Asian Journal of Chemistry Vol. 13, No. 3 (2001), 1127–1132

Studies of Proton-Ligand and Metal-Ligand Stability Constants of Cu(II) and Ni(II) Complexes of Substituted 1,3-Thiazines

S.R. DIGHADE*, M.L. NARWADE† and M.M. CHINCHOLKAR†
Department of Chemistry, R.D.I.K. College, Badnera-444 701, India

The interactions of Cu(II) and Ni(II) metal ions with (i) 4-(2-hydroxy-5-methylphenyl)-5-benzoyl-6-(2′-furyl)-2-imino-6H-2,3-dihydro-1,3-thiazine (L_1). (ii) 4-(2-Hydroxy-5-methylphenyl)-6-(4-methoxyphenyl)-2-imino-6H-2,3-dihydro-1,3-thiazine (L_2) have been studied at 0.1 M ionic strength. It is observed that and Cu(II) and Ni(II) metal ions form 1 : 1 and 1 : 2 complexes with L_1 and L_2. The substituted 1,3-thiazines show formation of stepwise complexes. The order of proton-ligand stability constant is as $pK_{L_1} > pK_{L_2}$. The data obtained for pK and log K are used (i) to see the effect of substitutents, (ii) to check the validity of $\log K = a\,pK + b$. Here proton-ligand and metal-ligand stability constants have been studied pH-metrically by Calvin-Bjerrum titration technique.

INTRODUCTION

1,3-Thiazines and their derivatives are biologically important compound having antibacterial[1–2], antiumour[3], antimicrobial[4] properties. Shelke *et al.*[5] have investigated the interaction between UO_2(II) and Cu(II) with dicarboxylic acids in dioxane-water mixture. Narwade *et al.*[6] have studied the equilibrium constants of Cu(II) complexes with some substituted chalcones at 0.1 M ionic strength potentiometricly. Sawalake and Narwade[6] have studied stability constants of Cu(II) complexes with some substituted chalcones at 0.1 M ionic strength. Rajput[7] has studied proton-ligand stability constants with some chlorosubstituted pyrazolines, isoxazolines, pyrazoles and isoxazoles. Deshmukh[8] has studied proton-ligand stability constants with some dichlorosubstituted pyrazolines, isoxazolines, pyrazoles and isoxazoles. Banerjee *et al.*[9] have synthesised number of mixed ligands of alkaline earth metal complexes with a view to understand the bio-inorganic chemistry of metal ions. Raghuwanshi *et al.*[10] have studied stability constants of Cu(II) complexes with some substituted isoxazolines in 70% dioxane-water mixture spectrophotometrically. Mandakmare *et al.*[11] have studied the interaction between UO_2(II) and substituted coumarins at 0.1 M ionic strength potentiometrically and spectrometrically. Recently Palaskar[12] has studied the

---

†Vidarbha Mahavidyalaya, Amravati (India) 444 604

effect of ionic strength and dielectric constant of Cu(II)-3-nitrophthalic acid potentiomehtrically at 0.02, 0.04, 0.06, 0.08 and 1.0 M ionic strength in aqueous medium at 30°C. The present work deals with the study of complex formation between Ni(II) and Cu(II) ions and substituted 1,3-thiazines and determination of proton-ligand and metal ligand-stability constants of some substituted 1,3-thiazines pH-metrically by Calvin-Bjerrum titration technique.

EXPERIMENTAL

Substituted 1,3-thiazine ligands L_1 and L_2 were synthesised in the laboratory and their purity was checked by TLC on microscopic slides with silica gel-G layer of thickness 0.3. The structures of L_1 and L_2 were confirmed by IR and NMR spectra.

Synthesis of Ligands

4-(2-Hydroxy-5-methylphenyl)-5-benzoyl-6-(2′-furyl)-2-imino-6H-2,3-dihydro-1,3-thiazine, (mp 83°C) (L_1) is synthesised from 3-benzoyl-2-(2′-furyl)-6-methylchromanone, (m.p. 125°C), by known method using thiourea and pyridine as solvent.

4-(2-Hydroxy-5-methylphenyl)-6-(4-methoxyphenyl)-2-imino-6H-2,3-dihyro-1,3-thiazine (L_2) is synthesised from 2′-hydroxy-5′-methyl-4-methoxychalcone, (m.p. 100.5°C), by known method using thiourea and pyridine as solvent.

IR studies (L_1): 3755–3680 (w, b) O—H streching, 3436–3000 (w, b) C—N—H stetching, 2930 (s) C=N—H stetching, 2854 (m) C—H stretching and aliphatic due to CH_3 group, 1597 (s) C=O stretching of aroyl group, 1483 (s) C=N stretching and C=C stretching vibration in aryl group, 1294 (d) C—N stretching. ^{1}HNMR: 2.30–2.40 (s) 3H Ar—CH_3, 3.10 (d) 1H, 1H, H_B, 3.7 (d) 1H, 1H, H_A, 5.20 (d) 1H, 1H, H_C, 5.9 (d) 1H, NH, N—H_H, 6.20 (d) 1H, 1H, N—H_B, 6.37–7.9 (m) 9H, Ar—H, 11.9 (s) 1H, Ar—OH.

IR studies (L_2): 3760–3370 (s) (broad) O—H stretching, 3374 (s) C—N—H stretching, 3014.5 (s) C=N—H streching, 1690–1638 (s) >C=N streching, 1485 (s) C=C streching vibration in aryl 1421 (s) —CH_3 group, 1288–1223 (d) C—N stretching, 1223.8–1175 (m) Ar—O streching. ^{1}HNMR: 2.35–2.40 (s) 3H, Ar—CH_3, 2.8 (d) 1H, CH_A, 3.2 (dd) 1H, CH_B, 3.7–3.9 (s) 3H, Ar—OCH_3, 4.05 (d) 1H, N—H_A, 5.4 (d) 1H, N—H_B, 6.9–7.41 (m) 7H, Ar—H, 12.75 (s) 1H, Ar—OH.

The solutions of ligands were prepared in 70% ethanol-water mixture. The solutions of NaOH, HNO_3, KNO_3 and metal ions ($CuNO_3$, $NiNO_3$) were obtained from BDH grade chemicals.

The pH measurements were carried out with 335 Systronic pH-meter (accuracy ±0.05 units) using glass and calomel electrodes at 30° ± 1°C.

The B values (pH-meter reading in 70% ethanol-water mixture) were converted to pH values by applying the corrections given by Van Viterts and Hass. pH meter was calibrated by standard buffer solutions (pH 4.01, 7.00 and 9.15).

Experimental procedure involves following three sets of titrations:

(i) Free acid titration ($HNO_3 + 1 \times 10^{-2}$ M).

(ii) Free acid + ligand titration (ligand 20×10^{-4} M).

(iii) Free acid + ligand + metal ion titration (4×10^{-4} M) were carried out with standard NaOH solution (0.1050 M) in presence of an inert atmosphere by bubbling a constant flow of nitrogen gas.

RESULTS AND DISCUSSION

The ligands are monobasic containing only one OH group; hence its dissociation is represented as below.

$$HL \rightleftharpoons H^+ + L^-$$

The derivations between acid curves (acid + ligand curves) started at about pH 2.6–3.0 for L_2 for all the systems this deviation gradually increases up to pH 12.00 which shows the dissociation of —OH group of ligands.

Determination of proton-ligand formation numbers ($\bar{n}A$)

The values of $\bar{n}A$ are estimated by using Irving and Rossotti experiments. Formation curves are prepared by plotting values of $\bar{n}A$ *vs.* pH which are shown in Figs. 1 and 2.

PLOT BETWEEN $\bar{n}A$ *vs.* pH

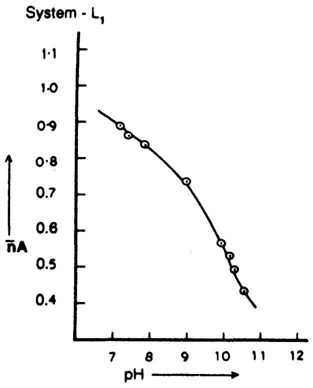

Fig. 1

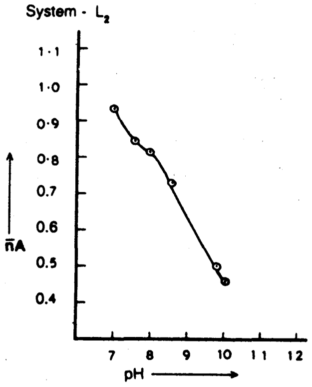

Fig. 2

Calculations

The values of pK are calculated from formation curves (i.e., half integral method). The pH at $\bar{n}A = 0.5$ corresponds the proton-ligand stability constant (pK). The order of proton-ligand stability constant is $pKL_2 > pKL_1$. The correct values are also calculated by pointwise calculation method. The pK values for L_1, L_2 are given in Table-1.

The slight reduction in pK value of ligand L_2 is due to presence of —OCH_3 group attached to phenyl ring as electron withdrawing group. In case of ligand L_1, the inductive effect of benzoyl group may be compensated due to the presence of furyl as electron releasing group that results in an increase in the pK value of ligand L_1.

TABLE-1
DETERMINATION OF PROTON LIGAND STABILITY CONSTANTS (pK)

Medium: 70% Ethanol-water $\mu = 0.1$ M $T_L^o = 20 \times 10^{-4}$ M
$T_m^o = 4 \times 10^{-4}$ M N = 0.150 M V° = 50 mL
E° = 1×10^{-2} M = 0.01 M Temp. = 30° ± 1°C

System	Constant (pK)	
	Half integral method	**Pointwise calculations**
Ligand L_1	10.30	10.25 ± 0.04
Ligand L_2	9.70	9.62 ± 0.03

Determination of Metal-Ligand Stability Constants

The deviation between (acid + ligand) and (acid + ligand + metal) curves started from pH 3 and increased continuously up to pH 7. It shows the commencement of complex-formation. Intense colouration was observed which also indicated the formation of complex.

Calculations of $\bar{n}$ values and determination of log K_1 and log K_2 values

The values of $\bar{n}$ are estimated by applying Irving-Rossotti expression.

The maximum value of $\bar{n}$ was obtained at about pH 2.00. This showed the formation of 1 : 1 and 1 : 2 complexes. The formation curves between $\bar{n}$ *vs.* pH are constructed as shown in Figs. 3–6.

The values of log K_1 and log K_2 for 1 : 1 and 1 : 2 complexes respectively are calculated and presented in Table-2.

PLOT BETWEEN $\bar{n}$ *vs.* pH

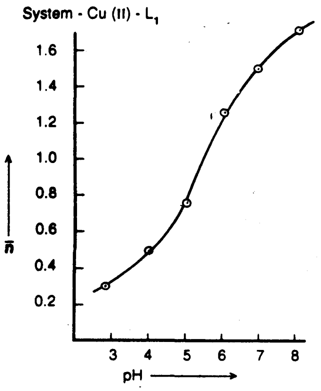

Fig. 3

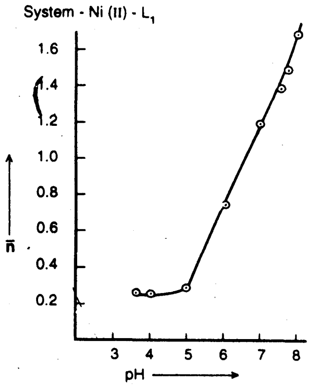

Fig. 4

PLOT BETWEEN $\bar{n}$ *vs.* pH

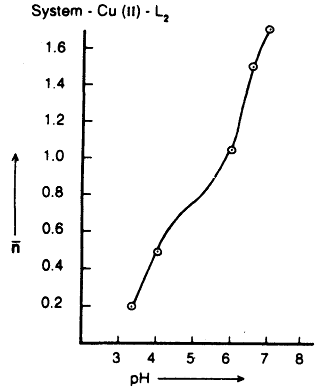

Fig. 5

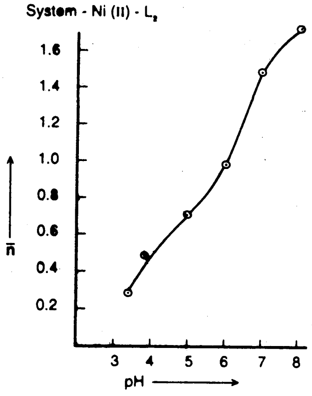

Fig. 6

TABLE-2
METAL-LIGAND STABILITY CONSTANTS OF Cu(II) AND Ni(II) METAL IONS WITH SUBSTITUTED 1,3 THIAZINAS IN 70% ETHANOL-WATER MIXTURE

Medium: 70% Ethanol-water	$T_L^\circ = 20 \times 10^{-4}$ M	$\mu = 0.1$ M
N = 0.150 M	$T_m^\circ = 4 \times 10^{-4}$ M	$E^\circ = 1 \times 10^{-2}$ M = 0.01 M
V° = 50 mL	Temp. = 30°C ± 1°C	

System	Metal-ligand stability constants (log K)			
	Half integral		Poinstwise calculations	
	log K_1	log K_2	log K_1	log K_2
Cu(II)-L_1 complex	9.04	6.35	9.10 ± 0.03	6.30 ± 0.03
Ni(II)-L_1 complex	8.54	5.35	8.50 ± 0.03	5.38 ± 0.02
Cu(II)-L_2 complex	8.64	5.95	8.50 ± 0.03	5.85 ± 0.03
Ni(II)-L_2 complex	8.50	5.26	8.89 ± 0.04	5.30 ± 0.02

From Table-2, the order of log K_1 is presented as below:

(I) log K_1 for Cu(II) complexes:

$$Cu(II)L_1 > Cu(II)L_2$$

(II) log K_1 for Ni(II) complexes

$$Ni(II)L_1 > Ni(II)L_2$$

It could be seen from Table-3 that the difference between log K_1 and log K_2 is greater (> 1) which shows formation of stepwise complex. If the difference is very smaller that indicates the formation of simultaneously complex formation.

TABLE-3
METAL LIGAND STABILITY CONSTANTS AT 0.1 M IONIC STRENGTH

System	$\log K_1 - \log K_2$		$\log K_1/\log K_2$	
	Half integral	Pointwise calculation	Half integral	Pointwise calculation
Cu(II)-L_1 complex	2.69	2.80	1.42	1.44
Ni(II)-L_1 complex	3.19	2.62	1.59	1.58
Cu(II)-L_2 complex	2.49	2.65	1.41	1.45
Ni(II)-L_2 complex	3.24	3.69	1.61	1.67

ACKNOWLEDGEMENT

The authors are thankful to RSIC/CIL Chandigarh for spectral analysis; similarly, the authors are thankful to Principal, Govt. Vidarbha Mahavidyalaya, Amravati and Principal, R.D.I.K. College, Badnera for providing facilities.

REFERENCES

1. M.A. Ramekar and M.M. Chincholkar, *J. Indian Chem. Soc.*, **71**, 199 (1994).
2. H.S. Patel, and N.P. Patel, *Orient. J. Chem.*, **13**, 69 (1997).
3. H.I. El-Subbagh, A.H. Abadi, I.E. Al-Khawad, K.A. Al-Rashood, *Arch. Pharm.*, **332**, 19 (1999).
4. A.W. Raut and A.G. Doshi, *Orient J. Chem.*, **11**, 205 (1995).
5. D.N. Shelke and D.V. Jahagirdar, *J. Indian Chem. Soc.*, **53**, 613 (1976).
6. M.L. Narwade and P.D. Sawalakhe., *J. Indian Chem. Soc.* **70**, 201 (1993).
7. P.R. Rajput., Ph.D. Thesis, Amravati University (1993).
8. M.S. Deshmukh., Ph.D. Thesis, Amravati University (1996).
9. A.K. Banarjee and T.V.R.K. Rao, *J. Indian Chem. Soc.*, **63**, 480 (1986).
10. P.B. Raghuwanshi, A.G. Doshi and M.L. Narwade, *Asian J. Chem.*, **8**, 211 (1996).
11. A.U. Mandakmare and M.L. Narwade, *Acta Ciencia Indica*, **16C**, 30 (1994).
12. N.G. Palaskar, *Samyak J. Chem.*, **2**, 26 (1998).

(*Received:* 1 March 2001; *Accepted:* 28 April 2001) AJC-2329