

Experimental and theoretical studies of a triazole ligand and complexes formed with the lanthanides

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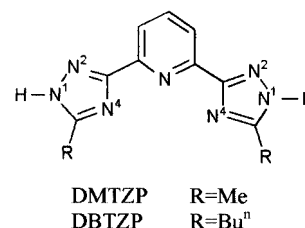
The crystal structure of 2DBTZP·H₂O [DBTZP = 2,6-bis(5-butyl-1,2,4-triazol-3-yl)pyridine] has been determined and shows a dimeric structure in which two ligands, with different protonation patterns, form four hydrogen bonds with an enclosed water molecule. Several crystal structures have been determined of lanthanide complexes with the corresponding 5-methyl derivative (DMTZP) which cover the lanthanide series. Four different structural types are reported: La^{III} forms [La(DMTZP)(NO₃)(H₂O)₅][NO₃]₂; Nd^{III}, Sm^{III} and Tb^{III} in the first part of the lanthanide series form [M(DMTZP)(NO₃)(H₂O)] which is crystallographically disordered over a two-fold axis, Ho^{III} forms [Ho(DMTZP)(NO₃)(H₂O)], with one monodentate nitrate giving nine co-ordination, while Er^{III} and Yb^{III} form [M(DMTZP)(NO₃)₃] complexes which are also nine-co-ordinate.

Introduction

One possible future scenario in nuclear reprocessing is the conversion or transmutation of the long-lived minor actinides, such as americium, into short-lived isotopes by irradiation with neutrons.^{1,2} In order to achieve this transmutation it is necessary to separate the trivalent minor actinides from the trivalent lanthanides by solvent extraction, otherwise the lanthanides absorb neutrons effectively and hence prevent neutron capture by the transmutable actinides.³

For many years we have been designing and testing ligands for the co-extraction of lanthanides and actinides from nuclear waste and their subsequent separation.^{4,5} Various oligoamines have been shown selectively to extract actinides in preference to the lanthanides from nitric acid solutions into an organic phase. Particularly useful have been tridentate planar ligands such as 2,2':6',2''-terpyridine and 2,4,6-tris(4-*tert*-butyl-2-pyridyl)-1,3,5-triazine⁶ and tetradentate ligands such as tris[(2-pyridyl)methyl]amine and tris[(2-pyrazinyl)methyl]amine.⁷ Recently, the triazole ligands 2,6-bis(5-butyl-1,2,4-triazol-3-yl)pyridine, DBTZP, and 2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine, DMTZP, have been found to have good extraction properties. However, they have remarkable separation properties in synergistic combination with 2-bromohexanoic acid.⁸ Thus, at concentrations between 0.003 and 0.03 M, DMTZP was able to extract from an aqueous phase containing 0.05 M HNO₃ and 0.1 M NH₄NO₃ into paraffinic diluent TPH (hydrogenated tetrapropene) giving Am^{III}/Eu^{III} separation factors between 41 and 68. The compound DBTZP is an even better extractant and was found to extract from an aqueous phase containing 0.1 M HNO₃ and 0.1 M NH₄NO₃ into TPH to give Am^{III}/Eu^{III} separation factors up to 150 at low ligand concentrations between 0.014 and 0.055 M.⁸ We have, therefore, initiated experimental and theoretical studies of these ligands in order to establish why they have these remarkable properties.

We wished to establish the stoichiometries of the metal complexes extracted at low acid concentrations with a view to understanding the processes involved and hence to establish the best possible ligands for the An/Ln separations. We have



adopted a theoretical and experimental approach to the identification of these species. Quantum mechanical methods, were used to investigate the conformational preferences of the ligand; in addition we attempted preparation of solid complexes in order to provide evidence for the typical species involved in this type of extraction.

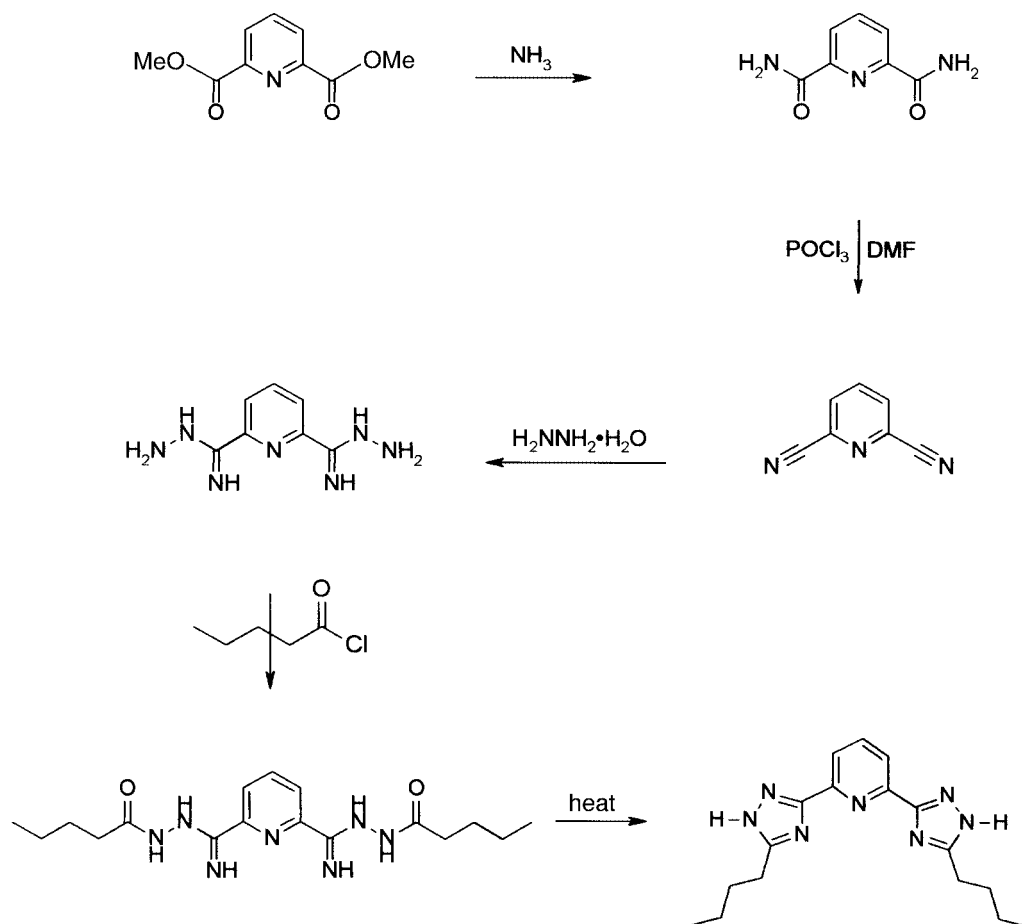
Experimental

Valeryl chloride (98%), lanthanum nitrate hexahydrate (99.999%), neodymium nitrate hexahydrate (99.9%), samarium nitrate hexahydrate (99.9%), terbium nitrate pentahydrate (99.9%), holmium nitrate pentahydrate (99.9%) and ytterbium nitrate pentahydrate (99.9%) were purchased from Aldrich; DMF (GPR, BDH) was dried over calcium hydride under nitrogen and then distilled under reduced pressure, acetonitrile was dried and stored over 3Å molecular sieves. The NMR spectra were run using a JEOL JNM-EX 400 spectrometer. Microanalyses were carried out by Medac Ltd., Brunel Science Centre and mass spectra were run on a VG autospec machine. Uncorrected melting points were obtained on a Stuart melting point apparatus.

Preparation of ligands

The ligand DMTZP was prepared according to the literature method.⁹ The synthesis of DBTZP has not been described in detail previously and we therefore report here the details.

The synthetic route is outlined in Scheme 1. Pyridine-2,6-dicarboxamide was prepared from dimethyl pyridine-2,6-



Scheme 1

dicarboxylate as described previously.¹⁰ Its conversion into 2,6-dicyanopyridine was effected using a Vilsmeier complex as dehydrating agent.¹¹ The preparation of pyridine-2,6-dicarbohydrazide imide was carried out by treating the cyanide with hydrazine hydrate in the absence of solvent.¹² The dicarbohydrazide imide was then converted into DBTZP as follows: 1 g (0.00518 mol) of it was initially suspended in DMF (20 cm³) under a nitrogen atmosphere. After the addition of 2 g of anhydrous sodium hydrogen carbonate the solution was cooled in an ice-bath and valeryl chloride (1.28 cm³, 0.01076 mol dissolved in 12 cm³ DMF) added dropwise with vigorous stirring. The cold solution was stirred for 1 h and during this time the dicarbohydrazide imide gradually dissolved and a yellow solid began to precipitate. After this time the solid divaleryl derivative was filtered off, washed with a large amount of water and then dried thoroughly under vacuum over calcium chloride. Yield 0.97 g, 52%, mp 186–188 °C. Found: C, 55.66; H, 7.48; N, 28.15. C₁₇H₂₇N₇O₂ requires C, 56.49; H, 7.53; N, 27.13%. ¹H NMR (DMSO): δ 0.93 (6 H, t), 1.33 (4 H, sex), 1.56 (4 H, qt), 2.19 (1 H, m), 2.61 (1 H, m), 6.95 (4 H, s), 7.84–7.89 (1 H, m), 8.03–8.11 (2 H, m) and 9.77 (2 H, m). Mass spectrum (CI): *m/z* 362 (MH⁺, 5), 344 (MH⁺ – H₂O, 22) and 326 (M⁺ – 2H₂O, 100%). The most abundant fragment ion indicates that the dicarbohydrazide imide loses two water molecules and cyclises to form 2,6-di(5-butyl-1,2,4-triazol-3-yl) pyridine DBTZP under the conditions used to obtain the mass spectrum.

The final product DBTZP was formed on heating the divaleryl derivative at 225 °C for 1 h in a nitrogen atmosphere. The dark brown solid residue obtained on cooling was dissolved in ethyl acetate–methanol (1 : 2) and then passed through a short silica gel column to remove decomposition products. The solvents were then removed and a white precipitate was obtained in 32% yield, mp 120–125 °C. Found: C, 59.64;

H, 7.01, N, 28.78. C₁₇H₂₃N₇·H₂O requires C, 59.45; H, 7.34; N, 28.55%. ¹H NMR (CDCl₃): δ 0.80 (6 H, t), 1.32 (4 H, sex), 1.73 (4 H, qt), 2.86 (4 H, t), 7.75–7.87 (1 H, m) and 8.01–8.19 (2 H, m). Crystals suitable for a single crystal X-ray analysis were obtained on dissolution in DMSO and very slow evaporation of the solvent at room temperature.

Preparation of metal complexes of DMTZP

The salt La(NO₃)₃·6H₂O (0.060 g, 0.14 mmol) dissolved in 0.5 cm³ CH₃CN was added to a vigorously stirred solution of DMTZP (0.030 g, 0.14 mmol) in 0.5 cm³ CH₃CN at *ca.* 50 °C. After slow evaporation of almost all the solvent over a period of two weeks crystals suitable for structure determination were obtained. Yield 9 mg, 20% [La(DMTZP)(NO₃)(H₂O)₅][NO₃]₂ **1**. Found: C, 20.20; H, 3.34; N, 20.97. C₁₁H₂₁LaN₁₀O₁₄ requires C, 20.13; H, 3.22; N, 21.34%. An additional water molecule was found in the lattice of the crystal used for the structure determination.

A solution containing Nd(NO₃)₃·6H₂O (0.030 g, 0.07 mmol) in 0.5 cm³ CH₃CN was added to a stirred solution of DMTZP (0.015 g, 0.07 mmol) in 1 cm³ CH₃CN at *ca.* 50 °C. Good quality crystals were formed after standing overnight at room temperature: [Nd(DMTZP)(NO₃)₃(H₂O)]·CH₃CN·2H₂O **2a** (12 mg, 26%). Found: C, 22.41; H, 2.40; N, 24.12. C₁₃H₂₀N₁₁NdO₁₂ requires C, 23.40; H, 3.02; N, 23.11%. The corresponding isomorphous complexes of Sm **2b** (22%) and Tb **2c** (46%) were obtained in the same way. Found: C, 22.25; H, 2.38; N, 23.94. C₁₃H₂₀N₁₁O₁₂Sm requires C, 23.21; H, 3.00; N, 22.90%. Found: C, 23.00; H, 2.46; N, 22.97. C₁₃H₂₀N₁₁O₁₂Tb requires C, 22.92; H, 2.96; N, 22.60%.

The salt Ho(NO₃)₃·5H₂O (0.0305 g, 0.07 mmol) in 1 cm³ CH₃CN was added slowly with stirring to DMTZP (0.015 g, 0.07 mmol) in 1 cm³ CH₃CN at *ca.* 50 °C. Crystals suitable for

X-ray analysis were formed after slow evaporation and standing at room temperature for three days. Yield 13 mg (29%) $[\text{Ho}(\text{DMTZP})(\text{NO}_3)_3(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ **3**. The sample sent for analysis indicated the presence of two additional water molecules rather than the acetonitrile found in the crystal structure. Found: C, 20.42; H, 2.52; N, 21.93. $\text{C}_{11}\text{H}_{17}\text{HoN}_{10}\text{O}_{12}$ requires C, 20.44; H, 2.65; N, 21.67%.

A solution containing $\text{Yb}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ (0.062 g 0.14 mmol) in 2 cm^3 CH_3CN was added to a stirred solution containing DMTZP (0.030 g, 0.14 mmol) in 3 cm^3 CH_3CN at ca. 50 °C. Crystals suitable for X-ray crystallography appeared after only 2 min at room temperature: $[\text{Yb}(\text{DMTZP})(\text{NO}_3)_3]\cdot \text{CH}_3\text{CN}$ **4**, yield 19 mg, 21%. Found: C, 24.00; H, 2.21; N, 23.61. $\text{C}_{13}\text{H}_{14}\text{N}_{11}\text{O}_9\text{Yb}$ requires C, 24.35; H, 2.20; N, 24.01%.

Crystallography

The structure of the DBTZP as a demihydrate, $2\text{DBTZP}\cdot\text{H}_2\text{O}$, was determined together with those of 6 metal complexes of DMTZP, viz $[\text{La}(\text{DMTZP})(\text{NO}_3)(\text{H}_2\text{O})_5][\text{NO}_3]_2\cdot\text{H}_2\text{O}$ **1**, $[\text{M}(\text{DMTZP})(\text{NO}_3)_3(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}\cdot 2\text{H}_2\text{O}$ (M = Nd **2a**, Sm **2b** or Tb **2c**) $[\text{Ho}(\text{DMTZP})(\text{NO}_3)_3(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}$ **3**, and $[\text{Yb}(\text{DMTZP})(\text{NO}_3)_3]\cdot\text{CH}_3\text{CN}$ **4**. Crystal data are given in Table 1 together with refinement details. Data for all 7 crystals were collected with Mo-K α radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. Ninety five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.¹³ Default refinement details are described here while differences for specific structures are included below. Structures were solved using direct methods with the SHELXS 86 program.¹⁴ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the carbon atoms and nitrogen atoms were included in calculated positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Hydrogen atoms on water molecules were not included. An empirical absorption correction was made for all lanthanide structures using the DIFABS program.¹⁵ All structures were refined on F^2 till convergence using SHELXL.¹⁶ All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

In the structure of $2\text{DBTZP}\cdot\text{H}_2\text{O}$ the ligand has crystallographic C_2 symmetry. A hydrogen atom found in a Fourier-difference map bonded to N(4) was included with 50% occupancy. Hydrogen atoms bonded to the water molecule or to any other nitrogen atom were not located and not included. The butyl chain was disordered and two sites with constrained dimensions were refined for the outermost three carbon atoms.

The structure of complex **1** showed some disorder. Two positions were refined for each of the methyl groups C(100) and C(300) each with 50% occupancy. The dipositive cation contained only one nitrate. One further ordered nitrate was located in the asymmetric unit while a second was disordered over two sets of positions both close to two-fold axes and were each refined with 50% occupancy. The structures of **2a–2c** were isomorphous and the metal atoms located on crystallographic two-fold axes. Initially the moiety containing the metal was determined as $[\text{M}(\text{DMTZP})(\text{NO}_3)_4]^-$ but this formulation was subsequently ruled out from unreasonable intramolecular contacts and high thermal parameters for two symmetry related nitrates. A successful structural model was found with a metal complex formulated as $[\text{M}(\text{DMTZP})(\text{NO}_3)_3(\text{H}_2\text{O})]$ with one nitrate and the water molecule disordered over the two-fold axis. This model was consistent with the presence of an acetonitrile solvent molecule also with 50% occupancy that was hydrogen bonded to the disordered water molecule. For **2a**, the R value was 0.0611 for the disordered model and 0.0714 for the tetranitrate model, thus confirming the accuracy of our disordered treatment. There was an additional water molecule

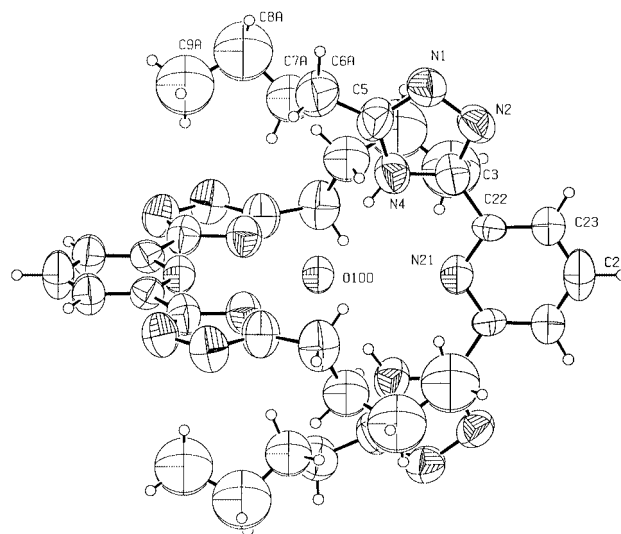


Fig 1 The structure of $2\text{DBTZP}\cdot\text{H}_2\text{O}$ with the atomic numbering scheme. Hydrogen atoms bonded to nitrogen and oxygen are not shown apart from those on N(4) (see text). Ellipsoids at 30% probability.

in the asymmetric unit given full occupancy. The structures of **3** and **4** were refined with the default methodology. Both contained a solvent acetonitrile molecule in the asymmetric unit. Relevant bond lengths in each structure are shown in Table 2. Hydrogen bonds lengths are shown in Table 3.

CCDC reference number 186/1507.

See <http://www.rsc.org/suppdata/dt/1999/2433/> for crystallographic files in .cif format.

Discussion

The crystal structure of $2\text{DBTZP}\cdot\text{H}_2\text{O}$ is shown in Fig. 1 together with the atomic numbering scheme. The ligand has crystallographic two-fold symmetry and the water molecule which occupies a crystallographic 222 position is also positioned on this axis. The N(4) atoms are mutually *cis* with the central pyridine nitrogen atom and all four N(4) atoms are 2.94(1) Å from the oxygen atom. The arrangement of the four N(4) nitrogen atoms around the oxygen atom is distorted tetrahedral with angles ranging from 107–112°. It seems unlikely that all four would be protonated with hydrogen atoms directed at the water molecule particularly as the latter has two hydrogen atoms of its own that can also form hydrogen bonds. A possible scenario therefore is for the oxygen atom to participate in two acceptor hydrogen bonds and two donor hydrogen bonds. This would be consistent with the fact that two of the five-membered rings (possibly in the same molecule but not necessarily so) would have their hydrogen atoms located on N(1) or N(2) rather than N(4). However, the Fourier-difference map gives no indication that N(1) or N(2) is protonated, indeed the evidence suggests that N(4) is the only atom protonated. However due to the poor quality of the data this result is not definitive. In this structure the two N(4)–C–N (py) torsion angles are *cis*. Quantum mechanics calculations (see below) in the absence of a water molecule show that the order of energies for this conformation, with N(4) atoms *cis* to the central pyridine nitrogen atom, with proton positions is $\text{N}(1) < \text{N}(4) < \text{N}(2)$. Thus, the results suggest that the scenario proposed above with the protons positioned on N(1) and N(4) in the two ligands is reasonable. These calculations were carried out in the absence of the water molecule and it can easily be envisaged how the configuration with N(4) protonated can be stabilised by the inclusion of a water molecule and the formation of hydrogen bonds. Of course, the same could be said for the configuration with N(1) or N(2) protonated but here the stabilisation would come from the donating hydrogen bond to N(4) from the water molecule. As is apparent from Fig. 1, the

hemihydrate structure is stabilised by the butyl chains which encapsulate the dimer. However these chains are disordered and two sets of positions were refined for each with occupancy factors of x and $1 - x$ respectively; x refined to 0.40(1).

The compound DBTZP can potentially bond to a metal in many different ways depending on the conformation of the ligand and which nitrogen atoms co-ordinate. We were unable to prepare any crystals of metal complexes containing this ligand due to solubility problems but instead formed many complexes with the methyl analogue DMTZP and report here the structures of six. In all cases, the ligand co-ordinates to a metal *via* the two N(4) atoms together with the central pyridine nitrogen atom to form a tridentate chelate. This co-ordination mode was also observed in the corresponding complexes with molecular formulae $\text{Fe}(\text{DMTZP})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{DMTZP})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$.⁹ Co-ordination through the other triazole nitrogen atom is also possible. In bis(2,2'-bipyridyl)-(3-methyl-5-pyridin-2-yl-1,2,4-triazole)ruthenium hexafluorophosphate tetrahydrate the Ru is bound to the N(2) triazole atom.¹⁷ The authors suggest that this is the most favoured mode of co-ordination because of steric hindrance caused by the methyl group in the 5 position. Our own structural and molecular modelling studies suggest, however, that this steric hindrance is not a significant factor.

The hydrogen atoms, present on N(4) in the "free" ligand, are then to be found on N(1) as shown by Fourier-difference maps and established by the pattern of intermolecular hydrogen bonds in all six structures. While these structures contain the DMTZP ligand, there seems no reason why the bonding pattern should be any different in DBTZP. This was confirmed by modelling studies where the methyl groups of the DBTZP ligand in the crystal structures were replaced by butyl groups and the resulting structures energy-minimised by molecular mechanics. It was found that these butyl groups did not cause any steric crowding and no adjustment of the co-ordination sphere was required.

The structure of the $[\text{La}(\text{DMTZP})(\text{NO}_3)(\text{H}_2\text{O})_3]^{2+}$ cation in complex **1** is shown together with the atomic numbering scheme in Fig. 2. Note that in this structure and the other lanthanide complexes the atoms in the five-membered rings are numbered N(n 1), N(n 2), C(n 3), N(n 4) and C(n 5), where n represents the ring number 1 or 3. The central pyridine has a ring number $n = 2$ and the nitrogen atom is numbered N(21). In **1** the metal atom is bound to the three nitrogen atoms of the DMTZP ligand with distances La–N(14) 2.713(18), La–N(21) 2.774(12), La–N(34) 2.724(17) Å. The remaining distances in the co-ordination sphere showed La–O (nitrate) distances of 2.60(2) and 2.72(2) Å and La–O (water) distances of 2.563(15)–2.641(15) Å. The co-ordination number is therefore 10, which is common for lanthanum with predominantly monodentate ligands although higher co-ordination numbers such as 11 and 12 are often found in co-ordination spheres with polydentate ligands. However this cation has an unexpected stoichiometry especially in comparison with that found for the other lanthanides in that only one of the nitrates is bound to the metal. We have carried out extensive structural studies of complexes of the lanthanide elements with a variety of terdentate ligands with nitrate anions and the vast majority of these complexes show the metal bonded to three nitrates to form a neutral species; occasionally cations with two nitrates are found but never before a dication with one nitrate. Search of the Cambridge Crystallographic Database confirmed that this type of compound is most unusual. This could be due to some special properties of the DMTZP ligand but this seems unlikely because of the other structures presented here. However we have often found in our studies of series of complexes with identical ligands across the lanthanide elements that lanthanum is very often the odd one out producing unique structures, no doubt because of its size and closed shell, although in this case we have been unable to prepare crystals of complexes with

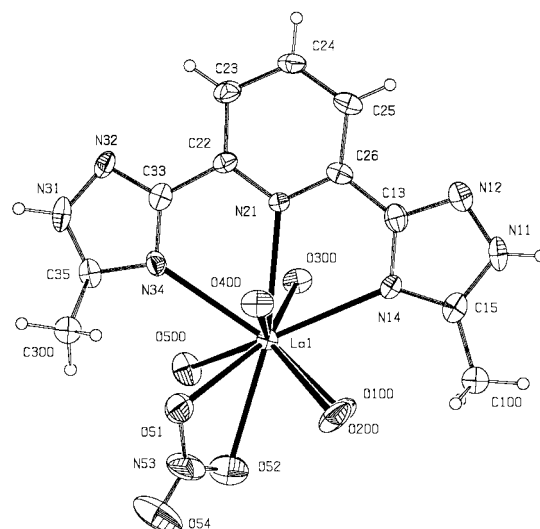


Fig. 2 The structure of complex **1** with the atomic numbering scheme. Ellipsoids at 30% probability. Hydrogen atoms on the water molecules could not be located.

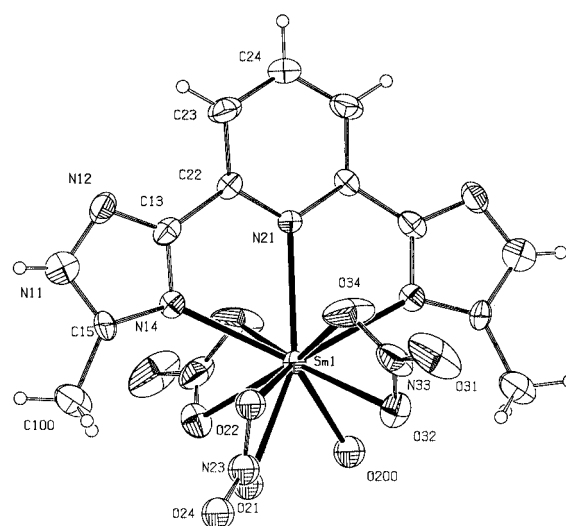


Fig. 3 The structure of complex **2b** with the atomic numbering scheme. Details as in Fig. 2.

the adjacent elements Ce and Pr which might have provided equivalent stoichiometries.

The structures of complexes **2a–2c** are isomorphous containing $[\text{M}(\text{DMTZP})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$. That of **2b** ($\text{M} = \text{Sm}$) is shown in Fig. 3. The metal atom is bonded to the three nitrogen atoms of the DMTZP ligand, six oxygen atoms from three nitrates and one water molecule making a co-ordination number of 10. The structure contains a two-fold axis and there is therefore disorder between one nitrate anion O(21), O(22), N(23), O(24) and the water molecule O(200). The dimensions for the three structures are compared in Table 2 and show consistent values with differences only due to the decrease in metal size ($\text{Nd} > \text{Sm} > \text{Tb}$). This result can be compared to the dimensions obtained for nitrogen donor tridentate planar ligands containing three six-membered rings. We have analysed complexes of 2,2':6',2'' terpyridine in the Cambridge Crystallographic Database. There were 262 examples of metals bonded to terpyridine. We plotted the difference Δ between the average M–N bond length for the two outer M–N bond lengths and the central bond against the central M–N bond length. We found a good correlation (though 3 outliers were rejected) with $r^2 = 0.620$. The linear equation is $\Delta = -0.163(\text{M–N}) + 0.421$ thus signifying that below 2.58 Å the outer M–N distance was greater than the inner M–N distance and above 2.58 Å the central M–N distances were the greater.

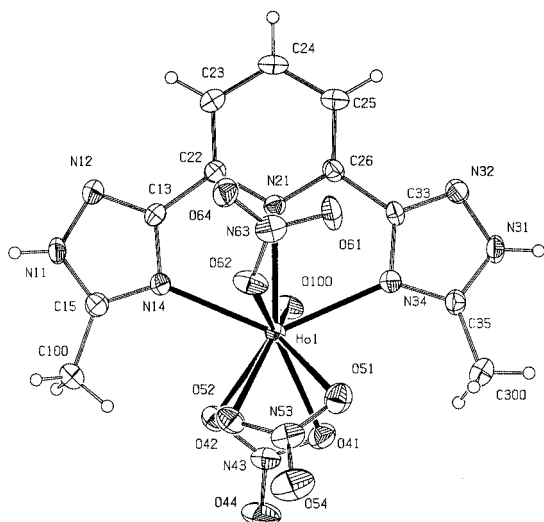


Fig. 4 The structure of complex **3** with the atomic numbering scheme. Details as in Fig. 2.

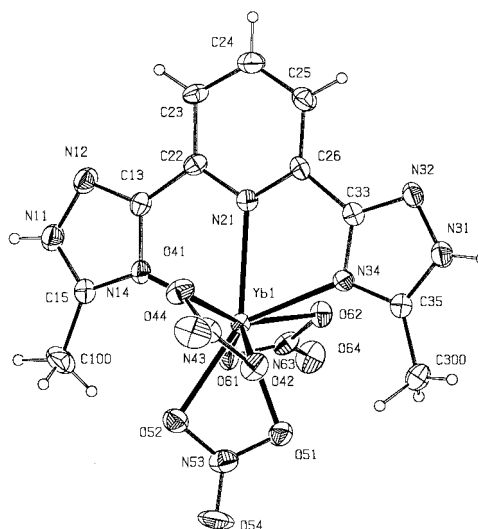


Fig. 5 The structure of complex **4** with the atomic numbering scheme. Ellipsoids at 30% probability.

In all the present triazole structures the outer M–N distances are less than the central M–N distance, while the opposite is the case for the aforementioned nickel and iron structures. It would appear that there are considerable similarities between the bonding pattern in the triazoles and the terpyridines. Though there are not enough examples of the triazoles to be conclusive, it would appear that the change in sign for Δ (differences in bond lengths) occurs at a smaller bond length than in terpyridine.

There is a significant amount of intermolecular hydrogen bonding in the isomorphous lattices. The solvent acetonitrile has 50% occupancy and forms a hydrogen bond to O(200) at 2.74(3) (Nd), 2.71(4) (Sm) and 2.78(4) Å (Tb). The water molecule forms two donating hydrogen bonds to N(12) and O(34) (2.97, 2.89, Nd; 3.00, 2.88, Sm; 3.00, 2.88 Å, Tb) while forming an accepting hydrogen bond from N(11) (2.73(2), Nd; 2.74(2), Sm; and 2.74(2) Å, Tb). Extensive intermolecular hydrogen bonding was also observed in the corresponding Fe^{II}/DMTZP complex involving triazole NH, nitrate anions and water molecules. The authors suggested that N–H...OH₂ hydrogen bonding would increase the acidity of the NH groups which would increase the acidity of the co-ordinating nitrogen atoms and as a result favour the singlet state of Fe^{II}.⁹ The opposite may also be the case because N...H₂O intermolecular hydrogen bonding is possible and this would result in a decrease in the electron density on the co-ordinating triazole nitrogen atoms. Intermolecular hydrogen bonding involving water molecules, anions and unco-ordinated triazole N atoms was also suggested as a significant factor in the stabilisation of the another Fe/triazole complex.¹⁸

The structure of complex **3** is shown in Fig. 4 and is very similar to the type **2** structures (though not isomorphous) except that one of the nitrate anions is monodentate with the Ho...O(61) distance 3.76 Å. Monodentate nitrates are not common but as is apparent from the Cambridge Crystallographic Database have been observed before in a few lanthanide structures. This structure also shows hydrogen atoms on N(*n*1) as confirmed by a similar hydrogen bond pattern to type **2** in that N(11) is hydrogen bonded to a nitrate oxygen O(64) at 2.87(2) Å and N(31) to an acetonitrile nitrogen atom at 2.89(2) Å. The water molecule O(100) which is co-ordinated to the metal is also hydrogen bonded to O(64) and N(32) in two other molecules.

The final complex in the series **4** is shown in Fig. 5 and shows a nine-co-ordinate structure with the terdentate ligand and three nitrate ligands bonded to the metal. Hydrogen bonds are also formed here from N(11) to an acetonitrile ligand at 2.91(2) Å and N(31) to a nitrate O(62) at 2.87(2) Å.†

It is interesting that in both complexes **3** and **4** intermolecular hydrogen bonds are formed to give polymeric one-dimensional chains. In **3** the N(*n*1)–H donor hydrogen bond is formed with a nitrate oxygen O(64) that is not bonded to the metal, while in **4** the bond is formed to O(62), an oxygen atom that is bonded to the metal. In all the other cases the N(*n*1)–H donor hydrogen bond is formed to solvent. Clearly the presence of these hydrogen bond interactions can facilitate the extraction process by forming complex agglomerates.

Theoretical structural analysis of DMTZP

Our purpose here was to study the energies of the possible structures of the DMTZP ligand. There are three possible conformations for DMTZP which can be characterised by the N(4)–C–C–N (py) torsion angles as *tt* (*trans,trans*), *ct* (*cis,trans*) and *cc* (*cis,cis*). In addition there is one hydrogen atom which can theoretically be attached in each five-membered ring to any one of the three nitrogen atoms N(1), N(2) or N(4). We made the assumption that the position of the hydrogen atom was equivalent in each of the two five-membered rings and this gave nine different possible structures for the DMTZP ligand which are denoted as 1-*cc*, 1-*ct*, 1-*tt*, 2-*cc*, 2-*ct*, 2-*tt* and 4-*cc*, 4-*ct*, 4-*tt*, the number indicating the nitrogen atom to which the proton is attached. If asymmetric models were considered, another 12 possible structures would need to be studied.

We have analysed these 9 structures for DMTZP using the GAUSSIAN 94 program.¹⁹ Starting models were built using the CERIUS 2 software²⁰ and the three rings were made approximately coplanar but no symmetry was imposed. Structures were then optimised using the 6-31G** basis set. Results are summarised in Table 4.

The lowest energy structure by quite a margin (>6.0 kcal mol⁻¹) was 2-*tt*. Here the two N(2) atoms are bound to a hydrogen atom while N(1) and N(4) are not, and the structure is stabilised by interactions between the protons and the central nitrogen N(21) of the pyridine ring. A similar stabilisation from intramolecular hydrogen bonds was also found in our study of the terpyridine ligand.⁵ For the latter (in which no nitrogen atoms are protonated) the *trans,trans* conformation was favoured but for the diprotonated terpyridine cation (in which the two nitrogen atoms in the outer pyridine rings were protonated) the *cis,cis* conformation had the lowest energy because

† The structure of the corresponding erbium complex was found to be isomorphous but the data were not of sufficient quality to report: $a = 16.123(17)$, $b = 8.211(11)$, $c = 16.625(14)$ Å, $\beta = 101.69(1)^\circ$, monoclinic, space group $P2_1/n$, $Z = 4$.

Table 1 Crystal data and structure refinement for the structures

	2DBTZP-H ₂ O	[LaL(NO ₃)(H ₂ O) ₃]- [NO ₃] ₂ ·H ₂ O 1	[NdL(NO ₃)(H ₂ O) ₃]- CH ₃ CN·2H ₂ O 2a	[SmL(NO ₃)(H ₂ O) ₃]- CH ₃ CN·2H ₂ O 2b	[TbL(NO ₃)(H ₂ O) ₃]- CH ₃ CN·2H ₂ O 2c	[HoL(NO ₃)(H ₂ O) ₃]- CH ₃ CN 3	[YbL(NO ₃)(H ₂ O) ₃]- CN 4
Empirical formula	C ₃₄ H ₄₈ N ₁₄ O	C ₁₁ H ₁₃ LaN ₁₀ O ₁₅	C ₁₂ H ₂₀ N ₁₁ NdO ₁₂	C ₁₃ H ₂₀ N ₁₁ O ₁₂ Sm	C ₁₃ H ₂₀ N ₁₁ O ₁₂ Tb	C ₁₃ H ₁₆ HoN ₁₁ O ₁₀	C ₁₃ H ₁₄ N ₁₁ O ₉ Yb
Formula weight	668.86	674.30	666.64	672.75	681.32	651.30	641.39
Crystal system, space group	Orthorhombic, <i>Fddd</i>	Triclinic, <i>P1</i>	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>	Triclinic, <i>P1</i>	Monoclinic, <i>P2₁/n</i>
<i>a</i> /Å	11.324(14)	9.830(12)	9.326(9)	9.353(12)	9.354(12)	8.563(9)	16.102(18)
<i>b</i> /Å	22.00(3)	11.254(14)	29.71(3)	29.59(3)	29.40(3)	11.095(14)	8.179(10)
<i>c</i> /Å	31.39(4)	13.787(17)	9.895(11)	9.889(12)	9.836(12)	13.346(16)	16.571(19)
<i>a</i> /°		73.96(1)				96.98(1)	
<i>β</i> /°		79.89(1)	113.03(1)	112.95(1)	112.52(1)	98.06(1)	101.69(1)
<i>γ</i> /°		67.60(1)				114.60(1)	
<i>V</i> /Å ³	7820	1351	2523	2521	2499	1118	1244
<i>Z</i> , <i>D_c</i> /Mg m ⁻³	8, 1.136	2, 1.658	4, 1.876	4, 1.773	4, 1.811	2, 1.934	4, 1.993
<i>μ</i> /mm ⁻¹	0.073	1.662	2.135	2.407	2.908	3.612	4.448
Reflections collected	3114	3412	4158	4050	3846	3873	6452
Unique reflections/ <i>R</i> (int)	1209/0.0949	3412	2293/0.0395	2221/0.0448	2190/0.0353	3873	3898/0.0291
Data/restraints/parameters	1209/12/112	3412/12/325	2293/0/162	2221/0/162	2190/0/163	3873/0/320	3898/0/334
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1215, 0.3668	0.1172, 0.3176	0.0611, 0.1555	0.0647, 0.1859	0.0618, 0.1668	0.0281, 0.0800	0.0447, 0.1230
(all data)	0.1890, 0.4110	0.1263, 0.3220	0.0669, 0.1584	0.0759, 0.1914	0.0671, 0.1721	0.0315, 0.0826	0.0614, 0.1344
Largest difference peak and hole/e Å ⁻³	0.269, -0.214	2.752, -1.544	1.448, -1.443	1.207, -0.970	2.767, -1.679	1.160, -1.219	2.085, -1.573

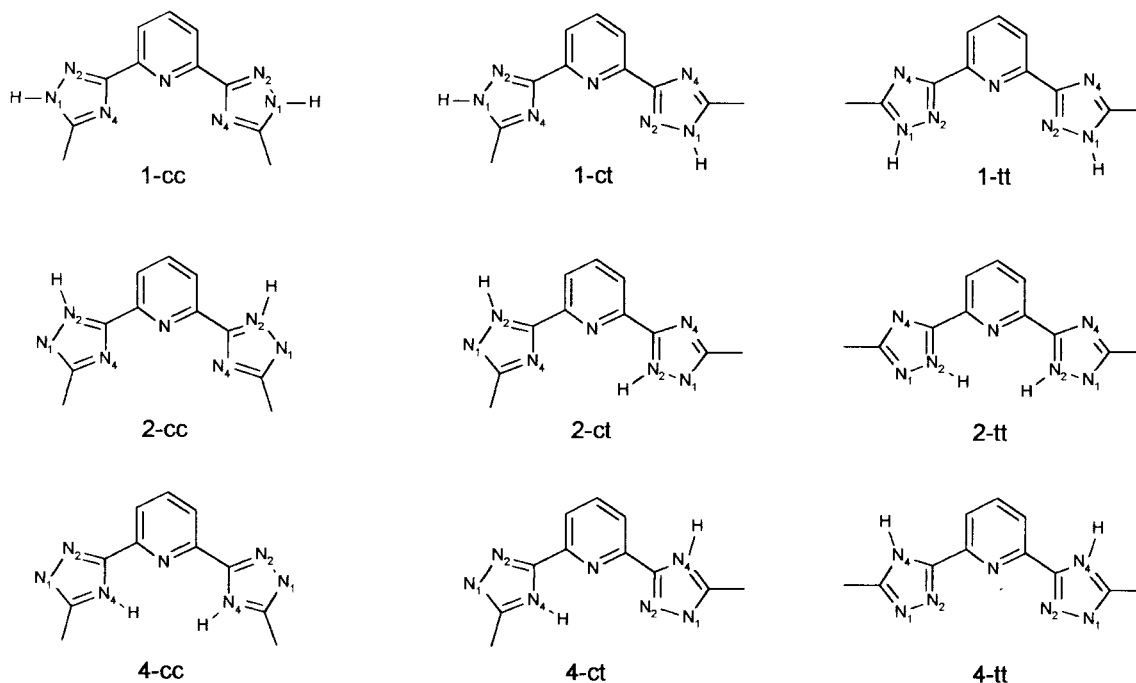


Table 2 Dimensions (bond lengths in Å, angles in °) in the metal coordination spheres of complexes **1**, **2a–2c**, **3** and **4**

1			
La(1)–O(100)	2.563(15)	La(1)–O(51)	2.60(2)
La(1)–O(200)	2.584(15)	La(1)–O(52)	2.72(2)
La(1)–O(300)	2.641(15)	La(1)–N(14)	2.713(18)
La(1)–O(400)	2.586(17)	La(1)–N(34)	2.724(17)
La(1)–O(500)	2.573(17)	La(1)–N(21)	2.774(12)
2a–2c			
	Nd	Sm	Tb
M(1)–O(200)	2.44(2)	2.44(2)	2.38(3)
M(1)–O(31)	2.496(9)	2.470(10)	2.428(9)
M(1)–O(32)	2.568(9)	2.525(10)	2.505(10)
M(1)–O(21)	2.577(15)	2.57(2)	2.540(18)
M(1)–O(22)	2.591(15)	2.588(19)	2.549(18)
M(1)–N(14)	2.629(7)	2.594(10)	2.582(9)
M(1)–N(21)	2.697(9)	2.687(12)	2.626(11)
3			
Ho(1)–O(100)	2.364(4)	Ho(1)–O(62)	2.392(4)
Ho(1)–O(51)	2.458(5)	Ho(1)–N(14)	2.460(4)
Ho(1)–O(52)	2.406(4)	Ho(1)–N(34)	2.462(5)
Ho(1)–O(41)	2.427(4)	Ho(1)–N(21)	2.518(4)
Ho(1)–O(42)	2.455(4)		
4			
Yb(1)–O(41)	2.356(6)	Yb(1)–O(62)	2.407(6)
Yb(1)–O(42)	2.433(7)	Yb(1)–N(14)	2.433(7)
Yb(1)–O(51)	2.372(7)	Yb(1)–N(34)	2.414(7)
Yb(1)–O(52)	2.360(6)	Yb(1)–N(21)	2.479(7)
Yb(1)–O(61)	2.451(7)		

of intramolecular hydrogen bonds between the two outer nitrogen atoms and the central nitrogen atom. The other energies listed in Table 4, together with the N(4)–C–N(py) torsion angles, show that the presence of the hydrogen atom on N(4) or N(2) *ortho* to the bridge to the central pyridine ring destabilises the structure when it is adjacent to a C–H bond on the central pyridine ring and torsion angles of 30–40° are found as the rings twist to reduce the steric interactions.

Clearly this low energy 2-*tt* configuration with N(2) bound to a hydrogen atom is not compatible with metal co-ordination. Although it is of course possible for the two five-membered rings to rotate to form the 2-*cc* configuration, this would lead to close N–H and C–H contacts. Not surprisingly this con-

Table 3 Hydrogen bonds (Å) in the structures

2DBTPZ·H₂O			
N(14A)···O(100)	2.94	N(14B)···O(100)	2.94
1			
N(11)···O(62 ¹)	2.93	O(200)···O(41 ⁴)	2.74
N(11)···O(61 ²)	3.04	O(200)···O(41 ⁵)	2.85
N(31)···O(71)	2.81	O(300)···N(12 ²)	2.88
N(31)···O(72)	3.09	O(400)···O(42 ⁴)	2.90
O(100)···O(700)	2.70	O(400)···N(32 ⁶)	3.24
O(100)···O(44 ³)	2.78		
Symmetry relations: 1 -x, 1 -y, 1 -z; 2 x, 1 +y, z; 3 x, y - 1, z; 4 x + 1, y, z; 5 -x, 1 -y, -z; 6 1 -x, -y, 1 -z.			
2a–2c			
	Nd	Sm	Tb
N(11)–O(100 ¹)	2.73	2.74	2.74
N(12)–O(100 ²)	2.97	3.00	3.00
N(100)–O(200)	2.74	2.71	2.78
O(100)–O(34)	2.89	2.88	2.88
Symmetry relations: 1 -x, y, $\frac{3}{2}$ -z; 2 x, 1 -y, $\frac{1}{2}$ +z.			
3			
O(100)···O(64 ⁴)	2.73	N(11)···O(64 ³)	2.87
O(100)···N(32 ²)	2.80	N(31)···N(100 ²)	2.89
Symmetry relations: 1 -x, y, z; 2 -x, -y, -z; 3 1 -x, 1 -y, 1 -z; 4 x - 1, y, z.			
4			
N(11)···N(100 ¹)	2.91	N(31)···O(62 ²)	2.87
Symmetry relations: 1 $\frac{1}{2}$ -x, y - $\frac{1}{2}$, $\frac{1}{2}$ -z; 2 $\frac{1}{2}$ -x, y + $\frac{1}{2}$, -z - $\frac{1}{2}$.			

figuration is not observed and for all the metal complexes reported here the 1-*cc* configuration is found. This not only presents a tridentate donor set to the metal for binding, but also because the hydrogen atom is positioned on N(1) rather than N(2) there are no close H···H contacts with the pyridine ring. In the unco-ordinated ligand all three conformations 1-*tt*, 1-*ct* and 1-*cc* have relatively low energies because of this lack of H···H contacts which is confirmed by the close coplanarity of the three rings so that the torsion angles are all less than 10.0° from planarity.

In the (DBTTPZ)₂ hydrate (Fig. 1) the two independent ligands also have the *cis, cis* conformation found in the metal

Table 4 Results from quantum mechanics calculations on DMTZP. Geometry optimisation was carried out using the 6-31G** basis set; energies in au (= 627.509 kcal mol⁻¹)

Structure		Energy	N(4)-C-C-N (py) torsion angle/°
H on N(1)	1-cc	-804.11510	-6.4, -6.4
	1-ct	-804.11644	-1.1, 179.8
	1-tt	-804.11763	179.4, 179.7
H on N(2)	2-cc	-804.10797	46.7, 46.7
	2-ct	-804.12327	-33.9, -177.6
	2-tt	-804.13301	180.0, 180.0
H on N(4)	4-cc	-804.11348	0.0, 0.0
	4-ct	-804.10453	-2.9, -153.9
	4-tt	-804.08451	141.3, 141.3

complexes. The positions of the protons were not established unequivocally but as detailed above it seems likely that one ligand has the structure 4-cc while the other could also be 4-cc but more likely is 1-cc.

As is apparent from Table 4 neither structure (4-cc or 1-cc) has a particularly low energy compared to other configurations, but given the presence of the water molecule it is easy to see why these particular configurations are favoured in the crystal structure. We have previously shown how the presence of a water molecule in the cavity can stabilise a tridentate planar ligand in the *cis*, *cis* conformation.⁵

Conclusion

We have shown that DMTZP (and by analogy DBTZP) forms a consistent series of structures across the lanthanide series with variations in stoichiometry due to the decreasing size of the metals across the series. Lanthanum as is often the case provides the only inconsistency. The reasons for the exceptional extraction properties of this ligand remain unclear. It has been suggested that the basicity of the heterocyclic nitrogen ligand has a big influence on the Am^{III}/Ln^{III} separations.⁶ A p*K*_a (base) value of 3.40 has been determined for 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole¹⁷ which indicates that this type of ligand has a lower basicity than, for example, pyridine (5.25)²¹ and bipyridine (4.45).²² Heterocyclic nitrogen ligands with lower basicities have been shown to give better Am^{III}/Ln^{III} separations.⁶ It is also clear that the addition of a weak acid, 2-bromohexanoic acid, is crucial to the ligands extraction performance.⁸ Therefore, although the solid Ln/DMTZP complexes isolated in this work are likely to give a good indication of the type of species which may be extracting, future work will include solution studies with and without 2-bromohexanoic acid, to establish better the nature of the extracting species in solution.

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