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Coordination Chemistry of Lanthanide Elements. II.[1] Cationic Lanthanide Complexes of Trimorpholino Phosphine Oxide

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In earlier studies,[2,3] it was found that the phosphoryl donor, hexamethyl phosphoramide (HMPA), formed six coordinate complexes with lanthanide ions. The occurrence of coordination number six for lanthanide ions, although not unique for this ligand, is unusual enough to warrant further study of the factors which give rise to it. The ligand, trimorpholino phosphine oxide exhibits behavior similar to that of HMPA[3] in forming complexes with transition metals. It was found that this ligand also gives complexes of the type $LnCl_3\cdot 3L$.[4] It was of interest to investigate cationic lanthanide complexes of this phosphoryl donor.

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[1] Part I: This Bulletin, **43**, 271 (1970).

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

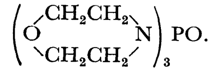
[3] J. T. Donoghue, E. Fernandez, J. A. McMillan and D. A. Peters, *Inorg. Chem.*, in press.

[4] J. T. Donoghue and E. Fernandez, This Bulletin, **43**, 271 (1970).

Table 1. Analytical data[a)]

Compound	% Carbon		% Hydrogen		% Nitrogen	
	Calcd	Found	Calcd	Found	Calcd	Found
L[b)]	46.2	46.0	8.0	8.3	13.8	13.5
$La(ClO_4)_3 \cdot 6L$	38.1	38.0	6.4	6.3	11.1	11.2
$Ce(ClO_4)_3 \cdot 6L$	38.1	37.8	6.4	6.8	11.1	11.2
$Pr(ClO_4)_3 \cdot 6L$	38.1	37.9	6.4	6.7	11.1	11.0
$Nd(ClO_4)_3 \cdot 6L$	38.0	37.9	6.4	6.4	11.1	11.0
$Pm(ClO_4)_3 \cdot 6L$	38.0	37.9	6.4	6.4	11.1	11.1
$Sm(ClO_4)_3 \cdot 6L$	37.9	38.1	6.4	6.4	11.1	11.1
$Eu(ClO_4)_2 \cdot 6L$	37.9	38.0	6.4	6.8	11.1	11.3
$Gd(ClO_4)_3 \cdot 6L$	37.8	37.6	6.3	6.7	11.0	11.0
$Tb(ClO_4)_3 \cdot 6L$	37.8	37.7	6.3	6.8	11.0	11.2
$Dy(ClO_4)_3 \cdot 6L$	37.7	37.6	6.3	6.5	11.0	11.2
$Ho(ClO_4)_3 \cdot 6L$	37.7	37.9	6.3	6.5	11.0	11.4
$Er(ClO_4)_3 \cdot 6L$	37.7	37.9	6.3	6.1	11.0	11.2
$Tm(ClO_4)_3 \cdot 6L$	37.6	37.9	6.3	6.1	11.0	11.1
$Yb(ClO_4)_3 \cdot 6L$	37.6	37.6	6.3	6.3	11.0	11.0
$Lu(ClO_4)_3 \cdot 6L$	37.5	37.5	6.3	6.3	10.9	11.0
$Y(ClO_4)_3 \cdot 6L$	38.9	38.5	6.5	6.3	11.4	11.1
$Sc(ClO_4)_3 \cdot 6L$	39.0	38.6	6.9	6.5	11.5	11.1

a) Nitrogen analyses by A. Bernhardt and W. Germany; C, H-analyses obtained on Coleman Analyzer.

b) L designates trimorpholino phosphine oxide 
$\left(O\begin{matrix}CH_2CH_2\\ \\ CH_2CH_2\end{matrix}N\right)_3PO.$

Experimental

Synthesis of Complexes. The complexes were synthesized by metathesis according to the equation

$$LnCl_3 + 3AgClO_4 + 6L \longrightarrow Ln(ClO_4)_3 \cdot 6L + 3AgCl.$$

0.001 mol of lanthanide halide was dissolved in 15 m*l* of hot alcohol. To this was added a solution of 0.003 mol of $AgClO_4$ in 15 m*l* of hot alcohol. The precipitated silver chloride was filtered after cooling. The filtrate, under nitrogen, was treated with 0.006 mol of ligand in 15 m*l* of hot alcohol. After the resulting solutions had cooled to room temperature, they were treated with 75 m*l* of absolute ether to precipitate the complexes. The solid complexes were filtered and dried under nitrogen and were stored *in vacuo* over H_2SO_4. Analytical results are presented in Table 1.

Infrared Spectra. Infrared spectra of Nujol mulls of the complexes and free ligand were obtained using a Perkin-Elmer, model 337, recording infrared spectrophotometer. In all complexes studied, the phosphoryl frequency of the ligand was displaced to lower energies on complexation. The results are shown in Table 2.

Conductance Measurements. Conductances of 0.001M solutions in nitromethane were obtained using an Industrial Instruments Conductivity Bridge which was frequently calibrated with 0.01N KCl. Results are presented in Table 3.

Reagents. The lanthanide halides were obtained from Trona Chemicals and were of 99.9$^+$% purity.

Trimorpholino phosphine oxide was obtained from Aldrich Chemical Co. and was used without further purification.

All other chemicals employed in this study were of reagent-grade quality.

Table 2. Phosphoryl absorption frequency, $\nu_{P=O}$ in cm^{-1}

Complex	$\nu_{P=O}$	Complex	$\nu_{P=O}$
L	1204	Tb	1191
La	1191	Dy	1192
Ce	1191	Ho	1191
Pr	1192	Er	1192
Nd	1191	Tm	1192
Pm	1193	Yb	1191
Sm	1192	Lu	1189
Eu	1190	Y	1191
Gd	1190	Sc	1192

Table 3. Molar conductivities of 10^{-3}M nitromethane solutions

Complex	Λ_{molar}	Complex	Λ_{molar}
La	258	Tb	257
Ce	265	Dy	255
Pr	267	Y	270
Nd	263	Ho	253
Pm	260	Er	252
Sc	261	Tm	253
Sm	261	Yb	251
Eu	258	Lu	251
Gd	256		

Results

Analytical. Analytical data for the ligand and its lanthanide complexes are given in Table 1.

Infrared. Absorption frequencies for the P=O group in the complexes are given in Table 2.

Conductivity. Molar conductivities obtained for 10^{-3}M solutions of the complexes in CH_3NO_2 are given in Table 3.

Discussion

The ligand trimorpholino phosphine oxide is similar to hexamethyl phosphoramide in many ways in that the infrared phosphoryl frequencies are nearly identical at 1204 cm^{-1} and 1208 cm^{-1} respectively. The coordination behavior of the two ligands toward transition metals is very similar in that both form pseudo tetrahedral complexes with nickel(II) and cobalt(II).[5,6] However, in terms of steric requirements, trimorpholino phosphine oxide,  $\left(\mathrm{O}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_2CH_2}}{\mathrm{CH_2CH_2}}{>}\mathrm{N}\right)_3\mathrm{PO}$, is expected to show a stronger resemblance to triphenyl phosphine oxide $(C_6H_5)_3PO$ than to HMPA, $[(CH_3)_2N]_3PO$.

The conductivity results indicate that the perchlorate anion is not coordinated in nitromethane. Unfortunately, strong ligand absorption in the infrared in the region expected for perchlorate absorption made it impossible to determine if perchlorate is weakly coordinated in the solid state. It must be assumed that the perchlorate anion is uncoordinated in the solid state as well as in nitromethane solution.

The behavior of trimorpholino phosphine oxide toward lanthanides was observed to be quite similar to that of HMPA and other oxygen donor ligands, such as diphenyl sulfoxide.[7,8]

On the basis of the data reported above, it is concluded that the apparent coordination number of the lanthanide elements in these complexes is uniformly six.

Obviously, the steric requirements of triphenyl phosphine oxide and trimorpholino phosphine oxide should be similar, but the coordination numbers exhibited for trimorpholino phosphine oxide in complexes of the type $[LnL_6]^{+3}$ are apparently six. Since the cationic lanthanide complexes of triphenyl phosphine oxide are unknown, a direct comparison between triphenyl phosphine oxide and trimorpholino phosphine oxide is not possible but is desirable. Future work will involve investigation of the cationic lanthanide complexes of triphenyl phosphine oxide.

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[5] J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 578 (1963).

[6] J. T. Donoghue and E. Fernandez, *ibid.*, in press.

[7] S. K. Ramalingam and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **20**, 1963 (1967).

[8] V. Krishnamurthy and S. Soundararajan, *Can. J. Chem.*, **45**, 189 (1967).