Structural studies of lanthanide complexes with new hydrophobic malonamide solvent extraction agents†

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Two new hydrophobic malonamide ligands butyl-N,N'-dimethyl-N,N'-diphenyl malonamide and ethoxyethyl-N,N'-dimethyl-N,N'-diphenyl malonamide and corresponding lanthanide complexes [Ln(NO$_3$)$_3$(L)$_2$], Ln = Nd or Pr, have been prepared and structurally characterised. The structural studies establish that the alkyl or alkyloxy groups attached to the central carbon atom of the malonamides do not effect the bidentate co-ordination of adjacent carbonyl oxygen atoms. All the metal complexes presented show the lanthanide to be 10-co-ordinate, being bonded to four oxygen atoms of two malonamides and six oxygen atoms of three nitrates. Malonamide ligands with alkyloxy groups have been shown previously to be better extractants for lanthanide(III) and actinide(III) ions than those with just alkyl groups. This solid state evidence seems to suggest that the enhanced extraction performance of ligands with an ether oxygen in the alkyloxy chain is not due to direct co-ordination between the metal ion and the ether oxygen.

Introduction

There is currently a great deal of interest in the methods used for the reprocessing of nuclear fuel. There are a number of processes already in operation that remove the most abundant radionuclides at the beginning of the nuclear fuel cycle. The PUREX process, utilising tributyl phosphate (TBP) as the solvent extraction reagent, has been used for a number of years to separate uranium and plutonium from irradiated fuel.[1] A more recent development, the TRUEX process, uses a mixture of TBP and (diisobutylcarbamoylmethyl)octyl(phenyl) phosphine oxide to separate not only uranium and plutonium but also trivalent actinides such as americium.[2] Our aim is to separate the long-lived minor actinide radionuclides such as Am^{III} from lanthanide(III) ions at the back end of the nuclear fuel cycle and to transmute them by nuclear means.[3] The final separation is necessary because the lanthanides will induce difficulties in the preparation of fuel targets for transmutation. Although the TRUEX process can separate americium(III) from the waste it does have an important drawback in the fact that the phosphorus containing reagents are not completely incinerable and as a result will generate secondary waste. We are interested in extracting agents that contain only carbon, hydrogen, nitrogen and oxygen and are thus completely incinerable at the end of process, producing carbon dioxide water and nitrogen that can be released freely into the atmosphere. Although the incineration of alpha contaminated waste is not possible in some countries, there are other methods that can be considered to achieve the same goal.

Among these are wet oxidation processes that can operate at room or temperatures below 100 °C. These include (i) silver(II) electromediated oxidation, (ii) hydrogen peroxide oxidation (Fenton reagent), (iii) UV-stimulated hydrogen peroxide oxidation and (iv) super-critical water wet oxidation that is carried out at a higher temperature but still well below that required for incineration.

One way to achieve the final americium(III) separation is first to coextract the chemically similar minor actinide(III) and

lanthanide(III) ions and then to develop another process to separate them. The DIAMEX process is currently under development for the coextraction step and involves the liquid–liquid extraction of both actinide(III) and lanthanide(III) ions using hydrophobic malonamides from the highly acidic raffinate issuing from the PUREX process.[4–6] A great deal of work has already been carried out to determine the optimum ligand for the coextraction.[7] Three factors are important. The ligand must show good affinity for the lanthanide(III) and actinide(III) ions, the formation of third phases during the solvent extraction is undesirable and the ligands should exhibit third phase boundaries at high nitric acid and metal concentrations. Two promising candidates N,N'-dibutyl-N,N'-dimethyl tetradecylmalonamide (L^1) and N,N'-diheptyl-N,N'-dimethyl(octyloxyethyl) malonamide (L^2) are shown together with the other malonamides discussed in this paper. Both L^1 and L^2 show good affinity for the metal ions. When 0.65 M solutions of each ligand in hydrogenated tetrapropylene were used to extract americium(III) and Ln from 2.96 M nitric acid solution, distribution ratios for Am and Eu were respectively 4.58 and 2.02 for L^1 and 9.1 and 4.54 for L^2.[7] Thus, L^2 is more efficient than L^1 for extraction by a factor of greater than 2 : 1, but it is not clear whether this is due to a structural difference, *i.e.* the participation of the ether oxygen atom from the R^3 chain in L^2 co-ordinating to the metal ions making L^2 a tridentate ligand, or to some other reason. This led us to conduct this study.

It is thought that at low nitric acid concentrations the actinide(III) and lanthanide(III) ions are extracted as co-ordination complexes and we have undertaken a systematic study of the metal-ion co-ordination behaviour of the malonamides.[8,9] Previous studies by us have shown that the malonamides complex to lanthanide ions through both carbonyl oxygen atoms. Either one or two malonamides are bound to the lanthanide and the co-ordination sphere of the metal is completed by nitrate ions and/or water molecules. It has been shown that there is a mixture of complexes in solution[10] and the nature of the solvent and substituents on the malonamide appears to determine which one crystallises out.[8,9] Thus crystal structures have been determined of [Nd(NO$_3$)$_3$(L^6)], L^6 = N,N'-dicyclohexyl-N,N'-dimethyl malonamide, [Nd(NO$_3$)$_3$(H$_2$O)(L^5)] (L^5 = N,N'-diphenyl-N,N'-dimethyl malonamide)

R^1 R^3 R^1

R^2-N C $N-R^2$

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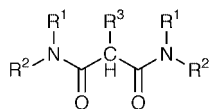
L^1 $R^1 = Me$, $R^2 = Bu^n$, $R^3 = (CH_2)_{13}CH_3$
L^2 $R^1 = Me$, $R^2 = (CH_2)_6CH_3$, $R^3 = (CH_2)_2O(CH_2)_7CH_3$
L^3 $R^1 = Me$, $R^2 = Ph$, $R^3 = Bu^n$
L^4 $R^1 = Me$, $R^2 = phenyl$, $R^3 = EtOEt$
L^5 $R^1 = Me$, $R^2 = Ph$, $R^3 = H$
L^6 $R^1 = Me$, $R^2 = cyclohexyl$, $R^3 = H$
L^7 $R^1 = Et$, $R^2 = cyclohexyl$, $R^3 = H$
L^8 $R^1 = Pr^i$, $R^2 = cyclohexyl$, $R^3 = H$
L^9 $R^1 = R^2 = Et$, $R^3 = EtOEt$
L^{10} $R^1 = Et$, $R^2 = Et$, $R^3 = H$

and $[Yb(NO_3)_3(H_2O)(L^5)]$.[9] All of these structural studies were undertaken on malonamides in which the central carbon atom was unsubstituted. The ligands used in the solvent extraction process have alkyl or oxyalkyl chains attached to the central carbon of the malonamide to make them more hydrophobic and we have now extended our structural studies to ligands of this type. Two new ligands have been synthesized. The first has a butyl chain on the central malonamide carbon, butyl-N,N'-dimethyl-N,N'-diphenyl malonamide (L^3), while the second has an ethoxy ethyl chain, ethoxy ethyl-N,N'-dimethyl-N,N'-diphenyl malonamide (L^4). Complexation studies with these new ligands should provide better models for the species which may be involved in the extraction process. The use of short rather than long chains facilitates the crystallisation of the metal complexes. We report here for the first time single crystal structures of lanthanide/hydrophobic malonamide complexes in which the ligands are more similar to those used in the actual extraction process.

Experimental

Sodium hydride, 1-bromobutane, bis(2-bromoethyl) ether, neodymium nitrate hexahydrate (99.9%), praseodymium nitrate hexahydrate (99.9%) (all Aldrich) and silica gel, particle size 40–63 μm (BDH), were used as received. Propan-2-ol (HPLC grade, Fisher) was dried and stored over 3 Å molecular sieves. N,N'-Dimethyl-N,N'-diphenylmalonamide (L^5) was prepared as described previously.[9] The NMR spectra were run on a JEOL JNM-EX 400 spectrometer. Microanalyses were carried out by Medac Ltd., Brunel Science Centre.

Preparations

Butyl-N,N'-dimethyl-N,N'-diphenyl malonamide (L^3). Sodium hydride (0.75 g of a 60% dispersion in mineral oil, 0.0184 M) was washed with light petroleum (bp 60–80 °C) and suspended in toluene (10 cm³). The compound N,N'-dimethyl-N,N'-diphenylmalonamide (L^5) (4 g, 0.0141 M) was added and the mixture heated at 90 °C for 30 min. 1-Bromobutane (1.94 g, 0.0141 M) dissolved in 15 cm³ toluene was added dropwise and the reaction mixture refluxed for 2.5 d. The toluene was removed under vacuum, water was added and the product extracted with CH_2Cl_2. After drying with sodium sulfate and removal of solvent, the crude product was purified using flash chromatography (BDH silica gel, particle size 40–63 μm) with light petroleum–ethyl acetate (2:1) as eluent. Suitable crystals for X-ray crystallography were obtained after the colourless oil had slowly crystallised at room temperature. In this manner, 1g (21%) of pure L^3 was obtained, mp 102–104 °C (Found: C, 75.10; H, 7.69; N, 8.21. $C_{21}H_{26}N_2O_2$ requires C, 74.52; H, 7.74; N, 8.28%); ^{1}H NMR (CDCl₃) δ 0.6–0.72 (3 H, br), 0.82–0.96 (4 H, br), 1.64–1.77 (2 H, br), 3.16 (6 H, s), 3.20–3.29 (1 H, br), 6.65–6.77 (4 H, m) and 7.28–7.37 (6 H, m).

Ethoxy ethyl-N,N'-dimethyl-N,N'-diphenyl malonamide (L^4). Compound L^4 was prepared in a similar manner to L^3, except

that bis(2-bromoethyl) ether (90%) was used as alkylating agent and the flash chromatography was carried out using light petroleum–ethyl acetate (1:1) as eluent. The oil slowly crystallised at room temperature to give colourless crystals which were suitable for X-ray crystallography. Thus, 0.24 g (38%) of pure L^4 was obtained, mp 90–91 °C (Found: C, 71.05; H, 7.45; N, 7.86. $C_{21}H_{26}N_2O_3$ requires C, 71.16; H, 7.39; N, 7.90%); ^{1}H NMR (C_6D_6) δ 0.92 (3 H, t), 2.10–2.27 (2 H, br), 2.81–2.97 (2 H, br), 3.04 (6 H, s), 3.40 (2 H, t), 3.67–3.79 (1 H, br), 6.47–6.68 (4 H, m) and 6.85–7.00 (6 H, m).

The neodymium complex of L^3 was prepared by dropwise addition of a solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.0324 g, 0.07 mM) in 3 cm³ propan-2-ol to a stirred solution containing L^3 (0.0250 g, 0.07 mM) in 3 cm³ of propan-2-ol–toluene (2:1). Crystals suitable for X-ray crystallography were formed after 1 h at room temperature (Found: C, 48.78; H, 5.13; N, 9.43. $C_{42}H_{52}N_7NdO_{13} \cdot H_2O$ requires C, 49.21; H, 5.31; N, 9.56%).

The neodymium complex of L^4 was prepared as follows: 0.0139 g of $Nd(NO_3)_3 \cdot 6H_2O$ (0.03 mM) dissolved in 0.5 cm³ propan-2-ol was added dropwise to a stirred solution of 0.011 g L^4 (0.03 mM) in 0.5 cm³ propan-2-ol. The solution was allowed slowly to evaporate at room temperature for one week and after cooling to 4 °C for two days crystals suitable for X-ray crystallography were obtained (Found: C, 46.26; H, 4.89; N, 9.55. $C_{42}H_{52}N_7NdO_{15} \cdot 3H_2O$ requires C, 46.14; H, 5.35; N, 8.97%).

The corresponding praseodymium complex was prepared by adding 0.0136 g of $Pr(NO_3)_3 \cdot 6H_2O$ (0.03 mM) dissolved in 0.2 cm³ propan-2-ol to a stirred solution of L^4 (0.011 g, 0.03 mM) in 0.15 cm³ propan-2-ol. Suitable crystals for X-ray crystallography were obtained after one day at room temperature (Found: C, 48.23; H, 5.04; N, 9.41. $C_{42}H_{52}N_7PrO_{15}$ requires C, 48.70; H, 5.06; N, 9.46%).

Crystallography

Data for all 5 crystals were collected with Mo-Kα radiation using the MARresearch Image Plate System. Details are listed in Table 1. The crystals were positioned 70 mm from the Image Plate; 95 frames were measured at 2° intervals with a counting time of 2 min at 298 K. Data analysis was carried out with the XDS program.[11] Structures were solved using either direct or heavy atom methods with the SHELXS 86 program.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was made for all lanthanide structures using the DIFABS program.[13] All structures were refined on F^2 till convergence using SHELXL.[14]

CCDC reference number 186/1631.

See http://www.rsc.org/suppdata/dt/1999/3605/ for crystallographic files in .cif format.

Molecular modelling

Models were obtained from crystal structures and modified where necessary using the CERIUS 2 software.[15] Molecular mechanics was carried out using the Universal force field.[16] However the default methodology in the software is unsuitable for lanthanide complexes because it relies on ideal angles and there are no such angles subtended at the metal by pairs of donor atoms in high-co-ordinate complexes. We therefore used our published technique[17] in which the M–L bonds are removed and replaced by M–L parabolic constraints. The removal of the bonds also removes the L–M–L angles and X–L–M–L torsion angles (L = donor atom, X = any atom) from the molecular mechanics summation but allows the introduction of non-bonded van der Waals interactions between donor atoms and these repulsive forces are used to obtain a low-energy arrangement of the co-ordination sphere. Quantum mechanics calculations were carried out with the

Results and discussion

The crystal structures of ligands L^3 and L^4 are shown in Fig. 1. Both structures show similar conformations both to each other and to that previously obtained for the corresponding unalkylated ligand L^5 in that the carbonyl groups are also in the *cis* conformation, the O=C$\cdots$C=O torsion angle being 60.6 (L^3), 55.2 (L^4) and 57.2° (L^5).[9] It is interesting that with different substituents at the nitrogen atoms, *e.g.* in *N,N'*-dicyclohexyl-*N,N'*-diethyl malonamide (L^7) and *N,N'*-dicyclohexyl-*N,N'*-diisopropyl malonamide (L^8), a *trans* conformation is found in which the O=C$\cdots$C=O torsion angle is 180°.[9] Quantum mechanics calculations[9] had verified that the *cis* conformation gave the lowest energy for L^5, and the *trans* conformation for L^6 and L^7, and it seems unlikely that these conformational preferences would be altered by the substituents on the central carbon atom. This was confirmed from both experimental and theoretical observations. Thus the structures of L^3 and L^4 were compared to that of L^5 in detail. When the $C_2NC(O)CC(O)NC_2$ backbone was considered, the r.m.s. deviations between L^3 and L^5, and between L^4 and L^5, were calculated to be 0.109 and 0.136 Å respectively. In order to check whether the geometry of L^3 and L^4 was affected by packing effects in the crystal, the two structures were optimised *via ab initio* quantum mechanics calculations using the 6-31G** basis set. Very little change in the structures were observed with r.m.s. deviations of 0.064, 0.064 Å respectively for the 11 atoms in the backbone and so it can be concluded that the conformations in the crystal structure represent low energy conformations.

The first attempts to prepare complex single crystals were carried out with a ligand having just alkyl and alkyloxy chains, ethoxy ethyl-*N,N,N',N'*-tetraethyl malonamide (L^9), as this was thought to be a better analogue for the promising candidates L^1 and L^2, which are already used in solvent extraction processes. These attempts were unsuccessful and so the two new ligands L^3 and L^4 were synthesized containing aryl groups as an aid to crystallisation. Our previous studies have shown no significant variations in the structure of the metal complex with the nature of the malonamides.[8,9] This experimental result was investigated with molecular mechanics calculations starting from the structure of $[Nd(NO_3)_3(L^6)_2]$.[9] In this 10-co-ordinate structure the geometry can best be described in terms of a pentagonal bipyramid with each bidentate nitrate occupying one site. Thus the two axial positions are occupied by nitrates, while the equatorial plane contains four oxygen atoms from two malonamides (angle of intersection of the two NdO_2 moieties 2.9°) together with a nitrate perpendicular to the plane so that one oxygen is above and one oxygen is below the plane. An equivalent geometry is found for the structure of $[La(NO_3)_3(L^{10})_2]$ where the angle between the two NdO_2 moieties is 14.5°. In this geometry there is only one possible significant steric interaction namely that between two R groups on adjacent malonamides in the equatorial plane. This manifests in the distance between carbon atoms in the ethyl groups of L^{10} being 3.58 Å in $[La(NO_3)_3(L^{10})_2]$, while in the $[Nd(NO_3)_3(L^6)_2]$ structure close contacts are avoided by one of the R groups being a methyl group which is too small to impact upon the adjacent cyclohexyl group. Models were built in which the R groups on the nitrogen atoms were successively replaced by a variety of N-substituents, phenyls, substituted phenyls, alkyl chains, branched alkyl chains and cyclic alkanes, but on energy minimisation there proved to be no significant change in the geometry of the metal co-ordination sphere. The only exception to this was when the aforementioned methyl group was replaced by a bulky substituent.

The structural effects of substitution on the central carbon atom of the malonamides were next investigated *via* crystal
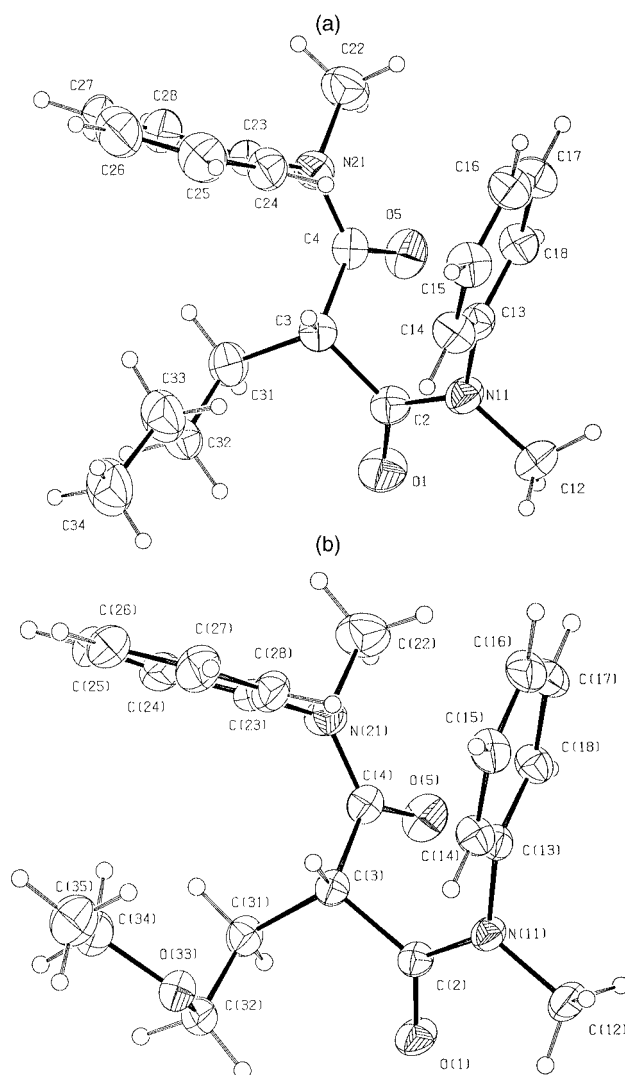

Fig. 1 Structures of (a) L^3 and (b) L^4 with ellipsoids at the 30% probability level.

structures of their metal complexes. The neodymium complex of L^3 (Fig. 2) has a crystallographic twofold axis with two malonamide ligands and three bidentate nitrate ions to make up a 10-co-ordinate environment. Bond lengths are listed in Table 2 and show as usual that the bonds to malonamide, 2.444(4) and 2.456(4) Å, are significantly shorter than bonds to nitrate, 2.560(6), 2.581(5) and 2.606(5) Å. Interestingly, the same complex was also isolated in 16% yield from an 8 M nitric acid solution. The complex was prepared in HNO_3 because the ligands are used to extract the metal ions from this medium in the solvent extraction process. The geometry of the co-ordination sphere is significantly different from the pentagonal bipyramid obtained for $[La(NO_3)_3(L^{10})_2]$ and $[Nd(NO_3)_3(L^6)_2]$[8,9] and described above. In particular the two malonamides are on the same side of the metal such that the angle between the NdO_2 planes is 72.0° rather than the values of 2.9 and 14.5° found in the L^6 and L^{10} complexes.

We next investigated structures containing L^4 which is equivalent to L^3 but with an alkyloxy chain instead of an alkyl chain on the central carbon atom. The two crystal structures obtained with Pr and Nd and L^4 are isomorphous, having the formulation $[Ln(NO_3)_3(L^4)_2]$ (Fig. 3). Both show two molecules in the asymmetric unit. The metal atoms are 10-co-ordinate being bonded to two bidentate malonamides and three bidentate nitrates. As well as the equivalent stoichiometry, it is clear that the geometry of the co-ordination sphere is similar to that found in the above mentioned $[Nd(NO_3)_3(L^3)_2]$ complex in that the angle between malonamide NdO_2 moieties is 70.6°. The

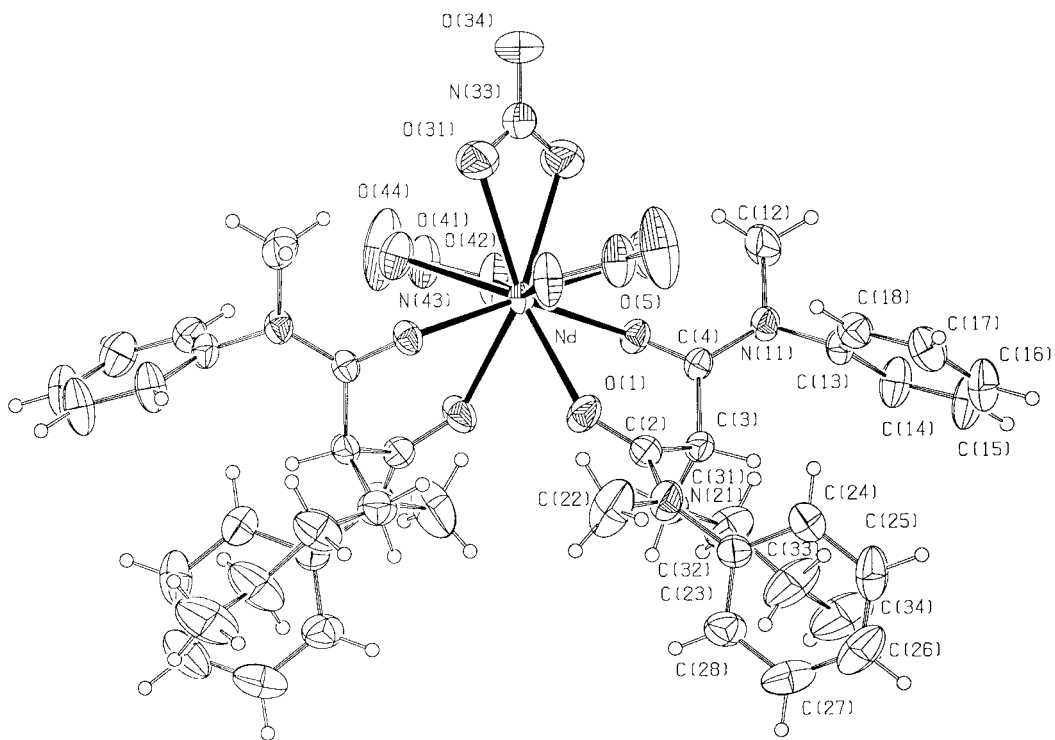**Fig. 2** The structure of [Nd(NO$_3$)$_3$(L^3)$_2$] with ellipsoids at the 30% probability level. The structure has crystallographic C_2 symmetry.

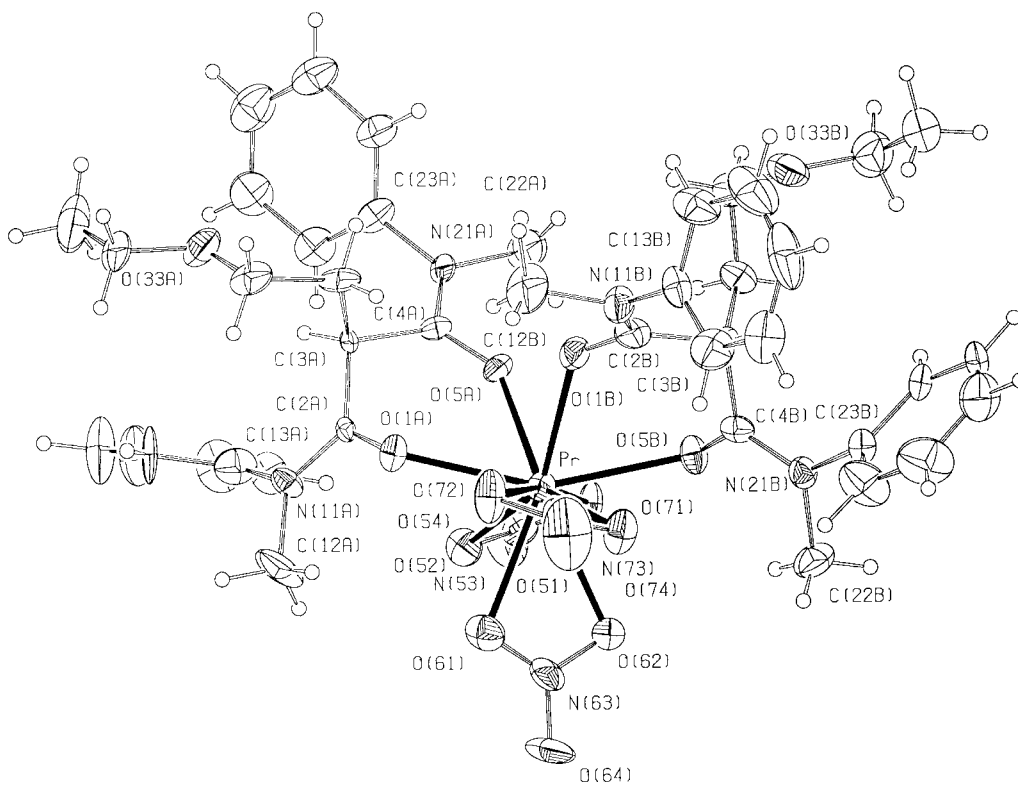**Fig. 3** The structure of [Pr(NO$_3$)$_3$(L^4)$_2$] with ellipsoids at the 30% probability level. There are two molecules in the asymmetric unit. The [Nd(NO$_3$)$_3$(L^4)$_2$] complex is isomorphous.

Nd–O distances show similar differences in that Nd–O (malonamide) range from 2.43 to 2.49 and Nd–O (nitrate) from 2.54 to 2.64 Å. The distances in the analogous praseodymium complex are slightly longer (2.45 to 2.49, 2.56–2.67 Å) reflecting the increased size of the metal ion. The structure confirms that the alkyloxy ether oxygen atom has no direct interaction with the metal ion in the solid state. The Nd$\cdots$O distance is 6.674 Å which is comparable with the Nd$\cdots$C distance (6.937 Å) to the equivalent carbon atom in L^3. Torsion angles along the chain

are however somewhat different. For the C(2)–C(3)–C(31)–C(32)–X(33)–C(34) linkage the three torsion angles are 63.8, 51.6, 76.5° for X = O in L^4 and 69.2, 57.7 and 174.8° for X = C in L^3. In L^4 the final torsion angle in the chain C(32)–O(33)–C(34)–C(35) for which there is no equivalent in L^3 is 174.1°. The close similarity between the two co-ordination spheres of these neodymium complexes is illustrated by the fact that the r.m.s. deviation between the two MO$_{10}$ moieties is only 0.138 Å.

We investigated whether the interesting structural change

Table 1 Crystal data and structure refinement for the structures

	L^3	L^4	$[Nd(NO_3)_3(L^3)_2]$	$[Nd(NO_3)_3(L^4)_2]$	$[Pr(NO_3)_3(L^4)_2]$
Empirical formula	$C_{21}H_{26}N_2O_2$	$C_{21}H_{26}N_2O_3$	$C_{42}H_{52}N_7NdO_{13}$	$C_{42}H_{52}N_7NdO_{15}$	$C_{42}H_{52}N_7O_{15}Pr$
Formula weight	338.44	354.44	1007.15	1039.14	1039.19
Crystal system, space group	Monoclinic, $P2_1/a$	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
$a/\text{Å}$	8.910(12)	9.080(9)	26.48(3)	27.76(3)	27.79(3)
$b/\text{Å}$	26.75(3)	9.666(12)	9.833(12)	18.22(2)	18.26(2)
$c/\text{Å}$	9.245(9)	13.158(14)	18.58(2)	19.12(2)	19.16(2)
$\alpha/°$		76.50(1)			
$\beta/°$	117.61(1)	81.19(1)	96.72(1)	97.73(1)	97.80(1)
$\gamma/°$		61.32(1)			
$V/\text{Å}^3$	1952	984	4805	9583	9631
$Z, D_c/\text{Mg m}^{-3}$	2, 1.943	2, 1.196	4, 1.392	8, 1.442	8, 1.430
μ/mm^{-1}	0.074	0.080	1.147	1.156	1.084
Reflections measured	4290	3463	7521	33036	31539
Unique reflections (R_{int})	2636 (0.0194)	3463	4354 (0.0477)	17449 (0.0426)	16889 (0.0548)
Data/restraints/parameters	2636/0/230	3463/0/239	4354/0/290	17449/0/1183	16889/0/1184
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0527, 0.1465	0.0571, 0.1641	0.0503, 0.1253	0.0709, 0.1716	0.1119, 0.1745
(all data)	0.0699, 0.1596	0.0866, 0.1837	0.0647, 0.1333	0.1254, 0.2022	0.1504, 0.1922

Table 2 Dimensions (Å) in the metal co-ordination spheres

$[Nd(NO_3)_3(L^3)_2]$

Nd–O(5)	2.444(4)	Nd–O(41)	2.581(5)
Nd–O(1)	2.456(4)	Nd–O(42)	2.606(5)
Nd–O(31)	2.560(6)		

$[Nd(NO_3)_3(L^4)_2]$ $[Pr(NO_3)_3(L^4)_2]$

Nd(1)–O(1A)	2.431(5)	2.456(7)
Nd(1)–O(1B)	2.452(5)	2.466(7)
Nd(1)–O(5B)	2.462(5)	2.494(7)
Nd(1)–O(5A)	2.494(5)	2.495(7)
Nd(1)–O(62A)	2.545(6)	2.609(8)
Nd(1)–O(61A)	2.548(6)	2.567(8)
Nd(1)–O(52A)	2.571(5)	2.601(8)
Nd(1)–O(51A)	2.596(5)	2.629(8)
Nd(1)–O(71A)	2.604(6)	2.633(8)
Nd(1)–O(72A)	2.643(6)	2.667(8)
Nd(2)–O(1D)	2.431(5)	2.445(7)
Nd(2)–O(5C)	2.444(5)	2.458(7)
Nd(2)–O(5D)	2.452(5)	2.467(7)
Nd(2)–O(1C)	2.485(5)	2.504(7)
Nd(2)–O(71C)	2.545(6)	2.563(9)
Nd(2)–O(72C)	2.571(6)	2.598(8)
Nd(2)–O(61C)	2.574(5)	2.576(8)
Nd(2)–O(62C)	2.587(5)	2.612(8)
Nd(2)–O(51C)	2.590(6)	2.594(8)
Nd(2)–O(52C)	2.639(6)	2.657(8)

between the L^6 and L^{10} complexes on the one hand and the L^3 and L^4 complexes on the other hand was due to the steric effects of substitution at the central carbon atom. Accordingly we took the structure of $[Nd(NO_3)_3(L^6)_2]$ and added a butyl group to the malonamide ligands, on the central carbon atom in axial positions and replaced the cyclohexyl rings by phenyl rings thus producing the $[Nd(NO_3)_3(L^3)_2]$ complex. On molecular mechanics minimisation the energy was 65.51 kcal mol⁻¹ with an intermalonamide angle of 21.3°. However starting from the crystal structure the energy became 63.84 kcal mol⁻¹ with an intermalonamide angle of 60.7°. It proved impossible to interconvert the two conformations and it seems likely that the repositioning of the malonamides can only be achieved by first removing one of the nitrate anions. The two conformations are comparable in energy and it is not obvious that the inclusion of the substituent butyl group in the malonamide destabilises the pentagonal bipyramidal structure found for complexes of L^6 and L^{10}.

While the crystal structures show there is no interaction between the metal atoms and the ether oxygens, it cannot be ruled out *de facto* that such an interaction does occur in solution and so the possibility of such an interaction was investigated *via* molecular mechanics calculations. We do not know

the structure of the extractant species or indeed the ratio of metal to malonamide although extraction experiments have suggested that ratios of 1:1, 1:2 or 1:3 are possible.[19,20] However in our structural studies only 1:1 and 1:2 complexes have been found and therefore these were investigated in detail. Three basic structural models $[Yb(NO_3)_3(H_2O)(L^4)]$, $[Nd(NO_3)_3(H_2O)(L^4)]$ and $[Nd(NO_3)_3(L^4)_2]$ were investigated. We first considered the nine-co-ordinate monohydrate ytterbium structure.[9] Using the method described above and constraining the Yb–O bonds to experimental values, the model refined to an energy of 96.52 kcal mol⁻¹. This structure contained one water molecule and because this molecule was on the same side of the molecule as one of the hydrogen atoms in the central CH_2 group in the bonded malonamide it was changed to the ether oxygen atom and the CH_2CH_2 linkage formed. This seemed the most likely procedure; that the water molecule would be removed from the co-ordination sphere and replaced by the ether oxygen from the malonamide thus keeping the same co-ordination number. The substitutions were completed with the addition of the terminal ethyl group to form the nine-co-ordinate complex $[Yb(NO_3)_3(L^4)]$. This structure was then energy-minimised to 129.26 kcal mol⁻¹. When the ether oxygen atom is not bonded to the metal then the energy is minimised at 101.91 kcal mol⁻¹. This result shows that there is significant steric strain in allowing the oxygen atom to approach the metal atom. The 10-co-ordinate neodymium dihydrate structure was also considered and the energy of the model taken from the crystal structure minimised to 38.01 kcal mol⁻¹. Again there was an obvious replacement of a water molecule by an ether oxygen and the structure $[Nd(NO_3)_3(H_2O)(L^4)]$ was built and energy minimised to 54.31 kcal mol⁻¹. When the bond from the ether oxygen to the metal was broken, the energy was reduced to 44.61 kcal mol⁻¹. While these results do not rule out formation of the terdentate structure, they make it seem rather unlikely although it is interesting that the energy increase on ether co-ordination is rather less for the larger neodymium ion than for the smaller ytterbium ion.

The $[Nd(NO_3)_3(L^4)_2]$ structure containing the metal atom in a ten-co-ordinate environment with two co-ordinated malonamides was also considered. Co-ordinates were taken from the crystal structure reported here and the structure was minimised to an energy of 129.03 kcal mol⁻¹. There are several different models that could be considered and the values given in parentheses are the minimum energies obtained. One model was used in which the metal co-ordination sphere is expanded to 11 donor atoms by including one ether oxygen atom (157.37 kcal mol⁻¹) and then expanded to 12 donor atoms by including both ether oxygen atoms (215.78 kcal mol⁻¹). Both these structures seem unlikely and perhaps a more realistic model would be one in which the co-ordination sphere remains with ten donor atoms. This could be achieved for one co-ordinating ether

oxygen by one of the nitrate anions becoming monodentate for which there are some precedents in lanthanide structural chemistry (150.68 kcal mol^{-1}). However if both ether oxygen atoms were to be co-ordinated, then the most likely scenario is for 10-co-ordination to be maintained by removing one nitrate altogether from the co-ordination sphere to give a cation complex $[Nd(NO_3)_2(L^4)_2]^+$ (155.71 kcal mol^{-1}).

It can be concluded from these calculations that it is most unlikely that the ether oxygen will bond to the metal in any environment. It should be noted that these calculations were carried out in the gas phase. In solution it is even less likely because the ether oxygen atom is likely to be hydrogen bonded to the solvent and will not be able easily to approach the metal atom. We are currently carrying out EXAFS studies on the complexes in solution to see if this conclusion can be validated directly by experimental results.

However experimental investigations do show that the presence of an ether oxygen in the malonamides definitely enhances the extraction of Eu and Am^{III} and in fact L^2 is a strong candidate as the ligand to be used in the actual DIAMEX process.[7] The exact reason for its good performance is not certain, but our solid-state structural studies and theoretical calculations now confirm that this is not due to direct co-ordination of the ether oxygen atom to the metal ion. It may be due to the fact that ligands of the L^2 type (with alkyloxy chains) are more weakly basic than the corresponding ligands with straight alkyl chains.[10,21] or possibly that the interaction of the ether oxygen with the solvent proves advantageous in some way to the extraction process. Although it is not possible for us to determine crystal structures of actinide complexes such as those of Am^{III} it is quite likely that these structures would be the same as those prepared with the chemically similar lanthanide(III) ions.

Acknowledgements

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Paper 9/05579G