Stability Constants of Transition Metal Complexes with Aryl Schiff Bases

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Proton ligand stability constants of *p*-bromo-OHA-N-(4′-methylphenyl) imine (R_1), 5-bromo-OHA-N-(5-nitrophenyl) imine (R_2) and 5-bromo-OHA-N-(2-chloro-5-nitrophenyl) imine (R_3) and metal-ligand stability constants of their complexes with transition metals Cu(II), Ni(II), Co(II), Mn(II) and Cd(II) have been determined at 25°, 35° and 45°C (± 0.1°C) and $\mu = 0.1$ M ($NaClO_4$) in 50 : 50 ethanol-water medium. The thermodynamic parameters for the formation of 1 : 1 and 1 : 2 complexes have been calculated. The effect of substituent and the dependence of stability constants on the atomic size has been discussed.

INTRODUCTION

The chemistry of Schiff base complexes continues to attract many researchers because of its applications in various fields like food industry, dyes, catalysis, analytical and biological studies. The condition required for the complex formation may be predicted on the basis of its stability constants in solutions. The study of the stability constants of these complexes shows 1 : 1 and 1 : 2 stoichiometry. Extensive stability studies of transition metal complexes in solution are available with a variety of bidentate and tridentate Schiff bases[1–3]. However, there is no systematic solution study of the complexes of transition metals with present Schiff bases. In view of the above facts, the study of their binary complexes with some transition metals has been undertaken.

EXPERIMENTAL

The Schiff bases were synthesized by the method reported in earlier publications[4]. The purity of Schiff bases was checked by nitrogen analysis and IR spectra. All the chemicals used were of AR grade. All the solutions were prepared in double glass distilled water. The initial ionic strength of all the solutions was maintained at 0.1 M by $NaClO_4$. A digital pH meter (Elico, Model LI–120) in conjunction with a combined electrode was used for pH measurements. The method of Calvin and Bjerrum as modified by Irving and Rossotti[5] was used to obtain pK and log K values. The measurements were made at 25°, 35° and 45°C at $\mu = 0.1$ M ($NaClO_4$) in 50% aq. ethanol. The pK and log K values were computed by half integral method, pointwise calculations and also by the

method of least squares. In all the calculations, pH correction and volume correction factors have been applied for the ethanol-water mixture. The average log K values were used to calculate the free energy change (ΔG) from the van't Hoff's isotherm. The ΔH and ΔS values were calculated from the van't Hoff's isochore and the equation $\Delta G = \Delta H - T\Delta S$ respectively. The data are listed in Table-1.

TABLE-1
FORMATION CONSTANTS, FREE ENERGY, ENTHALPY AND ENTROPY CHANGES IN THE COMPLEXATION EQUILIBRIA OF TRANSITION METAL IONS WITH R_1

Temp. 25 ± 0.1°C μ = 0.1 M $NaClO_4$

Complex	log K_1	log K_2	log β	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	$-\Delta S_2$
				(kJ mol^{-1})					
Cu(II)	7.65	6.28	13.93	43.652	35.834	14.970	15.630	96.247	67.800
Ni(II)	7.36	6.25	13.61	41.997	35.663	14.451	15.258	92.437	68.474
Cd(II)	6.92	5.96	12.88	39.486	34.008	16.319	16.650	77.743	58.250
Co(II)	7.01	6.13	13.14	40.001	34.978	15.178	15.411	83.295	65.663
Mn(II)	5.92	5.08	11.00	33.780	28.987	14.506	13.359	64.679	52.443
Zn(II)	6.86	5.90	12.76	39.144	33.666	15.950	18.681	77.832	50.286

With R_2 and R_3

Complexes	log K	log β	−ΔG	−ΔH	ΔS
			(kJ mol^{-1})		
Cu(II) R_2	6.99	6.99	39.886	18.806	70.738
Cu(II) R_3	6.87	6.87	39.201	18.842	68.319
Ni(II) R_2	5.12	5.12	29.155	15.666	45.468
Ni(II) R_3	5.06	5.06	28.873	11.554	58.117
Cd(II) R_2	4.77	4.77	27.218	13.359	46.507
Cd(II) R_3	4.67	4.67	26.647	16.319	34.660
Co(II) R_2	4.64	4.64	26.476	12.765	46.101
Co(II) R_3	4.24	4.25	24.251	14.573	32.477
Mn(II) R_2	4.39	4.39	25.050	13.925	37.332
Mn(II) R_3	4.10	4.10	23.395	14.361	30.316
Zn(II) R_2	5.52	5.52	31.497	19.332	40.825
Zn(II) R_3	5.51	5.51	31.440	13.076	61.627

RESULTS AND DISCUSSION

Due to the presence of azomethine nitrogen in the present ligands, protonation takes place in the initial stages of titration. The proton association constant (pK_1) and the proton dissociation constant (pK_2) from —OH group were determined at $\bar{n}_A = 1.5$ and 0.5 respectively. The values were further checked from

the plots of log $\{(2 - \bar{n}_A)/(\bar{n}_A - 1)\}$ *vs.* B and log $\bar{n}_A/(1 - \bar{n}_A)$ *vs.* B (B = pH) meter reading) and are given in Table-2.

TABLE-2

		Temp. (°C)		
		25	35	45
Ligand R_1	pK_1	4.66	4.54	4.42
	pK_2	9.74	9.60	9.47
Ligand R_2	pK_1	—	—	—
	pK_2	9.76	9.63	9.51
Ligand R_3	pK_1	—	—	—
	pK_2	9.77	9.64	9.41

It is observed from Table-2 that the ligand R_1 shows pK_1 which represents the deprotonation of —NH group at azomethine nitrogen atom whereas it is absent in the remaining ligands. This can be explained on the basis of the effect of substituent in the phenyl ring of the amine component of Schiff bases on the electron density at the azomethine nitrogen.

The Schiff base R_2 bears NO_2 group at 4-position to azomethine nitrogen of the Schiff base and it does not display pK_1 values. Similar observation is noticed in case of R_3 which has —NO_2 group at 4 and —Cl at 2 position with respect to azomethine nitrogen. The absence of pK_1 values in these ligands may be due to strong electron withdrawing effects of —NO_2 as well as —Cl group present in the ligand. The electron density on the azomethine nitrogen is almost totally withdrawn by these groups, resulting in the generation of positive charge on the azomethine nitrogen. Due to this, protonation of azomethine nitrogen does not take place resulting in the absence of pK_1 values. Thus the observed order of pK_2 values of the Schiff bases are $R_1 \approx R_2 \approx R_3$.

It is evident from Table-1 that in all Schiff bases the values of ΔG and ΔH are negaitve while ΔS values are all positive. This indicates that the dissociation of —OH group is favoured by free energy, enthalpy and entropy factors.

The stability constants of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) complexes with R_1 follow the order Cu > Ni > Co > Cd > Zn while the complexes of R_2 and R_3 follow the order Cu > Zn > Ni > Cd > Co > Mn. The values of stability constants of the complexes decrease with the increase in temperature which indicates that high temperature does not favour the formation of stable complexes. The above stabilities of the metal complexes of R_2 and R_3 are similar to observations made by a number of workers[6–9] and are in accordance with the Irving-Williams order[10]. The complexes of R_1 follow the order in accordance with Meller and Malley[11].

The change in free energy is directly related to the log K values. The ΔG cannot always be used as a diagnostic of the type of ion association reactions taking place, without the knowledge of enthalpy and entropy changes. To interpret the relative stabilities of proton-ligand and metal-ligand complexes, the knowledge of enthalpy and entropy changes essential. The ΔS values of Cu(II)

complexes are relatively highr than those of other metal complexes. The negative values of ΔG indicate that the formations of 1 : 1 and 1 : 2 metal ligand complexes in all cases are thermodynamically favoured processes. The negative values of ΔH also lead to the same inference. The high positive values of ΔS in these cases indicate that the entropy effect is predominant over enthalpy effect.

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