Molecular Interaction of Diaryl and Dicyclohexyl Phosphine Oxides with some Lanthanide(III) Chlorides

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Abstract

Lanthanide chlorides form six-coordinate octahedral adducts of the type $[LnCl_3(R_2P(O)H)_3]$ (where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy or Yb and R = C_6H_{11}, p-$CH_3C_6H_4$, p- or m-$CF_3C_6H_4$) when interacted with diaryl and dicyclohexyl phosphine oxides in dry ethanol. Complexes were recrystallised from n-hexane and on the basis of elemental analysis, infrared, and ^{31}P NMR spectral studies, it is concluded that these phosphine oxides coordinate to the lanthanide metal atom through the oxygen atom which shows the greatest affinity for lanthanides in these adducts.

Introduction

The coordination chemistry of the lanthanides has been extensively studied and is the subject of various reviews [1–3]. Although lanthanides form very stable chelate complexes with multidentate ligands, few less-stable complexes with monodentate have been reported [4]. This situation is characteristic of metals which form labile complexes, whilst among the more inert complexes formed by such acceptors as Pt(IV) or Co(III) are many containing monodentate ligands. In the case of lanthanides this behaviour arises from the thermodynamic instability of the complexes relative to the hydrated ion, coupled with their kinetic instability. However, this does not mean that lanthanide complexes are weak in the sense of having a low metal–ligand bond energy. No numerical values for the latter quantity have been determined, but observed thermal stabilities of solid complexes are often very high and constitute strong evidence for the existence of a fairly high bond energy. Complexes of a monodentate ligand should provide a flexible system for the study of preferred coordination number and its variations along the lanthanide series and of dissociative equilibria.

Phosphine oxides are suitable uncharged ligands for such studies because the ligand atom is oxygen, for which element the lanthanides are experimentally found to show their greatest affinity, and moderately high electric charge separation along the P–O bond will tend to increase metal ligand bond strength.

It was considered of interest to synthesise the lanthanide chloride complexes of diaryl and dicyclohexyl phosphine oxides, because these have not been reported in the literature although complexes of the type $[EuCl_3(OPPh_3)_3]$, $[Ln(NO_3)_3(OPPh_3)_3]$ with triphenylphosphine oxides have been reported [5–7], in which three oxygen atoms coordinate to the lanthanide atom. These phosphine oxide complexes of lanthanides find application in the solvent extraction of lanthanides [8–10].

Experimental

All-glass apparatus with standard quickfit joints was used throughout the experiments. Strict precautions were taken to exclude moisture.

Reagents

Lanthanide chlorides of 99.9% metal purity, obtained from M/s Indian Rare Earth Ltd., were used without purification. Anhydrous lanthanide chlorides were acquired by heating under a continuous stream of hydrogen chloride gas. The diaryl and dicyclohexylphosphine oxides were prepared as previously described [11, 12].

Ethanol was dried and purified by the standard method.

The IR spectra were recorded on a Perkin–Elmer 621 spectrophotometer using nujol mulls or KBr pellets. The ^{31}P NMR spectral data were recorded on Bruker WP-60 and Jeol FX-100 instruments. Chemical shifts, δ, are reported to the high frequency of external H_3PO_4.

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Analysis

The complexes were analysed for their metal and chloride parts. The metal content was estimated by the oxalate–oxide method and chloride was estimated as AgCl.

Preparation of Trichlorotris(di-cyclohexylphosphine oxide)lanthanum(III)

A boiling ethanolic solution (15 ml) of anhydrous lanthanum chloride (0.24 g) was added to a boiling ethanolic solution (10 ml) of dicyclohexylphosphine oxide (0.64 g) and the mixture was refluxed in an oil bath at 90 ℃ for six hours. The complex is extremely soluble in ethanol and was dried at 70 ℃ and 0.5 mmHg for 3 h. A solid complex was thus obtained and recrystallised from n-hexane. The yield was 70%. The corresponding Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb complexes were also prepared by the same method (Table I).

Preparation of Trichlorotris(di-paratolylphosphine oxide)lanthanum(III)

Di-*para*tolylphosphine oxide (0.21 g) dissolved in 20 ml of warm ethanol was added to a boiling ethanolic solution (20 ml) of anhydrous lanthanide chloride. Small colourless crystals appeared. The mixture was refluxed for 6 h in an oil bath at 90 ℃. The compound was then dried at 70 ℃ at 0.5 mmHg pressure for 5 h. The compound was recrystallised from hot n-hexane. The corresponding Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb complexes were also prepared by the same method (Table I).

Preparation of Trichlorotris(di-metatrifluorotolylphospine oxide)lanthanum(III)

Anhydrous lanthanum chloride (0.12 g) dissolved in 15 ml of warm ethanol was added to a warm ethanolic solution (20 ml) of trifluorotolylphosphine oxide (0.50 g). The clear solution was refluxed for eight h, when a few white crystals appeared. The complex was dried at 80 ℃ and at 0.5 mmHg pressure for 3 h. The complex was recrystallized from hot n-hexane. The Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb complexes were also prepared by the same method (Table I).

Synthesis of Trichlorotris(di-paratrifluorotolylphosphine oxide)lanthanum(III)

Anhydrous lanthanum chloride (0.10 g) dissolved in 20 ml of warm ethanol was added to a warm ethanolic solution (15 ml) of paratrifluorotolylphosphine oxide (0.41 g). The clear solution was refluxed for eight h, when a few white crystals appeared. The complex was dried at 80 ℃ and 0.5 mmHg pressure for 4 h. The complex was recrystallised from hot n-hexane. The Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb complexes were also prepared by the same method (Table I).

Results and Discussion

A boiling ethanolic solution of anhydrous lanthanum chloride was treated with excess of diaryl or dicyclohexyl phosphine oxides $R_2P(O)H$ (where $R = C_6H_{11}$, p-$CH_3C_6H_4$, p- or m-$CF_3C_6H_4$) in boiling ethanol and then refluxed for a few hours. The solvent was then removed under reduced pressure and the residue was recrystallised from n-hexane to give complexes of the type $[LnCl_3(R_2P(O)H)_3]$. The reaction can be shown as:

$$\underset{}{LnCl_3} + \underset{\text{(Excess)}}{R_2P(O)H} \longrightarrow [LnCl_3(R_2P(O)H)_3]$$

(where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy or Yb and $R = C_6H_{11}$, p-$CH_3C_6H_4$, p- or m-$CF_3C_6H_4$)

All these complexes are high melting solids (colour of the complexes is given in experimental section) soluble in ethanol and sparingly soluble in benzene and hexane.

Infrared Spectral Studies

Due to the strong a-character of the lanthanide(III) ions, the coordination of the secondary phosphine oxide group occurs via the oxygen of the P → O moiety. There is no evidence for the formation of phosphide complexes as no evolution of HCl was observed during the reaction. In most cases the P → O stretch of $R_2P(O)H$ frequency is found to occur at ~1165–1170 cm^{-1}. Coordination of $R_2P(O)H$ with metal ions via oxygen of the PO group has the effect of lowering the PO stretching frequencies. The stronger the M–O bond, the weaker the P–O bond and hence the lowering of its stretching frequency.

A decrease of the PO stretching frequency by about 25–40 cm^{-1} has been observed (Table II) in these complexes. This observation agrees well with the reported decrease of the P–O frequency in hexamethylphosphoramide complexes of lanthanide nitrates [13]. The P–H stretching frequency was found to be very weak and no appreciable shift was observed. It has also been observed that there is a slight increase in the ν(P–O) with decreasing lanthanide ion radius for these complexes. A similar trend has also been reported [6, 14] in the case of lanthanide complexes with triphenylphosphine oxide. This is due to an increase in the Ln–O bond strength with an increase in the atomic number of the lanthanide ions. This trend is also explained on the basis of the relative influence of attractive and repulsive forces in these complexes. As the size of the lanthanide ion decreases, the repulsive forces increase more rapidly than do the attractive forces. The Ln–O bond becomes gradually weaker and the P–O bond becomes progressively stronger, as indicated by the increase in ν(P–O).

TABLE I. Experimental and Analytical Data for the Diaryl and Dicyclohexyl Phosphine Oxide Complexes of Lanthanons.

Reagent		Molar ratio	Refluxing time	Product	Analysis: Found (Calcd) %	
					Metal	Chloride
$LaCl_3$	0.24 g	1:3	6	$[LaCl_3(DCHPO)_3]$	15.50	11.80
DCHPO	0.64 g			White solid	(15.60)	(11.90)
Ethanol	20 ml					
$PrCl_3$	0.14 g	1:3	7	$[PrCl_3(DCHPO)_3]$	15.60	11.76
DCHPO	0.37 g			Pale green solid	(15.70)	(11.90)
Ethanol	20 ml					
$NdCl_3$	0.11 g	1:3	7	$[NdCl_3(DCHPO)_3]$	16.10	11.76
DCHPO	0.28 g			Light blue solid	(16.00)	(11.80)
Ethanol	20 ml					
$SmCl_3$	0.24 g	1:3	7	$[SmCl_3(DCHPO)_3]$	16.64	11.69
DCHPO	0.61 g			Pale yellow solid	(16.70)	(11.80)
Ethanol	30 ml					
$EuCl_3$	0.20 g	1:3	8	$[EuCl_3(DCHPO)_3]$	16.79	11.80
DCHPO	0.50 g			White solid	(16.80)	(11.70)
Ethanol	20 ml					
$GdCl_3$	0.20 g	1:3	8	$[GdCl_3(DCHPO)_3]$	17.30	11.60
DCHPO	0.49 g			White solid	(17.30)	(11.50)
Ethanol	20 ml					
$TbCl_3$	0.36 g	1:3	8	$[TbCl_3(DCHPO)_3]$	17.38	11.60
DCHPO	0.89 g			White solid	(17.40)	(11.60)
Ethanol	30 ml					
$DyCl_3$	0.34 g	1:3	9	$[DyCl_3(DCHPO)_3]$	17.72	11.58
DCHPO	0.82 g			White solid	(17.72)	(11.59)
Ethanol	20 ml					
$YbCl_3$	0.10 g	1:3	9	$[YbCl_3(DCHPO)_3]$	18.80	11.48
DCHPO	0.24 g			White solid	(18.70)	(11.50)
Ethanol	20 ml					
$LaCl_3$	0.21 g	1:3	7	$[LaCl_3(DPTPO)_3]$	14.80	11.60
DPTPO	0.60 g			White solid	(14.80)	(11.40)
Ethanol	20 ml					
$PrCl_3$	0.15 g	1:3	7	$[PrCl_3(DPTPO)_3]$	15.00	11.36
DPTPO	0.42 g			Light green solid	(15.10)	(11.40)
Ethanol	25 ml					
$NdCl_3$	0.13 g	1:3	7	$[NdCl_3(DPTPO)_3]$	15.26	11.30
DPTPO	0.36 g			Light blue solid	(15.30)	(11.30)
Ethanol	20 ml					
$SmCl_3$	0.25 g	1:3	7	$[SmCl_3(DPTPO)_3]$	15.88	11.19
DPTPO	0.67 g			Pale yellow solid	(15.90)	(11.20)
Ethanol	30 ml					
$EuCl_3$	0.22 g	1:3	8	$[EuCl_3(DPTPO)_3]$	15.89	11.20
DPTPO	0.56 g			White solid	(16.00)	(11.20)
Ethanol	30 ml					
$GdCl_3$	0.26 g	1:3	8	$[GdCl_3(DPTPO)_3]$	16.49	11.10
DPTPO	0.67 g			White solid	(16.50)	(11.00)
Ethanol	20 ml					
$TbCl_3$	0.21 g	1:3	9	$[TbCl_3(DPTPO)_3]$	16.59	11.20
DPTPO	0.55 g			White solid	(16.60)	(11.12)
Ethanol	20 ml					

(Continued overleaf)

TABLE I. *(Continued)*

$DyCl_3$	0.30 g	1:3	9	$[DyCl_3(DPTPO)_3]$	16.95	11.08
DPTPO	0.77 g			White solid	(16.95)	(11.09)
Ethanol	25 ml					
$YbCl_3$	0.21 g	1:3	9	$[YbCl_3(DPTPO)_3]$	17.88	11.10
DPTPO	0.55 g			White solid	(17.91)	(11.11)
Ethanol	20 ml					
$LaCl_3$	0.10 g	1:3	8	$[LaCl_3(DPTFTPO)_3]$	11.03	8.60
DPTFTPO	0.41 g			White solid	(11.00)	(8.50)
Ethanol	15 ml					
$PrCl_3$	0.12 g	1:3	8	$[PrCl_3(DPTFTPO)_3]$	11.20	8.23
DPTFTPO	0.49 g			Pale green solid	(11.12)	(8.24)
Ethanol	15 ml					
$NdCl_3$	0.11 g	1:3	8	$[NdCl_3(DPTFTPO)_3]$	11.50	8.50
DPTFTPO	0.44 g			Pale yellow solid	(11.40)	(8.40)
Ethanol	15 ml					
$SmCl_3$	0.13 g	1:3	9	$[SmCl_3(DPTFTPO)_3]$	12.20	8.03
DPTFTPO	0.50 g			Pale yellow solid	(12.30)	(8.04)
Ethanol	15 ml					
$EuCl_3$	0.11 g	1:3	9	$[EuCl_3(DPTFTPO)_3]$	12.20	8.30
DPTFTPO	0.43 g			White solid	(12.01)	(8.40)
Ethanol	20 ml					
$GdCl_3$	0.13 g	1:3	9	$[GdCl_3(DPTFTPO)_3]$	12.29	8.29
DPTFTPO	0.98 g			White solid	(12.30)	(8.30)
Ethanol	15 ml					
$TbCl_3$	0.13 g	1:3	9	$[TbCl_3(DPTFTPO)_3]$	12.38	8.40
DPTFTPO	0.50 g			White solid	(12.40)	(8.32)
Ethanol	20 ml					
$DyCl_3$	0.20 g	1:3	9	$[DyCl_3(DPTFTPO)_3]$	12.67	8.29
DPTFTPO	0.98 g			White solid	(12.67)	(8.29)
Ethanol	20 ml					
$YbCl_3$	0.26 g	1:3	10	$[YbCl_3(DPTFTPO)_3]$	13.36	8.21
DPTFTPO	0.94 g			White solid	(13.40)	(8.20)
Ethanol	20 ml					
$LaCl_3$	0.12 g	1:3	8	$[LaCl_3(DMTFTPO)_3]$	11.01	8.51
DMTFTPO	0.50 g			White solid	(11.01)	(8.50)
Ethanol	20 ml					
$PrCl_3$	0.10 g	1:3	8	$[PrCl_3(DMTFTPO)_3]$	11.10	8.38
DMTFTPO	0.40 g			Light green solid	(11.10)	(8.43)
Ethanol	20 ml					
$NdCl_3$	0.14 g	1:3	8	$[NdCl_3(DMTFTPO)_3]$	11.40	8.41
DMTFTPO	0.56 g			Light blue solid	(11.40)	(8.40)
Ethanol	20 ml					
$SmCl_3$	0.14 g	1:3	9	$[SmCl_3(DMTFTPO)_3]$	12.38	8.36
DMTFTPO	0.54 g			Pale yellow solid	(12.41)	(8.41)
Ethanol	20 ml					
$GdCl_3$	0.26 g	1:3	10	$[GdCl_3(DMTFTPO)_3]$	12.30	8.27
DMTFTPO	0.99 g			White solid	(12.30)	(8.30)
Ethanol	30 ml					
$EuCl_3$	0.16 g	1:3	9	$[EuCl_3(DMTFTPO)_3]$	12.21	8.39
DMTFTPO	0.57 g			White solid	(12.10)	(8.42)
Ethanol	25 ml					

(Continued on facing page)

TABLE I. *(Continued)*

$TbCl_3$ DMTFTPO Ethanol	0.12 g 0.47 g 20 ml	1:3	9	$[TbCl_3(DMTFTPO)_3]$ White solid	12.36 (12.41)	8.41 (8.32)
$DyCl_3$ DMTFTPO Ethanol	0.27 g 1.02 g 25 ml	1:3	9	$[DyCl_3(DMTFTPO)_3]$ White solid	12.67 (12.67)	8.29 (8.29)
$YbCl_3$ DMTFTPO Ethanol	0.13 g 0.40 g 20 ml	1:3	10	$[YbCl_3(DMTFTPO)_3]$ White solid	13.36 (13.41)	8.20 (8.20)

TABLE II. IR Absorption Spectral Bands of Complexes of the Type $[LnCl_3(R_2P(O)H)_3]$.

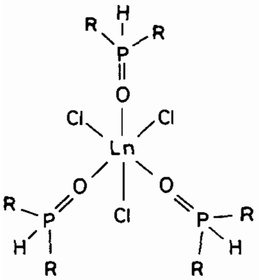
Compound	$(p\text{-}CH_3C_6H_4)_2P(O)H$ (P=O) = 1165	$(m\text{-}CF_3C_6H_4)_2P(O)H$ (P=O) = 1170	$(p\text{-}CF_3C_6H_4)_3P(O)H$ (P=O) = 1170	$C_6H_{11}P(O)H$ (P=O) = 1165
$LaCl_3L_3$	1135	1140	1135	1140
$PrCl_3L_3$	1135	1140	1130	1140
$NdCl_3L_3$	1135	1140	1130	1135
$SmCl_3L_3$	1135	1145	1130	1135
$GdCl_3L_3$	1140	1145	1135	1140
$EuCl_3L_3$	1140	1145	1140	1145
$TbCl_3L_3$	1140	1145	1140	1145
$DyCl_3L_3$	1140	1145	1140	1145
$YbCl_3L_3$	1140	1145	1140	1145

TABLE III. ^{31}P NMR Data of the Lanthanide–Phosphine Oxide Complexes.

Compound	$(p\text{-}CH_3C_6H_4)_2P(O)H$ 21.98	$(m\text{-}CF_3C_6H_4)_2P(O)H$ 17.98	$(p\text{-}CF_3C_6H_4)_2P(O)H$ 19.55	$(C_6H_{11})P(O)H$ 49.45
$LaCl_3L_3$	24.40	18.99	26.89	54.50
$PrCl_3L_3$	53.7 (Broad)	36.38 (Broad)	62.12 (Broad)	105.84 (Broad)
$NdCl_3L_3$	47.64 (Broad)	39.70 (Broad)		111.77 (Broad)
$SmCl_3L_3$	25.13	31.85	18.71	55.08
$GdCl_3L_3$	24.48	21.30	27.49	58.20
$EuCl_3L_3$			26.52	
$TbCl_3L_3$		19.01		56.19
$DyCl_3L_3$	21.13		27.0	
$YbCl_3L_3$	18.69	23.12	26.95	52.11

^{31}*P NMR Spectra*

The ^{31}P NMR spectra of the complexes were obtained in $CDCl_3$. The diamagnetic lanthanum complexes $[LaCl_3L_3]$ ($L = (C_6H_{11})_2P(O)H, p\text{-}CH_3C_6H_4)_2\text{-}P(O)H$, $(p\text{-}CF_3C_6H_4)_2P(O)H$, $(m\text{-}CF_3C_6H_4)_2P(O)H$ give singlets shifted to high frequencies of the resonances when compared with the free ligands, by about 1–6 ppm. This change in the chemical shift on coordination is much less than that normally observed if a phosphorus atom is directly bonded to the metal atom, indicating that the ligands are bonded through the oxygen atom. For the remaining complexes which are paramagnetic, signals are observed in most cases although some are considerably broadened. For the Pr and Nd complexes large downfield shifts of 18–60 ppm are observed with considerable broadening of the signals. The remaining complexes showed only small downfield shifts (Table III). On the basis of above studies the following structure may tentatively be assigned to these adducts:



(where Ln = La, Pr, Nd, Sm, Gd, Eu, Tb, Dy or Yb and L = C_6H_{11}, *p*-$CH_3C_6H_4$, *p*- or *m*-$CF_3C_6H_4$).

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