

Synthesis & Characterisation of Some Lanthanide Perchlorate Complexes of 4-Nitrosoantipyridine

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Seven lanthanide perchlorate complexes of 4-nitrosoantipyridine (NAP) of the general formula $\{Ln(NAP)_4ClO_4\}(ClO_4)_2$ (where Ln = La, Pr, Nd, Sm, Gd, Dy and Y), have been synthesised and characterised by elemental analyses, molecular weights, conductances, magnetic moments and infrared and electronic spectral data. In these nine-coordinated complexes, all the four NAP molecules are coordinated bidentately and one of the perchlorate groups is coordinated monodentately.

As part of our programme on the synthesis and characterisation of solid lanthanide complexes¹⁻⁴, we now report herein seven lanthanide perchlorate complexes of 4-nitrosoantipyridine (NAP), in which one of the perchlorate groups is also coordinated. In this respect, these complexes are very interesting. The ligand NAP has two donor sites, namely the ring carbonyl and the nitroso group and, therefore, it is expected to behave like a bidentate ligand forming a stable six-membered ring with the metal ion.

Perchlorates of La, Pr, Nd, Sm, Gd, Dy and Y were prepared from the respective oxides (99.9% pure) as reported earlier¹. The ligand NAP, was prepared by the literature method⁵ and its purity checked by elemental analyses and IR spectral data, m.p. 192° (lit.⁵ m.p. 192°).

Solutions containing lanthanide perchlorates (2 mmol) and NAP (8.1 mmol) in minimum quantity of hot ethanol were kept under reflux for 2 hr and cooled to room temperature ($28 \pm 2^\circ\text{C}$). To the reaction mixture was added ether in small portions with vigorous stirring. The precipitates obtained were filtered, washed repeatedly with hot benzene and ether and dried *in vacuo* over phosphorus pentoxide. The complexes were analysed for the metal and perchlorate contents by the conventional methods^{6,7}.

The molar conductances of $10^{-3}M$ solutions of the complexes in nitrobenzene, methanol and acetonitrile were determined at room temperature ($28 \pm 2^\circ\text{C}$) on an ELICO M 82T conductivity bridge with a dip-type cell and platinum electrodes (cell constant = 1.56 cm^{-1}). The room temperature magnetic susceptibilities of the complexes were measured by the Gouy method using mercury(II) tetrathiocyanate

tocobaltate(II) as the calibrant⁸. Molecular weights of the complexes were determined by the Rast method using biphenyl as the solvent⁹. The IR spectra of the ligand and the complexes were recorded in KBr on a Perkin-Elmer 397 IR spectrophotometer in the range $4000-400\text{ cm}^{-1}$. The electronic spectra of $10^{-4}M$ solutions of the ligand and the complexes in acetonitrile were recorded on a Hitachi 220A UV-visible spectrophotometer.

The analytical, molecular weight, molar conductivity and magnetic data of the complexes are presented in Table 1. All the seven complexes are reddish brown, non-hygroscopic solids. These are soluble in acetone, acetonitrile, nitrobenzene, methanol and ethanol and insoluble in benzene, petroleum ether and ether. The complexes can be represented by the general composition $Ln(NAP)_4(ClO_4)_3$ (where Ln = La, Pr, Nd, Sm, Gd, Dy and Y, and NAP = 4-nitrosoantipyridine).

The molar conductances of the complexes correspond to 2:1 electrolytes, indicating that one of the perchlorate ions is coordinated to the metal ions. However, slightly higher conductances of Gd and Dy complexes in acetonitrile are probably due to partial substitution for the coordinated perchlorate ions by the solvent molecules (acetonitrile). In fact, these higher values are always much less than those expected for a 3:1 electrolyte.

The room temperature magnetic data show that all the complexes, except those of La and Y, are paramagnetic; La and Y complexes are diamagnetic as expected. The observed magnetic moments are generally found to agree well with the theoretical values calculated by the Van-Vleck formula¹⁰.

The IR spectrum of the free ligand exhibits $\nu\text{C}=\text{O}$ and $\nu\text{N}=\text{O}$ modes as strong bands at 1680 and 1410 cm^{-1} respectively, which are shifted to 1630 and 1390 cm^{-1} , respectively in the complexes. These shifts to lower wavenumbers indicate that NAP is coordinated to the lanthanide ion through the oxygen atoms of these two groups. Comparatively, smaller shift ($\Delta\nu = 20\text{ cm}^{-1}$) in the $\nu\text{N}=\text{O}$ mode on coordination is probably due to its coupling with other stretching vibrations of the ligand¹¹.

The IR spectra of the complexes exhibit strong, doubly split band with band maxima at 1110 and 1090 cm^{-1} which are assigned to the ν_3 vibration of the monodentately coordinated perchlorate ion having C_{3v} symmetry¹². Two more additional bands, a medium band at 925 and a strong band at 620 cm^{-1} , which are unsplit and absent in the spectrum of the ligand are

Table 1 – Analytical, Conductance, Magnetic and Molecular Weight Data of Lanthanide(III) Perchlorate Complexes of 4-Nitroantipyrine

Complex	Found (Calc)%		Mol wt*	Molar conductivity (ohm ⁻¹ cm ² mol ⁻¹)			Magnetic moment* (B.M.)
	Metal	Perchlorate		Nitrobenzene	Methanol	Acetonitrile	
[Pr(NAP) ₄ ClO ₄](ClO ₄) ₂	10.74 (10.78)	22.46 (22.82)	1268 (1307)	73.92	189.40	293.88	3.60 (3.62)
[Nd(NAP) ₄ ClO ₄](ClO ₄) ₂	11.20 (11.01)	22.38 (22.76)	1281 (1310)	77.14	185.09	282.80	3.68 (3.68)
[Sm(NAP) ₄ ClO ₄](ClO ₄) ₂	11.87 (11.42)	22.32 (22.65)	1292 (1317)	75.70	158.20	257.58	1.63 (1.55-1.65)
[Gd(NAP) ₄ ClO ₄](ClO ₄) ₂	11.63 (11.88)	21.81 (22.53)	1265 (1324)	76.50	218.54	374.94	7.70 (7.94)
[Dy(NAP) ₄ ClO ₄](ClO ₄) ₂	11.76 (12.23)	21.91 (22.46)	1301 (1328)	76.59	214.47	330.90	10.61 (10.60)
[Y(NAP) ₄ ClO ₄](ClO ₄) ₂	7.01 (7.08)	23.50 (23.76)	1205 (1255)	70.24	184.18	288.47	0.00 (0.00)

* Values given in brackets are the theoretical values

assigned to the ν_1 and ν_4 vibrations, respectively of the perchlorate ion.

The electronic spectrum of the ligand displays three intense absorption bands at 30.86 ($n \rightarrow \pi^*$), 43.10 ($\pi \rightarrow \pi^*$) and 46.29 kK ($\pi \rightarrow \pi^*$). All these bands are red shifted in the spectra of the complexes. The very strong band observed in the visible region with absorption maximum in the region 26.59 – 28.09 kK may be assigned to the strong L → M charge-transfer (CT) transition. Most of the absorption bands due to $f-f$ transitions of the lanthanide ions in the visible region are obscured in the complexes and are replaced by broad CT bands (L → M) that spread over the whole visible region.

On the basis of the above discussion and the molecular weights of the complexes (Table 1), the lanthanides in the present series of complexes which are represented by the general formula $[Ln(NAP)_4ClO_4](ClO_4)_2$ are assigned a coordination number of nine.

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