

NOTES

**Stability Constants of 2N-(3,5-Diiodo Salicylidene)-5-Phenyl
1,3,4-Thiadiazole Complexes with Cu^{2+} , Ni^{2+} and Fe^{3+}**

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In the present communication the stability constants of 2N-(3,5-diiodo salicylidene)-5-phenyl 1,3,4-thiadiazole complexes with Cu^{2+} , Ni^{2+} and Fe^{3+} are reported.

In the present communication the dissociation constant of the 2N-(3,5-diiodo salicylidene)-5-phenyl 1,3,4-thiadiazole and formation constant of its Cu^{2+} , Ni^{2+} and Fe^{3+} chelates have been determined potentiometrically following the Bjerrum-Calvin^{1,2} pH titration technique as adopted by Irving and Rossotti³ at $25 \pm .1^\circ\text{C}$ at 0.1μ ionic strength in 50% (v/v) dioxane-water medium. The appropriate corrections in all pH meter readings were made on account of solvent as suggested by Van-Uitert *et al.*⁴

The ligand 2N-(3,5-diiodo salicylidene)-5-phenyl 1,3,4-thiadiazole was prepared by refluxing the equimolar quantities of 2-amino-5-phenyl-1,3,4-thiadiazole with 3,5-diiodo salicylaldehyde in absolute alcohol for 3 hrs. on a water bath and was repeatedly crystallised in the dioxane to get an analytical pure compound, m.pt. 185°C . The compound was characterized by elemental analysis (calculated: C 33.77%, S 6.00%, N 7.87%; found: C 33.77%, S 5.50%, N 7.80%).

All chemicals used in the present work were of reagent grade. Standard solutions of copper sulphate, nickel sulphate and ferric perchlorate were prepared in conductivity water. The metal contents were estimated by standard methods⁵. The solution of 2N-(3,5-diiodo salicylidene)-5-phenyl 1,3,4-thiadiazole (DISPT) was prepared in dioxane. 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.

The Ellico-pH meter, Model Lt-10, having glass and saturated calomel electrode was used for the titrations. The pH-meter was calibrated with potassium hydrogen phthalate solution (pH 4.05).

Proton Ligand Stability Constant

In the ligand it is the phenolic (OH) group that takes part in complex formation and proton is replaced from it by metal ions during chelation. Since only one

proton per ligand molecule is liberated during complexation, the number of dissociable protons, Y , attached to ligand molecule is one.

Calculation of proton ligand stability constants was carried out by plotting a graph of $\bar{n}H$ against pH and the value of pK_1^H was evaluated from the half integral point at $\bar{n}H = 0.5$. The plot of $\log(\bar{n}H/1 - \bar{n}H)$ vs pH was also drawn. From this pK_a was evaluated. This value agrees quite well with that obtained by half integral method.

Metal Ligand Stability Constant

The $\log K_1$ and $\log K_2$ values for Cu^{2+} , Ni^{2+} and Fe^{3+} system were determined by half integral method plotting the \bar{n} values against pL . These values were further confirmed by the various computational methods⁶ viz. interpolation at half \bar{n} values, midpoint method and interpolation at various \bar{n} values.

The observed order of stabilities for the above metal ions is $Cu(II) > Ni(II) > Fe(III)$ and conforms to Irving Williams⁷ order of stability. It is ordinarily expected that on account of the increased charge on the ion, Fe^{3+} complexes may be more stable than their Cu^{2+} and Ni^{2+} counterparts. The observations, however, are not in keeping with this expectation and can hardly be explained entirely on the basis of the difference between their ionic radii and the polarizing action of the central metal ions. The following explanation may account for this observation. Yatsimirki⁸ and Irving⁹ have pointed out that when dative bond is formed inside the complex particles between the ligand and the central metal atom, the exceptional behaviour as recorded above is noted. This happens because the strength of the dative bond decreases with increase in the charge of the central ion.

The formation of six-membered ring in the complex has created a very unusual feature 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 and single bond in the formation of metal chelates which is also responsible for the higher stability data.

TABLE 1
PROTON LIGAND AND METAL LIGAND STABILITY
CONSTANT AT $25 \pm 1^\circ C$, $\mu = 0.1 M$

Metals		I	II	III
	$\log K_1^H$	*6.90		
		†6.90		
Cu(II)	$\log K_1$	3.86	3.80	4.14
	$\log K_2$	3.64	3.58	3.63
	$\log \beta_n$	7.50	7.38	7.77

Table 1 Contd.

Metals		I	II	III
Ni(II)	log K ₁	3.50	3.50	3.54
	log K ₂	3.26	3.26	3.21
	log β _n	6.76	6.76	6.75
Fe(III)	log K ₁	3.22	3.35	3.48
	log K ₂	2.95	3.08	2.58
	log β _n	6.17	6.43	6.06

*Interpolation at half $\bar{n}H$ values

†Linear plot method.

I = Interpolation at half \bar{n} values.

II = Mid point method.

III = Interpolation of various \bar{n} values.

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