

4-Nitro and 4-chloro pyridine-N-oxide complexes of lanthanide perchlorates

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Abstract. Adducts of lanthanide perchlorates with 4-nitro and 4-chloro pyridine-N-oxides (4-NPNO and 4-CPNO respectively) have been synthesised for the first time and characterised by analysis, electrolytic conductance, infrared, proton-NMR and electronic spectral data. The complexes are of the compositions $\text{Ln}_2(\text{NPNO})_4(\text{ClO}_4)_6$ ($\text{Ln} = \text{La, Pr, Nd and Gd}$), $\text{Tb}(\text{NPNO})_7(\text{ClO}_4)_8$, $\text{Ln}_2(\text{NPNO})_{12}(\text{ClO}_4)_6$ ($\text{Ln} = \text{Dy, Ho, and Yb}$); $\text{Ln}(\text{CPNO})_8(\text{ClO}_4)_8$ ($\text{Ln} = \text{La, Pr, Nd, Tb, Dy, Ho and Yb}$) and $\text{Ln}(\text{CPNO})_7(\text{ClO}_4)_8$ ($\text{Ln} = \text{Sm and Gd}$). Conductivity and IR data provide evidence for the non-coordinated nature of the perchlorate groups. IR and NMR spectra suggest coordination *via* the oxygen of the N-oxide group. Electronic spectral shapes of the Nd^{+3} and Ho^{+3} complexes are interpreted in terms of eight- and seven-coordinate environments in the case of 4-NPNO complexes and eight-coordinate in the case of 4-CPNO complexes. IR data indicate bridged structure in NPNO complexes of lanthanides other than Tb.

Keywords. Lanthanide perchlorates; 4-nitro pyridine-N-oxide; 4-chloro pyridine-N-oxide; electrolytic conductance; proton-NMR; electronic spectra.

1. Introduction

Coordination compounds of a variety of lanthanide salts with pyridine-N-oxide (PyO) and methyl substituted pyridine-N-oxides have been extensively studied. It has been found that the substitution of the methyl group (Me) at the 3- and 4-positions of the PyO moiety have no influence on the coordination number around the lanthanide ions and the complexes have the formula $[\text{LnL}_8](\text{ClO}_4)_3$, $\text{L} = \text{PyO}$, 3-MePyO and 4-MePyO (Krishnamurthy and Soundararajan 1967; Koppikar and Soundararajan 1976; Harrison and Watson 1970). We have now initiated a systematic programme involving adducts of lanthanide salts with pyridine-N-oxides, having substituents other than the methyl group. As a part of such studies we report in this paper the preparation and characterisation of complexes of lanthanide perchlorates with 4-nitro and 4-chloro pyridine-N-oxides, with an attempt to compare the nature of the complexes formed by these ligands with those of

4-MePyO (Harrison and Watson 1970). The isolated complexes have been characterised by analysis, conductance, IR, NMR, and electronic spectra.

2. Experimental

2.1. Materials

Lanthanide oxides (99.9% pure) were obtained from Indian Rare Earths Ltd., Kerala State. All other chemicals used were of the reagent grade. Solvents were purified by standard methods.

2.2. Preparation of the ligands

4-Nitropyridine-1-oxide (4-NPNO) was prepared by the nitration of pyridine-1-oxide as described by Katritzky *et al* (1957) and was purified by recrystallisation from acetone (mp 158° C, lit 159.5° C).

4-Chloro pyridine-1-oxide (4-CPNO) was prepared by the reaction of 4-NPNO with acetyl chloride according to the method given by Ochai (1953) and recrystallised from acetone (mp 165° with decomposition, lit 169.5°).

2.3. Preparation of lanthanide perchlorates

The hydrated lanthanide perchlorates were prepared by dissolving the corresponding oxides in less than the required quantity of 50% perchloric acid and filtering off the excess oxide. The solution was evaporated to dryness on a steam bath.

2.4. Preparation of the complexes

2.4.1. *Preparation of the 4-NPNO complexes* : Hydrated lanthanide perchlorate (0.6 mM), dissolved in ethyl acetate (5 ml), was added drop by drop to a boiling solution of 4-NPNO (5.7 mM) in chloroform (30 ml), with vigorous stirring. Boiling and stirring was continued till the complex was completely precipitated. The complex was filtered from the hot mixture through a sintered crucible (grade-3). The crystalline solid was washed 3-4 times with hot chloroform and finally with ether and dried over phosphorus (V) oxide in a vacuum desiccator overnight.

2.4.2. *Preparation of the 4-CPNO complexes* : To a boiling solution of 4-CPNO (6.2 mM) in 25 ml of chloroform, a solution of hydrated lanthanide perchlorate (0.6 mM) in ethyl acetate (5 ml) was added drop by drop with vigorous stirring. The mixture was cooled and stirred till the complete precipitation of the complex resulted. The complex was filtered through a sintered crucible (grade-3), washed and dried as in the case of 4-NPNO complexes.

2.5. Analyses

The metal in the complexes was estimated by complexometric titration with EDTA using xylenol orange as indicator (Kolthoff and Elwing 1963). Perchlorate was determined by gravimetric precipitation with nitron as described by Welcher (1947).

The ligands, 4-NPNO and 4-CPNO, were analysed spectrophotometrically at 314 nm and 264 nm respectively, by the calibration curve method.

2.6. Physical methods

The infrared spectra of the ligands and complexes in nujol mulls in the region 400–4000 cm^{-1} were recorded on a Carl-Zeiss-UR-10 infrared spectrophotometer.

Proton NMR spectra of the complexes and the ligands were recorded on a Varian T-60 instrument using CH_3CN as solvent and TMS as the internal standard.

Electronic spectra of the Nd and Ho complexes in acetonitrile solutions were recorded in the region 350–700 nm on a Beckman Model-25 spectrophotometer. Solid state spectra for the complexes in nujol mull were obtained on a Unicam SP 700 spectrometer.

Conductance measurements in acetonitrile 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.

3. Results and discussion

The complexes of both 4-NPNO and 4-CPNO are non-hygroscopic and are soluble in solvents like methanol, acetone, acetonitrile, dimethyl formamide and insoluble in benzene, nitrobenzene, chloroform and carbon tetrachloride. The colours of the 4-NPNO complexes resemble the yellow colour of the ligand, while the 4-CPNO complexes retain the colours of the parent lanthanide salts.

Analytical and conductance data for all the complexes are presented in table 1. Analytical data show that the 4-NPNO complexes have the formulae $\text{Ln}_2(\text{NPNO})_{15}(\text{ClO}_4)_6$ ($\text{Ln} = \text{La, Pr, Nd and Gd}$), $\text{Tb}(\text{NPNO})_7(\text{ClO}_4)_3$ and $\text{Ln}_2(\text{NPNO})_{13}(\text{ClO}_4)_6$ ($\text{Ln} = \text{Dy, Ho and Yb}$). The 4-CPNO complexes analyse for the formulae $\text{Ln}(\text{CPNO})_8(\text{ClO}_4)_3$ ($\text{Ln} = \text{La, Pr, Nd, Tb, Dy, Ho and Yb}$), and $\text{Ln}(\text{CPNO})_7(\text{ClO}_4)_3$ ($\text{Ln} = \text{Sm and Gd}$).

Molar conductance data in acetonitrile, for the complexes of both 4-NPNO and 4-CPNO are in the range expected for 1 : 3 electrolytes, in this solvent (Geary 1971). This suggests that the perchlorates are not coordinated to metal ion.

Infrared data for the ligands and the complexes along with the assignments are presented in table 2. The characteristic features of the IR spectra are (i) a shift of the N–O stretching frequency from 1280 cm^{-1} in 4-NPNO and 1255 cm^{-1} in 4-CPNO to 1250 cm^{-1} and 1240 cm^{-1} respectively in the corresponding complexes, which can be taken as evidence for the coordination of the oxygen of the N-oxide group, (ii) splitting of the N–O stretching vibration of the NPNO complexes of lanthanides other than Tb, can be taken to mean bridged structure in these complexes (Isobe *et al* 1974) (figure 1), and (iii) the retention of the characteristic vibrations pertaining to the perchlorate group. The ν_3 mode of the ClO_4^- group occurring at 1080–1100 cm^{-1} , as a very strong band and ν_4 mode at 625–626 cm^{-1} as a medium band remain unsplit showing that the perchlorate groups in the complexes have the T_d symmetry. This is in line with the evidence for the ionic nature of the perchlorate group confirmed by the conductivity data,

Table 1. Analytical and molar conductance data.

Complex	% Metal		% Ligand		% ClO ₄ ⁻		Δ_m^*	Conc. moles $\times 10^{-3}$
	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.		
La ₂ (NPNO) ₁₅ (ClO ₄) ₆	9.46	9.34	70.01	70.62	20.30	20.05	401.2	0.764
Pr ₂ (NPNO) ₁₅ (ClO ₄) ₆	9.56	9.45	71.04	70.53	387.5	0.815
Nd ₂ (NPNO) ₁₅ (ClO ₄) ₆	9.73	9.66	71.08	70.39	393.8	0.752
Gd ₂ (NPNO) ₁₅ (ClO ₄) ₆	10.51	10.46	70.90	69.79	20.10	19.82	391.4	0.760
Tb(NPNO) ₇ (ClO ₄) ₃	11.15	11.05	69.60	68.16	21.08	20.76	396.0	0.749
Dy ₂ (NPNO) ₁₃ (ClO ₄) ₆	12.01	11.84	66.77	66.37	22.00	21.76	384.3	0.821
Ho ₂ (NPNO) ₁₃ (ClO ₄) ₆	12.12	12.00	66.90	66.27	383.4	0.824
Yb ₂ (NPNO) ₁₃ (ClO ₄) ₆	12.45	12.51	64.65	65.89	21.83	21.60	391.3	0.759
La(CPNO) ₈ (ClO ₄) ₂	9.43	9.44	70.69	70.33	20.50	20.26	413.7	0.715
Pr(CPNO) ₈ (ClO ₄) ₂	9.52	9.55	69.89	70.22	411.4	0.723
Nd(CPNO) ₈ (ClO ₄) ₂	9.61	9.76	70.46	70.08	20.40	22.18	401.6	0.742
Sm(CPNO) ₇ (ClO ₄) ₂	11.03	11.09	66.65	66.89	22.41	22.03	394.1	0.751
Gd(CPNO) ₇ (ClO ₄) ₂	11.52	11.54	66.96	66.56	398.6	0.741
Tb(CPNO) ₈ (ClO ₄) ₂	10.49	10.64	68.86	69.38	20.20	19.99	396.3	0.758
Dy(CPNO) ₈ (ClO ₄) ₂	10.59	10.85	68.61	69.18	416.9	0.710
Ho(CPNO) ₈ (ClO ₄) ₂	11.12	11.00	68.81	69.08	406.4	0.730
Yb(CPNO) ₈ (ClO ₄) ₂	11.31	11.48	69.06	68.74	20.10	19.81	409.1	0.723

*Molar Conductance in acetonitrile at 25° C ohms⁻¹ cm² mole⁻¹ for monomers.

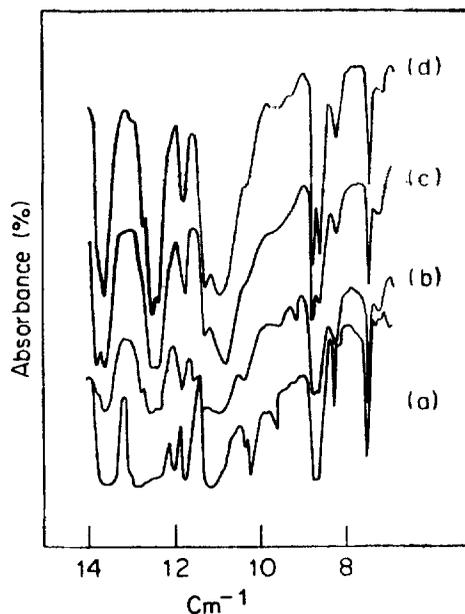


Figure 1. IR spectra in nujol mull of (a) NPNO and of the complexes of (b) La, (c) Tb and (d) Dy perchlorates.

The extent of shift to a lower frequency, of the ν_{N-O} can be related to the metal-N-O bond strength. The greater $\Delta \nu_{N-O}$ in the 4-NPNO complexes compared to that in the corresponding complexes of 4-CPNO, suggest a stronger metal-ligand bond in 4-NPNO complexes. This could be attributed to the greater electron withdrawing ability of NO_2 group in the ligand. A similar effect has been found in the complexes of the corresponding 4-substituted pyridine-N-oxides with a variety of transition metal ions (Herlocker *et al* 1966).

The proton NMR spectra of the diamagnetic La^{+3} complexes are sharp and well resolved. The doublets occurring at 1.70τ and 1.86τ in the 4-NPNO and those at 1.83τ and 2.58τ in the 4-CPNO correspond to the signals of α and β protons respectively. The shifts in the ring proton signals of the ligands (13 Hz for αH and 7 Hz for βH in the 4-NPNO complex, 7 Hz in the 4-CPNO complex for both α and β protons) 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 difference between the chemical shifts for the α protons in the free ligand and in the complex, being greater in the case of diamagnetic 4-NPNO complex, is indicative of a stronger metal-ligand bond in the 4-NPNO complexes as was found by Kanekar and Venkata Setty (1965), in the NMR study of 4-substituted pyridine-N-oxide UO_2Cl_2 complexes, which also corroborates the infrared evidence. The relevant NMR data are given in table 3.

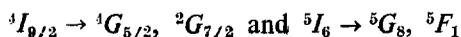
The isotropic shifts for the paramagnetic complexes show that both contact and pseudo-contact interactions are operative. The broadening of α proton signals in all paramagnetic complexes is due to the relaxation effects.

Table 3. Proton NMR spectral data.

Compound	αH	βH
4-NPNO	1.70	1.86
La ₂ (NPNO) ₁₅ (ClO ₄) ₆	1.48	1.73
Pr ₂ (NPNO) ₁₅ (ClO ₄) ₆	-0.75	1.05
Nd ₃ (NPNO) ₁₅ (ClO ₄) ₆	0.43	1.25
Tb(NPNO) ₇ (ClO ₄) ₃	-2.43 (α and βH)	
Dy ₂ (NPNO) ₁₃ (ClO ₄) ₆	-2.03 (α and βH)	
Ho ₂ (NPNO) ₁₃ (ClO ₄) ₆	-0.22 (α and βH)	
4-CPNO	1.83	2.58
La(CPNO) ₈ (ClO ₄) ₃	1.71	2.46
Pr(CPNO) ₈ (ClO ₄) ₃	1.10	2.15
Nd(CPNO) ₈ (ClO ₄) ₃	1.75	2.23
Sm(CPNO) ₈ (ClO ₄) ₃	1.58	2.38
Tb(CPNO) ₈ (ClO ₄) ₃	-0.52 (α and βH)	
Dy(CPNO) ₈ (ClO ₄) ₃	-2.72 (α and βH)	
Ho(CPNO) ₈ (ClO ₄) ₃	1.05 (α and βH)	
Yb(CPNO) ₈ (ClO ₄) ₃	1.25	1.88

Spectra of 4-NPNO, 4-CPNO and of their complexes were obtained in CH₃CN. TMS was used as the internal reference. Chemical shifts are given in τ .

The shapes of the hypersensitive electronic spectral bands have been found to be dependent on the coordination number around the tripositive lanthanide ion. The shapes of the hypersensitive bands



for Nd⁺³ and Ho⁺³-4-NPNO complexes respectively, in the solid state and in the solution resemble those of the eight and seven coordinate complexes studied by Karraker (1967) (figure 2). The electronic spectra of the corresponding 4-CPNO complexes show that the band shapes are identical to those of the eight coordinate β -diketonate (Karraker 1967) (figure 2).

Thus, the proton NMR data along with the IR data for both 4-NPNO and 4-CPNO complexes indicate the coordination of the ligands through the oxygen of N-O group, and a weaker metal-ligand bond in the 4-CPNO complexes.

The conductivity data for the 4-NPNO complexes along with the electronic spectral data for the complexes of Nd⁺³ and Ho⁺³ point to a coordination number of 8 in the complexes of La, Pr, Nd and Gd and of 7 in Tb, Dy, Ho and Yb complexes, with one ligand probably bridging in nature in all the complexes except in the case of Tb. The data for the 4-CPNO complexes suggest a coordination number of 7 in the complexes of Sm and Gd and of 8 in La, Pr, Nd, Tb, Dy, Ho and Yb complexes.

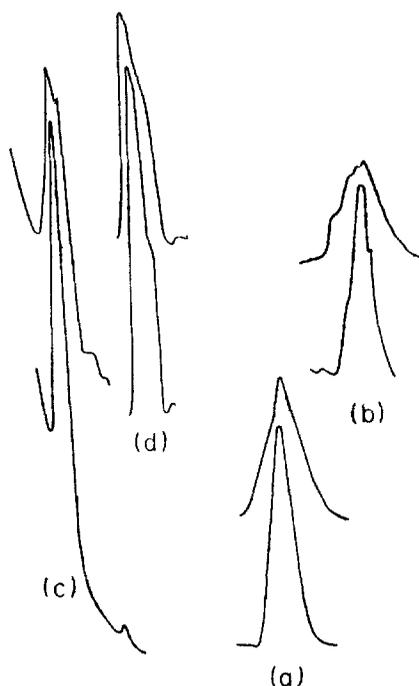


Figure 2. Electronic spectra of (a) $\text{Nd}_2(\text{NPNO})_{15} \cdot 6 \text{ClO}_4$, (b) $\text{Nd}(\text{CPNO})_8 \cdot 3 \text{ClO}_4$, (c) $\text{Ho}_2(\text{NPNO})_{15} \cdot 6 \text{ClO}_4$ and (d) $\text{Ho}(\text{CPNO})_8 \cdot 3 \text{ClO}_4$ (upper curve = solid state spectra; lower curve = solution spectra).

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