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Complexes of lanthanide chlorides with tricyclohexylphosphine oxide. The single crystal X-ray structures and solution properties of pentagonal bipyramidal complexes $[Ln(H_2O)_5(Cy_3PO)_2]^{3+} \cdot Cy_3PO \cdot 3Cl^-$ Ln = Dy, Er

The crystal structures of the complexes $Ln(Cy_3PO)_n(H_2O)_5 \cdot L \cdot 3Cl \cdot H_2O \cdot EtOH$ show a pentagonal bipyramidal geometry about the lanthanide ion.
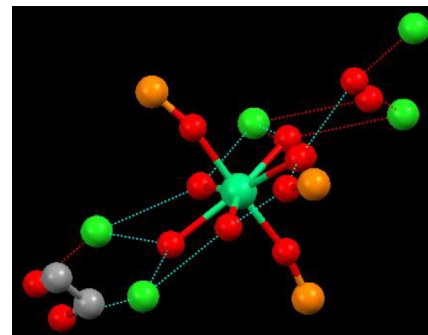
Complexes of lanthanide chlorides with tricyclohexylphosphine oxide. The single crystal X-ray structures and solution properties of pentagonal bipyramidal complexes $[Ln(H_2O)_5(Cy_3PO)_2]^{3+}\cdot Cy_3PO\cdot 3Cl^-$ Ln = Dy, Er

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ABSTRACT

The products of the reactions of tricyclohexylphosphine oxide, $Cy_3PO = L$, 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 Ln^{3+} ion with two Cy_3PO in axial positions and five water molecules in the equatorial plane with molecular formulae $LnL_n(H_2O)_5\cdot L\cdot 3Cl\cdot H_2O\cdot EtOH$. An extensive H-bonding network links the remaining Cy_3PO and the chloride ions to the coordinated water molecules to form a polymeric unit. The variable temperature solution ^{31}P NMR spectra in CD_2Cl_2 and $CDCl_3$ indicate that the solid state and solution structures are similar and that exchange between H-bonded and lanthanide bonded Cy_3PO 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 R_3PO to be directly bonded to the lanthanide metal via the oxygen atom, as expected [6–8] with *trans* $[LnCl_2(Ph_3PO)_4]^+$ and *mer* $[LnCl_3(Ph_3PO)_3]$ being isolated depending on reaction conditions. Reaction of cerium (III) chloride with the less sterically demanding trimethylphosphine oxide leads to the isolation $CeCl_3(Me_3PO)_4(H_2O)_4$ which contains an 8-coordinate $[Ce(Me_3PO)_4(H_2O)_4]^{3+}$ 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 $Ln(NO_3)_3(H_2O)_3$ 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 $Co(acac)_3$ 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, $Cy_3PO = L$ 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 with low ligand to metal ratios and 1:3 complexes obtained at higher ratios.

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Complexes with four L were not obtained under the reaction conditions employed. Elemental analysis indicates the compounds are $LnL_n(H_2O)_5Cl_3 \cdot H_2O \cdot EtOH$ (Ln = Dy, Yb (n = 3), 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 $La(Cy_3PO)_3(H_2O)_5Cl_3$ and $La(Cy_3PO)_2$ $(H_2O)_5Cl_3$ in approximately 1:2 ratio based on the elemental analysis. No solid material could be obtained from reactions with $NdCl_3$.

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 $Er(Cy_3PO)_3(H_2O)_5Cl_3$ and is isostructural with the Dy complex. It is thus is not representative of the bulk sample for which the elemental analysis as $Er(Cy_3PO)_2(H_2O)_5Cl_3 \cdot H_2O \cdot EtOH$ was satisfactory. The infrared spectra of the isolated complexes show the bands expected for coordinated phosphine oxides with v_{PO} between 1102–1105 cm^{-1} compared to 1158 cm^{-1} in the free ligand [19]. In additional to absorptions due to the cyclohexyl groups peaks characteristic of hydrogen bonded OH groups are clearly seen between 3400 and 3130 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 $LnX_3(R_3PO)_3$ complexes [6–8].

The geometry is a slightly distorted pentagonal bipyramid in which two Cy_3PO 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 ±0.15 Å of the equatorial plane defined by the coordinated water molecules and the $(H_2O)O-Ln-O(H_2O)$ angles range between 69.3° and 74.7° for both structures with an average of 72.05° Close to the ideal angle of 72°. Similarly the $(P)O-Ln-O(H_2O)$ angles fall with an 85.95–93.73° range with the average again close to the 90° idea for a pentagonal bipyramid at 90.03° both complexes.

The P–O distances at 1.510 Å (Dy) and 1.518 Å (Er) are essentially the same as observed previously in $Ln(NO_3)_3(Cy_3PO)_3$ complexes where the average of 1.510(5) Å was found to be independent of the lanthanide [20]. These value are longer than those found in Cy_3PO itself where the P–O distances are about 1.490 Å [21]. It is interesting that the PO distance in the hydrogen bonded ligand is essentially the same as in the lanthanide bonded Cy_3PO molecules, suggesting that the P=O–Ln and P=O···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 $Ph_2POC_4H_8POPh_2$ 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 Cy_3PO 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 Ln···Cl3···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 Cy_3PO 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···O distances between the Cy_3PO and coordinated water are significantly smaller than the sum of Van der Waals radii for oxygen (3.04 Å) and are essentially the same for both complexes at 2.62 Å. Similarly the hydrogen bonded distances between the chloride ions and coordinated water molecules average at 3.05 and 3.06 Å, 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 Å). The lattice H_2O is hydrogen bonded to only one of the coordinated water molecules with the O(10)···O(6) distance of around 2.6 Å in both Dy and Er complexes. The lattice ethanol is more weakly H-bonded to Cl(1) with an O(9)···Cl(1) distance just under 3.2 Å only slightly shorter than the sum of the Van der Waals radii.

The solid state ^{31}P NMR spectrum of the solid obtained from the lanthanum reaction showed two peaks; a signal at 59.3 ppm assigned to metal bound ligand and a lower intensity signal at 62.1 ppm is assigned to hydrogen bonded Cy_3PO.

3. Solution properties

The behaviour of the complexes in solution was investigated by ^{31}P NMR spectroscopy in both CD_2Cl_2 and $CDCl_3$. The results are shown in Table 3. In CD_2Cl_2 at room temperature the La complex shows a single broad resonance at 60.7 ppm ($W_{1/2}$ = 130 Hz) indicative of rapid exchange between the two Cy_3PO environments in $[La(H_2O)_5L_3]^{3+}$ which is also in rapid exchange with $[La(H_2O)_5L_2]^{3+}$ on the NMR timescale. On cooling the solution of the La complex to -40 °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 Cy_3PO to the larger La^{3+} ion compared with the smaller Dy, Er and Yb centres. We have previously observed similar lanthanide dependent fluxional behaviour in $Ln(NO_3)_3(R_3PO)_3$ complexes [20,23–25].
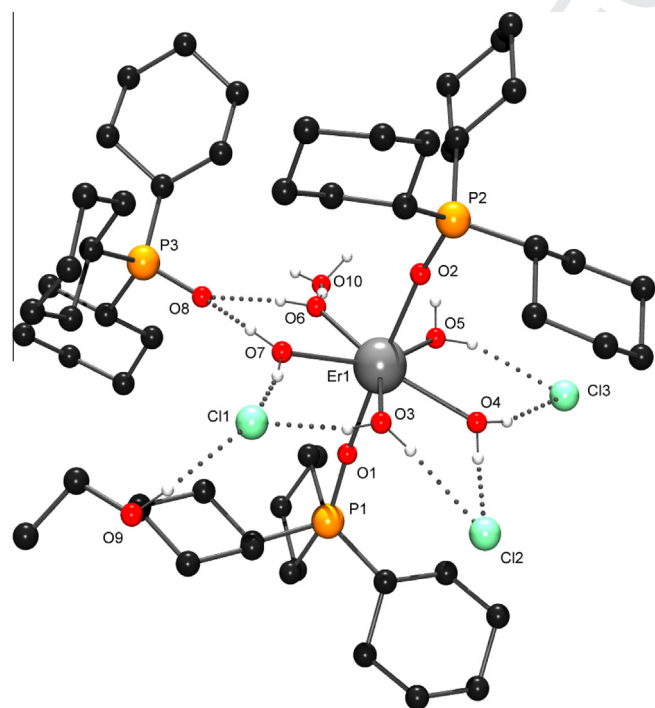

Fig. 1. The structure of $Er(Cy_3PO)_2(H_2O)_5 \cdot (Cy_3PO) \cdot 3Cl \cdot EtOH \cdot H_2O$ (cyclohexyl, methylene and methyl H-atoms omitted for clarity).

3

Table 1
Data collection and refinement.

Compound	[Dy(H₂O)₅(Cy₃PO)₂] (Cy₃PO)(H₂O)Cl₃·CH₃CH₂OH	[Er(H₂O)₅(Cy₃PO)₂] (Cy₃PO)(H₂O)Cl₃·CH₃CH₂OH
Crystal data		
Molecular formula	$C_{56}H_{117}Cl_3DyO_{10}P_3$	$C_{56}H_{117}Cl_3ErO_{10}P_3$
Molecular weight, M_r		
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	11.72450(10)	11.7738(6)
b (Å)	29.4136(4)	29.5356(16)
c (Å)	19.3908(2)	19.4461(9)
α (°)	90	90
β (°)	97.4860(10)	97.418(2)
γ (°)	90	90
Cell volume, U (Å³)	6630.11(13)	6705.7(6)
Formula units/unit cell, Z	4	4
Density (calc.), D_x (Mg m⁻³)	1.315	1.305
m (mm⁻¹)	1.370	1.492
$F(000)$	2780	2788
Reflections to obtain cell parameters	67912	51754
T (K)	120(2)	120(2)
Crystal description	rod	rod
	colourless	colourless
Dimensions (mm³)	0.03 × 0.07 × 0.26	0.14 × 0.04 × 0.04
θ (°)	2.92–27.54	2.95–25.00
Index ranges		
h	−15 → 15	−13 → 12
k	−36 → 38	−35 → 35
l	−25 → 25	−23 → 23
Measured reflections	82001	32561
Independent reflections (R_{int})	15195 (0.1022)	10594 (0.0748)
Data completeness	to θ = 27.54° 99.4%	to θ = 25.00° 89.9%
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
T_{max}/T_{min}	0.9601/0.7171	0.9427/0.8184
Refinement method	full matrix least squares on F^2	full matrix least squares on F^2
Data/restraints/parameters	15195/14/697	10594/103/697
Goodness-of-fit of F^2	1.046	1.152
Final R indices [$F_o > 2s(F_o)$]	$R_1 = 0.0486, wR_2 = 0.1184$	$R_1 = 0.1155, wR_2 = 0.2716$
R Indices [all data]	$R_1 = 0.0713, wR_2 = 0.1296$	$R_1 = 0.1329, wR_2 = 0.2913$
$(\Delta\sigma)_{max}$	0.002	0.002
Largest difference in peak and hole (e Å⁻³)	1.912 and −2.066	3.585 and −1.889
Absolute structure parameter	–	

The ambient temperature spectra of the other complexes show signals assigned to both the lanthanide bound and hydrogen bonded Cy₃PO groups, the latter being assigned on the basis of the larger paramagnetic shift from the position of Cy₃PO. The presence of two signals for the H-bonded ligands for the Er and Yb complexes can be explained by the possible formation of two species in solution which differ in their H-bonding patterns. Possible structures are indicated schematically in Fig. 3.

The appearance of the spectra in CDCl₃ is somewhat different. For example the Er complex shows a very broad time averaged signal at ambient temperature at 61.3 ppm ($W_{1/2}$ = 4 kHz) whilst the Yb complex shows a broadened signal at 12.9 ppm due to Cy₃PO–Yb and a sharper peak at 50.5 ppm due to the hydrogen bonded ligand. Heating the solution causes changes in the appearance of the spectra that would be expected from increasingly rapid exchange. Thus the spectra for the Er complex become relatively sharper with single peak at −41.4 ppm and $W_{1/2}$ = 960 Hz at 60 °C whilst for the Yb complex coalescence of the signals does not occur at 60 °C.

The difference in spectra between CD₂Cl₂ and CDCl₃ probably arises from the difference in hydrogen bonding capacity of the two solvents. Chloroform would be expected to disrupt the H-bonding in the complexes to a greater extent by virtue of the greater polarity of its C–D bond. The stronger H-bonding implied for the Yb complex compared to the Er analogue might be expected on the basis of the increased polarising power of the Yb³⁺ ion.

4. Experimental

4.1. Crystal structure determinations

Data were collected by the National Crystallography Service at the University of Southampton using previously described procedures [26–31].

Structures were solved using direct methods (SHELXS-97) [32,33]. All remaining non-H atom positions were obtained through subsequent fourier syntheses (SHELXL-97) [34], and refinement was by full-matrix least-squares on F^2 data using SHELXL-97 [34] from within the WinGX [35] suite of software.

In each of the structures, all non-H atoms were refined anisotropically. All ethanol and cyclohexyl H atoms were refined at calculated idealised positions using a riding model (methyl C–H = 0.98 Å, methylene C–H = 0.99 Å, methine C–H = 1.00 Å, O–H = 0.84 Å). The H atoms of water molecules were located close to their final positions, and restrained as necessary to give idealised H–O–H geometry. H atoms in each structure were assigned a common, refined, H atom isotropic displacement parameter.

The quality of the data for the Er structure was poor due to the crystal quality, and high angle data was incomplete. The R and weighted R factors in the final model were high. Adopting a fully anisotropic model, the thermal ellipsoids of the C atoms in some of the cyclohexyl rings displayed marked librational elongation suggesting overlapping disorder. An adequate disordered model

Table 2
Selected bond distances (Å) and angles (°) in [Ln(Cy₃PO)₂(H₂O)₅](Cy₃PO)(EtOH)(H₂O)Cl₃.

	Dy	Er
Ln(1)–O(1)	2.214(3)	2.208(10)
Ln(1)–O(2)	2.210(3)	2.207(10)
Ln(1)–O(3)	2.369(3)	2.353(9)
Ln(1)–O(4)	2.362(3)	2.358(10)
Ln(1)–O(5)	2.364(3)	2.338(10)
Ln(1)–O(6)	2.326(3)	2.327(10)
Ln(1)–O(7)	2.352(3)	2.345(11)
P(1)–O(1)	1.509(3)	1.521(11)
P(2)–O(2)	1.515(3)	1.517(11)
P(3)–O(8)	1.506(3)	1.517(11)
Ln(1)···P(1)	3.7013(10)	3.705(4)
Ln(1)···P(2)	3.6998(10)	3.701(4)
O(1)–Ln(1)–O(2)	175.63(10)	175.6(4)
O(1)–Ln(1)–O(3)	92.42(10)	92.3(4)
O(1)–Ln(1)–O(4)	85.96(10)	85.9(4)
O(1)–Ln(1)–O(5)	89.62(10)	88.9(4)
O(1)–Ln(1)–O(6)	86.70(11)	86.7(4)
O(1)–Ln(1)–O(7)	91.89(11)	91.8(4)
O(2)–Ln(1)–O(3)	90.16(10)	90.0(4)
O(2)–Ln(1)–O(4)	91.50(10)	91.3(4)
O(2)–Ln(1)–O(5)	86.27(10)	87.1(4)
O(2)–Ln(1)–O(6)	93.44(10)	93.7(4)
O(2)–Ln(1)–O(7)	92.32(11)	92.5(4)
O(3)–Ln(1)–O(4)	71.63(10)	72.1(4)
O(3)–Ln(1)–O(5)	145.65(10)	146.0(4)
O(3)–Ln(1)–O(6)	141.97(10)	141.8(4)
O(3)–Ln(1)–O(7)	69.50(10)	69.3(4)
O(4)–Ln(1)–O(5)	74.33(9)	74.1(4)
O(4)–Ln(1)–O(6)	145.91(10)	145.6(4)
O(4)–Ln(1)–O(7)	140.94(9)	141.2(3)
O(5)–Ln(1)–O(6)	72.38(10)	72.2(4)
O(5)–Ln(1)–O(7)	144.71(10)	144.7(4)
O(6)–Ln(1)–O(7)	72.52(10)	72.5(4)
P(1)–O(1)–Ln(1)	167.20(17)	167.1(6)
P(2)–O(2)–Ln(1)	166.44(17)	167.2(6)
Ln(1)–O(1)	2.214(3)	2.208(10)
Ln(1)–O(2)	2.210(3)	2.207(10)
Ln(1)–O(3)	2.369(3)	2.353(9)
Ln(1)–O(4)	2.362(3)	2.358(10)
Ln(1)–O(5)	2.364(3)	2.338(10)
Ln(1)–O(6)	2.326(3)	2.327(10)
Ln(1)–O(7)	2.352(3)	2.345(11)

could not be refined, so thermal and geometrical restraints (SIMU and DELU) were applied to maintain the cyclohexyl rings in a reasonable chair conformation.

Although precision was poor, we are confident in the characterisation, which shows the complex to be isostructural with the neighbouring Dy complex for which better quality data was obtained.

Molecular graphics were generated using ORTEP-3 [36].

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 951904 (Dy) and 951905 (Er). Copies of this information may be obtained free of charge from The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Infrared spectra were recorded with a resolution of ±2 cm⁻¹ on a Thermo Nicolet Avatar 370 FT-IR spectrometer operating in ATR mode. Samples were compressed onto the optical window and spectra recorded without further sample pre-treatment.

NMR spectra were recorded on a JEOL ECX 400 in CD_2Cl_2 or $CDCl_3$ solutions approximately 20 mg of complex dissolved in approximately 0.75 ml of solvent.

4.2. Synthesis

The same general procedure was adopted for the synthesis of all the complexes. The lanthanide chloride and tricyclohexylphosphine oxide were dissolved in hot ethanol. Heating was continued for 1 h and the solution was allowed to slowly evaporate at room temperature during which time crystalline material formed. The crystals were filtered, washed with cold ethanol and dried at the pump.

4.3. Mixture of [La(H₂O)₅(Cy₃PO)₃Cl₃][La(H₂O)₅(Cy₃PO)₃Cl₃]₂

Solutions of LaCl₃7H₂O (0.42 g 1.2 mmol) in 10 g EtOH and Cy₃PO (0.36 g 1.21 mmol) in 3.5 g EtOH were treated as above gave 0.33 g white powder.

Analysis for [La(H₂O)₅(Cy₃PO)₃Cl₃][La(H₂O)₅(Cy₃PO)₃Cl₃]₂ required (found) C 49.12 (49.16) H 8.54 (8.93); IR/cm⁻¹: 3297 (m, br) OH, 1636 (w, br) OH, 1102 (s) PO.
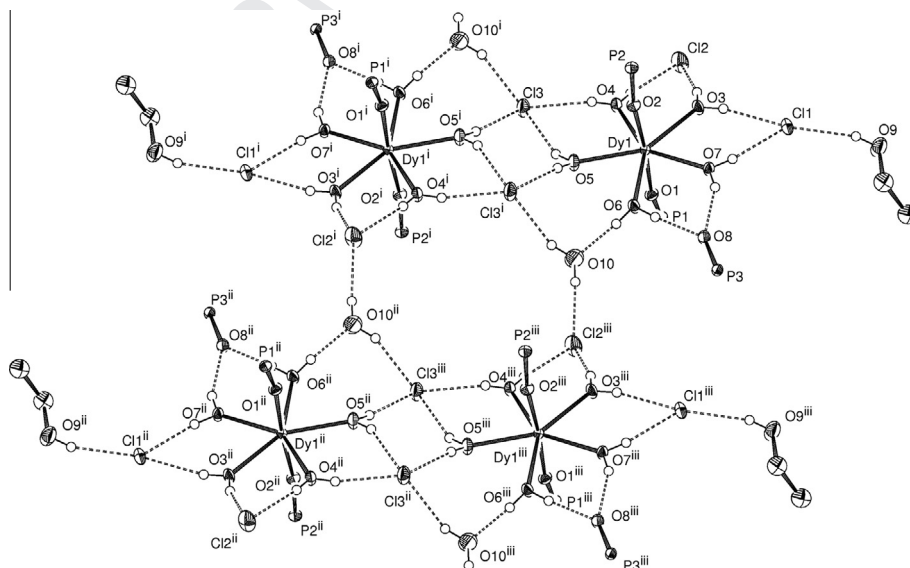
Fig. 2. The intra- and intermolecular hydrogen bonding network in Dy(Cy₃PO)₂(H₂O)₅·3Cl·EtOH·H₂O. Displacement ellipsoids are drawn at the 50% probability level. (Cyclohexyl groups and methyl and methylene H atoms omitted for clarity). [Symmetry codes: (i) 1 − x, −y, 1 − z; (ii) 1 + x, y, z; (iii) 2 − x, −y, 1 − z].

5

Table 3
Solution ^{31}P NMR data for $Ln(H_2O)_5(Cy_3PO)_2\cdot2Cy_3PO\cdot3Cl$.

Lanthanide Solvent	La[a]	Dy	Er		Yb	
	CD_2Cl_2	CD_2Cl_2	CD_2Cl_2	$CDCl_3$	CD_2Cl_2	$CDCl_3$
P=O–Ln	60.2	50.1	−82.7	−63.1	12.5	13.0
P=O–H₂O–Ln	61.5, 61.6	570.4	−14.1, 51.3		52.8, 74.7	50.5

[a] From a mixture of $Ln(H_2O)_5(Cy_3PO)_2\cdot2Cy_3PO\cdot3Cl$ and $Ln(H_2O)_5(Cy_3PO)_3\cdot2Cy_3PO\cdot3Cl$ at −40 °C.
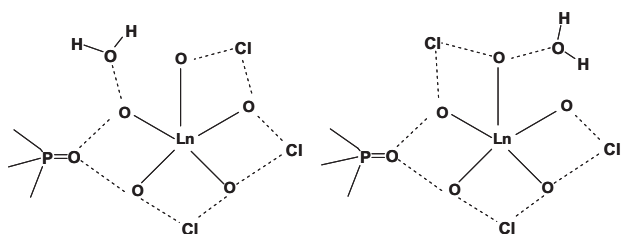
Fig. 3. Schematic representations of possible solution structures of the complexes viewed along the PO–Ln–OP axis.

4.4. [Dy(OH₂)₅(Cy₃PO)₃]·3Cl·H₂O·EtOH

Solutions of $DyCl_3 6H_2O$ (0.15 g 0.41 mmol) in 4.2 g EtOH and Cy_3PO (0.48 g, 1.62 mmol) in 3.8 g EtOH were treated as above gave 0.19 g (35%) crystals suitable for X-ray analysis. Analysis for [Dy(OH₂)₅(Cy₃PO)₃]·3Cl·H₂O·EtOH required (found) C51.25 (51.28) H 8.99 (8.79); IR/cm^{-1}: 3173 (m, br) OH, 1630 (w, br) OH, 1102 (s) 1081 (m) PO.

4.5. [Er(OH₂)₅(Cy₃PO)₂]·3Cl·2H₂O·EtOH

Solutions of $ErCl_3 6H_2O$ (0.25 g, 0.66 mmol) in 6.0 g EtOH and Cy_3PO (0.29 g, 0.96 mmol) in 4.8 g EtOH were treated as above gave 0.20 g (20%). Analysis for [Er(OH₂)₅(Cy₃PO)₂]·3Cl·2H₂O·EtOH required (found) C43.56 (43.61) H 8.12 (8.16); IR/cm^{-1} 3174 (m, br) OH, 1635 (w, br) OH, 1121 (m) 1105 (s) PO.

4.6. [Yb(OH₂)₅(Cy₃PO)₃]·3Cl·2H₂O·EtOH

Solutions of $YbCl_3 6H_2O$ (0.16 g, 0.40 mmol) in 4.8 g EtOH and Cy_3PO (0.43 g, 1.46 mmol) in 5.0 g EtOH were treated as above gave 0.29 g (54%). Analysis for [Yb(OH₂)₅(Cy₃PO)₃]·3Cl·2H₂O·EtOH required (found) C50.16 (49.93) H 8.95 (8.78); IR/cm^{-1} 3170 (m, br) OH, 1653 (w, br) OH, 1105 (s), 1100 (m) PO.

Acknowledgements

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