



## Potentiometric and IR spectral studies of Binary and ternary complexes of $\text{La}^{3+}$ , $\text{Sm}^{3+}$ , $\text{Gd}^{3+}$ and $\text{Dy}^{3+}$ with all cis-1,2,3,4-cyclopentanetetra carboxylic acid(CPTA) and Furan-2-carboxylic acid(FCA)

Richa Gupta\*, Nisha Agrawal and K. C. Gupta

Department of Chemistry, B. S. A. (P.G.) College, Mathura, India

### ABSTRACT

The stability constants of 1:1 binary complexes of some lanthanide metal ions like  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  with all cis-1,2,3,4-cyclopentanetetra carboxylic acid(CPTA) and Furan-2-carboxylic acid (FCA) and ternary complexes of them with all cis-1,2,3,4-cyclopentanetetra carboxylic acid(CPTA) as a primary ligand and Furan-2-carboxylic acid (FCA) as secondary ligand were determined potentiometrically at constant ionic strength  $\mu=0.2\text{M}(\text{KNO}_3)$  in aqueous solution at  $30^\circ\text{C}$ ,  $40^\circ\text{C}$  and  $50^\circ\text{C}$ . The stability constants calculated follows the order:  $\text{La}^{3+} < \text{Sm}^{3+} < \text{Gd}^{3+} \approx \text{Dy}^{3+}$ . The thermodynamic parameters like free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) have also been calculated using the standard thermodynamic equations. The infra red studies of 1:1 binary complexes of  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  with all cis-1,2,3,4-cyclopentanetetra carboxylic acid (CPTA) and Furan-2-carboxylic acid (FCA) were also carried out.

**(Keywords :** Stability constants; ternary complexes; cis-1,2,3,4-cyclopentanetetra carboxylic acid (CPTA); Furan-2-carboxylic acid; free energy; enthalpy; entropy).

### INTRODUCTION

All cis-1,2,3,4-cyclopentanetetra carboxylic acid (CPTA) is an extensively studied ligand. Lanthanide complexes of CPTA have also been investigated earlier.[1-6]

CPTA is useful in solution varnishes and baths for electroplating. Prostaglandins are a group of naturally occurring hydroxy cyclopentane acids derived from fatty acids isolated from mammalian's tissues and are believed to be regulators of various functions such as lipid metabolism, central nervous system, cardiovascular and reproductive physiology.

Furan-2-carboxylic acid (FCA) is a heterocyclic aromatic compound with five-membered ring structure consisting of four  $\text{CH}_2$  groups, one oxygen atom and a carboxylic group. There are two isomers at 2 or 3 position. 2-Furoic acid is called pyromucic acid. It is a volatile and mildly toxic liquid, can be obtained from wood oils. It is used as a solvent as well as in the synthesis of furfural and other organic compounds. It is also used as a preservative and bactericide and as a starting material of numerous furoate esters. Its sulfur-substituted derivatives are widely used as flavouring agents and nitro-substituted derivatives in medicinal preparations and in biological research.[7-10] Furan-2-Carboxylic acid derivatives are capable of activating AMP-activated protein kinase (AMPK) which is useful for the prevention and treatment of metabolic syndromes including diabetes, obesity, hyperlipidemia,

hypercholestromia, fatty liver and steatohepatitis factors . 4-amino-furan-2-carboxylic acid (proximicin) is an antibiotic which shows a weak antibacterial activity but a strong cytostatic effect to various human tumor cell lines.[11-13] Naphtho [2,1- b] furan derivatives have antioxidant activities and can be used as a powerful source used for suppression of pimples.[14]

In view of the importance of all cis-1,2,3,4-cyclopentanetra carboxylic acid(CPTA) and Furan-2-Carboxylic acid (FCA) and their metal derivatives in various physiological reactions, it was considered worthwhile to study the binary and ternary complexes of all cis-1,2,3,4-cyclopentanetra carboxylic acid (CPTA)and Furan-2-carboxylic acid (FCA) with some lanthanide metal ions like  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  to throw some light upon the further applications of these complexes.

The paper consists the results of pH-metric studies on the binary 1:1 and ternary1:1:1 complexes of  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  with all cis-1,2,3,4-cyclopentanetra carboxylic acid (CPTA)and Furan-2-carboxylic acid (FCA). I.R. studies of binary complexes have also been done to find out the coordination sites of the ligand. On coordination to a metal, the ligand bands are shifted to lower or higher frequencies with variation in intensity. It is possible, therefore, to interpret the interaction of metal with the ligand by comparing the infra red spectrum of the ligand with that of the metal bound ligand, the shifts in frequencies of functional group present in the ligand.

From the shifts in the functional group frequencies of the ligand, it is possible to establish the strength of the metal ligand bond.

#### MATERIALS AND METHODS

CPTA (Matheson, Colemon and Bell Co. U.S.A.), Furan-2-carboxylic acid (merck), lanthanides (Indian Rare Earths Ltd) and other chemicals of A.R., B.D.H. and Merck were used.

Solutions of metal nitrate were prepared by dissolving respective metal carbonates in calculated amount of nitric acid till no further salt was soluble, then the solution was filtered through the G-4 crucible of sintered glass and metal ion was estimated as per standard method.[15] CPTA solution was prepared in conductivity water by dissolving calculated weighed quantity of CPTA. Similarly the solution of FCA was prepared.

#### Preparation of binary complexes

The solid complexes of  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  with CPTA and FCA were isolated from the mixture of equimolar solutions of metal nitrates and ligands. The pH of the mixture was adjusted to 7 pH by adding dilute solutions of KOH. The mixture was refluxed in ethanol (15-20 ml) for 3-4 hours on a steam bath. The clear solution gave a solid mass on cooling, which was filtered through G4 glass crucible and washed several times with the mixture of doubly distilled water and alcohol. It was recrystallised to give pure crystal and then dried at  $60^{\circ}$ - $70^{\circ}\text{C}$ .

#### Procedure

##### Potentiometric measurements

The potentiometric titrations were carried out with the help of Systronics digital pH meter model 335 with accuracy in the pH range 0.1 unit at  $30^{\circ}\text{C}$ ,  $40^{\circ}\text{C}$  and  $50^{\circ}\text{C}$  ( $\pm 1^{\circ}\text{C}$ ). Solution temperature was maintained by using refrigerated water bath with circulating system with accuracy  $\pm 1^{\circ}\text{C}$  (Tanco). Initial volume of each solution to be titrated was kept 50c.c. and its ionic strength was kept constant  $\mu=0.2\text{M}$  ( $\text{KNO}_3$ ). The following solutions were titrated in duplicate against 0.2M KOH at different temperatures using modified Irving and Rossotti method.[16-17]

- 0.02M  $\text{HNO}_3$  + 0.18M  $\text{KNO}_3$
- 0.02M  $\text{HNO}_3$  + 0.002M FCA + 0.18M  $\text{KNO}_3$
- 0.02M  $\text{HNO}_3$  + 0.002M CPTA + 0.18M  $\text{KNO}_3$
- 0.02M  $\text{HNO}_3$  + 0.002M metal nitrate + 0.002M CPTA + 0.176M  $\text{KNO}_3$
- 0.02M  $\text{HNO}_3$  + 0.002M metal nitrate + 0.002M FCA + 0.176M  $\text{KNO}_3$
- 0.02M  $\text{HNO}_3$  + 0.002M metal nitrate + 0.002M CPTA + 0.002M FCA + 0.176M  $\text{KNO}_3$

The pKa values of ligands were determined by Martell and Chaberek method [18] and compared with the literature values.

**Spectroscopic studies**

The Perkin-Elmer model-RX100 automatic recording spectrophotometer was used for the recording of IR spectra of the complexes in solid state. The complexes were run as pressed KBr disks medium. Approximately 3-5 mg of the complex compounds were mixed with 100 mg of KBr for each disk. The chart speed maintained was 5 to 12 minutes and were recorded at room temperature.

**Calculations**

The pH titration technique of Irving and Rossotti and its modified form were employed in the present study to determine the stability constants of the complexes.

The titration curves were used to evaluate the value of  $\bar{n}H$  (the average number of protons attached the secondary ligand) from the following equation.

$$\bar{n}H = \gamma T_{CL}^0 + \frac{(V_1 - V_L)(N + E^0)}{(V_0 + V_1)} / T_{CL}^0$$

Where,

$E^0$  = initial strength of acid in the system.

$N$  = normality of alkali used.

$V_0$  = total volume of mixture taken initially.

$V_1$  = total volume of alkali required in the titration of mineral acid ( $HNO_3$ ).

$\gamma$  = total number of replaceable hydrogen atoms in secondary ligand

$T_{CL}^0$  = total conc. of secondary ligand in solution.

$V_L$  = total volume of alkali required in the titration of secondary ligand.

The values of  $\bar{n}$  (average number of secondary ligand molecules attached to the primary complex) were calculated from the following equation.[19]

$$\bar{n} = \frac{(V_3 - V_2)(N + E^0)}{(V_0 + V_1)\bar{n}H T_{CM}^0}$$

Where,

$T_{CM}^0$  = total conc. of metal ion in solution.

$V_2$  and  $V_3$  are the differences in volume of alkali added between the curves (c) and (d) and between the (a) and (b) respectively (Fig.1).

The pL values were calculated at  $\bar{n} = 0.5$  from the following equation.

$$pL = \log \frac{\sum_{n=0}^{n=j} \beta_n^H (1 / \text{anti log } \beta)^n}{T_{CL}^0 - \bar{n}T_{CM}^0} \cdot \frac{V_0 + V'''}{V_0}$$

Where,

$\beta_n^H$  is overall practical proton ligand stability constant and  $V'''$  is the volume of alkali required for curve (d) at the same pH and are summarized in Table 1. The error limit is 0.07 log units;

The thermodynamic parameters like change in free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) have been calculated at different temperatures and at constant ionic strength  $\mu = 0.2M(KNO_3)$  using following equations.

$$\Delta G^0 = -2.303 RT \log K_{MAL}^{MA}$$

Where,

$\Delta G^0$  = Standard free energy change.

R= Gas constant.

T= Absolute Temperature.

$K_{MAL}^{MA}$  =The formation constant of the 1:1:1 ternary complex.

$$\Delta H^0 = \frac{2.303 RT_1 T_2 (\log B_2 - \log B_1)}{T_2 - T_1}$$

Where,

$\Delta H^0$ = Standard enthalpy change.

$B_1$  and  $B_2$  are the stability constants at the temperature  $T_1$  and  $T_2$  respectively.

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

Where,

$\Delta S^0$ = Standard entropy change.

## RESULTS AND DISCUSSION

### Binary complex systems

The stability constants of 1:1 binary complexes of CPTA and FCA with  $La^{3+}$ ,  $Sm^{3+}$ ,  $Gd^{3+}$  and  $Dy^{3+}$  were calculated using the Irving-Rossotti method. To evaluate the formation constant of the formed complexes, the values of  $\bar{n}$  and pL are needed at different pH values. According to Irving-Rossotti the values of  $\bar{n}$  and pL were calculated and the experimental formation curves were constructed by plotting  $\bar{n}$  vs. pL. The stability constants of binary complexes of  $La^{3+}$ ,  $Sm^{3+}$ ,  $Gd^{3+}$  and  $Dy^{3+}$  with CPTA and FCA were calculated from the titration graphs in which the metal to ligand ratio was 1:1 are listed in table (1).

Inspection of IR spectra of binary complexes reveals that all the spectra are identical in all respects indicating that the bonding pattern must be the same in all the complexes. The comparison of IR spectrum of the parent ligand with that of its each metal complex has revealed certain characteristic differences as in fig.2.

One of the significant difference to be expected between the IR spectrum of the parent ligand and its metal complex is the presence of more broadened bands in the region of  $3200-3600\text{ cm}^{-1}$  for the metal complex as the oxygen of the O-H group of the ligands forms a coordinate bond with the metal ions.[20-22] This is explained by the fact that water molecules might have strongly absorbed to the metal chelate sample during their formation.

Another noticeable difference is that the infra red spectra of binary complexes do not display the band due to free carboxylic group indicating the coordination through carboxylic group. It is a simple rule that unionized and uncoordinated  $COO^-$  stretching band occurs at  $1750-1700\text{ cm}^{-1}$ , whereas the ionized and coordinated  $COO^-$  stretching band occurs at  $1610-1550\text{ cm}^{-1}$  and  $1400-1300\text{ cm}^{-1}$  which correspond to antisymmetrical and symmetrical vibrations of the carboxyl group. The later frequencies depend upon the nature of the metals.

### Ternary Complex Systems

The potentiometric titration curve for  $Sm^{3+}$ -CPTA-FCA in a 1:1:1 molar ratio at  $30^\circ\text{C}$  is shown in figure 1. Similar titration curves were obtained at the other studied temperatures and metal ion. The primary complex curve (c) and mixed ligand curve (d) overlap each other up to  $\text{pH}=3.50$ . This indicates that in this pH range when primary ligand combines with metal, combination of secondary ligand does not take place. Curve (d) diverges from curve(c) after  $\text{pH}=3.50$  showing that at this pH combination of secondary ligand with primary complex starts. The horizontal distance  $V_2$  between the curve (a) and (b) indicates the protons released due to the self dissociation of secondary ligand and the difference  $V_3$  between the curve (c) and (d) indicates the protons released due to the self dissociation of secondary ligand plus the protons released due to the formation of mixed ligand complex. Thus  $(V_3-V_2)$  accounts for the total protons released due to the formation of mixed ligand complex. By using these values  $\bar{n}$  values were calculated. The pL values were calculated at  $\bar{n} = 0.5$  and are summarized in Table 1.

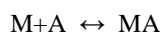
The stabilities of ternary complexes as compared to binary complexes can be quantified by the calculation of  $\Delta \log K$  which is given by the following expressions.

$$\Delta \log K = \log K_{MAL}^{MA} - \log K_{ML}^M$$

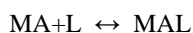
Or more appropriately as,

$$\Delta \log K = \log K_{MAL}^M - \log K_{ML}^M - \log K_{MA}^M$$

(A=CPTA and L=FCA) where  $\log K_{MA}^M$ ,  $\log K_{MAL}^{MA}$  and  $\log K_{MAL}^M$  can be expressed by the following equilibrium reactions (charges have been omitted for simplicity)



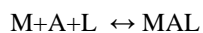
$$K_{MA}^M = \frac{[MA]}{[M][A]}$$



$$K_{MAL}^{MA} = \frac{[MAL]}{[MA][L]}$$

The overall stability constant for the mixed ligand complex MAL is given by the following equation

In the above equations M represents metal ion, A represents the primary ligand and L is the secondary ligand, which leads to the formation of a ternary or mixed ligand complex MAL.



$$\log K_{MAL}^M = \frac{[MAL]}{[M][A][L]}$$

**Table 1- Stability constants and Thermodynamic parameters of mixed ligand complexes at different temperatures ( $\mu=0.2M KNO_3$ )**

System	Temp.	$K_{MA}^M$	$K_{ML}^M$	$K_{MAL}^{MA}$	$\Delta \log K$	$\Delta G^0$	$\Delta H^0$	$\Delta S^0$
La <sup>3+</sup> +CPTA+FCA	30 <sup>0</sup> C	11.74	1.81	2.32	0.51	-3.21	-10.52	-24.08
	40 <sup>0</sup> C	11.59	1.72	2.09	0.37	-2.99		
	50 <sup>0</sup> C	11.36	1.64	1.85	0.21	-2.73		
Sm <sup>3+</sup> +CPTA+FCA	30 <sup>0</sup> C	9.53	1.66	2.27	0.61	-3.14	-7.16	-13.16
	40 <sup>0</sup> C	9.39	1.57	2.13	0.56	-3.05		
	50 <sup>0</sup> C	9.15	1.49	1.95	0.46	-2.88		
Gd <sup>3+</sup> +CPTA+FCA	30 <sup>0</sup> C	9.33	1.61	1.82	0.21	-2.52	-3.80	-4.27
	40 <sup>0</sup> C	9.20	1.52	1.73	0.21	-2.47		
	50 <sup>0</sup> C	8.86	1.44	1.65	0.21	-2.44		
Dy <sup>3+</sup> +CPTA+ FCA	30 <sup>0</sup> C	11.32	1.76	2.32	0.56	-3.21	-3.80	-1.97
	40 <sup>0</sup> C	11.19	1.67	2.23	0.56	-3.19		
	50 <sup>0</sup> C	11.16	1.54	2.15	0.61	-3.17		

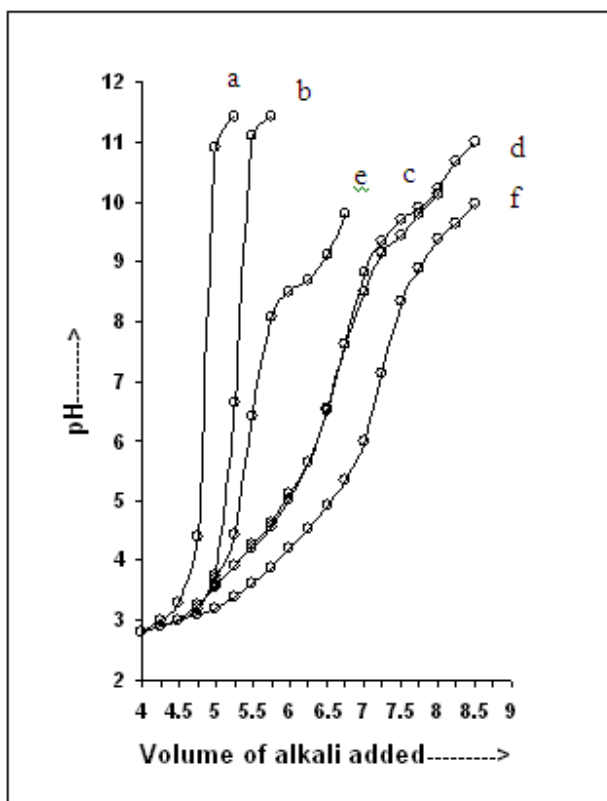


Fig. 1 Titration curve for  $\text{Sm}^{3+}$ -CPTA-FCA ( $30^{\circ}\text{C}$ )

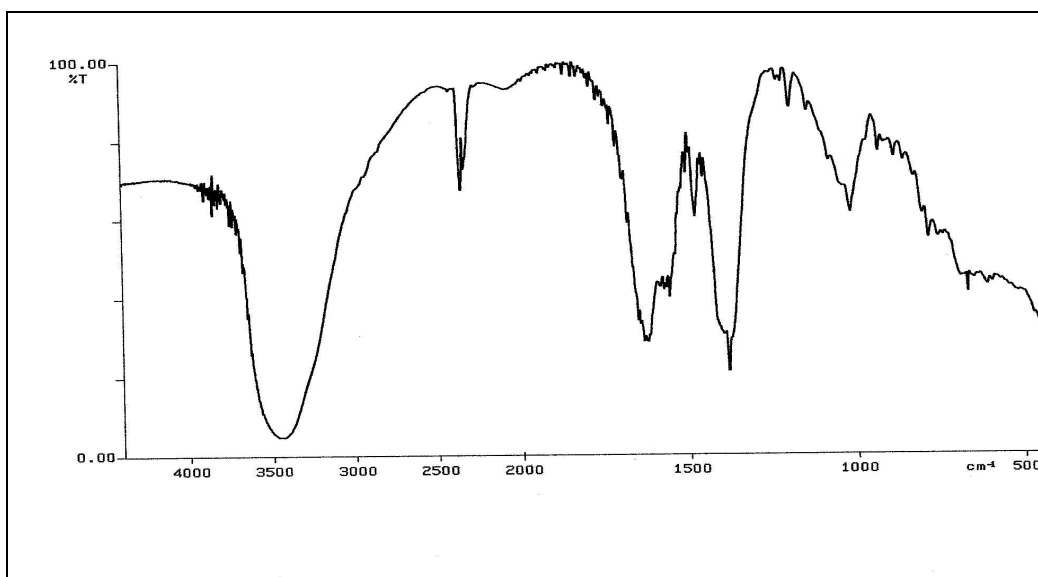


Fig. 2 The infrared spectrum of binary complex of  $\text{Sm}^{3+}$  and Furan-2-carboxylic acid (FCA)

**Table 2-The important infrared frequencies (in cm<sup>-1</sup>) of FCA, CPTA and their metal complexes**

System	$\nu_{(\text{OH})}$	$\nu_{\text{a}(\text{COO})}$	$\nu_{\text{s}(\text{COO})}$
FCA	3457	1696	
La <sup>3+</sup> +FCA	3435	1637	1569
Sm <sup>3+</sup> +FCA	3448	1636	1384
Gd <sup>3+</sup> +FCA	3447	1636	1419
Dy <sup>3+</sup> + FCA	3435	1421	1346
CPTA	3449	1676	
La <sup>3+</sup> +CPTA	3448	1636	1560
Sm <sup>3+</sup> +CPTA	3448	1540	1450
Gd <sup>3+</sup> CPTA	3449	1610	1400

### CONCLUSION

From Table (1) it can be seen that the stability constants of the binary complexes with each of the ligands decrease with increasing temperature; and that the complexation is exothermic. The stability constants of metal ions follow the order, La<sup>3+</sup> < Sm<sup>3+</sup> < Gd<sup>3+</sup> ≈ Dy<sup>3+</sup>.

It is further observed that with increase in temperature, the stability constants of the ternary complexes decrease. The major driving force of the ternary complex series with all the metal ions is entropically supported.

It can be observed from the result that log KMAL values for all the Metal–CPTA–FCA 1:1:1 system are higher than that of the log KML 1:1 complexes resulting in positive value of log K. The reason for the extra stability of ternary complexes may be due to interaction outside the coordination sphere such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization, chelate effect and stacking interactions.[23-24]

However, the binary complexes of metal ions with CPTA are found to be more stable than ternary complexes because the electrostatic theory of binary complex formation and statistical arguments suggest the availability of additional coordination position of the hydrated metal ion for the first ligand than for the second. Hence the usual order of stability  $K_{MA}^M > K_{MAL}^{MA}$  applies.

The results of IR spectral studies of binary complexes provide strong evidence for the complexation of the ligands with metal ion through carboxyl group.

Binary complexes of La (III), Sm (III), Gd (III) and Dy (III) with Furan-2-carboxylic acid (FCA) were synthesized and characterized. All the complexes exhibited considerable antifungal activity against *Aspergillus niger*, *Aspergillus fumigatus* and *Aspergillus flavus* and antibacterial properties against (gram negative) *Escherichia coli* and (gram positive) *Staphylococcus aureus*. Preliminary results indicate that newly synthesized rare earth complexes with FCA exhibited promising antibacterial and antifungal activities and they warrant more consideration as prospective antimicrobials.

### Acknowledgement

The authors thank Dr. Virendra Mishra, Principal, B.S.A. College, Mathura for providing necessary facilities.

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