



Inner and outer sphere coordination of tricyclohexylphosphine oxide with lanthanide bromides



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ABSTRACT

Complexes of lanthanide bromides with tricyclohexylphosphine oxide (Cy₃PO) form three distinct structural classes. Type I complexes LnBr₃(Cy₃PO)₃ have been structurally characterised for Ln = La, Pr, Nd, Gd and Ho and are molecular 6 coordinate with a distorted meridional octahedral arrangement. Type II complexes are based on pentagonal bipyramidal [Ln(Cy₃PO)_n(H₂O)₅]³⁺ structures and fall into three subsets; *n* = 2 and 3 have been isolated for Ln = Lu and *n* = 4 with Ln = La, Dy, Er and Yb. The structures of [Lu(Cy₃PO)₂(H₂O)₅]Br₃·2EtOH and [Ln(Cy₃PO)₂(H₂O)₅]Br₃ (Ln = Dy, Er, Yb) have been determined. When *n* = 2 both ligands are directly coordinated to the metal whilst complexes in which *n* = 4 have two ligands bonded to the metal and two hydrogen bonded to the coordinated water molecules. Analysis of the bond distances shows that the lanthanide contraction accounts for about 99% of the observed trends. The infrared spectra of the complexes give a good means of identifying the structural types produced. ³¹P NMR show that the Type I complexes are fluxional in solution and that the Type II complexes undergo ligand exchange between metal and H-bonded ligands. Analysis of the lanthanide induced shifts indicates that the Type II complexes are isostructural in solution.

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1. Introduction

The coordination complexes formed between lanthanide metal ions and phosphine oxides have been studied since the late 1960s [1]. Continued interest in this area comes as a result of the use of phosphine oxides in the solvent extraction in nuclear fuels reprocessing [2]. The phosphine oxide ligands are normally bonded in the first coordination sphere of the lanthanide ions. There are, however, numerous reports of other ligands binding to lanthanide ions by hydrogen bonding to coordinated water molecules. Thus 18-crown-6 has been shown to bind to lanthanide nitrates either in the primary or secondary coordination sphere depending on the ionic radius of the metal [3]. Similarly linear polyethers form outer sphere complexes with heavier lanthanide nitrates (Ho–Lu) [4], whilst scandium chloride forms inner sphere complexes with a variety of crown ethers which on hydrolysis are converted to outer sphere complexes [5]. The outer sphere coordination of water to gadolinium has significance in the effectiveness of MRI

contrast agents [6]. Solution studies have shown a variety of coordination behaviours for bromo complexes of lanthanides in *N,N*-dimethylacetamide, *N,N*-dimethylformamide and their mixtures: inner and outer sphere coordination is observed dependent upon solvent composition [7]. In even concentrated solutions of perchlorate and halite ions only outer sphere coordination of the anion is observed [8].

Complexes between lanthanide chlorides and simple phosphine oxides have been reported and show the ligand to be directly bonded to the lanthanide metal as expected [9]. Although the corresponding complexes of lanthanide bromides and iodides are less well reported, similar *trans* octahedral [MX₂L₄]⁺ structures are formed with X = Br when L = Ph₃PO [10], [11] and with X = I when L = (Me₂N)₃PO [12]. We have previously shown that lanthanide chlorides do not give the expected type of complexes with the bulkier tricyclohexylphosphine oxide, Cy₃PO but rather form [Ln(Cy₃PO)₂(H₂O)₅](Cy₃PO)Cl₃ where the phosphine oxide binds in both the primary and secondary coordination sphere: LnCl₃L₃ complexes were not isolated [13]. Here we report the synthesis, structures and properties of a range of complexes of tricyclohexylphosphine oxide with lanthanide bromides.

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2. Results

2.1. Synthesis

Mixing 95% ethanol solutions of hydrated lanthanide bromides and tricyclohexylphosphine oxide at $\sim 70^\circ\text{C}$ led to the isolation of two distinct series of complexes. The bulk compositions $\text{LnBr}_3(\text{Cy}_3\text{PO})_3 \cdot 0.5\text{H}_2\text{O}$, designated as Type I, and $[\text{Ln}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5](\text{Cy}_3\text{PO})_n\text{Br}_3$, Type II have been confirmed by elemental analysis and by the structural determination of selected compounds by single crystal X-ray diffraction (discussed below). The Type I complexes can be crystallised for the lighter lanthanides La–Ho, albeit often as minor products, by cooling the reaction mixture to room temperature and standing overnight. Type II complexes $[\text{Ln}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5](\text{Cy}_3\text{PO})_2\text{Br}_3$ can be obtained for all the lanthanides on slow evaporation of the cooled solutions following filtration of any Type I complexes initially formed. With intermediate metal to ligand ratios it was in one instance possible to isolate different Type II complexes with $n = 2$ (Type IIa) and $n = 3$ (Type IIb). $[\text{Lu}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5]\text{Br}_3$ is less soluble in ethanol than $[\text{Lu}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5](\text{Cy}_3\text{PO})\text{Br}_3$ and both types of complex could be obtained by fractional crystallisation of the reaction mixture.

During slow evaporation of ethanol solutions of reaction mixtures containing the lighter lanthanides, the increasing concentration of water led to the isolation of complexes which have infrared spectra very similar to those of the crystallographically characterised $[\text{Ln}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5](\text{Cy}_3\text{PO})_2\text{Br}_3$. Thus the “cut off” between Type I and Type II structures cannot be considered to be a clean one; Type II complexes were obtained for La, Ce and Nd when reactions were carried out in dilute solutions necessitating a longer crystallisation time in an increasingly water rich environment. We have not, however, been able to prepare Type I complexes of the heavier lanthanides by reacting the bromides with tricyclohexylphosphine oxide in concentrated solution, these reactions led to the crystallisation of Type II complexes exclusively in good yield.

The tendency of the lighter lanthanides to form complexes with directly bonded bromide, whilst the heavier metals form hydrated complexes in preference, may be related to increased steric effects for the smaller lanthanides, but also to the structures of the hydrated bromides themselves [14], where 9-coordinate La and Ce, and 8-coordinate Pr–Dy have two bromides bonded to the metal whereas the smaller Ho–Lu ions are all 8-coordinate $[\text{Ln}(\text{OH}_2)_8]^{3+}$ in the solid state. Although caution must be exercised in correlating solid state structures with solution processes it seems possible here that the Type I complexes form by coordination to an LnBr_2^+ based cation whilst the formation of Type II proceeds via $[\text{Ln}(\text{OH}_2)_8]^{3+}$. The nature of the complexes which crystallise from solution also depends on the reaction conditions and may be strongly influenced by the solubilities of the complexes. Thus the isolation of $\text{LnBr}_3(\text{Cy}_3\text{PO})_3$ for the lighter lanthanides may be due to their lower solubility in the reaction media than similar complexes for the heavier metals, for which hydrated complexes only are isolated.

2.2. Infrared spectroscopy

The infrared spectra are typical of those expected for anhydrous or hydrated phosphine oxide complexes of lanthanides, and can be used to identify their structural type. The main features of the spectra are summarised in Table 1 for the crystallographically confirmed complexes. The P=O stretches show the expected shift to lower wavenumber on coordination to the metal ($\Delta\bar{\nu} \sim 60 - 70 \text{ cm}^{-1}$ or on hydrogen bonding to the coordinated water molecules ($\Delta\bar{\nu} \sim 40 \text{ cm}^{-1}$). The values for metal coordinated ligands are similar to those obtained for Cy_3PO complexes with lanthanide nitrates

Table 1

Infrared spectra of crystallographically confirmed structures of the lanthanide bromide complexes.

	Type I	Type IIa	Type IIb	L
ν_{OH}	3250(w)	3122(m)	3170–3180(m)	
ν_{CH}	2924(m), 2850(m)	2927(m), 2850(m)	2927(m), 2852(m)	2923(s),2850 (s)
δ_{OH}		1617(w)	1633(w)	
$\nu_{\text{P=O}}$	1088–1095(s), 1073(m)	1110(s)	1118(m) 1095– 1103(m)	1147(s), 1138(s)

[15] and the complexes $\text{CuCl}_2(\text{Cy}_3\text{PO})_2$ [16] and *cis*- $\text{Rh}(\text{CO})_2\text{Cl}(\text{Cy}_3\text{PO})$ [17]. The Type I complexes have a weak OH stretch due to lattice water and an intense PO stretch with a weaker absorption $15\text{--}20 \text{ cm}^{-1}$ lower, tentatively assigned to the “*trans*” and “*cis*” PO groups respectively on the basis of their relative intensities. The Type II complexes have a strong OH stretch due to the coordinated water, the position of which (below 3200 cm^{-1}) is typical of hydrogen bonded water molecules. These water molecules are H-bonded to either to bromide or to both bromide and phosphoryl groups. The complex $[\text{Lu}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5]\text{Br}_3$ gives a single PO stretch due to the mutually *trans* ligands whilst $[\text{Ln}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5](\text{Cy}_3\text{PO})_2\text{Br}_3$ show an additional peak about $15\text{--}20 \text{ cm}^{-1}$ higher due to the presence of the hydrogen bonded Cy_3PO ligands. The spectra of the two lutetium complexes clearly demonstrate the ease with which assignments can be made and are shown in Fig. 1. The smaller shift in $\nu_{\text{P=O}}$ for the H-bonded Cy_3PO implies a weaker interaction between the phosphoryl group when hydrogen bonding to the coordinated water. This is confirmed by X-ray crystallography described below which shows the lanthanide bound P=O bond to be more weakened than the H-bonded group. Hydrogen/deuterium exchange was carried out by recrystallization from MeOD in an attempt to further confirm the assignment, but apart from the large changes in ν_{OH} and δ_{OH} there was no discernible effect on the infrared spectrum.

2.3. Structures

The crystal structures have been determined for representative examples of the Type I and Type II complexes. Details of the data collection and refinement are given in Table 2 and selected bond distances and angles in Tables 3 and 4 for the Type I and II complexes respectively. The structures of Type I complexes have been determined for Ln = La, Pr, Nd, Gd and Ho. The lanthanum complex is anhydrous compared with the hemihydrate for the remaining

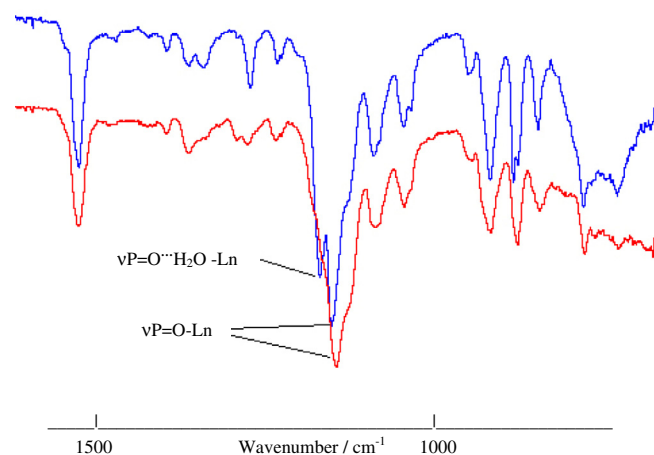


Fig. 1. The infrared spectra of $[\text{Lu}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5]\text{Br}_3$ (lower) and $[\text{Lu}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5](\text{Cy}_3\text{PO})_2\text{Br}_3$ (upper). The differences in $\nu_{\text{P=O}}$ are indicated.

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