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## A mixture of ethanolic solution of Magnetic Studies of Some Transition Metal Complexes

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### **ABSTRACT**

A number of new mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) containing diphenylamine-2-carboxylic acid (DPHC) and furfural dine-2-amino thiazole (FAT) have been synthesized and characterized by elemental analysis, TLC, conductivity measurements and IR spectral data.

**Key Words:** Synthesis, Transition metal, Complexes, Diphenylamine, Schiff base.

Complexes besides being academically important<sup>1</sup> have assumed analytical<sup>2</sup>, industrial<sup>3</sup>, pharmaceutical, medical, toxicological<sup>4</sup> and biochemical importance<sup>5</sup>. The metal complexes of nitrogen containing ligands have been found more biologically active<sup>6</sup> in comparisons to the ligand having other donor sites.

The present paper describes the mixed – ligand complexes<sup>7</sup> of  $M^{2+}$  ions ( $M=Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $Zn(II)$ ) with diphenylamine-2-hydroxy-2-carboxylic acid as primary ligand and furfural dine-2-aminothiazole as secondary ligand.

(a) Synthesis of diphenylamine-2-hydroxy-2-carboxylic acid (DPHC): Both o-chlorobenzoic acid (0.003M) and o-aminophenol (0.003M) were taken in 1:1 molar ratio in 100ml distilled water in flask fitted with a water condenser. The mixture was slightly alkaline with  $K_2CO_3$  solution and a little copper oxide was added to it. The contents were refluxed on water – both for about 5 h . After decolorizing with charcoal, the contents were filtered, concentrated and cooled. The obtained solution was acidified with dilute HCL in excess till the precipitation of the resultant product was complete. It was filtered in cold, dried and re-crystallized from alcohol to obtain a brown powder.

(b) Synthesis of furfural dine- 2-aminothiazole (FAT): A mixture of furan – 2 – aldehyde 1.70ml ( $2 \times 10^{-2}$  mole) and 2- aminothiazole 2.0g ( $2 \times 10^{-2}$ mole) in 50 ml dry ethanol was dissolved and refluxed for 12h over a water- bath. The solution thus obtained was cooled at room temperature and the excess of ethanol was almost distilled off under pressure. On keeping the obtained viscous solution at room temperature for one week a solid product was obtained. It was washed with acetone followed by ether and finally re- crystallized from methanol and dried.

### **Synthesis of Metal Complexes**

A mixture of ethanolic solution of metal acetates [ 0.10g (AcO)<sub>2</sub> Cu H<sub>2</sub>O) 0.12g (AcO)<sub>2</sub> Ni 4H<sub>2</sub>O, 0.13g (AcO)<sub>2</sub> Co.H<sub>2</sub>O, 0.11g (AcO)<sub>2</sub> Zn. 2H<sub>2</sub>O] DPHC (0.13g X  $10^{-4}$  mole) and FAT (0.98g,  $5 \times 10^{-4}$ mole) was refluxed for 3h after maintaining pH ca,6. On cooling, the complex precipitated out, which was filtered,wased with ethanol and dried in a vacuum desiccators over anhydrous CaCl<sub>2</sub>.N,S and metal in complexes were determined by the standard method<sup>9</sup> C and H analyses were performed (table-1).Molar conductance was measured in  $10^{-3}$  M<sup>3</sup> dry DMF solution using Toshniwal Conductivity bridge; IR spectra were recorded on Perkin- Elmer Model 577 (Table- 2). Antimicrobial data was shown in table- 3

### **RESULT AND DISCUSSION**

Analytical data of complexes suggest their 1: 1: 1(MLL) stoichiometry and the conductivity measurement reveal their non- electrolytical nature.

The ligand DPHC revealed characteristic IR band one at  $3010\text{cm}^{-1}$  and  $1750\text{cm}^{-1}$  ( $>\text{OH}$  and  $>\text{C}=\text{O}$  carboxylic stretching vibration). In the IR spectra of metal complexes, the band due to ( $-\text{NH}$ ) is shifted to negative side by  $30-40\text{cm}^{-1}$  which indicates the involvement of this ligand in bonding with metal ions through nitrogen atom. The OH band of carboxylic group disappeared on complexation with metal ions due to the deprotonation from (M\_ OOC) bond. Another ligand FAT exhibits IR bands at  $1650\text{cm}^{-1}$  ( $>\text{C} = \text{N}$  azometine stretching ),  $1485\text{cm}^{-1}$  and  $1525\text{cm}^{-1}$  (breathing vibration of thiophene and furan ring) in the lower frequency region showing the coordination of metal with ligand. Some new band corresponding to (M-O), (M- N), (M-S) also

present in the IR spectra of the complexes respectively at 550, 445 and 335  $\text{cm}^{-1}$  which further support the chelation the two ligands with metal ions through the coordination site. The ligands and there metal complexes were screened for antibacterial and antifungal activities against two bacterial, staphylococcus aureus and Escherichia coli and two common fungi. Aspergillus and Candida albicans, by serial dilution method.

**TABLE – 1****PHYSICAL AND ANALYTICAL DATA OF SYNTHESIZED COMPOUND**

Compound (m.f)	Colour	Mw Found (Calcd.)	m.p/d.p.(°C)	% Analysis Found (Calcd.)				
				C	H	N	S	M
DPHC ( $\text{C}_2\text{H}_{11}\text{NO}_3$ )	Brown	245 (229)	144	69.20 (68.11)	4.93 (4.80)	5.91 (6.12)	-	-
FAT ( $\text{C}_8\text{H}_6\text{N}_2\text{O}_5$ )	Brown	196 (178)	126	54.52 (53.93)	3.86 (3.37)	15.26 (15.73)	17.72 (17.91)	-
CO(II)-DPHC-FAT ( $\text{C}_{21}\text{H}_{16}\text{O}_4\text{N}_3\text{SNi}$ )	Blackish Brown	396 (376)	270	38.60 (38.32)	5.55 (5.05)	10.57 (11.17)	8.11 (8.51)	0.644 (0.156)
Ni(II)-DPHC-FAT ( $\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}_4\text{SNi}$ )	Brown	400 (376)	250	38.64 (37.32)	5.58 (5.07)	10.67 (11.17)	8.08 (8.51)	0.648 (0.156)
Cu(II)-DPHC-FAT ( $\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}_4\text{SCu}$ )	Brownish Black	410 (381)	260	38.09 (37.79)	5.40 (4.98)	10.52 (11.02)	7.89 (8.39)	15.99 (16.79)
Zn(II)-DPHC-FAT ( $\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}_4\text{SZn}$ )	Brown	405 (381)	230	38.15 (37.89)	5.37 (5.00)	11.73 (11.03)	7.92 (8.42)	15.67 (16.57)

**TABLE -2**

KEY INFRARED SPECTRAL BANDS (Cm<sup>-1</sup>) OF METAL COORDINATION COMPOUNDS

DPHC	FAT	Co(II)	Ni(II)	Cu(II)	Zn(II)	Probable assignments
		DPHC- FAT	DPHC- FAT	DPHC- FAT	DPHC- FAT	
3350	-	-	-	-	-	V(OH)(phenolic)
3300	-	-	-	-	-	V(OH)(carboxylic)
3010	-	2990	2995	2990	2995	V(NH)
1750	-	1720	1725	1725	1730	>C=O(Carboxylic)
-	1625	1615	1610	1615	1610	>C=N( azomethine stretching)
-	1525	1510	1510	1515	1505	Breathing vibration of furan ring
-	1485	1475	1470	1465	1460	Breathing vibration of thiophene ring
-	-	545	540	540	535	v(M- o)
-	-	440	445	435	440	v(M-N)
-	-	335	340	335	340	v(M- S)

**TABLE -3**

ANTIMICROBIAL ACTIVITY DATA (MIC VALUES) IN MOLAR CONCENTRATION (X 10<sup>-5</sup>) OF SYNTHESIZED COMPOUNDS

S.No	Compound	Bacterial		Fungi	
		S. aureus	E.coli	A.nidulans	C. albicans
1	DPHC	20.80	20.80	41.60	41.60
2	FAT	7.20	7.20	14.40	14.40
3	Co(II)-DPHC-	4.82	4.82	9.64	9.64
4	Ni(II)- DPHC-FAT	4.80	4.80	9.60	9.60
5	Cu(II)- DPHC-FAT	4.70	4.70	9.40	9.40

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6	Zn(II)- DPHC - FAT	4.81	4.81	9.62	9.62
7	Standard	4.36	4.36	8.30	8.30

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Abbreviation: S. aureus - Staphylococcus aureus, E. coli - Escherichia coli

A. Nidulans - Aspergillus nidulans, C. albicans- Candida albicans.

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