

## 2,4-Lutidine-1-oxide complexes of lanthanide perchlorates

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**Abstract.** 2,4-Lutidine-1-oxide (2,4-LutO) complexes of lanthanide perchlorates of the formulae  $\text{Ln}_3(2,4\text{-LutO})_3(\text{ClO}_4)_6$  ( $\text{Ln} = \text{Pr}$  and  $\text{Nd}$ ) and  $\text{Ln}_4(2,4\text{-LutO})_{15}(\text{ClO}_4)_6$  ( $\text{Ln} = \text{La}$ ,  $\text{Tb}$ ,  $\text{Dy}$ ,  $\text{Ho}$  and  $\text{Yb}$ ) have been prepared and characterised by chemical analysis, IR, NMR, conductance and electronic spectral data. Proton NMR data along with the IR data show that the ligand coordinates to the metal ion through the oxygen. Conductance data of the complexes in acetone and nitrobenzene indicate that the perchlorate is not coordinated to the metal ion.

**Keywords.** Lanthanide perchlorates; 2,4-Lutidine-1-oxide; hypersensitive bands.

### 1. Introduction

Lanthanide perchlorate complexes of 2-picoline-1-oxide (2-PicO) have a higher ligand to metal ratio compared to that in the corresponding complexes of 2,6-lutidine-1-oxide (2,6-LutO), suggesting thereby a greater steric hindrance in the 2,6-LutO complexes (Koppikar and Soundararajan 1975, 1976). In an attempt to ascertain the coordination number of the lanthanide ion in the complexes of 2,4-lutidine-1-oxide with the lanthanide perchlorates, we report in this paper the preparation of the complexes and characterisation of them by analytical, IR, NMR, conductance and electronic spectral data. The physico-chemical properties of the complexes have been compared with those of the corresponding complexes of 2-PicO and 2,6-LutO.

### 2. Experimental

#### 2.1. Materials

2,4-Lutidine was obtained from Aldrich Chemical Co., USA. Lanthanide oxides (99.9% pure) were obtained from Indian Rare Earths Ltd., Kerala State. All the other chemicals used, were of reagent grade. The solvents were purified by standard methods.

## 2.2. *Preparation of the ligand*

2,4-Lutidine-1-oxide was prepared according to the method given by Ochiai (1953) by the N-oxidation of 2,4-lutidine and purified by distillation under reduced pressure (110°/1 mm Hg).

## 2.3. *Preparation of the hydrated lanthanide perchlorates*

The hydrated lanthanide perchlorates were prepared by dissolving the corresponding oxides in 50% perchloric acid and evaporating the solution on a steam bath.

## 2.4. *Preparation of lanthanide perchlorate complexes*

Hydrated lanthanide perchlorate (0.6 mM) dissolved in ethyl acetate (5 ml) was treated with the ligand (6 mM) with stirring. A heavy oily layer settled within about 5 min. The supernatant liquid was decanted and the oily substance was washed repeatedly with ethyl acetate, to remove the excess of ligand. The resulting oil was dissolved in chloroform (5–10 ml) and the solution evaporated to dryness in air. Ether (5 ml) was added and stirred to get a granular solid. This was filtered through a sintered crucible (grade 3), washed with ether and dried over phosphorus (V) oxide in a vacuum desiccator.

## 2.5. *Analyses*

The metal content of the complexes was estimated by EDTA titrations using xylenol orange as the indicator (Kolthoff and Elwing 1963). The perchlorate was estimated by gravimetric precipitation with nitron as described by Welcher (1947). The ligand 2,4-LutO was estimated spectrophotometrically at 254 nm using the calibration curve method. The analytical data are presented in table 1.

## 2.6. *Physical methods*

The IR spectra of the complexes in KBr pellets and of the ligand (neat) were recorded on a Carl-Zeiss UR-10 infrared spectrophotometer. The principal IR bands and their tentative assignments are given in table 2.

Proton NMR spectra of the complexes and the ligand were recorded on a Varian T-60 instrument using  $\text{CDCl}_3$  as the solvent and TMS as the internal standard (table 3).

Electronic spectra of Nd and Ho complexes in acetone were recorded in the visible region on a Beckmann Model-25 spectrophotometer.

Conductance measurements in acetone and nitrobenzene were carried out in a Siemen's conductivity bridge using an immersion cell (type LTA), previously calibrated with standard KCl solution. The concentrations of the solutions used were of the order of 0.001M (table 1).

## 3. *Results and discussion*

All the complexes are hygroscopic and are soluble in solvents like acetone, nitrobenzene, while La, Pr and Nd complexes are soluble in chloroform, the other

Table 1. Analytical and molar conductance data.

Complexes	% Metal		% Ligand		% ClO <sub>4</sub>		A* <sub>m</sub>	
	Fd	Cal	Fd	Cal	Fd	Cal	Acetone	Nitrobenzene
La <sub>3</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	10.21	10.22	69.47	67.80	22.26	21.95	231.8	66.62
Pr <sub>3</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	11.38	11.37	66.80	64.54	23.53	24.09	228.3	66.48
Nd <sub>3</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	11.53	11.61	66.40	64.37	..	..	231.8	80.65
Tb <sub>3</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	11.54	11.52	68.10	66.83	21.90	21.63	223.8	76.49
Dy <sub>3</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	11.73	11.74	67.35	66.68	..	..	234.6	84.45
Ho <sub>3</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	11.80	11.90	67.29	66.55	..	..	282.4	72.76
Yb <sub>3</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	12.31	12.41	66.97	66.16	..	..	254.7	84.28

\* Molar conductance—Ohms<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup> for monomer.

Table 2. IR spectra of 2,4-LutO complexes of lanthanide perchlorates in KBr pellets.

2,4-LutO*	La	Pr	Nd	Tb	Dy	Ho	Yb	Assignment
1245vs	1238s	1238s	1238s	1238s	1238s	1238s	1238s	$\nu$ N—O
800s	810s	810s	810s	810s	812s	810s	812s	C—H out-of-plane
830s	825sh	825sh	825sh	825sh	825sh	830sh	830sh	N—O bending
1485s	1500s	1500s	1500s	1500s	1500s	1500s	1500s	Ring breathing
	1100s	1100s	1100s	1100s	1100s	1100s	1100s	$\nu_2$ - ClO <sub>4</sub>
	627m	627m	627m	627m	627m	627m	627m	$\nu_4$ - ClO <sub>4</sub>

\* Ligand = neat; vs = very strong; s = strong; m = medium; sh = shoulder.

Table 3. Proton NMR spectral data

Compound	6-H	3, 5-H	2-CH <sub>3</sub>	4-CH <sub>3</sub>
2,4-LutO	1.94	3.04	7.57	7.72
La <sub>2</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	1.55	2.9	7.54	7.67
Pr <sub>2</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	-0.6	1.17 (3-H) 1.95 (5-H)	6.85	6.77
Nd <sub>2</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	0.39	1.94 (3-H) 2.44 (5-H)	7.64	7.2
Yb <sub>2</sub> (LutO) <sub>15</sub> (ClO <sub>4</sub> ) <sub>6</sub>	2.64	3.42 (3-H) 3.1 (5-H)	6.6	7.87

Spectra of 2,4-LutO and its complexes were obtained in CDCl<sub>3</sub>. TMS was used as the internal reference. Chemical shifts are given in  $\tau$ .

complexes are sparingly soluble in this solvent. All the complexes are insoluble in solvents like benzene. The colours of the complexes resemble those of the parent salts but appear to be less intense.

Analytical data show that the complexes have the formulae Ln<sub>2</sub>(2,4-LutO)<sub>15</sub>(ClO<sub>4</sub>)<sub>6</sub> (Ln = Pr and Nd) and Ln<sub>2</sub>(2,4-LutO)<sub>15</sub>(ClO<sub>4</sub>)<sub>6</sub> (Ln = La, Tb, Dy, Ho and Yb). The ligand to metal ratio is different from those of the corresponding complexes of 2-PicO and 2,6-LutO.

Molar conductance data in nitrobenzene and acetone indicate that all the complexes behave as 1 : 3 electrolytes in these solvents (Geary 1971) suggesting thereby that the perchlorate is not coordinated to the metal ion.

The IR spectra of the complexes are characterised by (i) a decrease of  $\sim 7$  cm<sup>-1</sup> in the N-O stretching frequency of the ligand, 2,4-LutO, at 1245 cm<sup>-1</sup>, indicative of coordination of the ligand through oxygen; (ii) increase in the C-H out of plane bending frequency of the ligand at 800 cm<sup>-1</sup> by about 10 cm<sup>-1</sup>, indicative of the drainage of electron density from the pyridine ring through the oxygen to the metal ion; and (iii) bands that are characteristic of only ionic perchlorate groups at 1100 cm<sup>-1</sup> and 627 cm<sup>-1</sup>.

The  $\Delta\nu_{N-O}$  ( $\sim 7$  cm<sup>-1</sup>) in these complexes, being less than that observed for the corresponding complexes of 2-PicO ( $\sim 13$  cm<sup>-1</sup>) and 2,6-LutO ( $\sim 18$  cm<sup>-1</sup>) (Koppikar and Soundararajan 1975, 1976), suggests a weaker metal ligand bond. Both  $\nu_3$  (1100 cm<sup>-1</sup>) and  $\nu_4$  (627 cm<sup>-1</sup>) modes of the ionic perchlorate group ( $T_d$  symmetry) remain unsplit showing that the perchlorate groups are not coordinated to the metal ion.

The proton NMR spectra of the diamagnetic La-complex are sharp and well resolved. The doublet occurring at 1.94  $\tau$  in the free ligand corresponds to the 6-H signal, while that at 3.04  $\tau$  is due to the 3-H and 5-H and those at 7.57 $\tau$  and 7.72  $\tau$  to the 2-methyl and the 4-methyl proton signals respectively. A significant shift of the aromatic proton signals of the ligand in the diamagnetic complex arises from a deshielding of the protons due to the drainage of the electron density from the ligand to the metal, on coordination. The assignments of 3-H and 5-H signals have been made as per the data given for 2-PicO complexes of lanthanide

iodides (Ramakrishnan and Soundararajan 1977). The broadening of the 5-H signal compared to that of 3-H in Pr(III), Nd(III) and Yb(III) complexes is indicative of the proximity of the 5-H of the ligand to the metal ion. The broadening of the 6-H signal in all the paramagnetic complexes is due to the relaxation effects.

The electronic spectra indicate that the shape of the hypersensitive bands  $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$  for Nd<sup>+3</sup>-complex and  $^5I_6 \rightarrow ^5G_8, ^5F$  for Ho<sup>+3</sup>-complex, resemble those of the corresponding seven and eight coordinate complexes studied by Karraker (1967). Conductance data (1 : 3 electrolytic behaviour) of the complexes along with I.R. data and electronic spectral data suggest a coordination number of 7 for Pr and Nd complexes and of 8 for other complexes.

#### 4. Bonding and coordination number

The proton NMR data along with the IR data for the complexes indicate the coordination of the ligand through the oxygen of the N-O group and a weaker metal-ligand bond compared to that of the corresponding complexes of 2-PicO and 2,6-LutO.

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#### References

- Geary W J 1971 *Coord. Chem. Rev.* **7** 81  
Karraker D G 1967 *Inorg. Chem.* **6** 1863  
Kolthoff I M and Elwing P J 1963 *Treatise on analytical chemistry*, Part II, Vol. 8, p. 57 (New York : Interscience)  
Koppikar D K and Soundararajan S 1975 *J. Indian Inst. Sci.* **57** 461  
Koppikar D K and Soundararajan S 1976 *Inorg. Nucl. Chem. Lett.* **12** 459  
Ochiai E 1953 *J. Org. Chem.* **18** 548  
Ramakrishnan L and Soundararajan S 1977 *Proc. Indian Acad. Sci.* **A86** 59  
Welcher F J 1947 *Organic analytical reagents* (New York : Van Nostrand)