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Note

STEPWISE STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF SOME TRANSITION METAL COMPLEXES OF 5,5-DIMETHYLCYCLOHEXANE-2-(2-HYDROXYPHENYL)-HYDRAZONO-1,3-DIONE

AJAY K. JAIN, R.N. GOYAL and D.D. AGARWAL

Chemistry Department, University of Roorkee, Roorkee-247672 (India)

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A literature survey shows that hydrazones [1] have been used in the selective and sensitive determination of metals but no study has been made with 5,5-dimethylcyclohexane-2-(2-hydroxyphenyl)hydrazono-1,3-dione (DCPHD), which is used as an intermediate for the synthesis of antineoplastic [2] and antidiabetic [3] compounds. The present work describes the determination of the proton—ligand and the metal—ligand stability constants with divalent and trivalent metal ions using the Bjerrum—Calvin titration technique as modified by Irving and Rossotti [4,5].

REAGENT AND PROCEDURE

DCPHD was synthesised by the method of Garg and Prakash [6]. All chemicals used were of AR quality. The metal salt (nitrate) solutions were prepared in doubly 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 metal salt solution (0.01 M) + 1.0 ml of water.

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

RESULTS AND DISCUSSION

Proton—ligand stability constant

The average number of protons associated with the ligand ($\bar{n}_{\mathrm{H}}$) was determined from the acid—ligand titration curves employing the equation of

TABLE 1

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

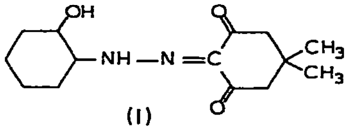
Cation	25°C			30°C			35°C		
	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2
H^+	8.50			8.40			8.10		
Fe^{3+}	5.18	4.67	9.85	5.47	4.93	10.40	5.82	5.23	11.05
Ni^{2+}	4.93	4.47	9.40	5.38	4.77	10.15	5.52	4.95	10.47
Fe^{2+}	4.95	4.40	9.35	5.35	4.60	9.95	5.52	4.83	10.35
Co^{2+}	4.85	4.30	9.15	5.30	4.55	9.85	5.40	4.65	10.05
Mn^{2+}	4.70	4.37	9.07	5.20	4.60	9.80	5.20	4.77	9.97

TABLE 2

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

Cation	$-\Delta G^0$ (kcal/mole^{-1})			ΔH^0 (kcal mole^{-1})			ΔS^0 (cal mole^{-1})		
	$-\Delta G_1$	$-\Delta G_2$	$-\Delta G^0$	ΔH_1	ΔH_2	ΔH^0	ΔS_1	ΔS_2	ΔS^0
H^+			11.64			16.80			93.86
Fe^{3+}	7.59	6.83	14.42	27.33	23.51	52.89	115.25	100.13	222.15
Ni^{2+}	7.49	6.62	14.11	26.45	21.16	47.02	112.01	91.68	201.75
Fe^{2+}	7.42	6.38	13.80	24.89	18.40	43.44	106.63	81.78	188.91
Co^{2+}	7.35	6.31	13.66	24.20	15.11	39.40	104.12	70.69	175.12
Mn^{2+}	7.21	6.38	13.59	21.16	16.93	38.47	93.63	76.92	171.82

Irving and Rossotti. It is seen from structure (I) of the ligand that only one proton per ligand molecule is released on chelation. The maximum value of $^{-}n_H$ was found to be less than one in all cases. The protonation constant (log K^H) was calculated at half integral value from the plot of $^{-}n_H$ 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.



(I)

Metal—ligand stability constant

The metal titration curves were well separated from the ligand titration curves. From the titration curves of solutions (2) and (3), the average number of ligand molecules attached per metal ion (n^{-}) and free ligand exponent pL were calculated. The ^{-}n values were plotted against the corresponding pL values to obtain the formation curves of the complexes. In all cases, the values of n^{-} were found to be less than two, showing the formation of only two complexes, viz. 1 : 1 and 1 : 2. The values of log K_1 and log K_2 were calculated from the formation curves using Bjerrum half n^{-} method. The metal—ligand stability data, log K_1 (±0.04), log K_2 (±0.05) and log β_2 (±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 [7].

The higher stability of the Fe^{2+} complex has been observed in many cases, particularly with aromatic ligands, e.g. riboflavin [8], folic acid [8], *o*-phenenthroline [9], 1-(2,3-dihydroxy-4-pyridylazo)benzene-4-sulphonic acid [10], and may be attributed to the resonance stabilisation energy of Fe^{2+} complexes of ligands having an aromatic ring system [9]. The higher stability of the Fe(III) complex compared with divalent metal complexes is expected on the basis of charge and ionisation potential of the metal ions. The stability constant of the mercury complex could not be determined because precipitation occurred at the initial stage.

The free energy, enthalpy and entropy changes have been evaluated by 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 to be equivalent to $-\Delta H/4.57$. These thermodynamic functions are summarised in Table 2. The negative ΔG^0 values and the increase in stability constant with increase in temperature show (Table 1) that complex formation is spontaneous and is favoured at higher temperatures. Further, the positive 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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