. The detected complexes and their relative abundances are normalised to 100%

	HNO_3/CH_3OH (%)	HNO_3/C_3H_7OH (%)	$C_6H_{13}OH$ (%)	$C_8H_{17}OH$ (%)
$[Eu(BTP)(NO_3)_2]^+$	—	—	—	3.1
$[Eu(BTP)_2(NO_3)]^{2+}$	—	40.0	2.2	5.8
$[Eu(BTP)_2(NO_3)_2]^+$	—	—	94.2	88.4
$[Eu(BTP)_3]^{3+}$	16.8	17.0	—	—
$[Eu(BTP)_3(NO_3)]^{2+}$	83.2	43.0	3.6	2.7

system were repeated. In agreement,[19] the exclusive formation of $[Ln(BTP)_3(NO_3)]^{2+}$ and $[Ln(BTP)_3]^{3+}$ complexes, even at sub-stoichiometric BTP concentrations, was confirmed. Although the mass spectrometer allows the detection of minor species suppressed by a factor of approximately 200, no fragmentation products, such as 2 : 1 complexes, were found, delivering the required proof of low invasiveness. We systematically extended the chain length of the alcohols from methanol, through 2-propanol and 1-hexanol, to 1-octanol. Table 1 shows the relative abundances of the detected Eu-BTP complexes in the different solution systems ([Eu] = 5 × 10^{-5} M, ligand to metal ratio 2 : 1; if nitric acid was used, the pH of the $Eu(NO_3)_3·6H_2O$ stock solutions was adjusted to 4.3). This approach shows a strong influence of the diluent on complex speciation.

The measurements in HNO_3/propanol show the following: besides the $[Eu(BTP)_3]^{3+}$ (*m*/*z* = 455.5 u/e, 17.0%) and $[Eu(BTP)_3(NO_3)]^{2+}$ complexes (*m*/*z* = 714.3 u/e, 43.0%), a considerable amount of $[Eu(BTP)_2(NO_3)(C_3H_7OH)]^{2+}$ (*m*/*z* = 542.2 u/e, 40.0%) complex was found. Due to the soft ionisation method and the high relative abundance of the 2 : 1 complexes, it is unlikely that these are fragmentation products.

Besides the complexes listed in Table 1, two-fold charged dimeric species of the $[Ln(BTP)_2(NO_3)_2]^+$ and $[Ln(BTP)(NO_3)_2]^+$ complexes (*i.e.* $[Ln_2(BTP)_4(NO_3)_4]^{2+}$ and $[Ln_2(BTP)_3(NO_3)_4]^{2+}$) were observed in the measurements in 1-hexanol and 1-octanol. The abundances of these dimers are weighted to the number of lanthanide atoms and are listed separately in Table 2.

Fig. 3 shows the spectrum of a solution with [Pr] = 10^{-5} M and [BTP] = 2 × 10^{-5} M in 1-octanol. The measured data are plotted in black, while the calculated fits are plotted in colour. The dominating species is the $[Pr(BTP)_2(NO_3)_2]^+$ complex (*m*/*q* = 1075.4 u/e, 44.2%; blue), overlapped by dimeric complex $[Pr_2(BTP)_4(NO_3)_4]^{2+}$ (*m*/*q* = 1075.4 u/e, 22.5%; red). Two-fold charged species (dimers) are identified from the reduced distance between the isotope peaks. From the abundances of the two-fold charged dimers with an odd number of water molecules, which do not interfere with the singly-charged monomers, the contribution of the overlapping dimers to the peaks of the monomer can be estimated by optimising all the ratios simultaneously (see Fig. 4 for the measurement of [Pr] = 10^{-5} M, [BTP] = 10^{-4} M).[32] Besides the 2 : 1 complex, even a 1 : 1 complex can be identified, namely $[Pr(BTP)(NO_3)_2(C_8H_{17}OH)_2]^+$ (*m*/*q* = 930.4 u/e, 13.1%; yellow); $[Pr(BTP)_3(NO_3)]^{2+}$ (*m*/*q* = 710.3 u/e) was not detected. Free ligand species $[BTP(H)]^+$ (*m*/*q* = 406.3 u/e; green) and $[BTP(Na)]^+$(*m*/*q* = 428.2 u/e; green) with both water and 1-octanol adducts were detected.

The spectrum of the analogous Tb measurement is plotted in Fig. 5. In contrast to the case of Pr, the 3 : 1 complex ($[Tb(BTP)_3(NO_3)]^{2+}$, *m*/*q* = 718.3 u/e, 17.8%; magenta) was found in significant quantities. Therefore, the formation of the 2 : 1 complex ($[Tb(BTP)_2(NO_3)_2]^+$, *m*/*q* = 1093.4 u/e, 39.7%; blue) still seems to be favoured. The overlapping dimeric complex plays only a subordinate role (*m*/*q* = 1093.4 *u*/*e*, 2.9%; red).

All of the detected Ln-BTP complexes from the ESI MS measurements of solutions containing [Ln] = 10^{-5} M and [BTP] = 2 × 10^{-5} M are summarised in Table 2(a). The relative abundances are normalised to 100% with respect to the total amount of detected Ln-BTP complexes. The difference in behaviour of the respective lanthanides is obvious. The fraction of 3 : 1 complexes continuously increases from La (0%) to Lu (24.2%) (Fig. 6). Most detected species remain in a solvation shell, consisting of some water and/or 1-octanol molecules. The occurrence of the water molecules might be due to the relatively high solubility of water in 1-octanol and the additional uptake of water from the air during the ESI process under ambient conditions. However, the presence of such a solvation shell shows the soft (*i.e.* low declustering) conditions of the measurement process.

Measurements were also performed with an excess of BTP (for the detected complexes see Table 2(b)). The excess BTP causes a general increase in the fraction of 3 : 1 complexes, whereas 1 : 1 complexes are almost completely absent. The general trend, however, of the increasing abundance of 3 : 1 complexes observed from La through to Lu is unaffected and remains clearly visible.

The high abundance of protonated BTP in the spectra does not reflect the fraction of protonated BTP in the octanolic

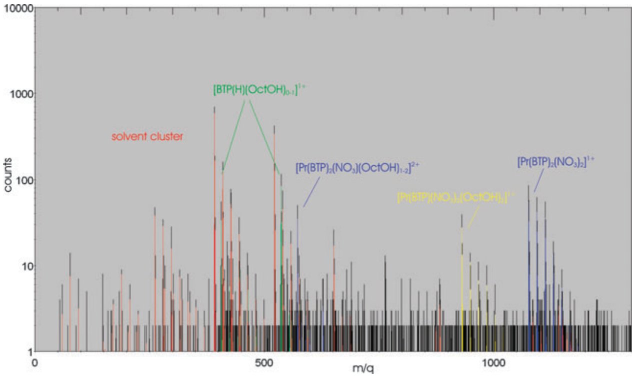

Fig. 3 The mass spectrum of an octanolic solution of [Pr] = 10^{-5} M and [BTP] = 2 × 10^{-5} M.

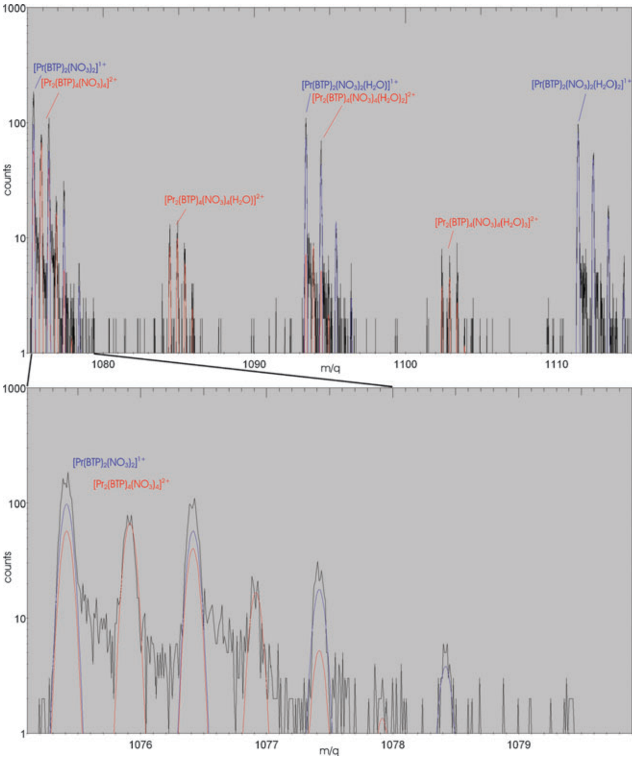

Fig. 4 A portion of the mass spectrum of an octanolic solution of [Pr] = 10^{-5} M and [BTP] = 10^{-4} M. Top: The region of m/q = 1075–1118 u/e shows that dimeric molecules with odd numbers of waters do not interfere with the singly-charged monomers. Bottom: The isotopic distribution of $[Pr(BTP)_2(NO_3)_2]^+$ (blue) and $[Pr_2(BTP)_4(NO_3)_4]^{2+}$ (red); these can be clearly separated due to their different charges. The isotopic pattern (resulting from the carbon, nitrogen and oxygen isotopes) act as a fingerprint of the respective species. Their theoretical distributions (blue and red) agree with the measured spectrum. Note that the overlapping theoretical fits have to be added to describe the peak.

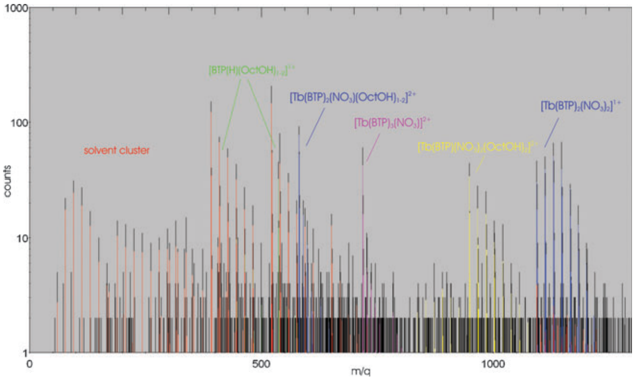

Fig. 5 The mass spectrum of an octanolic solution of [Tb] = 10^{-5} M and [BTP] = 2×10^{-5} M.

solution. As we conducted our measurements in positive ion mode, there is proton input to the solutions during measurements. The low concentration of protons in 1-octanol should not be able to produce as high a $BTP(H)^+$ signal as we found in our measurements.

4. Discussion

The influence of the diluent on the formation of the complexes is striking. Diluent effects on the distribution ratios for the extraction of lanthanides and actinides have been reported before.[10,21,22] The exclusive formation of 3 : 1 complexes obtained in the nitric acid/methanol system could not be observed when alcohols with longer chain lengths were applied. This finding confirmed our assumption that measurements must be performed directly in the extraction-relevant diluent 1-octanol, avoiding the dilution of the octanolic solutions in standard solvents for ESI investigations. In those measurements, 2 : 1, and even 1:1, complexes were detected. Three-fold positive-charged 3 : 1 complexes ($[Ln(BTP)_3]^{3+}$) were not detected. The relative abundances of the $Ln(BTP)_3$ complexes (dimers excluded) shown in Fig. 6 correlate with the distribution ratios for extraction to the organic phase depicted in Fig. 2. The more a 3 : 1 complex is formed, the better the metal ion can be shielded by the hydrophobic moieties of the ligands. This results in better extraction to the organic phase. Comparative TRLFS studies of Eu and Cm with BTP showed that the exclusive formation of $Cm(BTP)_3$ can be observed at a much lower excess of BTP ligand than that of $Eu(BTP)_3$.[13,15] Similar results were obtained by X-ray diffraction studies of the BTP ligand with the whole lanthanide series, where 3 : 1 complexes were only observed for the relatively small lanthanides.[38,39] The authors deduce that the extraction properties of the BTP ligands are connected with the ability to form 3 : 1 complexes with the respective metal ion. We find that, compared to $[Ln(BTP)_3(NO_3)]^{2+}$ complexes, lanthanide BTP complexes with lower BTP ratios have a bigger water shell. This reflects their poorer extraction ability due to the reduced hydrophobic character of those complexes.

In the second measurement series concerning the selected five lanthanides, the concentration of the BTP ligand was increased to 10 equivalents. This is an additional step towards extraction-relevant conditions, where ligand concentrations of several 10 mM are used. Obeying the law of mass action, the abundances of the 3 : 1 complexes increase in general. Only Tb and Lu form 1 : 1 complexes in detectable quantities. The higher abundance of the 1 : 1 complex for Lu compared to Tb might explain the lower distribution ratio for extraction to the organic phase (compare in Fig. 2). Fig. 7 displays the relative abundances of the Ln-BTP complexes (summarised in Table 2), disregarding the dimers. The trend in the relative abundances of the 3 : 1 complexes agrees with the results obtained for the first measurement series. Even with an excess of ligand, the formation of the 3 : 1 complex is not favoured for La, Pr and Eu.

For both measurement series, the abundance of the dimers decreases with decreasing ionic radius; lighter lanthanides are known to form dimeric complexes.[40] For lanthanum and the lanthanides Pr through to Tb, the decreasing ionic radius causes an increasing binding attraction due to steric factors and a stabilisation of the 3 : 1 complex. Further contraction of the ions from Tb through to Lu leads to a steric misfit of the small cations. The steric factors become clear in a comparison

Table 2 Nano-ESI TOF MS measurements of [Eu] = 10^{-5} M with ligand-to-metal ratios of (a) 2 : 1 and (b) 10 : 1 in 1-octanol. The detected complexes and their relative abundances are normalised to 100% and weighted to the number of Ln atoms per complex

(a) Ligand-to-metal ratio 2 : 1

	$[Ln(BTP)(NO_3)_2]^+$		$[Ln(BTP)_2(NO_3)]^{2+}$		$[Ln(BTP)_2(NO_3)_2]^+$		$[Ln(BTP)_3(NO_3)]^{2+}$		$[Ln_2(BTP)_4(NO_3)_4]^{2+}$		$[Ln_2(BTP)_3(NO_3)_4]^{2+}$	
	m/q	%	*m/q*	%	*m/q*	%	*m/q*	%	*m/q*	%	*m/q*	%
La	928.4	51.9	570.7	9.9	1073.4	21.1	708.3	—	1073.4	17.1		
Pr	930.4	13.1	571.8	12.0	1075.4	44.2	709.3	—	1075.4	22.5	872.8	8.2
Eu	941.4	12.2	576.8	15.1	1085.4	50.7	715.3	1.5	1085.4	17.7	882.8	2.8
Tb	948.4	23.7	580.8	18.8	1093.4	38.2	718.3	17.8	1093.4	2.9		
Lu	964.5	31.8	588.8	34.4	1109.4	8.9	726.3	24.2	1109.4	1.2		

(b) Ligand-to-metal ratio 10 : 1

	$[Ln(BTP)(NO_3)_2]^+$		$[Ln(BTP)_2(NO_3)]^{2+}$		$[Ln(BTP)_2(NO_3)_2]^+$		$[Ln(BTP)_3(NO_3)]^{2+}$		$[Ln_2(BTP)_4(NO_3)_2]^{2+}$	
	m/q	%	*m/q*	%	*m/q*	%	*m/q*	%	*m/q*	%
La	928.4	—	570.7	16.8	1073.4	55.0	708.3	2.6	1073.4	25.6
Pr	930.4	—	571.8	1.5	1075.4	75.2	709.3	2.1	1075.4	21.2
Eu	941.4	—	576.8	3.9	1085.4	49.6	714.3	13.9	1085.4	32.6
Tb	948.4	0.6	580.8	3.9	1093.4	26.5	718.3	63.8	1093.4	5.2
Lu	964.5	1.9	588.8	11.8	1109.4	6.3	726.3	78.6	1109.4	1.4

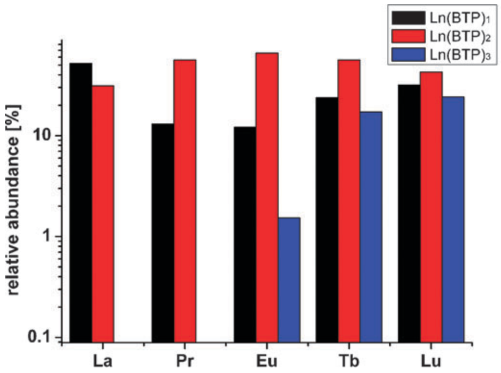

Fig. 6 The relative abundances of the $Ln(BTP)_{1-3}$ complexes detected in lanthanide nitrate/BTP solutions in 1-octanol (ligand-to-metal ratio 2 : 1) normalised to 100%.

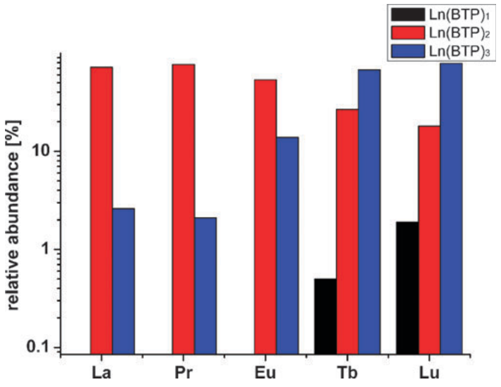

Fig. 7 The relative abundances of the $Ln(BTP)_{1-3}$ complexes detected in lanthanide nitrate/BTP solutions in 1-octanol (ligand-to-metal ratio 10 : 1) normalised to 100%.

between BTP and BPP ligands (BPP = 2,6-bis(5-alkyl-4*H*-pyrazol-3-yl)pyridine). Due to the wider nitrogen cavity of BPP ligands, the maximum value for $D_{M(III)}$ is found for Nd (Ho for BTP; see Fig. 2).[41]

5. Conclusions

We have shown that nano-ESI MS investigations on the complexation behaviour of lanthanides with BTP is possible directly in extraction-relevant diluents. These measurements show that the diluent influences the formation of the complexes drastically; this means that the measurements must be performed in the diluent to be studied without further dilution. The results of our measurements reflect the extraction behaviour of the lanthanides: the high abundance of the 2 : 1 complexes and the appearance of 1 : 1 complexes for all lanthanides points to the selectivity of extraction of Am(III) and Cm(III) over the lanthanides with BTP ligands. The ability to form 3 : 1 complexes correlates with their stability in the organic phase due to hydrophobic shielding of the metal ions by the ligand; these complexes are extraction relevant.[13,15,39] The 2 : 1 and 1 : 1 complexes attach more water molecules in the ESI process, which is evidence for the lower hydrophobic character of these complexes. Their appearance result in lower distribution ratios for extractions.

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