



# Complexes of lanthanide chlorides with tricyclohexylphosphine oxide. The single crystal X-ray structures and solution properties of pentagonal bipyramidal complexes $[\text{Ln}(\text{H}_2\text{O})_5(\text{Cy}_3\text{PO})_2]^{3+} \cdot \text{Cy}_3\text{PO} \cdot 3\text{Cl}^-$ Ln = Dy, Er



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## ABSTRACT

The products of the reactions of tricyclohexylphosphine oxide,  $\text{Cy}_3\text{PO} = \text{L}$ , with lanthanide chlorides (Ln = La, Dy, Er, Yb) have been investigated by solution NMR spectroscopy and single crystal X-ray crystallography (Dy, Er). The structures of the complexes are based on a pentagonal bipyramidal arrangement around the central  $\text{Ln}^{3+}$  ion with two  $\text{Cy}_3\text{PO}$  in axial positions and five water molecules in the equatorial plane with molecular formulae  $\text{LnL}_n(\text{H}_2\text{O})_5 \cdot \text{L} \cdot 3\text{Cl} \cdot \text{H}_2\text{O} \cdot \text{EtOH}$ . An extensive H-bonding network links the remaining  $\text{Cy}_3\text{PO}$  and the chloride ions to the coordinated water molecules to form a polymeric unit. The variable temperature solution  $^{31}\text{P}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  and  $\text{CDCl}_3$  indicate that the solid state and solution structures are similar and that exchange between H-bonded and lanthanide bonded  $\text{Cy}_3\text{PO}$  occurs. This exchange is rapid for La but slower for the Er and Yb complexes. Differences in the spectra between the two solvents are discussed in terms of the polarity of the C–D bonds.

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## 1. Introduction

The coordination chemistry of lanthanide metal ions with phosphine oxides has a long history [1–3]. One of the main reasons for the continued interest in this chemistry lies in the use of phosphine oxides as extractants in nuclear fuels reprocessing [4,5]. There are numerous reports of complexes between lanthanide chlorides and simple phosphine oxides. These show  $\text{R}_3\text{PO}$  to be directly bonded to the lanthanide metal via the oxygen atom, as expected [6–8] with *trans*  $[\text{LnCl}_2(\text{Ph}_3\text{PO})_4]^+$  and *mer*  $[\text{LnCl}_3(\text{Ph}_3\text{PO})_3]$  being isolated depending on reaction conditions. Reaction of cerium (III) chloride with the less sterically demanding trimethylphosphine oxide leads to the isolation  $\text{CeCl}_3(\text{Me}_3\text{PO})_4(\text{H}_2\text{O})_4$  which contains an 8-coordinate  $[\text{Ce}(\text{Me}_3\text{PO})_4(\text{H}_2\text{O})_4]^{3+}$  ion [9]. Similarly there are numerous reports of ligands binding to lanthanide ions in their second coordination sphere by hydrogen bonding to coordinated water molecules. For instance coordination of 18-crown-6 to lanthanide nitrates is in the primary coordination sphere for the lighter lanthanides whilst heavier metals adopt structures in which the crown ether is hydrogen bonded to the  $\text{Ln}(\text{NO}_3)_3(\text{H}_2\text{O})_3$  moiety [10]. Similar behaviour has been reported for the coordination complexes of linear polyethers where heavier lanthanide nitrates (Ho–Lu) form outer sphere complexes [11], and whilst scandium chloride forms inner sphere complexes with a variety of crown

ethers, which on hydrolysis these are converted to outer sphere complexes [12]. Of particular importance is the outer sphere coordination of water which has significance in the effectiveness of gadolinium based MRI contrast agents [13–15]. Solution studies have been used to demonstrate a variety of coordination behaviours, with dimethylacetamide being bound in both the inner and outer coordination spheres depending on its concentration in solution [16] whilst the perchlorate and halite ions remain in the outer sphere of the lanthanide ions even at high concentrations [17]. The presence of both inner and outer sphere coordinated  $\text{Co}(\text{acac})_3$  in the solvent extraction of lanthanide ions also has been examined [18].

We report here the synthesis, structures and properties of complexes of tricyclohexylphosphine oxide with lanthanide chlorides which show unexpected structures with one of the phosphine oxide ligands hydrogen bonded to coordinated water, a bonding mode not previously reported for lanthanide complexes where the phosphine oxide is usually in the primary coordination sphere.

## 2. Results and discussion

The reactions of hydrated lanthanide chlorides with tricyclohexylphosphine oxide,  $\text{Cy}_3\text{PO} = \text{L}$  in ethanol led to the crystallisation of well defined complexes for the heavier lanthanides. The composition of the complexes depends on the ratio of reactants used in the synthesis with 1:2 complexes formed

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with low ligand to metal ratios and 1:3 complexes obtained at higher ratios. Complexes with four L were not obtained under the reaction conditions employed. Elemental analysis indicates the compounds are  $\text{LnL}_n(\text{H}_2\text{O})_5\text{Cl}_3 \cdot \text{H}_2\text{O} \cdot \text{EtOH}$  ( $\text{Ln} = \text{Dy}, \text{Yb}$  ( $n = 3$ ),  $\text{Er}$  ( $n = 2$ )), the value of  $n$  reflecting the reaction ratio in the preparation. Attempted preparation of similar complexes with the lighter lanthanides was of limited success and with lanthanum chloride a mixture was obtained consisting of  $\text{La}(\text{Cy}_3\text{PO})_3(\text{H}_2\text{O})_5\text{Cl}_3$  and  $\text{La}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5\text{Cl}_3$  in approximately 1:2 ratio based on the elemental analysis. No solid material could be obtained from reactions with  $\text{NdCl}_3$ .

Single crystal X-ray crystallography has been carried out on the Dy and Er complexes (see below). The crystal selected for analysis from the erbium complex was found to be based on  $\text{Er}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5\text{Cl}_3$  and is isostructural with the Dy complex. It is thus representative of the bulk sample for which the elemental analysis as  $\text{Er}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5\text{Cl}_3 \cdot \text{H}_2\text{O} \cdot \text{EtOH}$  was satisfactory. The infrared spectra of the isolated complexes show the bands expected for coordinated phosphine oxides with  $\nu_{\text{P=O}}$  between  $1102\text{--}1105\text{ cm}^{-1}$  compared to  $1158\text{ cm}^{-1}$  in the free ligand [19]. In addition to absorptions due to the cyclohexyl groups peaks characteristic of hydrogen bonded OH groups are clearly seen between  $3400$  and  $3130\text{ cm}^{-1}$ . The La and Yb complexes have infrared spectra which strongly resemble those of the Dy and Er complexes and it seems reasonable to suppose that the structures are similar.

The single crystal X-ray structures were determined for the Dy and Er complexes and the Er complex is shown in Fig. 1. Details of the data collection and refinement are shown in Table 1 and selected bond distances and angles in Table 2. The structures are unusual for this type of lanthanide complex in that they are not based on the *mer* – octahedral geometry observed for other  $\text{LnX}_3(\text{R}_3\text{PO})_3$  complexes [6–8].

The geometry is a slightly distorted pentagonal bipyramid in which two  $\text{Cy}_3\text{PO}$  groups occupy axial positions, five water molecules make up the equatorial plane and the third phosphine oxide is hydrogen bonded to the coordinated water molecules. All the O and Ln atoms lie within  $\pm 0.15\text{ \AA}$  of the equatorial plane defined by

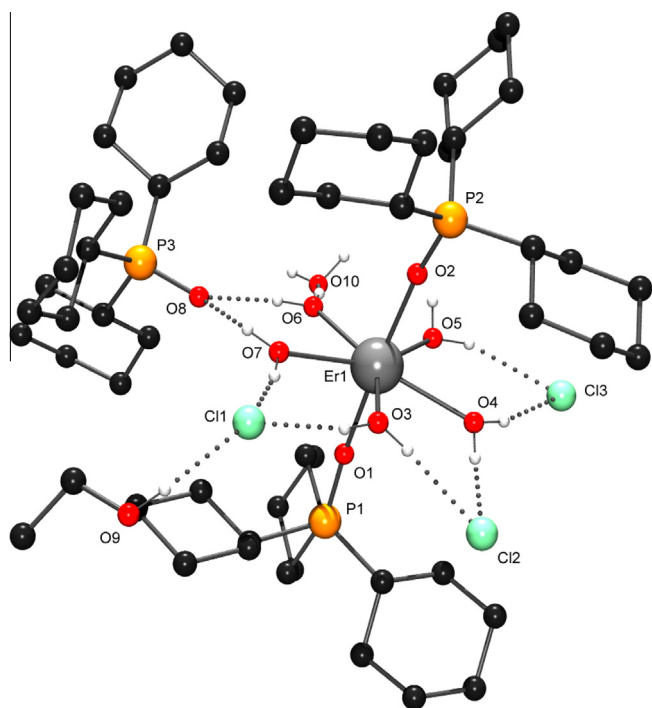


Fig. 1. The structure of  $\text{Er}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5(\text{Cy}_3\text{PO})_3\text{Cl} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$  (cyclohexyl, methylene and methyl H-atoms omitted for clarity).

the coordinated water molecules and the  $(\text{H}_2\text{O})\text{O} \cdot \text{Ln} \cdot \text{O}(\text{H}_2\text{O})$  angles range between  $69.3^\circ$  and  $74.7^\circ$  for both structures with an average of  $72.05^\circ$  Close to the ideal angle of  $72^\circ$ . Similarly the  $(\text{P})\text{O} \cdot \text{Ln} \cdot \text{O}(\text{H}_2\text{O})$  angles fall with an  $85.95\text{--}93.73^\circ$  range with the average again close to the  $90^\circ$  idea for a pentagonal bipyramid at  $90.03^\circ$  for both complexes.

The mean P–O distances at  $1.510\text{ \AA}$  (Dy) and  $1.518\text{ \AA}$  (Er) are essentially the same as observed previously in  $\text{Ln}(\text{NO}_3)_3(\text{Cy}_3\text{PO})_3$  complexes where the average of  $1.510(5)\text{ \AA}$  was found to be independent of the lanthanide [20]. These values are longer than those found in  $\text{Cy}_3\text{PO}$  itself where the P–O distances are about  $1.490\text{ \AA}$  [21]. It is interesting that the PO distance in the hydrogen bonded ligand is essentially the same as in the lanthanide bonded  $\text{Cy}_3\text{PO}$  molecules, suggesting that the  $\text{P}=\text{O} \cdot \text{Ln}$  and  $\text{P}=\text{O} \cdot \cdot \text{H}$  interactions are of similar strength. This is similar to our previous observation of the P=O bond distances in manganese and cobalt nitrate complexes of  $\text{Ph}_2\text{POC}_4\text{H}_8\text{POPh}_2$  where the bis-phosphine oxide which is hydrogen bonded to coordinated water molecules has slightly longer P=O distances [22].

An extensive hydrogen bonding network exists between all the coordinated water molecules, the chloride ions, the third  $\text{Cy}_3\text{PO}$  and lattice ethanol and water molecules.

Within the H-bonding network, pairs of complexes form dimers linked by coordinated water molecules H-bonded to chloride ion Cl3 about a rotational symmetry centre. These dimers are prevented from forming chains along the  $\text{Ln} \cdot \cdot \cdot \text{Cl3} \cdot \cdot \cdot \text{Ln}$  axis by termination of the H-bonding network with both chloride ion Cl1 (itself H-bonded to the lattice ethanol molecule) and the third  $\text{Cy}_3\text{PO}$  molecule. The dimers are linked into a continuous ladder motif along the crystallographic *a* axis by H-bonding between coordinated water molecules, the lattice water molecule (O10) and chloride ion Cl2. Fig. 2 shows the H-bonding network for the Dy complex.

The O  $\cdot \cdot \cdot$  O distances between the  $\text{Cy}_3\text{PO}$  and coordinated water are significantly smaller than the sum of Van der Waals radii for oxygen ( $3.04\text{ \AA}$ ) and are essentially the same for both complexes at  $2.62\text{ \AA}$ . Similarly the hydrogen bonded distances between the chloride ions and coordinated water molecules average at  $3.05$  and  $3.06\text{ \AA}$ , respectively for the Dy and Er complexes. These values are also shorter than the sum of Van der Waals radii of oxygen and chlorine ( $3.27\text{ \AA}$ ). The lattice  $\text{H}_2\text{O}$  is hydrogen bonded to only one of the coordinated water molecules with the  $\text{O}(10) \cdot \cdot \cdot \text{O}(6)$  distance of around  $2.6\text{ \AA}$  in both Dy and Er complexes. The lattice ethanol is more weakly H-bonded to Cl(1) with an  $\text{O}(9) \cdot \cdot \cdot \text{Cl}(1)$  distance just under  $3.2\text{ \AA}$  only slightly shorter than the sum of the Van der Waals radii.

The solid state  $^{31}\text{P}$  NMR spectrum of the solid obtained from the lanthanum reaction showed two peaks; a signal at  $59.3\text{ ppm}$  assigned to metal bound ligand and a lower intensity signal at  $62.1\text{ ppm}$  is assigned to hydrogen bonded  $\text{Cy}_3\text{PO}$ .

### 3. Solution properties

The behaviour of the complexes in solution was investigated by  $^{31}\text{P}$  NMR spectroscopy in both  $\text{CD}_2\text{Cl}_2$  and  $\text{CDCl}_3$ . The results are shown in Table 3. In  $\text{CD}_2\text{Cl}_2$  at room temperature the La complex shows a single broad resonance at  $60.7\text{ ppm}$  ( $W_{1/2} = 130\text{ Hz}$ ) indicative of rapid exchange between the two  $\text{Cy}_3\text{PO}$  environments in  $[\text{La}(\text{H}_2\text{O})_5\text{L}_3]^{3+}$  which is also in rapid exchange with  $[\text{La}(\text{H}_2\text{O})_5\text{L}_2]^{3+}$  on the NMR timescale. On cooling the solution of the La complex to  $-40^\circ\text{C}$  the line sharpens and two additional signals are seen which mimic the room temperature spectra of the Er and Yb complexes, discussed below. The dynamic exchange observed for the La complex probably is a result of the weaker bonding of  $\text{Cy}_3\text{PO}$  to the larger  $\text{La}^{3+}$  ion compared with the smaller Dy, Er and Yb centres. We

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