

4-Nitro 2-picoline-1-oxide complexes of lanthanide perchlorates

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Abstract. 4-Nitro 2-picoline-1-oxide (NPicO) complexes of the formulae $\text{La}(\text{NPicO})_5(\text{ClO}_4)_3$, $\text{Ln}_2(\text{NPicO})_6(\text{ClO}_4)_6$ ($\text{Ln} = \text{Pr, Nd, and Gd}$) and $\text{Ln}(\text{NPicO})_4(\text{ClO}_4)_3$ ($\text{Ln} = \text{Tb, Dy, Ho and Yb}$) have been synthesised and characterised by analysis, electrolytic conductance, infrared, proton NMR and electronic spectral data. A tentative coordination number of 6 for all the complexes have been assigned.

Keywords. Lanthanide perchlorates ; 4-Nitro 2-picoline-1-oxide. electrolytic conductance ; electronic spectra.

1. Introduction

Among the disubstituted pyridine-1-oxides only 2,6-lutidine-1-oxide (2,6 LutO) has been used for complexing with lanthanide salts (Koppikar *et al* 1978). 2,6-LutO complexes of lanthanide perchlorates have the composition $\text{Ln}(2,6\text{-LutO})_3(\text{ClO}_4)_3$ (Koppikar and Soundararajan 1975) and $\text{Ln}(2,6\text{-LutO})_5(\text{ClO}_4)_3$ (Karayannis *et al* 1974), suggesting that the steric hindrance due to the methyl groups at 2 and 6 positions of the pyridine-1-oxide moiety, is sufficiently large to stabilise complexes with lower L : M compared to that in the corresponding complexes of pyridine-1-oxide. We have now initiated a systematic programme involving adducts of lanthanide salts with 2,4-disubstituted pyridine-1-oxides. As a part of such studies, we have reported 2,4-lutidine-1-oxide (2,4-LutO) complexes of lanthanide perchlorates with the compositions $\text{Ln}_2(2,4\text{-LutO})_{16}(\text{ClO}_4)_6$ and $\text{Ln}_2(2,4\text{-LutO})_{13}(\text{ClO}_4)_6$ (Navaneetham and Soundararajan 1979). In continuation of such studies, we have now prepared the complexes of 4-nitro 2-picoline-1-oxide with lanthanide perchlorates. We report in this paper the preparation of the complexes and their characterisation 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 2,4-LutO.

2. Experimental

2.1. Materials

2-Picoline was obtained from S.D's Laboratory, Bombay. Lanthanide oxides (99.9% pure) were obtained from Indian Rare Earths Ltd., Kerala State. All

other chemicals used were of reagent grade. The solvents were purified by standard methods.

2.2. Preparation of the ligand NPicO

2-Picoline-1-oxide was prepared according to the method given by Ochiai (1953) by the N-oxidation of 2-picoline. NPicO was prepared by the nitration of 2-picoline-1-oxide as described by Katritzky *et al* (1957) for the preparation of 4-nitropyridine-1-oxide, and was purified by recrystallisation from acetone (m.p. 153° C lit. 154° C).

2.3. Preparation of the hydrated lanthanide perchlorates

The hydrated lanthanide perchlorates were prepared by dissolving the corresponding oxides in a little less than the required quantity of 50% perchloric acid and evaporating the filtrate on a steam bath.

2.4. Preparation of the lanthanide perchlorate complexes of NPicO

Hydrated lanthanide perchlorate (0.6 mM) dissolved in ethyl acetate (5 ml) was added drop by drop to a boiling solution of NPicO (6 mM) in chloroform with vigorous stirring. Boiling and stirring was continued till a solid was formed. The complex was filtered hot through a sintered crucible and washed 3-4 times with hot chloroform and finally with ether. While the complex was still covered with a little ether, the crucible was transferred to a vacuum desiccator, and the complex dried over phosphorous (V) oxide.

2.5. Analyses

The metal content of the complexes was estimated by EDTA titrations using xylenol orange as the indicator (Kolthoff and Ewing 1963). The perchlorate was estimated by gravimetric precipitation with nitron as described by Welcher (1947). The ligand NPicO was analysed spectrophotometrically at 350 nm by measuring the optical densities on a Beckmann Model-25 spectrophotometer. The analytical data are presented in table 1.

2.6. Physical methods

The IR spectra of the complexes and the ligand in KBr pellets in the region 400-4000 cm^{-1} were recorded on a Carl-Zeiss-UR-10 infrared spectrophotometer. Proton NMR spectra of the ligand and the La-complex were recorded on a Varian T-60 instrument using CH_3CN as solvent and TMS as the internal standard.

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

Conductance measurements in nitromethane 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 are given in table 1.

Table 1. Analytical and molar conductance data for NPicO complexes.

Complexes	% Metal		% Ligand		% ClO ₄		Λ_m°	Conc. moles $\times 10^3$
	Found	Calculated	Found	Calculated	Found	Calculated		
La(NPicO) ₃ (ClO ₄) ₃	11.57	11.51	63.54	63.78	24.32	24.71	175.7	0.997
Pr ₂ (NPicO) ₃ (ClO ₄) ₆	12.38	12.44	61.41	61.20	26.01	26.34	178.4	0.809
Nd ₂ (NPicO) ₃ (ClO ₄) ₆	12.50	12.71	61.16	61.03	174.9	0.813
Gd ₂ (NPicO) ₃ (ClO ₄) ₆	13.76	13.68	59.89	60.36	25.61	25.98	179.6	0.854
Tb(NPicO) ₄ (ClO ₄) ₅	14.64	14.79	57.91	57.38	27.29	27.77	169.6	0.962
Dy(NPicO) ₄ (ClO ₄) ₅	14.90	15.09	57.61	57.23	170.9	0.989
Ho(NPicO) ₄ (ClO ₄) ₅	14.98	15.27	56.93	57.07	171.4	0.958
Yb(NPicO) ₄ (ClO ₄) ₅	16.07	15.90	57.01	56.65	26.98	27.43	174.1	0.959

* Molar conductance in nitromethane: ohms⁻¹ cm² mole⁻¹ for monomers.

3. Results and discussion

All the complexes are hygroscopic and are soluble in solvents like nitromethane, acetonitrile, but insoluble in nitrobenzene, chloroform and benzene. The colours of the complexes resemble the yellow colour of the ligand.

Analytical data show that the NPicO complexes have the formulae $\text{La}(\text{NPicO})_6(\text{ClO}_4)_3$, $\text{Ln}_2(\text{NPicO})_9(\text{ClO}_4)_6$ ($\text{Ln} = \text{Pr, Nd, and Gd}$) and $\text{Ln}(\text{NPicO})_4(\text{ClO}_4)_3$ ($\text{Ln} = \text{Tb, Dy, Ho and Yb}$). The ligand to metal ratio is less than that in the corresponding complexes of 2,4-LutO (table 1).

Molar conductance data indicate that all the complexes behave as 1 : 2 electrolytes in nitromethane (Geary 1971) suggesting thereby that one of the three perchlorates is coordinated to the metal.

The IR frequencies for NpicO and its complexes along with the assignments are presented in table 2. The characteristic features of the IR spectra are (i) the N-O stretching frequency of the ligand occurring at 1275–1300 cm^{-1} as a strong and broad band split into a strong and sharp band at 1295 cm^{-1} and a shoulder at 1275 cm^{-1} in all complexes except the La-complex, where only a band at 1295 cm^{-1} results, (ii) increase in the C-H out-of-plane bending frequency of the ligand at 792 cm^{-1} by about 3–8 cm^{-1} and that of the ring stretch at 1520 cm^{-1} by about 5 cm^{-1} and (iii) bands that are assignable to both ionic and coordinated perchlorate groups.

Suszko and Szafran (1962) have found that the N-O of NPicO in benzene occurs at 1300 cm^{-1} . In view of this, a negative shift of the $\nu_{\text{N-O}}$ by about 5 cm^{-1} appearing in the complexes of NpicO, indicates the coordination of the ligand through the oxygen of the N-O group. The splitting of the $\nu_{\text{N-O}}$ in the complexes of lanthanides other than La, can be taken to mean bridged structures in these complexes (Isobe *et al* 1974). A similar observation was made by Ramakrishnan and Soundararajan (1977) in the lanthanide iodide complexes of 2,6-LutO. The $\nu_{\text{N-O}}$ in these complexes being less than that in the corresponding complexes of 2,4-LutO ($\sim 7 \text{ cm}^{-1}$) (Navaneetham and Soundararajan 1979) suggests a weaker metal-ligand bond. This may be due to the electron-withdrawing nature of NO_2 group coupled with the absence of back bonding.

The increase in C-H out-of-plane bending and ring stretch reveals that the electron density flows from the aromatic ring to the metals ion upon coordination.

The presence of a coordinated perchlorate group having C_{3v} symmetry is shown by the appearance of bands at 1158, 1030, 920 and 648 cm^{-1} in the IR spectra (Hathaway and Underhill 1961; Hathaway *et al* 1963). The existence of bidentate perchlorate (C_{2v}) in complexes is rare (Rosenthal 1973). However, the absence of bands at 1170 cm^{-1} and at 928 cm^{-1} in the IR spectra indicate the absence of the bidentate perchlorate group (Rosenthal 1973). Ionic perchlorate has four fundamental modes of vibration, two of which are active in the IR between 1075–1100 cm^{-1} for ν_3 and at 626 cm^{-1} for ν_4 .

The IR spectra of the NpicO complexes (table 2) show two bands, one in the range 1095–1100 cm^{-1} and the other at 625 cm^{-1} which have been assigned to the ν_3 and ν_4 vibrations respectively, of the perchlorate group (T_d symmetry). Also evidence for the presence of the coordinated perchlorate group (C_{3v}) is revealed by two bands—one in the region 1135–1155 (ν_4) and the other at 638 cm^{-1} (ν_3). The other bands at 940 and 1030 cm^{-1} , probably merge with the ligand bands

Table 2. Important IR bands (cm^{-1}) and their assignments for NPicO complexes.

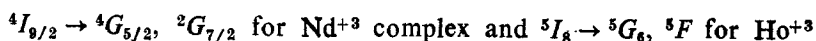
NPicO	La	Pr	Nd	Gd	Tb	Dy	Ho	Yb	Assignments
1275—	1295s	1295s	1295s	1294s	1295s	1295s	1294s	1295s	$\nu_{\text{N-O}}$
1300 s, b	1275sh	1275sh	1275sh	1275sh	1275m	1275m	1275m	1275m	$\delta_{\text{N-O}}$
850m	841m	841m	850m	852m	851m	850m	850m	851m	$\gamma_{\text{C-H}}$
792m	800m	800m	800m	795w	795w	795w	795w	795w	Ring stretch
1520s	1525s	1525s	1525s	1525s	1525s	1525s	1525s	1525m	$\nu_4 \text{ClO}_4$
	1135sh	1155s	1155s	1152s	1150s	1155s	1155s	1150s	$\nu_1 \text{ClO}_4 + \text{Ligand}$
1045m	1045sh	1040sh	1045sh	1045sh	1045sh	1045sh	1045sh	1040sh	$\nu_2 \text{ClO}_4 + \text{Ligand}$
940s	940s	940s	940s	940s	940s	940s	940s	940m	$\nu_3 \text{ClO}_4$
	636sh	635sh	638sh	637sh	638sh	638sh	638sh	638sh	$\nu_2 \text{ClO}_4$
	1100vs	1105vs	1095vs	1095vs	1095vs	1095vs	1095vs	1095vs	$\nu_2 \text{ClO}_4^-$
	625m	627m	627m	627m	627m	627m	627m	627m	$\nu_4 \text{ClO}_4^-$

vs = very strong, s = strong, m = medium, sh = shoulder, w = weak, b = broad.

occurring in the same regions. As there are no bands at 1170 cm^{-1} and at 928 cm^{-1} we conclude that the bidentate perchlorate groups are absent. These assignments indicating the presence of perchlorate groups of both T_d and C_{3v} symmetries are in line with the 1 : 2 electrolytic conductivity evidence for the presence of one coordinated perchlorate group and two ionic perchlorate groups.

The proton NMR spectra of the diamagnetic La^{+3} complex are sharp and well resolved. The doublet occurring at 1.77τ in the free ligand corresponds to the 6-H signal, and that at 1.94τ is due to the 5-H. The singlet at 1.83τ corresponds to the 3-H. The shifts in the ring proton signals of the ligand (7 Hz for 6-H, 4 Hz for 5-H and 3-H) arise from a deshielding of the protons due to the drainage of the electron density from the ligand to the metal ion on coordination of the N-oxide group.

The electronic spectra in nitro-methane indicate that the shapes of the hypersensitive bands



complex resemble those of the six coordinate complexes studied by Karnaker (1967).

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 the IR data suggest a weaker metal-ligand bond compared to that in the corresponding complexes of 2,4-LutO. The 1 : 2 electrolytic conductance along with the IR and electronic spectral data point to a coordination number of 6 in all the complexes with the possibility of an aromatic amine oxide bridged structure for all the complexes except the La-complex.

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