

## Synthesis and Characterization of Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) Chelates of *o*-(N-Thiophene-2-Chloroimino) Benzoic acid, *o*-(N-Thiophene-2-Chloroimino) Propanoic acid and *o*-(N-Furan-2-Acetylimino)Benzoic acid

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The stability constants of chelates of Cr(II), Mn(II) Co(II), Ni(II) and Cu(II) with *o*-(N-thiophene-2-chloroimino) benzoic acid (HTB), *o*-(N-thiophene-2-chloroimino) propanoic acid (HTP) and *o*-(N-furane-2-acetylimino) benzoic acid (HFB) have been determined potentiometrically using Calvin extension of Bjerrum method in 30% (v/v) aqueous-ethanol ( $\mu = 0.1, 0.05$  and  $0.01N NaClO_4$ ) at 25°, 35° and 45°C respectively. Thermodynamic parameters have been evaluated. Magnetic, conductance and spectral data of the solid chelates have been employed to characterize them.

### INTRODUCTION

A survey<sup>1,2</sup> of the literature has indicated that no work has been done on Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) chelates of *o*-(N-thiophene-2-chloroimino) benzoic acid (HTB), *o*-(N-thiophene-2-chloroimino) propanoic acid (HTP) and *o*-(N-furane-2-acetylimino) benzoic acid (HFB) hence the same was undertaken and the findings are reported in the present paper.

The physicochemical investigation on the bivalent metal chelates of HTB, HTP and HFB was carried out by potentiometric, magnetic and spectral techniques with the object to compare their properties.

### EXPERIMENTAL

#### Synthesis of HTB, HTP and HFB and their bivalent(II) chelates

HTB, HTP and HFB and their bivalent(II) chelates were synthesised by the procedure reported<sup>3</sup> earlier. M.pt. (HTB) 172°C, (HTP) 103°C and (HFB) 95°C. For HTB found-C, 54.14; H, 3.00; N, 5.09; S, 11.89; and Cl, 12.32; calcd. C, 54.24; H, 3.02; N, 5.27; S, 12.05; and Cl, 12.37%, for HTP found-C, 44.06; H, 3.57; N, 6.32; S, 14.59 and Cl, 16.24; calcd. C, 44.16; H, 3.68; N, 6.44; S, 14.71 and Cl, 16.32% and for HFB found-C, 67.30; H, 4.59; N, 5.97, calcd. C, 68.02; H, 4.78 and N, 6.11%.

The purity of the ligand was checked by TLC and spectral data. The

following solutions (A-C) were prepared in 30% v/v aqueous-ethanol and potentiometric studies were carried out by Calvin's extensions of Bjerrum method<sup>4</sup>. ( $\mu = 0.01, 0.05$  and  $0.1\text{ M NaClO}_4$ ) at 25, 35 and 45°C.

(A) 10.0 ml of 0.01 M ligand + 4.0 ml 1.0 N  $\text{NaClO}_4$  + 26.0 ml of 30% water-ethanol mixture.

(B) 10.0 ml of 0.01 M ligand + 4.0 ml 1.0 N  $\text{NaClO}_4$  + 0.01 M metal ion solution + 16.0 ml of 30% water-ethanol mixture.

(C) 20.0 ml of 0.01 M ligand + 4.0 ml 1.0 N  $\text{NaClO}_4$  + 10.0 ml 0.01 M metal ion solution + 6.0 ml of 30% water-ethanol mixture.

The C, H, N, S and Cl contents of the metal complexes were determined microanalytically and the metal contents were estimated by the standard method. From the results of elemental analysis and molecular weight data 1 : 2 (metal-ligand) stoichiometry was observed.

Conductance measurement were made on a Toshaniwal Conductivity bridge. A digital pH meter type DPH-77 equipped with a glass-calomel electrode assembly was used for pH determination. Molecular masses were determined ebulliometrically in dioxane. Magnetic measurements at room temperature were made on a Gouy magnetic balance using  $\text{Hg}[\text{Co}(\text{CNS})_4]$  as the calibrant. The i.r. spectra were recorded in Nujol on a Perkin-Elmer spectrophotometer using pallets. The  $^1\text{H}$  NMR spectra were recorded on a varian-model EM-390 using  $\text{CDCl}_3$  solvent and TMS as the reference.

## RESULTS AND DISCUSSION

The values of dissociation constants (pK) of HTB, HTP and HFB as determined by interpolation of half  $\bar{n}$  values method and algebraic method, were found to be 6.22, 7.30 and 5.80 at 25°C; 6.06, 7.15 and 5.57 at 35°C; and 5.88, 6.96 and 5.45 at 45°C respectively (at  $\mu = 0.1\text{ M NaClO}_4$ ) revealing monoprotic nature of the ligands. By plotting  $\bar{n}$  vs  $-\log[\text{A}^-]$ , the formation curves of the metal-ligand system were obtained. The formation curves were refined by different computational methods<sup>5</sup> and their average values are found to follow the order in agreement with Irving-Williams<sup>6</sup> rule.

### Thermodynamic Parameters

The  $\Delta G^\circ$  of all the chelates have more negative values at 45°C than at 35°C and 25°C (accuracy  $\pm .01$ ).  $\Delta H^\circ$  values are also found negative in all the cases suggesting endothermic nature of reactions.

The positive entropy ( $\Delta S^\circ$ ) term is favourable for chelation, on incorporation of the data in Harned eqn.<sup>7</sup> the values of  $\theta$ ,  $\text{pK}_m^H$  and  $\Delta H^*$  were found to be 167.14, 4.6652, 25.59; 160.0, 5.8739, 22.71 and 224.64, 2.68, 35.25 for HTB, HTP and HFP respectively.

The magnetic moments of the hydrated chelates of HTB, HTP and

HFB with Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) were found to be 4.82, 4.79 and 4.83; 5.85, 5.84 and 5.65; 4.77, 4.81 and 4.73; 3.40, 3.34 and 3.16 and 1.85, 1.79 and 1.81 respectively. On this basis, a high-spin octahedral geometry is suggested for Cr(II), Mn(II), Co(II), and Ni(II) chelates and the Cu(II) chelates appear to have a distorted octahedral geometry.

### Electronic Spectra

The electronic spectrum of HTB, HTP and HFP chelates are summarised in Table 1.

### I.R. Spectra

In the i.r. spectra of all the ligand three major bands were observed in the regions 1700–1730, 3400–3500 and 1600–1615  $\text{cm}^{-1}$  assignable to  $\nu_{>\text{C=O}}$ ,  $\nu_{-\text{OH}}$  of COOH group and  $\nu_{>\text{C=N}}$  respectively.

TABLE 1  
ELECTRONIC SPECTRA OF Cr(II), Mn(II), Co(II),  
Ni(II) and Cu(II) OF HTP, HTB AND HFB

| Metal ion | Absorption peaks $\text{cm}^{-1}$ |              |              | Assignments   |
|-----------|-----------------------------------|--------------|--------------|---|
|           | HTP chelates                      | HTB chelates | HFB chelates |   |
| Cr(II)    | 15285                             | 15350        | 15495        | ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$                        |
| Mn(II)    | 18050                             | 17800        | 17190        | ${}^6\text{A}_{1g}(\text{s}) \rightarrow {}^4\text{T}_{1g}(\text{G})$ |
|           | 21450                             | 21560        | 21290        | ${}^6\text{A}_{1g}(\text{s}) \rightarrow {}^4\text{T}_{2g}(\text{G})$ |
|           | 26575                             | 26600        | 26120        | ${}^6\text{A}_{1g}(\text{s}) \rightarrow {}^4\text{T}_{1g}(\text{G})$ |
| Co(II)    | 8740                              | 8680         | 8720         | ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$           |
|           | 18530                             | 18590        | 17910        | ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{E})$           |
|           | 20790                             | 20810        | 19490        | ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$           |
| Ni(II)    | 10820                             | 10930        | 10340        | ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$           |
|           | 17500                             | 17390        | 17830        | ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$           |
|           | 22150                             | 22075        | 22650        | ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$           |
| Cu(II)    | 12510                             | 12480        | 12320        | ${}^2\text{E}_g \rightarrow {}^2\text{T}_{1g}$                        |

In their metal chelates peaks in the range 3400–3500  $\text{cm}^{-1}$  disappeared suggesting the deprotonation on complexation.

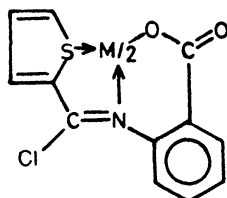
In all ligands the bands in the region 1600–1615  $\text{cm}^{-1}$  were shifted to lower frequency (15–25  $\text{cm}^{-1}$ ) in the complexes indicating coordination through azomethine nitrogen. In the i.r. spectra of the metal chelates two new broad bands were observed in the range 490–500 and 390–420 assignable to  $\nu_{\text{M-O}}$ ,  $\nu_{\text{M-N}}$  respectively and an additional band was observed in the range 280–300 due to  $\nu_{\text{M-S}}$  in HTB and HTP chelates.

**<sup>1</sup>H NMR Spectra**

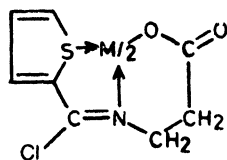
To substantiate further the bonding in these chelates <sup>1</sup>H NMR spectra of HTB, HTP and HFB. and their bivalent(II)-chelates were recorded in CDCl<sub>3</sub>/TMS. The chemical shifts values ( $\delta$ , ppm) of the different protons are as follows. The signals at  $\delta$  11.6, 11.3 and 11.5 ppm in HTB, HTP and HFB respectively due to —COOH protons disappeared in the spectra of the corresponding metal chelates. The signals due to thiophene ring sulphur both in HTB and HTP and due to furane ring oxygen in HFB appearing at  $\delta$  7.42, 7.59 ppm and 8.32 ppm respectively, shifted towards higher field in the metal chelates (*ca.*  $\delta$  0.15 to 0.2 ppm) indicating donation of lone pair of electrons to the central metal atom.

The position of signals due to —CH<sub>2</sub>—CH<sub>2</sub> multiplets in HTP at  $\delta$  3.05–3.12 ppm, signals due to methyl proton in HFB and signals due to aromatic proton multiplets both in HTB and HFB at  $\delta$  7.03 and 7.08 ppm respectively, were found unchanged in the metal chelates.

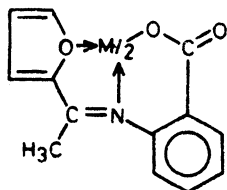
Based on the above evidences the metal chelates may be represented by the structures as shown in Fig. 1.



HTB-CHELATES



HTP-CHELATES



HFB-CHELATES

Where M = Cr(II), Mn(II), Co(II), Ni(II) and Cu(II)

Fig. 1. Structure of Bivalent Metal Chelates of *o*-(N-Thiophene-2-Chloroimino) Benzoic Acid (HTB), *o*-(N-Thiophene-2-Chloroimino) Propanoic Acid (HTP) and *o*-(N-Furane-2-Acetylimino) Benzoic Acid (HFB).

TABLE 2

THERMODYNAMIC CONSTANTS AND RELATED PARAMETERS OF BIVALENT METAL CHELATES OF *o*-(N-THIOPHENE-2-CHLORO/MINO) BENZOIC ACID (HTB), *o*-(N-THIOPHENE-2-CHLORO/MINO) PROPANOIC ACID (HTP) AND *o*-(N-FURANE-2-ACETYLMINO) BENZOIC ACID (HFB) AT 25°, 35° AND 45°C ( $\mu = 0$ )

| Metal ion | log $\beta_0$              |                            |                            | $-\Delta G^\circ$ kJ/mole   |                             |                             | $-\Delta H^\circ$ kJ/mole at 35°C | $\Delta S^\circ$ J/mole/K at 35°C |
|-----------|----------------------------|----------------------------|----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------------|-----------------------------------|
|           | 25°C                       | 35°C                       | 45°C                       | 25°C                        | 35°C                        | 45°C                        |                                   |                                   |
| Cr(II)    | 8.95<br>(8.98)<br>[8.30]   | 8.70<br>(8.80)<br>[8.06]   | 8.60<br>(8.65)<br>[7.83]   | 51.07<br>(51.24)<br>[47.36] | 51.30<br>(51.90)<br>[47.53] | 52.37<br>(52.67)<br>[47.66] | 31.75<br>(29.94)<br>[42.64]       | 63.47<br>(71.30)<br>[15.87]       |
|           | 9.35<br>(9.58)<br>[8.60]   | 9.14<br>(9.30)<br>[8.38]   | 8.95<br>(9.15)<br>[8.17]   | 55.35<br>(54.66)<br>[49.07] | 53.90<br>(54.85)<br>[49.42] | 54.50<br>(55.71)<br>[49.73] | 36.39<br>(39.01)<br>[39.01]       | 57.17<br>(51.43)<br>[33.79]       |
|           | 9.90<br>(10.15)<br>[8.85]  | 9.72<br>(9.88)<br>[8.63]   | 9.52<br>(9.75)<br>[8.40]   | 56.49<br>(57.92)<br>[50.49] | 57.32<br>(58.27)<br>[50.89] | 57.97<br>(59.37)<br>[51.15] | 34.48<br>(36.29)<br>[40.82]       | 74.16<br>(71.36)<br>[32.69]       |
| Ni(II)    | 10.50<br>(10.48)<br>[9.25] | 10.22<br>(10.20)<br>[9.05] | 10.00<br>(10.10)<br>[8.81] | 59.91<br>(59.80)<br>[52.78] | 60.27<br>(60.16)<br>[58.37] | 60.89<br>(61.50)<br>[53.64] | 45.36<br>(34.48)<br>[39.91]       | 48.41<br>(83.38)<br>[46.94]       |
|           | 10.90<br>(10.78)<br>[9.40] | 10.63<br>(10.55)<br>[9.16] | 10.42<br>(10.30)<br>[8.92] | 62.20<br>(61.51)<br>[53.63] | 62.69<br>(62.22)<br>[54.02] | 63.45<br>(62.71)<br>[54.31] | 43.55<br>(43.50)<br>[43.54]       | 62.14<br>(60.60)<br>[38.92]       |

The value in parentheses are those of the HTP-Chelates and those in square brackets are of HFB-chelates.

From the stability data and the characterization data of the metal chelates in solid state, it is suggested that they are fairly stable both in solution as well as in the solid state.

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