Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 9209

www.rsc.org/dalton

PAPER

Complexation of lanthanides, actinides and transition metal cations with a 6-(1,2,4-triazin-3-yl)-2,2′:6′,2″-terpyridine ligand: implications for actinide (III)/lanthanide(III) partitioning†

Frank W. Lewis,*[a] Laurence M. Harwood,*[a] Michael J. Hudson,[a] Michael G. B. Drew,[a] Michal Sypula,[b] Giuseppe Modolo,[b] Daniel Whittaker,[c] Clint A. Sharrad,[c] Vladimira Videva,[d,e] Véronique Hubscher-Bruder[d,e] and Françoise Arnaud-Neu[d,e]

Received 5th March 2012, Accepted 17th May 2012
DOI: 10.1039/c2dt30522d

The quadridentate *N*-heterocyclic ligand 6-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2′ : 6′,2″-terpyridine ($CyMe_4$-hemi-BTBP) has been synthesized and its interactions with Am(III), U(VI), Ln(III) and some transition metal cations have been evaluated by X-ray crystallographic analysis, Am(III)/Eu(III) solvent extraction experiments, UV absorption spectrophotometry, NMR studies and ESI-MS. Structures of 1 : 1 complexes with Eu(III), Ce(III) and the linear uranyl (UO_2^{2+}) ion were obtained by X-ray crystallographic analysis, and they showed similar coordination behavior to related BTBP complexes. In methanol, the stability constants of the Ln(III) complexes are slightly lower than those of the analogous quadridentate bis-triazine BTBP ligands, while the stability constant for the Yb(III) complex is higher. ^{1}H NMR titrations and ESI-MS with lanthanide nitrates showed that the ligand forms only 1 : 1 complexes with Eu(III), Ce(III) and Yb(III), while both 1 : 1 and 1 : 2 complexes were formed with La(III) and Y(III) in acetonitrile. A mixture of isomeric chiral 2 : 2 helical complexes was formed with Cu(I), with a slight preference (1.4 : 1) for a single directional isomer. In contrast, a 1 : 1 complex was observed with the larger Ag(I) ion. The ligand was unable to extract Am(III) or Eu(III) from nitric acid solutions into 1-octanol, except in the presence of a synergist at low acidity. The results show that the presence of two outer 1,2,4-triazine rings is required for the efficient extraction and separation of An(III) from Ln(III) by quadridentate N-donor ligands.

Introduction

A major goal in the future treatment of used nuclear fuel is the reduction in the long-term radiotoxicity of the waste by the removal of the long-lived minor actinides. In the partitioning and transmutation (P&T) strategy,[1] it is intended that, following their separation from the trivalent lanthanides, the trivalent minor actinides Am(III) and Cm(III) will be converted into shorter-lived or stable elements by neutron bombardment. Since many lanthanides have high neutron capture cross sections, efficient transmutation of the actinides is only possible once they have first been separated (partitioned) from the lanthanides.[2]

Although the chemical properties of An(III) and Ln(III) are similar,[3] it has been shown that ligands containing soft N- and S-donor atoms are capable of separating the two groups of elements.[4] The selectivity of these reagents for An(III) over Ln(III) is believed to arise from a more covalent interaction between the donor atoms of the ligands and the 5f orbitals of An(III).[5] Within the soft N-donor ligands, bis-(1,2,4-triazine) ligands show the highest selectivities and optimum extraction performances to date. The terdentate 2,6-bis(1,2,4-triazin-3-yl)pyridine (BTP)[6] and the quadridentate 6,6′-bis(1,2,4-triazin-3-yl)-2,2′-bipyridine (BTBP)[7] ligands have been the focus of intensive research. The annulated ligand $CyMe_4$-BTBP **1**[8] (Fig. 1) is currently the most suitable for An(III)/Ln(III) separations, as recently demonstrated under process conditions.[9] It has also been shown that the extraction properties of **1** can be markedly improved by pre-organization of the ligand using a 1,10-phenanthroline moiety.[10]

[a]*Department of Chemistry, The University of Reading, Whiteknights, Reading RG6 6AD, UK. E-mail: f.lewis@reading.ac.uk, l.m.harwood@reading.ac.uk; Fax: +44 (0)118 378 6121; Tel: +44 (0)118 378 7417*
[b]*Forschungszentrum Jülich GmbH, Sicherheitsforschung und Reaktortechnik, D-52425 Jülich, Germany. E-mail: g.modolo@fz-juelich.de; Tel: +492 46161 4896*
[c]*The Mill-C40, School of Chemical Engineering and Analytical Science, The University of Manchester, Manchester M13 9PL, UK. E-mail: clint.a.sharrad@manchester.ac.uk; Tel: +44 (0)161 275 4657*
[d]*Université de Strasbourg, IPHC, 25 Rue Becquerel, 67087 Strasbourg, France. E-mail: veronique.hubscher@unistra.fr; Tel: +33 (0) 368 852 751*
[e]*CNRS, UMR 7178, 67037 Strasbourg, France*

†Electronic supplementary information (ESI) available: Procedures and characterization data for known compounds, Mercury plot of ligand **2** and its Eu, Ce and U complexes, NMR stack plots and species distribution curves, enlargements of mass peaks for La(III), Eu(III), Cu(I) and Ag(I) complexes of **2**. CCDC 869233–869236. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30522d

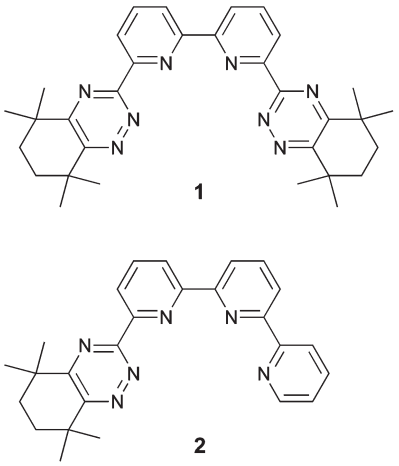


Fig. 1 Structures of $CyMe_4$-BTBP **1** and $CyMe_4$-hemi-BTBP **2**.

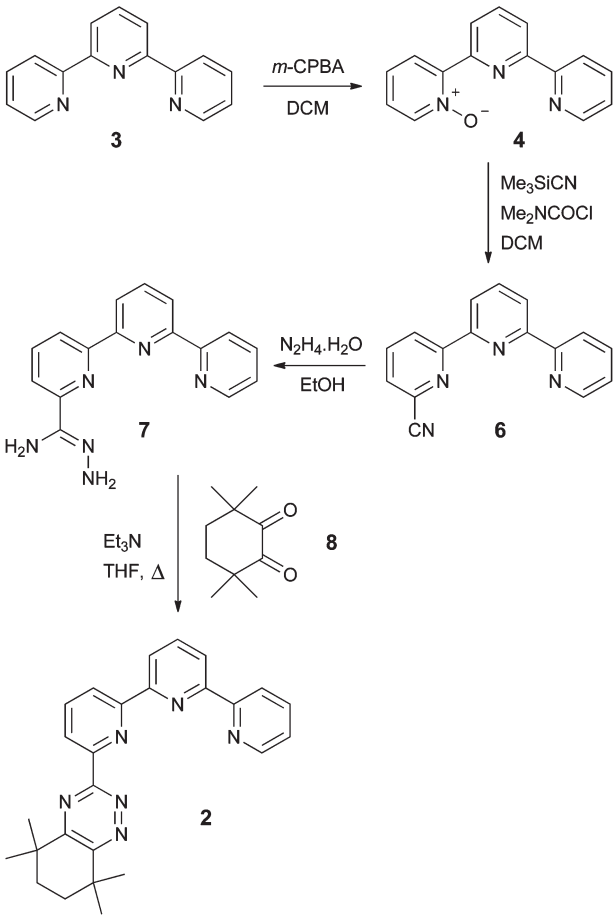
Despite intensive research,[11] a fundamental understanding of the origins of the high selectivity and excellent extraction properties shown by bis-(1,2,4-triazine) ligands is still limited, with the result that further improvements in ligand design continue to be made largely on a trial and error basis using chemical intuition. Previous studies on tridentate heterocyclic N-donor ligands have shown that the 6-(1,2,4-triazin-3-yl)-2,2′-bipyridine ligands (hemi-BTPs)[12] have properties between those of the BTPs and the 2,2′ : 6′,2″-terpyridine ligands (TERPY).[13] However, the hemi-BTPs more closely resemble the TERPY ligands in their extraction behaviour (*i.e.*, only 1 : 1 complexes are formed in contrast to the more hydrophobic 1 : 3 complexes formed by the BTPs, extraction only occurs at low acidity and a synergist is required for extraction to take place). With the aim of furthering our understanding of the quadridentate BTBP ligands, herein we report the results of our investigations on a closely related quadridentate 6-(1,2,4-triazin-3-yl)-2,2′ : 6′,2″-terpyridine (hemi-BTBP) ligand $CyMe_4$-hemi-BTBP **2** (Fig. 1), in which one of the triazine rings of **1** has been replaced by a pyridine ring.

Results and discussion

Synthesis and X-ray crystallography

The new ligand $CyMe_4$-hemi-BTBP **2** was synthesized in four steps, as shown in Scheme 1. Oxidation of 2,2′ : 6′,2″-terpyridine **3** with 3-chloroperoxybenzoic acid (*m*-CPBA)[14] generated a mixture of mono-*N*-oxide **4**,[15] bis-*N*-oxide **5**[16] and unreacted **3** from which pure **4** was obtained in 52% yield after separation by column chromatography. A modified Reissert–Henze reaction[17] of **4** with trimethylsilyl cyanide and *N*,*N*-dimethylcarbamyl chloride afforded the nitrile **6**[18] in high yield (**CAUTION**: trimethylsilyl cyanide is a volatile hydrogen cyanide equivalent). The reaction of **6** with hydrazine hydrate gave the carbohydrazonamide **7**[19] which, on treatment with 3,3,6,6-tetramethylcyclohexane-1,2-dione **8**[20,21] in THF/Et_3N at reflux, furnished the ligand **2** in 93% yield (see the ESI† for the synthesis of compounds **4**–**7**).

The X-ray crystal structure of **2** is shown in Fig. 2 together with the atomic numbering scheme. The four aromatic rings are



Scheme 1 Synthesis of $CyMe_4$-hemi-BTBP **2**.

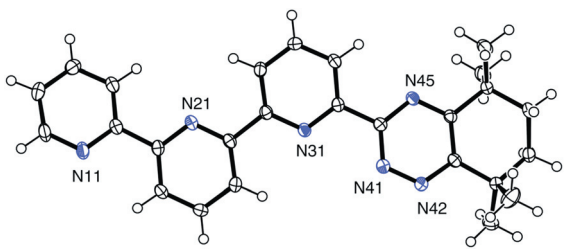


Fig. 2 X-Ray crystal structure of $CyMe_4$-hemi-BTBP **2**.

in a mutually *trans*-arrangement with respect to the pyridine nitrogen atoms. Thus the N(11)–C–C–N(21), N(21)–C–C–N(31) and N(31)–C–C–N(41) torsion angles are −157.7(2), −172.7(2) and −19.1(2)°, respectively. This *trans*, *trans*-arrangement of adjacent pyridine rings has been shown by quantum mechanics calculations[12] to be the most energetically favourable arrangement, primarily because there are no close H–H contacts between adjacent rings. Clearly, this conformation needs to change before the ligand can bind to a metal cation through its four nitrogen atoms. In previous work on multidentate N-donor ligands containing 1,2,4-triazine rings, it was found that binding always occurs through the nitrogen in position 2 of the triazine ring.[22] The packing of **2** in the crystal is shown in Fig. 17 in the ESI.† The molecules pack in pairs across a centre of symmetry,

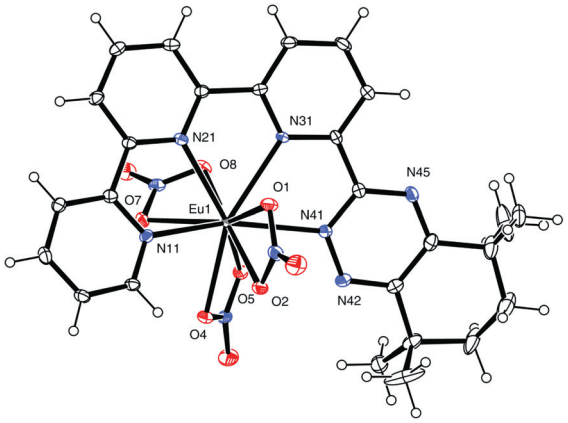


Fig. 3 X-Ray crystal structure of [Eu(**2**)$(NO_3)_3$]·2MeCN. Ellipsoids are shown at 30% probability. Solvent molecules are omitted for clarity.

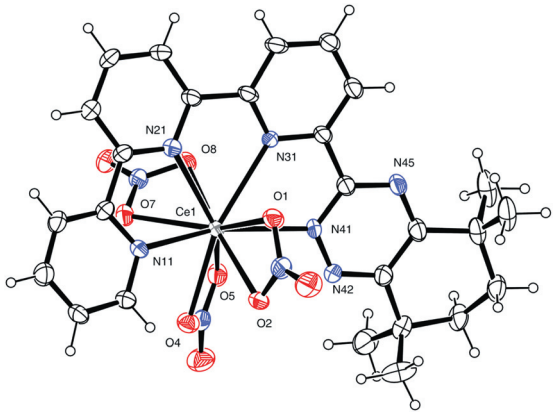


Fig. 4 X-Ray crystal structure of [Ce(**2**)$(NO_3)_3$]·C_7H_8. Ellipsoids are shown at 30% probability. Solvent molecules are omitted for clarity.

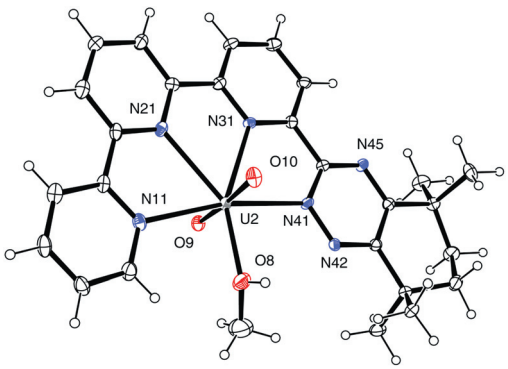


Fig. 5 X-Ray crystal structure of [UO_2(**2**)MeOH][$UO_2(NO_3)_4$]. Ellipsoids are shown at 30% probability. The counterion is not shown.

enabling π–π stacking between their central pyridine rings. The distance between these central pyridine rings (containing N(31)) is 3.32 Å.

We also synthesized the 1 : 1 complexes of **2** with the lanthanide nitrates $Eu(NO_3)_3$ and $Ce(NO_3)_3$ by admixture of dichloromethane solutions of **2** with a solution of the lanthanide nitrate salt in CH_3CN, followed by evaporation of the solvent. Coordination of the paramagnetic lanthanides to ligand **2** induced marked shifts in the ^{1}H NMR spectra of the complexes, particularly in the case of Eu(III). In the Eu(III) complex, three of the aromatic protons of **2** are shifted upfield to 3.44, 4.02 and 4.91 ppm relative to the free ligand **2**, while the methyl resonances are shifted downfield from 1.48 and 1.53 ppm to 2.68 and 2.91 ppm. The methylene protons appear as a multiplet at 3.04–3.14 ppm. Slow evaporation of solutions of the Eu and Ce complexes of **2** in MeOH/dichloromethane/toluene afforded crystals of the complexes suitable for X-ray analysis. The X-ray crystal structure of the Eu complex of **2** is shown in Fig. 3.

As is evident, the ligand coordinates in an approximately distorted planar tetradentate fashion to the Eu metal centre which is 10-coordinate. The remainder of the metal's inner coordination sphere is made up of three bidentate nitrate ions. The Eu–N bond distances range from 2.523(4) to 2.564(4) Å. A similar structure was also obtained with $Ce(NO_3)_3$ (Fig. 4). The Ce–N bond distances in this structure range from 2.605(8) to 2.621(8) Å. The difference in M–N bond lengths reflect the smaller size of the Eu ion compared to the Ce ion. The coordination mode of ligand **2** in these complexes is quite similar to that observed in the 1 : 1 complexes formed by the analogous BTBP ligands with trivalent lanthanide nitrates,[23] while the bond lengths are comparable. Some notable differences are that, in the present case, ligand **2** is significantly more distorted from planarity than the BTBP ligands in their 1 : 1 lanthanide complexes, and the orientation of the three nitrate ligands relative to the equatorial plane of the ligand is also different. The N(11)–C–C–N(21), N(21)–C–C–N(31) and N(31)–C–C–N(41) torsion angles for the Eu and Ce complexes are 2.0(6), 14.3(6), 2.1(6)°, and −2.0(7), 19.5(4) and −0.5(3)°, respectively, which may indicate that the Eu(III) ion is a better fit into the coordination cavity of **2** than the larger Ce(III) ion. The metal is oriented well away from the plane of the four ligating nitrogen atoms in the Eu and Ce structures (r.m.s. deviations of Eu and Ce from the plane of the four nitrogen atoms are 0.52(1) and 0.48(1) Å, respectively).

The addition of **2** in dichloromethane to a solution of $UO_2(NO_3)_2·6H_2O$ in methanol/acetonitrile afforded a sample of the uranyl complex [UO_2(**2**)MeOH][$UO_2(NO_3)_4$] from which crystals suitable for X-ray analysis were obtained following slow evaporation. The X-ray structure of this complex is presented in Fig. 5. The uranyl ion is coordinated in a classic pentagonal bipyramidal configuration that is well known for actinyl ions.[24] In contrast to the Eu and Ce structures, ligand **2** is almost planar and coordinates to the metal perpendicular to the linear UO_2^{2+} axis. The four U–N bond lengths range from 2.517(6) to 2.580(5) Å while the U═O bond lengths are U(2)–O(9) = 1.767(5) and U(2)–O(10) = 1.766(5) Å, which are typical of uranyl complexes. The UO_2^{2+} cation is almost linear (O(9)–U(2)–O(10) bond angle = 175.6(2)°). The remaining coordination site in the equatorial plane is occupied by a MeOH molecule. The structure is almost identical to analogous uranyl structures derived from $CyMe_4$-BTBP **1** that were reported previously, and there are no significant differences in the U–N bond lengths.[25]

Similarly, Cu(I) and Ag(I) complexes of **2** were prepared by admixture of **2** with $[Cu(MeCN)_4]BF_4$ and $[Ag(MeCN)_4]BF_4$, respectively. Detailed NMR and ESI-MS studies (*vide supra*) revealed that the stoichiometries of these complexes were 2 : 2 and 1 : 1, respectively. Unfortunately, despite repeated attempts

Table 1 Extraction of Am(III) and Eu(III) by $CyMe_4$-hemi-BTBP **2** into 1-octanol (0.01 M) as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C)

$[HNO_3]$	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.01	0.0003 ± 0.0001	0.0004 ± 0.0001	0.7 ± 0.1
0.1	0.0005 ± 0.0001	0.0003 ± 0.0001	1.6 ± 0.3
1.0	0.0007 ± 0.0001	0.0003 ± 0.0001	2.2 ± 0.4
2.0	0.0010 ± 0.0002	0.0013 ± 0.0003	0.8 ± 0.2
3.0	0.0015 ± 0.0003	0.0019 ± 0.0004	0.8 ± 0.2
4.0	0.0021 ± 0.0004	0.0021 ± 0.0004	1.0 ± 0.2

at growing crystals, efforts to characterize these complexes by X-ray crystallographic analysis were unsuccessful.

Solvent extraction studies

Ligand **2** was studied for its ability to extract and separate Am(III) and Eu(III) from nitric acid solutions into *n*-octanol, one of the most common diluents used for An/Ln separations. The distribution ratios and separation factors for the extraction of Am(III) and Eu(III) from nitric acid solutions by **2** dissolved in *n*-octanol (0.01 M) are shown in Table 1. Low distribution ratios ($D < 0.01$) were obtained for both Am(III) and Eu(III) at all nitric acid concentrations from 0.01–4 M, and essentially no significant extraction of either metal ion takes place. Furthermore, the ligand **2** shows no significant selectivity for Am(III) over Eu(III). These results are in marked contrast to those obtained for related quadridentate bis-triazine ligands such as $CyMe_4$-BTBP **1** which can extract ($D_{Am} > 1$) and separate Am(III) from Eu(III) with high selectivities ($SF_{Am/Eu} \sim 100$) under similar conditions.[8]

Previous studies on polydentate heterocyclic N-donor ligands have shown that extraction of An(III) and Ln(III) from nitric acid can be considerably improved by including a lipophilic anion source (*e.g.*, 2-bromodecanoic acid) as a synergist in the organic phase.[13] However, this effect only takes place at low acidity because dissociation of the synergist is suppressed at low pH. Thus, the extraction experiments with **2** were repeated in the presence of 2-bromohexanoic acid (see Table 1 and Fig. 18 in the ESI†). As expected, the extraction of Am(III) improves at low $[HNO_3]$ (D_{Am} = 1.3 at 0.001 M HNO_3) but the distribution ratios decrease at higher acidities. These results demonstrate that replacement of one of the 1,2,4-triazine rings in the BTBP ligands with a pyridine ring leads to a marked decrease in extraction performance and selectivity, and show that two 1,2,4-triazine rings are important for optimum results. A similar effect has previously been observed when one of the 1,2,4-triazine rings of the tridentate BTP ligands was replaced with a pyridine ring.[12]

Metal ion complexation studies

Using previously published methods,[26] the complexing properties of **2** with three lanthanide ions (La(III), Eu(III) and Yb(III)) and two transition metal ions (Cu(II) and Ni(II)) were studied in methanol and nitrate media using absorption-spectrophotometry. For comparison, the same measurements were also performed with the related ligand $CyMe_4$-BTTP **9** (Fig. 6).[27]

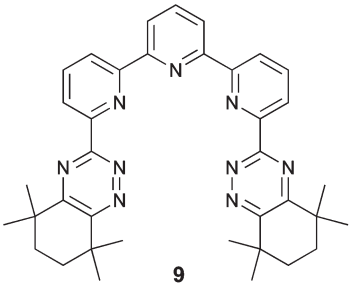


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Fig. 6 Structure of the ligand $CyMe_4$-BTTP **9**.

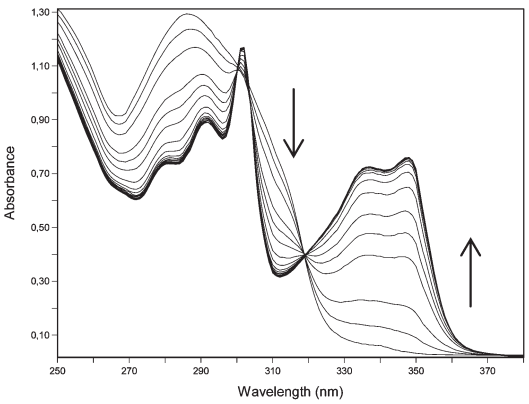

Fig. 7 Spectrophotometric titration of $CyMe_4$-hemi-BTBP **2** ($C_L = 5.16 \times 10^{-5}$ M) with $Yb(NO_3)_3$ in methanol ($0 \leq C_M/C_L \leq 1.94$) (T = 25 °C, $I = 10^{-2}$ M Et_4NNO_3).

Initially, the stability of the ligand solutions over time was monitored spectrophotometrically. In addition, we investigated the absorbance over time of mixtures of the ligands in the presence of *ca.* one equivalent of the metal. Although the equilibria were always reached within the time scale of the measurements for La(III) and Cu(II), it was necessary to wait longer to reach the equilibrium for Eu(III) (10 min with $CyMe_4$-BTTP **9**) and particularly for Yb(III) (10 min with $CyMe_4$-hemi-BTBP **2** and 15 min with $CyMe_4$-BTTP **9**) and Ni(II) (15 min with $CyMe_4$-hemi-BTBP **2**). For every system studied, complexation led to significant spectroscopic changes and in most cases gave rise to one or more isosbestic points. The spectrophotometric titration of $CyMe_4$-hemi-BTBP **2** with Yb(III) is presented in Fig. 7 as an example.

As regards lanthanide complexation, the best fit of the experimental data is obtained by assuming the formation of 1 : 1 complexes of $CyMe_4$-hemi-BTBP **2** and of $CyMe_4$-BTTP **9** with the two cations Eu(III) and Yb(III). With both ligands and Yb(III), the fit is improved by considering an additional 1 : 2 complex. The 1 : 1 stoichiometries of the lanthanide(III) nitrate complexes with ligand **9** are consistent with those found in the solid state and in liquid–liquid extraction of Eu(III) from nitric acid into octanol.[27] For La(III), the best interpretation indicates the formation of an exclusive 1 : 1 complex with **2** and a 1 : 2 complex with **9**. The corresponding stability constants (log β) are given in Table 2. The results show that, in the case of **2**, the stability constants of the 1 : 1 complexes with La(III) and Eu(III) are slightly lower than those found for the analogous $CyMe_4$-BTBP **1** (determined

Table 2 Stability constants (log β) of some lanthanide(III) and nickel(II) complexes with ligands **1**, **2** and **9** in methanol (T = 25 °C, $I = 10^{-2}$ M Et_4NNO_3) determined by UV-vis spectrometry

Ligand	Complex	La(III)	Eu(III)	Yb(III)	Ni(II)[b]
1[a]	1 : 1	4.4	6.5	5.9	—
	1 : 2	8.8	11.9	—	—
2	1 : 1	4.29 ± 0.08	5.6 ± 0.4	7.3 ± 0.2	—
	1 : 2	—	—	12.4 ± 0.2	9.95 ± 0.08
	1 : 3	—	—	—	15.4 ± 0.1
9	1 : 1	—	5.5 ± 0.2	5.6 ± 0.1	—
	1 : 2	8.2 ± 0.3	—	9.9 ± 0.5	12.1 ± 0.2
	1 : 3	—	—	—	16.9 ± 0.2

[a] Determined previously.[26] [b] One experiment.

previously),[26] while the corresponding complex with Yb(III) is more stable. The stability constants of the complexes of the same stoichiometry with $CyMe_4$-BTTP **9** and the related $CyMe_4$-BTBP **1** are of the same order of magnitude (except for Eu(III)), suggesting similar coordination. Regarding Ni(II), the best model corresponds to the formation of complexes of 1 : 2 and 1 : 3 stoichiometries for each ligand, although the formation of 1 : 3 complexes with Ni(II) is unlikely. No satisfactory model has been found so far for the complexation of Cu(II) by either ligand.

NMR titrations

The coordination chemistry and speciation of $CyMe_4$-hemi-BTBP **2** with selected trivalent lanthanide nitrates and transition metals was studied by ^{1}H NMR titration.[28] This technique is a useful tool for the determination of the solution behaviour of ligands with metal cations.[29] The formation of metal complexes of **2** was followed by recording the ^{1}H NMR spectra of **2** (0.01 M) in CD_3CN to which solutions of the metal salts (0.01 M in CD_3CN) were added. In the titration of **2** with $La(NO_3)_3$, both 1 : 1 and 1 : 2 complexes were observed. The 1 : 2 species is the major solution species present at low metal : ligand ratios. However, at higher metal : ligand ratios the 1 : 1 complex becomes the dominant solution species and this is the only species present after 1.3 equivalents of $La(NO_3)_3$ have been added (see Fig. 19 and 20 in the ESI†). Clearly, both 1 : 1 and 1 : 2 complexes are in equilibrium, and their relative ratio depends on the metal : ligand ratio. The species distribution curve, presented in Fig. 8, was calculated from the normalized relative ratios of each of the species present (obtained by integration of a given resonance for each species).

The stoichiometry of the 1 : 1 species formed at the end of the titration was confirmed by ESI-MS (see Fig. 21 in the ESI†). A mass peak corresponding to $[La(\mathbf{2})(NO_3)_2]^+$ was observed at m/z = 685.1039. The isotope distribution pattern of this peak was in agreement with that expected for $[La(\mathbf{2})(NO_3)_2]^+$. In a related ESI-MS study on BTBP ligands, only the 1 : 2 complexes were formed with lanthanides under extraction conditions.[30]

In the case of $Eu(NO_3)_3$, only a 1 : 1 species was formed during the course of the titration with **2**, and the resonances of the free ligand completely disappear after 1.1 equivalents of Eu(III) have been added. The paramagnetic Eu(III) ion induced pronounced shifts in some of the aromatic protons of **2**, although

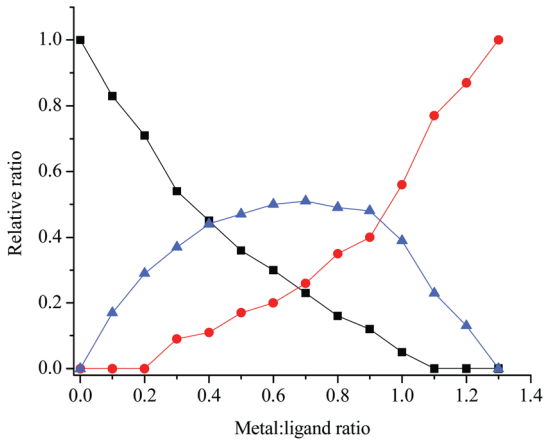

Fig. 8 ^{1}H NMR titration of $CyMe_4$-hemi-BTBP **2** with $La(NO_3)_3$ in CD_3CN (■ = free ligand, ● = 1 : 1 complex, ▲ = 1 : 2 complex).

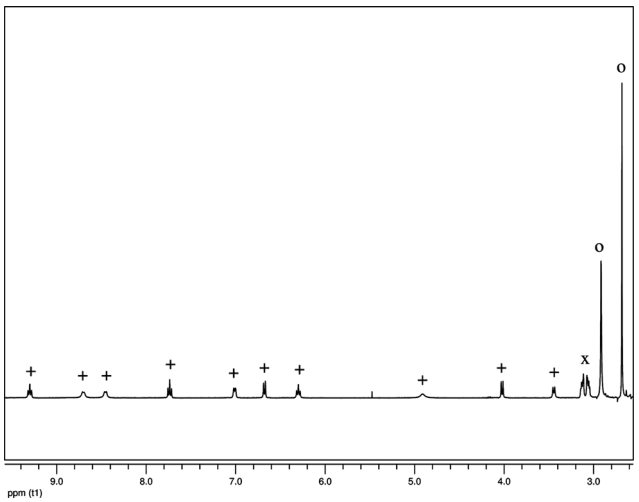

Fig. 9 ^{1}H NMR spectrum of the 1 : 1 complex $[Eu(\mathbf{2})(NO_3)_3]$ in CD_3CN (Assignments: o = methyl groups, x = methylene protons, + = aromatic protons).

the spectra obtained were well resolved (see Fig. 22 and 23 in the ESI†).[31] This is often the case with Eu(III) complexes because the Eu(III) cation usually causes minimal broadening of NMR peaks. The species distribution curve (see Fig. 24 in the ESI†) displayed a slightly asymptotic behaviour at the beginning of the titration, suggesting that the complexation reaction was incomplete. A straight line would be expected if all of the added Eu(III) was complexed by **2**. A slow complexation reaction was ruled out on the basis that no spectroscopic changes were observed as a function of time. The ^{1}H NMR spectrum of the 1 : 1 complex $[Eu(\mathbf{2})(NO_3)_3]$ is shown in Fig. 9. In the ESI-MS spectrum of the final solution species, a mass peak corresponding to $[Eu(\mathbf{2})(NO_3)_2]^+$ was observed (see Fig. 25 in the ESI†). The stoichiometries of the La(III) and Eu(III) complexes deduced from ^{1}H NMR and ESI-MS are in agreement with those determined spectrophotometrically in methanol.

Similar results were observed for the titration of **2** with $Ce(NO_3)_3$. Only a 1 : 1 complex was formed during the titration,

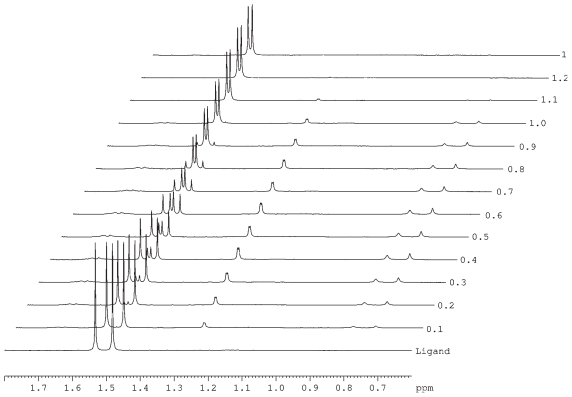

Fig. 10 Aliphatic region of the stack plot for the titration of $CyMe_4$-hemi-BTBP **2** with $Y(NO_3)_3$. First (bottom) spectrum = free ligand. Each subsequent spectrum corresponds to the addition of 0.1 eq. of $Y(NO_3)_3$.

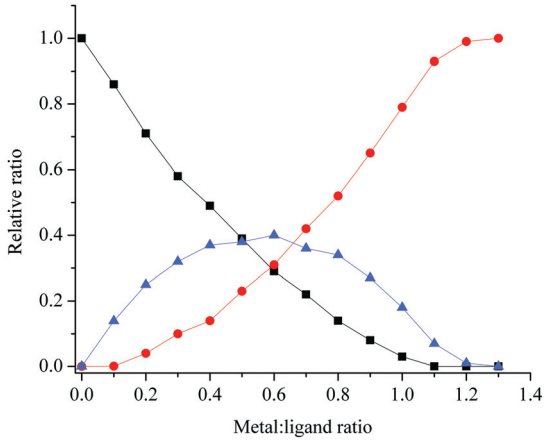

Fig. 11 ^{1}H NMR titration of $CyMe_4$-hemi-BTBP **2** with $Y(NO_3)_3$ in CD_3CN (■ = free ligand, ● = 1 : 1 complex, ▲ = 1 : 2 complex).

and the resonances of the free ligand had disappeared after 1.0 equivalents of Ce(III) had been added. The aromatic region of the stack plot of the NMR spectra is shown in Fig. 27 in the ESI.† Well resolved NMR spectra were obtained, which showed pronounced paramagnetic shifts for some resonances. Once again the species distribution curve showed asymptotic behavior (see Fig. 28 in the ESI†), suggesting incomplete complexation at the beginning of the titration. It is interesting to note that both **2** and $CyMe_4$-BTTP **9**, two ligands that share similar extraction properties, form only 1 : 1 complexes with Ln(III) in nitrate media by NMR (except for **2** with La(III) and Y(III)).

In contrast to the above results, the titration of **2** with $Yb(NO_3)_3$ gave rise to very broad resonances with no coupling information, making interpretation of the spectra difficult (see Fig. 29 and 30 in the ESI†). The calculation of the species distribution was thus not possible with any certainty. However, a 1 : 1 species is probably formed judging by the disappearance of the free ligand resonances only after 1.0 equivalents of Yb(III) have been added. Although solution structures of Yb(III) complexes can be determined unambiguously by analysis of the paramagnetic shifts that they induce (which are essentially dipolar in nature),[32] this can only be applied to symmetrical complexes such as those formed by $CyMe_4$-BTTP **9**[27] or a related phenanthroline based bis-triazine ligand.[10] Such an analysis of the Yb(III) complex of **2** is therefore not possible.

The titration of **2** with $Y(NO_3)_3$ gave very similar results to that with $La(NO_3)_3$. Both 1 : 1 and 1 : 2 species are formed, with the 1 : 2 species being the major species at low metal : ligand ratios. The 1 : 1 species becomes the only solution species present at high (>1.2 equivalents Y(III)) metal : ligand ratios. In the aliphatic region, the methyl resonances for the 1 : 2 complex of **2** appear as four singlets (Fig. 10). An expansion of the ^{1}H NMR spectrum that shows the aliphatic resonances of the 1 : 1 and 1 : 2 complexes is shown in Fig. 33 in the ESI.† Such a 1 : 2 complex with the non-symmetric ligand **2** is chiral and the aliphatic gem-dimethyl groups of the bis-complex are thus diastereotopic. The observation of four methyl resonances is therefore in agreement with the formation of a 1 : 2 bis-complex (see the ESI† for a full discussion and explanation). Only two methyl resonances are observed for the 1 : 1 complex, as expected. The species distribution curve for the titration of **2** with $Y(NO_3)_3$ is displayed in Fig. 11.

We then extended our NMR study to the complexation of **2** with Cu(I) and Ag(I). Extensive studies on oligopyridine coordination chemistry[33] by Constable and others have shown that the quaterpyridine ligands typically form planar mononuclear 1 : 1 complexes with metals that favour square planar or octahedral coordination geometries (*e.g.*: Ni(II), Pd(II), Fe(II), Co(II)).[34,35] On the other hand, metals that favour tetrahedral coordination geometries (*e.g.*: Cu(I), Ag(I)) usually form dinuclear double-helical 2 : 2 complexes,[36] although some rare exceptions have been noted.[37] Non-symmetrical quaterpyridine ligands are of particular interest as they are capable of forming directional isomers (head-to-head or head-to-tail isomers) when they form dinuclear double-helicates.[38] $CyMe_4$-hemi-BTBP **2** can be considered as a non-symmetrical quaterpyridine mimic, and we thus studied its complexation with $CuBF_4$ and $AgBF_4$ by NMR spectroscopy.

During the titration of **2** with $CuBF_4$, seven new resonances were observed for the methyl groups while the methylene protons appeared as a complex multiplet at 1.81–1.93 ppm (see Fig. 35–37 in the ESI†). Four methyl group resonances would be expected for a single isomer of a 2 : 2 helical complex (such a complex would be chiral with a screw axis, and the methyl groups would be diastereotopic) while only two would be expected for an achiral 1 : 1 complex. Two directional isomers of a dinuclear double-helical 2 : 2 complex are thus apparently formed (two of the resonances are overlapping).

Another possibility is that the ligand forms a 1 : 2 complex with each ligand being bidentate. Such a complex would also be chiral and four resonances would then be expected for the methyl groups. However, no directional isomerism is possible in such a structure and the maximum number of methyl resonances observed would only be four. The aliphatic region of the ^{1}H NMR spectrum of the final species formed after 1.2 equivalents of Cu(I) have been added is shown in Fig. 12. The 2 : 2 stoichiometry of the complex was also verified by ESI-MS (see Fig. 39 in the ESI†). The isotope distribution pattern of the mass peak (m/z = 485.1490) was consistent with a species containing two Cu(I) ions (7 mass peaks separated by 0.5 mass units).[39]

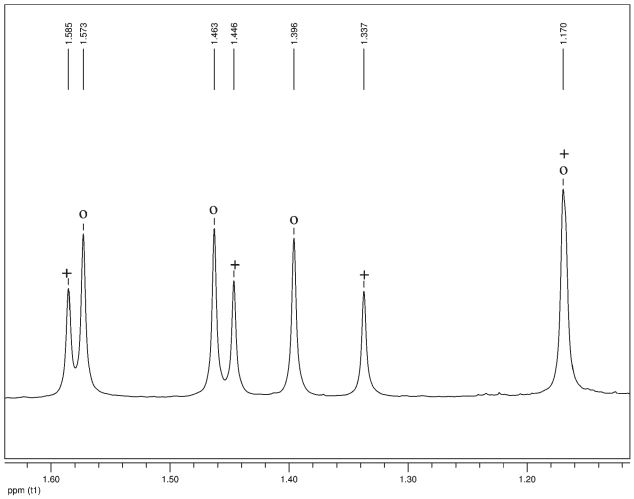

Fig. 12 Aliphatic region of the ^{1}H NMR spectrum of $[Cu_2(\mathbf{2})_2](BF_4)_2$ in CD_3CN (Assignments: o = methyl groups of the major isomer, + = methyl groups of the minor isomer).

The relative ratios of the methyl resonances are not equal and the ratio of directional isomers was calculated as 1.4 : 1 based on the relative integrations of the two sets of methyl resonances. Further evidence for the formation of two isomers of a 2 : 2 complex is found in the ^{13}C NMR spectrum of the final complex, which shows double the expected resonances (*i.e.*: 8 methyl groups, 4 methylene carbons, 20 aromatic carbons). The calculated species distribution curve is shown in Fig. 38 in the ESI.† The linear shape of the curve is indicative of a complexation reaction that goes to completion.

In contrast to the above results, the titration of **2** with $AgBF_4$ did not show separate resonances for the free ligand and the complexes. Instead, an averaged NMR spectrum of both species was observed throughout the titration (see Fig. 40 and 41 in the ESI†). Only one set of resonances was observed (two methyl peaks, one methylene resonance, one set of aromatic peaks), with minor changes in chemical shift occurring in some cases until 1.1 equivalents of metal had been added, after which no further spectroscopic changes were observed. This suggests that a rapid exchange process is taking place faster than the NMR timescale can detect. The presence of only two resonances for the methyl groups indicates that an achiral 1 : 1 complex is formed. A helical structure can thus be ruled out. The 1 : 1 complex stoichiometry was verified by ESI-MS (see Fig. 42 in the ESI†). In this case, the formation of a 1 : 1 complex is likely to be due to a better fit of the larger Ag(I) ion in the planar tetradentate coordination cavity of **2**. Although rare, examples of planar 1 : 1 complexes of Ag(I) with analogous quaterpyridine[37] and quinquepyridine[40] ligands have been reported.

Conclusions

We have synthesized the quadridentate N-donor ligand **2**, which is related to the established BTBP ligands that are currently the benchmark ligands for An(III)/Ln(III) separations. One of the outer 1,2,4-triazine rings of the BTBP ligand has been replaced by a pyridine ring in ligand **2**. The extraction selectivity for An(III) over Ln(III), and the extraction performance were found to be inferior to those of the BTBPs, possibly due to competing protonation of the ligand. Interestingly, the extraction performance of the ligand is comparable to that of $CyMe_4$-BTTP **9** (Fig. 6), which was capable of forming only 1 : 1 complexes in nitrate media.[27] Solid state structures of the 1 : 1 complexes of the ligand with Eu(III), Ce(III) and U(VI) were solved by X-ray crystallographic analysis. The lanthanide complexes showed a greater degree of ligand distortion compared to the 1 : 1 lanthanide BTBP complexes reported previously. Complexation results obtained in methanol show the formation of 1 : 1 complexes with all Ln(III) nitrates and an additional 1 : 2 complex in the case of Yb(III). In acetonitrile, ligand **2** formed only 1 : 1 complexes with these cations, except for La(III) and Y(III) where equilibrium mixtures of 1 : 1 and 1 : 2 species were observed. This contrasts with the BTBP ligands, which form predominantly 1 : 2 complexes in solution. The new ligand may be considered as an unsymmetrical quaterpyridine mimic, and the formation of two isomers of a chiral dinuclear double-helicate in solution was found with Cu(I). We suggest that the extraction ability of the quadridentate 1,2,4-triazine-based ligands is related to the relative ratios of the 1 : 1 and 1 : 2 complexes formed. Thus the BTBPs form predominantly hydrophobic 1 : 2 complexes with An(III) and are able to extract An(III) from a nitric acid medium, whereas in the present case, the hemi-BTBP ligand **2** forms only 1 : 1 complexes (except with the early lanthanides) that are less hydrophobic and thus more difficult to extract. The presence of at least two covalent interactions between 1,2,4-triazine rings and An(III) is obviously important for the formation of hydrophobic extractable 1 : 2 complexes by quadridentate N-donor ligands. The results highlight the importance of the two outer 1,2,4-triazine rings as an important feature in extractant design. This work furthers our understanding of the origins of the excellent extraction performances and An(III)/Ln(III) selectivities shown by bis-(1,2,4-triazine) N-donor ligands.

Experimental

Uncorrected melting points were obtained on a Stuart SMP10 instrument. IR spectra were recorded as Nujol® mulls on a Perkin Elmer RX1 FT-IR instrument. ^{1}H, ^{13}C–{^{1}H} and ^{13}C NMR spectra were recorded using either a Bruker AMX400, an Avance DFX400 or an Avance DPX250 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Assignments were verified with ^{1}H–^{1}H and ^{1}H–^{13}C COSY experiments as appropriate. Mass spectra were obtained under electrospray conditions on a Thermo Scientific LTQ Orbitrap XL instrument. Elemental microanalyses were performed by Medac Ltd, Chobham, Surrey (UK). All organic reagents were obtained from either Acros or Aldrich, while inorganic reagents were obtained from either BDH or Aldrich and used as received.

6-(5,5,8,8-Tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2′ : 6′,2″-terpyridine 2

2,2′:6′,2″-Terpyridine-6-carbohydrazonamide **7**[19] (1.51 g, 5.20 mmol) was suspended in THF (150 mL) and 3,3,6,6-tetramethylcyclohexane-1,2-dione **8** (1.05 g, 6.24 mmol, 1.2 eq.) was

added. Triethylamine (10 mL) was added and the suspension was heated under reflux for 24 hours. The solution was allowed to cool to room temperature and stirring was continued for a further 12 hours. The solvent was removed *in vacuo* and the residue was purified by chromatography, eluting first with DCM, then with 5% MeOH in DCM to afford the title compound **2** as a yellow solid (2.05 g, 93%). Mp 182–184 °C (from MeOH/DCM). Found: C, 73.91; H, 6.20; N, 19.88%; $C_{26}H_{26}N_6$ requires C, 73.74; H, 6.24; N, 19.67%. ν_{max}(Nujol®)/cm^{-1} 2926, 1580, 1560, 1507, 1458, 1375, 1263, 1141, 1075, 1042, 988, 920, 847, 811, 781, 737, 677, 629. δ_H(400.1 MHz; $CDCl_3$; Me_4Si) 1.47 (6H, s, 2 × Me), 1.52 (6H, s, 2 × Me), 1.88 (4H, s, 2 × CH_2), 7.33 (1H, ddd, *J* 7.6, 4.8 and 1.1, 4″-H), 7.86 (1H, td, *J* 7.6 and 1.8, 5″-H), 8.00 (1H, t, *J* 7.8, 4′-H), 8.05 (1H, t, *J* 7.8, 4-H), 8.47 (1H, dd, *J* 7.8 and 1.0, 5′-H), 8.54 (1H, dd, *J* 7.7 and 1.0, 3-H), 8.65 (1H, dt, *J* 7.8 and 1.1, 6″-H), 8.71 (1H, ddd, *J* 4.8, 1.8 and 1.1, 3″-H), 8.80 (1H, dd, *J* 7.8 and 1.0, 5-H), 8.82 (1H, dd, *J* 7.8 and 1.0, 3′-H). δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 29.2 (2 × Me), 29.7 (2 × Me), 33.2 (*C*H_2), 33.7 (*C*H_2), 36.4 (quat), 37.2 (quat), 121.1 (C-6″), 121.2 (C-5′), 121.6 (C-3′), 122.2 (C-5), 123.6 (C-3), 123.7 (C-4″), 136.8 (C-5″), 137.7 (C-4), 137.9 (C-4′), 149.1 (C-3″), 152.9 (quat), 155.0 (quat), 155.1 (quat), 156.2 (quat), 156.3 (quat), 160.9 (quat), 163.0 (quat), 164.4 (quat). *m*/*z* (CI) 423.2298 ([M + H]$^+$); $C_{26}H_{27}N_6$ requires 423.2297.

$Eu(NO_3)_3$ complex of $CyMe_4$-hemi-BTBP 2

The ligand **2** (0.1065 g, 0.2522 mmol) was dissolved in DCM (5 mL). To this solution was added a solution of $Eu(NO_3)_3{\cdot}5H_2O$ (0.1079 g, 1 eq.) in CH_3CN (4 mL). The two solutions were mixed and the solvents were allowed to evaporate over several days to afford the complex as a yellow solid (0.1791 g, 93%). Mp 236–238 °C (decomposition). Found: C, 40.82; H, 3.68; N, 16.25%; $C_{26}H_{26}O_9N_9Eu$ requires C, 41.06; H, 3.45; N, 16.57%. ν_{max}(Nujol®)/cm^{-1} 3103, 2936, 2869, 1643, 1598, 1575, 1463, 1447, 1430, 1373, 1298, 1273, 1246, 1183, 1166, 1149, 1112, 1066, 1027, 1014, 926, 844, 814, 780, 738, 721, 681, 653, 643, 630, 563. δ_H(400.1 MHz; CD_3CN) 2.68 (6H, s, 2 × Me), 2.91 (6H, s, 2 × Me), 3.04–3.07 (2H, m, CH_2), 3.11–3.14 (2H, m, CH_2), 3.44 (1H, d, *J* 7.8, Ar*H*), 4.02 (1H, d, *J* 7.8, Ar*H*), 4.91 (1H, br s, Ar*H*), 6.29 (1H, t, *J* 7.8, Ar*H*), 6.67 (1H, d, *J* 7.8, Ar*H*), 7.01 (1H, d, *J* 7.1, Ar*H*), 7.73 (1H, t, *J* 7.9, Ar*H*), 8.45 (1H, d, *J* 7.1, Ar*H*), 8.70 (1H, d, *J* 5.8, Ar*H*), 9.29 (1H, t, *J* 7.8, Ar*H*). δ_C(100.6 MHz; CD_3CN) 29.4 (2 × Me), 32.1 (2 × Me), 32.8 (*C*H_2), 33.8 (*C*H_2), 36.2 (quat), 40.6 (quat), 93.6 (Ar*C*), 94.4 (Ar*C*), 95.9 (Ar*C*), 98.8 (Ar*C*), 100.4 (Ar*C*), 110.7 (Ar*C*), 116.9 (Ar*C*), 131.8 (quat), 147.9 (Ar*C*), 150.5 (Ar*C*), 152.1 (Ar*C*), 157.2 (quat), 174.6 (quat), 182.5 (quat), 191.2 (quat), 193.2 (quat), 193.3 (quat), 197.9 (quat). *m*/*z* (CI) 699.1210 (M$^+$); $[C_{26}H_{26}O_6N_8Eu]^+$ requires 699.1184. The complex (*ca*. 0.06 g) was dissolved in DCM (2 mL), toluene (5 mL) and CH_3CN (2 mL), and the resulting yellow solution was allowed to slowly evaporate affording crystals suitable for X-Ray analysis.

$Ce(NO_3)_3$ complex of $CyMe_4$-hemi-BTBP 2

The ligand **2** (0.1063 g, 0.2517 mmol) was dissolved in DCM (5 mL). To this solution was added a solution of $Ce(NO_3)_3{\cdot}6H_2O$ (0.1093 g, 1 eq.) in CH_3CN (4 mL). The two solutions were mixed and the solvents were allowed to evaporate over several days to afford the complex as a yellow solid (0.1490 g, 79%). Mp > 300 °C (from DCM/MeCN). Found: C, 41.54; H, 3.41; N, 16.57%; $C_{26}H_{26}O_9N_9Ce$ requires C, 41.71; H, 3.50; N, 16.83%. ν_{max}(Nujol®)/cm^{-1} 3093, 2968, 2933, 2871, 1632, 1597, 1575, 1529, 1460, 1445, 1428, 1372, 1290, 1245, 1182, 1149, 1112, 1065, 1026, 1009, 926, 844, 815, 781, 752, 733, 721, 681, 642, 541. δ_H(400.1 MHz; CD_3CN) 0.00 (6H, s, 2 × Me), 0.50 (6H, s, 2 × Me), 0.79–0.82 (2H, m, CH_2), 0.90–0.93 (2H, m, CH_2), 3.87 (1H, br s, Ar*H*), 6.07 (1H, d, *J* 7.0, Ar*H*), 6.40 (1H, d, *J* 8.2, Ar*H*), 6.94 (1H, t, *J* 7.8, Ar*H*), 6.98 (1H, d, *J* 8.0, Ar*H*), 8.43 (1H, t, *J* 8.1, Ar*H*), 8.50 (1H, d, *J* 7.8, Ar*H*), 9.20 (1H, t, *J* 8.0, Ar*H*), 9.51 (1H, d, *J* 8.0, Ar*H*), 10.09 (1H, d, *J* 8.3, Ar*H*). δ_C(100.6 MHz; CD_3CN) 26.2 (2 × Me), 27.4 (2 × Me), 30.8 (*C*H_2), 31.4 (*C*H_2), 34.3 (quat), 36.8 (quat), 123.4 (Ar*C*), 124.3 (Ar*C*), 126.2 (Ar*C*), 127.0 (Ar*C*), 128.5 (Ar*C*), 130.4 (Ar*C*), 131.9 (Ar*C*), 137.5 (Ar*C*), 141.7 (Ar*C*), 142.0 (Ar*C*), 144.9 (quat), 146.8 (quat), 150.3 (quat), 154.8 (quat), 156.8 (quat), 157.7 (quat), 161.6 (quat), 164.7 (quat). The complex (*ca*. 0.045 g) was dissolved in DCM (2 mL), toluene (5 mL) and CH_3CN (2 mL), and the resulting yellow solution was allowed to slowly evaporate affording crystals suitable for X-ray analysis.

$UO_2(NO_3)_2$ complex of $CyMe_4$-hemi-BTBP 2

The ligand **2** (0.015 g, 0.0355 mmol) was dissolved in DCM (1 mL). To this solution was added a solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (0.0179 g, 0.0356 mmol, 1 eq.) in MeOH (1 mL). To the resulting yellow solution was added CH_3CN (2 mL) and the solution was left to slowly evaporate affording crystals suitable for X-ray crystallographic analysis. (**Caution**: Natural uranium was used during the course of these experiments. As well as the radioactive hazards associated with ^{238}U and ^{235}U, uranium is a toxic metal, and care should be taken with all manipulations).

$CuBF_4$ complex of $CyMe_4$-hemi-BTBP 2

The ligand **2** (0.0313 g, 0.07413 mmol) was dissolved in DCM (5 mL). To this solution was added a solution of $[Cu(MeCN)_4]BF_4$ (0.0233 g, 1 eq.) in CH_3CN (4 mL). The two solutions were mixed and the solvents were allowed to evaporate over several days to afford the complex as a black solid (1.4 : 1 mixture of directional isomers, 0.0412 g, 97%). Mp 265–268 °C (from DCM/MeCN). Found: C, 54.28; H, 4.85; N, 14.33; F, 12.97%; $C_{52}H_{52}N_{12}B_2F_8Cu_2$ requires C, 54.51; H, 4.57; N, 14.66; F, 13.27%. ν_{max}(Nujol®)/cm^{-1} 3082, 2967, 2933, 2869, 1596, 1570, 1525, 1455, 1426, 1388, 1344, 1247, 1184, 1165, 1146, 1053, 816, 778, 750, 721, 680, 644, 625, 541. δ_H(400.1 MHz; CD_3CN) 1.16 (s, Me *major* and Me *minor*), 1.33 (Me *minor*), 1.39 (Me *major*), 1.44 (Me *minor*), 1.46 (Me *major*), 1.57 (Me *major*), 1.58 (Me *minor*), 1.81–1.93 (2 × CH_2 *major* and 2 × CH_2 *minor*), 7.30–7.36 (m, Ar*H major* and *minor*), 7.89–7.92 (m, Ar*H major* and *minor*), 7.94–8.10 (m, Ar*H major* and *minor*), 8.14 (t, *J* 7.7, Ar*H major*), 8.28 (qu, *J* 4.1, Ar*H minor*), 8.33 (dd, *J* 7.7 and 1.1, Ar*H major*). δ_C(100.6 MHz; CD_3CN)

27.5 (Me *major*), 27.7 (Me *minor*), 28.3 (Me *major*), 28.5 (Me *minor*), 28.5 (Me *minor*), 28.6 (Me *minor*), 28.6 (Me *major*), 28.8 (Me *major*), 31.7 (*C*H_2 *minor*), 31.7 (*C*H_2 *major*), 32.5 (*C*H_2 *minor*), 32.6 (*C*H_2 *major*), 36.2 (quat), 36.3 (quat), 37.5 (quat), 37.5 (quat), 121.6 (Ar*C*), 121.7 (Ar*C*), 122.0 (Ar*C*), 122.1 (Ar*C*), 123.1 (Ar*C*), 123.4 (Ar*C*), 125.2 (Ar*C*), 125.4 (Ar*C*), 126.5 (Ar*C*), 126.5 (Ar*C*), 127.4 (Ar*C*), 127.5 (Ar*C*), 137.6 (Ar*C*), 137.9 (Ar*C*), 138.8 (Ar*C*), 138.9 (Ar*C*), 139.2 (Ar*C*), 139.5 (Ar*C*), 148.6 (Ar*C*), 148.6 (Ar*C*), 148.7 (quat), 149.0 (quat), 150.0 (quat), 150.1 (quat), 151.2 (quat), 151.4 (quat), 152.8 (quat), 153.2 (quat), 153.5 (quat), 153.8 (quat) 156.6 (quat), 156.8 (quat), 164.6 (quat), 164.8 (quat), 165.1 (quat), 165.7 (quat). *m*/*z* (CI) 485.1490 (M^{2+}); $[C_{52}H_{52}N_{12}Cu_2]^{2+}$ requires 485.1509.

$AgBF_4$ complex of $CyMe_4$-hemi-BTBP 2

The ligand **2** (0.0349 g, 0.08265 mmol) was dissolved in DCM (5 mL). To this solution was added a solution of $[Ag(MeCN)_4]$-BF_4 (0.0297 g, 1 eq.) in CH_3CN (4 mL). The two solutions were mixed and the solvents were allowed to evaporate over several days to afford the complex as a light brown solid (0.0488 g, 95%). Mp > 300 °C (from DCM/MeCN). Found: C, 50.32; H, 4.17; N, 13.25; F, 11.96%; $C_{26}H_{26}N_6BF_4Ag$ requires C, 50.60; H, 4.25; N, 13.61; F, 12.31%. ν_{max}(Nujol®)/cm^{-1} 3092, 2971, 2934, 2872, 1630, 1592, 1574, 1523, 1457, 1445, 1427, 1389, 1246, 1167, 1052, 1000, 922, 847, 816, 784, 747, 680, 639, 539. δ_H(400.1 MHz; CD_3CN) 1.21 (6H, s, 2 × Me), 1.50 (6H, s, 2 × Me), 1.84–1.87 (2H, m, CH_2), 1.89–1.92 (2H, m, CH_2), 7.28 (1H, ddd, *J* 7.9, 5.0 and 1.1, Ar*H*), 7.83–7.85 (2H, m, 2 × Ar*H*), 7.94 (1H, td, *J* 7.8 and 1.8, Ar*H*), 8.09 (1H, d, *J* 4.2, Ar*H*), 8.11 (1H, d, *J* 3.5, Ar*H*), 8.15–8.22 (3H, m, 3 × Ar*H*), 8.52 (1H, dd, *J* 7.2 and 1.5, Ar*H*). δ_C(100.6 MHz; CD_3CN) 28.2 (2 × Me), 28.6 (2 × Me), 31.8 (*C*H_2), 32.4 (*C*H_2), 36.1 (quat), 37.3 (quat), 122.9 (Ar*C*), 123.3 (Ar*C*), 124.3 (Ar*C*), 125.5 (Ar*C*), 125.9 (Ar*C*), 127.5 (Ar*C*), 138.9 (Ar*C*), 140.1 (Ar*C*), 140.4 (Ar*C*), 149.0 (quat), 150.2 (Ar*C*), 150.3 (quat), 151.8 (quat), 154.6 (quat), 154.9 (quat), 156.1 (quat), 164.8 (quat), 166.8 (quat). *m*/*z* (CI) 529.1274 (M^+); $[C_{26}H_{26}N_6Ag]^+$ requires 529.1264.

X-Ray crystallography

For the structure of **2** and its uranyl complex, data were collected with Mo Kα radiation at 100 K using the Oxford Diffraction X-Calibur CCD System (Oxford Diffraction XCalibur2 diffractometer equipped with an Oxford Cryosystems low temperature device). The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. For the structure of **2**, data analysis was carried out with the CrysAlis program.[41] The structure was solved using direct methods with the Shelxs97 program.[42] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using Shelxl97.[42] For the uranyl structure, data were corrected for Lorenz and polarization factors and absorption corrections applied to all data. Using Olex2,[43] the structure was solved with the XS structure solution program using direct methods and refined with the XL refinement package using least squares minimisation.[42] For the Eu and Ce structures, data were collected with Cu Kα radiation at 100 K using a Bruker APEX2 diffractometer using φ and ω scans.[44] The crystals were maintained at 100 K during data collection. Bruker APEX2 was used to guide the diffractometer to collect a full set of diffraction images and perform unit cell determination. Data reductions were carried out by SAINT PLUS and multiscan absorption corrections were performed using SADABS.[45] The structures were solved using SUPERFLIP.[46] Using Olex2,[43] the structures were refined with the XL refinement package using least squares minimisation.[42] Crystal Data have been deposited at the Cambridge Crystallographic Data Centre as CCDC 869233–869236.‡

Solvent extraction studies

The aqueous solutions were prepared by spiking nitric acid solutions (0.001–4 mol dm^{-3}) with stock solutions of ^{241}Am and ^{152}Eu tracers (10 μL) in nitric acid. The radiotracers ^{241}Am and ^{152}Eu were supplied by Isotopendienst M. Blaseg GmbH, Waldburg (Germany). Solutions of $CyMe_4$-hemi-BTBP **2** (0.01 mol dm^{-3}) were prepared by dissolving **2** in *n*-octanol, with or without added 2-bromohexanoic acid. Each organic phase (500 μL) was shaken separately with each of the aqueous phases (500 μL) for one hour at 22 °C using an IKA Vibrax Orbital Shaker Model VXR (2200 rpm). The contact time of one hour was sufficient to attain distribution equilibrium. After phase separation by centrifugation, 200 μL aliquots of each phase were withdrawn for radio analysis. Activity measurements of the γ-ray emitters ^{241}Am and ^{152}Eu were performed with a HPGe γ-ray spectrometer, EG-G Ortec. The γ-lines at 59.5 keV, and 121.8 keV were examined for ^{241}Am, and ^{152}Eu, respectively. The acidities of the initial and final aqueous solutions were determined by potentiometric titration against sodium hydroxide solution (0.1 mol dm^{-3}) using a Metrohm 751 GPD Titrino device. The distribution ratio *D* was measured as the ratio between the radioactivity in the organic and the aqueous phase. Distribution ratios

‡Crystal data for **2**: $C_{26}H_{26}N_6$, *M* = 422.53, triclinic, spacegroup $P\bar{1}$, *Z* = 2, *a* = 8.5515(11), *b* = 8.5740(11), *c* = 16.214(2) Å, α = 81.677(11), β = 85.060(11), γ = 66.015(12)°, *T* = 100(2) K, *U* = 1074.2(2) Å^3, D_c = 1.306 g cm^{-3}, μ = 0.081 mm^{-1}, 5965 independent reflections, 2754 data ($I > 2\sigma(I)$), R_1 = 0.0539, wR_2 (all data) = 0.1063, CCDC 869235. Crystal data for $[Eu(\mathbf{2})(NO_3)_3]\cdot 2MeCN$: $C_{30}H_{32}EuN_9O_9$, *M* = 842.63, monoclinic, space group $P2_1/c$, *Z* = 4, *a* = 12.8212(3), *b* = 14.9805(4)(8), *c* = 18.2654(5) Å, β = 102.155(2)°, *T* = 100.15 K, *U* = 3429.6(2) Å^3, D_c = 1.632 g cm^{-3}, μ = 13.688 mm^{-1}, 54 007 independent reflections, 5561 data ($I > 2\sigma(I)$), R_1 = 0.0458, wR_2 (all data) = 0.1417, CCDC 869234. Crystal data for $[Ce(\mathbf{2})(NO_3)_3]\cdot$toluene: $C_{33}H_{34}CeN_9O_9$, *M* = 840.81, monoclinic, space group $P2_1/n$, *Z* = 4, *a* = 15.4789(8), *b* = 15.3507(8), *c* = 16.4216(8) Å, β = 112.897(3)°, *T* = 100.15 K, *U* = 3594.5(3) Å^3, D_c = 1.554 g cm^{-3}, μ = 13.052 mm^{-1}, 37 812 independent reflections, 4468 data ($I > 2\sigma(I)$), R_1 = 0.0690, wR_2 (all data) = 0.1827, CCDC 869233. Crystal data for $2[UO_2(\mathbf{2})MeOH][UO_2(NO_3)_4]$: $U_3C_{54}H_{60}N_{16}O_{20}$, *M* = 1966.7, triclinic, space group = $P\bar{1}$, *Z* = 1, *a* = 11.1976(8), *b* = 11.5470(8), *c* = 13.3767(10)Å, α = 113.4860(10), β = 99.1500(10), γ = 94.8080(19)°, *T* = 100(2) K, *U* = 1545.29(19) Å^3, D_c = 2.113 g cm^{-3}, μ = 7.929 mm^{-1}, 12 300 independent reflections, 6198 data ($I > 2\sigma(I)$), R_1 = 0.0501, wR_2 (all data) = 0.0903, CCDC 869236.

between 0.1 and 100 exhibit a maximum error of ±5%. The error may be up to ±20% for smaller and larger values.

Complexation studies

The apparent stability constants β, equal to the molar ratio $[M_xL_y^{xn+}]/[M^{n+}]^x[L]^y$ (M^{n+} = cation, L = ligand), were determined by UV absorption spectrophotometry at 25.0 ± 0.1 °C in methanol at a constant ionic strength provided by 10^{-2} M Et_4NNO_3. The experimental procedure was previously described in detail.[26] The spectral changes of 2 mL solutions of ligand **2** upon stepwise additions (50 μL) of metal nitrate solution directly into the measurement cell were recorded from 250 to 370 nm with a Cary 3 (Varian) spectrophotometer. The ligand concentration was in the range 10^{-5}–10^{-4} M. The data thus obtained were treated with the program Specfit.[47]

NMR titrations

Stock solutions (0.01 M) of the ligand **2** and of the metal salts $La(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}5H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $Yb(NO_3)_3{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, $[Cu(MeCN)_4]BF_4$ and $[Ag\text{-}(MeCN)_4]BF_4$ (Aldrich) were prepared in CD_3CN. A 0.5 mL aliquot of the ligand solution **2** was placed in an NMR tube and the ^{1}H NMR spectrum was recorded. The appropriate metal salt solution was added to the NMR tube in 50 μL aliquots (*i.e.*, 0.1 equivalents each time) using a calibrated Eppendorf 100 μL micropipette, the tube was inverted several times to ensure complete mixing and the ^{1}H NMR spectrum was recorded after each successive addition until the resonances of the free ligand had completely disappeared and/or until no further spectroscopic changes were observed. The relative ratios of the different species present were calculated from the relative integrals of a suitable one-proton resonance of **2**. These values were normalized such that, for a given one-proton resonance, the total integration for all species present equalled one. The species distribution at different metal : ligand ratios was calculated from these normalized relative ratios.

Acknowledgements

We thank the Nuclear Fission Safety Program of the European Union for support under the ACSEPT (FP7-CP-2007-211 267) contract, the RCUK Energy Programme through its support of the MBase consortium and EPSRC for funding a Nuclear FiRST DTC studentship (DW). We also thank the EPSRC and the University of Reading for funds for the X-Calibur system. Use of the Chemical Analysis Facility at the University of Reading is gratefully acknowledged.

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