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Structural Studies of the Complexes of Lanthanides(III) with N-m-Methylbenzene Oxamic Acid

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Potentiometric studies have been cited for the formation of 1 : 3 lanthanide N-m-methylbenzene oxamic acid (NMMBOA) complexes. The complexes are found insoluble in common organic solvents but soluble in hot mineral acids and strong alkali. They are sufficiently thermally stable upto 240°C. The complexes have been characterised on the elemental analysis, thermal and infra red studies. The ligand behaves as a monobasic bidentate O-O donor.

INTRODUCTION

The synthesis of *o*, *p* and *m*-toluidinyl oxamic acids and their utility for the gravimetric estimation of some lanthanides have already been described by Sharma and coworkers[1] . The earlier report described the analytical use of *m*-methylbenzene oxamic acid for the determination of some lanthanides[2]. The present study reports the potentiometric studies and characterisation of N-m-methylbenzene oxamic acid (NMMBOA) complexes of La(III), Pr(III), Nd(III), Gd(III) and Dy(III) metal ions. The ligand behaves as a bidentate coordinating through the two oxygen atoms only.

EXPERIMENTAL

All the solutions of A.R. grade chemical were prepared in double distilled water. Metal nitrate solutions were prepared by dissolving their analaR grade oxide in minimum quantity of nitric acid and standardised by titrating the precipitate metal oxalate with standard $KMnO_4$ solution[3] or complexometrically with EDTA solution[4]. The solutions of desired concentration were prepared by subsequent dilution of their stock solutions. N-m-methylbenzene oxamic acid (NMMBOA) was synthesised and purified by earlier reported method[2]. The pH titrations were carried out by Philips pH meter (PR 9404) standardised with 0·01M potassium hydrogenphthalate solution for pH-4. The IR spectra were recorded in KBr on a Perkin Elmer 783 spectrophotometer with region 4000–200 cm^{-1}. The thermal analyses of the complexes were recorded on stanten (mass flow type) automatic recording thermogravimetric balance at a heating rate 5°C/min.

RESULTS AND DISCUSSION

The pH titration of the following system were carried out keeping the total volume (50 cc) and ionic strength (μ0.1 M KNO_3) constant against 0.1 M potassium hydroxide solution at room temperature.

10 cm^3 of (0.025 M) metal nitrate solution of La(III), Pr(III), Nd(III), Gd(III) and Dy(III) has been taken and titrated against potassium hydroxides solution. The KOH is added slowly and slowly with continuous stirring of the solution. A sharp single inflection has been recorded after the mixing of 2.5 mole of potassium hydroxide. The pH of the solution at this time was 8.5. This inflection shows the formation of basic salt formation of the metal ion[4]. In another set of titration 10 cm^3 of (0.025 M) N-m-methylbenzene oxamic acid (NMMBOA) has been taken and titrated against potassium hydroxide. After the 1 mole of KOH adding a single sharp inflection at pH $\approx$ 5 has been recorded. This sharp inflection indicates the neutralization of carboxylic proton of the oxamic acid. The absence of second inflection, however, indicates that proton attached to the imino group is not titrated upto pH $\approx$ 11

$$CH_3\text{-}C_6H_4NHCOCOOH + KOH \xrightarrow{m=1} CH_3-C_6H_4NHCOCOOK + H_2O$$

In another set of titration 10 cm^3 of metal nitrate solution (0.025 M) has been taken and 10 cm^3 of (0.025 M) NMMBOA added slowly with the pipette. The pH of the set is lowered from 4.5 to 4.0 and a white precipitate formed right from the beginning of titration.

Then the system is titrated against potassium hydroxide. Two inflections have been observed, first inflection is at pH 5.5 and another at pH 8.5 after addition of 1 mole and 3 moles of KOH respectively. The first inflection indicates the formation of 1 : 3 neutral species and second shows the precipitation of remaining metal nitrate as metal hydroxide.

$$Ln^{3+} + CH_3\text{-}C_6H_4\,NHCOCOOH + OH^- \xrightarrow{m=1}$$

$$\tfrac{1}{3}(CH_3\text{—}C_6H_4NHCOCOO)_3Ln + \tfrac{2}{3}Ln^{3+} + H_2O$$

$$\tfrac{2}{3}Ln^{3+} + 2\,OH^- \xrightarrow{m=3} \tfrac{2}{3}\,Ln(OH)_3$$

Ln = La, Pr, Nd, Gd or Dy.

In the next set of potentiometric titration 10 cm^3 of (0.025 M) different metal nitrate has been taken and 20 cm^3 of (0.025 M) NMMBOA added very slowly . The pH of the set is lowered from 4.5 to 3.5 and appearance of a solid phase from beginning of the addition of reagent observed. The system is titrated against potassium hydroxide. The first inflection is at 2 moles of KOH, at pH = 5 and second inflection is at 3 moles of KOH addition at pH 8.5. The formation of precipitate, lowering of pH and two inflection shows the formation of 1 : 3 complex. The second inflection is due to the precipitation of remaining metal nitrate as metal hydroxide.

$$Ln^{3+} + 2CH_3\text{–}C_6H_4NHCOCOOH + 2OH^- \xrightarrow{m\,=\,2} \tfrac{2}{3}Ln(CH_3\text{–}C_6H_4COCOO)_3 + 2H_2O + \tfrac{1}{3}Ln^{3+}$$

$$\tfrac{1}{3}Ln^{3+} + OH \xrightarrow{m\,=\,3} \tfrac{1}{3}Ln(OH)_3$$

In the final titration of 10 cm^3 of metal nitrate (0.025 M) and 30 cm^3 of (0.025M) NMMBOA against potassium hydroxide (0.1 M) only one inflection has been recorded at pH 4 at 3 moles of addition of KOH. The pH of the system has been lowered from 3.5 to 2.5 after adding NMMBOA and formation of a solid mass, right from the beginning of mixing of the reagent observed. The presence of only one inflection indicates the formation of 1 : 3 metal-ligand complex.

$$Ln^{3+} + 3CH_3\text{–}C_6H_4NHCOCOOH + 3OH^- \rightarrow Ln(CH_3\text{–}C_6H_4NHCOCOO)_3 + 3H_2O$$

Preparation of Complexes

All the complexes of lanthanides(III) were prepared by taking aliquot of respective metal nitrate solution to which 1% alcoholic solution of the ligand NMMBOA was gradually added with constant stirring till the complete precipitation was achieved. The precipitated complexes were filtered and washed with hot water and finally with 1% of alcohol and dried at 110°C. All the complexes are insoluble in benzene, chloroform, alcohol and ether and soluble in strong alkali and acids. Microanalytical methods were used for elemental analysis of carbon, hydrogen and nitrogen. The metal contains estimated using appropriate method of analysis[3-4]. The data are collected in Table 1.

TGA data of these complexes shows that complexes are stable upto 240°C and this study indicates that chelates do not contain any water molecule in its structure. The DTG records indicate their decomposition in two steps; most of the complexes show major mass loss within region 380–630°C and final residue in oxides of lanthanides in each case.

The IR spectrum of ligand has strong absorption band in the region 3240 cm^{-1} can be assigned to the mixed stretching vibration of –OH and –NH– indicating intra and intermolecular hydrogen bonding[5-7]. A strong absorption band at 1760 cm^{-1} and 1700 cm^{-1} are assigned to ketonic and $\nu(C{=}O)$ bond of free COO^- group[8,9] respectively. The NH bond frequency is observed in the region of 1515 cm^{-1} indicating coupling of –NH bond with amide band (–NH–CO).

Pertinent IR bands of the complexes listed in Table 1 with their most

TABLE 1

ANALYTICAL, SPECTRAL AND THERMAL DATA OF LANTHANIDES COMPLEXES OF N-m-METHYLBENZENE OXAMIC ACID

Complexes	Elemental analysis*				I-R bands (cm^{-1})		Thermal data*		
	% Metal	C%	H%	N%	>NH	>CO	Mass loss starts at (°C)	Final phase reached at	Total mass loss %
$La(C_9H_8NO_3)_3$	20.78 (20.65)	48.30 (48.14)	3.70 (3.75)	6.10 (6.24)	3340	1650	240	600	75.60 (75.80)
$Pr(C_9H_8NO_3)_3$	20.48 (20.88)	48.15 (48.01)	3.85 (3.56)	6.05 (6.22)	3345	1680	245	630	75.30 (75.57)
$Nd(C_9H_8NO_3)_3$	21.20 (21.77)	48.00 (47.77)	3.60 (3.54)	6.00 (6.18)	3355	1680	240	610	74.85 (75.20)
$Gd(C_9H_8NO_3)_3$	22.90 (22.75)	47.00 (46.87)	3.60 (3.47)	5.90 (6.08)	3360	1660	240	630	73.50 (73.78)
$Dy(C_9H_8NO_3)_3$	23.40 (23.23)	46.80 (46.20)	3.60 (3.45)	5.90 (6.03)	3345	1660	245	630	72.90 (73.22)

(Theoretical Values in brackets).

probable assignments. All the complexes show broad intense frequency in the region 3340–3360 cm^{-1}. This indicates that the intra and inter-hydrogen bonding is absent which was observed in free ligand. The —NH frequency observed in ligand (3240 cm^{-1}) is shifted to higher region (3340–3360 cm^{-1}) in the spectra of complexes indicating the non-participation of (—NH) in coordination. The ketonic frequency in the complexes is shifted towards lower region 1650 to 1680 cm^{-1} indicating participation of oxygen atom of ketonic group in coordination. $\nu(C = O)$ bond of free COOH group (of the ligand at 1700 cm^{-1}) is shifted in all these complexes indicating the absence of free COOH group[10,11]. ν_{as} and ν_s vibrations of the COO^- group appearing at 1550 and 1370 cm^{-1} respectively with $\Delta\nu$ value of 240 cm^{-1} indicate that carboxylate acts as unidentate coordinating agent[12]. Thus the ligand in complex is acting as an O—O donor leaving the —NH— group free.

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