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PHYSICO-CHEMICAL STUDIES OF THE BIVALENT METAL CHELATES OF SOME MONOPROTIC TRIDENTATE SCHIFF BASES

o-(*N*- α -furfuralideneimino) benzene sulphonic acid (HFB) and *o*-(*N*- α -furfuralideneimino) ethane sulphonic acid (HFE), Schiff bases function as monoprotic tridentate ligands and form solid chelates with Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II). These chelates have been characterised by elemental analysis, molecular weight determination, magnetic susceptibility and conductance measurements, electronic absorption and IR spectra. The presence of nitrogen atom of the azomethine group in β -position to the sulphonic group is responsible for the general similarity in the behaviour of the chelates of the two Schiff bases.

A survey of literature^{1,2} shows that no systematic study has been carried out using orthanilic acid and taurine Schiff bases with furfuraldehyde. Taurine and orthanilic acid contain an open chain molecule and phenyl radical, respectively. Both form monoprotic tridentate Schiff bases with furfuraldehyde and these are structurally similar.

HFB and HFE were prepared by the method of Pfeiffer *et al.*³ and their metal chelates with Cr(II), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) were synthesised similar to the procedure described by Yamada *et al.*^{4,5}.

Elemental analysis and molecular weight determinations of the solid chelates indicated 1:2 metal-ligand stoichiometry. Magnetic susceptibility measurements were carried out using Gouy magnetic balance with mercury(II) tetrathiocyanatocobaltate as the reference⁶. The magnetic moments at 308° K of the Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) chelates were found 4.84, 5.92, 5.46, 5.18, 3.14 and 1.96 B.M. for HFB chelates and 4.81, 5.91, 5.41, 5.13, 3.12 and 1.92 B.M. for HFE chelates

which indicate the presence of 4, 5, 4, 3, 2 and 1 unpaired electrons, respectively.

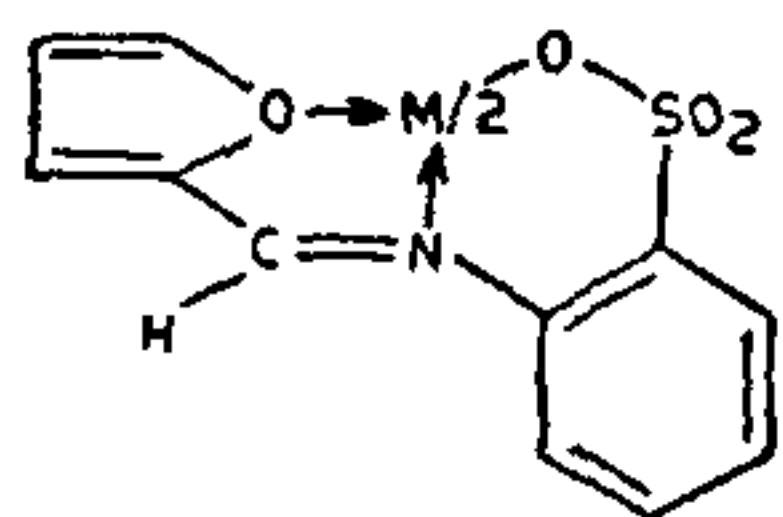
The metal chelate solutions in DMF (10⁻³ M) display negligibly small molar conductance values (3.5 to 8.7 ohm⁻¹ cm² mole⁻¹) which suggest the non-electrolytic nature of these compounds.

The electronic absorption spectra of the chloroform solution of the Cr(II) chelates of both the Schiff bases gave one absorption band at ~ 14600 cm⁻¹ ($\epsilon = 43$ – 51 mole⁻¹ cm⁻¹) assignable to the transition ${}^5E_g \rightarrow {}^5T_{2g}$. The Mn(II) chelate solutions gave two bands at ~ 24800 cm⁻¹ ($\epsilon = 52$ – 67 mole⁻¹ cm⁻¹) and ~ 29700 cm⁻¹ ($\epsilon = 70$ – 82 mole⁻¹ cm⁻¹) which can be assigned to the transitions ${}^6A_{1g} \rightarrow {}^4E_g$ (G) and ${}^6A_{1g} \rightarrow {}^4E_g$ (D) respectively. Fe(II) chelates solutions gave one absorption peak at ~ 10700 cm⁻¹ ($\epsilon = 65$ – 73 mole⁻¹ cm⁻¹) assignable to the transition ${}^5T_{2g} \rightarrow {}^5E_g$ (D). The Co(II) chelate solutions gave three bands at ~ 8700 , ~ 19800 ($\epsilon = 67$ – 72 ; 80 – 88 mole⁻¹ cm⁻¹) and ~ 21200 cm⁻¹ ($\epsilon = 92$ – 99 mole⁻¹ cm⁻¹) assignable to the transitions ${}^4T_{1g}$ (F) \rightarrow ${}^4T_{2g}$ (F), ${}^4T_{1g}$ (F) \rightarrow ${}^4A_{2g}$ (F), ${}^4T_{1g}$ (F) \rightarrow ${}^4T_{1g}$ (P), respectively. Similarly the chloroform solutions of the Ni(II) chelates gave three absorption bands with their peaks at ~ 8800 , ~ 13900 ($\epsilon = 69$ – 78 ; 87 – 94 mole⁻¹ cm⁻¹) and ~ 25700 cm⁻¹ ($\epsilon = 98$ – 108 mole⁻¹ cm⁻¹) which can be assigned to the transitions ${}^2A_{2g}$ (F) \rightarrow ${}^3T_{2g}$ (F), ${}^3A_{2g} \rightarrow$ ${}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow$ ${}^3T_{1g}$ (P), respectively. The Cu(II) chelate solutions gave only one absorption band with its peak at ~ 12600 cm⁻¹ ($\epsilon = 118$ – 130 mole⁻¹ cm⁻¹) assignable to the transition ${}^2E_g \rightarrow {}^2T_{2g}$. These data including the low molar extinction coefficient values suggest octahedral structure for all the metal chelates under investigation.

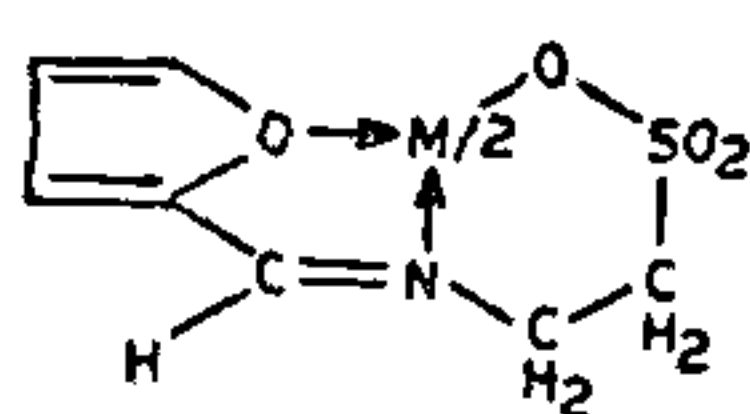
IR spectra of HFB and HFE consist of two bands in the narrow ranges of 1150–1140 cm⁻¹ and 1610–1600 cm⁻¹ assignable, respectively to ν -SO₃H and ν C=N. In the spectra of the metal chelates the bands in the range of 1150–1140 cm⁻¹ are absent suggesting co-ordination through sulphonic group. ν C=N of HFB and HFE in the range of 1610–1600 cm⁻¹ was shifted to lower frequency side on complexation suggesting participation of azomethine nitrogen in co-ordination. The appearance of two new bands in the ranges of 620–610 cm⁻¹ and 550–540 cm⁻¹ in the metal chelates indicate the formation of M-O and M-N bonds, respectively, in them.

Based on the above data the metal chelates may have the structure as shown in Fig. 1.

The results so far obtained conclusively show that the general similarities of the chelates of HFB and HFE are not due to the presence or absence of an open chain or a six-membered ring but it is due to the presence of nitrogen atom of the azomethine group in β -position to the sulphonic group. This result is also in agreement with an earlier finding⁷.



HFB-CHELATES



HFE-CHELATES

WHERE $M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II)$ AND $Cu(II)$

FIG. 1 METAL CHELATES OF *o*-(*N*- α -FURFURALIDENE IMINO) BENZENE SULPHONIC ACID (HFB) AND *o*-(*N*- α -FURFURALIDENE IMINO) ETHANE SULPHONIC ACID (HFE).

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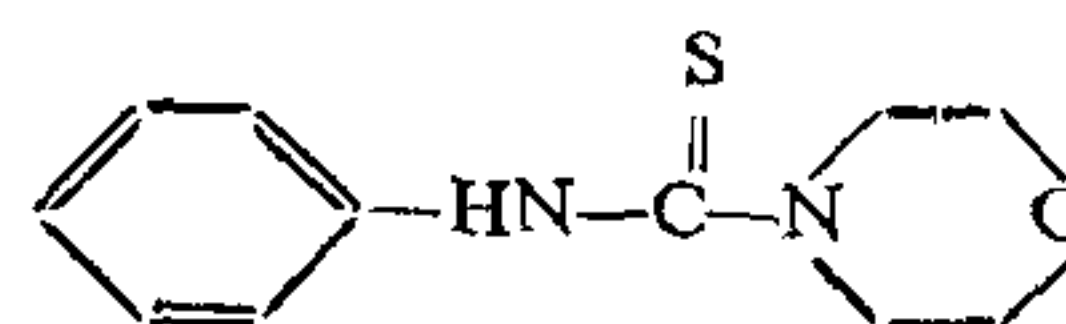
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COMPLEXES OF MORPHOLINE-4-THIOCARBONIC ACID ANILIDE WITH TELLURIUM(IV) AND TELLURIUM(II)

TETRAMETHYLTHIOUREA has been reported to form complexes with both $Te(IV)^{1-3}$ and $Te(II)^4$ whereas thiourea and its other substituted derivatives studied

have been shown to stabilise only $Te(II)^5$. While extending on the reported work⁶ on complexation tendencies of morpholine-4-thiocarbonic acid anilide (MTA),



we found that this ligand interacted with $Te(IV)$ in hydrochloric and hydrobromic acid media to yield $TeCl_4 \cdot 2MTA$ (A) and $TeBr_4 \cdot 2MTA$ (B), respectively and in hydroiodic acid medium to yield $TeI_2 \cdot 2MTA$ (C). This is the only second example where a thio-urea is shown to form $Te(IV)$ complexes.

Complexes A and B were prepared by treating 0.8 g (5 mM) of TeO_2 dissolved in 7 ml conc. HCl/HBr with 2.2 g (10 mM) of MTA dissolved in 30 ml acetone. Both A and B were precipitated in near quantitative yield and were washed with dilute HCl/HBr and dried in vacuum. The complex C was precipitated slowly in 30 minutes on mixing solutions of 0.4 g (2.5 mM) TeO_2 in 30 ml of 2M HI and of 3.3 g (15 mM) MTA in 30 ml acetone.

The analytical data on the complexes is reported in Table I. The oxidation state of tellurium, in addition to being derived from elemental analysis, was also checked by treatment of the complexes in hydrohalic acid media with excess sodium diethyldithiocarbamate (Na DDTC) and testing by analysis whether the resulting dithiocarbamate preparations were Te^{IV} (DDTC)₄⁷ or Te^{II} (DDTC)₂⁸. Iodide has been recently reported⁹ to cause greater redox reactivity in complexes of tellurium with sulphur ligands and this is illustrated in the present work also. The complexes were indefinitely stable under non-humid conditions and were readily decomposed on contact with water, methanol and ethanol in absence of hydrohalic acids.

$TeCl_4 \cdot 2MTA$ and $TeBr_4 \cdot 2MTA$ were nonconducting in dichloromethane solutions and osmometric studies (concentration range : 0.0003 M; solvent:

TABLE I

Compound	Colour	% composition					
		Te	X	C	H	N	S
$TeCl_4 \cdot 2MTA$ (A)	Yellow	17.60 (17.86)	19.61 (19.86)	37.10 (36.99)	3.90 (3.95)	7.50 (7.84)	9.20 (8.96)
$TeBr_4 \cdot 2MTA$ (B)	Orange	13.40 (14.31)	36.30 (35.83)	30.00 (29.62)	3.10 (3.16)	6.40 (6.28)	7.30 (7.19)
$TeI_2 \cdot 2MTA$ (C)	Red orange	15.71 (15.45)	31.40 (30.73)	31.80 (31.99)	3.36 (3.41)	6.69 (6.78)	7.83 (7.76)

X = halide; expected values in parenthesis.