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Formation Constants and Thermodynamic Parameters of Transition Metal Chelates Derived from Schiff Base of 4-Benzoyl-1-(*p*-nitrophenyl)-3-methyl-2-pyrazolin-5-ones with Some Diamines

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Stability constants and thermodynamic data of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} chelates of Schiff base of 4-benzoyl-1-(*p*-nitrophenyl)-3-methyl-2-pyrazolin-5-ones with ethylene diamine, *m*-phenylene diamine, benzidine have been determined at 25 and 35 °C in 70:30 (v/v) dioxane-water media and 0.1 M KNO_3, using Calvin-Bjerrum technique as applied by Irving and Rossotti. The stability constants at both the temperatures is found to be Mn < Co < Ni < Cu > Zn for all systems. ΔG, ΔH, and ΔS for the complexation have been derived.

Key Words: Potentiometric study, Formation constant, Thermodynamic parameters, Transition metal chelates, 4-Benzoyl-1-(*p*-nitro phenyl)-3-methyl-2-pyrazolin-5-ones, Schiff base.

INTRODUCTION

In continuation with our studies on potentiometric studies of 4-substituted-2-pyrazolin-5-one[1-4], herein the stability constants of some chelates formed by 4-benzoyl-1-(*p*-nitrophenyl)-3-methyl-2-pyrazolin-5-ones with ethylene diamine, *p*-phenylene diamine, benzidine with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} by Calvin-Bjerrum technique as applied by Irving and Rossotti[6] at 25 and 35 °C are reported. For all these systems, stability constants were calculated using different computational methods, *viz.*, half integral, point-wise, mid-point slope, linear plots and least-squares[5,6]. Using the mean log β_2, the thermodynamic parameters such as ΔG (free energy change), ΔH (enthalpy change) and ΔS (entropy change) have also been computed for the following equilibrium:

$$[M(H_2O)_X]^{2+} + H_2L = ML(H_2O)_{X-Y} + YH_2O + 2H^+ (aq)$$

where $[M(H_2O)_X]^{2+}$ = aquated divalent transition metal ion and H_2L = ligand.

EXPERIMENTAL

The ligands H_2BNPMP-END, H_2BNPMP-PPDA, H_2BNPNP-BZ were prepared by the literature method[7,8]. The solutions of the ligands were prepared in distilled dioxane. Metal nitrate solutions were prepared by dissolving the corresponding nitrates (AnalaR) in double distilled water. Potassium nitrate (AnalaR) was used to

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keep ionic strength constant. Standard carbonate-free sodium hydroxide solution was also prepared[9]. The pH-metric titrations were carried out against 0.1 M KOH solution with a Systronic 331 digital pH-meter using glass and calomel electrodes. The instrument was standardized against 0.005 M potassium hydrogen phthalate solution (pH = 4) in the beginning of each titration. The total volume 50 mL and (μ = 0.1 M KNO_3) of each system were kept constant in the beginning of each titration.

RESULTS AND DISCUSSION

The proton ligand stability constant for ligand was calculated from the pH-metric titration curve of nitric acid in the presence and the absence of the ligand. All the ligands show a maximum nA = 2.00 in dioxane-water media, indicating that ligands have two dissociable proton. The 2-pyrazolin-5-one ring does not show aromatic stability, although in many cases it assumes an aromatic structure[10]. The possible resonance structure of the 4-benzoyl-1-(*p*-nitrophenyl)-3-methyl-2-pyrazolin-5-ones are:

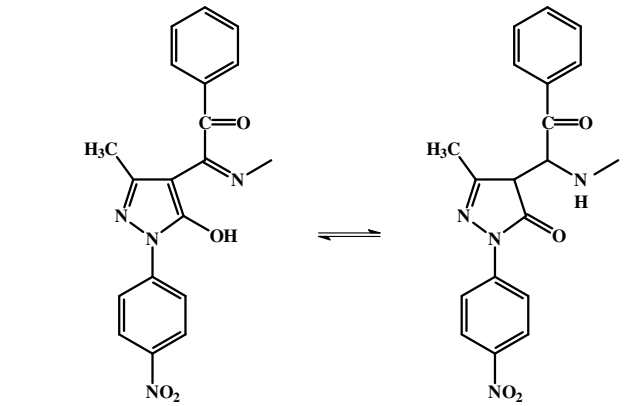

TABLE-1
DISSOCIATION OF H_2BNPMP-END, H_2BMPMP-PPDA, H_2BNPMP-BZ

Ligand	Half integral method		Point wise calculation		Average log PKH	
	25 ºC	35 ºC	25 ºC	35 ºC	25 ºC	35 ºC
H_2BNPMP-END	7.91	7.81	7.88	7.80	7.89	7.80
H_2BNPMP-PPDA	8.23	7.97	8.22	7.96	8.20	7.96
H_2BNPMP-BZ	8.28	8.13	8.29	8.12	8.30	8.12

There is no experimental evidence concerning these structures. From the above resonance structures these compounds may be considered to exist in hydroximine form at least in the solution studies by the characterization[11].

Metal ligand stability constants: It is observed that maximum values of 'n' for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} are more than one. This indicates the formation of 1:1 as well as 1:2 complexes. For all these systems log K_1 and log K_2 have been evaluated (Table-2) by (1) half integral method, (2) point-wise calculation method, (3) mid-point slope method, (4) linear plots method and (5) least squares method. The values of log β obtain by all these methods. The order of stability constants (log β) as regards to the metal ions with particular ligands is found to be $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ which is in agreement with Irving and Williams order[12].

The thermodynamic parameters (ΔG, ΔS) were calculated using the relationships

$$\Delta G = -2.303RT \log K; \quad T\Delta S = \Delta G - \Delta H$$

The calculated ΔG values are given in Table-3 is for a particular metal ion with different ligands[3]. It is interesting to note that the ΔG values for metal ions with particular ligand and its log β values are in the same order.

The ΔS values at 25 and 35 °C have also been calculated using $\Delta H_C = \Delta G + T\Delta S$ are given in Table-4. The observed positive values of ΔS indicate spontaneous formation of the complex. The ΔS values are higher at 35 than at 25 °C for all the systems indicating that the formation of a complex is more favourable at 35 °C. The negative free energy change ΔG in each case indicates that the chelation is spontaneous.

In the calculation of ΔH_L values (Table-6), the heat of complex formation ΔH_C (Table-4) and theoretical heat of hydration ΔH_H for metal ions have been used.

The transition series contraction energy E_r (Mn–Zn) has been calculated from the following equation:

$$E_r = -[\Delta H_H(Zn^{2+}) + \Delta H_C(Zn^{2+})] + [\Delta H_H(Mn^{2+}) + \Delta H_C(Mn^{2+})] \quad (2)$$

where $\Delta H_C(Mn^{2+})$ is the heat of complex formation (Table-4).

The average log β values are used to evaluate heat of complex. Formation ΔH_C using the following equation:

$$\log [\beta_{T_1}/\beta_{T_2}] = -\Delta H/2.303R[(T_2-T_1)/T_1T_2] \quad (3)$$

TABLE-2
FORMATION CONSTANT OF Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} AND Zn^{2+} WITH H_2BNPMP-END, H_2BNPMP-PPDA, H_2BNPMP-BZ

Ligand	Temp. (ºC)	Method of calculation					Mean	Stability constant
		Half integral	Point-wise slope	Mid-point slope	Linear plots	Least square		
				Cu^{2+}				
H_2BNPMP-END	25	6.68	6.67	6.69	6.69	6.70	6.68	log K_1
		4.21	4.21	4.19	4.19	4.21	4.21	log K_2
		10.89	10.88	10.88	10.88	10.91	10.89	log β
	35	6.45	6.47	6.44	6.46	6.44	6.46	log K_1
		4.27	4.26	4.26	4.26	4.28	4.26	log K_2
		10.72	10.73	10.70	10.72	10.72	10.72	log β
H_2BNPMP-PPDA	25	6.93	6.95	6.96	6.95	6.94	6.95	log K_1
		5.88	5.86	5.85	5.85	5.87	5.86	log K_2
		12.81	12.81	12.81	12.80	12.81	12.81	log β
	35	6.85	6.91	6.92	6.92	6.89	6.91	log K_1
		5.78	5.77	3.76	5.76	5.79	5.77	log K_2
		12.68	12.68	12.68	12.68	12.68	12.67	log β
H_2BNPMP-BZ	25	7.13	7.14	7.12	7.12	7.13	7.12	log K_1
		6.50	6.48	6.46	6.49	6.51	6.49	log K_2
		13.63	13.62	13.55	13.61	13.64	13.61	log β
	35	6.81	6.81	6.80	6.80	6.81	6.81	log K_1
		6.71	6.72	6.71	6.13	6.74	6.72	log K_2
		13.53	13.53	13.51	13.53	13.55	13.53	log β
				Ni^{2+}				
H_2BNPMP-END	25	4.62	4.61	4.59	4.60	4.62	4.60	log K_1
		4.22	4.24	4.24	4.24	4.22	4.23	log K_2
		8.84	8.85	8.83	8.84	8.84	8.84	log β
	35	5.13	5.15	5.15	5.16	5.14	5.14	log K_1
		3.56	3.56	3.56	3.54	3.54	3.56	log K_2
		8.69	8.71	8.71	8.70	8.68	8.70	log β
H_2BNPMP-PPDA	25	5.70	5.70	5.69	5.71	5.69	5.69	log K_1
		4.20	4.22	4.21	4.20	4.22	4.21	log K_2
		9.90	9.93	9.90	9.91	9.91	9.91	log β
	35	5.83	5.81	5.83	5.82	5.83	5.83	log K_1
		3.91	3.91	3.90	3.90	3.90	3.90	log K_2
		9.74	9.73	9.73	9.72	9.73	9.73	log β
H_2BNPMP-BZ	25	5.73	5.71	5.74	5.71	5.74	5.73	log K_1
		4.91	4.92	1.89	4.90	4.89	4.90	log K_2
		10.64	10.63	40.63	10.61	10.63	10.63	log β
	35	5.91	5.89	5.90	5.91	5.92	5.91	log K_1
		4.54	4.57	4.55	4.55	4.56	4.55	log K_2
		10.45	10.46	10.45	10.46	10.48	10.46	log β

				Co^{2+}				
H_2BNPMP-END	25	4.81	4.83	4.81	4.84	4.84	4.83	log K_1
		3.61	3.62	3.64	3.63	3.61	3.62	log K_2
		8.42	8.45	8.45	8.47	8.45	8.45	log β
	35	4.37	4.36	4.38	4.39	4.39	4.38	log K_1
		3.95	3.96	3.93	3.94	3.93	3.94	log K_2
		8.32	8.32	8.31	8.33	8.31	8.32	log β
H_2BNPMP-PPDA	25	4.64	4.65	4.66	4.64	4.64	4.65	log K_1
		3.17	3.18	3.15	3.17	3.15	3.16	log K_2
		7.81	7.83	7.81	7.81	7.79	7.81	log β
	35	4.45	4.48	4.47	4.48	4.46	4.65	log K_1
		3.21	3.21	3.14	3.21	3.19	3.20	log K_2
		7.66	7.69	7.66	7.69	7.67	7.67	log β
H_2BNPMP-BZ	25	4.88	4.90	4.84	4.88	4.87	4.89	log K_1
		4.09	4.10	4.42	4.11	4.10	4.10	log K_2
		8.98	9.00	9.01	8.99	8.97	8.99	log β
	35	4.90	4.89	4.88	4.89	4.87	4.88	log K_1
		3.95	3.95	3.93	3.94	3.96	3.95	log K_2
		8.84	8.84	8.91	8.83	8.83	8.83	log β
				Mn^{2+}				
H_2BNPMP-END	25	3.89	3.91	3.92	3.90	3.89	3.90	log K_1
		3.49	3.49	3.47	3.48	3.50	3.49	log K_2
		7.38	7.41	7.39	7.38	7.39	7.39	log β
	35	3.49	3.50	3.52	3.52	3.50	3.51	log K_1
		3.68	3.68	3.69	3.68	3.69	3.68	log K_2
		7.17	7.18	7.21	7.20	7.19	7.19	log β
H_2BNPMP-PPDA	25	3.46	3.45	3.48	3.47	3.47	3.47	log K_1
		3.68	3.68	3.68	3.66	3.67	3.67	log K_2
		7.14	7.13	7.16	7.13	7.14	7.14	log β
	35	3.19	3.19	3.19	3.18	3.18	3.19	log K_1
		3.79	3.81	3.81	3.81	3.73	3.80	log K_2
		6.98	7.00	7.01	6.99	6.97	6.99	log β
H_2BNPMP-BZ	25	3.59	3.59	3.59	3.61	3.60	3.59	log K_1
		3.41	3.42	3.39	3.40	3.40	3.40	log K_2
		7.00	7.01	6.98	7.01	7.00	6.99	log β
	35	3.81	3.81	3.79	3.79	3.82	3.81	log K_1
		3.02	3.03	3.05	3.05	3.02	3.03	log K_2
		6.83	6.84	6.84	6.84	6.84	8.64	log β
				Zn^{2+}				
H_2BNPMP-END	25	3.83	3.84	3.84	3.82	3.85	3.84	log K_1
		3.80	3.79	3.82	3.82	3.80	3.80	log K_2
		7.63	7.63	7.66	7.64	7.65	7.64	log β
	35	3.55	3.55	3.55	3.56	3.57	3.56	log K_1
		3.92	3.90	3.89	3.92	3.89	3.90	log K_2
		7.46	7.45	7.44	7.48	7.46	7.46	log β

		4.00	3.99	3.99	4.01	3.99	3.99	log K_1
	25	3.78	3.79	3.79	3.78	3.78	3.79	log K_2
H_2BNPMP-PPDA		7.78	7.78	7.78	7.79	7.77	7.78	log β
		3.76	3.76	3.77	3.78	3.76	3.76	log K_1
	35	3.81	3.81	3.83	3.81	3.82	8.32	log K_2
		7.57	7.57	7.60	7.59	7.58	7.58	log β
		4.19	4.18	4.18	4.18	4.19	4.19	log K_1
	25	3.52	3.49	3.49	3.51	3.52	3.50	log K_2
H_2BNPMP-BZ		7.71	7.67	7.67	7.69	7.71	7.69	log β
		3.92	3.91	3.93	3.94	3.94	3.92	log K_1
	35	3.65	3.64	3.63	3.64	3.65	3.65	log K_2
		7.57	7.55	7.56	7.58	7.59	7.57	log β

TABLE-3
FREE ENERGY OF FORMATION OF METAL CHELATES ΔG (kcal/mol)

Ligand	Temp. (ºC)	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
H_2BNPMP-END	25	10.39	14.85	12.03	11.51	10.08
	35	10.50	15.09	12.25	11.72	10.14
H_2BNPMP-PPDA	25	10.58	17.44	13.48	10.64	9.70
	35	10.67	17.85	13.72	10.80	9.85
H_2BNPMP-BZ	25	10.50	18.57	14.49	12.26	9.53
	35	10.08	19.06	14.73	12.45	9.63

TABLE-4
ENTHALPY OF FORMATION OF METAL CHELATES ΔHc (kcal/mol)

Ligand	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
H_2BNPMP-END	7.58	7.15	5.87	5.46	8.39
H_2BNPMP-PPDA	8.42	5.47	7.55	5.87	6.29
H_2BNPMP-BZ	5.16	3.79	7.13	6.71	6.71

TABLE-5
ENTROPY FORMATION OF METAL CHELATES ΔS (kcal/mol)

Ligand	Temp. (ºC)	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
H_2BNPMP-END	25	2.83	7.71	6.15	6.03	1.66
	35	2.93	7.97	6.35	6.24	1.72
H_2BNPMP-PPDA	25	2.21	11.98	5.93	4.77	3.44
	35	2.28	12.39	6.13	4.93	3.55
H_2BNPMP-BZ	25	5.44	14.80	7.74	5.53	2.83
	35	5.02	15.30	7.56	5.72	2.93

Assuming that all metals studied are known to form complexes having the same symmetry, ΔH for the complexes of first transition series can be calculated by:

$$\partial H(M^{2+}) = \Delta H_C(Mn^{2+})-(n-5)/5\ E_r-\Delta H_C(Mn^{2+}) + \Delta H_H(Mn^{2+})-\Delta H_H(M^{2+}) \quad (4)$$

The values for ΔH_H (M^{2+}) have been taken from the literature[13].

The ∂H value depends on the number of 3*d*-electrons and has been evaluated using the George-McClure method[14]. E_r and ∂H values (Table-6) suggest the coordination for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions with H_2BNPMP-END, H_2BNPMP-PPDA, H_2BNPNP-BZ

TABLE-6
STABILIZATION ENERGY (∂H) OF METAL CHELATES

Parameters		Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
	ΔH_H	655.00	698.00	717.00	717.90	702.10
H_2BNPMP-END	ΔH_C	8.39	5.45	5.87	7.15	7.58
	$\Delta H_H + \Delta H_C = \Delta H_L$	663.39	703.45	722.87	725.05	709.68
	$E_r \frac{n-5}{5}$	–	18.50	27.75	37.00	46.26
	∂H	–	28.94	38.10	31.03	–
H_2BNPMP-PPDA	ΔH_C	6.29	5.87	7.55	5.47	8.42
	$\Delta H_H + \Delta H_C = \Delta H_L$	660.29	702.87	723.55	722.37	709.52
	$E_r \frac{n-5}{5}$	–	19.68	29.52	39.36	49.20
	∂H	–	28.17	39.00	26.99	–
H_2BNPMP-BZ	ΔH_C	6.71	6.71	7.13	3.79	5.06
	$\Delta H_H + \Delta H_C = \Delta H_L$	660.71	703.71	723.13	720.69	706.16
	$E_r \frac{n-5}{5}$	–	18.16	27.26	36.33	45.42
	∂H	–	30.05	39.84	27.43	–

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