Asian Journal of Chemistry Vol. 15, Nos. 3 & 4 (2003), 1275–1283

Formation Constants and Thermodynamic Parameters of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} Chelates of Some 4-Formyloxime-2-Pyrazolin-5-ones

R.R. SHAH†, K.S. SOLANKI‡, D.K. BHOI**, Mohammad J. KHARODAWALA, H.R. DABHI* and D.S. RAJ††

Department of Chemistry, Navjivan Science College, Dahod-389 151, India

Stability constants and thermodynamic data of the chelates of 4-formyloxime-1,3-diphenyl-2-pyrazolin-5-one, 4-formyloxime-1-(2′,4′-dinitrophenyl)-3-phenyl-2-pyrazolin-5-one and 4-formyloxime-1-(2′,4′-dinitrophenyl)-3-methyl-2-pyrazolin-5-one with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} have been deterrnined of 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 data have been calculated using the different computational methods. The order of stability constants at both the temperatures is found to be Mn < Co < Ni < Cu > Zn for all systems. ΔG, ΔH and ΔS for the cornplexation have been dcrived.

Key Words: Formation constants, Thermodynamic parameters, Contraction energy, Potentiometric study, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} chelates.

INTRODUCTION

In continuation with our studies on potentiometric studies of 4-substituted-2-pyrazolin-5-one[1–4], here we report the stability constants of some chelates formed by 4-formyloxime-1,3-diphenyl-2-pyrazolin-5-one (HFDPPZ), 4-formyloxime-1-(2′,4′-dinitrophenyl)-3-methyl-2-pyrazolin-5one (HFMNPPZ) and 3-methyl-4-formyloxime-1′(2′,4′-dinitrophenyl)-3-phenyl-2-pyrazolin-5-one (HFPNPPZ) 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. 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 been computed for the following equilibrium:

$$[M(H_2O)_x]^{2+} + 2HL \;=\; ML_2(H_2O)_{x-y} + yH_2O + 2H^+(aq)$$

†Maninagar Science College, Ahmedabad, India.
‡B.M.S. Chemicals, Padra, India.
**J. & J. College of Science, Nadiad, India.
††M.B. Patel Science College, Anand, India.

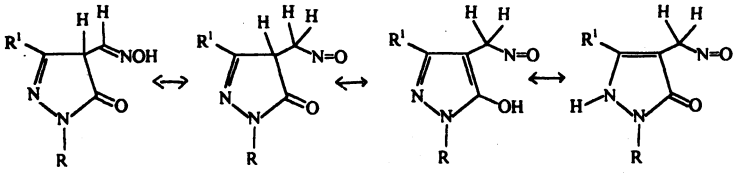
$[M(H_2O)_x]^{2+}$ represents the aquated divalent transition metal ion and HL is the ligand.

EXPERIMENTAL

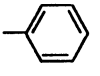
The ligands HFDPPZ, HFMNPPZ and HFPNPPZ were prepared by the literature method[7,8]. The solutions of the ligands were prepared in distilled dioxane. Metal nitrate solutions were prepared by dissolving the corresponding nitrates (AnalaR) in double distilled water. Potassium nitrate (AnalaR) was used to keep ionic strength constant. Standard carbonate-free sodium hydroxide solution was prepared by the method of Allen and Law[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.

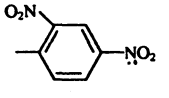
RESULTS AND DISCUSSION

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 $n_A = 1.0$ in dioxane-water media, indicating that ligands have one dissociable proton. The results obtained in Table-1 suggest that there is very little effect of substitution of 3-position and 1-position. It is interesting to indicate the log pK_H values in relation to the structural features of the ligands. 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 1,3-disubstituted-4-formyloxime-2-pyrazolin-5-one are:



[A] [B] [C] [D]

R and R' =  [HFDPPZ],

R =  and R' =  [HFPNPPZ],

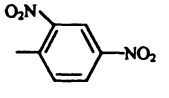
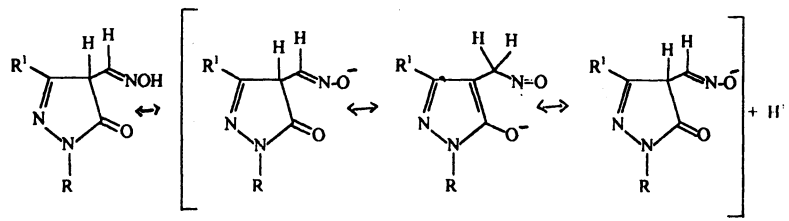
R =  and R' = $-CH_3$ [HFMNPPZ].

TABLE-1
DISSOCIATION OF HFDPPZ, HFMNPPZ AND HFPNPPZ

Ligand	Half integral method (Temp., °C)		Pointwise calculation (Temp., °C)		Average log pK_H (Temp., °C)	
	25	35	25	35	25	35
HFDPPZ	7.92	7.80	7.89	7.79	7.90	7.79
HFMNPPZ	8.22	7.98	8.21	7.97	8.21	7.97
HFPNPPZ	8.29	8.12	8.30	8.11	8.29	8.11

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

The negative charge on the nitrozonium (= N—O⁻) may also be stabilized on ketonic oxygen as follows:-



Acid strength of the compounds depends on electron density which is delocalized by the presence of substituted group and acid strengths are higher at higher temperature.

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 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

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

The calculated ΔG value 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

$\Delta H_C = \Delta G + T\Delta S$ 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 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:

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

TABLE-2
FORMATION CONSTANT OF Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} AND Zn^{2+} WITH HFDPPZ, HFMNPPZ AND HFPNPPZ

Ligand	Temp. (°C))	Method of calculation					Mean	Stability constant
		Half integral	Pointwise slope	Midpoint slope	Linear plots	Least square		
				Cu^{2+}				
HFDPPZ	25	6.67	6.67	6.69	6.68	6.69	6.68	$\log K_1$
		4.21	4.20	4.19	4.19	4.21	4.20	$\log K_2$
		10.88	10.87	10.88	10.87	10.90	10.88	$\log \beta$
	35	6.45	6.46	6.44	6.46	6.44	6.45	$\log K_1$
		4.27	4.26	4.25	4.25	4.27	4.26	$\log K_2$
		10.72	10.72	10.69	10.71	10.71	10.71	$\log \beta$
HFMNPPZ	25	6.93	6.94	6.95	6.95	6.93	6.94	$\log K_1$
		5.87	5.86	5.85	5.85	5.87	5.86	$\log K_2$
		12.80	12.80	12.80	12.80	12.80	12.80	$\log \beta$
	35	6.84	6.90	6.91	6.91	6.89	6.90	$\log K_1$
		5.78	5.77	3.76	5.76	5.78	5.77	$\log K_2$
		12.67	12.67	12.67	12.67	12.67	12.67	$\log \beta$
HFPNPPZ	25	7.12	7.13	7.11	7.11	7.13	7.12	$\log K_1$
		6.50	6.48	6.46	6.49	6.50	6.49	$\log K_2$
		13.62	13.61	13.54	13.60	13.63	13.61	$\log \beta$
	35	6.81	6.80	6.79	6.79	6.81	6.80	$\log K_1$
		6.71	6.72	6.71	6.13	6.73	6.72	$\log K_2$
		13.52	13.52	13.50	13.52	13.54	13.52	$\log \beta$

Contd.

TABLE-2 (*Contd.*)

				Ni^{2+}				
HFDPPZ	25	4.61	4.60	4.59	4.59	4.61	4.60	$\log K_1$
		4.22	4.24	4.23	4.24	4.22	4.23	$\log K_2$
		8.83	8.84	8.82	8.83	8.83	8.83	$\log \beta$
	35	5.13	5.14	5.15	5.15	5.13	5.14	$\log K_1$
		3.56	3.56	3.55	3.54	3.54	3.55	$\log K_2$
		8.69	8.70	8.70	8.69	8.67	8.69	$\log \beta$
HFMNPPZ	25	5.69	5.70	5.68	5.70	5.68	5.69	$\log K_1$
		4.20	4.22	4.21	4.20	4.22	4.21	$\log K_2$
		9.89	9.92	9.89	9.90	9.90	9.90	$\log \beta$
	35	5.82	5.81	5.83	5.81	5.83	5.82	$\log K_1$
		3.91	3.91	3.89	3.90	3.89	3.90	$\log K_2$
		9.73	9.72	9.72	9.71	9.72	9.72	$\log \beta$
HFPNPPZ	25	5.72	5.71	5.73	5.71	5.73	5.72	$\log K_1$
		4.91	4.91	1.89	4.90	4.89	4.90	$\log K_2$
		10.63	10.62	10.62	10.61	10.62	10.62	$\log \beta$
	35	5.90	5.89	5.89	5.91	5.91	5.90	$\log K_1$
		4.54	4.56	4.55	4.54	4.56	4.55	$\log K_2$
		10.44	10.45	10.44	10.45	10.47	10.45	$\log \beta$
				Co^{2+}				
HFDPPZ	25	4.81	4.82	4.81	4.83	4.83	4.82	$\log K_1$
		3.61	3.62	3.63	3.63	3.61	3.62	$\log K_2$
		8.42	8.44	8.44	8.46	8.44	8.44	$\log \beta$
	35	4.36	4.36	4.37	4.38	4.38	4.37	$\log K_1$
		3.95	3.95	3.93	3.94	3.93	3.94	$\log K_2$
		8.31	8.31	8.30	8.32	8.31	8.31	$\log \beta$
HFMNPPZ	25	4.63	4.65	4.65	4.64	4.63	4.64	$\log K_1$
		3.17	3.17	3.15	3.16	3.15	3.16	$\log K_2$
		7.80	7.82	7.80	7.80	7.78	7.80	$\log \beta$
	35	4.45	4.47	4.46	4.47	4.45	4.64	$\log K_1$
		3.20	3.21	3.14	3.21	3.19	3.20	$\log K_2$
		7.65	7.68	7.65	7.68	7.64	7.66	$\log \beta$
HFPNPPZ	25	4.88	4.89	4.84	4.87	4.87	4.88	$\log K_1$
		4.09	4.10	4.11	4.11	4.09	4.10	$\log K_2$
		8.97	8.99	9.00	8.98	8.96	8.98	$\log \beta$
	35	4.89	4.88	4.87	4.89	4.87	4.88	$\log K_1$
		3.95	3.95	3.93	3.93	3.95	3.94	$\log K_2$
		8.83	8.83	8.90	8.82	8.82	8.82	$\log \beta$

Contd.

TABLE-2 (*Contd.*)

				Mn^{2+}				
HFDPPZ	25	3.89	3.91	3.91	3.90	3.89	3.90	log K_1
		3.48	3.49	3.47	3.47	3.49	3.48	log K_2
		7.37	7.40	7.38	7.37	7.38	7.38	log β
	35	3.49	3.50	3.51	3.51	3.49	3.50	log K_1
		3.67	3.67	3.69	3.68	3.69	3.68	log K_2
		7.16	7.17	7.20	7.19	7.18	7.18	log β
HFMNPPZ	25	3.45	3.45	3.47	3.46	3.47	3.46	log K_1
		3.68	3.67	3.68	3.66	3.66	3.67	log K_2
		7.13	7.12	7.15	7.12	7.13	7.13	log β
	35	3.18	3.19	3.19	3.17	3.17	3.18	log K_1
		3.79	3.80	3.81	3.81	3.79	3.80	log K_2
		6.97	6.99	7.00	6.98	6.96	6.98	log β
HFPNPPZ	25	3.58	3.59	3.58	3.60	3.60	3.59	log K_1
		3.41	3.41	3.39	3.40	3.39	3.40	log K_2
		6.99	7.00	6.97	7.00	6.99	6.99	log β
	35	3.81	3.80	3.79	3.79	3.81	3.80	log K_1
		3.02	3.03	3.04	3.04	3.02	3.03	log K_2
		6.83	6.83	6.83	6.83	6.83	6.83	log β
				Zn^{2+}				
HFDPPZ	25	3.82	3.83	3.84	3.82	3.84	3.83	log K_1
		3.80	3.79	3.81	3.81	3.80	3.80	log K_2
		7.62	7.62	7.65	7.63	7.64	7.63	log β
	35	3.55	3.54	3.54	3.56	3.56	3.55	log K_1
		3.91	3.90	3.89	3.91	3.89	3.90	log K_2
		7.46	7.44	7.43	7.47	7.45	7.45	log β
HFMNPPZ	25	4.00	3.98	3.98	4.00	3.99	3.99	log K_1
		3.77	3.79	3.79	3.78	3.77	3.78	log K_2
		7.77	7.77	7.77	7.78	7.76	7.77	log β
	35	3.75	3.76	3.77	3.77	3.75	3.76	log K_1
		3.81	3.80	3.82	3.81	3.82	3.81	log K_2
		7.56	7.56	7.59	7.58	7.57	7.57	log β
HFPNPPZ	25	4.19	4.17	4.17	4.18	4.19	4.18	log K_1
		3.51	3.49	3.49	3.50	3.51	3.50	log K_2
		7.70	7.66	7.66	7.68	7.70	7.68	log β
	35	3.91	3.91	3.92	3.93	3.93	3.92	log K_1
		3.65	3.63	3.63	3.64	3.65	3.64	log K_2
		7.56	7.54	7.55	7.57	7.58	7.56	log β

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+}
HFDPPZ	25	10.40	14.84	12.04	11.50	10.06
	35	10.50	15.10	12.24	11.71	10.12
HFMNPPZ	25	10.59	17.45	13.50	10.63	9.72
	35	10.66	17.86	13.70	10.79	9.84
HFPNPPZ	25	10.47	18.56	14.48	12.24	9.53
	35	10.05	19.05	14.72	12.43	9.63

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

Ligand	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
HFDPPZ	7.56	7.14	5.88	5.46	8.40
HFMNPPZ	8.40	5.46	7.56	5.88	6.30
HFPNPPZ	5.04	3.78	7.14	6.72	6.72

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

Ligand	Temp. (°C)	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
HFDPPZ	25	2.84	7.70	6.16	6.04	1.66
	35	2.94	7.96	6.36	6.25	1.72
HFMNPPZ	25	2.19	11.99	5.94	4.75	3.42
	35	2.26	12.40	6.14	4.91	3.54
HFPNPPZ	25	5.43	14.78	7.76	5.52	2.81
	35	5.01	15.27	7.58	5.71	2.91

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

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

The values for $\Delta H_H(M^{2+})$ 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 ideal coordination for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions with HFDPPZ, HFPNPPZ and HFMNPPZ ligand.

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

Parameters		Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
	ΔH_H	654.00	697.00	716.00	716.90	701.10
HFDPPZ	ΔH_C	8.40	5.46	5.88	7.14	7.56
	$\Delta H_H + \Delta H_C = \Delta H_L$	662.40	702.46	721.88	724.04	708.66
	$E_r \frac{n-5}{5}$	—	18.50	27.75	37.00	46.26
	∂_H	—	27.94	38.11	31.00	—
HFDPPZ	ΔH_C	6.30	5.88	7.56	5.46	8.40
	$\Delta H_H + \Delta H_C = \Delta H_L$	660.30	702.88	723.56	722.36	709.50
	$E_r \frac{n-5}{5}$	—	19.68	29.52	39.36	49.20
	∂_H	—	27.18	38.02	26.98	—
HFDPPZ	ΔH_C	6.72	6.72	7.14	3.78	5.04
	$\Delta H_H + \Delta H_C = \Delta H_L$	660.72	703.72	723.14	720.68	706.14
	$E_r \frac{n-5}{5}$	—	18.16	27.25	36.33	45.42
	∂_H	—	29.52	20.87	8.43	—

E_r = Contraction energy,
n = Number of electrons,
ΔH_L = Enthalpy changes,
∂_H = Heat of hydration of the transition metal ion,
ΔH_C = Experimental values of for heat of complex formation,
ΔH_H = Theoretical values for heat of hydration of transition metal ion

ACKNOWLEDGEMENTS

The authors are thankful to the Principal, J. & J. College of Science, Nadiad; to Dr. A.K. Rana, Principal, Navjivan Science College, Dahod; to the Nadiad Education Society, Nadiad and the Dahod Anaj Mahajan Sarvajanik Education Society; and to Late Shri Girdharlal Sheth and Shri N.K. Shah, Dahod for laboratory facilities.

REFERENCES

1. M.J. Kharodawala, D.S. Raj, D.K. Bhoi, R.R. Shah, H.R. Dabhi and M.B. Chauhan, *Orient. J. Chem.*, **17**, 327 (2001).
2. ———, *Orient. J. Chem.*, **17**, 241 (2001).
3. M.J. Kharodawala, D.K. Bhoi, D.N. Dave, D.M. Suthar, J.M. Patel and H.R. Dabhi, *Acta Cienc. Indica*, **26C**, 137 (2000).
4. K.T. Joshi, H.R. Dabhi, R.K. Rai, A.M. Pancholi and A.K. Rana, *Acta Cienc. Indica*, **25C**, 1013 (1999).
5. J. Bjerrum, Metal Amine Formation in Aquous Solution, in: P. House and H. Rossotti, Determination of Stability Constants, McGraw-Hill, New York (1961).
6. J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950); H. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
7. M.J. Kharodawala and A.K. Rana, *Asian J. Chem.*, **14**, 703 (2002).
8. ———, *Asian J. Chem.*, **14**, 979 (2002).
9. N. Allen and G.W. Low, *Ind. Eng. Chem.* (1993).
10. H. Wiley Richard and Paul Wiley, Pyrazolones, Pyrazolines and Derivatives, Interscience, New York (1964).
11. N.R. Shah, Ph.D. Thesis, S.P. University, Vidyanagar (1980).
12. H. Irving and R.J.P. Williams, *Nature*, **162**, 746 (1948).
13. P. Georgy and D.S. McClure, Progress in Inorganic Chemistry, Interscience, New York (1959).
14. ———, Inner Orbital Splitting in Progress in Inorganic Chemistry, Interscience, New York, p. 428 (1959).

(*Received*: 24 August 2002; *Accepted*: 26 March 2003) AJC-3019