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Effect of Schiff Bases on Stabilities of Copper(II) Complexes

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Some substituted Schiff bases *viz.*, cyano acetyl benzalidene hydrazone (CABH), cyano-acetyl salicylidene hydrazone (CASH) and cyanoacetyl 3:5 diiodo salicylidene hydrazone (CAISH) have been synthesized and the effect of substitution in the ligand molecule on stabilities of Cu(II) complexes has been studied. The metal ligand ratio was found to be 1:1 conductometrically following job's method. The stabilities of the complexes have been determined by Bjerrum-Calvin pH titration technique. The log k_H values of these ligands were found to be 9.24 (CABH), 9,10 (CASH) and 10.15 (CAISH). The order of stabilities of Cu(II) complexes with these ligands has been found to be Cu-CABH > Cu-CASH > Cu-CAISH which has been explained on the basis of π electron delocalization possible in the ligand molecules.

Key Words: Cu(II) complex, Stabilities, Schiff base.

INTRODUCTION

Cyano derivatives have been extensively used in medicine as drugs[1,2]. It has also been observed that the activity of the cyano compounds increases with chelation. The literature survey indicate that no attempt has been made for separating the solid complexes of cyano acetyl benzalidene hydrazone (CABH), cyano acetyl salicylidence hydrazone (CASH) and cyano acetyl 3.5 diiodo salicylidene hydrazone (CAISH) and to determine their stability constants with copper ions. The present communication is aimed to determine the compositions and to study the effect of substitution in the ligand molecules on the stability of Cu(II) complexes following Bjerrum Calvin pH titration technique.

EXPERIMENTAL

All reagents and chemicals used were of AnalaR/BDH grade. Carbon dioxide free sodium hydroxide was prepared from AR reagent. Perchloric acid of 0.1 M and $NaClO_4$ of 2 M were prepared in double distilled water. Copper(II) salt solution was also prepared in double distilled water and was estimated by EDTA.

Conductivity bridge (Elico-CM-82) was used to determine conductance. While pH meter (Elico model LI-10) with wide range calomel electrode was used for pH measurements.

RESULTS AND DISCUSSION

Synthesis of ligands: The cyanoacetic acid hydrazide by known method[3] was prepared and condensed in equimolar proportiosn with benzaldehyde, salicyladeyde and 3.5 di-iodo salicylaldehyde dissolved in minimum quantity of ethanol. On keeping the well-stirred solution overnight, needle shaped crystals separated. They were filtered and recrystallized repeatedly from ethanol and dried in vaccum over $CaCl_2$. The purity of the compound was confirmed by elemental analysis. The nitrogen was estimated by semimicro Dumas method.

Ligand	m.f.	Nitrogen Calcd. (Found) (%)
Cyanoacetyl benzalidene hydrazone (CABH)	$C_{10}H_9N_3O$	22.46 (22.45)
Cyanoacetyl salicylidene hydrazone (CASH)	$C_{10}H_9N_3O_2$	19.54 (19.50)
Cyanoacetal-3,5-diiodo-salicylidene hydrazone (CAISH)	$C_{10}H_7N_2O_2$	9.24 (9.20)

Composition of complexes: Job's method[4] was employed to establish the composition of the complexes conductometrically. The method of continuous variation in equimolar solutions was applied and found that the complexes contain metal and ligand in 1:1 ratio. All measurements were made in 50 % aqueous ethanol medium.

Potentiometric titrations: The following solutions were titrated[5,6] separately against 0.1 M NaOH solution keeping the total volume as 50.0 mL in 70/30 (v/v) ethanol-water medium: (i) 5.0 mL 0.1 M $HClO_4$ + 5.0 mL 2 M $NaClO_4$ + 5.0 mL H_2O + 35 mL ethanol, (ii) 5.0 mL 0.0 M $HClO_4$ + 5.0 mL 2 M $NaClO_4$ + 5.0 mL H_2O + 35 mL 0.005 M ligand, (iii) 5.0 mL 0.1 M $HClO_4$ + 5.0 mL 2 M $NaClO_4$ + 35 mL 0.005 M ligand + 5.0 mL 0.001 M copper(II).

The 100 mL tipless pyrex beakers containing solution were kept immersed in thermostat maintained at 25 ± 0.5ºC and kept covered with a Perspex cover with holes to admit electrodes, burette and the glass stirrer. The pH was noted after each addition of 0.10 mL of the alkali. The $\bar{n}H$, $\bar{n}$ and pL were calculated by employing the formulae of Irving and Ressotti[7].

From the proton ligand stability curve plotted between $\bar{n}H$ *vs.* pH and log K_1H value was read directly at 0.5 $\bar{n}H$ (Fig. 1).

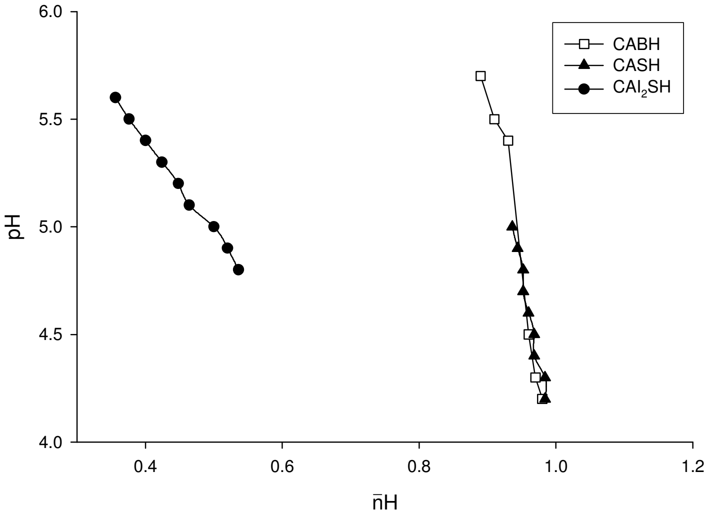


Fig. 1. Proton ligand stability curves

The metal ligand stability constants were calculated by plotting a graph between $\bar{\eta}$ and pL (Fig. 2) the values of log k_1 and log k_2 were calculated from this curve. Employing the method of interpolation at 0.5 $\bar{\eta}$ value, interpolation at mid-point interpolation at 1.5 $\bar{\eta}$ value and interpolation at various $\bar{\eta}$ values. These values have been tabulated in Table-1.

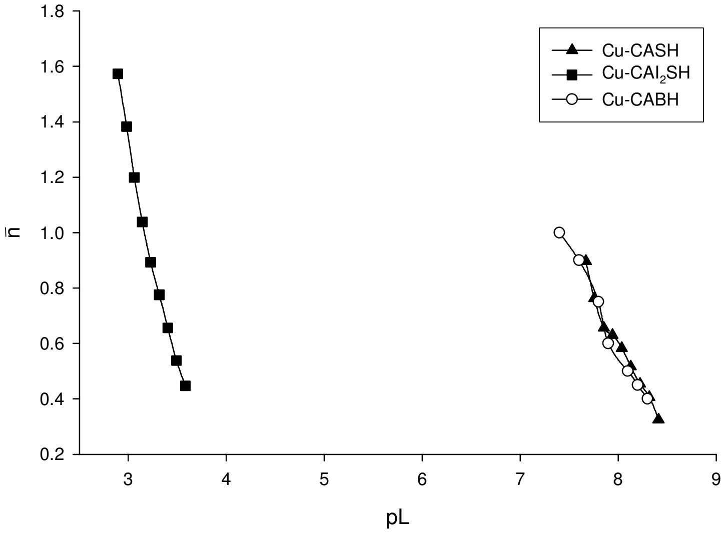
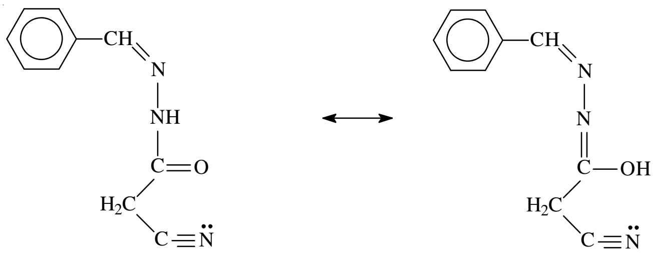


Fig. 2. Metal ligand stability curves

TABLE-1
VALUES OF STABILITY CONSTANTS OF Cu(II) COMPLEXES OF CYANOACETYL HYDRAZONES

	log k 9.24 Cu-CASH			log k_1 9.10 Cu-CASH			log k_1 10.15 Cu-CAISH		
	log k_1	log k_2	log/Bn	log k_1	log k_2	log/Bn	log k_1	log k_2	log/Bn
Interpolation at 0.5 $\bar{\eta}$ value	8.120	–	–	7.590	–	–	5.720	–	–
Interpolation at mid points	–	6.780	–	–	5.730	–	–	5.160	–
Interpolation at various $\bar{\eta}$ value	–	–	–	–	6.040	–	–	5.120	–
Interpolation at various $\bar{\eta}$ value	8.086	6.377	–	6.593- 5.995	–	5.712	-	5.070	–
Mean average value	8.103	6.678	14.681	7.091	5.921	13.012	5.716	5.116	10.832

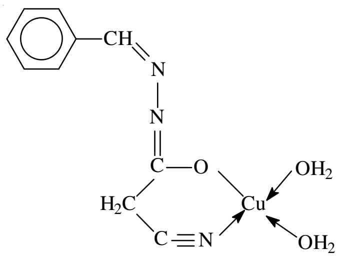
The cyanoacetyl benzalidene hydrazone (CABH) is bidentate in nature which exhibits imide-imidol tautomerism as under:



I
Imide form (CABH)

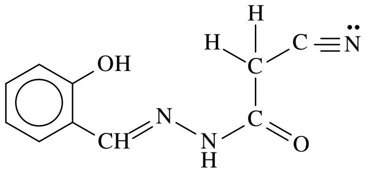
II
Imidol form (CABH)

As the metal complexes have been prepared in strong ammonical medium, it is obvious that the ligand forms the complex through its imidol form (**II**) by co-ordination through nitrogen of -CN group and by replacement of hydrogen as H^+ of the -OH group of the imidol form. The structure of the complex may be represented as follows:

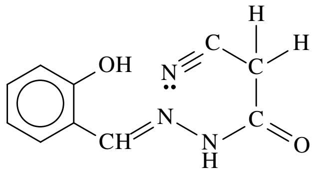


III

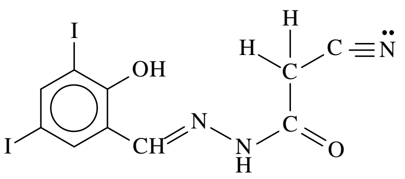
The cyano-acetyl salicylidene hydrazone (CASH) and cyanoacetyl 3.5 diiodo salicylidene hydrazone (CAISH) are tridentate ligands. Their strainless molecules may be represented by **IV** and **V** which change to **VI** and **VII** before complexation respectively in which the three coordinating centres come close to each other:



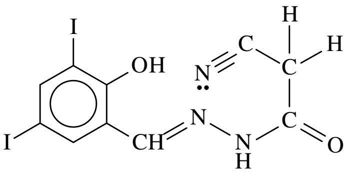
IV (CASH)



V (CASH)



VI (CAISH)



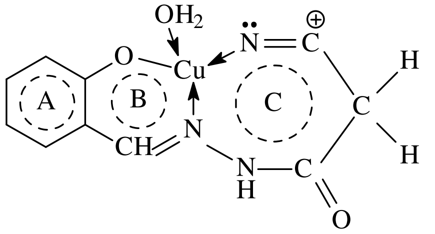
VII (CAISH)

The complexes of CASH (**VIII**) and CAISH (**IX**) are also formed by co-ordination through nitrogen atoms and by replacement of hydrogen as H^+ of the -OH group thus having two six membered rings (A) and (B) and one seven membered ring (C) analogous to trophylium ions fused with one another.

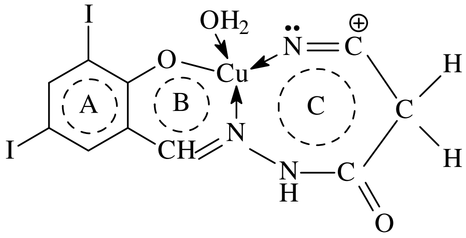
The stabilities of copper complexes for their order with the above igands can be very well explained on the basis of π electron delocalization.

The highest stability of CABH complex is due to the fact that it has a six membered planner ring structure with extensive π electron delocalization in it. The CASH and CAISH complexes can not have planner ring structure but puckered ones preventing thereby extensive electron delocalisation in them which is maximum in case of CABH complex.

The experimental data obtained for the stabilities of Cu(II) complexes with the said ligands (Table-1) clearly reveals that the stabilities of the complexes decrease with substitution of the ligand molecules and confirms the order as CABH > CASH > CAISH.



VIII Cu-CASH complex



(IX) Cu-CAISH Complex

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