

pectively and  $T_{OH}$  is the concentration of the base added to the reaction mixture during the titration, that under the condition  $T_M = T_A = T_L$ .

$$K_{MAL} = \frac{T_M - X[L^-]}{X[L^-]^2} \quad \dots(3)$$

where  $X = \frac{[H^+]}{k_1} + 1$  and

$$[L^-] = \frac{(2-m)T_M - [H^+] + [OH^+]}{[H^+]/k_1}$$

where  $k_1$  is the dissociation constant of the secondary ligand.

*Formation constants of the hydroxo derivative of 1:1:1 mixed ligand chelates* — A gradual increase in the values of  $\log K_{MAL}$  at  $m > 1.8$ ; 1.5, 1.32, 1.36; 1.56, 1.40 and 1.64 in the case of Ni(II)-bipy-gly, ala or norleu; Zn(II)-bipy-gly, ala or norleu; Cd(II)-bipy-gly, ala or norleu probably indicates that the addition of the hydroxyl groups starts before the complete formation of 1:1:1 mixed ligand chelate resulting in the formation of a hydroxo derivative. The equilibria involved in the formation of monohydroxo derivative of 1:1:1 mixed ligand chelate may be represented by



and the overall formation constant  $K_{MAL(OH)}$  of the monohydroxo derivative in these systems may be defined as:

$$K_{MAL(OH)} = \frac{[MAL(OH)]}{[MA^{2+}][L^-][OH^-]} \quad \dots(5)$$

Other pertinent equations are:

$$T_M = [MA^{2+}] + [MAL^+] + [MAL(OH)] \quad \dots(6)$$

$$T_{OH} + [H^+] - T_A - [OH^-] = [MAL^+] + 2[MAL(OH)] + [L^-] \quad \dots(7)$$

$$T_L = [MAL^+] + [MAL(OH)] + [HL] + [L^-] \quad \dots(8)$$

Eliminating  $[MAL(OH)]$  from Eqs. (6)-(8) and rearranging the terms, we obtain

$$a[MA^{2+}]^2 + b[MA^{2+}] - c = 0 \quad \dots(9)$$

where  $a = K_{MAL}$ ,  $b = \frac{2[H^+]}{k_1} + 1$  and  $c = \{(3-m)T_M - [H^+] + [OH^-]\}X$ .

The equilibrium concentration of  $MA^{2+}$  present in the reaction mixture may be obtained by solving Eq. (9) and the concentrations of other species involved in the equilibrium relations can then be calculated from the above equations and also the value of formation constant,  $K_{MAL(OH)}$ .

The values of the formation constants of the mixed ligand chelate  $K_{MAL}$  and its monohydroxo derivative  $K_{MAL(OH)}$  are presented in Table 1. The formation constants of monohydroxo derivative of Ni(II)-bipy-gly, Ni(II)-bipy-ala, Ni(II)-bipy-norleu, Zn(II)-bipy-ala and Zn(II)-bipy-norleu could not be calculated, as the precipitation occurs at an early stage after the addition of hydroxyl group starts.

The order of stability of mixed complexes in terms of metal ions is: Ni(II) > Zn(II) > Cd(II) as expected from Mellor and Maley order. Further, the order of stability in terms of secondary ligands has been found to be: gly > ala > norleu and this can be ex-

TABLE 1 — FORMATION CONSTANTS OF MIXED LIGAND CHELATE AND MONOHYDROXO DERIVATIVE

System	$\log K_{MAL}$	$\log K_{MAL(OH)}$
Ni(II)-bipy-gly	5.50 ± 0.03	—
Ni(II)-bipy-ala	5.15 ± 0.07	—
Ni(II)-bipy-norleu	4.90 ± 0.09	—
Zn(II)-bipy-gly	4.67 ± 0.04	9.90 ± 0.04
Zn(II)-bipy-ala	4.32 ± 0.13	—
Zn(II)-bipy-norleu	4.11 ± 0.12	—
Cd(II)-bipy-gly	3.97 ± 0.12	8.06 ± 0.07
Cd(II)-bipy-ala	3.72 ± 0.11	8.04 ± 0.07
Cd(II)-bipy-norleu	3.64 ± 0.08	7.92 ± 0.12

plained on the basis of the enlargement of the chain in  $\alpha$ -alanine and norleucine systems.

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#### Mixed Ligand Complexes of Lanthanides with Diacetylmonoxime as a Primary Ligand & N-Substituted Anthranilic Acids as Secondary Ligands

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**Mixed complexes of lanthanide ions  $Y^{3+}$ ,  $La^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Gd^{3+}$ ,  $Dy^{3+}$  with diacetylmonoxime as primary ligand and N-phenylanthranilic acid and N-methylanthranilic acid as secondary ligands have been synthesized and characterized on the basis of analytical, spectral and thermal data.**

SEVERAL simple lanthanide complexes with various oximes have been reported and characterized<sup>1-5</sup>. Mixed ligand complexes of lanthanides have also received much interest in recent years<sup>6-9</sup>. Mixed complexes of lanthanides using oximes as primary ligands and 1,10-phenanthroline, oxine and pyridine-2-aldoxime as the secondary ligands have also been reported<sup>10</sup>. Preparation and characterization of several mixed complexes of lanthanides using DAMO as the primary ligand and NPAA and NMAA<sup>11</sup> as the secondary ligands are reported in this note.

Lanthanide diacetylmonoximates were prepared by the method of Rao *et al.*<sup>5</sup> from specpure lanthanide oxides and reagent grade diacetylmonoxime. The mixed complexes were prepared adopting the following procedure:

Lanthanide diacetylmonoximate ( $\text{LnDAMO} \cdot \text{Cl}_3 \cdot 4\text{H}_2\text{O}$ , 200 mg) was dissolved in ethanol (30 ml) and mixed with calculated amount (mole ratio 1:3) of the N-phenyl or N-methyl anthranilic acids; these acids were prepared by literature method<sup>11</sup>. The pH of the solution was adjusted to 5.8 by the addition of alcoholic ammonia. The resulting solution was evaporated on a steam bath and the solid obtained washed with ether to remove excess ligand; yield 75%. All the compounds were dried *in vacuo* over fused calcium chloride for 48 hr. Analytical data are given in Table 1.

In their UV spectra DAMO exhibits a band at  $\sim 220$  nm ( $\log \epsilon$  4.04), NPAA at 290 nm ( $\log \epsilon$  4.28) and NMAA at 220 ( $\log \epsilon$  4.65) and 255 nm ( $\log \epsilon$  4.13). The bands around 220 and 255 nm could be due to  $\pi \rightarrow \pi^*$  and around 290 nm be due to  $n \rightarrow \pi^*$  transitions. In the several lanthanide mixed complexes both the characteristic band maxima of primary and secondary ligands have been observed with slight shift in their positions and change in intensity. The  $\log \epsilon$  values in the complexes are of the order of 4.92-5.17. This observation gives an indication that both the ligands are attached to the metal ion.

Characteristic bands of  $\text{Pr}^{3+}$  could not be located in the mixed complexes reported in this note. Among the  $\text{Nd}^{3+}$  complex only  $\text{Nd}^{3+}$  DAMO-NPAA showed a band around 470-490 nm ( $\log \epsilon$  2.82). The characteristic band of  $\text{Sm}^{3+}$  ion around 402 nm is also absent in the mixed complexes. Such a disappearance of lanthanide ion bands in their mixed complexes has been reported<sup>10</sup>. The disappearance of the bands, as a first approximation, can be taken as an evidence of strong complex being formed.

In the IR spectra (KBr) of the complexes of  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$  and  $\text{Pr}^{3+}$  with DAMO and NPAA the  $\nu\text{OH}$  and  $\nu\text{NH}$  overlap and appear at lower frequency (3300-3320  $\text{cm}^{-1}$ ). In the case of  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  these bands are shifted to a slightly higher frequency (3400  $\text{cm}^{-1}$ ). The  $\nu\text{C}=\text{O}$  band at 1655 in DAMO and at 1650  $\text{cm}^{-1}$  in NPAA disappear in all the complexes except in  $\text{La}^{3+}$  and  $\text{Pr}^{3+}$  where they are located at 1605 and 1645  $\text{cm}^{-1}$  respectively. These changes indicate that the C=O groups of both the ligands are involved in bond formation. The changes observed in the other groups such as C=C phenyl, C=C phenyl conjugated, substituted phenyl, COOH and  $\text{C}_6\text{H}_5\text{NH}$  are in conformity with the observations made in lanthanide N-phenylanthranilates<sup>12</sup>. The 975  $\text{cm}^{-1}$  band due to  $\nu\text{N}-\text{O}$  of oxime could not be located in these complexes.

In the mixed complexes of  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$  with DAMO and NMAA  $\nu\text{OH}$  (3350  $\text{cm}^{-1}$ ) and  $\nu\text{NH}$  (3375  $\text{cm}^{-1}$ ) of DAMO and NMAA respectively appear as broad split band slightly shifted to lower frequency region (3360-3340  $\text{cm}^{-1}$ ). Only broadening is observed in  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  complexes. The  $\nu\text{C}=\text{O}$  of both the ligands (1650  $\text{cm}^{-1}$ ) appear at

TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES

Compound	M (%)		N (%)	
	Calc.	Found	Calc.	Found
Y(DAMO) <sub>1</sub> (NPAA) <sub>3</sub>	10.75	10.6	6.77	6.20
La(DAMO) <sub>1</sub> (NPAA) <sub>3</sub>	15.86	15.17	6.39	6.33
Pr(DAMO) <sub>1</sub> (NPAA) <sub>3</sub>	16.04	15.75	6.378	6.1
Nd(DAMO) <sub>1</sub> (NPAA) <sub>3</sub>	16.36	16.20	6.35	6.20
Sm(DAMO) <sub>1</sub> (NPAA) <sub>3</sub>	16.94	16.70	6.31	6.26
Gd(DAMO) <sub>1</sub> (NPAA) <sub>3</sub>	17.58	17.48	6.26	5.9
Dy(DAMO) <sub>1</sub> (NPAA) <sub>3</sub>	18.06	18.00	6.22	6.05
Pr(DAMO) <sub>1</sub> (NMAA) <sub>3</sub>	20.35	19.91	8.09	8.03
Nd(DAMO) <sub>1</sub> (NMAA) <sub>3</sub>	20.74	20.42	8.05	8.00
Sm(DAMO) <sub>1</sub> (NMAA) <sub>3</sub>	21.44	21.28	7.98	7.94
Gd(DAMO) <sub>1</sub> (NMAA) <sub>3</sub>	22.20	21.7	7.907	7.51
Dy(DAMO) <sub>1</sub> (NMAA) <sub>3</sub>	22.17	22.12	7.85	7.62

DAMO = diacetylmonoxime; NPAA = N-phenylanthranilic acid; NMAA = N-methylanthranilic acid.

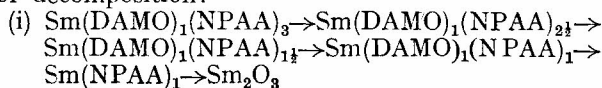
TABLE 2 — THERMAL BEHAVIOUR OF SAMARIUM DIACETYL-MONOXIME AND ITS MIXED COMPLEX WITH N-PHENYL-ANTHRANILIC ACID

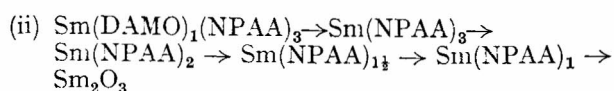
Temp. °C	Weight loss (%)		Probable composition of the residue
	Theor.	Exptl	
Sm(DAMO) <sub>1</sub> Cl <sub>3</sub> 4H <sub>2</sub> O			
140	16.74	16	Sm(DAMO) <sub>1</sub> Cl <sub>3</sub>
340	28.49	30	Sm(DAMO) <sub>1</sub> Cl <sub>3</sub>
520	40.23	40	SmCl <sub>3</sub>
580	58.75	56	Sm <sub>2</sub> O <sub>3</sub>
Sm(DAMO) <sub>1</sub> (NPAA) <sub>3</sub>			
260	11.95	11	Sm(DAMO) <sub>1</sub> (NPAA) <sub>2½</sub>
360	35.83	33	Sm(DAMO) <sub>1</sub> (NPAA) <sub>1½</sub>
460	47.23	50	Sm(DAMO) <sub>1</sub> (NPAA) <sub>1</sub>
520	58.96	56	Sm(NPAA) <sub>1</sub>
820	80.09	80	Sm <sub>2</sub> O <sub>3</sub>

lower frequency (1620  $\text{cm}^{-1}$ ) suggesting involvement of C=O group in bond formation.

NMAA exhibits bands at 1440 and 1240  $\text{cm}^{-1}$  due to COOH group. The 1440  $\text{cm}^{-1}$  band is absent in  $\text{Pr}^{3+}$ ,  $\text{Gd}^{3+}$  complexes while it is lowered in  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$  complexes. The 1240  $\text{cm}^{-1}$  band is shifted to higher frequency and located around 1280  $\text{cm}^{-1}$  in the complexes. Similar effect on this band is observed in DMG-NPAA mixed complexes<sup>13</sup>. The anilino (1575  $\text{cm}^{-1}$ ) and the phenyl group (1510  $\text{cm}^{-1}$ ) frequencies are slightly shifted. The  $\nu\text{N}-\text{O}$  of DAMO could not be isolated in these mixed complexes.

Thermal analysis of samarium diacetyl monoxime indicates the dehydration at 140° and confirms that the compound is a tetrahydrate. There is an endothermic peak at 340° corresponding to a loss of 30% on TGA curve. This corresponds to a loss of half a molecule of DAMO. However, the complete removal of DAMO is observed at 520° leading to the formation of sesquioxide at 900°. Thermal study of mixed complex gives interesting results. By comparison of weight losses at 260° one can postulate the following two routes for decomposition:





From comparison of the thermal analysis of simple LnDAMO and LnNPAA complexes<sup>12</sup> with those of their mixed complexes it can be concluded that the mode of decomposition of the mixed complexes follows the first route postulated. The thermal data are detailed in Table 2.

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### Mixed Ligand Complexes of Sc(III), Y(III), La(III), Nd(III) & Sm(III) with EDTA as Primary Ligand & Catechol-3,5-disulphonic Acid (Tiron) as Secondary Ligand

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Stability constants of the mixed ligand complexes, MAL, where M=Sc(III), Y(III), La(III), Pr(III), Nd(III) or Sm(III); A=ethylenediaminetetraacetic acid (EDTA); and L=catechol-3,5-disulphonic acid have been determined at 30° and  $\mu=0.2M$  (NaClO<sub>4</sub>) using a modified form of Irving-Rossotti pH-titration technique. In all the cases, stabilities of the ternary complexes are found to be less than those of the correspond-

ing binary complexes. The stability constants increase with decrease in ionic radii for binary as well as ternary complexes.

THE role of catechol-3,5-disulphonic acid (Tiron) as a secondary ligand in mixed ligand complexes of many metal ions<sup>1-6</sup> has been extensively investigated. We report here the results of our studies on the mixed ligand complexes of Sc(III), Y(III), La(III), Pr(III), Nd(III) and Sm(III) with EDTA as the primary ligand and catechol-3,5-disulphonic acid as the secondary ligand. The stability constants of the binary and ternary complexes have been determined using the Irving-Rossotti pH-titration technique<sup>7</sup>, as modified for the mixed complexes.

All the chemicals used were of AR grade. Rare earth perchlorates were prepared from the corresponding oxides<sup>8,9</sup> and standardised by complexometric methods<sup>10</sup>. The following solutions were titrated against CO<sub>2</sub>-free 1.26M NaOH. The titrations were carried out under N<sub>2</sub> atmosphere. The total volume in each case was 100 ml and ionic strength was 0.2M (NaClO<sub>4</sub>).

- (i) 0.02M HClO<sub>4</sub>+0.18M NaClO<sub>4</sub>
- (ii) 0.02M HClO<sub>4</sub>+0.006M tiron+0.174M NaClO<sub>4</sub>
- (iii) 0.02M HClO<sub>4</sub>+0.006M tiron+0.002M metal salt+0.172M NaClO<sub>4</sub>
- (iv) 0.02M HClO<sub>4</sub>+0.002M EDTA+0.002M metal salt+0.176M NaClO<sub>4</sub>
- (v) 0.02M HClO<sub>4</sub>+0.002M EDTA+0.002M metal salt+0.006M tiron+0.170M NaClO<sub>4</sub>

The "practical" proton-ligand stability constants obtained using half  $\bar{n}$  values method were  $\log K_1^H=12.60$  and  $\log K_2^H=7.59$ . The metal-ligand stability constants of the binary complexes were determined as reported earlier<sup>8,9</sup> by plotting  $\bar{n}$  against  $pL$ . In all the cases, the value of  $\bar{n}$  exceeded 1.5, which reveals the formation of 1:1 as well as 1:2 complexes. The values of stepwise stability constants for the binary complexes as obtained by half  $\bar{n}$  value method are given in Table 1.

*Mixed ligand stability constants*—The primary complexation of rare earth with EDTA takes place at a very low pH and the complex remains stable even in the higher pH range.

To prove the existence of mixed ligand complex formation, a composite curve was drawn assuming that there was no mixed complex formation, and only species present during the titration were 1:1 M(EDTA) and the free secondary ligand. This composite curve was compared with the experimental mixed ligand complex curve.

TABLE 1—STEPWISE STABILITY CONSTANTS OF BINARY COMPLEXES AT 30° AND  $\mu=0.2M$  (NaClO<sub>4</sub>)

Metal	$\log K_1$	$\log K_2$	$\log \beta$
Sc(III)	17.78	9.32	27.10
Y(III)	14.20	8.75	22.95
La(III)	12.65	4.40	17.05
Pr(III)	13.40	4.95	18.35
Nd(III)	13.50	4.98	18.48
Sm(III)	14.15	5.90	20.05

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