Chemicals:

All chemicals were of AnalaR grade unless otherwise mentioned. The list of chemicals and their source of supply has been given below:

Perchloric acid, 4-methoxy benzoic acid (Riedel, Germany). Nitrobenzoic acids and all dicarboxylic acids (B.D.H., London). Benzoic acid and sodium hydroxide (GR grade, Sarabhai Merck India). Methoxy substituted benzoic acids (purum, Fluka, Germany).

Copper nitrate (B.D.H., London).

Uranyl nitrate (May and Baker).

Beryllium nitrate (E. Merk).

Rare earth nitrates (Rare earth India, & Bhabha Atomic Research Centre, Bombay, India).

Fluorine substituted hydroxy chalcones prepared in our research laboratory.

Citric acid, Oxalic acid, Malonic acid, Tartaric acid, and Malic acid (B.D.H., London).

Tryptically Distilled water; (Carbon di-oxide free), with pH 6.6, was prepared on an all glass distillation plant, supplied by Scientific Instruments, New Delhi.
India; by repeated distillation, which was finally distilled over alkaline potassium permanganate.

**Solvents:**

The solvents like dioxane, benzene, carbon tetrachloride, m-xylene, hexane, chloroform, toluene were purified by the known standard methods\(^1\).

**Purification of dioxane:**

Dioxane was purified by the method described by Vogel\(^1\) and stored. Its purity was checked from time to time by potassium iodide solution because upon exposure to air or on standing dioxane decomposes to peroxide; which gives yellowish colour with potassium iodide solution. Even if slight traces of peroxide were detected, it was redistilled before use.

**Purification of benzene:**

Benzene may contain thiophene as an impurity which cannot be separated by distillation or by fractional crystallization. Thiophene is more readily sulphonated than benzene. The solvent is,
therefore, shaken repeatedly with about 15% of its volume of concentrated sulphuric acid in a stoppered separatory funnel until the acid layer remains colourless or pale yellow on standing. After each shaking the mixture is allowed to settle and the lower layer of acid is drawn off. The benzene is then shaken twice with water in order to remove most of the acid, once with 10% sodium carbonate solution and again with water. Finally it is dried over anhydrous calcium chloride, filtered and distilled. Fraction of distillate at 80–81°C is collected.

**Purification of carbon tetrachloride:**

Carbon tetrachloride may contain carbon di sulphide as an impurity.

One litre of carbon tetrachloride is treated with potassium hydroxide 60 gms. (1.5 times the quantity required to combine with carbon di sulphide) dissolved in equal weight of water and 100 ml of rectified spirit and the mixture is vigorously shaken for 30 minutes between 50–60°C. This was accomplished by intermittently heating on a mantle and shaking on a
shaker. After washing with water the process is repeated with half the quantity of potassium hydroxide. The alcohol is then removed by shaking several times with 500 ml of water followed by shaking with small portions of concentrated sulphuric acid until there is no further colouration. The carbon tetrachloride is then washed with water, dried over anhydrous calcium chloride and distilled. The pure solvent is collected at 70°C.

m-Xylene, hexane and chloroform, of A.R. grade, were double distilled freshly before use.

**Solutions**:

Sodium hydroxide solution - Sodium hydroxide pellets of A.R. quality were rinsed rapidly with water to remove the carbonate formed on the surface and then the solution is prepared which is satisfactory for most of the titration purposes.

The aqueous solutions of beryllium nitrate, copper nitrate and uranyl nitrate were prepared in 0.1 M perchloric acid.
The rare earth nitrate solutions were prepared in 0.1 M perchloric acid. The solutions were analysed for metal contents by standard procedure.

**pH meter:**

The pH meter assembly consisted of an Elico model LIX120 digital pH meter (with an accuracy of +0.01 pH unit), an Elico glass electrode and a saturated calomel electrode. The readings were recorded only when the instrument showed a steady pH. The pH meter was standardized at the experimental temperature, before each run with phthalate buffer and borax buffer solutions. The pH meter scale was calibrated by titrating aqueous solution of 0.025 M H₅IO₄ against standard NaOH. The pH values measured and those calculated from the analytical concentration of H₅IO₄ and activity co-efficients agreed within the accuracy of the instrument.

For any erratic behaviour of the pH meter it was calibrated by dipping the glass electrode and calomel electrode pair in phthalate and borax buffers.
alternately and adjusting the digital pH reading to 4.01 and 9.14 respectively by operating the standardization knob. When the adjustment of the knob did not work, the screw marked 'pH calibration' on the back side of the instrument, was adjusted.

The pH meter readings obtained for the dioxane-water medium are designated as 'B'. They have been converted to the real thermodynamic pH values by the correction of Van Uitert and Hess 4.

The details of various types of glass electrodes, supplied by the Elico Pvt. Ltd., Hyderabad (India) have been tabulated below for ready reference.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>pH Range</th>
<th>Temp. °C</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0 – 11</td>
<td>0 – 40</td>
<td>EK 62 A</td>
</tr>
<tr>
<td>2.</td>
<td>0 – 12</td>
<td>0 – 100</td>
<td>EN 66</td>
</tr>
<tr>
<td>3.</td>
<td>0 – 13</td>
<td>20 – 75</td>
<td>EN 60</td>
</tr>
<tr>
<td>4.</td>
<td>0 – 14</td>
<td>20 – 100</td>
<td>EL 60</td>
</tr>
</tbody>
</table>

These glass electrodes were used in this work.
The characteristics and other information about the glass electrode have been discussed in detail, by Cole.  

**Experimental procedures:**

For convenience the procedure of Section-I is given in Chapter on 'Results and discussion'.

**Section - II**

The metal ligand potentiometric titrations.

Calvin - Bjerrum titration technique has been used. The following carbonate free solutions with ionic strength = 0.1M NaClO₄ were titrated against standard NaOH under inert nitrogen atmosphere.

1) 3 ml HClO₄ (0.1 M) + 5 ml NaClO₄ (1.0 M) + 25 ml dioxane + 17 ml water (Acid titration, A curve).

2) 3 ml HClO₄ (0.1 M) + 5 ml NaClO₄ (1.0 M NaClO₄) + 10 ml ligand (1 x 10⁻² M) in dioxane + 15 ml dioxane + 17 ml water (Acid + ligand titration, A + L curve).
3) 1 ml \( \text{HClO}_4 \) (0.1 M) + 5 ml \( \text{NaClO}_4 \) (1.0 M) + 10 ml ligand (1 \( \times \) 10\(^{-2} \) M) in dioxane + 2 ml (1 \( \times \) 10\(^{-2} \) M) metal solution in (0.1 M) \( \text{HClO}_4 \) in water + 15 ml dioxane + 17 ml water (Acid + ligand + metal titration, \( A + L + M \) curve).

The composition of dioxane-water mixture was 50/50 (v/v). The potentiometric titration curves (fig. 1) represent the plot of pH meter readings (E) against the addition of alkali, in ml (v).

The proton ligand formation number \( n_h \) was calculated by the Irving-Rossotti\(^6 \) expression,

\[
\tilde{n}_h = \frac{Y \cdot (V_0 - V_1) (N + E_0)}{(V_0 + V_1) x T_0^0}
\]  \( \ldots (2.1) \)

where \( V_0 \) = initial volume of the solution.

\( E_0 \), \( T_0^0 \) are initial concentrations of perchloric acid and ligand respectively. \( V_1 \) and \( V_2 \) are the volumes of alkali of given normality \( N \) required during acid and (acid + ligand) titrations at a given pH. \( Y \) is the number of replaceable hydrogen ions from the ligand.
$\text{UO}_2^{2+} - 3'$-FLUORO-4'-HYDROXY-
-3-(2''-THIENYL)-ACRYLOPHENONE.

MEDIUM 50 % DIOXANE
TEMP. 30 °C

A

A + L

A + L + M

Vol. of NaOH (ml)

pH

FIG. 1
The proton ligand stability constants were calculated by (i) half integral method, and (ii) method of pointwise calculations. The various terms used to calculate the \( pK \) values for two representative systems have been given in Tables A-7, A-8 and A-9.

**Calculations of metal ligand stability constants:**

Metal-ligand complex formation in all cases commenced before the onset of hydrolysis of the metal ions.

The solutions employed were so dilute that the probability of existence of polynuclear species under experimental conditions was negligible. The metal ligand formation number \( \bar{n} \) is given by the expression

\[
\bar{n} = \frac{(V_3-V_2)\left\{\frac{K[E^0+T_L^0]}{(Y-\bar{n})}\right\}^2}{(V_1^0+V_2)\ T_M^0 \bar{n}^2} \quad \ldots \quad (2.2)
\]

\( V_3 \) is the volume of NaOH (in \( A+L+M \)) curve at a pH corresponding to \( V_1 \) and \( V_2 \).

\( T_M^0 \) = metal concentration.
The $PL = \log [L]$ free ligand concentration was calculated by the expression

$$PL = \log \frac{1 + [H]/K_2 + [H]^2/K_1K_2}{(T_L^0 - \bar{n}T_M^0)} \times \frac{V^0 + V_3}{V_3} \quad \cdots \ (2.3)$$

Calculations of $\log K$ Values:

Half-integral method: Values of $\bar{n}$ have been plotted against $PL$ to obtain the formation curve. (Refer figures (3-6) in Section II, Chapter 3). Approximately the values of $PL$ at $\bar{n}=0.5$ and 1.5 are equal to $\log K_1$ and $\log K_2$ respectively.

The method of pointwise calculations: The accurate $\log K$ values were calculated by this method. For calculations of $\log K_1$ the expression

$$\log \frac{\bar{n}}{1-\bar{n}} = \log K_1 + PL \quad \cdots \ (2.4)$$

was solved for $\bar{n}$ values between 0.2 and 0.8. The plots of log term versus $PL$ were obtained. The data for calculations of $\log K_1$ values for two representative systems has been given in Table A-10 and A-11.

Similarly $\log K_2$ was calculated using the expression $\cdots$
$\text{UO}_2^{+2} - 3'$-FLUORO-4'-HYDROXY-3-($^2''$-THIENYL)-ACRYLOPHENONE

$\text{Gd}^{+3} - 3'$-FLUORO-4'-HYDROXY-3-($^2''$-PYRIDYL)-ACRYLOPHENONE

\[\begin{array}{c}
\text{FIG. 3} \\
\text{FIG. 4} \\
\end{array}\]

$\text{UO}_2^{+2} - 3'$-FLUORO-4'-HYDROXY-3-($^3''$-PYRIDYL)-ACRYLOPHENONE

$\text{Tb}^{+3} - 3'$-FLUORO-4'-HYDROXY-3-($^2''$-FURYL)-ACRYLOPHENONE

\[\begin{array}{c}
\text{FIG. 5} \\
\text{FIG. 6} \\
\end{array}\]
\[ \log \frac{\bar{n} - 1}{2 - \bar{n}} = \log K_2 + pL \quad \ldots \quad (2.5) \]

for \( \bar{n} \) values between 1.2 and 1.8.

**Section-III**

**Experimental procedure for (metal) mixed ligand complexes:**

The experimental procedure involved potentiometric titrations under oxygen free nitrogen atmosphere of carbonate free aqueous solutions given below, in 50 ml total volume.

1) HSO$_4$A
2) HSO$_4$ + ligand (L)
3) HSO$_4$ + ligand (L) + metal ion (M)
4) HSO$_4$ + ligand (A)
5) HSO$_4$ + ligand (A) + metal ion (M)
6) HSO$_4$ + ligand (L) + ligand (A) + metal ion (M)

against standard NaOH. Here 'L' and 'A' are the two ligands. The ionic strength of solutions was maintained constant at 0.1 M by the addition of requisite amount of 1M sodium perchlorate solution.
Calculation of stability constants of mixed-ligand Complexes:

The pK and logK values for binary systems were calculated by the procedure described earlier. This is necessary for calculation of stability constants of mixed-ligand complexes.

In the titration of metal ion-mixed-ligand system against standard sodium hydroxide, the following equilibria are possible:

\[ M + L \rightleftharpoons ML, \quad ML + A \rightleftharpoons MLA \quad \text{stepwise equilibrium} \]
\[ M + A \rightleftharpoons MA, \quad MA + L \rightleftharpoons MLA \quad \text{equilibrium} \]
\[ M + L + A \rightleftharpoons MLA \quad \text{simultaneous equilibrium} \]

where 'M' represents the metal ion, 'L' and 'A' represent the two ligands.

i) Stepwise equilibrium:

The combination of 'L' and 'A' with the metal ion 'M' would be by a stepwise equilibrium if the mixed ligand titration curve could be superimposed over the 1:1 ML or MA titration curve. The stability constants for the stepwise equilibrium of the mixed ligand complex MLA formed from ML or MA may be
calculated by the replacement of \( M = [L] \) by \( ML \) or \( MA \) in the following expression:

\[
K_{ML} = \frac{T_M - [L]X}{[L]^2 X} \quad \ldots (2.6)
\]

where \( T_M \) = metal ion concentration,

\([L]\) = free ligand concentration

and \( X = \frac{[L]^2}{K_1K_2} + \frac{[A]}{K_2} + 1 \quad \ldots (2.7)\)

ii) Simultaneous equilibrium:

when the mixed ligand titration curve does not coincide with either \( ML \) or \( MA \) curve, the equilibrium involved is simultaneous. For the determination of stability constants, the concentration of total (first and second) free ligand and the value of \( X \) were calculated by the following expression obtained by the modification of Thompson and Larsema method,\(^7\)

\[
K_S = \frac{T_M - \frac{1}{2}[A]X}{1/8[A]^3X} \quad \ldots (2.8)
\]

when \( T_M = T_L = T_A \)

\[
K_S = \frac{\frac{1}{2}(T_L + T_A) - [A]X}{2(T_L + T_A) - [A]X} \quad \frac{1}{\frac{1}{2}[A]^3X} \quad \ldots (2.9)
\]
when \( T_R \neq T_L \neq T_A \)

where

\[
A = \frac{2T_L + 2T_A + P - T_{OH}}{4[H]^2 + \frac{2[H]}{K_1K_2 + K_1K'_1 K_2 + K'_2}} \quad \ldots \quad (2,10)
\]

and

\[
x = 1 + \frac{2[H]^2}{K_1K_2 + K_1K'_1 K_2 + K'_2} \quad \ldots \quad (2,11)
\]

where \( T_R, T_L, T_A \) represent the concentrations of total metal ion, the primary ligand and the secondary ligand respectively, \( P \) is the initial concentration of \( H\text{E}10_4 \) and \( T_{OH} \) is the concentration of \( \text{NaOH} \). \( K_1K_2 \) and \( K_1K'_1 K_2 + K'_2 \) are the first and second dissociation constants of the two ligands. The value of the stability constant of the mixed-ligand complex is given by

\[
K_{M,LA} = \frac{T_R - \frac{1}{3}[A]_x}{1/3[A]^3 \cdot x} \quad \ldots \quad (2,12)
\]

\( x \) is the end.
REFERENCES


