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# Synthesis, structures and mass spectrometry of lanthanide nitrate complexes with tricyclohexylphosphine oxide

Ann P. Hunter<sup>a</sup>, Anthony M.J. Lees<sup>b</sup>, Andrew W.G. Platt<sup>b,\*</sup>

<sup>a</sup> EPSRC National Mass Spectrometry Service Centre, Chemistry Department, University of Wales, Swansea, Singleton Park, Swansea SA2 8PP, UK <sup>b</sup> Faculty of Sciences, Staffordshire University, College Road, Stoke-on-Trent, ST4 2DE, UK

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### Abstract

The complexes  $Ln(NO_3)_3(OPCy_3)_3(EtOH)_x$  (Cy = cyclohexyl,  $C_6H_{11} x = 0$  for Ln = Eu, Er, x = 0.5 for Ln = La, Nd and x = 1 for Ln = Tm, Yb) have been prepared by reaction of lanthanide nitrates with Cy<sub>3</sub>PO in ethanol. The single crystal X-ray structures for Ln = La, Nd, Eu, Er, Tm and Yb are reported. The structures for Ln = La-Eu have two molecules in the unit cell in which the nitrates are all bound as bidentate ligands. The unit cell for Ln = Er contains two distinct molecules; one with three bidentate nitrates and one with two bidentate and one monodentate nitrate. The Tm and Yb complexes have one molecule in the unit cell with two bidentate and one monodentate nitrates are hydrogen bonded to ethanol in the Tm and Yb structures but not in the Er complex. The infrared spectra of the three classes of complex do not readily permit identification of the monodentate nitrate groups. Electrospray mass spectrometry indicates that redistribution/ionisation reactions occur in solution. Ions formed by solvolysis reactions are attributed to gas phase processes associated with the electrospray technique. Tandem mass spectrometry for the La, Ho and Yb complexes shows that in the gas phase loss of Cy<sub>3</sub>PO is the sole fragmentation pathway for all but the Yb complex where the higher energy required for initial fragmentation leads to a more complex fragmentation pattern. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Crystal structures; Tandem mass spectrometry; Lanthanide nitrate; Complexes; Tricyclohexylphosphine oxide

# 1. Introduction

Complexes of lanthanide nitrates with phosphine oxide donors have been extensively studied [1]. One of the main reasons for this interest lies in their use in nuclear fuels reprocessing [2] where the high affinity of phosphine oxides for lanthanide and actinide metals, together with the ready adaptation of their peripheral structure to enhance solvent extraction properties and their chemically robust nature facilitates application. Many ligand systems with multiple donors have been synthesised to increase selectivity in the extraction process [3]. The chemically simpler triphenylphosphine oxide systems have been structurally investigated [4–6]. Here it is found that complexes of varying

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E-mail address: A.Platt@staffs.ac.uk (A.W.G. Platt).

stoichiometry can be isolated depending on the metal to ligand ratio. Complexes such as Ce(NO<sub>3</sub>)<sub>3</sub>(Ph<sub>3</sub>PO)<sub>2</sub>(CH<sub>3</sub>-CH<sub>2</sub>OH) can be formed with low Ln: phosphine oxide ratios [4]. With Ln:Ph<sub>3</sub>PO ratios of approximately 1:3 nine-coordinate Ln(NO<sub>3</sub>)<sub>3</sub>(Ph<sub>3</sub>PO)<sub>3</sub> are formed and with more ligand rich reaction media Ln(NO<sub>3</sub>)<sub>3</sub>(Ph<sub>3</sub>PO)<sub>4</sub> can be isolated [5]. Structurally characterised complexes in the tetrakis(triphenylphosphine oxide) series show that for the lighter lanthanides two nitrates are chelating whilst one is monodentate and that as the ionic radii of the lanthanide decreases the monodentate nitrate is expelled from the primary coordination sphere giving cationic complexes,  $[Ln(NO_3)_2(Ph_3PO)_4]^+NO_3^-$  [5]. The replacement of the phenyl by the more sterically demanding cyclohexyl group in ligands has been shown to give significant changes in structures. For instance 1:1 and 1:2 complexes are formed between Ln(NO<sub>3</sub>)<sub>3</sub> and 2,6(CH<sub>2</sub>P(O)R<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>NO when

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R = Ph whilst with the bulkier ligand (R = Cy) only a 1:1 complex was isolated [3c] and  $[\text{Li}(R_2\text{PC}(N^i\text{Pr})_2]_n$  forms a dimer with R = Ph, but a less sterically crowded hexamer for R = Cy [7].

We examined a series of lanthanide nitrate complexes with tricyclohexylphosphine oxide to investigate the effect of increasing the steric bulk of the ligand on the structural properties of the resulting complexes. The increased lipophilicity of  $Cy_3PO$  compared to  $Ph_3PO$  may make its complexes more suited to solvent extraction. In this respect any transition from a neutral to cationic complex may also provide a mechanism for increased selectivity in extraction, with ionic complexes having lower affinity to a non-aqueous phase.

# 2. Results and discussion

#### 2.1. Synthesis and structures

The reaction of lanthanide nitrates with tricyclohexylphosphine oxide in metal to ligand ratios between 1:3 and 1:4 led to the isolation of  $Ln(NO_3)_3(OPCy_3)_3$  as ethanol solvates except for the Eu and Er complexes. The 1:4 complexes which can be formed with Ph<sub>3</sub>PO [5] and the smaller Ph<sub>2</sub>MePO [8] cannot be obtained with the more bulky Cy<sub>3</sub>PO under these conditions. The complexes formed in high yield giving crystals suitable for X-ray diffraction.

The structures comprise two molecules in the unit cell for the La, Nd, Eu and Er complexes and one for Tm and Yb. Details of the data collection and refinement are given in Table 1 and selected bond lengths and angles in Table 2. The geometries about the metals are all distorted *mer*-octahedra if the nitrate ligands are considered to act as pseudo-monodentate ligands bonded via the nitrogen atoms. The "*cis*" angles range from 104.5° to 74.0° with an average of 90.9° over all the complexes, whilst the "*trans*" angles range from 153.4° to 176.9° with an average of 164.7°.

The coordination mode of the nitrate ligands changes with the decrease in the ionic radius of the lanthanide ion. Thus for the larger ions La-Eu the nitrates all act as bidentate ligands and the complexes are 9-coordinate. Where the unit cells contain ethanol molecules, they are not hydrogen bonded to any of the nitrate ligands. The structure of one of the molecules in the unit cell of the lanthanum complex is shown in Fig. 1. The Er structure has two molecules in the unit cell which differ in the binding of the nitrates. One molecule has three bidentate nitrates and a similar overall structure to those of the La, Nd and Eu complexes, whilst the other has two bidentate and one monodentate nitrate and is hence eight-coordinate. It is interesting to note here that the monodentate nitrate is not hydrogen bonded to the lattice ethanol, and this appears to lead to relatively symmetrical bonding to the metal with non-bonded distances between the O-Er of 3.940(6) and 3.979(5) Å. The structures of the Tm and

Yb complexes have one molecule in the unit cell in which there are two bidentate and one monodentate nitrate ligands. The structure of the Tm complex is shown in Fig. 2.

In these complexes the monodentate nitrate is hydrogen bonded to the lattice ethanol and this causes a distinct asymmetry in the bonding of the monodentate nitrate. The H-bonded oxygen–Ln distance is over 4.4 Å whilst the non-H-bonded distances are in the region of 3.5 Å for the Tm and Yb complexes.

The Ln–O distances have a good linear correlation with the nine-coordinate (La to Er) and eight-coordinate (Er to Yb) ionic radii of the respective lanthanide ions [9]. A plot of the Ln–O(N<sub>bidentate</sub>) and Ln–O(P) distances versus ionic radius is shown in Fig. 3.

In the Er structure the monodentate nitrate has an Er– O(N) distance of 2.287(5) Å compared with longer distances for the Tm (2.310(2) Å) and Yb (2.304(2) Å), respectively. This discrepancy can be explained by the hydrogen bonding between the nitrate and ethanol. In the Tm and Yb complexes, the O···O contacts between the nitrate and ethanol of 2.932(5) Å (Tm) and 2.943(5) Å (Yb) are shorter than the sum of the Van der Waals radius for oxygen (3.04 Å) and are thus indicative of a hydrogen bond.

#### 2.2. Infrared spectroscopy

Infrared spectroscopy has routinely been used as a means of identifying the coordination mode of nitrate ligands to metals [10]. Thus although monodentate and bidentate coordinated nitrates have the same local symmetry the splitting of the N–O stretching modes has been taken as a means of assigning structures. Further, ionic nitrate, with a higher local symmetry should be readily distinguishable by the number of bands observed alone.

We have recently encountered complexes in which formally ionic nitrates are hydrogen bonded to lanthanide coordinated ligands or lattice solvent molecules [11]. The spectra in these instances are typical of bidentate nitrates. It was thus apparent that the use of spectroscopy alone in determining the coordination mode of nitrate ligands was prone to uncertainties when H-bonding ligands were present.

The infrared spectra of the  $Cy_3PO$  complexes are as expected for complexes of phosphine oxides with lanthanide nitrates. The P=O stretch decreases on coordination from 1146 cm<sup>-1</sup> to about 1100 cm<sup>-1</sup> on coordination to the metal. The spectra of the N–O region in these complexes differ only subtly despite the presence of monodentate nitrates in the Er, Tm and Yb complexes. All complexes show absorptions typical of coordinated nitrate with strong bands in the 1480–1450 cm<sup>-1</sup> and 1300– 1290 cm<sup>-1</sup> region and a weaker absorption around 1040 cm<sup>-1</sup>. Complexes which contain both monodentate and bidentate nitrates do not display features which would allow unambiguous identification of the presence of monodentate nitrates.

Crystal data, data collection	and refinement parameters					
Compound	[La(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] · 0.25EtOH	[Nd(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] · 0.25EtOH	$[Eu(Cy_3PO)_3(NO_3)_3]$	$[Er(Cy_3PO)_3(NO_3)_3]$	$[Tm(Cy_3PO)_3(NO_3)_3] \cdot EtOH$	[Yb(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] · EtOH
Crystal data						
Molecular formula	$C_{108}H_{198}La_2N_6O_{24}P_6 + CH_3O_{0.5}$	$C_{108}H_{198}N_6Nd_2O_{24}P_6 + CH_3O_{0.5}$	$C_{108}H_{198}Eu_2N_6O_{24}P_6$	$C_{108}H_{198}Er_2N_6O_{24}P_6$	$C_{54}H_{99}N_3O_{12}P_3Tm + C_2H_6O$	$C_{54}H_{99}N_3O_{12}P_3Yb + C_2H_6O$
Molecular weight, $M_r$	2451.40	2462.06	2454.46	2485.06	1290.27	1294.38
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	P2 <sub>1</sub>	$P2_1$	$P2_1$	$P2_1$	$Pc2_1n$	$Pc2_1n$
Unit cell dimensions	-	-	-	-	-	
a (Å)	11.7015(7)	11.6360(4)	11.6216(2)	11.62110(10)	14.2639(2)	14.25470(10)
$b(\mathbf{A})$	18.7997(6)	18.7227(12)	18.7278(4)	18.6661(2)	22.2990(4)	22.3444(2)
$c(\mathbf{A})$	28.6979(16)	28.4733(17)	28.4435(6)	27.9691(4)	19.1100(3)	19.13000(10)
α(°)	90	90	90	90	90	90
β(°)	100.953(2)	101.063(3)	101.5490(10)	99.1778(4)	90	90
ν (°)	90	90	90	90	90	90
Cell volume, $V(Å^3)$	6198.3(5)	6087.8(6)	6065.3(2)	5989.40(12)	6078.33(17)	6093.15(8)
Formula units/unit cell.	2	2	2	2	4	4
Z						
$D_{\rm calc}$ (Mg m <sup>-3</sup> )	1.313	1.343	1.344	1.378	1.410	1.411
F(000)	2594	2606	2592	2612	2720	2724
Reflections to obtain cell	98420	55177	135855	102414	28935	75486
parameters						
$\theta$ (°)	2.91-26.73	2.92-26.01	2.91-27.48	2.95-27.46	2.91-27.48	2.91-27.49
$\lambda$ (Mo Ka) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu (\mathrm{mm}^{-1})$	0.825	0.991	1.171	1.540	1.600	1.675
$T(\mathbf{K})$	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal description	block	plate	block	block	prism	shard
Colour	colourless	colourless	colourless	colourless	colourless	colourless
Dimensions (mm)	$0.3 \times 0.16 \times 0.14$	$0.1 \times 0.1 \times 0.02$	$0.1 \times 0.08 \times 0.04$	$0.2 \times 0.1 \times 0.1$	$0.3 \times 0.2 \times 0.2$	$0.38 \times 0.18 \times 0.12$
Data collection and SORTAV	absorption correction [19]					
$T_{\rm max}$	0.97779	1.01367	1.35378	1.09172	1.00179	0.80646
$T_{\min}$	0.92571	0.95229	0.68948	0.86566	0.90410	0.72406
Measured reflections	34864	37736	73696	80937	13116	68372
Independent reflections	20342	19181	24697	26588	13116	13420
Observed reflections	14127 (n = 4)	14798 (n = 4)	20285 (n = 4)	20777 (n = 4)	11568 (n = 4)	11804 (n = 4)
$(F_{\alpha} > n\sigma F_{\alpha}))$						~ /
R <sub>int</sub>	0.0703	0.0706	0.1465	0.1293	0.0000	0.0710
$\theta_{\rm max}$ (°)	26.73	26.01	27.45	27.46	27.48	27.49
h	$-14 \rightarrow 13$	$-12 \rightarrow 14$	$-15 \rightarrow 14$	$-15 \rightarrow 15$	$-18 \rightarrow 18$	$-18 \rightarrow 18$
k	$-23 \rightarrow 20$	$-23 \rightarrow 21$	$-22 \rightarrow 24$	$-24 \rightarrow 24$	$-28 \rightarrow 28$	$-27 \rightarrow 29$
l	$-28 \rightarrow 36$	$-34 \rightarrow 35$	-36  ightarrow 36	$-36 \rightarrow 36$	$-24 \rightarrow 24$	$-24 \rightarrow 24$
Refinement on $F^2$						
Scattering factors from Inter	rnational Tables for Crystalla	ography (vol. C)				
Reflections	20342	19181	24697	26588	13116	13420
Parameters/	1342/1	1342/1	1317/37	1307/1	691/1	690/1
restraints		,	.,	··· <b>,</b>	,	.,

Table 1

(continued on next page)

Table 1 (continued)

Compound	[La(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] · 0.25EtOH	[Nd(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] · 0.25EtOH	$[Eu(Cy_3PO)_3(NO_3)_3]$	$[Er(Cy_3PO)_3(NO_3)_3]$	[Tm(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] · EtOH	[Yb(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] · EtOH
Weighting scheme, w <sup>a</sup>	$[\sigma^2(F_o^2) + (0.0354P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.0331P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.0901P)^2 + 7.72P]^{-1}$	$[\sigma^2(F_o^2) + (0.0599P)^2 + 0.81P]^{-1}$	$[\sigma^2(F_o^2) + (0.0426P)^2 + 14.02P]^{-1}$	$[\sigma^2(F_0^2) + (0.0365P)^2]^{-1}$
Final <i>R</i> indices <sup>b</sup>	n = 4	n = 4	n = 4	<i>n</i> = 4	<i>n</i> = 4	n = 4
$(F_{\rm o} > n\sigma F_{\rm o})$						
R(F)	0.0585	0.0546	0.0734	0.0634	0.0307	0.0305
$wR_2(F^2)$	0.0981	0.0889	0.1756	0.1339	0.0630	0.0646
S	0.987	1.007	1.091	1.031	1.046	1.014
Final R indices	$b^{b}$ (all data)					
R(F)	0.1093	0.0862	0.0924	0.0887	0.0416	0.0395
$wR_2(F^2)$	0.1086	0.0960	0.1867	0.1456	0.0663	0.0679
$(\Delta/\sigma)_{\rm max}$	0.001	0.002	0.001	0.001	0.002	0.002
$\Delta \rho_{\rm max}$ (e Å <sup>-3</sup> )	1.24	0.51	2.77	1.07	0.999	1.08
$\Delta \rho_{\rm min} ({\rm e}{\rm \AA}^{-3})$	-1.38	-0.77	-3.17	-1.85	-0.623	-0.99
Extinction correction	none	none	none	none	none	none
Absolute structure parameter	-0.011(10)	-0.014(8)	-0.017(10)	-0.020(7)	0.520(5) <sup>c</sup>	-0.030(4)

<sup>a</sup>  $P = [\max(F_o^2, 0) + 2F_c^2]/3.$ <sup>b</sup>  $R_1 = \sum ||F_o|| - F_c || / \sum |F_o; wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}.$ <sup>c</sup> Batch scale factor for TWIN refinement.

	[Ln(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub> )	$[Ln(Cy_3PO)_3(NO_3)_3] \cdot 0.25C_2H_5OH$		O <sub>3</sub> ) <sub>3</sub> ]	[Ln(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub>	$[Ln(Cy_3PO)_3(NO_3)_3] \cdot C_2H_5OH$	
	La	Nd	Eu	Er	Tm	Yb	
Ln(1)–O(1a)	2.596(5)	2.534(5)	2.493(6)	2.444(5)	2.449(3)	2.450(2)	Ln(1)-O(1)
Ln(1)-O(3a)	2.609(5)	2.552(5)	2.515(6)	2.431(5)	2.411(2)	2.405(2)	Ln(1)-O(3)
Ln(1)-O(4a)	2.616(5)	2.549(5)	2.526(6)	2.441(5)	2.442(2)	2.439(2)	Ln(1)-O(4)
Ln(1)–O(6a)	2.610(5)	2.533(5)	2.509(7)	2.443(6)	2.440(2)	2.428(2)	Ln(1)–O(6)
Ln(1)–O(7a)	2.635(5)	2.558(5)	2.499(7)	2.287(5)	2.310(2)	2.304(2)	Ln(1)–O(7)
Ln(1)-O(9a)	2.618(5)	2.575(5)	2.546(7)				Ln(1)–O(9)
Ln(1)–O(10a)	2.420(5)	2.360(5)	2.313(6)	2.279(6)	2.219(2)	2.202(2)	Ln(1)–O(10)
Ln(1)–O(11a)	2.419(5)	2.348(4)	2.314(6)	2.225(4)	2.241(2)	2.228(2)	Ln(1)–O(11)
Ln(1)–O(12a)	2.424(4)	2.363(4)	2.333(6)	2.254(5)	2.220(2)	2.203(2)	Ln(1)–O(12)
$Ln(1) \cdots N(1a)$	3.014(7)	2.954(7)	2.944(8)	2.857(7)	2.852(3)	2.848(3)	$Ln(1) \cdots N(1)$
$Ln(1) \cdots N(2a)$	3.049(7)	2.977(7)	2.950(7)	2.880(7)	2.860(3)	2.854(3)	$Ln(1) \cdots N(2)$
$Ln(1) \cdots N(3a)$	3.030(7)	2.959(6)	2.961(9)	3.275(6)	3.322(3)	3.321(3)	$Ln(1) \cdots N(3)$
$Ln(1) \cdots P(1a)$	3.8906(20)	3.8263(20)	3.8029(22)	3.7423(22)	3.6995(9)	3.6858(8)	$Ln(1) \cdots P(1)$
$Ln(1) \cdots P(2a)$	3.9284(21)	3.8604(17)	3.8409(23)	3.7453(18)	3.7531(10)	3.7452(9)	$Ln(1) \cdots P(2)$
$Ln(1) \cdots P(3a)$	3.8809(19)	3.8175(19)	3.7959(21)	3.7195(20)	3.7129(9)	3.6971(8)	$Ln(1) \cdots P(3)$
Ln(2)–O(1b)	2.610(5)	2.534(5)	2.487(7)	2.422(5)			
Ln(2)–O(3b)	2.623(4)	2.541(5)	2.531(6)	2.459(5)			
Ln(2)-O(4b)	2.640(5)	2.567(5)	2.529(7)	2.461(6)			
Ln(2)–O(6b)	2.605(4)	2.526(5)	2.511(6)	2.410(6)			
Ln(2)–O(7b)	2.653(5)	2.581(5)	2.545(6)	2.497(6)			
Ln(2)-O(9b)	2.663(5)	2.596(4)	2.584(7)	2.545(7)			
Ln(2)–O(10b)	2.408(4)	2.340(4)	2.303(5)	2.262(4)			
Ln(2)–O(11b)	2.432(4)	2.366(3)	2.336(5)	2.273(4)			
Ln(2)–O(12b)	2.400(5)	2.338(5)	2.312(6)	2.255(6)			
$Ln(2) \cdot \cdot \cdot N(1b)$	3.031(6)	2.958(7)	2.912(7)	2.859(6)			
$Ln(2) \cdots N(2b)$	3.041(7)	2.979(7)	2.925(7)	2.880(7)			
$Ln(2) \cdot \cdot \cdot N(3b)$	3.066(9)	3.001(6)	2.967(9)	2.955(8)			
$Ln(2) \cdots P(1b)$	3.8787(20)	3.8079(17)	3.7875(19)	3.7329(18)			
$Ln(2) \cdots P(2b)$	3.9323(18)	3.8644(14)	3.8375(20)	3.7668(16)			
$Ln(2) \cdots P(3b)$	3.8818(22)	3.8062(22)	3.7677(25)	3.7242(24)			
$N(3a) \cdots Ln(1) \cdots P(2a)$	168.70(15)	167.40(13)	167.07(19)	172.35(13)	167.55(6)	167.30(6)	$N(3) \cdots Ln(1) \cdots P(2)$
$N(1a) \cdots Ln(1) \cdots N(2a)$	174.68(19)	175.52(19)	176.91(21)	173.39(20)	176.24(9)	176.44(8)	$N(1) \cdots Ln(1) \cdots N(2)$
$N(1a) \cdots Ln(1) \cdots N(3a)$	91.43(21)	92.21(20)	92.61(24)	83.19(19)	90.79(9)	91.00(9)	$N(1) \cdots Ln(1) \cdots N(3)$
$N(2a) \cdots Ln(1) \cdots N(3a)$	87.01(19)	86.29(19)	86.99(24)	93.08(19)	90.02(9)	89.52(8)	$N(2) \cdots Ln(1) \cdots N(3)$
$N(3a) \cdot \cdot \cdot Ln(1) - O(11a)$	168.72(19)	167.31(16)	166.64(24)	174.18(17)	166.75(9)	166.55(9)	N(3)··· $Ln(1)$ – $O(11)$
$P(1a) \cdots Ln(1) \cdots P(3a)$	162.64(4)	162.30(4)	161.57(5)	158.16(5)	156.19(2)	156.02(2)	$P(1) \cdots Ln(1) \cdots P(3)$
O(10a)-Ln(1)-O(11a)	86.61(16)	87.06(16)	86.95(22)	97.50(18)	92.91(11)	92.90(10)	O(10)–Ln(1)–O(11)
O(10a)-Ln(1)-O(12a)	156.51(15)	156.58(15)	155.10(21)	157.67(20)	160.15(9)	159.80(8)	O(10)-Ln(1)-O(12)
O(11a)–Ln(1)–O(12a)	85.42(16)	85.83(16)	85.83(22)	90.37(18)	95.61(9)	95.94(8)	O(11)-Ln(1)-O(12)

Table 2 Selected bond lengths (Å), bond angles (°) and geometry between non-bonded atoms of  $Ln(NO_3)_3(Cy_3PO)_3$ 

(continued on next page)

	[Ln(Cy <sub>3</sub> PO) <sub>3</sub> (NO <sub>3</sub>	$_{3}$ , $_{3}$ $] \cdot 0.25 C_{2} H_{5} OH$	$[Ln(Cy_3PO)_3(N$	$[O_3)_3]$	$[Ln(Cy_3PO)_3($	NO <sub>3</sub> ) <sub>3</sub> ] · C <sub>2</sub> H <sub>5</sub> OH	
	La	PN	Eu	Er	Tm	Yb	
$N(3b) \cdot \cdot \cdot Ln(2) \cdot \cdot \cdot P(2b)$	161.83(17)	162.63(13)	163.55(18)	163.49(18)			
$N(1b) \cdots Ln(2) \cdots N(2b)$	172.42(17)	173.71(19)	174.28(20)	175.38(19)			
$N(1b) \cdots Ln(2) \cdots N(3b)$	101.69(19)	99.76(18)	98.11(22)	96.44(21)			
$N(2b) \cdots Ln(2) \cdots N(3b)$	84.98(19)	84.97(18)	86.11(22)	85.32(20)			
N(3b) - Ln(2) - O(11b)	160.92(19)	161.65(16)	162.51(23)	162.68(21)			
$P(1b) \cdots Ln(2) \cdots P(3b)$	159.10(5)	159.22(4)	159.73(5)	158.08(5)			
O(10b)-Ln(2)-O(11b)	87.17(15)	86.86(13)	86.79(19)	87.35(15)			
O(10b)-Ln(2)-O(12b)	156.47(15)	156.60(16)	155.86(20)	154.61(19)			
O(111b)-Ln(2)-O(12b)	91.87(17)	90.97(16)	90.11(24)	88.59(20)			



Fig. 1. The structure of one of the molecules of  $La(Cy_3PO)_3(\kappa^2-NO_3)_3$ . Thermal ellipsoids are drawn at the 50% probability level and cyclohexyl groups have been omitted for clarity.



Fig. 2. The structure of  $Tm(Cy_3PO)_3(\kappa^1-NO_3)(\kappa^2-NO_3)_2$ . Thermal ellipsoids are drawn at the 50% probability level and cyclohexyl groups have been omitted for clarity.

# 2.3. Electrospray mass spectrometry

The solution properties of the complexes were examined by electrospray mass spectrometry in methanol solution, and the data and assignments for the complexes studied are given in Table 3. Assignments are made on the basis of calculated m/z ratios, all of which are within 0.5 Da of the theoretical values and the observation of analogous

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Fig. 3. The variation in Ln–O distances with ionic radius of the lanthanide ion.

Table 3 The electrospray mass spectra<sup>a</sup> of  $Ln(NO_3)_3L_3$  in methanol/water

	$[Ln(NO_3)_2L_3]^2$	$[Ln(NO_3)L_4]^{2+}$	$[Ln(NO_3)L_3]^{2+}$	$[Ln(OH)L_4]^{2+}$	$[Ln(OMe)L_4]^{2+}$	$[Ln(OMe)L_3]^{2+}$
La	1151.6(<5)	692.9(10)	544.8(<5)	670.4(10)		529.3(20)
Nd	1156.6(15)	695.5(50)	547.3(10)	672.8(30)	679.8(15)	531.7(20)
Eu	1165.7(<5)	700.0(10)	501.0(<5)	677.5(<5)		536.3(10)
Gd	1170.6(5)	702.3(15)	554.0(5)	680.0(15)	686.5(5)	538.8(10)
Tb	1171.6(20)	703.2(75)	554.5(15)	680.7(65)	687.0(10)	539.5(40)
Но	1177.6(20)	705.9(50)	557.5(10)	683.4(45)	690.0(5)	542.3(25)
Tm	1181.6(20)	709.9(10)	559.5(5)	685.4(10)		544.4(20)
Yb	1186.7(25)	710.4(50)	562.2(15)	687.9(45)	694.8(<5)	546.8(20)
Tandem mass spectr	a					
Precursor ion	$[Ln(NO_3)_2L_3]^+$	$[Ln(NO_3)L_4]^{2+}$		$\left[\operatorname{Ln}(\operatorname{OH})\operatorname{L}_{4}\right]^{2+}$		$[Ln(OMe)L_3]^{2+}$
Fragment ion	$[Ln(NO_3)_2L_2]^+$	$[Ln(NO_3)L_3]^{2+}$		$\left[\operatorname{Ln}(\operatorname{OH})\operatorname{L}_{3}\right]^{2+}$		$[Ln(OMe)L_2]^2+$
La	855.1	544.6		522.1		380.8
Но	881.2	557.5		534.9		394.0
Yb	890.0	562.1		539.6		398.4 <sup>b</sup>

<sup>a</sup> m/z (relative intensity %).

<sup>b</sup> Significant fragmentation of this ion was observed as discussed in the text.

species for the series of complexes studied. In addition the theoretical isotope patterns give excellent agreement with those observed. An example for the  $[Gd(NO_3)_2L_3]^+$  ion is typical and shown in Fig. 4. The spectra all show strong signals from  $[L+H]^+$ ,  $[L+Na]^+$ ,  $[2L+H]^+$  whilst those from lanthanide containing ions indicate that the complexes undergo redistribution reactions in solution. Such redistribution reactions are common for lanthanide complexes and have previously been observed for  $\beta$ -diketonate [12] and a variety of phosphine oxide [13] complexes. Peaks from  $[Ln(NO_3)_2L_3]^+$  are observed for all complexes, often as low intensity clusters of signals. The main lanthanide containing signals are derived from loss of nitrate to give

 $[Ln(NO_3)L_3]^{2+}$  and from loss of nitrate and attachment of further ligand to give  $[Ln(NO_3)L_4]^{2+}$ . There appears to be no correlation between the abundance of +2 cations and the presence of the monodentate nitrates observed in the solid state structures. In addition to these processes solvolysis reactions are also apparent giving rise to intense signals assigned to  $[Ln(OH)L_4]^{2+}$ ,  $[Ln(OMe)L_3]^{2+}$  and  $[Ln(OMe)L_4]^{2+}$ . Such solvolysis processes have been observed in the spectra of lanthanide salts and complexes before [14] and are thought to be due to gas phase processes rather than reflecting the nature of solution species. The mass spectra of several of the complexes were recorded again after the solutions had aged for about three weeks



Fig. 4. Theoretical isotope pattern for  $[Gd(NO_3)_2L_3]^+$  (L = Cy<sub>3</sub>PO) and that observed in the positive ion electrospray mass spectrum.

and showed no significant differences with spectra obtained from fresh solutions. The positive ion ESMS of  $Ho(NO_3)_3L_3$  is representative of the spectra obtained and is shown in Fig. 5. Selected ions were also examined by tandem mass spectrometry to investigate their behaviour in the gas phase. The ions were chosen to represent species which might be expected initially to be present in solution namely



Fig. 5. The positive ion Electrospray mass spectrum of  $Ho(NO_3)_3L_3$  (L = Cy<sub>3</sub>PO) in methanol/water with principal assignments.

 $[Ln(NO_3)_2L_3]^+$  and  $[Ln(NO_3)L_4]^{2+}$  and also ions which are more likely to have been formed as part of the electrospray process such as  $[Ln(OH)L_4]^{2+}$  and  $[Ln(OMe)L_3]^{2+}$ . The lanthanum, holmium and ytterbium complexes were stud-

ied to represent the range of lanthanides. The tandem mass spectra of most of the ions are simple, showing loss of only one tricyclohexylphosphine oxide ligand for all ions studied. The exception to this was  $[Yb(OMe)L_3]^{2+}$  which





Fig. 7. A possible fragmentation pathway for  $[Yb(OMe)L_3]^{2+}$  (L = Cy<sub>3</sub>PO).

required a higher collision offset (COFF) to induce fragmentation similar to that of the La and Ho complex ions. Typical spectra for the La and Yb complexes are shown in Fig. 6. The Yb complex ion required COFF 50 eV, whilst the corresponding La and Ho ions yielded simple and meaningful fragment ions with COFF 30-40 eV. The stability of the Yb complex to loss of ligand is presumably due to the higher charge density on the metal ion. Under the harsher conditions required for its fragmentation a more complex spectrum was produced. This showed loss of Cy<sub>3</sub>PO with further fragmentation due to loss of MeO', cyclohexyl radicals and possibly cyclohexadiene. Loss of cyclohexene and cyclohexyl radicals under electron impact has been observed previously in the mass spectra of aromatic cyclohexyl ethers [15] and in  $Cy_2P(O)C_2H_4P(O)Cy_2$ [16] and whilst electrospray ionisation is generally less energetic, the application of higher COFF in the tandem mass spectra of the Yb complex presumably supplies sufficient energy for radical formation.

The loss of  $H_2$  from a 2+ charged ion was also apparent by the presence of peaks separated by one m/z unit. Fig. 7 illustrates a possible fragmentation pathway which accounts for the presence of the major ions observed. It must be noted that the mechanism is tentative. Cleavage of the Yb–OMe bond leading to loss of MeO<sup>•</sup> generates an Yb(II) fragment which may explain why whilst further decomposition of  $[Yb(OMe)L_2]^{2+}$  was observed the corresponding ion for La and Ho, for which the divalent states are less stable, does not undergo this decomposition.

# 3. Experimental

#### 3.1. Crystal structure determinations

Data were collected by the EPSRC National Crystallography Service at the University of Southampton using previously described procedures [17–19].

The positions of the metal atoms in the La and Yb structures were estimated by Patterson methods using shelxs-97 [20], and all remaining non-H atom positions were obtained through subsequent Fourier syntheses (shelxl97) [21]. Refinement was by full-matrix least-squares on  $F^2$  data using SHELXL-97 [21]. Solutions and all refinements were conducted using SHELX-97 from within the WinGX [22] suite of software.

The Nd, Eu and Er structures were each refined in space group  $P2_1$  after isomorphous replacement into the La structure. The Tm structure was solved by similar replacement into the Yb structure (space group  $Pc2_1n$ ) after re-indexing the data and transforming the unit cell axes from the alternative space group setting,  $Pbn2_1$  for which the data were collected. The asymmetric unit in each of the La–Er structures consisted of two discrete lanthanidecontaining molecules. The asymmetric units of the Tm and Yb structures each consisted of a single lanthanidecontaining molecule.

Attempts to refine the Er structure after initial substitution into the La structure showed the positions of the atoms of one of the bidentate nitrate groups in one of the two molecules to be unstable. After deletion of nitrate atoms, peaks were re-located in subsequent Fourier syntheses to build a stable model containing a monodentate nitrate group – consistent with the molecular structure observed in the Yb and Tm complexes.

In each of the structures, non-H atoms were refined anisotropically with the exception of the C atoms of one of the cyclohexyl groups in each of the La and Nd structures and two cyclohexyl groups in the Er structure. The initial, fully anisotropic, models of the La–Er structures displayed marked librational elongation of the thermal ellipsoids of the C-atoms in these groups, and their geometry deviated from that expected for the cyclohexyl moiety. A disordered, isotropic, model consisting of two alternative sites with complementary site occupation factors was adopted for the La, Nd, and Er structures. SIMU restraints were applied to C-atoms of the corresponding group in the Eu structure for which data were poorer.

An ethanol molecule was located near to one of the nitrate groups in each of the La, Nd, Tm and Yb structures. The site occupation factors of the solvent molecules in the La and Nd lattices were initially refined, and finally fixed at half occupancy. A similar solvent molecule was located in the Er structure apparently H-bonded to one of the bidentate nitrate groups. This site occupation factor of this solvent refined to <0.6%, and made little improvement to the figures of merit. It was excluded from the final structure. No similar solvent could be located in the difference Fourier maps of the Eu structure.

All H atoms were included in the refinements at idealised positions riding on the atoms to which they were bonded (methane C-H = 1.00 Å, methylene C-H = 0.99 Å, methyl C-H = 0.98 Å, O-H = 0.84 Å) The H-atoms of each functional group were assigned a single, refined isotropic displacement parameter, except those of solvent molecules which were assigned a common, refined isotropic displacement parameter.

The non-centrosymmetric structures refined to give Flack absolute structure parameters of -0.011(10), -0.014(8), -0.017(10), -0.020(7), -0.030(4) for the La, Nd, Eu, Er and Yb structures, respectively. The absolute structure of the Tm complex could not be unambiguously determined. ROTAX analysis [23] of the Tm data indicated merohedral or pseudo-merohedral twinning. The Tm structure refinement was repeated assuming racemic twinning by using the default TWIN setting in SHELXL-97 [21], and refinement converged to yield a batch scale factor of 0.520(5).

Molecular graphics were generated using SNOOPI [24]

#### 3.2. Mass spectrometry

Electrospray mass spectra were recorded on a either a Waters ZO-4000 or a Micromass Quattro II for the MS/ MS measurements. Samples in methanol solution were loop injected into a flow of 1:1 methanol: water running at 40µL/min into the electrospray capillary. Nebulisation was pneumatically assisted by a flow of  $N_{2(g)}$  at 15 L/min and a drying gas of  $N_{2(g)}$  at 100 L/min warmed by a source temperature of 80 °C. The spray voltage was 3.5 kV and the cone voltage varied between 20 V and 90 V depending on the mass and charge of the ions of interest. For tandem mass spectra,  $Ar_{(g)}$  at a pressure of  $2 \times 10^{-3}$  mbar was introduced into the collision chamber (termed quadrupole 2 or Q2); ions formed during the ES process and mass selected for individual analysis by the first quadrupole (Q1), were accelerated through this region of relatively high pressure by a voltage termed the collision offset (COFF). The COFF voltage was adjusted to obtain optimal fragmentation for each precursor ion, and the resulting fragment ions analysed by Q3.

# 3.3. Infrared spectroscopy

Infrared spectra were recorded in the range  $400-4000 \text{ cm}^{-1}$  on a Thermo Nicolet Avatar 370 instrument operating in ATR mode. Samples were analysed without pre-treatment other than crushing onto the optical surface.

#### 3.4. Synthesis and characterisation

Tricyclohexylphosphine oxide was prepared by oxidation of an acetone solution of tricyclohexylphosphine with 30% H<sub>2</sub>O<sub>2</sub>. In a typical preparation the phosphine (20.04 g) was suspended in 100 ml of acetone and hydrogen peroxide (9.00 g 30% aqueous solution) was added in portions allowing the vigorous reaction to subside before the next addition. The resulting clear solution was allowed to cool to room temperature and the resulting crystalline solid filtered, washed with a little cold acetone and dried at the pump to give 19.18 g of a waxy colourless solid. NMR (acetone)  $\delta^{31}$ P 51.6, literature 50.0 [25]  $v_{PO}$  1146 cm<sup>-1</sup>.

The nitrate complexes were prepared by mixing hot solutions of tricyclohexylphosphine oxide with the appropriate lanthanide nitrate in ethanol. On cooling crystals formed in 80–100% yield. Representative syntheses and characterisation are described below.

 $La(NO_3)_3(Cy_3PO)_3 \cdot 0.5EtOH$ . La(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O (0.23 g 0.55 mmol) in 10 ml hot ethanol was mixed with Cy<sub>3</sub>PO (0.71 g 2.4 mmol) in 10 ml hot ethanol. The resulting solution was warmed for 15 min during which time crystals began to form. The mixture was cooled to room temperature and allowed to stand overnight. The colourless crystals were filtered, washed with a small quantity of cold ethanol and dried at the pump to give 0.65 g (99%),  $v_{PO}$  1097 cm<sup>-1</sup>.

*Anal.* Calc. for La(NO<sub>3</sub>)<sub>3</sub>(Cy<sub>3</sub>PO)<sub>3</sub> · 0.5EtOH: C, 53.39; H, 8.31; N, 3.40. Found: C, 52.88; H, 8.20; N, 3.28%.

 $Nd(NO_3)_3(Cy_3PO)_3 \cdot 0.5EtOH.$  Nd(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (0.26 g 0.59 mmol) in 5 ml hot ethanol was mixed with Cy<sub>3</sub>PO (0.66 g 2.2 mmol) in 10 ml hot ethanol. The mixture was cooled to room temperature and allowed to stand overnight. The lilac crystals which formed were filtered, washed with a small quantity of cold ethanol and dried at the pump to give 0.65 g (99%),  $v_{PO}$  1099 cm<sup>-1</sup>.

*Anal.* Calc. for Nd(NO<sub>3</sub>)<sub>3</sub>(Cy<sub>3</sub>PO)<sub>3</sub> · 0.5EtOH: C, 53.16; H, 8.27; N, 3.38. Found: C, 52.63; H, 8.19; N, 3.32%.

 $Eu(NO_3)_3(Cy_3PO)_3$ . Eu(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (0.26 g 0.58 mmol) in 10 ml hot ethanol was mixed with Cy<sub>3</sub>PO (0.72 g 2.4 mmol) in 10 ml hot ethanol. The mixture was cooled to room temperature and allowed to stand overnight. The colourless crystals which formed were filtered, washed with a small quantity of cold ethanol and dried at the pump to give 0.63 g (88%)  $v_{PO}$  1102 cm<sup>-1</sup>.

*Anal.* Calc. for Eu(NO<sub>3</sub>)<sub>3</sub>(Cy<sub>3</sub>PO)<sub>3</sub>: C, 52.85; H, 8.13; N, 3.42. Found: C, 52.38; H, 8.15; N, 3.23%.

 $Tm(NO_3)_3(Cy_3PO)_3$ . Tm(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (0.24 g 0.52 mmol) in 5 ml hot ethanol was mixed with Cy<sub>3</sub>PO (0.62 g 2.0 mmol) in 10 ml hot ethanol. The mixture was cooled to room temperature and allowed to stand overnight. The colourless crystals which formed were filtered, washed with a small quantity of cold ethanol and dried at the pump to give 0.55 g (84%),  $v_{PO}$  1104 cm<sup>-1</sup>.

*Anal.* Calc. for M(NO<sub>3</sub>)<sub>3</sub>(Cy<sub>3</sub>PO)<sub>3</sub>: C, 52.13; H, 8.02; N, 3.38. Found: C, 52.05; H, 8.20; N, 3.15%.

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#### Appendix A. Supplementary material

CCDC 602138 to 602143 contain the supplementary crystallographic data for La to Yb. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallo-graphic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.06.023.

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