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Synthesis and characterization of transition metal complexes of bidentate ligands and their antimicrobial studies

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ABTRACT

The solid complexes of Cu (II), Ni (II), Co (II), Zn (II), Mn (II) and Fe (III), were prepared from bidentate Schiff base derived from 2-aminopyridine and 2, 5-dihydroxy acetophenones. The synthesized metal complexes were characterized by molar conductivity, magnetic susceptibility, thermal analysis, FTIR, ^{1}HNMR, and UV-Visible spectra. The analytical data of these complexes show metal ligand ratio 1:2. The physicochemical study supports the square planar geometry around Cu (II), Zn (II), Mn (II) and octahedral geometry around Co (II), Fe (III) and Ni (II) ions. The molar conductance values of metal complexes suggest their non electrolytic nature. The IR spectral data reveals that the ligand behaves as bidentate with ON donor atoms sequence towards central metal ion.

Antibacterial and antifungal activities of ligands and its metal complexes were performed in vitro against *E.coli, S. typhi, S. aureus, B. subtilis* and against various fungi like *P.chrysogenum, A. niger, F. moniliformae, and A.Flavus.*

KEYWORDS

Bidentate schiff bases;
Metal complexes;
Spectral analysis;
Antibacterial activity;
Antifungal activity.

INTRODUCTION

The field of Schiff base complexes is fast developing because of the wide variety of possible structures for the ligands depending on the aldehyde and amine used. Many Schiff bases and their complexes have been widely studied because of their industrial and biological applications[1,2]. Schiff bases of hydroxyl aldehydes and ketones were widely used in the coordination chemistry for the preparation of metal complexes[3,4]. The Schiff bases of hydroxyl acetophenone and its complex have a variety of applications in biological, clinical, analytical and pharmacological areas[5-7].

Here we report the synthesis and characterization of such bidentate Schiff bases and their metal complexes. The literature survey reveals that the metal complexes of Schiff bases demonstrated more potent bacterial and fungicidal properties and their corresponding ligands.

EXPERIMENTAL

All melting points were determined in an open capillary tube and are uncorrected. Completion of the reaction was monitored by TLC on pre coated sheet of silica gel-G. All the reagents used were chemically pure and are of AR grade. Solvents were dried and distilled before use according to standard procedure[8].

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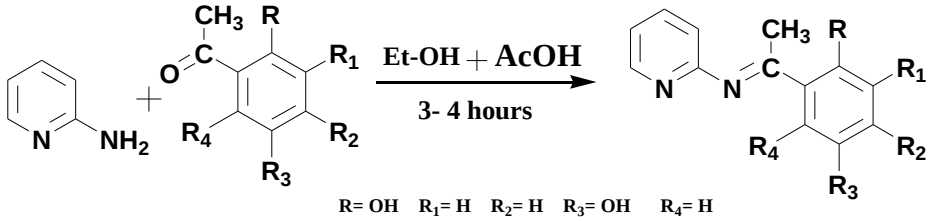


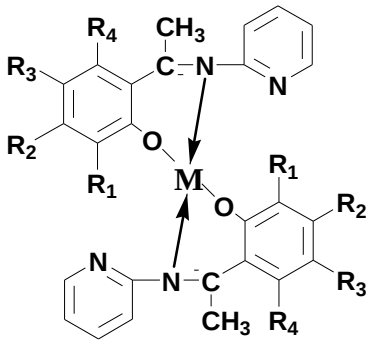
R= OH R_1= H R_2= H R_3= OH R_4= H

General procedure for the synthesis of schiff bases

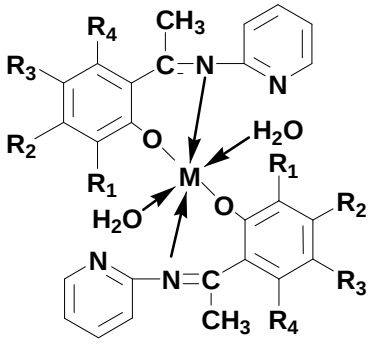
An equimolar mixture of 2-amino pyridine and substituted ketone (i.e.0.01mole) dissolved in ethyl alcohol and mixture was refluxed for 3-4 hours. The reaction mixture was then poured into ice cold water the solid separated was filtered washed with water and recrystallised from ethyl alcohol TABLE 1.

TABLE 1 : Physical data of synthesized metal complexes

Compound code	Molecular formula	Colour	Decomposition temp.°C	Yield %
L	$C_{13}H_{12}O_2N_2$	Yellow	220	82
La	$C_{26}H_{22}O_4N_4Cu$	Dark brown	278	68
Lb	$C_{26}H_{26}O_6N_4Co$	Brown	250	74
Lc	$C_{26}H_{26}O_6N_4Ni$	Orange	248	56
Ld	$C_{26}H_{24}O_6N_4Fe$	Brown	252	82
Le	$C_{26}H_{22}O_4N_4Zn$	Yellow	256	76
Lf	$C_{26}H_{22}O_4N_4Mn$	Brown	212	60



Where, M= Cu (II), Zn (II)



Where, M= Fe (III), Co (II), Ni (II)

Synthesis of metal complexes

The ligand (0.02 mole) and the metal salt (0.01 mole) in 50 ml ethanol was refluxed for 2 hours. In all the cases the ligand concentration was slight excess of 1:2 metal ligand molar ratio. After refluxing the solid mass separated filtered through a sintered glass crucible (G4) and the residue was washed several times with hot methanol until the washing were free of the excess of ligand these complexes finally dried under vacuum desiccator over fused calcium chloride.

Molar conductivity measurements were carried out in DMSO on an Elico digital conductometer model 180. The magnetic susceptibility measurements were made on Guoy balance at room temperature using Hg [Co (NCS) $_4$] as standard.

IR spectra of the metal in KBr pallets in the range of 4000-350 cm^{-1} were recorded making use of FTIR-SCHIMADZU 8400S spectrophotometer.

UV visible spectra in DMF were recorded on a SCHIMADZU multipurpose recording spectrophotometer model 1601 and ^{1}H-NMR spectra were recorded in DMSO on AVANCE 300 MHz spectrophotometer using TMS as an internal standard (δ ppm).

RESULTS AND DISCUSSION

All the complexes are coloured solids, air stable and having good solubility in polar solvents DMF and DMSO. The elemental analysis shows 1:2 (M: L) stoichiometry for all the complexes. The analytical data given in TABLE 1. The metal contents in complexes were analyzed by gravimetric analysis.

All the complexes show low conductance which indicates their non electrolytic nature. The magnetic measurement studies suggest that the Cu (II), Co (II), Mn (II) and Fe (III) complexes exhibit paramagnetic behavior where as the Ni (II) and Zn (II) show diamagnetic behavior.

^{1}H-NMR spectra

^{1}H-NMR spectra of synthesized ligand and its transition metal complexes where recorded in DMSO. The 1H-NMR spectra of ligand shows signals at 2.7δ (s,3H, -CH3), 7.20 δ - 7.87 δ (m,7H, Ar-H), 12.10 δ (s,2H, Ar-OH) ppm.

The ^{1}HNMR spectra of complexes show broad signals due to presence of metal ion and the conformation of each signal in the aromatic region is difficult due to complex pattern of splitting.

IR spectra

The FT-IR spectrum of the free ligand shows four characteristic bands at 3300 cm^{-1} (-OH stretch), 1538 (C=C Ar. str), 1640 (C=N str.), 1250 (C-O, Ar-OH).

Where as in the IR spectra of complexes there is one more additional absorption band appears at 420-474 cm^{-1} range due to M-O bond.

Thermal analysis

The thermo gram of Ni (II), Fe (III) Co (II) complexes confirms the presence two moles of coordinated water molecules where as there is absence of coordination of water molecule in Zn (II) and Cu (II) complexes.

Hence from TGA it is clear that the complex under study contains two moles of coordinated water molecules which are coordinated to central metal ion[9].

Magnetic moment

The $\mu_{eff.}$ values at room temperature for Cu (II) complexes are in the range of 1.78-1.86 B.M. usually observed for square planar geometry[10,11]. Ni (II) and Co (II) complexes have magnetic moment values in the range of 2.84-3.24 and 4.28-4.94 B.M. respectively. Whereas due to completely filled d-orbitals the Zn (II) ion complex is diamagnetic in nature.

Electron spin resonance study

From the ESR spectra the values of gπ and g⊥ have been calculated by Kneubehls methods[12]. The observed g-values point to the presence of the unpaired electron in the dx^2-y^2 orbital with gπ>g⊥ characteristic of square planar of elongated tetragonal geometry.

The gπ obtain obtained for the Cu (II) complexes is less than 2-3 indicating covalent character of the metal-ligand bond[13].

Antimicrobial activity

The antibacterial activity of the compounds was determined by agar diffusion method against various bacteria like *E.coli, S. typhi, S. aureus, and B. subtilis* at various concentrations such as 20, 50 and 100 µg /ml. The zone of inhibition was measured in mm and DMSO was used as solvent. Sterile nutrient agar was seeded with test organism and layered in sterile petri plate.

After solidification, agar cups were borered with cork borer 0.1 ml of the compound solution was added to the cup with the help of micropipettes, one cup in the plates was filled with solvent.

Standard penicillin (10v/ml) was used as reference drug. The plates were kept at low temperature (4°C) for 20 minutes to allow diffusion of the compound. Then the plates were incubated at 37 °C for 24 hr. After proper incubation the plates were observed for zone of no growth (zone of inhibition of growth) around the cup. Similarly the same compounds were screened for the antifungal activity against different organisms like *P.chrysogenum, A. niger, F. moniliformae,* and *A. Flavus* by using poison plate method. The compound was mixed with sterile potato dextrose agar medium so as to get final concentration 2%. It was then poured in sterile petri plate and allowed to solidify. Spots of test organisms were placed on the agar surface. A plate without compound was prepared for control. The plates were incubated at room temperature for 48 hr.

TABLE 2 : Antimicrobial activity of synthesized compounds

Product	Bacterial strain				Fungal strain			
	Ec	St	Sa	Bs	An	Pc	Fm	An
L_1	15	09	26	19	-ve	+ve	-ve	-ve
$[L_1.Cu.H_2O]$	13	17	12	21	+ve	-ve	-ve	-ve
$[L_1.Ni(H_2O)_2]$	09	11	22	13	-ve	+ve	-ve	-ve
$[L_1.Co(H_2O)_2]$	-	09	27	18	+ve	+ve	RG	+ve
$[L_1Mn]$	14	-	14	25	+ve	-ve	-ve	-ve
$[L_1,Fe(H_2O)_2]$	06	08	17	16	-ve	RG	-ve	+ve
$[L_1Zn]$	-	-	23	11	+ve	+ve	-ve	+ve
Pencillin	18	20	32	28	-ve	-ve	-ve	-ve
Grysofulvin	NA	NA	NA	NA	-ve	-ve	-ve	-ve

Ec-E.coli, St-S.typhi, Sa- S.aureus, Bs-B.subtilis; An-A.niger, Pc-P.chrysogenum, Fm-F.moneliformae, Ca-C.albicans; -ve: No growth of fungi,+ve: Growth of fungi, RG-Reduced growth, NA-Not Applicable, Zone of inhibition was measured in mm

After proper incubation plates were observed for

growth of the test organisms. The growth indicates that the compound is not antifungal while inhibition of growth of test organism indicates antifungal activity. The antifungal activities of the compounds were compared with standard grysofulvin.

The result of antimicrobial data of the ligand and complex shows that the complexes of the Schiff bases shows enhanced activity than their corresponding ligand.

CONCLUSION

From the result and the discussion and analytical data it is confirmed 1:2 stoichiometry And the electronic spectral data suggest that the Co (II), Ni (II),Fe (II) complexes have octahedral geometry where as Cu (II), Zn (II) and Mn (II) complexes have square planar geometry.

The antimicrobial studies show that the complexes of the corresponding Schiff bases show more potent activity than their corresponding ligand.

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