

THF and nitrobenzene. The molar conductance of these complexes in nitrobenzene show that they are non-electrolytes.

The IR spectra of the ligands in solution exhibit  $\nu$ N-H mode at  $3300\text{ cm}^{-1}$  which shifts to the lower frequency region in the spectra of their complexes suggesting the involvement of  $>\text{NH}$  group(s) in coordination. Amide-I band occurring in the region  $1720\text{--}1705\text{ cm}^{-1}$  in the spectra of all the ligands except PTSC shows negative shift in  $\text{SnX}_4\cdot\text{FPTSC}$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) and remains practically unchanged in  $\text{SnCl}_4\cdot\text{APTSC}$  and  $\text{SnCl}_4\cdot\text{IPTSC}$  suggesting the coordination of the keto group in the former and its non-involvement in the latter complexes. The  $\nu\text{C}=\text{S}$  band occurring in the region<sup>3</sup>  $1350\text{--}1285\text{ cm}^{-1}$  in the spectra of the ligands registers a negative shift in the complexes  $\text{SnCl}_4\cdot\text{PTSC}$ ,  $\text{SnCl}_4\cdot\text{APTSC}$ ,  $\text{SnCl}_4\cdot\text{IPTSC}$ ,  $\text{SnCl}_3\cdot(\text{APTSC-H})$  and  $\text{SnX}_3\cdot(\text{APTSC-H})$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ), a positive shift in the case of  $\text{SnX}_4\cdot\text{FPTSC}$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) and becomes weak or almost disappears in the complexes  $\text{SnCl}_3\cdot(\text{PTSC-H})$ ,  $\text{SnX}_2\cdot(\text{FPTSC-2H})$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ) suggesting the coordination of the ligand through sulphur of the thioketo group in the first category of complexes, non-participation in bonding in the second category of complexes and removal of  $>\text{C}=\text{S}$  group presumably via enolization in the third category of complexes.

The  $\nu\text{Sn-Cl}$  is reported at  $403\text{ cm}^{-1}$  (ref. 4, 5) in  $\text{SnCl}_4$  which shifts to the lower frequency side in the octahedral complexes<sup>5,6</sup>. The presently investigated tin(IV) chloride complexes show a broad band in the region  $325\text{--}280\text{ cm}^{-1}$  which may be due to a *cis*-octahedral geometry of the complexes.  $\text{SnCl}_3\cdot(\text{PTSC-H})$  shows two widely separated bands at  $358$  and  $280\text{ cm}^{-1}$  which may be explained by assuming a chlorine bridged dimeric structure for the above complex. The higher frequency band may be due to the terminal  $\nu\text{Sn-Cl}$  while the lower frequency band may be due to the bridging  $\nu\text{Sn-Cl}$  mode. The tin-bromine and tin-iodine vibrations could not be observed because they lie beyond the range of the infrared spectrophotometer used in the present studies. The non-ligand bands occurring in the regions  $490\text{--}480$ ,  $480\text{--}465$ ,  $416\text{--}400$  and  $270\text{--}230\text{ cm}^{-1}$  may be tentatively assigned to  $\nu\text{Sn-S}$  (ref. 7),  $\nu\text{Sn-O}$  (ref. 8),  $\nu\text{Sn}\leftarrow\text{O}$  (ref. 6) and  $\nu\text{Sn-N}$  (ref. 9) modes respectively.

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#### Stepwise Formation Constants of the Chelates of Substituted Azobenzenes with Cu(II), Ni(II), Co(II), Zn(II) & Cd(II)

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Stepwise formation constants of the chelates of 3-formyl-4-hydroxy-2'-nitroazobenzene (HF2NB), 3-formyl-4-hydroxy-3'-nitroazobenzene (HF3NB) and 3-formyl-4-hydroxy-4'-nitroazobenzene (HF4NB) with Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) have been determined using the Calvin-Bjerrum titration technique. The order of the formation constants considering  $\log K_1$  is found to be  $\text{Zn(II)} < \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Cd(II)}$ . Stability constants are in fair agreement with Irving-William's order.

IN continuation of our earlier work<sup>1,2</sup> on the chelates of substituted azobenzenes, we report in this note the synthesis of 3-formyl-4-hydroxy-3'-nitroazobenzene (HF3NB) and 3-formyl-4-hydroxy-2'-nitroazobenzene (HF2NB) and the stabilities of the complexes of these ligands along with those of 3-formyl-4-hydroxy-4'-nitroazobenzene (HF4NB) with Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) employing Calvin-Bjerrum *pH* titration technique<sup>3,4</sup>. The experiments were done in 60% (w/w) ethanol-water at  $28^\circ \pm 0.1^\circ$  and  $\mu = 0.2\text{ M}$  ( $\text{KNO}_3$ ).

The ligands HF3NB and HF2NB were prepared using Analar grade chemicals by a method similar to the one reported earlier<sup>1</sup>. The nitranilines employed were recrystallized from ethanol. HF2NB is a redish brown solid, m.p.  $149^\circ$  (Found: C, 57.56; H, 3.31; N, 15.48%). HF3NB is a yellowish red solid, m.p.  $159^\circ$  (Found: C, 57.53; H, 3.30; N, 15.51%). Both require C, 57.55; H, 3.32; N, 15.50%. The IR spectra of the ligands were compatible with their structures.

All solutions were prepared in doubly distilled,  $\text{CO}_2$ -free water. Nitrogen gas presaturated with the solvent was kept bubbling through the experimental solution so as to keep an inert atmosphere. The metal solutions were prepared from the respective nitrates. The corrections in *pH* were done according to Bates<sup>5</sup>. The following solutions (total volume 50 ml) were taken and titrated against  $0.2\text{ N}$  standard sodium hydroxide: (A) 1 ml of  $4 \times 10^{-2}\text{ M}$   $\text{HClO}_4$  + 10 ml of  $1.0\text{ M}$   $\text{KNO}_3$ ; (B) A + 25 ml of  $5 \times 10^{-3}\text{ M}$  ligand solution; and (C) B + 5 ml of  $5 \times 10^{-3}\text{ M}$  metal solution. Cu(II) precipitated at 4.0, 4.2, 4.3 *pH* in the case of HF3NB, HF2NB and HF4NB respectively. The other metals precipitated between *pH* 5.0 and 6.5 with the above ligands. In the case of solution (C), fall in *pH* was observed which clearly showed the formation of complexes.

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TABLE 1 — STEPWISE STABILITY CONSTANTS OF THE DIFFERENT COMPLEXES

Metal		HF3NB				HF2NB				HF4NB			
		log $K_1$	log $K_2$	log $\beta_2$	$-\Delta F$ kcal/ mole	log $K_1$	log $K_2$	log $\beta_2$	$-\Delta F$ kcal/ mole	log $K_1$	log $K_2$	log $\beta_2$	$-\Delta F$ kcal/ mole
Cu(II)	(a)	6.20	—	6.20	8.54	6.00	—	6.00	8.26	5.82	—	5.82	8.02
Ni(II)	(a)	5.95	—	5.95	8.19	5.65	—	5.65	7.78	5.45	4.47	9.92	13.67
	(b)										9.60		
Co(II)	(a)	5.65	4.18	9.83	13.55	5.42	3.75	9.17	12.63	5.05	—	5.05	6.97
	(b)			9.80									
Zn(II)	(a)	5.40	3.95	9.35	12.88	5.15	3.90	9.05	12.47	4.80	3.67	8.47	11.67
	(b)			9.10				9.20				8.40	
Cd(II)	(a)	5.20	—	5.20	7.16	4.85	—	4.85	6.68	4.60	3.52	8.12	11.19
	(b)											7.84	

(a) Bjerrum values and (b) midpoint slope.

All the ligands were monoprotic in nature and hence gave one buffer region in their titration curves, as a result of neutralizing one equivalent of base. The protonation constants ( $pK^H$ ) were found out by the method of Irving and Rossotti<sup>6</sup> to be 7.20 and 7.30 for HF2NB and HF3NB respectively. HF4NB gave a value ( $pK^H$ ) of 7.10 in good agreement with the value reported earlier<sup>2</sup>. The protonation constants were also calculated from Eq. (1) using the direct calculation method.

$$\log K_H = \log \frac{\bar{n}^H}{\bar{n}^H - 1} + p^H \quad \dots(1)$$

The values of  $\bar{n}$  and  $pA$ , where  $\bar{n}$  is the formation function, were calculated using the method devised by Bjerrum and Calvin and formation curves for different metal systems were plotted with  $\bar{n}$  against  $pA$ . The stepwise stability constants  $\log K_1$  and  $\log K_2$  were taken directly from formation curves at points corresponding to  $\bar{n} = 0.5$  and  $\bar{n} = 1.5$  respectively. These values along with the overall value of stability constants are given in Table 1. The values of stability constants were refined using computational methods devised by Rossotti and Rossotti<sup>7</sup>. Overall changes in free energy ( $\Delta F = -RT \ln K$ ) were also calculated at 28° (Table 1).

In all the cases, Cu(II) formed only 1:1 complexes. The stabilities of the chelates taking  $\log K_1$  into consideration were in the order: Zn(II) < Cu(II) > Ni(II) > Co(II) > Cd(II), in accord with Irving-Williams order<sup>8</sup> for bivalent metal ion of 3d-series. Even though Zn(II) and Cd(II) have got the same  $d^{10}$  configuration, Cd(II) has greater ionic radius than Zn(II) and hence it forms a less stable complex.

As is seen from the  $pK$  values, out of the three nitro substituted azobenzenes, HF3NB with  $pK$  value 7.30 forms the most stable set of complexes and HF4NB with  $pK$  value 7.10 forms the least stable ones. HF2NB with  $pK$  value 7.20 forms complexes of intermediate stability.

Considering the reported values of stability constants of the methyl substituted azobenzenes, it is observed that the nitro substituted series have, in general, a diminished complex forming capacity.

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#### Formation Constants of $UO_2^{2+}$ & Th(IV) Complexes of 2,5-Dimercapto, 1,3,4-thiadiazole (Bismuthiol I)

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Stability constants of the chelates of Bismuthiol I with  $UO_2^{2+}$  and  $Th^{4+}$  have been determined in aq. ethanol at  $25^\circ \pm 0.1^\circ$  and  $\mu = 0.05, 0.1$  and  $0.15M$  using Calvin-Bjerrum titration technique. While  $UO_2^{2+}$  forms only a 1:1 complex,  $Th^{4+}$  forms 1:1, 1:2 and 1:3 complexes.

THE analytical utility of 2,5-dimercapto, 1,3,4-thiadiazole (Bismuthiol I) is now well known. Recently we have reported the nature of its Cu(I) and Cu(II) complexes<sup>1</sup>. The stability constants of its chelates with  $UO_2^{2+}$  and  $Th^{4+}$  ions, have now been determined in aq. ethanol  $pH$ -metrically using Calvin-Bjerrum titration technique at  $25^\circ \pm 0.1^\circ$  and  $\mu = 0.0, 0.1$  and  $0.15M$  maintained by adding  $1.0M NaClO_4$ .