

Diethyl and Diisopropyl Phosphite Complexes of Lanthanide(III) Chlorides

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(Received May 15, 1986; revised August 21, 1986)

Abstract

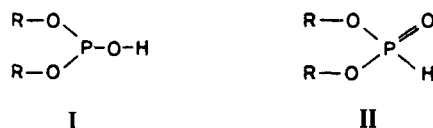
Lanthanide chlorides form adducts of the type $[\text{Ln}(\text{L})_n\text{Cl}_3]$ (where $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$, when $n = 6$; and $\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$ or Yb when $n = 5$; and $\text{L} = (\text{EtO})_2\text{P}(\text{O})\text{H}$ or $(\text{Pr}^i\text{O})_2\text{P}(\text{O})\text{H}$) upon interacting with the diethyl and diisopropyl phosphites in dry ethyl and isopropyl alcohol, respectively. Complexes were recrystallised from ethanol or isopropanol and washed with *n*-hexane. On the basis of elemental analysis, infrared, ^1H NMR and ^{31}P NMR spectral studies, it is concluded that these phosphites coordinate to the lanthanide metal atom through the oxygen atom which has the greatest affinity for lanthanides in these adducts.

Introduction

The ionic radii of the lanthanide ions are rather large and give rise to complexes with coordination numbers higher than those generally found in transition metals. In lanthanide complexes, the coordination number eight is common, but coordination numbers nine to twelve have also been observed in a few cases when suitable ligands are employed [1–5]. Observations indicate that bulkier or more basic ligands can stabilize complexes with low ligand:metal ratios. As the electronegativity, or size of the ligand increases, the ligand–ligand repulsions become more effective on heavy lanthanide ions as the size of the tripositive lanthanide ion decreases from $\text{La}(\text{III})$ to $\text{Lu}(\text{III})$.

In a previous publication [6] we have reported our studies on the reactions of diaryl and dialkyl phosphite oxides ($\text{R}_2\text{P}(\text{O})\text{H}$) ($\text{R} = \text{C}_6\text{H}_{11}$, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, *p*- or *m*- $\text{CF}_3\text{C}_6\text{H}_4$) with lanthanide(III) chlorides. In this communication, we have extended our studies to the reaction of lanthanide chlorides with diethyl phosphite and diisopropyl phosphites $(\text{RO})_2\text{P}(\text{O})\text{H}$ ($\text{R} = \text{C}_2\text{H}_5$, $(\text{CH}_3)_2\text{CH}$) in order to have a comparative study of the effect of these R and OR groups on the coordination behaviour of the ligands to the lantha-

nide chlorides. Although it has been reported [7] that dialkyl phosphites could exist in form I and II, the evidence gathered from NMR and IR studies [8] suggest that only form II is present in solution



Experimental

Physical measurements and experimental techniques were carried out as described elsewhere [6, 9].

Preparation of Trichlorohexakis(diethyl phosphite)-lanthanum(III)

A clear solution was obtained by dissolving anhydrous lanthanum chloride (0.36 g, 1.55 mmol) in 15 ml of dry ethyl alcohol. To this solution, diethyl phosphite (1.96 g, 14.19 mmol) was added and the mixture was refluxed over an oil bath temperature of 100°C for about seven hours. Then the reaction vessel was cooled to room temperature and kept overnight. A white crystalline mass precipitated on the walls of the vessel. The compound was filtered, washed with dry ethanol, and then dried at 65°C and 0.5 mm Hg for 2 h. On the basis of elemental analysis, it is concluded that the compound is of the type $[\text{La}(\text{EtO})_2\text{P}(\text{O})\text{H}_6\text{Cl}_3]$.

Other compounds were prepared similarly (Table I).

Results and Discussion

An ethanolic or isopropanolic solution of anhydrous lanthanide chloride was refluxed with an excess of diethylphosphite and diisopropyl phosphite, respectively. On cooling a crystalline solid was deposited on the walls of the reaction vessel. The product was filtered, washed with dry ethyl alcohol or isopropyl alcohol and dried under vacuum. On the basis of elemental analysis, it was observed that five

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TABLE I. Experimental Data

Reagent ^a	Refluxing time (h)	Product	Analysis, found (calculated) (%)		
			Metal	Chloride	
LaCl ₃ DEP Ethanol	0.38 g 1.96 g	7	La(DEP) ₆ Cl ₃ (white solid)	12.87 (12.93)	9.92 (9.90)
PrCl ₃ DEP Ethanol	0.41 g 2.24 g	7	Pr(DEP) ₆ Cl ₃ (pale green solid)	13.00 (13.10)	10.10 (9.89)
NdCl ₃ DEP Ethanol	0.54 g 2.86 g	7	Nd(DEP) ₆ Cl ₃ (light blue solid)	13.21 (13.37)	9.89 (9.85)
SmCl ₃ DEP Ethanol	0.43 g 2.44 g	7	Sm(DEP) ₆ Cl ₃ (pale yellow solid)	13.79 (13.86)	10.06 (9.80)
EuCl ₃ DEP Ethanol	0.42 g 2.32 g	7	Eu(DEP) ₆ Cl ₃ (white solid)	13.91 (13.98)	9.82 (9.78)
GdCl ₃ DEP Ethanol	0.39 g 2.00 g	8	Gd(DEP) ₅ Cl ₃ (white solid)	16.45 (16.38)	11.13 (11.15)
TbCl ₃ DEP Ethanol	0.29 g 2.10 g	8	Tb(DEP) ₅ Cl ₃ (white solid)	16.39 (16.63)	11.14 (11.13)
DyCl ₃ DEP Ethanol	0.36 g 1.92 g	8	Dy(DEP) ₅ Cl ₃ (white solid)	16.93 (16.94)	11.12 (11.09)
YbCl ₃ DEP Ethanol	0.31 g 1.66 g	8	Yb(DEP) ₅ Cl ₃ (white solid)	17.84 (17.84)	10.96 (10.97)
LaCl ₃ DIPP Isopropanol	0.44 g 2.51 g	7	La(DIPP) ₆ Cl ₃ (white solid)	11.90 (11.18)	8.57 (8.56)
PrCl ₃ DIPP Isopropanol	0.37 g 2.46 g	7	Pr(DIPP) ₆ Cl ₃ (pale green solid)	13.21 (13.52)	8.55 (8.55)
NdCl ₃ DIPP Isopropanol	0.64 g 3.00 g	7	Nd(DIPP) ₆ Cl ₃ (pale blue solid)	11.55 (11.56)	8.54 (8.53)
SmCl ₃ DIPP Isopropanol	0.32 g 0.91 g	7	Sm(DIPP) ₆ Cl ₃ (pale yellow solid)	11.77 (12.00)	8.55 (8.48)
EuCl ₃ DIPP Isopropanol	0.36 g 2.22 g	8	Eu(DIPP) ₆ Cl ₃ (white solid)	12.10 (12.01)	8.40 (8.48)
GdCl ₃ DIPP Isopropanol	0.36 g 2.12 g	8	Gd(DIPP) ₅ Cl ₃ (white solid)	15.35 (14.37)	9.73 (9.72)
TbCl ₃ DIPP Isopropanol	0.45 g 2.55 g	8	Tb(DIPP) ₅ Cl ₃ (white solid)	14.38 (14.50)	9.70 (9.70)

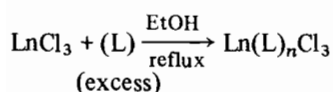
(continued)

TABLE I (continued)

Reagent ^a	Refluxing time (h)	Product	Analysis, found (calculated) (%)		
			Metal	Chloride	
DyCl ₃ DIPP Isopropanol	0.31 g 2.00 g	8	Dy(DIPP) ₅ Cl ₃ (white solid)	14.76 (14.78)	9.69 (9.76)
YbCl ₃ DIPP Isopropanol	0.53 g 2.67 g	8	Yb(DIPP) ₅ Cl ₃ (white solid)	15.61 (15.57)	9.58 (9.57)

^aDEP = Diethyl phosphite; DIPP = Diisopropyl phosphite.

to six molecules of ligand were attached to the lanthanide chlorides. These reactions are shown below:

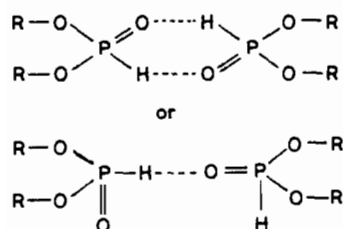


($n = 5$ for Gd, Tb, Dy or Yb and $n = 6$ for La, Pr, Nd, Sm or Eu. L = (EtO)₂P(O)H or (PrⁱO)₂P(O)H)

These complexes were crystallised from ethanol or isopropanol and washed with n-hexane. These are moderately high melting solids having the colour of the respective parent lanthanon.

Infrared Spectral Studies

The infrared spectra of the ligands [7] show a slightly broadened band at 2435 cm⁻¹ due to $\nu(\text{P-H})$, suggesting that in the ligand state the P-H bond may be associated in a bridge through oxygen atoms similar to the familiar hydrogen bridge in $-\text{O}-\text{H}-\text{O}-$ or $-\text{N}-\text{H}-\text{O}-$ systems, in this case leading to structures as shown below:



From the infrared spectral studies of these complexes, it appears that the coordination of the diethyl and diisopropyl phosphite groups to the lanthanon metal occurs via the oxygen of the P → O moiety. The (P → O) stretching frequency which occurs in the region 1265–1255 cm⁻¹ in free (RO)₂P(O)H has been shifted to lower frequency of about 100 cm⁻¹ (Table II). This can be explained on the basis of metal–oxygen bond formation which in turn weakens the (P → O) bond thus causing the lowering in the (P → O) stretching frequency. A similar observation

TABLE II. IR Spectral Data of Lanthanide(III) Chloride Phosphite Complexes (cm⁻¹)

Compound	(EtO) ₂ P(O)H		(Pr ⁱ O) ₂ P(O)H	
	(P=O) 1261s	(P-H) 2434m	(P=O) 1262s	(P-H) 2432m
LaL ₆ Cl ₃	1140s	2430m	1150s	2430m
PrL ₆ Cl ₃	1150s	2430m	1155s	2432m
NdL ₆ Cl ₃	1158s	2433m	1160s	2425m
SmL ₆ Cl ₃	1160s	2425m	1140s	2435m
EuL ₆ Cl ₃	1165s	2430m	1145s	2430m
GdL ₅ Cl ₃	1165s	2430m	1145s	2430m
TbL ₅ Cl ₃	1175s	2428m	1165s	2430m
DyL ₅ Cl ₃	1175s	2425m	1180s	2430m
YbL ₅ Cl ₃	1180s	2425m	1180s	2427m

has also been reported [10] in the case of lanthanide nitrate complexes with hexamethylphosphoramide. However, this shift (~100 cm⁻¹) is much larger than the shift observed in the case of secondary phosphine oxides [6], which may suggest the strong coordination of diethyl and diisopropyl phosphites to the lanthanide metal.

It has also been observed that there is a slight increase in the (P → O) stretching frequency with decreasing lanthanide ion radius. A similar trend has also been reported by Cousins and Hart [11, 12] and McRae and Karraker [13] in the case of lanthanide complexes with triphenylphosphineoxide. This is due to an increase in the Ln–O bond strength with an increase in atomic number of lanthanide ions. This observation has also been explained on the basis of 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 the attractive forces. The Ln–O bond becomes gradually weaker and P–O bond becomes progressively stronger as indicated by the increase in (P → O) stretching frequency. The effect of cation size on the the IR spectrum of ligand can be seen in the IR spectra of these complexes (Fig. 1). The (P–H)

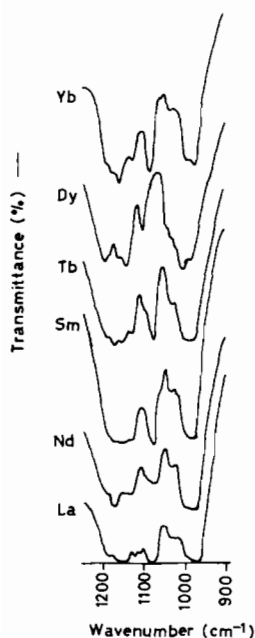


Fig. 1. Infrared spectra of $[\text{Ln}((\text{C}_3\text{H}_7)_2\text{P}(\text{O})\text{H})_n\text{Cl}_3]$ ($n = 5$: Gd, Tb, Dy, Yb; $n = 6$: La, Pr, Nd, Sm, Eu).

stretching frequency in these complexes was found to be very strong near $2435\text{--}2425\text{ cm}^{-1}$ and no appreciable shift was observed. The presence of the P–H stretching frequency as well as the non-evolution of HCl gas during the reaction confirm the non-formation of a bond between the phosphorus and lanthanide metal atoms.

However, the P–H band is observed with a small split which may indicate the presence of a different environment of P–H groups in $(\text{RO})_2\text{P}(\text{O})\text{H}$ coordinating to the metal atom. The (Ln–O) stretching frequency occurs around 400 cm^{-1} .

^1H NMR Spectral Studies

The ^1H NMR spectra of some of these complexes were obtained in deuteriochloroform. The diamagnetic lanthanum complex of the type $\text{La}(\text{L})_6\text{Cl}_3$ where $\text{L} = (\text{Pr}^{\text{I}}\text{O})_2\text{P}(\text{O})\text{H}$ shows a doublet centered at 6.8 ppm (for the free ligand it occurs at 6.78 ppm) due to the P–H proton. Thus, the confirmation of the presence of the P–H proton in these complexes further rules out the formation of a bond between the phosphorus atom of $(\text{RO})_2\text{P}(\text{O})\text{H}$ and the lanthanide metal atom. A multiplet at 1.35 ppm is assigned to the CH_3 protons. The signal due to the CH_3 protons appears at 1.07 ppm as a doublet in free ligand. The occurrence as a multiplet and the higher shift may be explained on the basis of the presence of a different environment of ligands in the lanthanide complexes. The CH protons are observed as a multiplet at 4.57

ppm. For other complexes which are paramagnetic, signals are observed with considerable broadening and the spectra are complicated. It was not possible to assign the various peaks with certainty.

^{31}P NMR Spectra

The ^{31}P NMR spectra of the complexes were obtained in CDCl_3 (Table III). All these complexes give singlets shifted to higher frequencies of the resonances, when compared with free ligands, by about 0.5–6.5 ppm. This change in the chemical shift on coordination is much less than that normally observed if the phosphorus atom is directly bonded to the metal atom, indicating that the ligands are bonded through the oxygen atom.

The square antiprism and tricapped trigonal prism structures may be assigned to the complexes $\text{Ln}(\text{L})_5\text{Cl}_3$ and $\text{Ln}(\text{L})_6\text{Cl}_3$, respectively [14, 15].

TABLE III. ^{31}P NMR Data of the Lanthanide (III) Chloride Complexes of Diethyl and Diisopropyl Phosphites (ppm)^a

Compound	$(\text{EtO})_2\text{P}(\text{O})\text{H}$ 7.99	$(\text{Pr}^{\text{I}}\text{O})_2\text{P}(\text{O})\text{H}$ 4.97
LaL_6Cl_3	9.32	8.62
PrL_6Cl_3	9.20 ^b	9.81 ^b
NdL_6Cl_3	9.91 ^b	11.25 ^b
SmL_6Cl_3	10.42	9.57
EuL_6Cl_3	9.77 ^b	7.38 ^b
GdL_5Cl_3	10.21	6.19
TbL_5Cl_3	8.48	8.12
DyL_5Cl_3	10.12 ^b	6.90
YbL_5Cl_3	9.20	10.42

^aRelative to an external H_3PO_4 standard. All spectra were taken in deuteriochloroform. ^bBroad.

Acknowledgements

Authors are grateful to Mobil Chemical Co., Richmond, Virginia, U.S.A. for the gift of $(\text{EtO})_2\text{P}(\text{O})\text{H}$ and $(\text{Pr}^{\text{I}}\text{O})_2\text{P}(\text{O})\text{H}$. R.S. is thankful to CSIR, New Delhi, India, for the research fellowship.

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