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Equilibrium Studies of Transition Metal Complexes with Tridentate Ligands Containing N, O, S as Donor Atoms

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Stability constants of complexes of Mn(II), Co(II), Ni(II) and Cu(II) chelates of 2-hydroxy-3-methoxy benzylidine thiosemicarbazone have been determined by Bjerrum's method of pH metric titration technique as followed by Irving and Rossotti. The stability constants of chelates of bivalent transition metals is in the order:

Cu(II) > Ni(II) > Co(II) > Mn(II)

From the value of observed K, free energy change of the complexation reaction have been calculated.

Key Words: Stability constant, pH metric titration, Mn(II), Co(II), Ni(II), Cu(II), Tridentate ligand, Free energy change of complexation.

INTRODUCTION

A number of complexes of transition metals with ligands containing the thiosemicarbazone have been reported because of their biochemical and analytical[1,2] importance. But less is known about their stability. Thus, this work undertaken is to investigate the stability constant of complexes of transition metals *i.e.*, Mn(II), Co(II), Ni(II) and Cu(II) with 2-hydroxy-3-methoxy benzylidine thiosemicarbazone (HMBTC). The proton ligand and metal ligand stability constants were reported in dioxane:water (50:50) medium at constant ionic strength 0.1 M KNO_3) at 35 ± 1 ºC employing Calvin-Bjerruim[3] pH titration technique as modified by Irrving and Rossotti[4-7].

EXPERIMENTAL

All the chemicals used were AnalaR quality of E. Merck or BDH. Metals were estimated complexometircally by EDTA and by other suitable methods as reported in literature[8].

Preparation of ligand: One gram of 2-hydroxy-3-methoxy benzaldehyde was weighed and dissolved in 20 mL of methanol. Required quantity of thiosemicarbazide was dissolved in water. Precipitate obtained by refluxing two solutions was filtered and washed with water. The precipitate was recrystallized twice to get in pure form and its melting point was determined and found to be 216 ºC. pH metric titration's

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were carried out with the help of pH meter (systronic model 331) supplied with calomel and glass electrodes in water thermostat maintained at 35 ± 1 ºC the titration cell consists of a long beaker (100 mL) accompanied with glass stirrer and a micro burette.

Titrations were done in dioxane-water (50:50) medium at constant ionic strength (0.1 M KNO_3). Nitrogen gas was bubbled through the mixture to keep an inert atmosphere. Acid mixture, a mixture of acid and ligand solutions and a mixture of acid + ligand solution + metal salt solution was titrated with standard alkali. The change in pH with each addition of alkali was recorded. During the titration the change of colour and appearance of turbidity at particular pH values were recorded simultaneously.

RESULTS AND DISCUSSION

A graph between pH meter reading [B] *vs.* volume of alkali added was plotted and three titration curves was obtained as shown in Table-1.

TABLE-1
pH METRIC TITRATION READING OF (a) ACID,
(b) ACID + LIGAND AND (c) ACID + LIGAND + METAL ION
Ionic strength μ = 0.1 M KNO_3; Temperature = 35 ± 1 ºC; Solvent = Dioxane:water (50:50)

Volume of alkali added (B)	pH-meter reading (B)					
	Acid	Acid + ligand	Acid + ligand + Cu(II) ion	Acid + ligand + Ni(II) ion	Acid + ligand + Co(II) ion	Acid + ligand + Mn(II) ion
0.00	2.10	2.50	2.50	2.50	2.50	2.50
1.00	2.30	2.70	2.70	2.70	2.70	2.70
1.05	2.32	2.80	2.80	2.80	2.80	2.80
1.10	2.35	2.90	2.90	2.90	2.90	2.90
1.15	2.40	3.20	3.20	2.30	2.30	2.30
1.20	2.45	3.40	3.40	3.40	3.40	3.40
1.25	2.52	3.60	3.60	3.60	3.60	3.60
1.30	2.60	3.75	3.75	3.75	3.75	3.75
1.35	2.72	3.90	3.90	3.79	3.79	3.79
1.40	2.75	4.10	4.10	3.95	3.95	3.95
1.45	2.85	4.25	-	4.15	4.15	4.15
1.50	3.00	4.50	4.25	4.30	4.30	4.30
1.55	3.20	7.75	-	4.60	4.60	4.60
1.60	3.45	5.25	4.62	4.80	4.80	4.80
1.65	3.90	5.50	-	5.05	5.05	5.05
1.70	8.00	7.25	5.15	5.40	5.62	5.45
1.75	10.80	9.15	-	5.70	5.60	6.45
1.80	11.40	9.60	6.00	6.60	6.50	7.37
1.85	12.00	9.80	6.75	-	7.60	8.30
1.90	-	10.00	7.10	7.00	8.20	8.80
2.00	-	10.50	-	-	-	-
2.10	-	11.05	-	-	-	-
2.20	-	11.30	-	-	-	-
2.30	-	11.50	-	-	-	-

The functions $\bar{n}_A$ and $\bar{n}$ were calculated using the standard expressions.

$$\bar{n}_A = 1 + \frac{V_1 - V_2}{V_0 + V_1} \times \frac{N + E}{T_L}$$

and

$$\bar{n} = \frac{V_3 - V_2}{V_0 + V_1} \times \frac{N + E}{\bar{n}_A T_M}$$

The ligand titration curve is well separated at pH 8.70 indicating the dissociation of ligand in the titration medium.

The ligand formation curve was plotted $\{\bar{n}_A \text{ vs. } [B]\}$. It extends between 0.5 to 2.9. The values of practical proton ligand stability constants were calculated by half integral methods (Table-2).

TABLE-2
2-HYDROXY-3-METHOXY BENZYLIDINE THIOSEMICARBAZONE AT THE TEMPERATURE 35 ± 1 ºC

[B]	$\bar{n}_A$	[B]	$\bar{n}_A$
3.00	2.93	10.00	1.60
3.50	2.82	10.10	1.56
3.80	2.39	10.20	1.51
4.00	2.55	10.30	1.45
4.30	2.37	10.40	1.41
4.50	2.25	10.50	1.35
4.75	2.15	10.60	1.31
5.00	2.11	10.70	1.29
5.25	2.06	10.80	1.25
9.00	1.94	10.90	1.22
9.10	1.81	11.00	1.18
9.20	1.89	11.10	1.09
9.30	1.88	11.20	1.03
9.40	1.85	11.30	0.97
9.50	1.81	11.40	0.89
9.60	1.79	11.50	0.78
9.70	1.75	11.60	0.73
9.80	1.63	11.75	0.63
9.90	1.68	–	–

The complex titration curve crossed the ligand curve and acid curve at pH 5.0 for Cu(II), 5.50 for Co(II) 4.0 for Ni(II) and for Mn(II) in beginning.

The value of $\bar{n}$ extended between 0.12 to 1.1 indicating the formation of ML type complex with all the metals. Thus the ratio of metal to ligand is 1.1.

An approximate value of stability constant of the metal complex was calculated by half integral method[3,4]. The value of pL corresponding to n = 0.5 gave the value of log K (Table-3).

TABLE-3
METAL(II) + 2-HYDROXY-3-METHOXY BENZYLIDINE THIOSEMICARBAZONE (HMBTC) SYSTEM AT 35 ± 1 ºC

[B]	V_3-V_2	$\bar{n}_A$	$\bar{n}$	pL
		Cu(II) + HMBTC		
5.0	0.010	2.10	0.06	14.36
5.2	0.040	2.06	0.24	14.01
5.3	0.050	2.05	0.30	14.03
5.5	0.080	2.04	0.49	13.91
5.6	0.085	2.03	0.52	13.23
6.0	0.115	2.02	0.70	12.44
6.5	0.135	2.01	0.73	11.49
6.8	0.150	2.00	0.92	11.96
7.0	0.165	1.99	1.03	10.47
7.1	0.750	1.99	1.09	10.28
		Ni(II) + HMBTC		
5.5	0.03	2.04	0.21	13.41
5.6	0.05	2.03	0.31	13.18
5.7	0.06	2.03	0.40	13.11
5.9	0.08	2.02	0.52	12.62
6.1	0.09	2.02	0.59	12.22
6.3	0.10	2.01	0.56	11.73
6.5	0.12	2.01	0.74	11.44
6.7	0.12	2.00	0.78	10.94
7.0	0.14	1.99	0.88	10.45
7.1	0.16	1.99	1.00	10.27
7.4	0.22	1.98	1.38	9.71
		Co(II) + HMBTC		
5.5	0.02	2.04	0.15	13.40
5.6	0.04	2.03	0.24	14.85
5.7	0.05	2.03	0.31	13.02
6.0	0.06	2.02	0.40	12.40
6.2	0.07	2.02	0.46	12.01
6.3	0.08	2.01	0.49	11.99
6.4	0.10	2.01	0.61	11.63
6.6	0.11	2.01	0.71	11.24
6.8	0.12	2.00	0.75	10.84
7.0	0.12	1.99	0.78	10.44
7.2	0.13	1.99	0.85	10.05
7.4	0.14	1.99	0.88	9.65
7.5	0.14	1.98	0.91	9.40
		Mn(II) + HMBTC		
5.7	0.02	2.03	0.12	12.52
6.0	0.03	2.02	0.22	12.39
6.3	0.05	2.01	0.31	11.80
6.3	0.05	2.01	0.31	11.80
6.5	0.06	2.01	0.37	11.40
6.9	0.08	1.99	0.50	10.61
7.2	0.09	1.99	0.56	10.02
7.4	0.10	1.98	0.63	9.63
7.5	0.10	1.98	0.66	9.43
7.7	0.11	1.97	0.73	9.05
7.9	0.12	1.96	0.76	8.64
8.1	0.13	1.96	0.82	8.25
8.4	0.14	1.96	0.89	7.65
8.5	0.14	1.96	0.92	7.47

pL values were calculated by using the

expressions $$pL = \left[\frac{\log[\sum_{n=0}^{n=j} PB_n^H}{(T_L^0 - nT_M^0)} \frac{1}{j(\text{Antilog}\,B)]} \times \frac{V_0 + V_3}{V_0} \right]$$

The values of stability constant was also obtained by straight line plot method[6]. A graph between log $\bar{n}/1-\bar{n}$ *vs.* pL was plotted and the pL value corresponding to zero of log $n/1-\bar{n}$ gave the value of log K (Table-4).

TABLE-4
METAL(II) + 2-HYDROXY-3-METHOXY BENZYLIDINE THIOSEMICARBAZONE (HMBTC) SYSTEM AT 35 ± 1 ºC

Cu(II) + HMBTC		Ni(II) + HMBTC		Co(II) + HMBTC		Mn(II) + HMBTC	
$\log \frac{\bar{n}}{n-\bar{n}}$	pL	$\log \frac{\bar{n}}{n-\bar{n}}$	pL	$\log \frac{\bar{n}}{n-\bar{n}}$	pL	$\log \frac{\bar{n}}{n-\bar{n}}$	pL
-0.50	14.01	-0.57	13.41	-0.75	13.39	-0.86	12.52
-0.37	14.09	0.35	13.18	-0.48	14.85	-0.55	12.39
-0.02	13.91	0.18	13.11	-0.35	13.02	-0.35	11.80
0.03	13.23	+0.03	12.62	-0.18	12.40	-0.23	11.40
+0.39	12.44	+0.16	12.22	-0.07	12.01	0.00	10.61
+0.69	11.49	+0.27	11.73	0.00	11.99	0.10	10.20
1.12	11.96	+0.45	11.44	0.21	11.63	0.23	9.63
–	–	+0.55	10.94	0.39	11.24	0.43	9.05
–	–	+0.86	10.45	0.48	10.84	0.50	8.64
–	–	–	–	0.55	10.44	0.66	8.25
–	–	–	–	0.75	10.05	0.91	7.65
–	–	–	–	0.87	9.65	–	–
–	–	–	–	1.00	9.45	–	–

Values 0.05 < $\bar{n}$ > 0.95 were used for the linear plot.

The average of the values of stability constants obtained by half integral method and straight line plot method was taken as the most representative value of stability constant (Table-5).

The standard thermodynamic expression[9] ($\Delta G^o = -2.303\ RT \log_{10} K$) was used to obtain the free energy change of the complexation reaction and recorded (Table-6).

The high negative values of free energy change indicates spontaneity of complexation reaction. For the given ligand the stability constants of metals shows the sequence Cu(II) > Ni(II) > Co(II) > Mn(II).

The values of stepwise stability constants by different computational method were recorded in the Table-6. The methods were: (a) half integral method (A), (b) straight line plot method (B).

TABLE-5
2-HYDROXY-3-METHOXY BENZYLIDINE THIOSEMICARBAZONE (HMBTC)
Ionic strength: 0.1 M KNO_3; Temperature: 35 ± 1 ºC; Medium: Aqueous dioxane (50:50) (v/v)

Cation	Method	log K	Average value
Cu(II)	A	13.30	13.33
	B	13.36	
Ni(II)	A	12.72	12.62
	B	12.52	
Co(II)	A	11.95	11.97
	B	12.00	
Mn(II)	A	10.60	10.55
	B	10.50	

Half integral method (A); Straight line plot method (B)

TABLE-6
VALUES OF FREE ENERGY CHANGE OF COMPLEXATION
Ligand: 2-hydroxy-3-methoxy benzylidine thiosemicarbazone (HMBTC)
Temperature: 35 ± 1 ºC; Ionic strength: 0.1 M KNO_3; Medium: Aqueous dioxane (50:50) (v/v)

Cation	ΔG (k. cals)
Cu(II)	18.91
Ni(II)	17.90
Co(II)	17.00
Mn(II)	14.98

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