

2-PICOLINE-N-OXIDE COMPLEXES OF RARE-EARTH CHLORIDES

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ABSTRACT

2-Picoline-N-Oxide (2-PicNO) complexes of seven rare-earth chlorides of the general formula $M(2\text{-PicNO})_n\text{Cl}_3$ where $n = 4$ for $M = \text{La}$ or Pr ; and $n = 5$ for $M = \text{Nd}, \text{Sm}, \text{Tb}, \text{Er}$ or Y have been prepared and characterized. Ligand is coordinated through oxygen of the N-O group and the chloride ions are non-ionic.

INTRODUCTION

IN continuation of our recent studies on 2-PicNO complexes of rare-earth bromides¹, iodides², nitrates³ and perchlorates⁵, the preparation and characterization of its complexes with rare-earth chlorides is undertaken.

EXPERIMENTAL

Preparation of the complexes:—One g of the ligand was added to about 0.5 g of the hydrated rare-earth chloride. The mixture was triturated and warmed on a water-bath for about 15 minutes. The fine crystalline product obtained after cooling was suspended in acetone in which only the free ligand is quite soluble. The product was filtered through a sintered crucible, washed well with acetone and dried in a desiccator over calcium chloride under reduced pressure.

Analyses: The metal content of the complexes was estimated by EDTA titrations using xylenol orange

RESULTS AND DISCUSSION

Results of analyses (Table I) conform to the general formula $M(2\text{-PicNO})_n\text{Cl}_3$ where $n = 4$ for $M = \text{La}$ or Pr ; and $n = 5$ for $M = \text{Nd}, \text{Sm}, \text{Tb}, \text{Er}$ or Y . Unlike in the corresponding bromide, iodide, nitrate and perchlorate complexes, the metal ligand ratio changes as one goes from lighter to heavier lanthanides. The stoichiometry of the complexes is different from that of the corresponding pyridine-N-oxide complexes⁶. While eight molecules of PyO are coordinated to all the rare-earth metal ions only four or five ligand molecules are coordinated in the present case. This is due to the steric effect of the methyl group at 2-position in the aromatic ring of PyO. It is interesting to observe that the reduction in the number of ligand molecules coordinated to rare-earth ions, as one goes from PyO to 2-PicNO complexes, is more in rare-earth halide complexes (3 or 4 molecules) than in the perchlorate complexes (1 molecule).

TABLE I
Analytical and conductance data for the complexes

Compound	Metal (%)		Chloride (%)		2-PicNO (%)		Molar conductance (ohm ⁻¹ cm ² mole ⁻¹) in	
	Calc.	Found	Calc.	Found	Calc.	Found	Methanol	Acetonitrile
La (2-PicNO) ₄ Cl ₃	20.39	20.52	15.62	15.46	64.03	64.20	126.7	..
Pr (2-PicNO) ₄ Cl ₃	20.61	20.67	15.57	15.61	63.84	63.79	126.0	..
Nd (2-PicNO) ₅ Cl ₃	18.12	18.04	13.37	13.52	68.52	68.43	127.6	..
Sm (2-PicNO) ₅ Cl ₃	18.74	18.59	13.26	13.40	67.98	68.02	129.7	..
Tb (2-PicNO) ₅ Cl ₃	19.59	19.45	13.12	13.02	67.28	67.50	130.8	34.64
Er (2-PicNO) ₅ Cl ₃	20.42	20.40	12.99	12.82	66.59	66.37	124.1	26.48
Y (2-PicNO) ₅ Cl ₃	12.00	11.96	14.36	14.15	73.64	73.81	124.0	33.56

as indicator; chloride was estimated by Volhard's method and 2-PicNO spectrophotometrically in aqueous solutions at 254 nm using the calibration curve method. The infrared, and conductivity measurements were carried out as described earlier⁵.

The complexes are hygroscopic, insoluble in non-polar solvents and acetone but soluble in alcohols, DMF and DMSO. While the complexes of La, Pr, Nd and Sm are insoluble in acetonitrile, those of Tb, Er and Y are slightly soluble. Though all the complexes

are soluble in chloroform, they separate out subsequently on standing except for the Er complex which does not separate from the solution. The colours of the complexes are similar to those of the corresponding rare-earth salts.

The Tb, Er and Y complexes behave as non-electrolytes in acetonitrile suggesting that all the chloride ions are coordinated to the metal. Hence a coordination number of seven for lighter lanthanides (La and Pr), and eight for heavier lanthanides and yttrium can be postulated. An increase in the coordination number on going from lighter to heavier lanthanides can be explained as follows. On going from La to Lu, the size of the trivalent lanthanide ion decreases and hence steric effect will influence the coordination number of the lanthanides leading to a lower coordination number for the heavier lanthanide. At the same time the ionic potential of the trivalent lanthanides increases on going from La to Lu. The heavier lanthanides attracting more number of ligands show that the influence of the second factor is dominant in the present case.

The infrared spectra of the complexes are similar showing no significant dependence on the central metal ion. The N-O stretching vibration of the ligand appearing at about 1255 cm^{-1} is shifted to about

1234 cm^{-1} in the complexes indicating bonding of the ligand through oxygen of the N-O group. The N-O bending vibration occurring at 855 cm^{-1} in the free ligand remains unshifted. The C-H out-of-plane vibration appearing at 775 cm^{-1} is shifted to slightly higher frequencies due to decrease in the electron density in the aromatic ring consequent upon the formation of the metal to ligand bond.

The extent of $\nu_{\text{N-O}}$ shift in the complexes which is a measure of the metal-oxygen bond strength is almost the same in rare-earth chloride, bromide and iodide complexes of 2-PicNO.

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PHYSICOCHEMICAL INVESTIGATION OF SOME TRIVALENT METAL-CHELATES OF *o*-(α -2-OXOPROPYLBENZYLIDENEIMINO) BENZENE SULPHONIC ACID

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A SURVEY of the literature¹ has revealed that no work has been done on the rare-earth chelates of *o*-(α -2-oxopropylbenzylideneimino) benzene sulphonic acid (H_2OB). Hence the physicochemical studies of the metal-chelates of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) with H_2OB have been carried out using potentiometric, magnetic and spectral techniques and their stoichiometry and structures have been established.

Potentiometric titrations of the mixtures containing (A) perchloric acid alone, (B) perchloric acid and the ligand (H_2OB) and (C) perchloric acid, ligand and metal-ion solution have been carried out by the method of Irving and Rossotti².

The mean values of dissociation constants ($\log K_1^{\text{H}}$ and $\log K_2^{\text{H}}$) as obtained by interpolation at half \bar{n} values method³ and interpolation of various \bar{n} values method⁴ have been found to be 9.755 and 3.030 at 25° and 9.355 and 2.880 at 35°, respectively. The formation curves for the metal-ligand system attain

maxima at $\bar{n} > 1.5$ which indicates that 1:1 and 1:2 chelates are formed. Since in all the cases $K_1/K_2 > 10^{2.5}$, the method of interpolation at half \bar{n} values is applicable besides the methods of successive approximation and correction term⁴. The values of the stability constants as obtained from these methods are in good agreement and the average values thus obtained are shown in Table I. Thus the stability of the chelates increases, with decreasing ionic size of the metal-ions, i.e., La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III). The values of their thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°), entropy change (ΔS°) and the energy of activation (E) have also been included in Table I. The more negative values of ΔG° at 35° C than at 25° C and the positive values of ΔH° in all the cases suggest the endothermic nature of these reactions. The positive values of ΔS° indicate that the entropy term is favourable for their formation. The positive values of energy of activation further confirm the endothermic nature of the reactions.