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The structures of CyMe$_4$-BTBP complexes of americium(III) and europium(III) in solvents used in solvent extraction, explaining their separation properties

Christian Ekberg,[a,*] Elin Löfström-Engdahl,[a] Emma Aneheim,[a] Mark R.StJ.Foreman,[a] Andreas Geist,[b] Daniel Lundberg,[c] Melissa Denecke,[d] and Ingmar Persson[c,*]

[a] Nuclear Chemistry / Industrial materials recycling, Chalmers University of Technology, SE-412 96 Göteborg, Sweden. E-mail: che@chalmers.se

[b] Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal (INE), 76021 Karlsruhe, Germany.

[c] Department of Chemistry and Biotechnology, Uppsala Biocenter, Swedish University of Agricultural Sciences, P.O. Box 7015, SE-750 07 Uppsala, Sweden. E-mail: ingmar.persson@slu.se

[d] Dalton Nuclear Institute, The University of Manchester, Manchester M13 9PL, United Kingdom.

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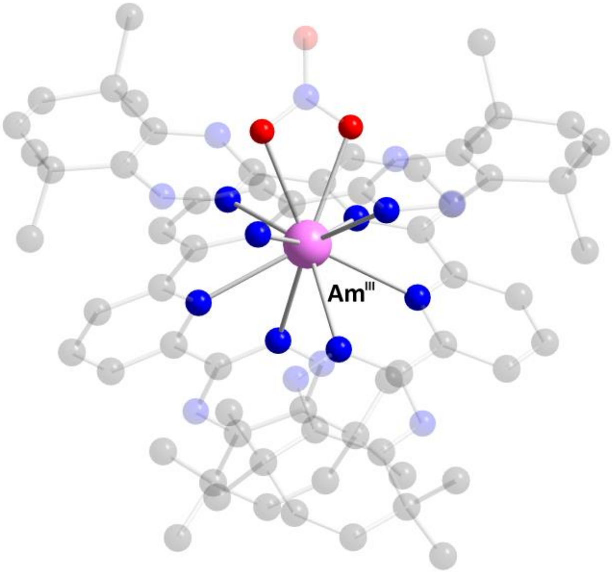
Graphical abstract

The structure around the absorbing atom in the dicomplexes of 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, with americium(III) and europium(III) have been determined by means of Am and Eu L$_3$ edge EXAFS spectroscopy in a series of solvents used to separate these metal ions using solvent extraction. The obtained structural information has been correlated with previously reported solubility and selectivity data as well as ionic radii in general terms.



Abstract

Separation of trivalent actinoid (An(III)) and lanthanoid (Ln(III)) ions is extremely challenging due to their similar ionic radii and chemical properties. Poly-aromatic nitrogen compounds acting as tetradentate chelating ligands to the metal ions in the extraction, have the ability to sufficiently separate An(III) from Ln(III). One of these compounds, 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzol[1,2,4]triazin-3-yl)[2,2]bipyridine, $CyMe_4$-BTBP, has proven to be resistant towards acidic environments and strong radiation from radioactive decomposition. EXAFS studies of the dicomplexes of $CyMe_4$-BTBP with americium(III) and europium(III) in nitrobenzene, cyclohexanone, 1-hexanol, 1-octanol and malonamide (DMDOHEMA) in 1-octanol have been carried out to get a deeper understanding of the parameters responsible for the separation. The predominating complexes independent of solvent used are $[Am(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$ and $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$, respectively, which are present as outer-sphere ion-pairs with nitrate ions in the studied solvents with low relative permittivity. The presence of a nitrate ion in the first coordination sphere of the americium(III) complex compensates the charge density of the complex considerably in comparison when only outer-sphere ion-pairs are formed as for the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complex. The stability and solubility of a complex in a solvent with low relative permittivity increase with decreasing charge density. The $[Am(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$ complex will therefore be increasingly soluble and stabilized over the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complex in solvents with decreasing relative permittivity of the solvent. The separation of americium(III) from europium(III) with $CyMe_4$-BTBP as extraction agent will increase with decreasing relative permittivity of the solvent, and thereby also with decreasing solubility of $CyMe_4$-BTBP. The choice of solvent is therefore a balance of a high separation factor and sufficient solubility of the $CyMe_4$-BTBP ligand.

Introduction

Approximately 12% of all electric energy in the world stems from nuclear power.[1] Today the utilisation of nuclear power is an effective way to produce electricity with very low emission of greenhouse gases,[2] which has increased the interest for the technique. However, a concern with nuclear power is the production of highly radioactive used nuclear fuel (UNF). The UNF is highly radiotoxic to mankind and the environment, and will continue to be so for a very long time due to the long life-times of several isotopes.[3] Some countries (UK, France, Russia, Japan, India) complement direct disposal of commercial UNF in deep underground geologic repositories by UNF reprocessing, whereby uranium and plutonium are reused or recycled as nuclear fuel. The associated highly radioactive waste from reprocessing, including fission products and the minor actinoids neptunium, americium and curium, is vitrified for ultimate disposal in a deep geologic repository. A future component in UNF handling is transmutation of the minor actinoids into less radiotoxic or less stable isotopes. By transmuting the actinoids, the waste volume, long-term heat load and radiotoxicity of the highly radioactive waste can be reduced significantly.[4-6] However, before their transmutation the actinoids must be separated from the UNF fission, corrosion and activation products. One way to achieve the required separation is through solvent extraction.

Separation of trivalent actinoid (An(III)) and lanthanoid (Ln(III)) ions represents one of the most challenging separations due to their similar ionic radii and chemical properties. Recent studies have shown that poly-aromatic nitrogen compounds, *N*-PAHs, acting as tetradentate chelating ligands to the metal ions in the extraction, have the ability to sufficiently separate An(III) from Ln(III).[7-10] One of these *N*-PAHs, 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzol[1,2,4]triazin-3-yl)[2,2]bipyridine, CyMe$_4$-BTBP (Figure 1), has promising process potential,[11-16] as it has proven to be resistant towards acidic environments[17-19] and strong radiation from radioactive decomposition[13,20] present at the separation process of actinoids from UNF. CyMe$_4$-BTBP extracts An(III) and Ln(III) from concentrated nitric acid or nitrate solutions to the organic phase by a complex formation mechanism of predominantly 1:2 complexes,[18,21] $[M(CyMe_4\text{-}BTBP)_2(NO_3)_n(solv)_m]^{(3-n)+}$, as does the structurally similar 6,6'-bis(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2']-bipyridine (C$_5$-BTBP) molecule, see Eq. 1.[22,23]

$$M^{3+}_{aq} + 3\,NO_3^{-}{}_{aq} + 2\,BTBP_{org} \rightleftharpoons \{[M(BTBP)_2(NO_3)_n(solv)_m]^{(3-n)+}\cdots(NO_3^{-})_{3-n}\}_{org} \quad \text{(Eq. 1)}$$

The 1:2 stoichiometry has been confirmed for different metals by electrospray ionisation mass spectrometry (ESI-MS), time-resolved laser-induced fluorescence spectroscopy (TRLFS), and extended X-ray absorption fine structure (EXAFS) in solution.[24-29] In the solid state, structures with both 1:1 and 1:2 stoichiometry have been reported.[17,27,28,30,31] Complexes with 1:2 stoichiometry may have different number of nitrate ions bound to the central metal ion depending on the experimental conditions during preparation; $[M(BTBP)_2]^{3+}$,[24,25] $[M(BTBP)_2(NO_3)]^{2+}$,[24,28,29,31] or $[M(BTBP)_2(H_2O)_n]^{3+}$.[25,26,28]

Qualitative reasoning concerning the Lewis basicity of the extractant and the somewhat softer character of the actinoid(III) ions compared to the lanthanoid(III) ones has been used to explain the An(III)/Ln(III) separation capacity of *N*-PAH ligands.[32,33] An(III)/Ln(III) separation by $CyMe_4$-BTBP has also been observed to vary with the solvent used.[18,34,35] In order to understand the fundamental basis for An(III)/Ln(III) separation properties of BTBP ligands, the speciation in detail, and the role of the solvent, EXAFS studies of these complexes have been carried out in solution. Analysis of EXAFS data gives information about the distances to the surrounding atoms which can be used to determine the structural environment around the absorbing atom and thereby the speciation in solution which may differ from the one in the solid state. In this study the americium(III) and europium(III) $CyMe_4$-BTBP complexes have been studied in selected solvents previously investigated for their potential in separation processes including nitrobenzene, cyclohexanone, 1-hexanol, and 1-octanol.[12,24,36,37]

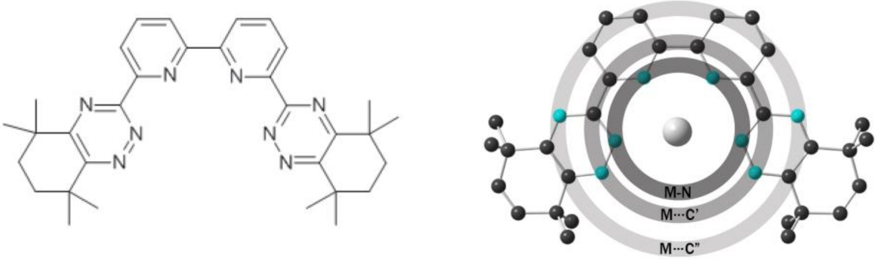


Figure 1. Molecular structure of 6,6’-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzol[1,2,4]triazin-3-yl)[2,2]bipyridine, $CyMe_4$-BTBP (left), and a graphical representation of the EXAFS single scattering pathways between a metal ion and one $CyMe_4$-BTBP ligand (right): M-N [dark grey], M···C’ [grey] and M···C” [light grey], where the two latter include six carbon and two nitrogen atoms per ligand, respectively. All hydrogen atoms have been omitted for clarity.

Malonamides such as *N*,*N*'-dimethyl-*N*,*N*'-dioctyl-2-(2'-hexyloxyethyl)-malonamide (DMDOHEMA) can be added to 1-octanol solutions of CyMe$_4$-BTBP to accelerate kinetics of the extraction system.[18,21] This addition results in a lowering of the An(III)/Ln(III) selectivity, which can be explained by a weak but unselective co-extraction of Am(III) and Eu(III) by DMDOHEMA.[18,21] Nevertheless, formation of mixed metal BTBP-DMDOHEMA complexes cannot be excluded, which is why a solution of CyMe$_4$-BTBP and DMDOHEMA in 1-octanol has been examined by EXAFS as well.

The results from the EXAFS studies have been correlated to previously reported solubility and extraction data of An(III)/Ln(III)-CyMe$_4$-BTBP complexes in these solvents, as well as their physical properties, Table 2. In addition, a conductivity study on extracted Ln(III)-CyMe$_4$-BTBP complexes has been performed, in order to elucidate the reasons for the observed differences in BTBP solubility and EXAFS bond distances in nitrobenzene compared to the other solvents; nitrobenzene has a high relative permittivity compared to the other solvents[38,39] could be able to dissociate the extracted ion pairs.[34,40] Conductivity measurements could identify if this is the case, resulting in deviations in solubility and extraction properties.

Experimental section

Sample preparation

The samples for EXAFS studies were prepared by extracting americium(III) or europium(III) from an aqueous solution into the organic solvents nitrobenzene, cyclohexanone and 1-hexanol, and 0.25 mol·dm^{-3} DMDOHEMA in 1-octanol containing 10 mmol·dm^{-3} CyMe$_4$-BTBP, and a saturated CyMe$_4$-BTBP solution, 8.2 mmol·dm^{-3}, in 1-octanol. The aqueous phase contained radioactive ^{241}Am(III) or ^{243}Am(III), or non-radioactive Eu(III) in 0.01–0.1 mol·dm^{-3} HNO$_3$ + 1.9–4.0 mol·dm^{-3} NaNO$_3$. The organic and aqueous phases were then equilibrated on a mechanical shaker for 1–3 hours. After centrifugation, an aliquot of the organic phase (typically several 100 µL) was transferred to the EXAFS sample holder made of Teflon and Kapton foil. The Am CyMe$_4$-BTBP samples contained approx. 1 mmol·dm^{-3} americium(III), and the Eu CyMe$_4$-BTBP samples several mmol·dm^{-3} europium(III).

EXAFS data collection

The EXAFS measurements of the Am-CyMe$_4$-BTBP complexes in nitrobenzene, cyclohexanone, 1-hexanol, 1-octanol and DMDOHEMA in 1-octanol were performed at the Am L$_3$ X-ray absorption edge. The data were collected at the wiggler beam line I811 at MAX-lab, Lund University, which operated at 1.5 GeV and a maximum current of 220 mA, and at the bending magnet INE-Beamline for actinide research at the synchrotron source ANKA operating at 2.5 GeV, and a maximum current of 200 mA. The synchrotron beam was monochromatised using a Si[311] or Ge[422] double crystal monochromator at MAX-lab and ANKA, respectively, with higher order harmonics reduced by detuning the second monochromator crystal to reflect 70% of maximum intensity at the end of the EXAFS range scanned. The measurements were performed in fluorescence mode using a PIPS® (Passivated Implanted Planar Silicon) detector (Canberra; http://www.canberra.com/products/438239.asp) at MAX-lab, and a Canberra LEGe 5-element solid state detector at ANKA. The spectrum of a zirconium metal foil was recorded simultaneously in transmission mode as reference; the first inflection point of metallic zirconium on the K edge is defined as 17.998 keV.[41] For each sample three to five scans were averaged by means of the EXAFSPAK program package.[42]

EXAFS measurements of corresponding Eu-CyMe$_4$-BTBP complexes were performed in transmission mode at the Eu L$_3$ X-ray absorption edge using same kind of energy dispersive solid state detector as for Am L$_3$ EXAFS at ANKA, *vide supra*. The data were collected at the wiggler beam line 4-3 at Stanford Synchrotron Radiation Lightsource (SSRL), Stanford University, USA (3.0 GeV, 97–100 mA in top-up mode), and at MAX-lab, beam-line I811, using a Si[111] double crystal monochromator. Higher order harmonics were reduced by detuning the second monochromator crystal to reflect 40% of maximum intensity at the end of the scans. The spectrum of a europium metal foil was recorded simultaneously in transmission mode as reference; the first inflection point of metallic europium on the L$_3$ edge is defined as 6977 eV.[41] For each sample five scans were averaged.

EXAFS data analysis

The EXAFS ocillations were extracted from raw averaged data using standard procedures for pre-edge subtraction, spline removal and data normalization. In order to obtain quantitative information of the coordination structure of the metal ions, the experimental k^3-weighted EXAFS oscillations were analysed by non-linear least-squares fits of the data to the EXAFS equation, refining the model parameters, number of backscattering atoms, N_i, mean interatomic distances R, Debye-Waller factor coefficients, σ^2, and threshold energy, E_o. Data analysis was performed using the EXAFSPAK program package.[42] Model fitting was performed with theoretical phase and amplitude functions calculated from models based on the previously reported solid structure of $[Eu(CyMe_4\text{-}BTBP)_2\text{-}\kappa_2(NO_3)](NO_3)_2\cdot C_8H_{17}OH$[31] using the *ab initio* code FEFF (version 7.02).[43] It included both single scattering paths (M-N, M···C or M···N, where M = Eu or Am) for the nearest and next-nearest neighbour distances, and multiple scattering paths with significant intensity, *i.e.* M-N-C' for 32 three-legged multiple scattering paths along the donor N atoms to the next-nearest neighbours back to the central metal cation and another 32 three-legged M-N-C" paths for multiple scattering paths along the donor N atoms to the C atoms in *ortho*-position and back to the central metal cation, Figure 1, right panel. Note that EXAFS cannot meaningfully differentiate between Z and Z+1 back-scatterers, meaning that N atoms cannot be differentiated from the C ones; such nearest and next-nearest neighbours are designated as C' and C", Figure 1.

The standard deviations reported for the obtained refined parameters listed in Tables 3 and 4 are those related to the least-squares refinements and do not include any systematic errors. Variations in the refined parameters obtained using different models and data ranges indicate that the accuracy of the distances given for the separate complexes is within ±0.005–0.02 Å, which is typical for well-defined interactions.

Conductivity measurements

Conductivity studies were performed in order to determine whether the extracted An(III)/Ln(III) $CyMe_4$-BTBP complexes were present as associated or dissociated ion-pairs in the studied solvents. The measurements were performed with a CDM210 (Radiometer Anayltical) instrument with a two electrode cell (CDC641T) using solutions of salts in water saturated nitrobenzene. To maintain a constant cell geometry the conductivity probe was inserted into a 17 mL polypropylene tube (Sarstedt, 15 mm internal diameter). The conductivity equipment was calibrated using tetraethyl ammonium perchlorate solutions before use. Details on the study in nitrobenzene can be found in the ESI section.†

Results and Discussion

EXAFS

Europium(III)-CyMe$_4$-BTBP complexes

The EXAFS data shows very clearly that the structure of the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complex with outer-sphere nitrate ion-pairs in 1-octanol solution is significantly different from solid $[Eu(CyMe_4\text{-}BTBP)_2\text{-}\kappa_2(NO_3)](NO_3)_2\cdot C_8H_{17}OH$,[31] Figure 1. On the other hand, the EXAFS spectra of the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complex in all the studied solvents are very similar, Figure 1. The Eu-N bond distance is on average 0.09 Å shorter in the complexes in solution in comparison to solid $[Eu(CyMe_4\text{-}BTBP)_2\text{-}\kappa_2(NO_3)](NO_3)_2\cdot C_8H_{17}OH$. This shows that the coordination number is lower in solution, and the observed difference strongly indicates a coordination number of eight in solution, thus neither any nitrate ions nor solvent molecules are directly bound to the central Eu ion. The observed shortening is well explained by a change in the coordination number from ten (solid state) to eight in solution.[31,44] The mean Eu-N bond distances in the Eu(III)-CyMe$_4$-BTBP complexes in the various solutions are given in

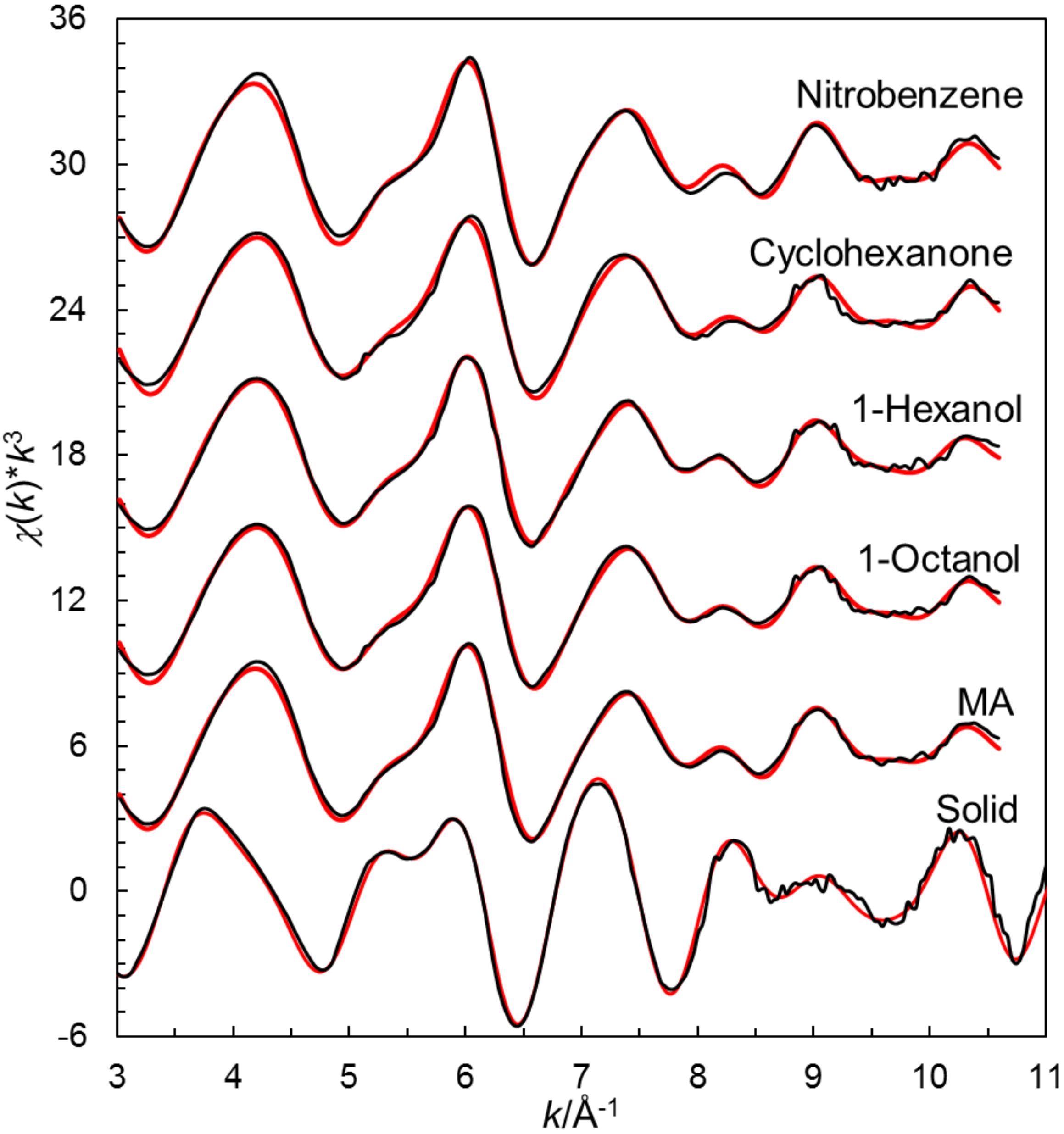


Figure 1. Fit (red) of experimental EXAFS data (black) of Eu(CyMe$_4$-BTBP)$_2$]$^{3+}$ complexes in nitrobenzene (offset: 30), cyclohexanone (offset:24), 1-hexanol (offset: 18), 1-octanol (offset: 12) and DMDOHEMA/1-octanol (MA) (offset:6) solution, and solid [Eu(CyMe$_4$-BTBP)$_2$-κ$_2$(NO$_3$)](NO$_3$)$_2$·C$_8$H$_{17}$O (no offset) with the structure parameters given in Table 1.

1, together with the Eu-N and Eu-O bond distances in solid [Eu(CyMe$_4$-BTBP)$_2$-κ$_2$(NO$_3$)](NO$_3$)$_2$·C$_8$H$_{17}$OH precipitated from a solution of Eu(CyMe$_4$-BTBP)$_2$(NO$_3$)$_3$ in 1-octanol. In the europium complex in the solid state europium bind eight nitrogen atoms from the CyMe$_4$-BTBP ligands at a mean Eu-N bond length of 2.57 Å and a bidentate nitrate ion at 2.56 Å.[27,28,31] Acceptable fits of the solution data was obtained using an *N* value of 8, without including any additional Eu-O distance, Table 1 and Figure 1. This suggests that the europium(III) ion is eight-coordinated, exclusively by two CyMe$_4$-BTBP ligands, in all the solvents studied. It must be stressed that the high solubility of the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complex in solvents with low relative permittivity strongly indicates that the counter nitrate ions must be very close to the highly charged complex as solvent-shared or solvent-separated ion pairs. However, such ions are not possible to observe by EXAFS as their mean distance is too long from the Eu ion and/or the mean distance distribution is too large causing very large Debye-Waller coefficients. The similarity of the EXAFS spectra in 1-octanol and CyMe$_4$-BTBP-DMDOHEMA mixtures shows that no detectable amounts of mixed Eu(III)-CyMe$_4$-BTBP-DMDOHEMA complexes are formed, Table 1 and Figure 1, nor after precipitation (data not shown).

Table 1. EXAFS refinement parameters for the Eu(III)-CyMe$_4$-BTBP fits shown in Figure 2; number of backscattering atoms, N, mean interatomic distance for single scattering paths Eu-N, Eu···C’ and Eu···C” or effective distance for multiple scattering paths Eu-N-C’ and Eu-N-C” (see Figure 1), R, Debye-Waller factor, σ^2, and the threshold energy, E_o/eV. S_o^2 is the amplitude reduction factor.

	N^*	R/Å	σ^2/Å^2	E_o	S_o^2
Nitrobenzene					
Eu-N	8	2.494(3)	0.0143(4)	6988.0(3)	0.93(5)
Eu···C’	16	3.494(4)	0.0171(5)		
Eu-N-C’	32	3.777(6)	0.0259(9)		
Eu···C”	16	4.928(6)	0.0094(6)		
Eu-N-C”	32	5.128(13)	0.025(2)		
Cyclohexanone					
Eu-N	8	2.494(3)	0.0133(4)	6988.9(3)	0.96(4)
Eu···C’	16	3.484(4)	0.0178(5)		
Eu-N-C’	32	3.767(6)	0.028(1)		
Eu···C”	16	4.92(1)	0.008(1)		
Eu-N-C”	32	5.12(1)	0.025(2)		
1-Hexanol					
Eu-N	8	2.481(2)	0.0144(4)	6987.4(3)	0.91(4)
Eu···C’	16	3.494(4)	0.0174(5)		
Eu-N-C’	32	3.7774(5)	0.0269(8)		
Eu···C”	16	4.951(5)	0.0111(7)		
Eu-N-C”	32	5.18(2)	0.031(3)		
1-Octanol					
Eu-N	8	2.474(2)	0.0127(3)	6987.1(3)	0.92(4)
Eu···C’	16	3.497(4)	0.0135(4)		
Eu-N-C’	32	3.786(5)	0.0198(8)		
Eu···C”	16	4.924(5)	0.0104(5)		
Eu-N-C”	32	5.12(2)	0.032(3)		
DMDOHEMA/1-Octanol (MA)					
Eu-N	8	2.491(6)	0.013(3)	6987.6(3)	0.95(4)
Eu···C’	16	3.473(9)	0.005(2)		
Eu-N-C’	32	3.75(2)	0.0232(8)		
Eu···C”	16	4.93(5)	0.016(1)		
Eu-N-C”	32	5.11(2)	0.032(3)		
Solid [Eu(CyMe$_4$-BTBP)$_2$(NO$_3$)](NO$_3$)$_2$					
Eu-N	8	2.572(6)	0.0085(3)	6988.1(4)	0.93(5)
Eu-O	2	2.56(2)	0.015(6)		
Eu···C’	12	3.452(3)	0.0054(3)		
Eu-N-C’	24	3.715(7)	0.025(2)		
Eu···C”	16	4.896(6)	0.008(1)		
Eu-N-C”	32	5.013(10)	0.014(2)		

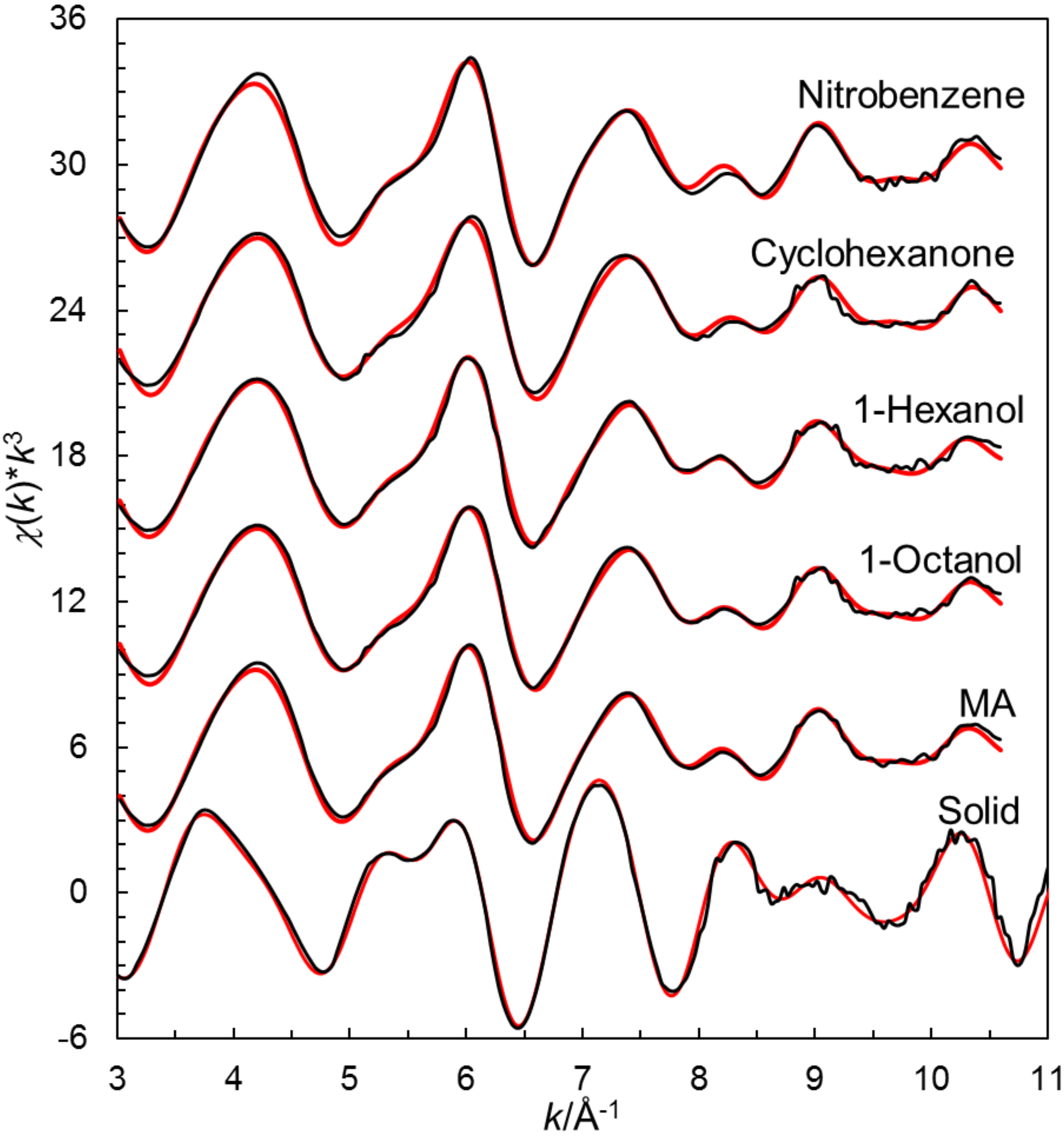


Figure 1. Fit (red) of experimental EXAFS data (black) of $Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complexes in nitrobenzene (offset: 30), cyclohexanone (offset:24), 1-hexanol (offset: 18), 1-octanol (offset: 12) and DMDOHEMA/1-octanol (MA) (offset:6) solution, and solid $[Eu(CyMe_4\text{-}BTBP)_2\text{-}\kappa_2(NO_3)](NO_3)_2\cdot C_8H_{17}O$ (no offset) with the structure parameters given in Table 1.

Americium(III)-CyMe$_4$-BTBP complexes

The structures of the americium(III)-CyMe$_4$-BTBP complexes in nitrobenzene, cyclohexanone, 1-hexanol, 1-octanol and DMDOHEMA/1-octanol have been determined by means of Am L$_3$ EXAFS data. The data quality of the Am(III) data is not as good as the corresponding europium(III) data due to lower concentrations. For this reason the available data range for the complex in nitrobenzene only allowed a single shell Am-N fit and the fits to the data sets for the Am(III)-CyMe$_4$-BTBP complexes in 1-hexanol and in DMDOHEMA/1-octanol did not include the multiple scattering on the more distant Am···C” shell. No crystal structure of any actinoid(III)-CyMe$_4$-BTBP complex has been reported to date.

Table 2. EXAFS refinement parameters for the Am L$_3$ EXAFS of Am(III)-BTBP fits shown in Figure 3: number of backscattering atoms, *N*, mean interatomic distance for single scattering paths Am-N, Am···C’ and Am···C” or effective distance for multiple scattering paths Am-N-C’ and Am-N-C” (see Figure 1), *R*, Debye-Waller factor, σ^2, and threshold energy, E_o/eV. S_o^2 is the amplitude reduction factor.

	N	*R*/Å	σ^2/Å^2	E_o	S_o^2
Nitrobenzene					
Am-N	8	2.590(13)	0.020(2)	18522.4(8)	0.86(8)
Cyclohexanone					
Am-O	2	2.376(7)	0.0014(7)	18522.8(3)	0.94(4)
Am-N	8	2.583(3)	0.0017(5)		
Am···C’	16	3.413(4)	0.0050(7)		
Am-N-C’	32	3.54(2)	0.0077(4)		
Am···C”	16	4.64(2)	0.011(3)		
Am-N-C”	32	4.94(1)	0.011(2)		
1-Hexanol					
Am-O	2	2.37(2)	0.004(2)	18522.1(5)	0.88(7)
Am-N	8	2.565(8)	0.0033(7)		
Am···C’	16	3.406(8)	0.0055(11)		
Am-N-C’	32	3.59(2)	0.008(2)		
Am···C”	16	4.62(2)	0.009(2)		
1-Octanol					
Am-O	2	2.35(6)	0.025(8)	18522.2(3)	0.87(10)
Am-N	8	2.556(5)	0.011(2)		
Am···C’	16	3.423(8)	0.011(2)		
Am-N-C’	32	3.65(6)	0.023(7)		
Am···C”	16	4.47(2)	0.013(3)		
Am-N-C”	32	4.97(2)	0.016(3)		
DMDOHEMA/1-Octanol (MA)					
Am-O	2	2.40(2)	0.008(2)	18522.5(3)	0.92(8)
Am-N	8	2.58(1)	0.007(3)		
Am···C’	16	3.44(1)	0.006(2)		
Am-N-C’	32	3.76(2)	0.008(4)		
Am···C”	16	4.53(2)	0.009(3)		

The fit parameters obtained for fits to the americium(III)-CyMe$_4$-BTBP complex data in solution are summarised in Table 2; the k^3-weighted EXAFS data and their corresponding fit are depicted in Figure 2. The fit of the EXAFS improved significantly applying a model with an additional short Am-O bond distance in all the solvents studied. About two nearest neighbour Am-O bond distances, most likely from one nitrate ion, gave the best fit to the experimental data, Table 2. Evidently, $[Am(CyMe_4\text{-}BTBP)_2(NO_3)_n]^{(3-n)+}$ complexes form. One possible reason for this is that, due to the ca. 0.04 Å larger americium(III) ion radius compared to that of europium(III) for a given coordination number,[44] americium(III) binds either solvent or water molecules or a bidentate nitrate ion in the americium(III)-$CyMe_4$-BTBP complex, which contrasts our findings for the corresponding europium(III) complex. Since an oxygen from nitrate, water or solvent has hard bonding properties, we do not consider any 'softer' binding properties of americium(III) compared to europium(III) as an explanation for the appearance of a short Am-O bond in the complexes and the reason seems to be purely sterical.

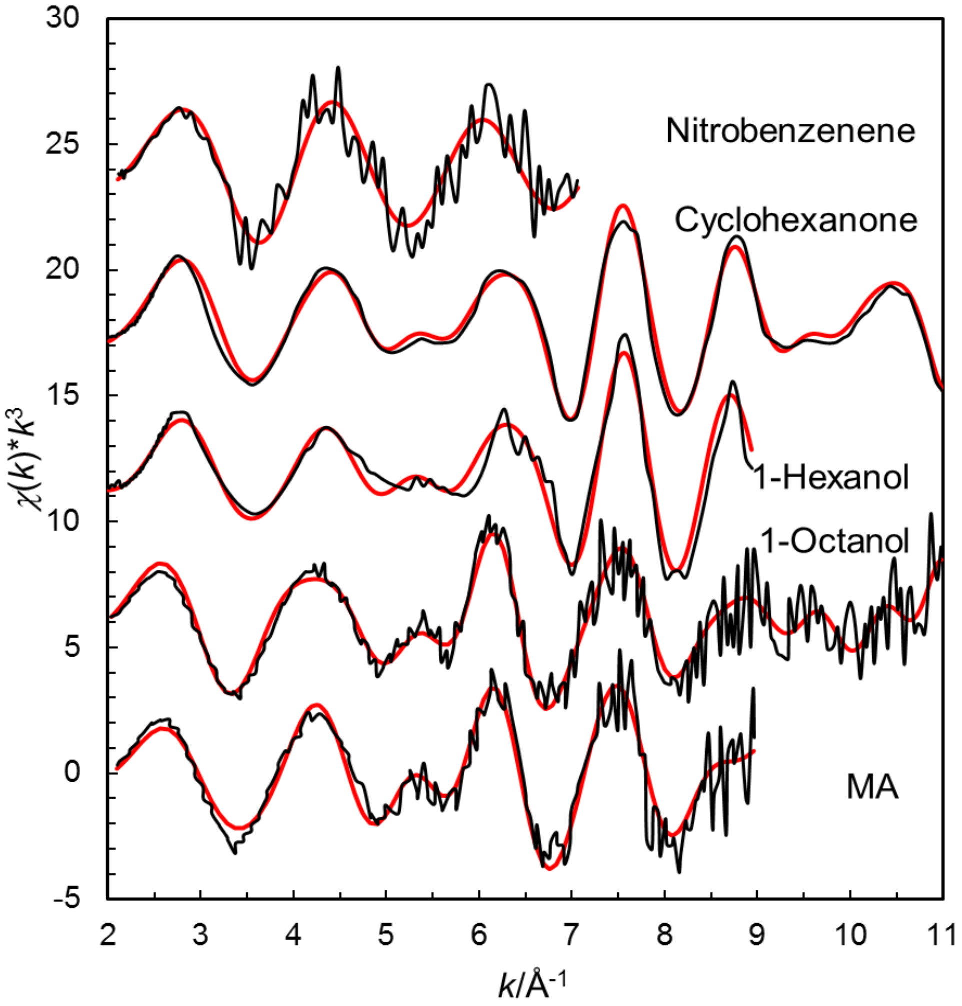


Figure 2. Fit (red) of experimental EXAFS data (black) of $Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complexes in nitrobenzene (offset: 24), cyclohexanone (offset:18), 1-hexanol (offset: 12), 1-octanol (offset: 6) and DMDOHEMA/1-octanol (MA) (no offset) solution with the structure parameters given in Table 2.

Structure of europium(III)- and americium(III)-CyMe$_4$-BTBP complexes in solute on

The EXAFS results point to that the europium(III) and americium(III) complexes have the compositions $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ and $[Am(CyMe_4\text{-}BTBP)_2(NO_3)_n(solv)_m]^{(3-n)+}$, respectively, independent of solvent used (nitrobenzene, cyclohexanone, 1-hexanol, 1-octanol and DMDOHEMA/1-octanol). The crystal structure of $[Eu(CyMe_4\text{-}BTBP)_2\text{-}\kappa_2(NO_3)](NO_3)_2\cdot C_8H_{17}OH$ clearly shows that the europium(III) ion is embedded in a cage made of the two CyMe$_4$-BTBP ligands and the nitrate ion, and has no possibility to be in contact with the solvent.[31] The solvation of the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complex should therefore only take place between the CyMe$_4$-BTBP ligands and the solvent through mainly van der Waals forces. The solvation of the CyMe$_4$-BTBP as ligand is principle proportional to the solubility of CyMe$_4$-BTBP. For the $[Am(CyMe_4\text{-}BTBP)_2(NO_3)_n(solv)_m]^{(3-n)+}$ complex, the observed short Am-O bond distance is either from a nitrate ion or solvent molecules. However, it is seems much more likely that it is nitrate oxygens as it would compensate the charge significantly, which is favourable in solvents with low relative permittivity, i.e. all solvents studied except nitrobenzene, Table 3. Therefore, the strength of the solvation of a $[Am(CyMe_4\text{-}BTBP)_2(NO_3)_n]^{(3-n)+}$ complex should also be proportional to the solubility of CyMe$_4$-BTBP in the studied solvents. This is supported by the EXAFS results showing that the M-N bond distances decrease very little with decreasing solvation (solubility) of the CyMe$_4$-BTBP ligand, Tables 1-3. The solubility of the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ and $[Am(CyMe_4\text{-}BTBP)_2(NO_3)_n]^{(3-n)+}$ complexes is surprisingly high considering the low relative permittivity of all the studied solvents (except nitrobenzene). It therefore seems very likely that the nitrate counter ions will be clustered close to the complex as ion-pairs to compensate the effective charge of the complex as much as possible. However, it has not been possible to detect presence of these nitrate ions with EXAFS as their mobility is too high.

Extraction and Solubility Correlations

By comparing the solubility of CyMe$_4$-BTBP in the studied solvents and the relative permittivity of the solvent a linear relationship is obtained, Figure 3, while the separation factor increases exponentially with decreasing relative permittivity, Figure 4, and thereby also by decreasing solubility of CyMe$_4$-BTBP in the solvent. This further supports that it is a nitrate ion which binds directly to americium(III) as a $[Am(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$ complex, thereby compensating the charge/charge density which increases extraction favourably with decreasing relative permittivity of the solvent. The choice of solvent is therefore a balance of a high separation factor and sufficient solubility of CyMe$_4$-BTBP ligand.

Table 5. Am-N and Eu-N bond distances, *R*/Å, in the first coordination spheres of the [Eu(CyMe$_4$-BTBP)$_2$]$^{3+}$ and [Am(CyMe$_4$-BTBP)$_2$(NO$_3$)$_n$(solv)$_m$]$^{(3-n)+}$ complexes, the separation factors, $SF_{\mathrm{Am/Eu}}$, and the solubility of CyMe$_4$-BTBP, in mmol·dm^{-3}, and the relative permittivity, ε_{r}, in the studied solvents.

Solvent	$R_{\mathrm{Am\text{-}N}}$	$R_{\mathrm{Eu\text{-}N}}$	$SF_{\mathrm{Am/Eu}}$ [a]	Solubility [b]	ε_{r} [c]
Nitrobenzene	2.590(13)	2.494(3)	89	51.3	35.6
Cyclohexanone	2.583(3)	2.494(2)	118	16.8	16.1
1-Hexanol	2.565(8)	2.481(2)	151	10	13.03
1-Octanol	2.556(5)	2.474(2)	147	8.2	10.30
1-Octanol/DMDOHEMA	2.580(10)	2.491(6)	120	-	

[a] Refs. 34 and 35 [b] Ref. 46 [c] Ref. 34

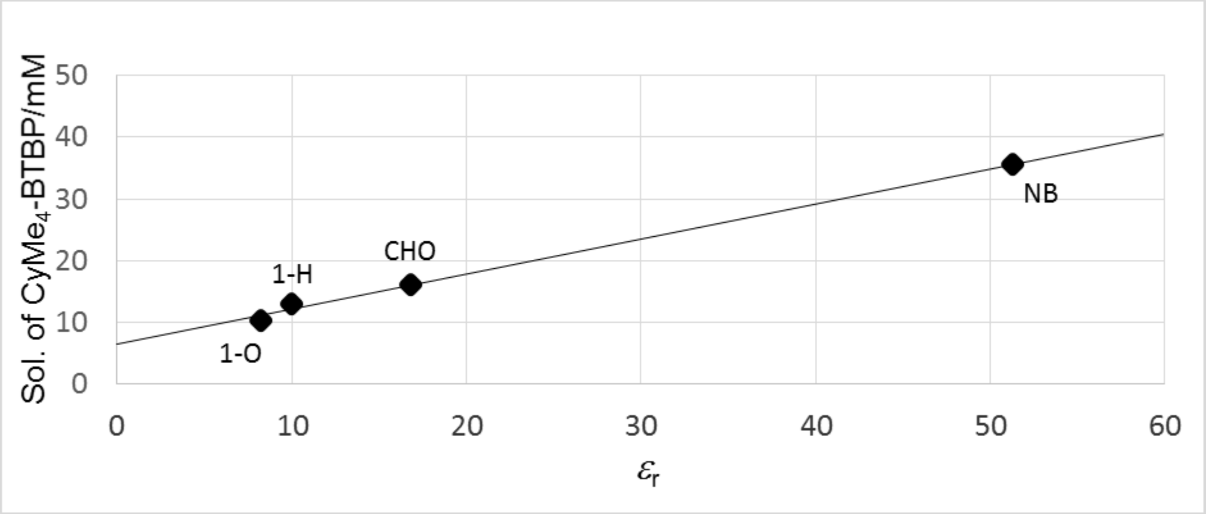


Figure 2. The linear relationship between the solubility and the relative permittivity of the solvent of CyMe$_4$-BTBP in 1-hexanol (1-H), 1-octanol (1-O), cyclohexanone (CHO) and nitrobenzene (NB).

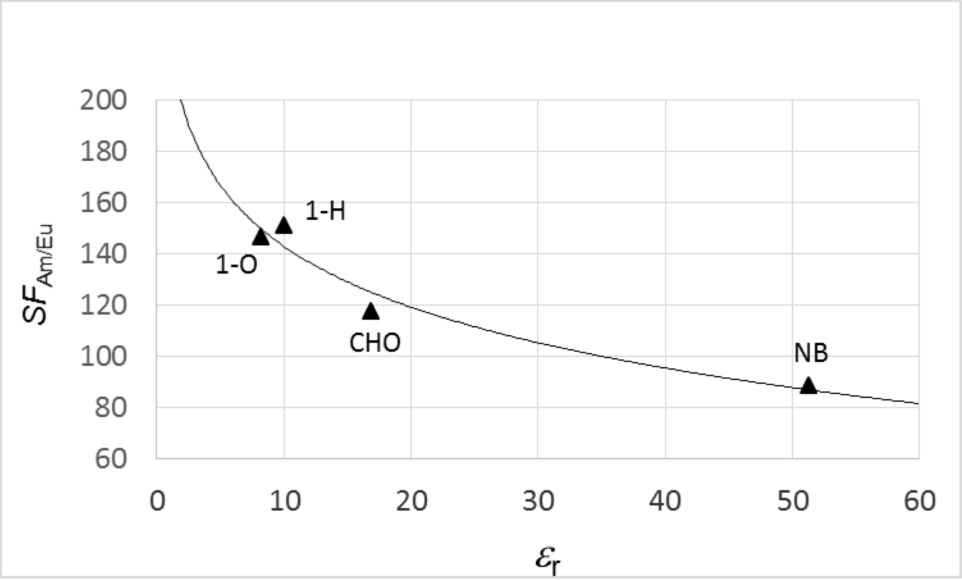


Figure 4. Relationship between the separation factor $SF_{\mathrm{Am/Eu}}$ and the relative permittivity of the solvent in 1-hexanol (1-H), 1-octanol (1-O), cyclohexanone (CHO) and nitrobenzene (NB); the approximate trendline follows a logarithmic function.

Conductivity measurements

The limiting conductivity of europium(III)-CyMe$_4$-BTBP complex in 1 mmol·dm^{-3} solution in nitrobenzene was observed to be 46.4 S cm^2 mol^{-1}. This value is smaller than expected for a fully dissociated salt (108 S cm^2 mol^{-1}), but still sufficiently high to assume that only some of the nitrates anions are associated with the [Eu(CyMe$_4$-BTBP)$_2$]$^{3+}$ complex. When attempts were made to conduct conductivity measurements in cyclohexanone, even tetraethyl ammonium perchlorate was found to be a weak electrolyte, meaning that there is a very strong association of the cations with the anions in this solvent. The [Eu(CyMe$_4$-BTBP)$_2$]$^{3+}$ and [Am(CyMe$_4$-BTBP)$_2$(NO$_3$)$_n$]$^{(3-n)+}$ complexes are hence associated with nitrate ions as ions pairs, explaining their relatively high solubility in solvents with low relative permittivity as 1-hexanol, 1-octanol and cyclohexanone, Table 3.

Conclusions

EXAFS studies of the dicomplexes of CyMe$_4$-BTBP with americium(III) and europium(III) in nitrate media in nitrobenzene, cyclohexanone, 1-hexanol, 1-octanol, and malonamide (0.25 mol·dm^{-3} DMDOHEMA) in 1-octanol have shown that predominating complexes are

$[Am(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$ and $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$, respectively, independent of solvent. The metal-nitrogen distance in the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complex is ca. 0.1 Å shorter than in the $[Am(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$ one. This difference is fully explained by assigning different coordination numbers to the americium(III) and europium(III) ions, ten and eight, respectively, and the fact that americium(III) is slightly larger than the europium(III) ion, also when they have the same coordination number.[44] The presence of a nitrate ion in the first coordination sphere of the americium(III) complex compensates the charge density of the complex considerably in comparison with when only ion-pairs are formed. The stability and solubility of complexes in solvents with low relative permittivity increases with decreasing charge density. The $[Am(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$ complex will therefore be increasingly soluble and stabilized over the $[Eu(CyMe_4\text{-}BTBP)_2]^{3+}$ complex in solvents with decreasing relative permittivity. The separation factor $SF_{\mathrm{Am/Eu}}$ increases accordingly with decreasing relative permittivity of the solvent, Figure 4. The separation of americium(III) from europium(III) with $CyMe_4$-BTBP as extraction agent will increase with decreasing relative permittivity of the solvent, and thereby also with decreasing solubility of $CyMe_4$-BTBP. The choice of solvent is therefore a balance of a high separation factor and sufficient solubility of the $CyMe_4$ ligand.

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Electronic Supplementary Information

Conductivity measurements in nitrobenzene

In order to be able to understand the results obtained with nitrate salts of BTBP complexes it is vital to know the limiting conductivity and hydrodynamic radius of a homoleptic *bis*-BTBP complex. The perchlorate salts of the C_2-BTBP complexes of four metals (cadmium, copper, lead and silver) were studied and for comparison the perchlorate salt of the bis-$CyMe_4$BTBP complex of lead was also studied. The cadmium and silver complexes were made using the literature method,[1] while the perchlorate salts of the lead complexes were obtained by a modified method. In place of potassium hexafluorophosphate, sodium perchlorate was used for anion metathesis. The copper complex was obtained by the treatment of a copper(II) salt with two equivalents of C_2-BTBP followed by anion metathesis with sodium perchlorate.

It was found that the mobility of the mononuclear complexes of divalent metals was independent of the nature of the metal and indeed a change of the radius of the coordinated central metal cation had little effect on the experimentally observed limiting conductivity of the mononuclear complexes (Table S1). Using literature data for the hydrodynamic radius of a perchlorate anion in nitrobenzene (2.51 Å)[2] it was then possible to estimate the hydrodynamic radii of these metal complexes (Figure S1, Table S1). However, on changing to the dinuclear silver(I) the hydrodynamic radius increased and as the charge on the *homoleptic* complex is identical to that of the cadmium, copper and lead complexes it can be concluded the difference in hydrodynamic radius is due to that fact that the complex has a different shape.

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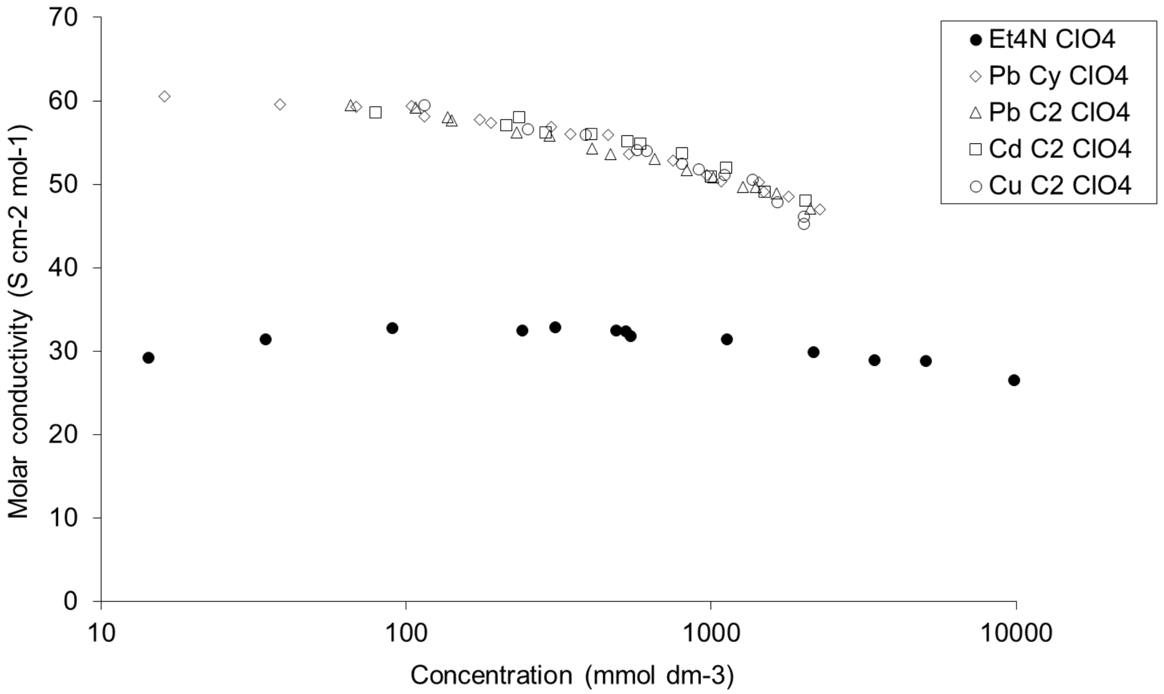

Figure S1. Molar conductivity of perchlorates of metal complexes and the tetraethyl ammonium ion in water saturated nitrobenzene.

Table S1. Measured limiting equivalent conductivity, $\Lambda_+°$, and calculated hydrodynamic radius, R_{hyd}, of different metal-BTBP complexes.

Complex	**$\Lambda_+°$ /S cm^2 mol^{-1}**	**R_{hyd}/Å**
$[Cu(C_2BTBP)_2]^{2+}$	27.7	3.21
$[Cd(C_2BTBP)_2]^{2+}$	26.6	3.34
$[Pb(C_2BTBP)_2]^{2+}$	25.9	3.43
$[Pb(CyMe_4BTBP)_2]^{2+}$	26.4	3.36
$[Ag_2(C_2BTBP)_2]^{2+}$	21.2	4.20