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Note

STEPWISE STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF 1-PHENYL-3-METHYL-4-(2-HYDROXYPHENYL)-HYDRAZONO-2-PYRAZOLINE-5-ONE COMPLEXES WITH TRANSITION METALS

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Potentiometric studies of the complexes of substituted azo-derivatives of phenyl-3-carbethoxy-4-pyrazolenes with a few metal ions have been reported [1], but no work has been done with 1-phenyl-3-methyl-4-(2-hydroxyphenyl)-hydrazono-2-pyrazoline-5-one (PMHP) which has been used as an antidiabetic agent [2]. In the present communication, stability constants and thermodynamic functions for the complexes of Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+} and Fe^{3+} with PMHP in 75 : 25 (v/v) methanol—water mixtures are reported. Stability constants were determined by the Bjeerum—Calvin titration technique as modified by Irving and Rossotti [3,4].

EXPERIMENTAL

The ligand was prepared by the method reported in the literature [5]. All chemicals used were of A.R. quality. The metal salt (nitrates) solutions were prepared in double distilled water. The stock solution (0.002 M) of the ligand was prepared in methanol as it was found to be insoluble in water. The pH of the solutions was measured using an ECIL expanded scale pH meter (accuracy ±0.02 pH units) fitted with glass and calomel electrodes. The pH meter was standardized with aqueous buffers. Sodium perchlorate was used to maintain the ionic strength.

The pH titrations of the following solutions thermostated at 25, 30 and 35 ± 0.1°C were carried out against standard 0.1 M sodium hydroxide.

(i) 4 ml $HClO_4$(0.04 M) + 4 ml $NaClO_4$(1.0 M) + 30 ml methanol + 2 ml water;

(ii) 4 ml $HClO_4$(0.04 M) + 4 ml $NaClO_4$(1.0 M) + 20 ml ligand (0.002 M) + 10 ml methanol + 2 ml water;

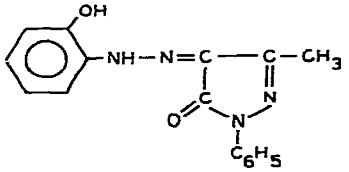
(iii) 4 ml $HClO_4$(0.04 M) + 4 ml $NaClO_4$(1.0 M) + 20 ml ligand (0.002 M) + 10 ml methanol + 1 ml metal solution (0.01 M) + 1 ml water.

The concentration of the ligand in the above solutions was kept four times that of the metal ion.

RESULTS AND DISCUSSION

Proton-ligand stability constant

From the titration curves of solutions (i) and (ii), $\bar{n}_H$, the average number of protons associated with the ligand, at different pH values was calculated using the method of Bjeerum and Calvin as modified by Irving and Rossotti [3,4]. It is seen from the structure [A] of the ligand that only one proton per ligand molecule can be released on chelation. Protonation constants were evaluated by plotting a graph of $\bar{n}_H$ vs. pH and the log K^H values calculated at $\bar{n}_H = 0.5$ are given in Table 1. Log K^H decreases with increase in temperature.



A

Metal—ligand stability constant

The metal titration curves are well separated from the ligand titration curve, indicating that the liberation of a proton is due to chelate formation. The average number of ligand molecules attached per metal ion ($\bar{n}$) and the free ligand exponent (pL) were calculated from the titration curves of solutions (ii) and (iii). The stability constants were evaluated from the formation curves using half $\bar{n}$ method. The values of log K_1(±0.03), log K_2(±0.05) and log β_2(±0.08) are given in Table 1.

For all the metal complexes investigated, values of $\bar{n}$ greater than 2 were not obtained. It is therefore concluded that not more than two complexes, i.e., 1 : 1 and 1 : 2 (M : L) are formed in each system. At 25°C the order of stability observed for these complexes is $Fe^{3+} > Co^{2+} > Ni^{2+} > Fe^{2+} > Mn^{2+}$.

TABLE 1

Stability constants of metal complexes with PMHP at different temperatures (μ = 0.10 M $NaClO_4$)

Cation	25°C			30°C			35°C		
	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2
H^+	8.70			8.40			8.00		
Fe^{3+}	7.88	5.68	13.56	7.63	5.65	13.28	7.58	5.23	12.81
Ni^{2+}	6.70	4.95	11.65	6.48	4.88	11.36	6.20	4.80	11.00
Co^{2+}	6.90	4.85	11.75	6.58	4.60	11.18	6.33	4.35	10.68
Fe^{2+}	6.20	4.83	11.03	5.88	4.50	10.38	5.43	4.23	9.66
Mn^{2+}	5.48	4.43	9.91	5.28	4.35	9.63	5.00	4.28	9.28

TABLE 2

Values of thermodynamic functions of metal complexes with PMHP at 30°C

Cation	$-\Delta G$(kcal mole^{-1})			$-\Delta H$(kcal mole^{-1})			$-\Delta S$(cal mole^{-1})		
	ΔG_1	ΔG_2	ΔG^0	ΔH_1	ΔH_2	ΔH^0	ΔS_1	ΔS_2	ΔS^0
Fe^{3+}	10.58	7.83	18.41	15.23	20.77	35.16	15.35	42.71	55.28
Ni^{2+}	8.98	6.76	15.74	24.73	7.62	31.56	51.98	2.84	52.21
Co^{2+}	9.12	6.38	15.50	27.73	24.05	50.78	61.42	58.32	116.44
Fe^{2+}	8.15	6.24	14.39	36.62	28.56	61.10	93.93	73.66	154.16
Mn^{2+}	7.31	6.03	13.34	23.46	7.15	32.64	53.50	3.70	63.70

The higher stability of Co(II) complex as compared with that of Ni(II) complexes may be attributed to Jahn—Teller distortion present in the former case. At 30 and 35°C the order of stability is in accordance with the Irving—Williams rule [6].

The higher stability of the Fe(III) complex as compared to the stability of bivalent metal complexes is justified on the basis of charge and ionization potential of ions. The stability constant for the Cu(II) complex could not be determined due to precipitation.

The overall free energy, enthalpy and entropy changes were evaluated using standard equations. The values of log β_2 obtained at different temperatures were plotted as a function of $1/T$. The gradient was taken as equivalent to $-\Delta H/4.57$, wherever a linear plot was not obtained a tangent was drawn to obtain the slope. The values of thermodynamic functions are summarized in Table 2. It is seen that values of ΔG^0 are negative, showing that complex formation is spontaneous. Further, the negative values of ΔH^0 and ΔS^0 indicate that complex formation is accompanied by liberation of energy and is an enthalpy directed process.

Potentiometric studies of the complexes shows that stability decreases with increase in temperature.

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REFERENCES

1 F.A. Snavely, M.N. Rosenblum, P.S. Danielson and R.L. Rill, J. Inorg. Nucl. Chem., 33 (1971) 455.
2 H.G. Garg and C. Prakash, J. Pharm. Sci., 60 (1971) 323.
3 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.
4 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1953) 3397.
5 C. Prakash, Ph.D. thesis, University of Roorkee, 1972.
6 H. Irving and R.J.P. Williams, J. Chem. Soc., (1953) 3192.