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Synthesis, Characterization and Antimicrobial Activity of Transition Metal Complexes of Schiff base

K. Venkatesh[a], L.Venkata Reddy[a], K.B.Chandra Sekhar[b], K.Mukkanti[a]*

Center for Chemical science & Technology, Institute of Science and Technology,
J.N.T.University, Hyderabad – 500072, India.

*Corres. author: kmukkanti@yahoo.com

Abstract: 2-(2,3Diemethyl-phenylamino)-benzoic acid hydrazide (DPBN) is a shiff base. DPBN is synthesized starting from Mefenamic acid. Due to higher biological activity of Schiff bases and their metal complexes, metal complexes of DPBN have been synthesized with Co (II), Zn (II) and Cu (II). The metal complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibility measurements and spectral analysis. The metal complexes were found to show higher antimicrobial sensitivity than DPBN.

Key words: DBPN, Metal complexes, Antimicrobial activity.

Introduction:

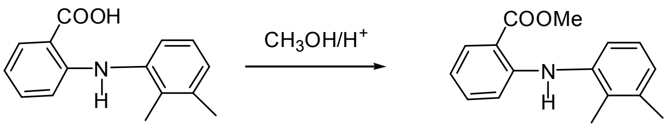
Mefenamic acid is a non-steroidal anti-inflammatory drug used to treat pain, including menstrual pain.[1]. Generally Schiff bases are used in chemical and pharmalogical properties. Recent interest in the synthesis and investigation of Schiff base chelates were supported to exhibit antimicrobacterial activity against *Salmonella* Typhai, *Enterococcus fecalis, and Eschesichia coli* by spore germination inhibition method [2-4]. The zinc (II) is found to occur in several enzymes such as dehydrogenases, aldoses, peptidases, phosphates, etc. Zinc is also necessary for the formation of tryptopham. Copper is found in both plants and animals [5]. A number of copper proteins, including enzymes have been isolated. Known copper proteins are predominantly oxidases or reversible oxygen carriers [6]. The complexes of Co (II) with Schiff base ligands have been studied with greater interest because of the varied structural types. The Schiff bases have been contributed to a large extent to the development of coordination chemistry of Co (II) [7].

Experimental

All the chemicals are reagent grade. Solvents were dried and distilled before use according to standard procedures [8].

Synthesis of Ligand:

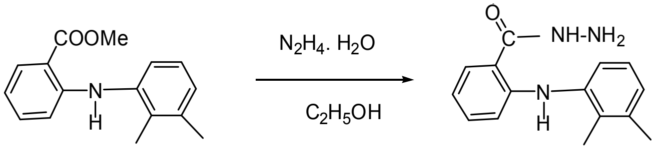
Step 1.



To a solution of Mefenamic acid (5.0gm,0.02mol) in MeOH (15ml) carefully.The solution was refluxed for 16-18 hours and the progress of the reaction ,solvent was evaporated .The crude was added to water ,neutralized by 2 mol NaOH (until ph is 7.0) and finally extracted with CHl3(3x25 mL).The combined chloroform layer was washed with brine . Dried over anhydrous Na2SO4 and con under the reduced pressure .The residue obtained was purified by column chromatography on silica gel to afford the desired product as white solid .

White solid………….. 4.1 gm,(yield 80%)
Melting point…………96-98
R_f……………… ….0.80 (3:2 ethyl acetate / n-hexane)

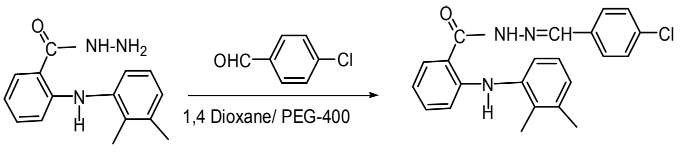
Step 2.



A solution of ester (1g,0.004 mol)in EtOH (10 mL) was added hydrazine hydrate (2 mL) drop wise and the solution was stirred .The temperature of the mixture was raised gradually to 95-100c and and was maintained for 12 hours .The aqueous layer was extracted with chloroform (3x25ml).The organic layer were collected .The combined washed with brain (10mL),dried anhydrous NaSO4 and concentrated under reduced pressure .The solid was purified by crystallization from EtOH, filterd and dried to give the desired compound as yellow colour solid.

White solid………….. 0.82 gm,(yield 80%)
Melting point………… 118-120c
R_f………………… 0.3 (3:2 ethyl acetate / n-hexane)

Step 3.



Solution of Acid hydrazine (2.65 g,0.01 mol) dissolved in 15 ml of 1,4 Dioxane stirred 10-15 minutes after the added aldehyde (P-chloro benzaldehyde) and the stirred at the room temperature .The progress of reaction monitored by TLC after the completion the reaction mixture was diluted by using ice cold water (25mL) with stirring. The solid separated was filtered, washed with ice cold water and recrystallisation from EtOH to afford the expected product(DPBN) obtain yellow colour solid.

White solid………….. 0.92 gm, (yield 80%)
Melting point………… 168-170c
R_f……………… 0.37 (3:2 ethyl acetate / n-hexane)

Synthesis of Metal complexes:
Analytical grade metal salts were oven dried overnight at 115^0C and stored in desiccators. DPBN complexes of Co (II), Cu (II), and Zn (II) were synthesized by refluxing the respective metal salt solution (0.135M, 20ml) and DPBN (0.05M, 20ml) in 1,4 Diaxane medium. The reaction mixture was refluxed for 2 hours. Then to provide basic medium for complexation dilute ammonium hydroxide solution was added. The mixture is refluxed further for 13-16 hours. The solid complexes separated out were filtered in hot condition, washed with hot 1,4 Diaxane and water to remove unreacted ligand and metal ion, then finally washed with petroleum ether and dried in vacuum. Recrystallization of complexes is effected from DMF-ethanol mixture. Yield 60-75%.

Results & Discussion

All the complexes are quite stable to air and moisture. All the complexes are amorphous and are readily soluble in 1, 4 Dioxan, DCM and PEG-400. From the elemental analysis it is evident that all the complexes of DPBN were formed in 1:2 compositions. From the conductivity data recorded with the solution prepared in, 1, 4 Dioxane it is evident that the complexes are non-electrolytes [9].

Magnetic moments
Co (II) complexes are showing the magnetic moment in the range of 5.05-5.14BM indicating that the Co (II) complexes are typically high spin complexes and having octahedral structure. The Cu (II) complexes are paramagnetic and give higher magnetic moment of 2.06-2.11BM as compared to spin only values is presumably due to spin-orbit coupling. The Zn (II) complexes are diamagnetic due to nonavailability of unpaired electrons [10-13].

Physical and analytical data of metal complexes are presented in table-1. The absence of chloride is indicated by negative test. This clearly indicates that chloride is neither present in coordination sphere nor out side the sphere of complex.

Table-1 Physical and analytical data of metal complexes

Ligand/ Complex	Mol. For	Mol.Wt	Yield	%C (%Cal)	%H (%Cal)	%N (%Cal)	%Metal (%Cal)	μ effect	Molar Conductance
DPBN	$C_{15}H_{17}N_3O$	255.3	80%	69.50 (70.56)	6.52 (6.71)	16.86 (16.46)		--	--
$Co(L)_2$	$(C_{15}H_{11}N_3O)_2Co$	565	66%	62.52 (63.71)	3.53 (3.89)	14.83 (14.86)	10.20 (10.26)	5.09	06
$Cu(L)_2$	$(C_{15}H_{15}N_3O)_2Cu$	572.1	71%	62.19 (62.92)	5.02 (5.24)	14.58 (14.68)	10.98 (11.08)	2.10	03
$Zn(L)_2$	$(C_{15}H_{15}N_3O)_2Zn$	574	73%	62.16 (62.72)	5.18 (5.22)	14.57 (14.63)	11.32 (11.37)	--	02

Table 2. Antimicrobial activity of the ligand DPBN and its complexes

S.No	Compound	Antimicrobial activity of zone of inhibition,mm		
		E.faecalis	*S.Typhi*	*E.Col*
1	DPBN	4	4	4
2	Co(II)-DPBN	6	5	8
3	Cu(II) -DPBN	5	5	5
4	Zn(II) -DPBN	8	7	8

IR spectrum of DPBN showed characteristic peaks at νNH_2 3321, Cm^{-1}, νNH (2^0) 3321.53 Cm^{-1}, $\nu C=O$ 1633.76 Cm^{-1}, $\nu C=N$ 1653 Cm^{-1}. IR spectra of complexes have been studied extensively, from the IR spectra of the complexes it is evident that $\nu C=O$ peak observed in ligand is shifted to lower frequencies in its complexes. The new peak in the region of 1670-1600Cm^{-1} in the complexes is due to formation of –C=N in ring during complex formation[14].

The carboxy stretching frequency observed at 1633.76 Cm^{-1} in the ligand IR spectrum is not observed in all the complexes and an extra peak observed in the region of 1200Cm^{-1} may be assigned to >C-O- in the complexes this also indicates deprotonation from oxygen via enol form [15]. The ligand exhibits three bands in the region of 3321-3100 Cm^{-1}, which are assigned to NH & NH_2 stretching. The intensity of these bands is considerably shifted in metal complexes. .In case of Cu (II) complexes, from HSAB principle it may be predicted that 'N' which is a borderline base would have more affinity towards Cu (II) ion, which is a borderline acid [16-17].

The electronic spectral data of Co (II), Cu (II) and Zn (II) complexes of the ligand DPBN were recorded. The electronic spectra of Co(II) exhibit bands in the region of 18123 – 20618 cm^{-1} and 27548 – 35211 cm^{-1} are attributed to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) , $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and CT/LC transitions respectively supporting the Octahedral geometry for Co(II) complex [18].

The electronic spectra of Cu (II) exhibit bands in the region of 22000 – 36231 cm^{-1} are attributed to $^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1) and CT/LC transitions respectively supporting the square planner geometry for Cu (II) complex. The electronic spectra of Zn (II) exhibit bands in the region of 24038 cm^{-1} are attributed to CT/LC transitions respectively supporting the tetrahedral geometry for Zn(II) complex [19] .

Antimicrobial activity:

Metal complexes were screened for antibacterial activity against gram-positive bacteria *Enterococcus faecalis (E.faecalis)*, Salmonella Typhi (*S.Typhi)* and gram-negative bacteria Eschesichia Coli (*E.Col)i.* The testing was carried out using 100µg/mL of sample in DMF. Sensitivity plates were seeded with bacterial inoculums of $1X10^6$ CIU/mL and each cup (dia 10mm) was loaded with 0.1mL of test solution. The DPBN zones of inhibition were recorded after incubation for 24hrs[20]. The zones of inhibitions of the antimicrobial activity have been presented in Table 2.

Conclusion:

The elemental analysis, Magnetic susceptibility, electronic, IR and conductivity studies suggests the Metal complexes are in 1:2 ratio and a square planer geometry for Cu(II) ,tetrahedral geometry for Zn(II) and an octahedral geometry for Co(II) complexes. On the basis of chelation theory, metal complexes have more biological activity than the free ligand.

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