

Complexes of lanthanide nitrates with O,O',N-triisopropyl phosphoramidate

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Abstract. A substituted phosphoramidate has been used as a ligand to lanthanides for the first time. New complexes of lanthanide nitrates with O,O',N-triisopropyl phosphoramidate (TIP) of the general formula $\text{Ln}(\text{TIP})_3(\text{NO}_3)_3$, where Ln = La - Yb and Y have been synthesised and characterised by chemical analysis, infrared and visible electronic spectra and electrical conductance.

Infrared spectra indicate the coordination of the ligand to the metal ions through the oxygen of the P = O group. IR and conductance show that the nitrate groups are all coordinated. Electronic spectral shapes have been interpreted in terms of an eight coordinate geometry around the metal ions.

Keywords. Lanthanide nitrate complexes; triisopropyl phosphoramidate; infrared spectra; visible electronic spectra; electrical conductance.

1. Introduction

The coordination of lanthanides with ligands containing P = O groups is not uncommon. Studies on complexes of lanthanides with phosphoramides (Sylvanovich and Madan 1972, Airoidi *et al* 1976), phosphonates (Stewart and Siddall 1971; Mikulski *et al* 1977), phosphinamides (Vicentini and Braga 1971; Vicentini and Dunstan 1972) and phosphine oxides (Cousins and Hart 1968; Donohogue and Fernandez 1970) have been reported. However, complexes of lanthanides with alkyl phosphoramidates are unknown. In this paper, we report the preparation and characterisation of new adducts of lanthanide nitrates with O,O',N-triisopropyl phosphoramidate. The characterisation and assignment of the nature of bonding of the complexes is based on infrared and electronic spectral data, chemical analysis and conductance measurements.

2. Experimental

2.1. Materials

The rare earth oxides were obtained in 99.9% purity from Indian Rare Earths Ltd, Kerala. The lanthanide nitrates were prepared by dissolving the appropriate

oxides in 50% nitric acid and evaporating the solution to dryness on a water bath. Solvents used were purified by standard methods.

2.2. Preparation of ligand

2.2a. Preparation of diisopropyl hydrogen phosphite : Diisopropyl hydrogen phosphite was synthesised by a method similar to that reported by Atherton *et al* (1945a).

Phosphorous trichloride (1 mol) dissolved in carbon tetrachloride (0.5 mol) was gradually run into isopropanol (3 mol) in carbon tetrachloride (2 mol) over a period of 15–20 min with stirring and cooling in an ice salt bath. Then the solution was kept for 90 min and subjected to reduced pressure. The temperature was raised slowly to remove all the carbon tetrachloride and hydrogen chloride. The residue was distilled at 80–81°/16 mm.

2.2b Preparation of *O,O',N*-triisopropyl phosphoramidate : Triisopropyl phosphoramidate was prepared from the phosphite as reported in literature (Atherton *et al* 1945b). To the phosphite (1 mol) in 20–25 ml of benzene was added carbon tetrachloride (1 mol). Isopropylamine (2.25 mol) was then added dropwise with cooling and stirring and the mixture was then stirred for 2 hr, the solid hydrochloride filtered off and the filtrate distilled at 120° C/6 mm.

2.3. Preparation of complex

The complexes were prepared by extraction into carbon tetrachloride. Less than the stoichiometric quantity of ligand in carbon tetrachloride was shaken with the hydrated lanthanide nitrate and boiled for 15 min on a water bath. After filtering off the unreacted metal nitrate from the carbon tetrachloride solution containing the complex, the solution was evaporated to dryness on the water bath. The resulting oily mass was scratched to obtain the solid complex.

2.4. Physical measurements

IR spectra were taken in nujol mulls with a Carl-Zeiss UR-10 spectrometer in the region 400–4000 cm^{-1} . Electronic spectra in solid state in the visible region were recorded with a Unicam SP-700A spectrophotometer. Samples were milled in nujol and smeared on Whatman filter paper strips. A blank strip smeared with nujol only was used as reference. Solution spectra in carbon tetrachloride were run on a Beckmann model 25 spectrometer.

2.5. Analysis

Metal content of the complexes were determined volumetric lly by EDTA titration using xylenol orange as indicator. The nitrate was estimated gravimetrically as nitron nitrate. Phosphorous was determined colorimetrically as the yellow molybdovanadophosphate complex by the method of Salvago and Dixon (1965).

3. Results and discussion

The analytical and conductivity data are summarised in table 1. The adducts are stable and non-hygroscopic for a reasonable length of time. The analytical data

suggest the formula $\text{Ln}(\text{TIP})_3(\text{NO}_3)_3$ where $\text{TIP} = \text{O}, \text{O}', \text{N}$ -triisopropyl phosphoramidate, for the complexes. The complexes are soluble in benzene, carbon tetrachloride, chloroform, dimethylsulphoxide and acetonitrile. The electrical conductivity values in acetonitrile show that all the three nitrate groups are coordinated. The important IR bands of the ligand and the complexes along with the assignments are presented in table 2. A considerable shift in the $\text{P}=\text{O}$ stretch to lower frequencies in the complexes compared to that in the ligand clearly proves that the coordination of the ligand to metal ion occurs through the oxygen of the $\text{P}=\text{O}$ group. In addition shifts to higher frequencies of some of the $\text{P}-\text{N}$ vibrations are also observed further confirming the coordination through oxygen of the $\text{P}=\text{O}$ group.

The IR spectra do not show bands indicative of ionic nitrates occurring at 1380 cm^{-1} and 830 cm^{-1} . Confirmatory evidence for this is provided by conductance values. Nitrate groups are capable of bonding to a metal ion in a unidentate or a bidentate fashion. Coordination involving either mode lowers the symmetry of the ionic nitrate from D_{3h} to C_2 . The two situations cannot, in general, be unambiguously distinguished on the basis of the IR data alone. The combination bands of the nitrate group which generally appear in the $1700\text{--}1800$ region have been used for structural assignments of the nitrate groups (Curtis and Curtis 1965; Lever *et al* 1971). In the present complexes, we find three weak bands in the said region, the separation between which suggest that both mono and bidentate nitrate groups are present in the complexes.

The strength of the metal nitrate coordination is related to the ν_4 mode of the nitrate group (Carpentier and Moeller 1970). In the TIP complexes of lanthanide nitrates the ν_4 is found between $1505\text{--}1520\text{ cm}^{-1}$. In the complexes of two other $\text{P}=\text{O}$ ligands, viz., diphenyl phosphinyl morpholide (DPPM) (Vicentini *et al* 1974) and trioctyl phosphine oxide (TOPO) (Manchanda *et al* 1977), this frequency occurs between $1475\text{--}1490\text{ cm}^{-1}$ and $1485\text{--}1510\text{ cm}^{-1}$ respectively. It

Table 1. Analytical and conductivity data.

Complex	Metal (%)		Phosphorus (%)		Anion (%)		Molar conductance CH_3CN at (25°C) ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$)
	Found	Theoretical	Found	Theoretical	Found	Theoretical	
La	13.84	13.98	2.99	3.12	18.56	18.71	14.8
Pr	14.03	14.16	2.94	3.11	18.34	18.67	17.2
Nd	14.54	14.42	3.01	3.10	18.28	18.62	13.0
Tb	15.51	15.68	2.89	3.05	18.19	18.34	19.4
Ho	15.98	16.17	2.94	3.04	18.03	18.24	24.0
Er	16.28	16.39	2.88	3.03	17.95	18.20	15.6
Yb	16.75	16.83	2.98	3.01	17.79	18.09	17.1
Y	9.36	9.43	3.23	3.28	20.64	20.89	21.0

Table 2. Important infrared frequencies (in cm^{-1}) and their assignments.

Ligand	La	Pr	Nd	Tb	Ho	Er	Yb	Y	Assignments
	1770w	1770w	1770w	1770w	1775w	1775w	1790w	1775w	$(\nu_2 + \nu_3)$
	1750w	1750w	1740w	1750w	1755w	1755m	1750w	1750w	Nitrate
	1735w	1730w	1725w	1730w	1725w	1730w	1735w	1735w	$(\nu_2 + \nu_3)$ Nitrate
..	1520w	1515sb	1505s	1510m	1515mb	1515s	1515s	1520sb	ν_4 Nitrate
..	1300s	1310vs	1295vs	1310s	1310sb	1310s	1310s	1310s	ν_1 Nitrate
1240vs	1215m	1210m	1210s	1220m	1220m	1220m	1225s	1220m	P=O stretching
..	1030s	1030sb	1025s	1040mb	1040mb	1035m	1035m	1030m	ν_2 Nitrate
995vs	1000s	1010m	1005s	1000sb	1005m	1010m	1010m	1005m	P-N stretching
900s	910m	910m	910m	910m	910m	910m	910m	910m	P-N stretching
..	825s	820s	820s	825s	825s	820s	820s	820s	ν_6 Nitrate
..	730w	730w	730m	730m	730m	730m	730m	730w	ν_5 Nitrate
..	740s	740s	740s	750s	750s	750s	750s	750s	
..	710w	710w	710w	710w	710w	710w	710w	710w	ν_5 Nitrate

Abbreviations : vs = very strong; s = strong; w = weak; m = medium; b = broad.

can therefore be suggested that the strength of the metal to nitrate bond in the complexes follows the order TIP > TOPO > DPPM. This order could be related to the bulk of the ligands which increases in the same order. The bulkier the ligand, lesser the chance for the nitrate groups to approach the metal ion and hence weaker the metal-nitrate bond.

The electronic spectral data in the visible region for the Nd^{3+} , Ho^{3+} and Er^{3+} complexes are presented in table 3. The $f-f$ electronic transitions of the lanthanides are found to be sharp and line-like. On complexation, the spectra tend to show band energy shifts as compared to the aquo ion complexes. In the present complexes small shifts to lower frequencies are found for all the bands. This red shift is called the nephelauxetic shift and has been related to covalency in the metal to ligand bond. Sinha (1966, 1971) has defined a parameter δ to measure the covalent character of the metal-ligand bond. This value is given by the relation

$$\delta (\%) = (1 - \beta)/\beta \times 100$$

where β is the average value of the ratio $\nu_{\text{complex}}/\nu_{\text{aquo}}$. The β and δ values calculated for these complexes are presented in table 3. The δ values of the TIP complexes are greater than those of oxalates, phthalates and dibenzolymethides reported by Sinha (1966) indicating greater covalency in the metal-ligand bond in the present complexes. However, they are much less compared to the complexes with nitrogen donor ligands such as terpyridyl and dipyrityl. Karraker (1968) has found that the shapes of some of the bands called hypersensitive bands are related to the coordination number around the metal ion. We find that the solid

Table 3. Electronic spectral data in the visible region for the Nd³⁺, Ho³⁺ and Er³⁺ complexes.

Nd ³⁺		Ho ³⁺		Er ³⁺	
J level	Energy (KK)	J level	Energy (KK)	J level	Energy (KK)
⁴ G _{9/2}	19.42	⁵ G ₆	27.55	⁴ G _{11/2}	26.50
⁴ G _{7/2}	18.98	⁵ G ₅	23.92	⁴ F _{3/2}	22.58
⁴ G _{5/2}	17.25	³ K ₆	22.10	⁴ F _{5/2}	22.22
			21.98		
² G _{7/2}	17.15	⁵ F ₃	20.51	⁴ F _{7/2}	20.53
..	..	⁶ S ₃ , ⁴ F ₄	18.52	² H _{11/2}	19.13
..	..	⁶ F ₆	15.49	⁴ F _{9/2}	15.33
$\beta = 0.9874$		$\beta = 0.9949$		$\beta = 0.9977$	
$\delta = 1.227$		$\delta = 0.5126$		$\delta = 0.2305$	

state spectral shapes closely resemble the hypersensitive spectral shapes in solution. This indicates a similarity in coordination number in the solid state and in solution. The shapes of the hypersensitive bands of the Nd³⁺, Ho³⁺ and Er³⁺—TIP complexes show marked resemblance to the shapes of the aqueous Nd³⁺, Ho³⁺ and Er³⁺ ions in concentrated electrolytes like LiCl, HCl where a coordination number of eight has been proposed.

4. Conclusion

The analytical, conductivity and infrared data coupled with electronic spectral data indicate that each of the lanthanide ion is surrounded by three TIP ligands coordinating via the oxygen of the P=O group and three nitrate groups. Of the three nitrate groups two are bonded in a bidentate fashion and one in a unidentate fashion. A probable coordination number of eight can thus be assigned on the basis of all these data.

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