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Studies on standard changes in entropy of complexes of Monothio-β-diketone and their medicinal significance

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Abstract- With good entropy change values, the complexes of Monothio-β-diketone have good therapeutic importance. These complexes play vital role in biological system in both human beings and plants. Overall Stability constants of bivalent complexes of Manganese, Nickel, Palladium and Platinum with para-chlorobenzoylthioacetophenone an organic ligand have been determined potentiometrically at three different temperatures viz. 10°C, 20°C and 30°C. From a knowledge of Stability Constant data, Standard Changes in Free energy, Enthalpy and Entropy were determined with the help of appropriate methods. The Standard change in entropy of the above complexes together with their medicinal significance have been discussed.

Key words: Overall Stability constant, Potentiometric technique, Standard change in Entropy, Medicinal significance, Therapeutic importance

INTRODUCTION

Para-chlorobenzoylthioacetophenone, the ligand of our research work is an organic compound belonging to Monothio-β-diketone class.[1-3] Complexation of this ligand were made with bivalent Mn, Ni, Pd and Pt. This ligand behaves as a uninegatively charged bidentate ligand after deprotonation through its enol or enethiol[4-6] form resulting in the formation of a six-membered resonance stabilised chelate[7] with metal ions. The structure of the ligand is presented below.

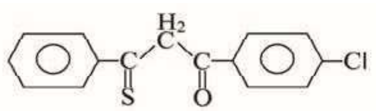

Fig. 1- Structure of p-chlorobenzoylthioacetophenone

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But no attempt has been made so far to study the solution equilibria of the ligand in question and its derived complexes with said metal ions as also the Standard Changes in Entropy of the above complexes and their medicinal values. This can help to understand the chelating ability of the said ligand, Standard Change in Entropy associated with these complexes and especially their medicinal values.

In this present communication we report Standard Changes in Entropy of the complexes formed with their medicinal values. The Overall Stability Constants[8-10] of the complexes of p-chlorobenzoylthioacetophenone with Mn(II), Ni(II), Pd(II) & Pt(II) at three different temperatures namely 10°C, 20°C and 30°C are obtained through Calvin-Bjerrum potentiometric technique[11-13] as modified by Irving and Rossotti.[13,14]

MATERIALS & METHODS

The ligand, in question was synthesised by Claisen condensation of o-ethylthiobenzoate with pchloroacetophenone in presence of sodamide as shown below. The ligand solution was prepared in dioxan.[15,16]

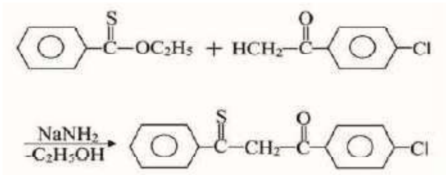

Fig. 2- Synthesis of p-chlorobenzoylthioacetophenone

Following three mixtures were prepared for potentiometric titration:

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

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

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

Total volume was maintained 50 ml in each experiment. The mixtures were titrated against 0.2 M Potassium hydroxide solution and the pH was measured in nitrogen atmosphere. The pH-meter readings and the volume of alkali were plotted in each case to obtain Acid, Ligand and Complex Titration Curves respectively.

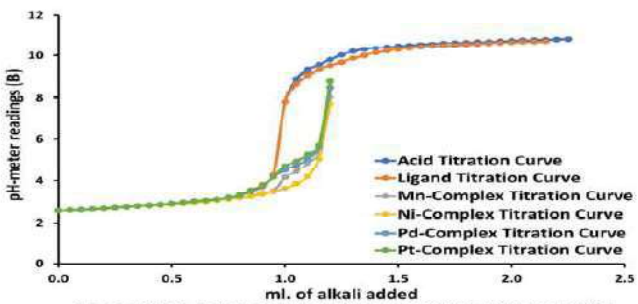

Figure 3: Acid, Ligand and Metal-Complex Titration Curve at 10°C

Similar acid, ligand and metal titration curves were obtained at 20°C and 30°C.

$\bar{n}_A$ values were obtained from acid and ligand titration curves to know the protonation constant (pKa) value of the ligand whereas $\bar{n}$ and pL were obtained by plotting $\bar{n}$ vs pL to know stepwise stability constant which final gave Overall stability constant values of the complexes formed. These values are mentioned 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+}	10.59	09.75	20.34	10.37	09.48	19.85	10.31	09.45	19.76
Mn^{2+}	09.48	08.79	18.27	09.32	08.69	18.01	09.24	08.55	17.79
Pd^{2+}	09.11	08.51	17.62	09.12	08.39	17.51	08.83	08.29	17.12
Pt^{2+}	08.93	08.39	17.32	08.77	08.23	17.00	08.63	08.14	16.77

The Standard change in Free energy[17,18] accompanying the above complexations was evaluated using the thermodynamic relation $\Delta G° = -2.303\ RT\ Log\ \beta$ where ΔG° and Log β are respectively Standard change in Free energy and Overall Stability constant values of the complexes. R and T have their usual meanings. Values of ΔG° are given in Table-2.

Table 2- ΔG° values of Bivalent Metal Complexes at different temperatures

Metal ions	-ΔG°(kcal/mol)		
	Temperatures		
	10 ± 1°C	20 ± 1°C	30 ± 1°C
Ni^{2+}	26.34	26.61	27.40
Mn^{2+}	23.66	24.15	24.67
Pd^{2+}	22.82	23.48	23.74
Pt^{2+}	22.43	22.79	23.25

The Standard change in Enthalpy (ΔH°) accompanying the above complex formation reactions was determined with the help of following isobar equation, It was also obtained by employing Gibbs-Helmholtz equation. The values of ΔH° obtained by Linear Plot Method and G-H eq^n are mentioned in Table-3.

Table 3- ΔH° values of Bivalent Metal Complexes in Kcals/mol

Metal ions	-ΔH° (kcal/mol)		
	By Linear Plot Method	By Gibbs-Helmholtz equation at 30 ± 1°C	Average values
Ni^{2+}	11.58	11.08	11.33
Mn^{2+}	09.44	09.35	09.39
Pd^{2+}	09.70	10.00	09.85
Pt^{2+}	10.85	10.77	10.81

Evaluation of Standard Changes in Entropy (ΔS°)

The related values of ΔS° were obtained using average value of ΔH° as mentioned in Table 3. In the calculation of ΔS°, the thermodynamic equation viz. $\Delta G° = \Delta H° - T\Delta S°$ was applied. The required ΔG° values present in Table-2 were used. The values of ΔS° obtained are arranged below in Table-4.

Table 4- ΔS° values of Bivalent Metal Complexes in Cals./deg/mol

Metal Ions	ΔS°(Cals./deg/mol)
Ni^{2+}	52.15
Mn^{2+}	50.37
Pd^{2+}	46.52
Pt^{2+}	40.89

RESULTS & DISCUSSION

From the data obtained, it is obvious that β increases as ΔG° becomes more negative. The value of ΔG° becomes more negative when that of ΔS° becomes more positive. More positive value of ΔS° will cause the formation of more stable complex. The entropy of a system is a measure of degree of disorderness of the system. The greater the amount of this disorder produced in the product, the greater will be the value of Entropy and hence greater will be the stability.

In the present investigation, we find that the thermodynamic parameters too in conformity with the stability order as mentioned in Table-1 follow the same order. Thus, at each temperature, the decrease in ΔG° follows the same trend (Table-2) which suggests the complexes formed are free energy stabilised. The negative values of ΔH° for each metal complex as listed in Table 3. indicate that complex formation reactions are exothermic in nature which reflects that all the complexes formed are enthalpy stabilised.

The data for Standard change in Entropy (ΔS°) furnished in Table-4 clearly support the stability order of the complexes (Table-1). Thus, the values of Standard change in Entropy follow the trend: $Ni^{II} > Mn^{II} > Pd^{II} > Pt^{II}$.

Complex compounds have special place in chemistry because of their structural arrangements and applications in various fields. These compounds known as coordination compounds play vital role in biological system in animals and plants. Complexes of p-chlorobenzoylthioacetophenone of Palladium and Platinum are anti-cancer drugs. These are also antibacterial.

CONCLUSIONS

Looking at the values of Standard Entropy change obtained for the complexes of Nickel,Manganese, Palladium and Platinum which come to be respectively 52.15, 50.37, 46.52 and 40.89 Cals/degree/mol clearly suggests that the complexes formed are considerably stable and therefore have good therapeutic values especially those of Palladium and Platinum. Higher values of entropy contribute much in stabilising the metal complexes which in turn have much therapeutic values.

In addition to be specific as anti-cancer drugs, these complexes have shown effective behaviour in Alzheimer and malaria.

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