Complexes formed between the quadridentate, heterocyclic molecules 6,6′-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridine (BTBP) and lanthanides(III): implications for the partitioning of actinides(III) and lanthanides(III)

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New hydrophobic, tetradentate nitrogen heterocyclic reagents, 6,6′-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridines (BTBPs) have been synthesised. These reagents form complexes with lanthanides and crystal structures with 11 different lanthanides have been determined. The majority of the structures show the lanthanide to be 10-coordinate with stoichiometry $[Ln(BTBP)(NO_3)_3]$ although Yb and Lu are 9-coordinate in complexes with stoichiometry $[Ln(BTBP)(NO_3)_2(H_2O)](NO_3)$. In these complexes the BTBP ligands are tetradentate and planar with donor nitrogens mutually *cis i.e.* in the *cis*, *cis*, *cis* conformation. Crystal structures of two free molecules, namely C2-BTBP and CyMe$_4$-BTBP have also been determined and show different conformations described as *cis*, *trans*, *cis* and *trans*, *trans*, *trans* respectively. A NMR titration between lanthanum nitrate and C5-BTBP showed that two different complexes are to be found in solution, namely $[La(C5\text{-}BTBP)_2]^{3+}$ and $[La(C5\text{-}BTBP)(NO_3)_3]$. The BTBPs dissolved in octanol were able to extract Am(III) and Eu(III) from 1 M nitric acid with large separation factors.

Introduction

There have been few studies of lanthanide- or actinide-(III) separation using tetradentate heterocyclic molecules as the extractants.[1,2] It has been shown by treatment of tetradentate ligands such as *N*,*N*′-bis(1-(pyridin-2-yl)ethylidene)ethane-1,2-diamine and *N*,*N*′-bis(1-(pyridin-2-yl)ethylidene)propane-1,3-diamine with nitrates of the lanthanides that neutral trinitrate metal complexes can be formed.[3] Since it was shown that tetradentate molecules are able to bind to and extract europium,[1] a more detailed study of the actinide and lanthanide chemistry of the tetradentate 6,6′-bis-1,2,4-triazin-3-yl-2,2′-bipyridines (BTBPs) was undertaken. The 5f (and 6d) atomic orbitals of the actinides are more able to interact with the molecular orbitals of potential ligands than the 4f orbitals of the lanthanides. Hence the actinides can form more stable complexes with molecules such as terpyridines and the 2,6-bis-1,2,4-triazin-3-yl-pyridines (BTPs) than can lanthanides.[4] It is likely that the smaller steric demands of the 1,2,4-triazin-3-yl ring by comparison with the 2-pyridinyl ring, which allows the nitrogen atoms to approach more closely to the metal atom, contributes to the greater ability of the BTP ligands to adopt the geometry required for metal binding. Currently, owing to their ease of synthesis and favourable metal extraction chemistry, the BTP ligands are the bench-mark reagents for the selective americium(III) extraction from nitric acid. It seems likely that the efficiency of the BTP ligands in this regard is also due to the formation of a single species, the cationic nine-coordinate lanthanide complex of the formula $[Ln(BTP)_3]^{3+}$,[5] in which the metal is completely enclosed by the organic ligands to the exclusion of both nitrate anions and water molecules. It was, therefore, decided to further investigate the structures of the complexes formed by the BTBP ligands with lanthanide(III) nitrates. The parent structures of the BTP and BTBP molecules studied are depicted in Fig 1. In order to permit solution state studies of the BTBP ligands in a wide range of organic solvents, new soluble derivatives (C4-BTBP and C5-BTBP) bearing n-alkyl groups have been prepared. Since it has been shown that nitrogen oxides and oxoacids are able to oxidize alkylarenes through abstraction of benzylic hydrogens,[6] a BTBP (CyMe$_4$-BTBP) bearing no benzylic hydrogens was also prepared.

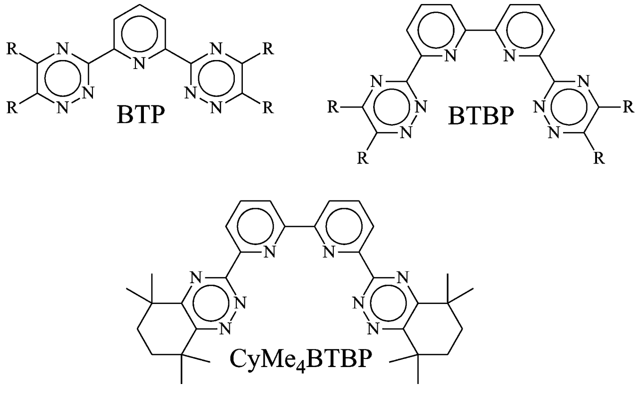

Fig. 1 The structures of tetrasubstituted BTP and BTBP molecules.

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Experimental

Radiochemical experiments were performed at the CEA (France) as previously described.[7,8] The nitric acid stability test was performed at the CEA by shaking solutions of the extractants (0.01 M) and *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexyloxy-ethyl)-malonamide (0.25 M, DMDOHEMA) in octanol nitric acid (1 M) at 25 °C for two h. Then the mixture was allowed to stand for 1 h and then the procedure was repeated. ^{1}H, ^{13}C–{^{1}H} and ^{13}C NMR spectra were recorded using either a Bruker AMX400 or an Avance DPX250 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane. All organic reagents were purchased from Acros or Aldrich, while inorganic reagents were obtained from either BDH or Aldrich. Dodecane-6,7-dione was obtained by the sequential reaction of ethyl hexanoate with sodium/trimethylchlorosilane, aqueous hydrochloric acid and copper(II) acetate. 3,3,6,6-Tetramethyl-cyclohexane-1,2-dione was obtained by the bromine oxidation of 3,3,6,6-tetramethyl-1,2-bis-(trimethylsilanyloxy)-cyclohexene.[9] The 6,6′-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridines (BTBPs) were obtained from the sequential reaction of 6,6′-dicyano-2,2′-bipyridine[10] with hydrazine[11] and then with a 1,2-diketone. The overall procedure by which the BTBPs were prepared is shown in Fig. 2. On cooling solutions of the tetraethyl (C2-BTBP) and CyMe$_4$-BTBP derivatives in THF, crystals were obtained.

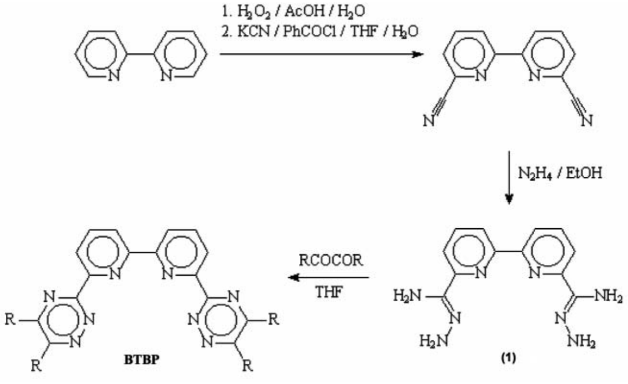

Fig. 2 Overall scheme for the synthesis of the BTBP ligands.

A typical procedure for the synthesis of a BTBP, C2-BTBP

Powdered 2,2′-bipyridine-6,6′-dicarboxbisamidrazone (1.85 g) (**1**) was added to a stirred solution of hexane-3,4-dione (11.5 mL) in tetrahydrofuran (500 mL), and the resulting mixture was heated over 45 min to the boiling point. After boiling under reflux (150 min), the mixture was allowed to cool. If the mixture was cloudy, it was filtered through Celite® before all volatile matter was removed under vacuum. To the residue was added ethanol (40 mL), and the resulting mixture was boiled briefly before being allowed to cool. The solid product (1.96 g, 67%) was then collected by filtration, washed with ethanol and then diethyl ether, and was then dried in air. Found: C, 67.1; H, 6.1; N, 26.1%; $C_{24}H_{26}N_8$ requires C, 67.6; H, 6.1; N, 26.3%. δ_H 8.85 (2H, dd, 7.9 and 0.9 Hz), 8.54 (2H, dd, 7.8 and 0.9 Hz), 7.99 (2H, dd, 7.9 and 7.8 Hz), 3.05 (4H, q, 7.5 Hz), 2.96 (4H, q, 7.4 Hz), 1.40 (12H, m) ppm. δ_C 162.77 (quat), 161.77 (quat), 160.61 (quat), 156.53 (quat), 153.10 (quat), 138.38, 124.47, 123.47, 27.51 (CH$_2$), 26.12 (CH$_2$), 12.71 and 11.60 ppm. MS(CI+) MH + 427, 317 and 207 *m*/*z*. Molecular ion found at 427.2349 ($^{12}C_{24}{}^1H_{27}{}^{14}N_8$ requires 427.2358, error of 2.2 ppm).

Synthesis of C4-BTBP

2,2′-Bipyridine-6,6′-dicarboxbisamidrazone (**1**) (810 mg) was reacted with of decane-5,6-dione (1.97 g) in tetrahydrofuran (175 mL) as described above so furnishing C4-BTBP (811 mg, 50%) after recrystallisation from hot ethanol. Found: C, 71.1; H, 7.8; N, 20.7%; $C_{24}H_{26}N_8$ requires C, 71.3; H, 7.9; N, 20.8%. δ_H 8.85 (2H, d, 7.1 Hz), 8.52 (2H, d, 7.8 Hz), 7.96 (2H, t, 7.9 Hz), 3.01 (4H, t, 7.7 Hz), 2.88 (4H, t, 7.7 Hz), 1.80 (8H, m), 1.45 (8H, m), 0.95 (12 H) ppm. δ_C 162.20 (quat), 161.62 (quat), 160.13 (quat), 156.53 (quat), 153.10 (quat), 138.37, 124.45, 123.47, 34.05 (CH$_2$), 32.51 (CH$_2$), 30.86 (CH$_2$), 29.96 (CH$_2$), 23.08 (CH$_2$), 22.99 (CH$_2$), 14.36 and 14.29 ppm.

Synthesis of C5-BTBP

2,2′-Bipyridine-6,6′-dicarboxbisamidrazone (**1**) (10.50 g) was reacted with dodecane-6,7-dione (23.69 g) in tetrahydrofuran (500 mL) as described above to furnish after a recrystallisation from ethanol C5-BTBP (14.62 g, 63%). Found: C, 72.6; H, 8.6; N, 19.0%; $C_{24}H_{26}N_8$ requires C, 72.7; H, 8.5; N, 18.8%. δ_H 8.94 (2H, dd, 7.9 and 1.0 Hz), 8.61 (2H, dd, 7.8 and 1.0 Hz), 8.07 (2H, t, 7.9 Hz), 3.09 (4H, t, 7.7 Hz), 2.96 (4H, t, 7.7 Hz), 1.90 (4H, m), 1.50 (8H, m), 0.98 (6H, m) ppm. δ_C 162.19 (quat), 161.63 (quat), 160.13 (quat), 156.53 (quat), 153.12 (quat), 138.35, 124.45, 123.44, 34.29 (CH$_2$), 32.78 (CH$_2$), 32.10 (CH$_2$), 32.02 (CH$_2$), 28.47 (CH$_2$), 27.55 (CH$_2$), 22.93 (CH$_2$), 22.88 (CH$_2$), 14.39 and 14.37 ppm.

Synthesis of C6-BTBP

2,2′-Bipyridine-6,6′-dicarboxbisamidrazone (0.844 g) (**1**) was reacted with tetradecane-7,8-dione (2.44 g) in a mixture of tetrahydrofuran (175 mL) and triethyl amine (2.5 mL) as described above to furnish C6-BTBP (0.689 g. 34%) (after titruration with diethyl ether rather than recrystallisation from ethanol). Found: C, 73.8; H, 9.0; N, 17.2%; $C_{24}H_{26}N_8$ requires C, 73.8; H, 9.0; N, 17.2%. δ_H 8.92 (2H, dd, 7.9 and 1.0 Hz), 8.61 (2H, dd, 7.8 and 1.0 Hz), 8.07 (2H, t, 7.9 Hz), 3.08 (4H, t, 7.7 Hz), 2.96 (4H, t, 7.7 Hz), 1.9 (4H, m), 1.4 (12 H, m), 0.93 (6H, m) ppm. δ_C 162.2 (quat), 161.6 (quat), 160.2 (quat), 156.5 (quat), 153.1 (quat), 138.4, 124.5, 123.5, 34.3 (CH$_2$), 32.8 (CH$_2$), 32.0 (CH$_2$), 32.0 (CH$_2$), 29.6 (CH$_2$), 29.6 (CH$_2$), 28.8 (CH$_2$), 27.8 (CH$_2$), 23.0, 14.5 ppm.

Synthesis of CyMe$_4$-BTBP

2,2′-Bipyridine-6,6′-dicarboxbisamidrazone (**1**) (2.01 g) was reacted with 3,3,6,6-tetramethyl-cyclohexane-1,2-dione (4.60 g) in a mixture of tetrahydrofuran (250 mL) and triethylamine (7.5 mL) as described above. The residue from the evaporation of the filtered reaction mixture (heavy oil) was triturated with petroleum ether (10 mL, bp 60–80 °C) before the crude solid (4.2 g) was collected by filtration. This solid was treated with ethanol (75 mL), the resulting mixture was briefly boiled before being allowed to cool. Subsequently the solid was collected by filtration. After washing twice with cold ethanol and three times with cold diethyl ether the canary yellow solid (2.40 g. 60%) was dried in air. Found: C, 71.5; H, 7.2; N, 20.7%; $C_{24}H_{26}N_8$ requires C, 71.9; H, 7.2; N, 21.0%. Mp 261–262 °C. δ_H 8.96 (2H, dd, 7.9 and 1.0 Hz), 8.55 (2H, dd, 7.8

and 1.0 Hz), 8.02 (2H, t, 7.9 Hz), 1.90 (8H, s), 1.53 (12H, s) and 1.48 (12H, s) ppm. δ_C 164.78 (quat), 163.42 (quat), 161.33 (quat), 156.47 (quat), 153.19 (quat), 138.27, 124.31, 123.28, 37.67 (quat), 36.90 (quat), 34.17 (CH_2), 33.71 (CH_2), 30.17 (CH_3) and 29.67 (CH_3) ppm.

Synthesis of lanthanide complexes of C2-BTBP

To a solution of C2-BTBP (60 mg) in dichloromethane (10 mL) was added a slight excess of the lanthanide nitrate dissolved in acetonitrile (10 mL). This mixture was allowed to stand for several days; if no solid had formed then the solution was allowed to slowly evaporate until crystals formed. The crystals were collected by filtration in a Hirsch funnel, washed with acetonitrile and dried in air (Table 1).

Crystallography

X-Ray diffraction data for the two ligands C2-BTBP and CyMe$_4$-BTBP and eight metal complexes of C2-BTBP (L) were collected with Mo-Kα radiation using the MAR research Image Plate System. Details are provided for all compounds in Table 2. The crystals were positioned 70 mm from the image plate. 100 frames were measured at 2° intervals with a counting time of 2 min or more where appropriate. Data analysis was carried out with the XDS program.[12] Structures of the ligands were solved using direct methods and for the metal complexes with the Patterson method using the Shelx86 program.[13] 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. In most structures the hydrogen atoms bonded to oxygen in water molecules could not be located. Empirical absorption corrections were carried out on all lanthanide structures using the DIFABS program.[14] The two structures involving Ce and Pr metals gave high residual electron density close to the metal position. Structures with La, Ce, Pr, Nd, Sm and Eu form an isomorphous series with the metal atom on a twofold axis. Structures with Dy, Ho, Er and Y complexes also form an isomorphous series but with the metal complex in a general position. The Yb and Lu complexes are also isomorphous. Structures were refined on F^2 until convergence using Shelxl.[15]

CCDC reference numbers 255384 and 280519–280531.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511321k

Computational chemistry

Density functional calculations were performed using the ADF program.[16] Slater-type orbital basis sets of triple zeta quality for the valence orbitals were employed with polarisation functions on the ligand atoms (2p for H, and 3d for C and N) and additional valence p orbitals on the metal atom. Scalar relativistic effects were included *via* the Zora protocol. The generalized gradient approximation was used with Becke88 exchange and Perdew86 correlation gradient corrections. The COSMO method[17] which provides a conductor-like screening method was used for solvent calculations. COSMO is a dielectric model in which the solute molecule is embedded in a molecular-shaped cavity surrounded by a dielectric medium with a given dielectric constant.

Results and discussion

NMR Titrations

Titrations of lanthanum nitrate with C5-BTBP were undertaken in order to provide an insight into the solution state coordination chemistry of the early lanthanides with C5-BTBP ligands. Owing to the low solubility of C5-BTBP in acetonitrile, the titration was performed in a 38 : 62 mixture of deuterated chloroform and acetonitrile. It was found that ligand exchange was relatively slow on the NMR time-scale, so the same methodology was employed as was used for the yttrium nitrate/dimethyl-*hemi*-BTP system.[8] The known concentrations of lanthanum and C5-BTBP allow calculation of the metal to C5-BTBP ratio ($[La]^{total}/[C5\text{-}BTBP]^{total}$). The integration heights of all peaks that were due to the pyridine proton environments of C5-BTBP and its lanthanum complexes were measured. The proton environments were assigned to either the free ligand, or one of two metal-containing species. The relative concentrations of each species were calculated using eqn (1)

$$\text{relative concentration} = \sum\text{integration for a given species}/\sum\text{integration for all species} \qquad (1)$$

Table 1 Details of the yttrium and lanthanide complexes of C2-BTBP (L)

				Found (%)			Theory (%)		
Metal	Formula	Yield (%)	Colour	C	H	N	C	H	N
Y	$[Y(NO_3)_3(L)]\cdot 1.5H_2O$	61	White	39.4	3.6	21.3	39.6	4.0	21.2
La	$[La(NO_3)_3(L)]\cdot 0.5MeCN$	88	White	39.1	3.6	20.9	38.9	3.6	20.9
Ce	$[Ce(NO_3)_3(L)]\cdot MeCN$	32	Orange	39.3	3.6	21.0	39.4	3.7	21.2
Pr	$[Pr(NO_3)_3(L)]\cdot MeCN$	41	Green	39.1	3.7	20.9	39.3	3.7	21.2
Nd	$[Nd(NO_3)_3(L)]\cdot MeCN$	40	White	39.1	3.7	20.9	39.2	3.6	21.1
Sm	$[Sm(NO_3)_3(L)]\cdot 0.3MeCN$	66	White	38.3	3.5	20.4	38.1	3.5	20.4
Eu	$[Eu(NO_3)_3(L)]\cdot 0.25MeCN$	67	White	38.2	3.5	20.3	38.0	3.5	20.3
Gd	$[Gd(NO_3)_3(L)]\cdot 0.5MeCN$	65	White	38.0	3.5	20.3	38.0	3.5	20.4
Tb	$[Tb(NO_3)_3(L)]\cdot 0.5MeCN$	49	White	38.0	3.5	20.3	39.9	3.5	20.3
Dy	$[Dy(NO_3)_3(L)]$	74	White	37.0	3.4	19.6	37.2	3.4	19.9
Ho	$[Ho(NO_3)_3(L)]$	51	White	37.1	3.4	19.8	37.1	3.4	19.8
Er	$[Er(NO_3)_3(L)]$	74	Orange	37.1	3.6	19.8	37.0	3.4	19.8
Tm	$[Tm(NO_3)_3(L)]$	52	Orange	36.9	3.6	19.7	36.9	3.4	19.7
Yb	$[Yb(NO_3)_3(L)]\cdot 2H_2O$	55	Yellow	35.2	3.6	18.6	35.1	3.7	18.8
Lu	$[Lu(NO_3)_3(L)]\cdot 2H_2O$	49	White	35.2	3.6	18.7	35.0	3.6	18.7

Table 2 Details of the crystal structures (L = C2-BTBP)

Structure	C2-BTBP	CyMe4BTBP·0.5CH_3OH	La(NO_3)L]·H_2O	[Ce(NO_3)L]·H_2O	[Pr(NO_3)L]·1.5H_2O	[Nd(NO_3)L]·H_2O	[Sm(NO_3)L]]·H_2O
Empirical formula	$C_{24}H_{26}N_8$	$C_{32.5}H_{40}N_8O_{0.5}$	$C_{24}H_{28}LaN_{11}O_{10}$	$C_{24}H_{28}CeN_{11}O_{10}$	$C_{24}H_{29}PrN_{11}O_{10.5}$	$C_{24}H_{28}N_{11}NdO_{10}$	$C_{24}H_{28}SmN_{11}O_{10}$
Formula weight	426.53	550.73	769.48	770.69	780.49	774.82	780.92
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2/c$	Monoclinic, $P2/c$	Monoclinic, $P2/c$	Monoclinic, $P2/c$	Monoclinic, $P2/c$
a/Å	7.881(9)	12.156(14)	8.853(9)	8.859(9)	8.809(9)	8.826(9)	8.820(9)
b/Å	8.831(9)	15.004(17)	12.008(14)	11.992(13)	11.928(13)	11.906(12)	11.867(12)
c/Å	8.889(9)	19.420(22)	15.904(17)	15.897(13)	15.846(18)	15.829(17)	15.842(17)
α/°	67.87(1)	(90)	(90)	(90)	(90)	(90)	(90)
β/°	83.94(1)	90.13(1)	99.88(1)	99.83(10)	99.98(1)	99.98(1)	99.74(1)
γ/°	90.19(1)	(90)	(90)	(90)	(90)	(90)	(90)
Volume/Å^3	592	3542	1666	1664	1640	1638	1646
Z, calculated density/Mg m^{-3}	1, 1.244	4, 1.033	2, 1.538	2, 1.566	2, 1.581	2, 1.571	2, 1.591
Absorption coefficient/mm^{-1}	0.079	0.065	1.349	1.434	1.555	1.652	1.869
Reflections collected/unique	2008	5542	2946	3201	2902	2765	3099
Data/restraints/parameters	2008/0/147	5542/0/390	2946/0/217	3811/36/213	2902/0/213	2765/0/212	3099/0/212
Final R indices [$I > 2\sigma(I)$]: $R1$, $wR2$	0.0798, 0.1669	0.1299, 0.3659	0.1063, 0.2186	0.1202, 0.3036	0.0363,0.0928	0.0357, 0.0956	0.0326, 0.0963
R indices (all data)	0.1721, 0.1921	0.1643, 0.3957	0.1462, 0.2517	0.1447, 0.3225	0.0381, 0.0938	0.0381, 0.0969	0.0353, 0.1080
Largest diff. peak and hole/e Å^{-3}	0.277, −0.255	0.370, −0.162	1.717, −3.810	9.701, −1.807	1.276, −1.445	2.585, −0.749	2.557, −0.639

Table 2 (*Contd.*)

Structure	[Eu(NO_3)$_3$L]·MeCN	[Dy(NO_3)$_3$L]·MeCN	[Ho(NO_3)$_3$L]·MeCN	[Er(NO_3)$_3$L]·MeCN	[Yb(NO_3)$_3$L(H_2O)]·H_2O	[Lu(NO_3)$_2$L(H_2O)](NO_3)(H_2O)	[Y(NO_3)$_3$L]·MeCN
Empirical formula	$C_{26}H_{29}EuN_{12}O_9$	$C_{26}H_{29}DyN_{12}O_9$	$C_{26}H_{29}HoN_{12}O_9$	$C_{26}H_{29}ErN_{12}O_9$	$C_{24}H_{28}N_{11}O_{11}Yb$	$C_{24}H_{28}N_{11}O_{11}Lu$	$C_{26}H_{29}N_{12}O_9Y$
Formula weight	805.57	816.12	816.54	820.88	819.61	821.54	742.52
Crystal system, space group	Monoclinic, $P2/c$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
a/Å	8.872(9)	9.988(12)	9.998(12)	10.054(14)	7.733(9)	7.736(9)	10.040(11)
b/Å	11.883(13)	10.147(14)	10.142(14)	10.202(14)	22.614(24)	22.660(24)	10.168(12)
c/Å	15.842(17)	16.915(8)	16.836(18)	16.868(18)	18.073(19)	18.083(19)	16.869(14)
α/°	(90)	92.49(1)	92.40(1)	92.50(1)	(90)	(90)	92.46(1)
β/°	99.74(1)	95.37(1)	95.25(1)	94.85(1)	92.10(1)	92.14(1)	95.23(1)
γ/°	(90)	106.59(1)	106.59(1)	106.75(1)	(90)	(90)	106.76(1)
Volume/Å^3	1646	1631	1625	1646	3158	3168	1638
Z, calculated density/Mg m^{-3}	2,1.625	2, 1.662	2, 1.673	2, 1.656	4, 1.720	4, 1.718	2, 1.506
Absorption coefficient/mm^{-1}	1.974	2.359	2.503	2.617	3.036	3.190	1.849
Reflections collected/unique	3096	5556	5711	5631	5704	5566	5348
Data/restraints/parameters	3096/0/209	5556/0/439	5711/0/439	5631/0/424	5704/0/438	5566/0/429	5348/0/438
Final R indices [$I > 2\sigma(I)$]: $R1$, $wR2$	0.0930, 0.2178	0.0611, 0.1436	0.0393, 0.1009	0.0755, 0.1988	0.0456, 0.0900	0.0592, 0.1179	0.1144, 0.2899
R indices (all data)	0.0980, 0.2245	0. 705, 0.1467	0.0418 0.1053	0.0812, 0.2021	0.0507, 0.0922	0.0709, 0.1213	0.1337, 0.3109
Largest diff. peak and hole/e Å^{-3}	8.909, −1.414	1.911, −1.826	2.165, −1.302	2.612, −3.008	1.380, −1.368	1.416, −1.726	1.641, −1.11

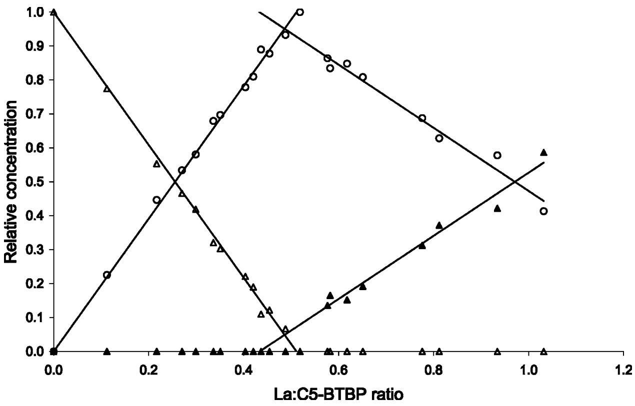

Fig. 3 Relative concentrations of the species containing C5-BTBP plotted against the C5-BTBP to lanthanum nitrate ratio. Key ▲ Free C5-BTBP, ○ $\{\mathrm{La}(\text{C5-BTBP})_2\}_n$ and ▲ $\{\mathrm{La}(\text{C5-BTBP})\}_n$.

and are plotted in Fig. 3.When less than 0.5 equivalent of lanthanum nitrate was present, the only species present were the free ligand and the metal complex A, which could be $[\mathrm{La}(\text{C5-BTBP})_2]^{3+}$, $[\mathrm{La}(\mathrm{H_2O})(\text{C5-BTBP})_2]^{3+}$ or $[\mathrm{La}(\mathrm{NO_3})(\text{C5-BTBP})_2]^{2+}$. It is impossible from the NMR experiment to distinguish between the three possible species all of which have a C5-BTBP to lanthanum ratio of 2 : 1. The slope of the line for $[\mathrm{A}]^{\mathrm{relative}}/([\mathrm{La}]^{\mathrm{total}}/[\text{C5-BTBP}]^{\mathrm{total}})$ when less than 0.5 equivalent of lanthanum nitrate is present is 1.96 ($r^2 = 0.997$) suggesting that under the conditions used, the measurement of the association constant for eqn (2)

$$\mathrm{La}^{3+} + x\mathrm{NO_3}^- + 2\ \text{C5-BTBP} \rightleftarrows [\mathrm{La}(\mathrm{NO_3})_x(\mathrm{H_2O})_n(\text{C5-BTBP})_2]^{(3-x)+} \qquad (2)$$

is impossible because of its large magnitude.When $[\mathrm{La}]^{\mathrm{total}}/[\text{C5-BTBP}]^{\mathrm{total}}$ was greater than 0.5, a new lanthanum-containing species which has a lanthanum to C5-BTBP ratio of 1 : 1 (metal complex B) was observed. The line for B has a slope of 0.93, suggesting that every additional atom of lanthanum converts one molecule of A into two molecules of B. It is clear that lanthanum complexes of C5-BTBP with two different stoichiometries can be obtained. When the experiment was repeated using yttrium nitrate, the results were identical suggesting that the later lanthanides are also able to combine with BTBP ligands to form complexes with similar ratios.

Crystal structures of the reagents

The structures of two of the reagents namely C2-BTBP and $\mathrm{CyMe_4}$-BTBP were determined by X-ray crystallography and are shown in Fig. 4 and 5. For C2-BTBP, the molecules pack in the *c* direction forming two-dimensional sheets. There exist weak hydrogen bonds between C(11)-H and N(1) (symmetry element $x, y, 1 + z$) with dimensions H···N 2.63 Å, C···N 3.53 Å and C···H–N 164°. In contrast, there are no such hydrogen bonds in $\mathrm{CyMe_4}$-BTBP and the ligands do not pack in sheets.

The solid state conformations of the two molecules are different. The conformation of the molecule can be described by the three torsion angles between aromatic rings, N(2)–C(3)–C(7)–N(8), N(8)–C(9)–C(29)–N(28) and N(22)–C(23)–C(27)–N(28) with *cis* (*c*) and *trans* (*t*) representing angles close to 0 and 180° respectively. Thus the conformation of C2-BTBP can be described as *ctc* with torsion angles of 0.9, 180.0, −0.9° and that of $\mathrm{CyMe_4}$-BTBP is

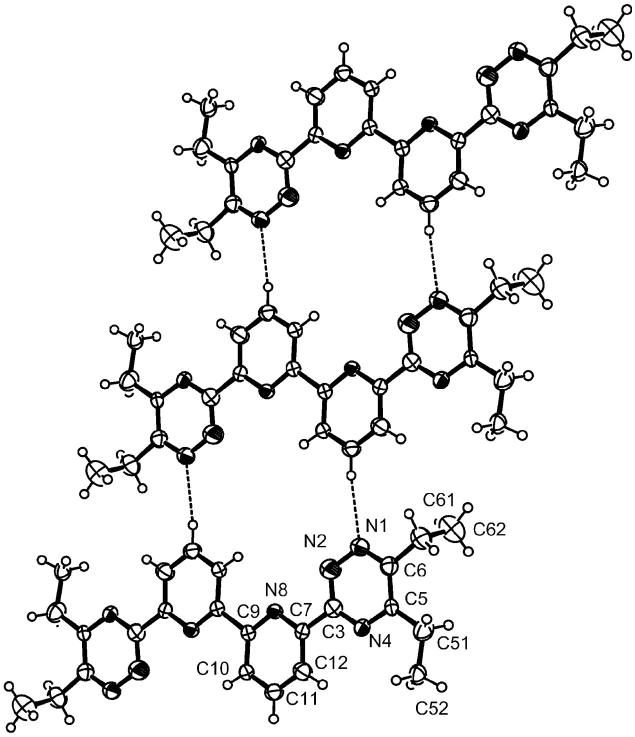

Fig. 4 The structure of C2-BTBP, which has the *ctc* conformation, with ellipsoids at 25% probability showing how the molecules pack in the *c* direction. Intermolecular hydrogen bonds are shown as dotted lines.

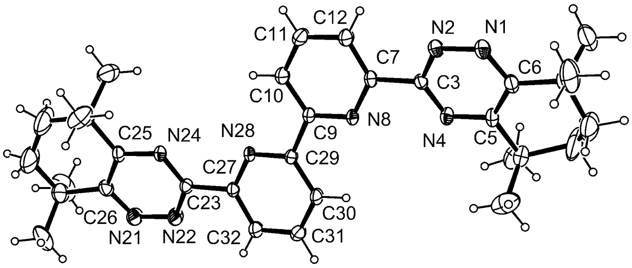

Fig. 5 The structure of $\mathrm{CyMe_4}$-BTBP, which has the *ttt* conformation, with ellipsoids at 25% probability.

ttt with torsion angles of −162.0, −178.2, 164.7°, thus the latter has shows a C_i rather than a C_2 distortion. This conformation found in C2-BTBP is unexpected as in previous structures of BTP ligands the equivalent N(2)–C(3)–C(7)–N(8) torsion angles are *trans* and not *cis* as is the case for $\mathrm{CyMe_4}$-BTBP. It seems likely that this particular conformation for C2-BTBP is stabilised by the hydrogen bond formation shown in Fig. 4.

Quantum mechanics calculations

Quantum mechanics calculations were carried out using C0-BTBP, the BTBP ligand with no substituent alkyl groups, at the TZP level with the ADF program.[14] The aim of these calculations was to evaluate the various possible conformations of the ligand both in the gas phase and in solution. The six possible conformations were considered and their geometry optimised energies are shown in Table 3. As expected in the gas phase the *ttt* conformation has the lowest energy. However, when solvent is included at various dielectric constants, calculations using the COSMO method[17]

Table 3 Relative energies (kJ mol^{-1}) of C0-BTBP in the six possible conformations in various dielectric constants calculated after geometry optimisation to convergence

	Dielectric constant			
Conformation	1.0	5.0	10.0	80.0
ccc	49.50	18.20	7.95	−0.47
ctc	2.57	−0.52	−0.86	−1.31
ctt	2.31	4.03	2.83	3.28
tcc	42.70	15.95	11.59	2.12
tct	39.97	13.48	6.85	1.15
ttt	0.00	0.00	0.00	0.00

show that the energy difference between the conformations becomes much smaller suggesting that electrostatic effects strongly influence their relative energies. Indeed at a dielectric constant of 80.0, the energies of the six conformations all fall within a range of 5 kJ mol^{-1}. It should be noted however that the organic layer in the separation process, consisting of hydrocarbons such as dodecane, has a dielectric constant of *ca.* 2.0, much less than the value in the aqueous layer that is *ca.* 80.

Considering first the gas phase energies, it can be seen that the conformations divide into two sets, those with a *trans* central torsion angle having a lower energy by *ca.* 40 kJ mol^{-1} than those with a *cis* angle. This result is consistent with the available experimental data. A search of the CCDC[18] shows that in compounds containing unchelating 2,2′-bipyridine, the two central rings have the *trans* conformation, the only exceptions being found when the *cis* conformation is stabilised by both nitrogens forming acceptor hydrogen bonds to a second species, for example a water molecule.

By comparison, the difference in energy between outer *cis* and *trans* conformations is an order of magnitude less at <4 kJ mol^{-1}. Even so it is somewhat of a surprise that the C2-BTBP molecule has the *ctc* conformation in the solid state. It has been found previously for all the BTP ligands[19] that the ligand adopts the *cc* conformation in order to bind to the metal indicating that the two outer rings rotate from the *tt* conformation established as the lowest energy conformation by quantum mechanics calculations and experimentally. Our calculations (see later) and experimental results confirm that BTBP will chelate to metals in the *ccc* conformation.

In the extraction process the dielectric constant of the aqueous solution will be high and, therefore, the energy differences between the conformations of the BTBPs will be quite low. Indeed, it is to be expected that there would be an equivalent population of *trans* and *cis* arrangements around the two outer bridgehead bonds. However, the preference for the central torsion angle between pyridine rings to be *trans* rather than *cis* is much higher and this conformation is likely to persist until metal complexation or protonation (see later).

The packing of the C2-BTBP molecules is shown in Fig. 6 and involves π-stacking of the planar molecules with interatomic distances of 3.4–3.6 Å. While two of the ethyl groups are within the approximate plane formed by the aromatic rings of the molecule, the other ethyl groups intrude into the holes that are present in another layer.

The Mulliken charges on the nitrogen atoms N(1), N(2), N(4), N(8) were for C0-BTBP −0.16, −0.18, −0.23, −0.28, for C2-BTBP −0.16, −0.21, −0.23, −0.28 and CyMe$_4$-BTBP −0.17, −0.20, −0.25, −0.28 respectively. The frontier orbitals for C0-BTBP, C2-BTBP and CyMe4-BTBP were calculated. For C0-BTBP, both frontier orbitals are degenerate and concentrated on one of the triazine rings, the HOMO being σ and the LUMO π*. A similar pattern is observed for C2-BTBP and CyMe$_4$-BTBP indicating that the electronic properties of the ligands are not affected significantly by substituents. The HOMO–LUMO energy gap for C0-BTBP is 2.283 eV, for C2-BTBP is 2.108 eV and for CyMe$_4$-BTBP is 2.130 eV.

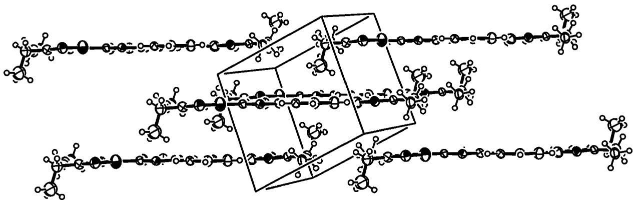

Fig. 6 The packing of the molecules of C2-BTBP in the unit cell.

These frontier orbitals are very similar to those found for C0-BTP which are also σ and π* and associated with the triazine rings. The HOMO–LUMO gap is somewhat smaller at 2.033 eV. One major difference between the BTBP and BTP ligands is the fact that in the former the energy required to change the conformation from the lowest energy form to that required for metal complexation is significantly greater. The energy difference between *cis*, *cis*, *cis* (*ccc*) and *trans*, *trans*, *trans* (*ttt*) forms in C0-BTBP is far greater at 49.50 kJ mol^{-1} than the energy difference between the *cc* and *tt* forms in C0-BTP which is only 1.02 kJ mol^{-1} because there are no H···H contacts in the latter. This means also that there is much less energy required to convert from the free conformation to that required for metal complexation which is calculated as 101.41 kJ mol^{-1} (rotating around 3 bonds) for C0-BTBP compared to 44.90 kJ mol^{-1} (rotating around 2 bonds) for C0-BTP although these energies would be reduced in the presence of solvent and by protonation (*vide supra*).

The separations of Am(III) from La(III) take place in acid media and therefore it is pertinent to consider the protonation properties of the BTBP ligands. Taking into account the symmetry of the molecule there are 4 protonation sites for the *ttt*, *ctc*, *ccc* and *tct* conformations, but 8 for the asymmetrical *tcc* and *ctt* conformations. The energies of the 32 unique mono-protonated structures were calculated for C0-BTBP. The numbering system is shown in Fig. 7. The conformation is described by the torsion angles N2–C3–C7–N8, N8–C9–C9′–N9′ and N8′–C7′–C3′–N2′ respectively.

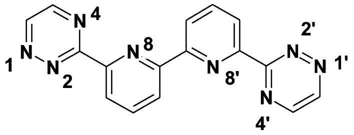

Fig. 7 The numbering system of the nitrogen atoms in C0-BTBP illustrated in the *ttt* conformation.

After protonation, the lowest energy structures are in order *tcc*-8 < *tcc*-8′ (relative energy 2.20 kJ mol^{-1}) < *ccc*-8 (2.52 kJ mol^{-1}) < *tct*-8 (5.74 kJ mol^{-1}) followed by *ctc*-8, *ctt*-8, *ctt*-8′, *ttt*-8, all in the range of 20–25 kJ mol^{-1} above the minimum. The next lowest energy configuration is *ctc*-1 at 97.31 kJ mol^{-1} above the minimum. Thus the four lowest energy conformations of similar energy all have a *cis* conformation at the central bridgehead and are protonated at N8 (or N8′) and therefore permit hydrogen bond interactions with either N4 or N2 and N8′ (or N8). It is interesting that the energy difference between the *cis* and *trans* arrangements around the central two rings which was calculated to be *ca*. 40 kJ mol^{-1}, is readily overcome by protonation. This change in conformation on protonation is also obtained for the BTPs[19,20] and produces the *cc* conformation required by metal complexation. It was argued previously that protonation might facilitate metal complexation by providing the impetus for conformational change. The same argument will also apply in this case to the BTBPs. However the protonation energy, defined as the difference between the energy of the free ligand and the protonated ligand both in their lowest energy conformation, required for the C0-BTBP ligand at 213.9 kJ mol^{-1} is comparable to that for C0-BTP at 201.8 kJ mol^{-1}.

The lowest energy conformations of protonated C0-BTBP were then studied in solvents with various dielectric constants and as expected the difference between the energies of the species is significantly reduced as the dielectric constant is increased. With a dielectric constant of 80.0, the four minimum energy configurations remain within 3.5 kJ mol^{-1} while the remaining three with N8 protonated are within 16 kJ mol^{-1} of the minimum. The most noticeable change is that the higher energy configurations have a much smaller energy difference, thus for example the *ctc*-1 configuration is now only 17.5 kJ mol^{-1} from the minimum rather than the 97.3 kJ mol^{-1} found in the gas phase.

However in the solvent extraction work no evidence of the protonation of BTBP extractants has been observed. It is thus clear that in the gas phase the rotation around the central dipyridine bridgehead bond is facilitated by protonation, while in condensed phases with high dielectric constants the difference in energy between the conformations becomes smaller so permitting the BTBP molecule to adopt the *ccc* conformation required for metal binding without recourse to protonation.

The steric effects of substituents on chelation

In order to establish whether the formation of metal complexes in which N2 was bound to the metal in the *ccc* conformation rather than N4 in the *tct* conformation was due to electronic or steric effects, calculations were carried out in the gas phase and in a solvent (water) for [M(BTBP)(NO$_3$)$_3$] using density functional theory *via* the ADF program with the results shown in Table 4. Starting models were based on the crystal structures reported here with imposed C_2 symmetry.

Table 4 Relative energies (kJ mol^{-1}) for various [M(BTBP)(NO$_3$)$_3$] structures after geometry optimisation (the energy of each *tct* complex is expressed relative to the *ccc* isomer)

Ligand					
Conformer		C0-BTBP		C2-BTBP	
Metal	Dielectric constant	*ccc*	*tct*	*ccc*	*tct*
La	1	0.00	−1.21	0.00	64.34
La	78.8	0.00	31.03	0.00	94.45
Lu	1	0.00	7.61	0.00	84.32
Lu	78.8	0.00	31.89	0.00	125.68

The calculations in the gas phase for C0-BTBP show that there is little difference in energy between the two conformations when bound to La or Lu. However, when the calculations were repeated for the C2-BTBP ligand then the *ccc* conformation was favoured in the gas phase by over 60 kJ mol^{-1}, which emphasises the importance of the steric effects of the ethyl groups which prevent complexation *via* N(4). In both cases adding solvent to the calculation increases the energy difference in favour of the *ccc* conformation by 20 to 30 kJ mol^{-1}.

Similar calculations were also carried out with bis-BTBP metal complexes and showed similar results—in particular that any change from the *ccc* conformation of the ligands led to steric clashes and higher energies although these changes were very low for C0-BTBP.

Crystal structures of the metal–BTBP complexes

It was found that the lanthanide series bar Yb and Lu formed two isostructural series with La, Ce, Nd, Sm, Eu forming one set with crystallographic C_2 symmetry and Gd,† Ho, Dy, Er the other with no imposed symmetry. In all of these solids a 1 : 1 metal to C2-BTBP ratio was observed, this contrasts with the observation of species with 1 : 2 metal to BTBP ratios in the NMR titration. It is possible that the 2 : 1 complexes have not been observed by crystallography simply because the 2 : 1 complexes do not form good quality crystals. It has been reasoned that the metal atoms within the 2 : 1 complexes are more completely enclosed by the BTBP molecules, so creating complexes which have lipophilic exteriors. In the first series there are two water molecules with 50% occupancy and in the second there is one acetonitrile molecule in the asymmetric unit. However in both series, the stoichiometry of the complex is [Ln(C2-BTBP)(NO$_3$)$_3$] with the metal in a 10-coordinate environment. The structures of [Nd(C2-BTBP)(NO$_3$)$_3$] and [Er(C2-BTBP)(NO$_3$)$_3$] are shown in Fig. 8 and 9 respectively and illustrate that there is little difference between the coordination spheres in the two compounds despite them not being isomorphous. Thus in all cases the ligand is approximately planar and one nitrate occupies the gap in this equatorial plane being

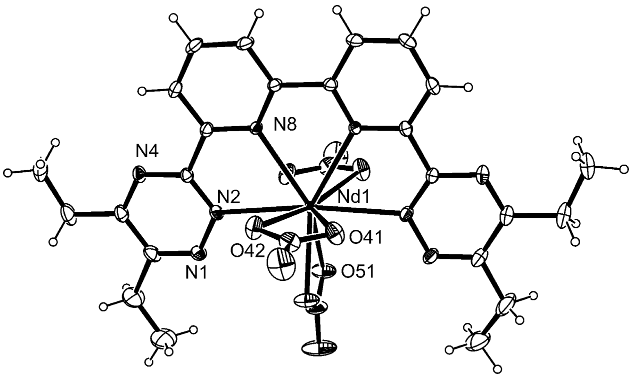

Fig. 8 The structure of [Nd(C2-BTBP)(NO$_3$)$_3$] with ellipsoids at 25% probability.

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† The Gd complex was isomorphous with Dy, Ho and Er complexes, thus triclinic, space group $P\bar{1}$ with cell dimensions $a = 9.972(12)$, $b = 10.121(12)$, $c = 17.063(19)$ Å, $\alpha = 92.58(1)$, $\beta = 95.77(1)$, $\gamma = 106.55(1)°$. While the intensity data were collected, they proved to be of insufficient quality for the structure to be reported here.

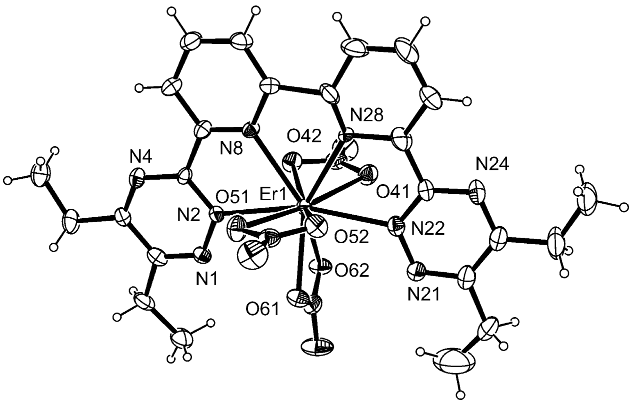

Fig. 9 The structure of [Er(C2-BTBP)$(NO_3)_3$] with ellipsoids at 25% probability.

perpendicular to this plane. The other two nitrates are respectively above and below the plane. Dimensions in the metal coordination sphere are compared in Tables 5 and 6.

The six structures of type 1 show the expected decrease in bond lengths when passing from La to Eu. In all cases, the bond lengths to the ligand are significantly greater than the bond lengths to the nitrates but this difference decreases along the series. The four structures of type 2 follow this pattern although it is noticeable that the changes in bond length from Dy to Yb are rather smaller than might be expected. This may be a consequence of the relatively rigidity of the tetradentate BTBP ligand. While ligands such as *N*,*N*′-bis(1-(pyridin-2-yl)ethylidene)ethane-1,2-diamine, which form complexes with similar stoichiometry,[20] have a flexible aliphatic section and so are able to change shape to suit the demands of the metal, the BTBP ligands are more rigid and, therefore, are less able to change shape to suit the metal. It is surprising that the overall coordination number of 10 (and indeed the stoichiometry) is identical along the series as more often than not the coordination number of La is greater than that of Yb. By contrast the Lu structure shown in Fig. 10 has the stoichiometry [Lu(C2-BTBP)$(NO_3)_2(H_2O)$] (NO_3), and is 9- rather than 10-coordinate, which reflects the fact that Lu is the smallest of the lanthanides.

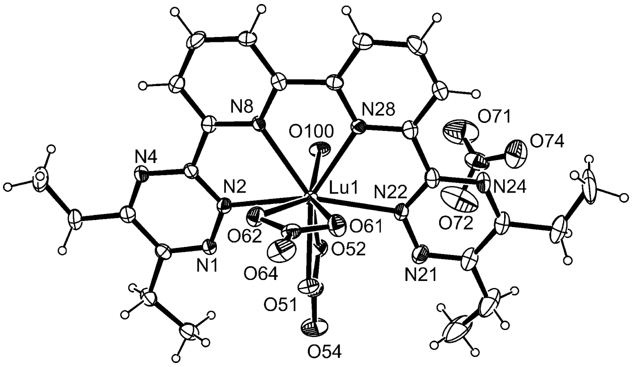

Fig. 10 The structure of the cation from the [Lu(C2-BTBP)$(NO_3)_2$-$(H_2O)]^+(NO_3)^-$ solid with ellipsoids at 25% probability. The hydrogen atoms bonded to the water molecule O(100) were not located and are not included.

It is noteworthy that these structures are, according to the CCDC, the first examples of lanthanides bonded to a tetradentate aromatic ligand though there are examples of tetradentate ligands

Table 5 Important dimensions (distance/Å, angles/°) for the complexes of the early lanthanides (La–Eu) with C2-BTBP

	Metal					
	La	Ce	Pr	Nd	Sm	Eu
M–O(41)	2.601(12)	2.570(15)	2.560(4)	2.547(4)	2.524(4)	2.543(9)
M–O(51)	2.604(13)	2.56(2)	2.542(4)	2.531(4)	2.501(4)	2.492(9)
M–O(42)	2.607(13)	2.584(14)	2.563(5)	2.555(5)	2.528(5)	2.542(10)
M–N(2)	2.704(13)	2.674(13)	2.650(4)	2.639(5)	2.617(4)	2.602(9)
M–N(8)	2.741(12)	2.699(13)	2.660(4)	2.635(4)	2.595(4)	2.604(8)
N(2)–M–N(2)$1	175.7(7)	175.1(6)	173.4(2)	172.3(4)	170.4(2)	169.6(4)

Symmetry element $1 is $-x, y, -z - 1.5$.

Table 6 Important dimensions (distance/Å, angles/°) for the complexes of the later lanthanides (Dy–Lu) and yttrium with C_2-BTBP

	Metal					
	Dy	Ho	Er	Yb	Lu	Y
M–O(42)	2.472(7)	2.466(5)	2.470(10)	—	—	2.478(8)
M–O(41)	2.552(8)	2.546(5)	2.551(11)	—	—	2.551(9)
M–O(61)	2.441(7)	2.416(4)	2.418(10)	2.471(5)	2.465(7)	2.416(7)
M–O(62)	2.468(7)	2.437(5)	2.442(11)	2.450(5)	2.442(7)	2.436(9)
M–O(51)	2.509(7)	2.511(5)	2.510(11)	2.355(5)	2.354(6)	2.503(9)
M–O(52)	2.492(7)	2.489(5)	2.484(10)	2.365(5)	2.359(7)	2.473(8)
M–O(100)	—	—	—	2.295(5)	2.285(7)	—
M–N(8)	2.521(7)	2.505(5)	2.508(10)	2.450(5)	2.448(8)	2.516(8)
M–N(22)	2.538(8)	2.514(5)	2.530(11)	2.439(5)	2.447(8)	2.515(9)
M–N(28)	2.477(7)	2.487(5)	2.383(13)	2.438(5)	2.433(7)	2.499(7)
M–N(2)	2.521(8)	2.509(5)	2.521(10)	2.461(5)	2.457(7)	2.525(8)
N(2)–M–N(22)	165.0(2)	164.2(2)	163.0(2)	158.8(2)	158.0(3)	164.3(2)

containing two pyridine rings linked by aliphatic diamines[20] where the donor atoms form an approximate plane with the metal. The pattern of bond lengths in the crystal structures show some trends. As expected the bond lengths decrease across the lanthanide series. For the larger elements, the bond lengths to oxygen are *ca.* 0.10 Å shorter than those to nitrogen but this difference is reduced along the series. Indeed for Y, there is little difference between the bond lengths to N and O. There is, however, no discernable pattern in the bond lengths to N(2) and N(8), which remain similar across the series. One distinguishable feature is the N(2)–M–N(22) angle, which ranges from 175.6(6) for La to 164.3(2)° for Y demonstrating that as the metal is decreased in size it is pulled more into the ligand cavity. Despite the tetra-coordination of the ligand, the bond lengths are similar to those found for tridentate ligands such as terpy and BTP. Thus for [Nd(C2-BTP)(NO_3)$_3$)(HOEt)],[5] Nd–N are 2.641 × 2, 2.162 Å compared to 2.639 × 2, 2.635 × 2 in [Nd(C2-BTBP)(NO_3)$_3$] and in [Yb(terpy)$_2$(NO_3)$_3$],[21] Yb–N are 2.417, 2.395, 2.419 Å compared to 2.450, 2.439, 2.438, 2.461 Å in [Yb(C2-BTBP)(NO_3)$_3$].

Nitric acid stability

Since benzylic hydrogens are particularly prone to abstraction by oxygen-centred free radicals the presence of such hydrogens in an extractant is undesirable.[21] Radicals, such as nitrogen dioxide and nitrogen trioxide, are likely to be present in many aqueous nitric acid solutions found within the nuclear industry, and consequentially a BTBP (CyMe$_4$-BTBP) bearing an alkyl group containing no benzylic hydrogens was made. After a mixture of CyMe$_4$-BTBP (0.01 M) and the diamide (0.25 M) was exposed to nitric acid (1 M) for 60 days it was not degraded. By comparison C5-BTBP under the same conditions was extensively degraded within one month.

Conclusions

It has been shown that the BTBP reagents are able to form complexes with metals and the crystal structures of 1 : 1 complexes with the majority of lanthanides have been determined. It has been shown by metal ligand titrations that lanthanum is able to form complexes with 2 : 1 BTBP to metal ratios as well as 1 : 1. The range of BTBP ligands has been increased by the reaction of larger diketones. The initial extraction test conducted with C2-BTBP[1] has been repeated in a non-halogenated solvent which is more amenable for industrialization. Further, more detailed investigations of the metal extraction and general chemistry of the BTBP ligands are being undertaken.

Acknowledgements

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