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Note

STEPWISE STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF SOME TRANSITION METAL COMPLEXES OF 2-(2-HYDROXYPHENYL)-HYDRAZONOPENTANE-2,4-DIONE (PHPD)

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Literature survey shows that hydrazones [1] are of importance because of their high physiological activity [2] and their use in analytical chemistry, but no study has been done with 2-(2-hydroxy phenyl)hydrazonopentane-2,4-dione which is used as an intermediate for the synthesis of antineoplastic [3] and antidiabatic [4] compounds. The present work describes the determination of proton ligand stability constant and metal–ligand stability constants with divalent and trivalent metal ions using the Bjerrum–Calvin titration technique as modified by Irving and Rossotti [5,6].

REAGENT AND PROCEDURE

PHPD was synthesized using the method of Garg and Prakash [7]. All chemicals used were of AR quality. The metal salt (nitrates) solutions were prepared in double distilled water and the stock solution (0.002 M) of the ligand was prepared in methanol. Since the ligand is inadequately soluble in water, studies were carried out in a 25:75 (v/v) water–methanol mixture. Sodium perchlorate was used to maintain the ionic strength. The following set of solutions were titrated pH-metrically on an ECIL expanded scale pH meter against 0.1 M standard sodium hydroxide at 25, 30 and 35 ± 0.1°C.

(1) 4.0 ml of $HClO_4$(0.04 M) + 4.0 ml of $NaClO_4$(1.0 M) + 30 ml of methanol + 2.0 ml of water;

(2) 4.0 ml of $HClO_4$(0.04 M) + 4.0 ml of $NaClO_4$(1.0 M) + 10 ml of methanol + 20 ml of ligand(0.002 M) + 2.0 ml of water;

(3) 4.0 ml of $HClO_4$(0.04 M) + 4.0 ml of $NaClO_4$(1.0 M) + 10 ml of methanol + 20 ml of ligand(0.002 M) + 1.0 ml of (0.01 M) metal salt solution + 1.0 ml of water.

The ligand to metal ratio was maintained at 4:1 in all the titrations.

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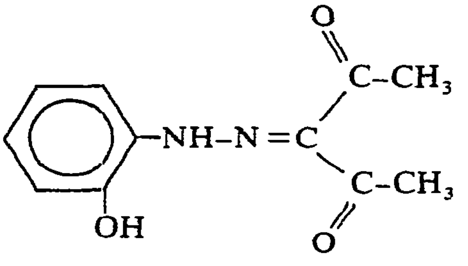
RESULTS AND DISCUSSION

Proton ligand stability constant

The average number of protons associated with the ligand ($\bar{n}_H$) was determined from the acid, ligand titration curves employing the equation of Irving and Rossotti. It is seen from structure (A) of the ligand that only one proton per ligand molecule is released on chelation. In all cases the maximum value of $\bar{n}_H$ was found to be less than 1. The protonation constant (log K^H) was calculated at the half integral value from the plot of $\bar{n}_H$ vs. pH. The proton ligand stability constants and their thermodynamic functions at different temperatures are given in Tables 1 and 2, respectively. It is seen from Table 1 that log K^H decreases with increase in temperature.



Metal–ligand stability constant

The metal titration curves were well separated from the ligand titration curves. From the titration curves of solutions (II) and (III), the average number of ligand molecules attached per metal ion ($\bar{n}$) and free ligand exponent pL were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to obtain formation curves of the complexes. In all cases the values of $\bar{n}$ were found to be less than 2, showing the formation of only two complexes, viz. 1 : 1 and 1 : 2 complexes. The values of log K_1 and log K_2 were calculated from the formation curves using the

Table 1

Stability constants of the metal complexes with PHPD at different temperatures μ=0.1 M $NaClO_4$

Cation	Temp (°C)								
	25			30			35		
	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^+	8.60			8.40			8.20		
Fe^{3+}	6.18	5.67	11.85	6.67	5.83	12.50	7.22	6.83	14.05
Ni^{2+}	6.00	5.47	11.47	6.60	5.55	12.15	7.02	6.45	13.47
Fe^{2+}	5.85	5.10	10.95	6.05	5.60	11.65	7.00	6.35	13.35
Co^{2+}	5.85	4.30	10.15	6.30	4.85	11.05	6.90	5.54	12.44
Mn^{2+}	5.00	4.42	9.42	6.00	4.80	10.80	6.20	5.47	11.67

Table 2

Values of thermodynamic functions of metal complexes of PHPD at 30°C

Cations	$-\Delta G^0$ (kcal mole^{-1})			ΔH^0 (kcal mole^{-1})			ΔS^0 (cal mole^{-1})		
	ΔG_1	ΔG_2	ΔG^0	ΔH_1	ΔH_2	ΔH^0	ΔS_1	ΔS_2	ΔS^0
H^+			11 70						
Fe^{3+}	9 25	8 08	17 33	42 84	48 72	96 60	171 90	187 46	376 00
Ni^{2+}	9 15	7 69	16 85	42 84	41 16	84 00	171 58	161 22	332 83
Fe^{2+}	8 39	7 76	16 15	48 30	52 50	100 80	187 09	198 88	385 97
Co^{2+}	8 73	6 72	15 32	44 10	52 08	96 18	174 36	194 05	369 04
Mn^{2+}	8 32	6 66	14 97	50 40	47 46	94 50	184 09	178 60	361 28

Bjerrum half $\bar{n}$ method. The metal—ligand stability data log $K_1(\pm 0.04)$. log $K_2(\pm 0.05)$ and log $\beta_2(\pm 0.09)$ at various temperatures are reported in Table 1. The order of stability for these complexes is found to be $Fe^{3+} > Ni^{2+} > Fe^{2+} > Co^{2+} > Mn^{2+}$. Only the stability order $Ni^{2+} > Co^{2+} > Mn^{2+}$ is consistent with the Irving-Williams Rule [8].

The higher stability of the Fe^{2+} complex has been observed in many cases, particularly with aromatic ligands, e.g. riboflavin [9], folic acid [9], *ortho*phenanthroline [10], 1-(2,3 dihydroxy-4-pyridylazo)-benzene-4-sulphonic acid [11], and may be attributed to the resonance stabilization energy of Fe^{2+} complexes of ligands having an aromatic ring system [10]. The higher stability of the Fe(III) complex as compared to that of divalent metal complexes is expected on the basis of the charge and ionization potential of the metal ions.

The free energy, enthalpy and entropy changes have been evaluated using standard relations. The values of ΔH were obtained from the slope of log K vs. $1/T$ plots. Wherever a linear plot was not obtained, a tangent was drawn to obtain the slope which was taken equivalent to $-\Delta H/4.57$. These thermodynamic functions are summarized in Table 2. The negative ΔG^0 values and the decrease in stability constant with increase in temperature show (Table 1) that complex formation is spontaneous and is favoured at higher temperatures. Further, the values of ΔH show that complex formation is endothermic and is, therefore, an entropy directed process, as is obvious from the positive ΔS values.

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