



SYNTHESIS, PHYSICO-CHEMICAL CHARACTERIZATION AND ANTIMICROBIAL STUDIES ON TRANSITION METAL COMPLEXES OF PHENYLHYDRAZONE LIGAND

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Abstract: The Mn(II), Cu(II), Zn(II) and Cd(II) complexes of Schiff base derived from phenylhydrazine and benzophenone have been synthesized and characterized. The structure of the ligand (L) was established on the basis of micro-elemental analysis, UV and IR data. The synthesized coordination complexes were characterized by elemental analysis (C,H,N), IR, UV-visible, conductivity and magnetic susceptibility measurements. The ligand is found to act as a neutral bidentate chelating one, binding through two amino N atoms. Both the ligand and its complexes were tested for antimicrobial properties and found that the metal complexes have higher antimicrobial activity than the free ligand.

Key Words: Phenylhydrazine, benzophenone, Schiff base, antimicrobial activity

INTRODUCTION

Schiff bases can be said to be one of the most researched group of chemical molecules, because of their versatility, stability, and ease of synthesis, which have resulted in their wide applications [1-3]. The azomethine functional group which they possess make contributions to their bioactivity [4]. The azomethine nitrogen C=N may interact and form intramolecular hydrogen bonding with a few responding sites within the cell structure, affects the regular cell processes and hence their biological significance [5-6]. Also the lone pair electron within the sp² hybridized orbital of the azomethine nitrogen is another reason for their chemical reactivity. To a great extent the properties of the Schiff base metal complexes depend on the nature of the ligand and that of the metal ion.

Hydrazones are the well known class of biologically active compounds in the discipline of synthetic chemistry. They own antimicrobial, antimalarial, antitubercular, anticonvulsant, Anti HIV, antiinflammatory, antihyperalgesic and other pharmacological properties. The rise in antibiotic-resistant micro-organisms in recent years has led to an increasing look for new antimicrobial agents. Further the complexation of hydrazones with metal ions may enhance their antimicrobial properties and this complexes may also be used as potent drugs in the treatment of infectious diseases [7-8]. In spite of these striking features one can see the glamour of hydrazones in the formation of complexes with various metals. And these complexes are proving to be of extremely good utility in pharmacy and industries. With the need of time and adaptability hydrazones have been applied as protecting groups for carbonyl compounds [9].

Keeping this in mind, an attempt has been made to synthesize a novel phenyl hydrazone ligand and its metal complexes with bivalent Mn, Cu, Zn and Cd, to characterize them and to screen their antimicrobial activities.

EXPERIMENTAL

Metal salts, phenyl hydrazine, benzophenone and other reagents were AR grade. Solvent used was ethanol. C, H and N contents of the ligand and the complexes were estimated by Heraous CHN-O-rapid analyzer. FTIR spectra were taken on a Perkin Elmer Spectrum 400 Instrument with PIKE GladiATR attachment and a DTGS detector in the 4000-400 cm^{-1} region. The electronic spectra of the complexes were recorded in HPLC grade DMSO on a Shimadzu spectrophotometer. Molar conductivity measurements were recorded on systronic conductivity meter type 304. Magnetic measurements of the complexes were performed on a Magway MSB Mk 1 susceptibility balance at room temperature.

Synthesis of the ligand

The Ligand(L) was prepared by the condensation of benzophenone and phenyl hydrazine in 1:1 molar ratio by refluxing in ethanol [10].

Preparation of metal complexes

The hot ethanolic solution (20 mL) of the hydrazone ligand, L (0.02 M) was added to the hot ethanolic solution (20 mL) of the metal salt (0.01 M) with vigorous stirring. Then the resulting solution was refluxed on a water bath for two hours. The solid complex formed in each case was filtered, washed with ethanol and dried in a *vacuum* desiccator over calcium chloride and preserved in the desiccator itself. The metal complexes thus obtained were subjected to physical, chemical and biological studies.

RESULTS AND DISCUSSION

All the complexes are stable at room temperature and non-hygroscopic. They are insoluble in common organic solvents like ether, acetone, benzene, carbon tetrachloride and nitrobenzene but are freely soluble in DMF and DMSO. The analytical data and empirical formulae of the complexes are presented in Table 1. The non-electrolytic nature of metal complexes suggests that the anions of the salts have coordinated to the metal ions.

Table 1
Elemental and other physico- chemical data of ligand and its complexes

Compound	M.P $^{\circ}\text{C}$	Colour	Found(Calcd.)%		
			C	H	N
HL	220	Light yellow	84.33 (83.79)	5.99 (5.92)	9.89 (10.29)
$[\text{MnL}_2(\text{CH}_3\text{COO})_2]$	266	Brown	70.02 (70.29)	5.98 (5.34)	7.23 (7.81)
$[\text{CuL}_2\text{Cl}_2]$	280	Deep Blue	67.89 (67.20)	4.23 (4.75)	7.86 (8.25)
$[\text{ZnL}_2(\text{NCS})_2]$	256	Yellow	69.46 (69.27)	5.03 (5.26)	6.98 (7.69)
$[\text{CdL}_2(\text{CH}_3\text{COO})_2]$	240	Yellow	65.00 (65.07)	4.57 (4.94)	7.34 (7.23)

Electrical conductance

Molar conductance measurements of the complexes were carried out in 10^{-3} M DMF solution. The conductance values of complexes are in the range and $12\text{-}20\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. This result shows that the complexes are non electrolytic in nature [11].

Magnetic behaviour

The magnetic moment values of the complexes are show that all the complexes except Zn(II) and Cd(II) are paramagnetic. The high spin d^5 configuration of Mn(II) gives spin only magnetic moment of 5.7 BM. For Cu(II) complex the measured value is 1.81 BM. Zn(II) and Cd(II) are found to be diamagnetic in nature.

Infrared spectra

The characteristic IR frequencies of the ligand and its complexes along with their assignments are listed in Table 2. The coordination of ligand to the metal causes shifts in the bands of the ligand to lower frequencies with different intensities. The mode of coordination has been assigned by comparing the spectra of metal complexes with that of ligand [12].

The IR Spectrum of ligand shows an intense band at 1680 cm^{-1} due to the presence of azomethine group. But in the spectra of complexes, this band was shifted to lower frequency range of $1610\text{ - }1650\text{ cm}^{-1}$ indicating the coordination of azomethine nitrogen to the metal ion. The broad band at 3450 cm^{-1} of ligand is due to the presence of N-H groups. On coordination, this band is shifted to lower frequencies. New bands are found in spectrum of complexes in the region of $510\text{ - }620\text{ cm}^{-1}$ indicates the presence of M – N coordination. IR data showed that the ligand is bidentate in complexes. The spectrum of the acetate-containing complexes display relatively strong bands around $1540\text{-}1580\text{ [}\nu_a(\text{COO})\text{]}$ and at $1340\text{-}1360\text{ cm}^{-1}\text{ [}\nu_s(\text{COO})\text{]}$ support the unidentate nature of the acetate group in this compound. The thiocyanate complexes show strong IR bands around $2060\text{-}2070\text{ cm}^{-1}$ attributed to the (C-N) stretching frequency. The position and intensity of these bands suggests the N-bonded nature of the thiocyanate group [13].

Table 2
Important IR spectral bands of ligand and its complexes

Compound	$\nu(\text{C}=\text{N})\text{cm}^{-1}$	$\nu(\text{N-H})\text{cm}^{-1}$	$\nu(\text{M-N})\text{cm}^{-1}$
L	1680	3450	-
$[\text{MnL}_2(\text{CH}_3\text{COO})_2]$	1640	3230	540
$[\text{CuL}_2\text{Cl}_2]$	1650	3350	580
$[\text{ZnL}_2(\text{NCS})_2]$	1670	3430	510
$[\text{CdL}_2(\text{CH}_3\text{COO})_2]$	1650	3240	620

Electronic spectra

The electronic spectra of the ligand in DMSO exhibit two spectral bands in the regions at 36030 cm^{-1} and 29550 cm^{-1} . But in complexes these bands show slight changes, which indicate coordination of ligand to metal. The bands around $24750\text{ - }25010\text{ cm}^{-1}$ for complexes may be due to charge transfer transitions.

Antimicrobial activity

The ligand and its metal complexes were screened *in vitro* for their antibacterial activity against two Gram-negative (*Escherichia coli* and *Salmonella typhimurium*) and two Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) bacterial strains using agarwell diffusion method using Imipenem as standard. The

results of antibacterial studies are presented in Table 3. A comparative study of the ligand and their metal complexes indicates that most of the metal complexes exhibit higher antimicrobial activity than that of the free ligand and the control. Hence complexation increases antimicrobial activity [14]. The enhanced activity of the complexes can be explained on the basis of Overtone's concept [15] and Tweedy's Chelation theory [16].

Table.3
Results of antibacterial assay (concentration used 1mg/mL of DMSO).
 <10: weak, Between 10 and 16: Moderate, >16: Significant

Compound	Gram-bacteria		Gram-positive	
	<i>E.coli</i>	<i>S.typhi</i>	<i>B.subtilis</i>	<i>S.aureus</i>
LH ₂	11	14	13	12
[MnL ₂ (CH ₃ COO) ₂]	18	16	08	13
[CuL ₂ Cl ₂]	14	18	17	17
[ZnL ₂ (NCS) ₂]	20	19	18	20
[CdL ₂ (CH ₃ COO) ₂]	12	21	19	19
SD*	32	28	31	33

*SD: standard drug-Imipenem

Conclusion

Analytical data show that all the complexes have the composition $[M(L_2)(X)_2]$, where M = Cu(II), Mn(II), Zn(II), Cd(II) and X = CH₃COO⁻, Cl⁻, and NCS⁻. The molar conductance values in DMF and the infrared spectral values show that all the complexes are non-electrolytes. Hence all the ionic groups are present inside the coordination sphere. In thiocyanato complexes the anion is coordinated through nitrogen atom. Infrared spectra of complexes reveal that L behaves as a neutral bidentate ligand coordinating through two nitrogen atoms. The infrared spectrum of the acetate complexes further attests the monodentate coordination of the acetate group. The magnetic moment values suggest that the complexes are paramagnetic except Zn(II) and Cd(II) complexes. A comparative study of the ligand and their metal complexes show that most of the metal complexes exhibit higher antibacterial activity than that of free ligand and the control. Hence complexation increases antibacterial activity.

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