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Formation constants and thermodynamic parameters of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} chelates derived from tetradentate Schiff-base of 4-substituted-2-pyrazolin-5 ones with diamines

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ABSTRACT

Stability constants and thermodynamic data of the chelates of Tetradentate Schiff– base of 4 - formyl-l-phenyl-3-methyl-2-pyrazolin-5-ones with ethelene diamine, hexamethelene diamine, benzedine with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} have been determined of 25° C 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 word: Formation constant, Thermodynamic parameters, Constraction energy, Potent iometric study, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} chelates

INTRODUCTION

In continuation with our studies on potentiometric studies of 4-substituted-2-pyrazolin -5-one1-4, here we report the stability constants of some chelates formed by 4-Formyl-1-Phenyl-3-Methyl-2-Pyrazolin-5-ones with ethelene diamine, hexamethelene diamine, benzedine with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} by Calvin-Bjerrum technique as applied by Irving and Rossotti6 at 25°C and 35° C. For all these systems, stability constants were calculated using different computational methods, viz.; half integral, point-wise, mid-point slope, linear plots and least – squares5,6. Using the mean log β_2, the thermodynamic parameters such as ΔG (free energy change), ΔH (enthalpy change) and ΔS (entropy change) have been computed for the following equilibrium:

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

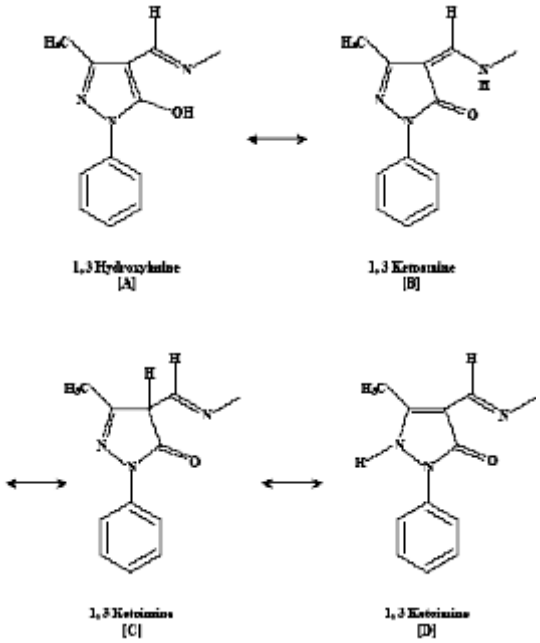
$[M(H_2O)X]^{2+}$ represents the aquated divalent transition metal ion and H2L is the ligand.

EXPERIMENTAL

The ligands H_2FPMP-END, H_2FPMP-HMDA, H2FPP – BZ were prepared by the literature method7,8. 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 keep ionic strength constant. Standard carbonate-free sodium hydroxide solution was prepared by the method of Allen and Law9. 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 µL and (m = 0.1 M KNO3) 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 structure10. The possible resonance structure of the 4-Formyl-1-Phenyl-3-Methyl-2- Pyrazolin-5-ones are :



Metal ligand stability constants

It is observed that maximum values of n for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} for all systems are more than one. This indicates the formation of 1:1 as well as 1:2 complexes. For all these systems log K1 and log K2 have been evaluated (Table-2) by (I) 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 b obtain by all these methods. The order of stability constants (log b) 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 order12.

The thermodynamic parameters (DG, DS) were calculated using the relationships $\Delta G = -2.303RT \log K$; $TDs = \Delta G - \Delta H$ The calculated ΔG value in Table 3 is for a particular metal ion with different ligands3. It is interesting to note that the ΔG values for metal ions with particular ligand and its log b values are in the same order.

The Δs values at 25 and 35° C have also been calculated using $\Delta H = \Delta G + TDS$ and 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 DG in each case indicates that the chelation is spontaneous.

In the calculation of ΔHL values (Table 6), the heat of complex formation ΔHC (Table 4) and theoretical heat of hydration ΔHH for metal ions have been used.

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

Table 1: Dissociation of H_2FPMP-END, H_2FPMP-HMDA, H_2FPMP-BZ

Ligand	Half integral method (Temp. °C)		Point wise calculations (Temp. °C)		Average Log PKH (Temp. °C)	
	25	35	25	35	25	35
H_2FPMP – END	7.90	7.78	7.86	7.78	7.88	7.77
H_2FPMP – HMDA	8.20	7.96	8.19	7.96	8.19	7.95
H_2FPMP – BZ	8.27	8.10	8.27	8.10	8.27	8.09

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].

Table 2: Formation constant of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with H_2FPMP-END, H_2FPMP-HMDA, H_2FPMP-BZ

Ligand	Temp (°C)	Method of calculation: Half integral	Pointwise slope	Midpoint slope	Linear plots	Least square	Mean	Stability constant
				Cu^{2+}				
		6.66	6.66	6.69	6.67	6.78	6.67	log K_1
	25	4.20	4.19	4.19	4.18	4.20	4.19	logK_2
		10.86	10.85	10.88	10.85	10.88	10.86	log β
	35	6.44	6.46	6.43	6.44	6.43	6.45	log K_1
		4.26	4.26	4.24	4.26	4.26	4.24	logK_2
H_2FPMP – END		10.70	10.72	10.67	10.69	10.69	10.69	log β
		6.91	6.93	6.94	6.95	6.92	6.92	log K_1
	25	5.87	5.85	5.84	5.85	5.87	5.86	log K_2
		12.78	12.78	12.48	12.80	12.79	12.78	log β
		6.82	6.90	6.90	6.90	6.80	6.90	log K_1
		5.78	5.75	3.75	5.75	7.77	5.75	log K_2
H_2FPMP – HMDA	35	12.65	12.65	12.65	12.65	12.65	12.65	log β
		7.10	7.11	7.11	7.10	7.11	7.12	log K_1
	25	6.50	6.48	6.46	6.48	6.50	6.47	log K_2
		13.60	13.59	13.54	13.58	13.60	13.59	log β
		6.81	6.80	6.78	6.78	6.80	6.80	log K_1
		6.71	6.70	6.70	6.12	6.71	6.70	log K_2
H_2FPMP – BZ	35	13.50	13.50	13.48	13.50	13.52	13.50	log β
				Ni^{2+}				
		4.60	4.60	4.58	4.59	4.61	4.60	log K_1
	25	4.21	4.22	4.22	4.20	4.24	4.23	log K_2
		8.81	8.82	8.80	8.81	8.81	8.83	log β
		5.12	5.12	5.14	5.13	5.13	5.13	log K_1
		3.55	3.56	3.54	3.54	3.54	3.54	log K_2
H_2FPMP – END	35	8.67	8.68	8.68	8.67	8.67	8.67	log β
		5.67	5.70	5.67	5.70	5.67	5.67	log K_1
	25	4.20	4.22	4.20	4.18	4.21	4.21	log K_2
		9.87	9.92	9.87	9.88	9.88	9.88	log β
		5.82	5.80	5.83	5.80	5.81	5.80	log K_1
		3.91	3.90	3.87	3.90	3.89	3.90	log K_2
H_2FPMP – HMDA	35	9.73	9.70	9.70	9.70	9.70	9.70	log β
		5.70	5.70	5.71	5.70	5.71	5.70	log K_1
	25	4.91	4.90	1.89	4.90	4.89	4.90	log K_2
		10.61	10.60	10.60	10.60	10.60	10.60	log β
		5.90	5.87	5.88	5.90	5.90	5.90	log K_1
		4.52	4.56	4.54	4.53	4.55	4.55	log K_2
H_2FPMP – BZ	35	10.42	10.43	10.42	10.42	10.45	10.45	log β
				Co^{2+}				
		4.80	4.80	4.81	4.83	4.81	4.82	log K_1
	25	3.60	3.62	3.61	3.63	3.61	3.60	log K_2
		8.40	8.42	8.42	8.46	8.42	8.42	log β
		4.35	4.35	4.35	4.38	4.37	4.38	log K_1
		3.95	3.95	3.93	3.94	3.94	3.93	log K_2

H_2FPMP – END	35	8.30	8.30	8.28	8.32	8.30	8.30	log β
		4.61	4.65	4.64	4.62	4.62	4.64	log K_1
	25	3.17	3.17	3.14	3.16	3.15	3.14	log K_2
		7.78	7.82	7.78	7.78	7.77	7.78	log β
		4.44	4.45	4.44	4.47	4.44	4.62	log K_1
		3.20	3.21	3.14	3.21	3.18	3.20	log K_2
H_2FPMP – HMDA	35	7.64	7.66	7.63	7.68	7.62	7.64	log β
		4.86	4.89	4.83	4.88	4.85	4.86	log K_1
	25	4.09	4.10	4.10	4.11	4.09	4.10	log K_2
		8.95	8.99	8.95	8.97	8.94	8.96	log β
		4.89	4.86	4.85	4.88	4.85	4.86	log K_1
		3.95	3.95	3.93	3.92	3.95	3.94	log K_2
H_2FPMP – BZ	35	8.83	8.81	8.88	8.80	8.80	8.80	log β
				Mn2+				
		3.87	3.90	3.90	3.90	3.89	3.90	log K_1
	25	3.48	3.49	3.47	3.45	3.47	3.46	log K_2
		7.35	7.40	7.37	7.35	7.36	7.39	log β
		3.47	3.50	3.51	3.50	3.48	3.50	log K_1
		3.67	3.65	3.69	3.67	3.68	3.66	log K_2
H_2FPMP – END	35	7.14	7.15	7.20	7.17	7.16	7.16	log β
		3.45	3.45	3.46	3.45	3.47	3.45	log K_1
	25	3.66	3.65	3.67	3.65	3.66	3.66	log K_2
		7.11	7.10	7.13	7.10	7.13	7.11	log β
		3.18	3.17	3.19	3.16	3.16	3.16	log K_1
		3.77	3.80	3.81	3.80	3.78	3.80	log K_2
H_2FPMP – HMDA	35	6.95	6.97	7.00	6.96	6.94	6.96	log β
		3.56	3.57	3.58	3.60	3.60	3.57	log K_1
	25	3.41	3.40	3.37	3.40	3.37	3.40	log K_2
		6.97	6.68	6.95	7.00	6.97	6.97	log β
		3.80	3.80	3.79	3.79	3.81	3.80	log K_1
		3.02	3.01	3.04	3.04	3.02	3.01	log K_2
H_2FPMP – BZ	35	6.82	6.81	6.83	6.83	6.83	6.81	log β
				Zn^{2+}				
		3.80	3.83	3.84	3.81	3.84	3.81	log K_1
	25	3.80	3.77	3.81	3.80	3.80	3.80	log K_2
		7.60	7.60	7.65	7.61	7.64	7.62	log β
		3.54	3.54	3.54	3.53	3.56	3.55	log K_1
		3.91	3.90	3.88	3.91	3.89	3.90	log K_2
H_2FPMP – END	35	7.45	7.44	7.42	7.44	7.45	7.45	log β
		4.00	3.97	3.98	4.00	3.99	3.99	log K_1
	25	3.75	3.78	3.79	3.72	3.77	3.76	log K_2
		7.75	7.75	7.77	7.76	7.76	7.75	log β
		3.75	3.74	3.75	3.76	3.74	3.76	log K_1
		3.81	3.80	3.82	3.81	3.82	3.81	log K_2
H_2FPMP – HMDA	35	7.56	7.54	7.57	7.57	7.56	7.57	log β
		4.19	4.16	4.16	4.18	4.19	4.17	log K_1
	25	3.51	3.48	3.49	3.50	3.51	3.50	log K_2
		7.70	7.64	7.65	7.68	7.70	7.67	log β
		3.90	3.91	3.90	3.93	3.91	3.92	log K_1
		3.64	3.62	3.63	3.63	3.65	3.64	log K_2
H_2FPMP – BZ	35	7.54	7.52	7.53	7.56	7.56	7.56	log β

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

where ΔHC(Mn2+) 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:

$$\log [\beta_{T1} / \beta_{T2}] = -\Delta H / 2.303R[(T_2 - T_1) / T_1T_2]$$

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

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

The values for ΔH_H (M^{2+}) have been taken from the literature13. The ∂H value depends on the number of 3d – electrons and has been evaluated using the George – McClure method14. 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_2FPMP – END, H_2FPMP – HMDA, H_2FPMP – BZ

Table 3: Free energy of formation of metal chelates ΔG (kcal / mol)

Ligand	Temp (°C)	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
	25	10.41	14.86	12.03	11.51	10.07
H_2FPMP – END	35	10.51	15.12	12.23	11.72	10.13
	25	10.58	17.43	13.51	10.61	9.70
H_2FPMP – HMDA	35	10.65	17.84	13.71	10.77	9.82
	25	10.45	18.57	14.49	12.22	9.51
H_2FPMP – BZ	35	10.03	19.06	14.73	12.41	9.61

Table 4: Enthalpy of formation of metal chelates ΔH_C (kcal / mol)

Ligand	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
H_2FPMP – END	7.51	7.13	5.87	5.45	8.39
H_2FPMP – HMDA	8.40	5.45	7.56	5.87	6.29
H_2FPMP – BZ	5.03	3.77	7.13	6.71	6.71

Table 5: Entropy formation of metal chelates ΔS (kcal / mol)

Ligand	Temp(°C)	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
	25	2.83	7.70	6.15	6.03	1.66
H_2FPMP-END	35	2.93	7.96	6.35	6.25	1.71
	25	2.18	11.92	5.94	4.74	3.42
H_2FPMP – HMDA	35	2.25	12.40	6.13	4.90	3.54
	25	5.42	14.78	7.75	5.51	2.81
H_2FPMP – BZ	35	5.00	15.26	7.58	5.70	2.90

Table 6: Stabilization energy (∂h) of metal chelates

Parameters	ΔHH	Zn^{2+} 654.00	Cu^{2+} 697.00	Ni^{2+} 716.00	Co^{2+} 716.90	Mn^{2+} 701.10
	ΔHC	8.41	5.45	5.87	7.13	7.55
	$\Delta H_H+\Delta H_C=\Delta H_L$	662.41	702.45	721.87	724.03	708.65
H2FPMP – END	$E_r\frac{n-5}{5}$	-	18.51	27.76	37.01	46.25
	∂H	-	27.92	38.09	31.10	-
	DHC	6.31	5.87	7.55	5.45	8.41
	$\Delta H_H+\Delta H_C=\Delta H_L$	660.31	702.87	723.55	722.35	709.51
H_2FPMP-HMDA		-	19.67	29.51	39.35	49.20
	∂H	-	27.18	38.02	26.98	-
	ΔHC	6.71	6.71	7.13	3.77	5.03
	$\Delta H_H+\Delta H_C=\Delta H_L$	660.72	703.71	723.13	720.67	706.13
H_2FPMP-BZ		-	18.15	27.24	36.32	45.42
	∂H	-	29.52	39.85	28.31	-

Er = Contraction energy, n = Number of electrons, DHL = Enthalpy changes, ∂H = Heat of hydration of the transition metal ion, ΔHC = Experimental values for heat of complex formation. ΔH_H = Theoretical values for heat of hydration of transition metal ion

$$E_r\frac{n-5}{5}$$

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