



NOTE

Furfural Hydrazone Complexes of Fe(II), Co(II), Ni(II) and Cu(II) Chlorides

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Furfural hydrazone and its Fe(II), Co(II), Ni(II) and Cu(II) chlorides complexes were synthesized and characterized. The Co(II) and Fe(II) complexes assume an octahedral geometry while the Ni(II) and Cu(II) complexes are probably of distorted octahedral geometry. The ligand coordinated *via* the furan oxygen and the azomethine nitrogen, the bioassay of the ligand and complexes are encouraging.

Key Words: Furfural hydrazone, Complexes, Fe(II), Co(II), Ni(II), Cu(II).

Considerable attention has been focused on the chemistry of hydrazones due to their pharmacological activity, specifically on the account of their antifungal and antibacterial activity^{1,2}. This interest is due to their versatility in their coordination ability to yield stereochemistry of higher coordination number³.

Quiet a number of shift bases contains N, S and O donors and their metal complexes are available in the literature⁴ this may be concern to their anticarcinogenic and antiviral activities⁵.

In this work, we reported the synthesis of furfural hydrazone and its complexes with Co(II), Ni(II), Fe(II) and Cu(II) chloride and of their microbial activity.

The reagents and chemicals are products of BDH Ltd. and were used without further purification. All the solvents used were of analytical grade.

Synthesis of ligand (FH): The ligand furfural hydrazone (FH) was prepared by adding furfural (31.4 mL, 0.38 mol) to anhydrous hydrazine (24 mL, 0.76 mol) in 50 mL absolute ethanol, containing 1 mL of glacial acetic acid in a 250 mL beaker. The mixture was stirred continuously for 0.5 h. The resultant precipitate was filtered, recrystallized in ethanol and dried over CaCl₂ in a vacuum desiccators.

Synthesis of complexes [Cu(FH)₂]Cl₂: 3 g of furfural hydrazone in 20 mL of ethanol was added to 15.29 g CuCl₂ in 20 mL of deionized water in 250 mL beaker, with stirring. The stirring was continued for further 0.5 h and the resulting crystals were filtered and recrystallized in methanol, dried and stored over CaCl₂ in a vacuum dessicater.

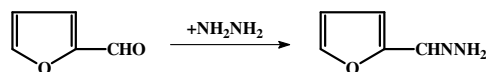
Similarly the following complexes were synthesized accordingly; [Fe(FH)₂]Cl₂, [Co(FH)₂]Cl₂ and [Ni(FH)₂]Cl₂.

The infrared spectra was run on a FTIR spectrophotometer, the electronic spectra on pye-unicam SP8-100 UV-

Visible spectrophotometer. The room temperature magnetic susceptibilities of the complexes were run on a MBS auto-magnetic susceptibility balance, while the melting point was taken on Gallenkamp melting point apparatus. The metals and chloride ion were determined titrimetrically, according to standard method⁶.

Microbial analysis: The microbial activity of the ligand and complexes were tested against *Staphylococcus aureus*, *Bacillus subtilis*, *Shigella flexneri*, *Pseudomonas aeruginosa* and *Klebstella pneumonias* by algal-well diffusion method⁷.

The furfural hydrazone (FH) synthesis was achieved with good yield. The crytal is soluble only in polar solvent with a melting point of 99 °C.



The complexes however were of low yields of between 22-38 % and equally soluble in polar solvents as shown by their physico-chemical properties (Table-1).

Infrared spectra: The IR spectra data as given in Table- 2, shows the $\nu(\text{OH})$ obscuring the $\nu(\text{NH})$ bands in both the ligand and complexes. The $\nu(\text{OH})$ of the ligand at 3407 cm^{-1} is attributed to the hydrogen bonding of the oxgen of the furfural hydrazone and hydrogen atom of the methine side chain. The $\nu(\text{OH})$ of the complexes are however due to the water molecule of the complexes. The $\nu(\text{C}=\text{N})$ band of the ligand was shifed between $6-8\text{ cm}^{-1}$ in the complexes, suggesting the participation of the azomethine nitrogen in the coordination⁷ while the $\nu(\text{C}=\text{O})$ band of the furfural at 1006 m^{-1} was shifted between $10-18\text{ cm}^{-1}$ in the metal complexes, indicates ligation of the oxygen atom of furfural to the metal.

TABLE-1
 PHYSICO-CHEMICAL DATA OF LIGAND AND ITS COMPLEXES

Compound	m.f.	m.w.	Colour	m.p. (°C)	Yield (%)	Solubility	C	H	N	M	Cl
FH	C ₅ H ₆ N ₂ O	110	Dark brown	99	84	EtOH, MeOH	54.46 (54.69)	15.380 (5.45)	25.24 (25.45)	-	-
Fe(FH) ₂ Cl ₂ ·H ₂ O	C ₁₀ H ₁₄ N ₂ O ₂ Cl ₂ Fe	321	Redish brown	192	33	EtOH	37.28 (37.38)	4.18 (4.36)	8.68 (8.72)	17.22 (17.44)	21.89 (22.1)
Co(FH) ₂ Cl ₂ ·H ₂ O	C ₁₀ H ₁₄ N ₂ O ₂ Cl ₂ Co	324	Light brown	129	22	EtOH, MeOH	36.86 (37.04)	4.24 (4.32)	8.58 (8.64)	21.88 (21.91)	18.18 (18.21)
Ni(FH) ₂ Cl ₂ ·H ₂ O	C ₁₀ H ₁₄ N ₂ O ₂ Cl ₂ Ni	324	Brown	102	38	EtOH, MeOH	36.92 (37.04)	4.12 (4.32)	8.74 (8.64)	21.82 (21.91)	18.14 (18.21)
Cu(FH) ₂ Cl ₂ ·H ₂ O	C ₁₀ H ₁₄ N ₂ O ₂ Cl ₂ Cu	324	Green	126	29	EtOH, MeOH	36.22 (36.47)	4.18 (4.25)	8.62 (8.51)	19.68 (19.45)	21.42 (21.58)

 TABLE-2
 IR DATA (cm⁻¹) OF FH AND ITS METAL COMPLEXES

Compound	v(OH, NH)	v(C=N)	v(C=O)	v(N-N)
FH	3407	1631	1006	1022
Fe(FH) ₂ Cl ₂ ·H ₂ O	33509	1625	1114	1018
Co(FH) ₂ Cl ₂ ·H ₂ O	3386	1625	1116	1018
Ni(FH) ₂ Cl ₂ ·H ₂ O	3411	1639	1120	1022
Cu(FH) ₂ Cl ₂ ·H ₂ O	3392	1623	1124	1022

Electronic studies: The electronic spectra of the complexes were run in ethanol (Table-3), the magnet moments values of Fe and Co complexes are 5.26 and 4.78 B.M., respectively, which is in the range of octahedral complexes³, while the Ni and Cu complexes have values of 2.21 and 1.18 B.M., respectively. The electronic spectral of the Co(FH)₂Cl₂·H₂O shows a band assigned to the ⁴T_{1g}→¹A_{2g} transition, that of Fe(AH)₂Cl₂·H₂O show a band at 30075 cm⁻¹, which is assigned to the ⁴T_{1g}→¹A_{2g} *e.g.* transition, both of which are of normal octahedral symmetry. On the other hand the complex Ni(FA)₂Cl₂·H₂O shows two bands which are assigned to the ³T_{2g}→³A_{1g} (p) and ³T_{2g}→³A_{1g}(F) transitions, while that of Cu(FH)₂Cl₂·H₂O shows a band which was assigned to *d-d* transitions, both of distorted octahedral symmetry⁸.

 TABLE-3
 ELECTRONIC AND MAGNETIC DATA

Compound	λ _{max} (cm ⁻¹)	Assignment	μ _{eff}	Symmetry
Fe(FH) ₂ Cl ₂ ·H ₂ O	30675	⁶ A _{1g} → 4A _{1g} , ⁴ E _g	5.28	Octahedral
Co(FH) ₂ Cl ₂ ·H ₂ O	28818	⁴ T _{1g} → 4A ₂	4.66	Octahedral
Ni(FH) ₂ Cl ₂ ·H ₂ O	25641 13793	⁶ A _{1g} → 4A _{1g} (P) ³ A _{2g} → 2T _{1g}	2.28	Distorted Octahedral
Cu(FH) ₂ Cl ₂ ·H ₂ O	12345	d - d	1.24	Distorted Octahedral

Microbial test: The result of the microbial screening of the ligand and four complexes as given in Table-4, show negative

activity of the ligand to the organisms with exception of *S. flexneri* and *P. aeruginosa*, which shows partial activity. The Cu(II) and Co(II) complexes shows moderate activity against *P. aeruginosa* and *S. flexneri*, respectively. Otherwise most of the complexes shows negative activity against the tested organisms. There is no correlation of the activity of ligand to the microbial organisms on complexation. In all, the activities of the compounds were only mild in the cases where it is positive.

 TABLE-4
 BIOASSAY OF THE COMPOUNDS

Compound	<i>S. aureus</i>	<i>B. subtilis</i>	<i>S. flexneri</i>	<i>P. aeruginosa</i>	<i>K. pneumoniae</i>
FH	-	-	=	+	-
Fe(FH) ₂ Cl ₂ ·H ₂ O	+	+	-	-	-
Co(FH) ₂ Cl ₂ ·H ₂ O	-	-	-	++	-
Ni(FH) ₂ Cl ₂ ·H ₂ O	-	-	-	-	-
Cu(FH) ₂ Cl ₂ ·H ₂ O	-	+	++	-	+

+ Fairly active, ++ moderately active, - non active

In conclusion, the shift in v(C=O) and v(C=N) implies the binding to the metal ion and the compound have low biological activity towards the tested organisms.

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