

Studies on Composition and Stability Constants of Complexes of Copper(II) and Nickel(II) with 2*N*-Salicylidene- and 2*N*-3,5-Dichlorosalicylidene-5-phenyl-1,3,4-thiadiazole Schiff Base

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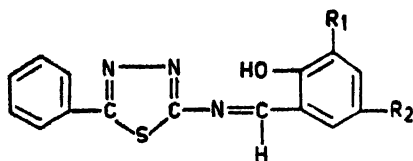
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The composition, protonation constants of 2*N*-salicylidene-5-phenyl-1,3,4-thiadiazole and 2*N*-3,5-dichlorosalicylidene-5-phenyl-1,3,4-thiadiazole and formation constants of their metal-chelates with Cu^{II} and Ni^{II} in 50% ethanol-water system have been determined by Irving-Rossotti method at various ionic strengths at 25±1°. The observed order of the ligands on the basis of relative strength is SPT > DCSP. The order of stability of the metal chelates is found to be Cu^{II} > Ni^{II}. Solid complexes were also separated. Chemical analyses suggest a 1 : 2 stoichiometry of metal ligand.

NO work on the reaction of Cu^{II} and Ni^{II} metals with 2*N*-salicylidene-5-phenyl-1,3,4-thiadiazole and 2*N*-3,5-dichlorosalicylidene-5-phenyl-1,3,4-thiadiazole is reported in the literature, which encouraged to carry out the present investigation.

Experimental

Synthesis of ligand : The ligands 2*N*-salicylidene-5-phenyl-1,3,4-thiadiazole and 2*N*-3,5-dichlorosalicylidene-5-phenyl-1,3,4-thiadiazole were prepared by refluxing the equimolar quantities of 2-amino-5-phenyl-1,3,4-thiadiazole with salicylaldehyde, and 3,5-dichlorosalicylaldehyde, respectively in absolute alcohol for 3 h on a water bath and were repeatedly crystallised in alcohol to get analytically pure compounds, m.p. 161° and 166°, respectively. The compound was characterised by elemental analyses and infrared spectral studies. The ligand may be represented as shown below.



where R₁, R₂ = H or R₁, R₂ = Cl

Separation of the metal chelates : Metal complexes of the appropriate Schiff bases were prepared by refluxing aqueous solution of the metal salt and alcoholic solution of the ligand in 1 : 2 molar ratio

for 2 to 3 h. The metal salts used were copper acetate and nickel acetate. The insoluble complexes that separated out on cooling, were filtered, washed, dried in vacuum and analysed for metal and nitrogen. The results are given in Table 1.

TABLE 1—ANALYTICAL DATA

Composition	Colour	Analysis% : Found/(Calcd.)	
		Metal	N
(C ₁₅ H ₉ N ₃ OS) ₂ Cu	Green	10.20 (10.22)	13.45 (13.51)
(C ₁₅ H ₉ N ₃ OS) ₂ Ni	Yellow green	9.48 (9.51)	13.67 (13.62)
(C ₁₅ H ₇ N ₃ Cl ₂ OS) ₂ Cu	Green	8.27 (8.37)	11.00 (11.06)
(C ₁₅ H ₇ N ₃ Cl ₂ OS) ₂ Ni	Yellow green	7.72 (7.78)	11.10 (11.13)

Materials : All chemicals used were of reagent grade. Standard solutions of copper sulphate and nickel sulphate were prepared in conductivity water. The metal content were estimated by standard methods¹.

The solutions of 2*N*-salicylidene-5-phenyl-1,3,4-thiadiazole (SPT) and 2*N*-3,5-dichlorosalicylidene-5-phenyl-1,3,4-thiadiazole (DCSP) were prepared in absolute alcohol. The carbonate free NaOH solution was prepared in conductivity water and used in potentiometric titrations. Stock solutions of sodium perchlorate (neutral) and perchloric acid were prepared in conductivity water.

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Apparatus : An Elico-Lt-10 pH meter having glass and saturated calomel electrode was used for the titrations. The pH meter was calibrated with potassium hydrogen phthalate solution (pH 4.05). An Elico CM-80 conductivity bridge having cell constant 1.09 was used for the determination of the composition of the complex.

Conductometric study : Jobs² method was employed to establish the composition of the complexes conductometrically.

Potentiometric study : Bjerrum-Calvin^{3,4} technique modified by Irving and Rossotti⁵ was employed for determining the stability constant of the metal complexes, for this purpose the following three mixtures were prepared.

Mixture A.	Perchloric acid 0.1 M
Mixture B.	Perchloric acid 0.1 M + Ligand solution 0.005 M
Mixture C.	Perchloric acid 0.1 M + Ligand solution 0.005 M + Metal solution 0.001 M

The concentration of the common ingredients were identical in different mixtures. An appropriate amount of the neutral sodium perchlorate (*M*) was added to maintain the desired ionic strength. These mixtures were titrated against standard sodium hydroxide solution (0.1 M). Since pH titrations were carried out in 50% v/v ethanol-water medium, appropriate corrections in all pH meter readings were made on account of the solvent as suggested by Van Uitert *et al*⁶.

A graph of pH vs the volume of alkali added was plotted. The three titration curves were referred as, (A) acid titration curve; (B) ligand titration curve, and (C) complex titration curve.

Results

Proton ligand stability constant : The values of $\bar{n}H$ at various pH values were calculated from the acid titration curve (A), and ligand titration curves (B) using the formula of Irving and Rossotti. Calculation of Proton-ligand stability constants was carried out by plotting a graph of $\bar{n}H$ vs pH. The pK_a values corresponding to $\bar{n}H=0.5$ was obtained from the curve. However, the best values of pK_a of the ligand was found from the plot of $\log \bar{n}H / (1-\bar{n}H)$ vs pH. The plot was found to be linear with intercept equal to pK_a and slope equal to unity, suggesting that only one proton was dissociated.

The values of proton ligand stability constants obtained at various ionic strengths are given in Table 2.

Metal ligand stability constant : From the three titration curves, \bar{n} values of the metal complex were determined at various pH values. From these data the corresponding pL values were calculated. The \bar{n} values were then plotted against the corresponding pL values to get the formation curves of the metal complex equilibria.

It is observed that the metal-ligand curve is well separated from the ligand titration curves, suggesting thereby that the liberation of proton is due to chelation. The \bar{n} values for each system were calculated until the pH of precipitation. Second buffer region starts after this pH, which explains the gradual consumption of hydrogen ion by metal in formation of metal hydroxide. The value of \bar{n} obtained for Cu^{II} and Ni^{II} system was less than 2 before the onset of precipitation. This indicates the formation of MR⁺ and MR₂ complex species in solution, where R is the ligand. The value of log K₁ and log K₂ for Cu^{II} and Ni^{II} were obtained by direct observation of the formation curves ($\bar{n}=0.5$ and 1.5) as shown in Table 3. The values of log K₁ and log K₂ was refined by computational methods⁷ viz. interpolation at various \bar{n} and interpolation at half \bar{n} values.

Discussion

As the ionic strength increases the values of log K₁ and log K₂ decrease. This observation is in agreement with the Debye-Huckel equation⁸. The observed order of stabilities for the above metal ions is Cu^{II} > Ni^{II} and conforms to Irving Williams⁹ order of stability.

The formation of six membered ring in the complex has created a very unusual features in the compound, i.e. a six and five membered ring is alternate to each other predicting the high stability which has actually been observed by the experimental data. Another phenomenon observed in the ligand molecule is the appearance of conjugated double bond in the formation of metal chelates which also is responsible for the higher stability data.

It is clear from Tables 2 and 3 that chloro group has marked influence on phenolic group. The observed order of ligand on the basis of relative acid strength is SPT > DCSPT. It is due to the presence of the electron withdrawing group, i.e. -I effect of the substituted group.

TABLE 2—PROTON LIGAND STABILITY CONSTANT AT 25±1°

Ligand	$\mu = 0.05$			$\mu = 0.10$			$\mu = 0.15$		
	I	II	Mean	I	II	Mean	I	II	Mean
SPT pK_a	8.50	8.48	8.49	8.45	8.46	8.46	8.35	8.36	8.36
DCSPT pK_a	7.86	7.86	7.86	7.25	7.25	7.25	7.17	7.18	7.18

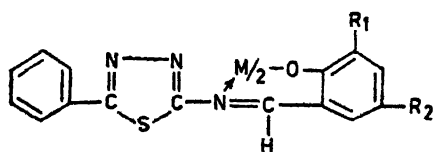
I = Interpolation at half $\bar{n}H$ values, II = linear plot method.

TABLE 3—METAL LIGAND STABILITY CONSTANT AT 25±1°

Ligand	Ionic strength	$\mu=0.05$			$\mu=0.10$			$\mu=0.15$		
		I	II	Mean	I	II	Mean	I	II	Mean
SPT Metal										
Cu ^{II}	log K ₁	7.84	7.94		7.62	7.75		7.48	7.39	
	log K ₂	6.18	6.09		6.38	6.42		6.04	5.93	
	log β_n	14.02	14.03	14.03	14.00	14.17	14.09	13.52	13.32	13.42
Ni ^{II}	log K ₁	6.30	6.39		5.62	—		5.46	5.85	
	log K ₂	5.54	5.51		4.12	—		4.12	3.85	
	log β_n	11.84	11.90	11.87	9.74	—	9.74	9.58	9.70	9.64
DCSPT Metal										
Cu ^{II}	log K ₁	7.46	7.56		6.94	7.05		6.73	6.86	
	log K ₂	6.54	6.38		6.72	6.84		5.86	5.89	
	log β_n	14.00	13.94	13.97	13.66	13.89	13.78	12.59	12.75	12.67
Ni ^{II}	log K ₁	5.84	5.93		5.54	5.44		4.72	5.05	
	log K ₂	4.92	4.90		4.20	4.05		4.18	4.10	
	log β_n	10.76	10.83	10.80	9.74	9.49	9.62	8.90	9.15	9.03

I = Interpolation at half \bar{n} method, II = interpolation at various \bar{n} values.

Conductometric study and chemical analyses of metal chelate suggest a 1 : 2 stoichiometry of metal : ligand. The probable structure to the 1 : 2 metal complex may be as written below.



where R₁, R₂ = H or R₁, R₂ = Cl

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