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Coordination Chemistry of Lanthanide Elements. I. Complexes of Trivalent Lanthanide Halides with Trimorpholino Phosphine Oxide

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In previous papers we have reported on complexes of lanthanides[2,3] and transition metals[4] with phosphoryl donors. The ligand hexamethyl phosphoramide $O=P[N(CH_3)_2]_3$ has been found to form two series of lanthanide complexes: $LnCl_3\cdot 3HMPA$ and $Ln(ClO_4)_3\cdot 6HMPA$ in which the coordination number was found to be six. This coordination number, although not unique for lanthanides, is sufficiently unusual to be of interest. For hexamethyl phosphoramide complexes, it was concluded that the steric requirements of the amide molecule were of prime importance in directing the coordination number of six for the lanthanides. The steric requirements of the amide are such as to obscure the natural tendency for coordination number to decrease from left to right in the lanthanide series. In this paper we report complexes of lanthanide halides with trimorpholino phosphine oxide.

Experimental

Preparation of Compounds. 0.001 mol of anhydrous lanthanide halide was dissolved in 25 m*l* of hot absolute alcohol. A solution of 0.003 mol of trimorpholino phosphine oxide in 25 m*l* of hot absolute ethanol was prepared. These solutions were mixed together and allowed to stir until cool. All reactions were carried out in a nitrogen atmosphere. After cooling, 75 m*l* of absolute ether were added to the solutions to complete precipitation. The solids were filtered under nitrogen and washed five times with 10 m*l* portions of cold, absolute ether. The dried solids were stored *in vacuo* over H_2SO_4. Analytical data for the ligand and its complexes are reported in Table 1.

Conductivity Measurements. Conductivities of nitromethane solutions of the complexes were obtained using an Industrial Instruments Inc. conductivity bridge which had been previously calibrated with 0.01 N KCl solution. The results are summarized in Table 1.

Spectral Measurements. Infrared spectra for the free ligand and its complexes were obtained using a Perkin-Elmer 337 spectrophotometer. The results for the phosphoryl stretching frequency $\nu_{P=O}$ of trimorpholino phosphine oxide and its complexes are reported in Table 1.

Reagents. Trimorpholino phosphine oxide was obtained from Aldrich Chemical Co. and was used without further purification. Analytical data are given in Table 1.

Lanthanide halides were obtained from American Potash and Chemical Corporation and were 99.9+% pure and were used without further purification.

All other chemicals used in this study were reagent grade.

Results. Analytical, conductivity, and infrared spectral data are summarized in Table 1.

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[2] J. T. Donoghue and D. A. Peters, *J. Inorg. Nucl. Chem.*, **31**, 467 (1969).

[3] J. T. Donoghue, E. Fernandez, J. A. McMillan and D. A. Peters, *ibid.*, in press.

[4] J. T. Donoghue, E. Fernandez and D. A. Peters, *Inorg. Chem.*, in press.

TABLE 1. PROPERTIES OF TRIMORPHOLINO PHOSPHINE OXIDE-LANTHANIDE COMPLEXES

$MCl_3\cdot 3L$[*4] M=	Analytical results[*1] Carbon Calcd	Found	Hydrogen Calcd	Found	Nitrogen Calcd	Found	Metal Calcd	Found	$\nu_{P=O}$,[*2] cm^{-1}	Conductivity[*3] mol at 25°C
L	46.2	46.5	8.0	7.9	13.8	13.9			1205	
Sc	40.5	40.1	6.8	7.0	11.8	11.5	4.2	4.6	1191	4.5
Y	38.8	38.7	6.5	6.8	11.4	11.5	8.0	8.0	1190	3.2
La	37.2	37.2	6.3	6.6	10.8	10.9	12.0	11.5	1191	2.2
Ce	37.1	37.1	6.3	6.6	10.8	10.7	12.1	11.7	1191	2.5
Pr	37.0	36.7	6.3	6.6	10.8	10.7	12.4	11.9	1191	2.0
Nd	36.9	37.2	6.3	6.3	10.8	10.7	12.6	12.3	1191	1.7
Pm	36.7	37.0	6.3	6.5	10.8	10.9	12.8	12.8	1195	2.0
Sm	36.7	37.0	6.2	6.5	10.7	10.9	13.0	13.2	1193	1.1
Eu	36.6	36.6	6.2	6.5	10.7	10.7	13.3	13.0	1195	2.5
Gd	36.6	36.4	6.2	6.2	10.7	10.7	13.5	13.0	1191	1.8
Tb	36.5	36.7	6.2	6.2	10.7	10.9	13.7	13.3	1191	1.9
Dy	36.5	36.6	6.1	6.1	10.6	10.4	13.9	14.1	1192	2.3
Ho	36.4	26.5	6.1	6.1	10.6	10.4	14.0	13.7	1191	2.3
Er	36.3	36.2	6.1	6.3	10.6	10.6	14.1	14.1	1191	2.5
Tm	36.2	36.2	6.1	6.3	10.6	10.3	14.3	14.0	1191	1.7
Yb	36.1	36.2	6.1	6.3	10.5	10.5	14.5	14.0	1191	1.9
Lu	36.0	36.2	6.1	6.3	10.5	10.5	14.7	14.0	1192	

[*1] Analytical work performed by A. Bernhardt, W. Germany.

[*2] Phosphoryl frequencies reported were obtained on Nujol mulls of ligand and complexes.

[*3] Conductivities of 1×10^{-4}M solutions were obtained at 25°C.

[*4] L denotes trimorpholino phoshine oxide $(\overline{O\quad N})_3PO$.

Discussion

All of the complexes studied were found to be quite hygroscopic and it was necessary to perform most operations with the exclusion of air. No attempts were made to record melting points for these complexes. The colors of the complexes were found to be essentially the same as those of the anhydrous chlorides.

The analytical data (Table 1) suggest that the complexes may be formulated as $LnCl_3\cdot 3L$ (L=trimorpholino phosphine oxide, $O{=}P{-}\ [N\langle{}^{CH_2CH_2}_{CH_2CH_2}\rangle O]_3$). No tendency to reduction of coordination number in progressing across the lanthanide series with decreasing crystal radius of the lanthanide ions was exhibited.

Infrared spectra of mulls of the ligand and its complexes were obtained and interpreted in terms of the location of the phosphoryl stretching frequency, $\nu_{P=O}$, of the ligand. The phosphoryl frequency (Table 1) was found to decrease on coordination in every case. Reductions are on the order of 15—20 cm^{-1}. This is taken as evidence that the site of coordination in the ligand is at the phosphoryl oxygen of the ligand. These shifts, though not as large as those noted for transition metal complexes,4) are in the same direction as those noted for transition metal complexes.

Conductivities of the complexes in nitromethane solutions suggest that the species are non-electrolytes in nitromethane and accordingly must contain coordinated halide ion. The species may be thus formulated as $[LnCl_3L_3]$ species.

The data presented may be collectively interpreted to infer that in these lanthanide complexes of trimorpholino phosphine oxide, the coordination number of the lanthanides is six for all cases studied. This is in agreement with results obtained when the ligand is hexamethyl phosphoramide2,3) or diphenyl sulfoxide.5)

The most common coordination numbers exhibited by lanthanides in complexes containing monodentate ligands are eight and seven.6–8) With hexamethyl phosphoramide as ligand, in the

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5) S. K. Ramalingam and S. Soundararajan, *Z. Anorg. Allg. Chem.*, **353**, 216 (1967); S. K. Ramalingam and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **20**, 1963 (1967); V. Krishnamurthy and S. Soundararajan, *Can. J. Chem.*, **45**, 189 (1967).

6) D. R. Cousins and F. A. Hart, *Chem. Ind.* (London), **1965**, 1259.

7) J. R. Ferraro and C. Cristallini, *J. Inorg. Nucl. Chem.*, **29**, 139 (1967).

8) T. Meoller and G. Vincenti, *ibid.*, **27**, 1477 (1965).

complexes $LnCl_3 \cdot 3HMPA$ and $Ln(ClO_4)_3 \cdot 6HMPA$, it was possible to interpret the failure of the lanthanides to achieve apparent maximum coordination numbers higher than six, as due to the steric requirements of the ligand itself.[2,3] However, for trimorpholino phosphine oxide the situation may involve other factors. In complexes of triphenylphosphine oxide, whose steric requirements are similar to those of trimorpholino phosphine oxide, coordination numbers higher than six have been found in derivatives of the type $LnX_3 \cdot xL$. It might be expected that trimorpholino phosphine oxide would exhibit similar behavior, but it does not. Clearly some factor other than ligand steric requirement is involved in determination of coordination number in lanthanide complexes of trimorpholino phosphine oxide.

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