

# POTENTIOMETRIC STUDIES ON THE TERNARY SYSTEMS: ALUMINIUM (III)/IRON (III)-AMINOPOLYCARBOXYLIC ACIDS-DICARBOXYLIC ACIDS

KM. USHA JAIN, KM. VINOD KUMARI AND G. K. CHATURVEDI

*Chemical Laboratories, Agra College, Agra*

## ABSTRACT

Potentiometric evidence has been cited for the formation of 1 : 1 : 1 ternary complexes in the systems:  $Al^{3+}$ -EDTA/NTA-OX/MALN and  $Fe^{3+}$ -EDTA-OX/MALN (where EDTA = ethylenediamine tetraacetic acid, NTA = nitrilotriacetic acid, OX = oxalic acid, MALN = malonic acid) and the hydrolytic behaviour of the mixed species resulting in the formation of hydroxo or polynuclear species has been discussed. The formation constants and free energies of formation have also been evaluated. The order of stability in terms of metal ion and dicarboxylic acids has been found to be  $Fe^{3+} > Al^{3+}$  and  $MALN > OX$ .

## INTRODUCTION

**B**INARY complexes of Al(III) and Fe(III) with aminopolycarboxylic acids and dicarboxylic acids have been extensively studied by several workers<sup>1-7</sup>, using different physico-chemical techniques. Survey of the literature, however, revealed that so far, very little work on the mixed ligand complexes of the above metals with aminopolycarboxylic acids has been reported<sup>8</sup>. The results of the investigations on the systems Al(III)-EDTA/NTA-OX/MALN and Fe(III)-EDTA-OX/MALN, have been discussed in the present communication.

## EXPERIMENTAL

Stock solutions of Al(III) and Fe(III) nitrates and those of the ligands (EDTA, NTA, OX and MALN) were prepared in double distilled water and the concentrations checked by standard methods. The pH measurements were recorded at  $35 \pm 1^\circ C$ . The titrations were carried out in duplicate, against 0.1 M potassium hydroxide keeping the total volume of the reaction mixture at 50 ml and the ionic strength ( $\mu = 0.1 M KNO_3$ ) constant at the beginning of the titration. The pH was plotted against moles of alkali ( $m$ ) added per mole of ligand or metal (Figs. 1 and 2).

## Calculations

The pK values of EDTA, NTA, OX and MALN acids were determined by the method of Chaberek and Martell<sup>9</sup> (Table I). The formation constants for the simultaneous addition of the two ligands to the central metal ion were calculated by the method of Ramamoorthy and Santappa<sup>10</sup>, according to which in the case of metal-dibasic acid monobasic acid systems

$$K_{MLL'} = \frac{T_M - 1/2 [A] X}{(1/2)^3 [A]^3 X}$$

where,

[A] = total free ligand concentration

$$= \frac{3T_M - T_{OH} - [H^+]}{2[H^+] + \frac{2[H^+]^2}{K'_1 K'_2}}$$

$$X = 1 + \frac{2[H^+]}{K'_2 + K_1} + \frac{[H^+]^2}{K'_1 K'_2}$$

where  $T_{OH} = KOH$ ,  $T_M$  = total metal ion concentration,  $K_1$  = dissociation constant of monobasic acid  $K'_1$  and  $K'_2$  = First and Second dissociation constants of dibasic acid,

and in the case of metal-dibasic acid-dibasic acid system

$$K_{MLL'} = \frac{T_M - (1/2) [A] X}{(1/2)^3 [A]^3 X}$$

where

$$[A] = \frac{4T_M - T_{OH} - [H^+]}{2[H^+] + \frac{4[H^+]^2}{K_2 + K'_2 + K_1 K_2 + K'_1 K'_2}}$$

$$X = 1 + \frac{2[H^+]}{K_2 + K'_2} + \frac{2[H^+]^2}{K_1 K_2 + K'_1 K'_2}$$

$K_1$ ,  $K_2$  and  $K'_1$  and  $K'_2$  being the first and second dissociation constants of the two dibasic acids respectively. In the pH range 2.00-3.00 where the values of  $\log K_{MLL'}$  have been evaluated the hydrolysis of the species has been taken to be negligible and, therefore, not taken into consideration.

The free energies of formation ( $\Delta F^\circ$ ) at  $35 \pm 1^\circ C$  were calculated by the expression

$$\Delta F^\circ = -RT \ln K_{MLL'}$$

TABLE I  
Ionization constants of the acids

Acids	$pK_1$	$pK_2$
EDTA	6.13	9.80
NTA	9.53	..
OX	1.65	4.24
MALN	2.94	5.84

The values of formation constants and free energies of formation evaluated for the above systems are recorded in Table II.

TABLE II  
Formation constants ( $\log K_{MLL'}$ ) and free energies of formation

System	$\log K_{MLL'}$	$\Delta F^\circ$ (K. cal/mole)
Al-EDTA-OX	$7.91 \pm 0.17$	-11.14
Fe-EDTA-OX	$10.20 \pm 0.14$	-14.37
Al-EDTA-MALN	$13.66 \pm 0.30$	-19.24
Fe-EDTA-MALN	$14.19 \pm 0.15$	-19.99
Al-NTA-OX	$8.64 \pm 0.15$	-12.17
Al-NTA-MALN	$12.38 \pm 0.20$	-17.44

### RESULTS AND DISCUSSION

A sharp inflection at  $m = 1$  ( $pH \sim 8$ ) in the case of disodium salt of EDTA and at  $m \sim 1$  ( $pH \sim 10$ ) in the case of disodium salt of NTA, may be ascribed to the titration of one of the two carboxy group protons of  $EDTANa_2$  and the remaining proton of  $NTANa_2$  respectively. The inflection at  $m = 2$  in the case of OX and MALN may be attributed to the titration of carboxylic protons of the compounds.

#### Al(III)/Fe(III)-EDTA

Curve *a* in Figs. 1 and 2 depicting the systems Al(III)/Fe(III)-EDTA exhibits the lowering in pH and inflection at  $m = 2$  which may be correlated to the formation of 1:1  $Al^{3+}/Fe^{3+}$ -EDTA complexes. Another inflection at  $m = 3.5$  and  $m = 3$  in the case of aluminium and iron systems respectively, may be ascribed to the formation of soluble hydroxo complexes which in the case of iron, probably, form the polynuclear species<sup>11</sup>.

#### Al(III)-NTA

Curve *b* Fig. 1, depicting the system Al(III)-NTA, shows inflections at  $m = 1$  and  $m = 3$ . The former inflection may be ascribed to the formation of a 1:1 complex and the latter one may be due to the formation of a hydroxo species.

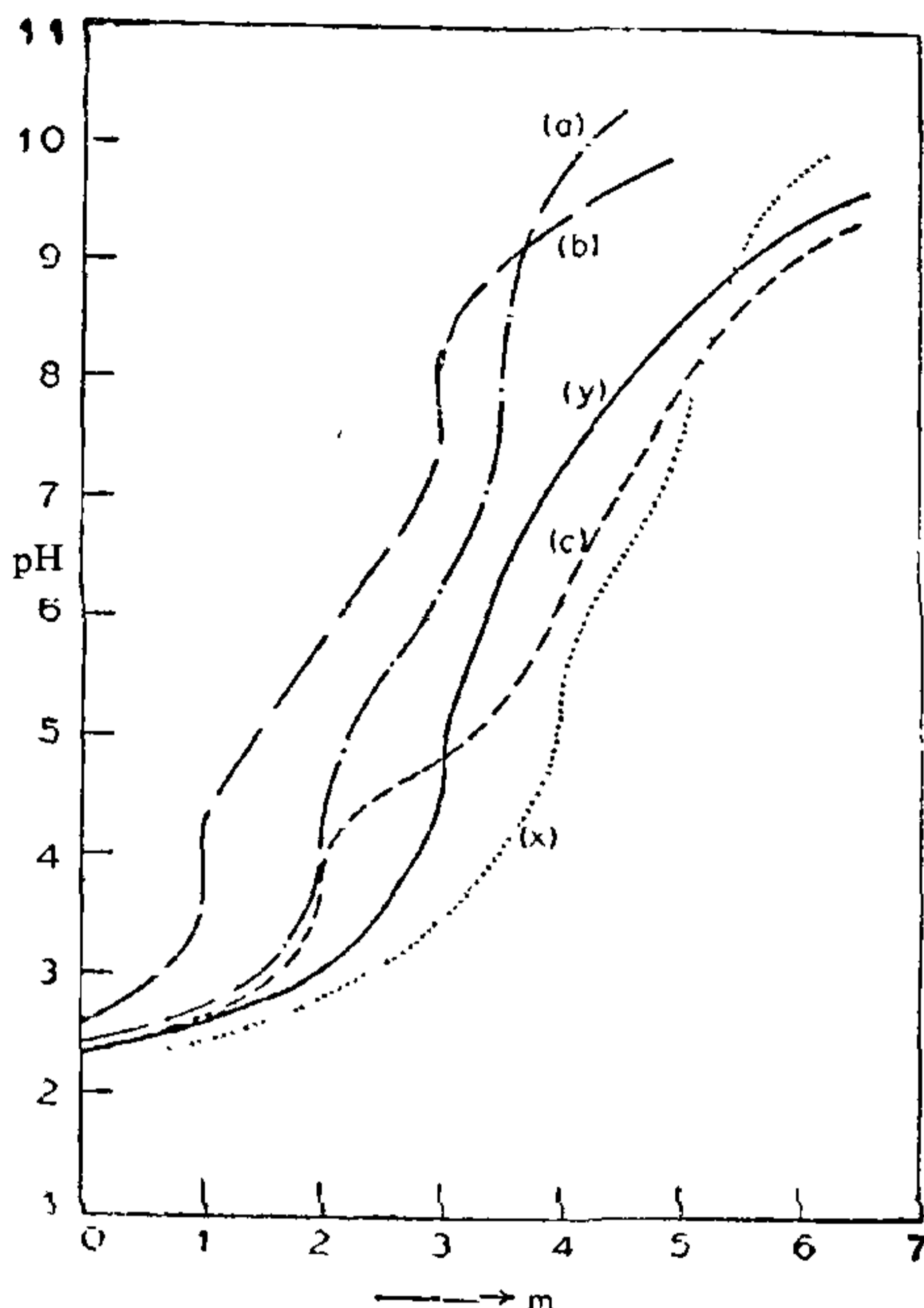


FIG. 1. Curve, *a* = 1:1 Al-EDTA, *b* = 1:1 Al-NTA, *c* = 1:1 Al-OX, *x* = 1:1:1 Al-EDTA-OX, *y* = 1:1:1 Al-NTA-OX.

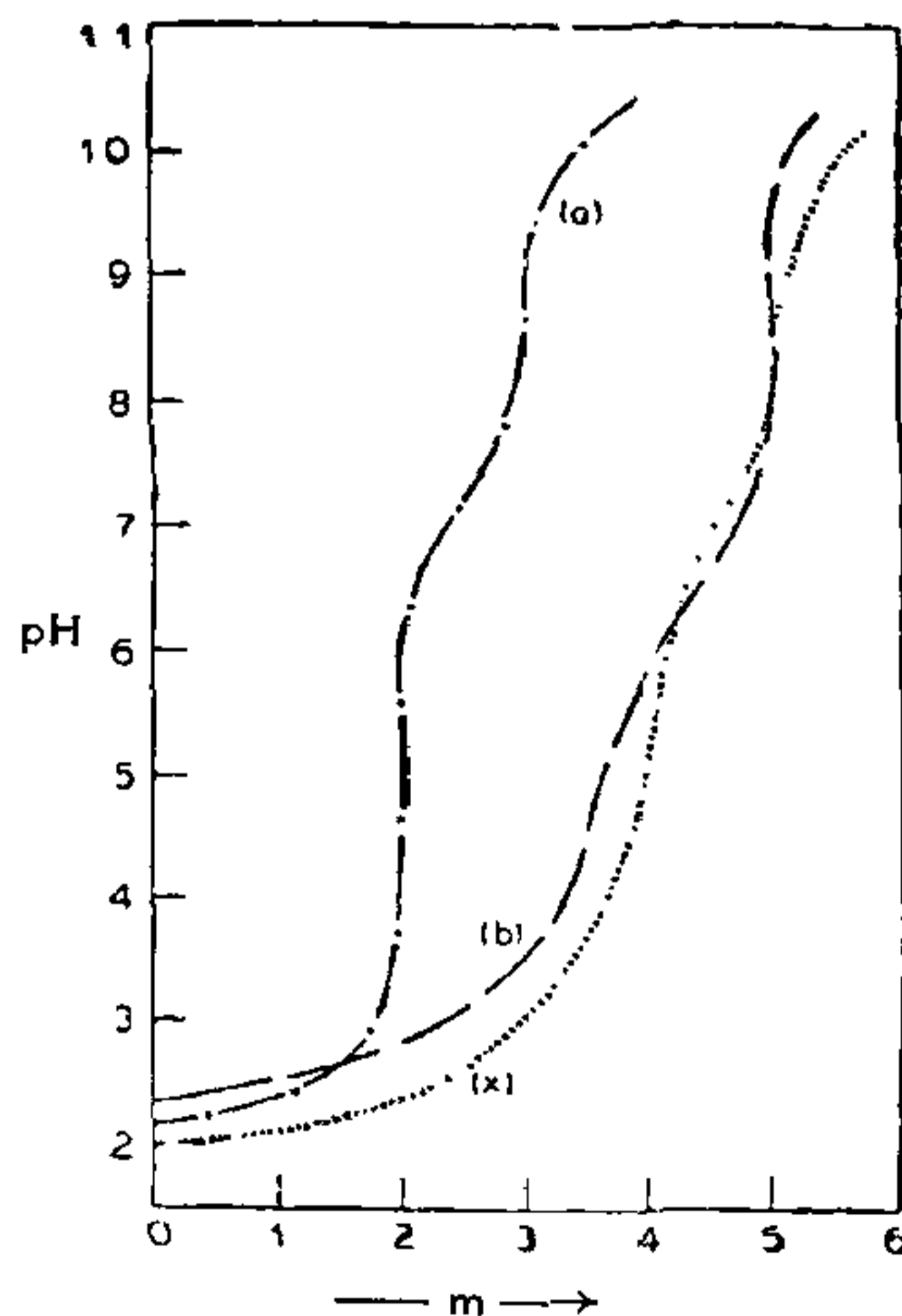


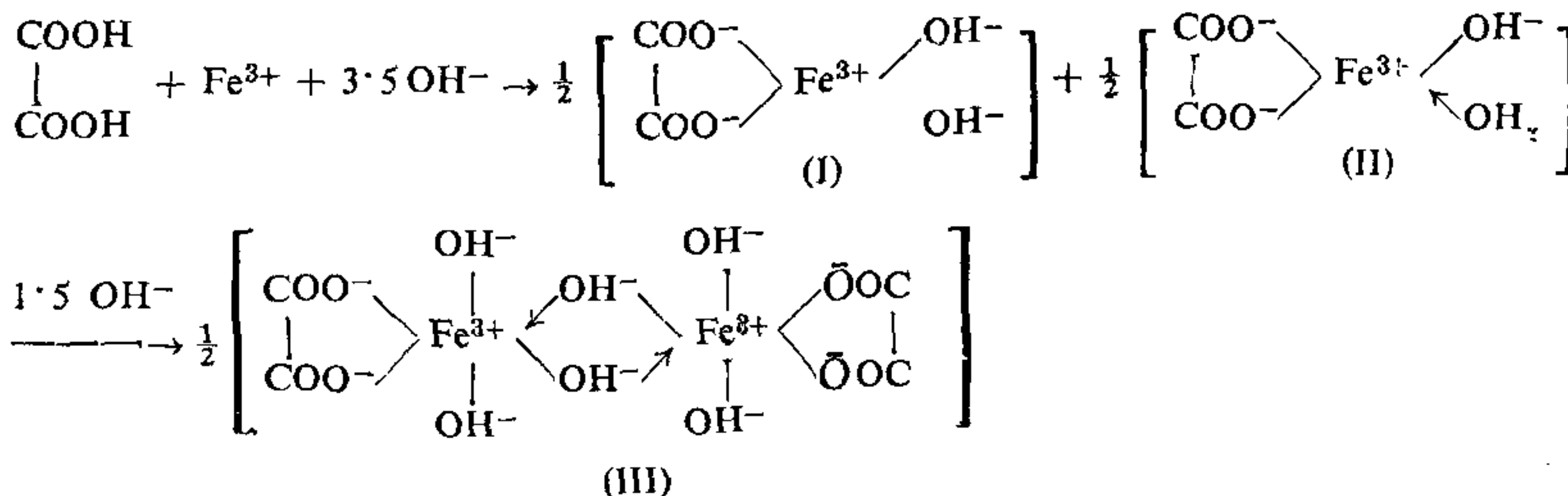
FIG. 2. Curve, *a* = Fe-EDTA, *b* = Fe-OX, *x* = 1:1:1 Fe-EDTA-OX.

*Al(III)/Fe(III)-OX/MALN*

Inflection at  $m = 2$ , representing the systems  $Al^{3+}$ -OX (curve *b*, Fig. 1 as representative)/MALN, may be attributed to the formation of 1:1 complex which on hydrolysis, gives an intermediate non-ionic species at  $m \sim 2$ . The slopy nature of the curves probably indicates the hydrolytic behaviour of this intermediate species. On further addition of the base at  $m > 3$ , the non-ionic species dissolves slowly giving a soluble hydroxo complex. The inflection at  $m = 4$  may, possibly, be attributed to the formation of the hydroxo species.

In the case of systems Fe(III)-OX (curve *b* Fig. 2 as representative)/MALN, two inflections at  $m \sim 3.5$  and 5 are observed. The former inflection may be correlated to the simultaneous formation of soluble species<sup>12</sup> (I and II). The latter one may, however, be ascribed to the further hydrolysis resulting in the formation of a polynuclear species<sup>13</sup> having hydroxo bridges (III).

The following mechanism has been shown for Fe(III)-OX system as representative:



*Al(III)-NTA-OX/MALN*

In the systems Al(III)-NTA-OX (curve *y* Fig. 1 as representative)/MALN inflection at  $m = 3$  is observed, which may be ascribed to the formation of 1:1:1 Al(III)-NTA-OX/MALN ternary species. The slopy nature of the curve indicates the hydrolytic behaviour.

The formation of the ternary species may be further supported by (i) the lowering of the pH, (ii) non-formation of the solid phase and (iii) significant colour changes in the case of Fe(III) systems.

The order of stabilities as observed in the terms of the metal ions and the dicarboxylic acids are:

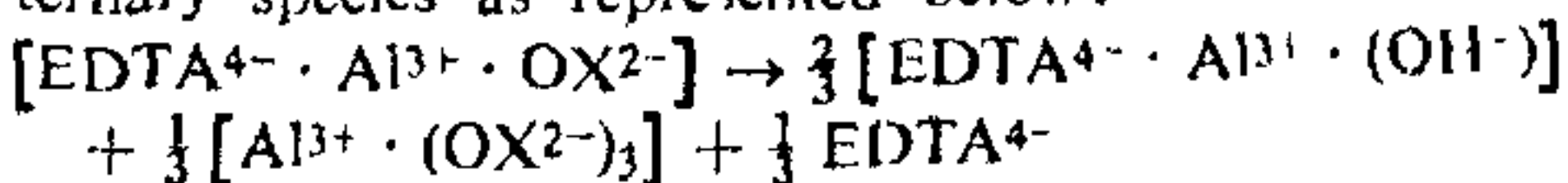
- (i) Fe(III) > Al(III)
- (ii) MALN > OX

The trend in the case of dicarboxylic acids may be attributed to the increasing basicity.

*Al(III)/Fe(III)-EDTA-OX/MALN*

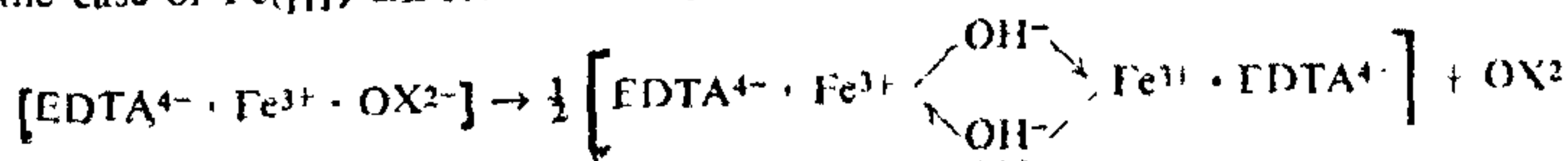
In the case of systems Al(III)-EDTA-OX (curve *x* Fig. 1 as representative)/MALN and Fe(III)-EDTA-OX (curve *x* Fig. 2 as representative)/MALN inflection at  $m = 4$ , may be attributed to the formation of 1:1:1 Al(III)/Fe(III)-EDTA-OX/MALN species by the simultaneous addition of both the ligands to the metal ion.

Another inflection at  $m \sim 5$  in the case of systems involving aluminium ion, may be ascribed to the probable disproportionation of the initially formed ternary species as represented below:



In the case of systems involving iron ion, the initially formed ternary species, however, appears to disproportionate resulting in the formation of a polynuclear species.

The mechanism can be illustrated as shown below as in the case of Fe(III)-EDTA-OX as representative:



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## COMPLEXES OF 4-AMINOANTIPYRINE WITH LANTHANIDE THIOCYANATES

[C. G. R. NAIR AND JACOB CHACKO\*

*Department of Chemistry, University of Kerala, Trivandrum 695 001*

### ABSTRACT

Complexes of lanthanide thiocyanates with 4-amino antipyrine have been synthesized for the first time. Unlike other lanthanide complexes, these complexes are quite novel in that the lanthanide ions themselves fall into two groups (the lighter ones and the heavier ones) as regards their coordinating ability. The complexes have been characterized using various physico-chemical techniques such as conductivity measurements, infrared spectroscopy, and thermal analysis (TG, DTG and DTA).

### INTRODUCTION

In earlier communications, we have reported on the preparation and characterization of complexes of 4-aminoantipyrine (*aap*) with lanthanide perchlorates<sup>1</sup> and nitrates<sup>2</sup> with the compositions  $[\text{Ln } aap_6] (\text{ClO}_4)_3$  and  $[\text{Ln } aap_3 (\text{NO}_3)_3]$  respectively. (Ln = La, Pr, Nd, Sm, Gd, Dy or Y). Similar complexes of *aap* with lanthanide thiocyanates are being reported here.

### EXPERIMENTAL

4-Aminoantipyrine used was of Analar grade (BDH). Lanthanide oxides (99.9%) obtained from M/s. Indian Rare Earths Ltd., Udyogamandal, Kerala, were used as such. Ammonium thiocyanate used was from E. Merck (Germany). All solvents used were purified by standard methods<sup>3</sup>.

#### *Preparation of the complexes*

The lanthanide oxides were converted into the corresponding nitrates by the methods described earlier<sup>2</sup>. All the complexes were prepared by the general procedure given below.

Lanthanide nitrate (1g, 2.3 mmol) and *aap* (1.5 mmol) were separately dissolved in minimum amount of cold water (0–5° C) and then mixed together. Any precipitate formed was filtered off. To the clear solution was added, dropwise, a cold (0–5° C) saturated solution of ammonium thiocyanate. The pasty mass which separated out was washed well with cold (0–5°

C) water. The mass was then dissolved in minimum amount of acetone and reprecipitated by addition of benzene or petroleum ether. The solid thus obtained was dried in vacuum over phosphorus (V) oxide.

The lanthanide content was determined gravimetrically by the oxalate-oxide method<sup>4</sup> and the thiocyanate content by the Volhard's procedure<sup>5</sup>.

Thermogravimetric studies were carried out on a Perkin-Elmer TGS-1 Thermobalance (heating rate: 5°/min; atmosphere: static air; chart speed: 40 cm per hour).

I.R. spectra were run on a Perkin-Elmer 237 i.r. spectrophotometer. KBr pellet technique was used. Conductance measurements were made at room temperature ( $28 \pm 2^\circ \text{C}$ ) using a Philips GM 4249 conductivity bridge with dip type cell and Pt black electrode (cell constant =  $0.7511 \text{ cm}^{-1}$ ).

### RESULTS AND DISCUSSION

The complexes are extremely hygroscopic, freely soluble in polar solvents and only sparingly soluble in non-polar solvents. The analytical data (Table I) suggest that they have the general formula  $\text{Ln } aap_3 (\text{CNS})_3 \cdot 4\text{H}_2\text{O}$ .

Thermogravimetric studies show that the complexes are stable upto  $\sim 100^\circ \text{C}$ . All the four water molecules are lost between 100 and  $200^\circ \text{C}$ . X-ray powder diffraction data of the ultimate thermal decomposition residues showed that they were  $\text{Ln}_2\text{O}_3$  in the case of La, Nd, Sm, Gd, Dy and Y;  $\text{Pr}_6\text{O}_{11}$  in the case of Pr.

\* Present address : Department of Marine Sciences, University of Cochin, Cochin 682 016.