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Studies on Standard changes in Free energy of Fluorobenzoylthioacetophenone complexes of Manganese, Nickel, Cadmium & Mercury with their Biological importance

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Abstract- Complexes of p-fluorobenzoylthioacetophenone, an organic ligand with transition metal ion acts as multitherapeutic agents. They act as catalyst and in photosynthesis. These complexes have many applications in the form of medicines. The formation constants of the complexes of the said ligand with bivalent Manganese, Nickel, Cadmium and Mercury were determined at three different temperatures through Irving and Rossotti method. From a knowledge of Overall formation constants, Standard change in Free energy were determined at the said temperatures using thermodynamic relation $\Delta G^\circ = -2.303\ RT\ Log\ \beta$. From the data obtained, the Standard Changes in free energy which contribute towards complex formation and which has a say in the therapeutic properties have been discussed.

Key words: Formation constants, Therapeutic properties, Free energy

INTRODUCTION

The ligand chosen for the complexation with Manganese, Nickel, Cadmium and Mercury is para-fluorobenzoyl thioacetophenone, whose structure is shown below. This ligand belongs to Monothio-β-diketone[1-3] class of compounds. It behaves as a uninegatively charged bidentate chelating agent resulting in the formation of six-membered chelates.[4] It deprotonates through enol or enethiol form.[5-7]

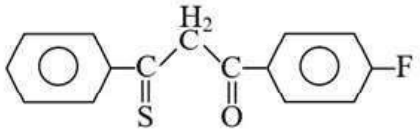

Fig. 1- p-fluorobenzoyl thioacetophenone

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However, attempt has not been made to study the therapeutic properties of the complexes of the said ligand with Mn, Ni, Cd and Hg – a work that can help to understand the contribution of Free energy Change associated with above complexes in order to know the therapeutic uses and biological importance of the complexes formed.

In this present communication we report the Formation Constants[8-10] of complexes of the said ligand with Manganese, Nickel, Cadmium and Mercury at three different tempts. viz 10°C, 20°C and 30°C as determined by Calvin-Bjerrum[11-13] pH-metric technique and as modified by Irving and Rossotti[13,14]. We also report the Standard Changes in Free energy accompanying above complexation together with chemotherapeutic significance of these complexes.

MATERIALS & METHODS

Para-fluorobenzoylthioacetophene, the ligand chosen with present research work was synthesised by Claisen condensation of o-ethylthiobenzoate with p-fluoroacetophenone in presence of sodamide as shown below.

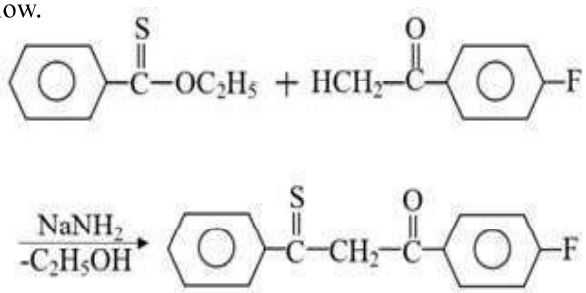

Fig. 2- Synthesis of p-fluorobenzoyl thioacetophenone

Standard solution of ligand was prepared in dioxan[15,16]

Procedure: Following three mixtures were prepared for potentiometric titration:

(i) Mixture (i): 5 ml 0.4 M Hydrochloric acid solution + 5 ml M Potassium Chloride solution

(ii) Mixture (ii): Mixture (i) + 5 ml 0.02 M Ligand solution

(iii) Mixture (iii): Mixture (ii) + 5ml 0.004 M Metal ion solution

Total volume in each titration was kept 50 ml. The mixtures were titrated against 0.2 M KOH solution and the pH was measured in O_2-free nitrogen atmosphere. The pH-meter readings were plotted against volume of alkali added in each case to get Acid, Ligand and Complex Titration Curves respectively.

$\bar{n}_A$ values at various B-values were obtained from acid and ligand titration curves. A plot of $\bar{n}$ versus B gave the Formation Curve of Ligand–Proton complex. Protonation constant value of the ligand was obtained by Half-Integral method from this curve (Log K_1^H = pKa = B at $\bar{n}_A$= 0.5). The values of $\bar{n}$ and pL were obtained from Ligand and Complex titration curves through appropriate equation. Formation Curves of complexes were drawn by plotting of $\bar{n}$ vs pL. These curves finally provided the data of Stepwise Stability Constants. These data are furnished in Table 1.

Table 1- Stepwise and Overall Stability Constant Data of Metal Complexes at different temperatures.

Metal Ions	Temperatures								
	10°C			20°C			30°C		
	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β
Ni^{2+}	10.47	09.43	19.90	10.21	09.38	19.59	10.18	09.31	19.49
Mn^{2+}	09.57	08.63	17.95	09.18	08.52	17.70	09.03	08.40	17.43
Cd^{2+}	08.94	08.35	17.29	08.76	08.16	16.92	08.59	08.05	16.64
Hg^{2+}	08.72	08.26	16.98	08.83	08.06	16.69	08.39	07.89	16.28

It is thus obvious from the table that stability constants of Metal complexes follow the trend: Ni(II) > Mn(II) > Cd(II)> Hg(II).

Evaluation of ΔG°

Standard change in Free energy[17,18] (ΔG°) values were assessed at a given temperature through the well-known thermodynamic expression, ΔG° = -2.303 RT Log β, where ΔG° = Standard change in free energy accompanying the complex formation reaction, β = overall Formation constant, T = Temperature and R = Constant.

These values of ΔG° for each metal for each metal complex are furnished below in Table 2.

Table 2- ΔG° values of Bivalent Metal Complexes at three different temperatures. (μ = 0.1 M KCl)

Metal ions	-ΔG°(kcal/mol) Temperatures		
	10 ± 1°C	20 ± 1°C	30 ± 1°C
Ni^{2+}	25.77	26.29	27.02
Mn^{2+}	23.24	23.73	24.16
Cd^{2+}	22.39	22.68	23.07
Hg^{2+}	21.98	22.37	22.57

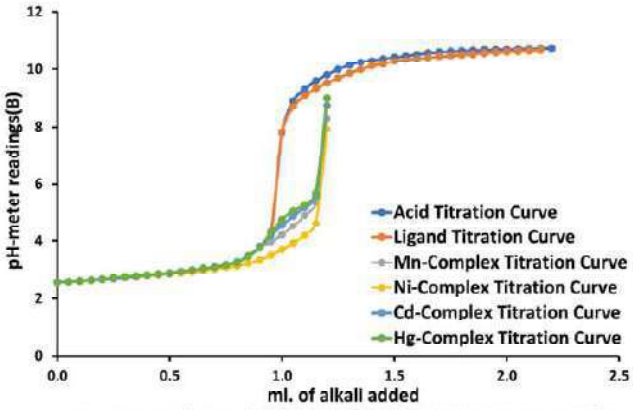

Figure 3: Acid, Ligand and Metal-Complex Titration Curve at 10°C

Similar graphs were obtained at 20°C and 30°C.

RESULTS & DISCUSSION

From the above table, it is obvious that the decrease in standard free energy change is higher at 20°C than at 10°C in the case of the complexes of each metal ion. Similarly, the decrease in free energy at 30°C is higher than at 20°C. Also, at each temperature, the decrease in Standard free change follows the trend: Ni(II) > Mn(II) > Cd(II)> Hg(II). Thus, the complexes are free energy stabilised. This trend in free energy change is in conformity with the stability order (mentioned in Table-1) of the complexes.

The decrease in free energy associated with the formation of complexes of these metal ions has some regularity which can be understood by looking at the values obtained. For example, ΔG° values at 10°C for the complexes of bivalent Ni, Mn, Cd and Hg are respectively 25.77, 23.24, 22.39 and 21.98 supporting the values of decrease in free energy have good curative power.

CONCLUSION

The above complexes of Mn, Ni, Cd and Hg have higher values of Stability constants showing that they are stable complexes. Also, values of Standard change in free energy accompanying above complexes are higher which make them have higher pharmaceutical values. Complexes of Cadmium with the ligand in question have numerous applications as pharmaceutical agents. These complexes also act as enzymes and thus regulate biological processes.

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