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Synthesis and spectral characterization of hydrazone Schiff base ligand, L derived from condensation of terephthalaldehyde and 2-furoic acid hydrazide and its binuclear complexes with Co(II), Ni(II), Cu(II) and Zn(II) : Comparative in-vitro microbiological evaluation of L and its Zn(II) coordination complex

Mohammad Shakir and Ambreen Abbasi*

Division Inorganic Chemistry, Department of Chemistry, Aligarh Muslim University, Aligarh, India

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ABSTRACT

The hydrazone Schiff base ligand, Furo-(phenyldimethine)-carbohydrazone, L was synthesized by reacting terephthalaldehyde with 2-furoic acid hydrazide in 1:2 molar ratio and binuclear complexes of type, $[M_2L\,(DMF)_4\,(CH_3COO)_4]$ were synthesized by reaction of Schiff base ligand, L with Co(II), Ni(II), Cu(II) and Zn(II) acetates. The Schiff base and its complexes have been characterized on the basis of the results of elemental analysis, molar conductance, magnetic susceptibility measurements and spectroscopic studies viz, FT-IR, ^{1}H NMR, UV-Vis, mass and EPR. The infrared spectral data suggested that the hydrazone Schiff base behaved as tetradentate ligand with ON NO donor sequence towards metal ions. The characteristic resonance signal in ^{1}H NMR spectrum indicated the presence of azomethine group as a result of condensation reaction. Magnetic moment data and reflectance spectra of Co(II), Ni(II), Cu(II) complexes revealed an octahedral geometry around metal ions with distortion in Cu(II) coordination complex. Low conductance value of Zn(II) complex in DMSO indicated its non electrolytic nature. Schiff base, L and its Zn(II) complex have been screened for their antibacterial (Escherichia coli, Methicillin resistant Staphylococcus aureus , Pseudomonas aeruginosa, Streptococcus pyogenes and Klebsiella pneumoniae) and antifungal activities (Candida albicans, Aspergillus fumigatus, Penicillium marneffei and Trichophyton mentagrophytes (recultured). Complex show more activity than free Schiff base.

Keywords: Hydrazone Schiff base; spectroscopic studies; octahedral geometry; antimicrobial studies.

INTRODUCTION

The hydrazone functional group (>N-N=C<) belongs to a large class of azomethines which are distinguished from other members of this class (e.g. imines, oximes) by presence of two adjacent N atoms. Hydrazone Schiff bases of acyl, aroyl and heteroaroyl compounds have an additional donor sites like >C=O. The additional donor sites make them more flexible and versatile. This versatility has made hydrazones good poly dentate chelating agents that can form a variety of complexes with various transition and inner transition metals and have attracted the attention of many researchers.

Various hydrazones are obtained depending on the experimental conditions which have application as biologically active compounds [1], as analytical agents [2] and as hole transporting agents in organic layer photo conductors. As biologically active compounds, hydrazones find applications in the treatment of diseases such as cancer [3], schizophrenia, tuberculosis [4], leprosy and mental disorder. Tuberculostatic activity is attributed to the formation of stable chelates with transition metals present in the cell. Thus many vital enzymatic reactions catalyzed by these transition metals cannot take place in presence of hydrazones [5-7]. Hydrazones and their metal compounds are of interest for their physicochemical properties and find applications in many important chemical processes that include sensors, non linear optics and others [8-10]. It has been suggested that nucleophilic substitution of hydrazone ligands maybe an important route to assemble nanoscale molecular clusters [11]. Qi and Wang have reported the preparation of novel dendritic mixed valence ruthenium complexes, which can act as variable attenuators for the control of optical signals [12].

Hydrazones are used as plasticizers and stabilizers for polymers, polymerization initiators, antioxidants, etc., they act as intermediates in preparative chemistry. In analytical chemistry, hydrazones find application in detection, determination and isolation of compounds containing the carbonyl group. More recently, they have been extensively used in detection and determination of several metals. They also find application as indicators and spot test agents [2].

A number of Schiff base hydrazones and their complexes have been synthesized from 2-furoic acid hydrazide [13-15]. In this paper, we report synthesis, characterization and spectroscopic properties of aroyl hydrazone Schiff base, Furo-(phenyldimethine)- carbohydrazone, L derived from reaction between terephthalaldehyde and 2-furoic acid hydrazide and its Co(II), Ni(II), Cu(II) and Zn (II) coordination complexes where metal ions are in an octahedral environment. Schiff base and its Zn (II) complex have been screened for their antibacterial (*Escherichia coli, Methicillin resistant Staphylococcus aureus , Pseudomonas aeruginosa , Streptococcus pyogenes and Klebsiella pneumoniae*) and antifungal activities (*Candida albicans, Aspergillus fumigatus, Penicillium marneffei* and *Trichophyton mentagrophytes* (recultured). Complex show more activity than free Schiff base.

EXPERIMENTAL SECTION

2.1. Materials and Instrumentation

The metal salts, $MX_2.nH_2O$ [X= CH_3COO^{-1} , M= Co, n=4; M=Ni, n= 4 ; M=Cu, n= 1 ; M=Zn, n= 2] (All Aldrich) were commercially pure samples. The chemicals terephthalaldehyde and 2- furoic acid hydrazide (both Acros) were used as received. Solvents DMF, DMSO and ethanol (AR) were used without further purification. The elemental analysis were obtained from micro-analytical laboratory of CDRI, Lucknow using Perkin–Elmer 2400 CHNO Elemental Analyzer. The metal content was determined by volumetric method . The FT-IR spectra (4000-400 cm^{-1}) were recorded as KBr pellets on Shimadzu 8201 PC spectrophotometer. ^1H NMR spectra in DMSO-d_6 were recorded using Bruker Avance II 400 NMR spectrometer at room temperature. The reflectance spectra of the coordination complexes were recorded in the range 1700-350 nm as MgO discs on a Beckman DK-2A spectrophotometer. The magnetic susceptibility measurements were carried on Lakeshore VSM 7410 from Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Madras, Chennai, India. EPR spectra of Cu(II) coordination complex in solid state at 300 K was recorded on Varian E-4 X band using DPPH as a g marker from IIT Bombay. Mass spectrum of Schiff base was recorded on JEOL GC mate from IIT Madras whereas mass spectrum of Zn(II) complex was recorded on JEOL-Accu TOF JMS-T100 LC mass spectrometer having DART source. The given sample was subjected as such in front of DART source. Dry helium was used with 4 LPM flow rate at 350 ^{0}C. The molar conductivity of 10^{-3} M solution of Zn(II) complex in DMF was obtained on a Systronic type 302 conductivity bridge equilibrated at 25 $^\circ$C ± 0.01 $^\circ$C.

2.2. Synthesis of Furo-(phenyldimethine) carbohydrazone, L.

A solution of 2-furoic acid hydrazide (2mmol, 0.256gm) in 20 ml ethanol was treated with terephthaldehyde (1mmol, 0.134 gm) dissolved in same solvent (20ml). The reaction mixtute was magnetically stirred for 24 hours at room temperature leading to isolation of off white coloured solid product which was filtered and washed with ethanol and diethyl ether and dried in vacuum over anhydrous calcium chloride.

2.3 Synthesis of coordination complexes

A solution of hydrated metal acetates (1.43mmol) in DMF (20 ml) was added slowly to solution of L (0.716 mmol) in same solvent (20 ml) and the resulting mixture was heated under reflux for 5 hours. The coloured microcrystalline products that separated on cooling the reaction flask to ambient temperature were filtered off and dried in vacuum over anhydrous calcium chloride.

2.4. Pharmacology

In-vitro antibacterial and antifungal assays

The biological activities of newly synthesized Schiff base, L and its Zn(II) coordination complex have been studied for their antibacterial and antifungal activities by disc diffusion method and measured by Halo Zone Test. The antibacterial activity was done using following organisms (*Escherichia coli* (ATCC-25922), Methicillin resistant *Staphylococcus aureus* (MRSA +Ve), *Pseudomonas aeruginosa* (ATCC-27853), *Streptococcus pyogenes* and *Klebsiella pneumoniae* (Clinical isolate)). A standard inoculums (1-2 × 10^7 c.f.u. /ml 0.5 McFarland standards) was introduced on to the surface of sterile agar plates, and a sterile glass spreader was used for even distribution of the inoculums. The discs measuring 6 mm in diameter were prepared from Whatmann no. 1 filter paper and sterilized by dry heat at 140 °C for 1 h. The sterile discs previously soaked in a known concentration of the test compounds were placed in nutrient agar medium. Solvent and growth controls were kept. Ciprofloxacin was used as positive control. While the disk poured in DMSO was used as negative control. The plates were inverted and incubated for 24 h at 37 °C. The susceptibility was assessed on the basis of diameter of zone of inhibition against Gram-positive and Gram-negative strains of bacteria. Inhibition zones were measured and compared with the controls.

Minimum inhibitory concentrations (MICs) were determined by broth dilution technique. The nutrient broth, which contained logarithmic serially two fold diluted amount of test compound and controls were inoculated with approximately 5×10^5 c.f.u. /ml of actively dividing bacteria cells. The cultures were incubated for 24 h at 37 °C and the growth was monitored visually and spectrophotometrically. The lowest concentration (highest dilution) required to arrest the growth of bacteria was regarded as minimum inhibitory concentration (MIC). To obtain the minimum bacterial concentration (MBC), 0.1 ml volume was taken from each tube and spread on agar plates. The number of c.f.u. was counted after 18-24 h of incubation at 35 °C. MBC was defined as the lowest drug concentration at which 99.9% of the inoculums were killed. Antifungal activity was also done by disk diffusion method. For assaying antifungal activity *Candida albicans*, *Aspergillus fumigatus*, *Penicillium marneffei* and *Trichophyton mentagrophytes* (recultured) in DMSO by agar diffusion method. Sabourands agar media was prepared by dissolving peptone (1 g), D-glucose (4 g) and agar (2 g) in distilled water (100 ml) and adjusting pH to 5.7. Normal saline was used to make a suspension of spore of fungal strain for lawning. A loopful of particular fungal strain was transferred to 3 ml saline to get a suspension of corresponding species. Twenty millilitres of agar media was poured into each petridish. Excess of suspension was decanted and the plates were dried by placing in an incubator at 37 °C for 1 h. Using an agar punch, wells were made and each well was labelled. A control was also prepared in triplicate and maintained at 37 °C for 3-4 days. The fungal activity of each compound was compared with Greseofulvin as standard drug. Inhibition zones were measured and compared with the controls. The fungal zones of inhibition values are given in Table 3. The nutrient broth, which contained logarithmic serially two fold diluted amount of test compound and controls was inoculated with approximately 1.6×10^4 - 6×10^4 c.f.u. /ml. The cultures were incubated for 48 h at 35 °C and the growth was monitored. The lowest concentration (highest dilution) required to arrest the growth of fungus was regarded as minimum inhibitory concentration (MIC). To obtain the minimum fungicidal concentration (MFC) 0.1 ml volume was taken from each tube and spread on agar plates. The number of c.f.u. was counted after 48 h of incubation at 35 °C. MFC was defined as the lowest drug concentration at which 99.9% of the inoculums were killed.

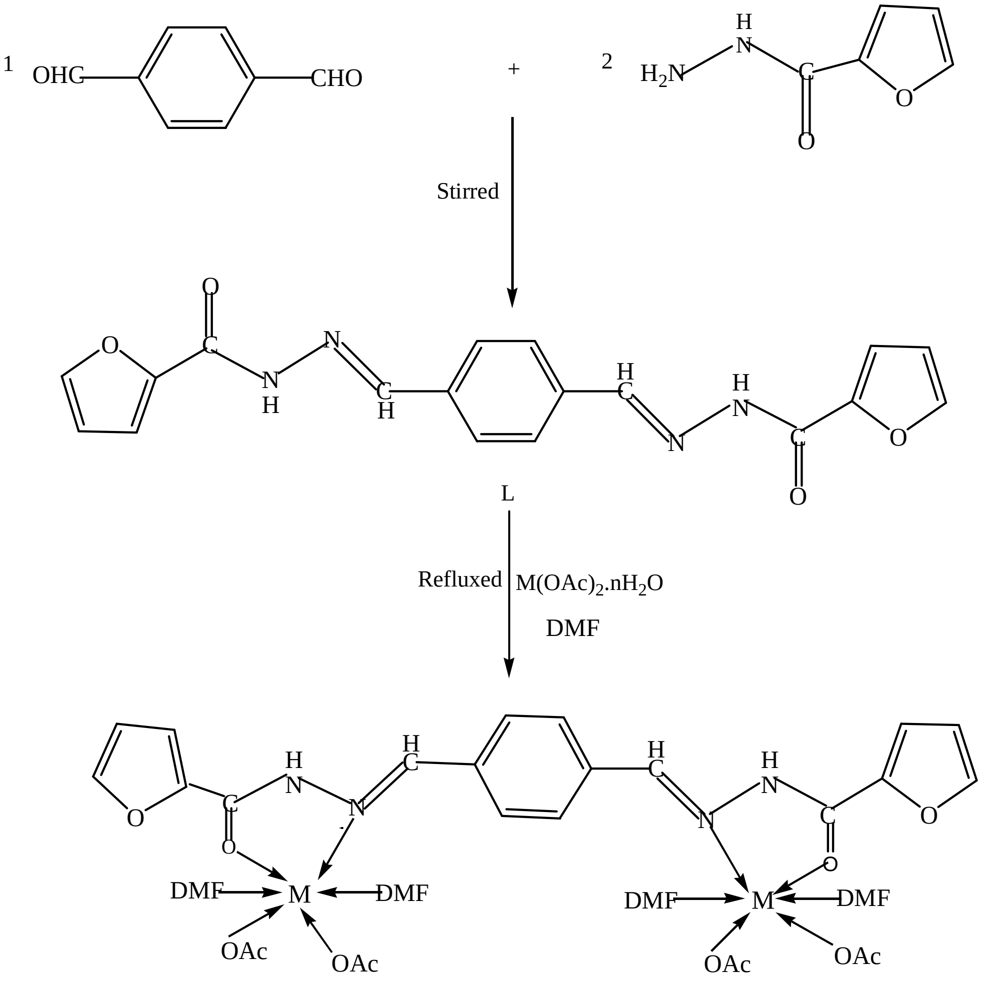
RESULTS AND DISCUSSION

Schiff base ligand, L was synthesized by condensation of terephthalaldehyde and 2-furoic acid hydrazide in 1:2 molar ratio dissolved in ethanol. The coordination complexes of type $[M_2L(DMF)_4(CH_3COO)_4]$ were synthesized by reaction of L and metal salt in 1:2 molar ratio dissolved in DMF (Scheme).

All coordination complexes were stable at room temperature and were insoluble in water and common organic solvents and were only partially soluble in DMSO except Zn(II) complex which was completely soluble in DMSO and DMF. The analytical data along with some physical properties of Schiff base ligand and its coordination complexes are summarized in Table 1.

Table 1: Analytical data, % yield, colour, melting point of Schiff base ligand, L and its coordination complexes

Compound / Empirical formula Of monomer unit	Found (calcd) %				Yield %	Colour	M.P (^{0}C)
	C	H	N	O			
L	61.74	4.04	16.01	18.29	50	Off White	>300
$C_{18}H_{14}N_4O_4$	(61.71)	(4.03)	(15.99)	(18.27)			
$[Co_2L(DMF)_4(CH_3COO)_4]$	44.49	6.00	11.51	26.43	38	Pink	>300
$C_{36}H_{54}Co_2N_8O_{16}$	(44.45)	(5.595)	(11.52)	(26.32)			
$[Ni_2L(DMF)_4(CH_3COO)_4]$	44. 51	6.01	11.55	26.41	44	Green	>300
$C_{36}H_{54}Ni_2N_8O_{16}$	(44.47)	(5.598)	(11.53)	(26.33)			
$[Cu_2L(DMF)_4(CH_3COO)_4]$	44.08	5.59	11.48	26.11	46	Green	>300
$C_{36}H_{54}Cu_2N_8O_{16}$	(44.03)	(5.54)	(11.41)	(26.07)			
$[Zn_2L(DMF)_4(CH_3COO)_4]$	43.91	5.57	11.41	26.01	42	Light brown	>300
$C_{36}H_{54}Zn_2N_8O_{16}$	(43.87)	(5.52)	(11.37)	(25.97)			



Scheme

The formation of Schiff base ligand, L and its coordination complexes and bonding modes were inferred from characteristic band positions in FT-IR spectra. The octahedral geometry around Co(II), Ni(II) and Cu(II) ions in the complexes were deduced from the positions of absorption bands observed in the reflectance spectra and magnetic moment values. The low molar conductance value (17.5 $Ohm^{-1}cm^{2}mol^{-1}$) of Zn(II) complex in DMF (10^{-3}M solution) indicate its non electrolytic nature of complex [16].

3.1. Infrared Spectra

The prominent bands observed in the IR spectra of the Schiff base ligand, L and its coordination complexes are listed in Table 2. In order to study the bonding mode of Schiff base ligand to the metal ions in coordination complexes, the IR spectrum of the free ligand was compared with the spectra of the corresponding coordination complexes. The IR spectrum of ligand, L showed broad bands at 3435 cm^{-1} and 3218 cm^{-1} due to υ(NH) vibrations of hydrazone. These bands were assigned to υ_{asy} (NH) and υ_{sy} (NH) vibrations, respectively, of secondary amide. According to Halli et al [17], coordination of NH through N should cause splitting and shifting of bands to lower frequency side or decrease in intensity. In the present study no such changes were observed indicating non participation of N atom of NH in bonding with metal ions.

The amide I, υ(C=O) band is observed at 1662 cm^{-1} in free ligand, L. This band shifted to lower wave numbers in all metal coordination complexes and appear in the region 1600-1641 cm^{-1} indicating bonding of oxygen of (>C=O) to metal ions [18].

A medium intensity band at 1604 cm^{-1} in free Schiff base is attributed to υ(C=N) vibration [19]. Spectra of all complexes exhibited a band in the region 1561-1592 cm^{-1} corresponding to υ(C=N) which undergoes a negative shift (12 – 43 cm^{-1}) in comparison to free Schiff base indicating that azomethine nitrogens were coordinated to metal ions.

The band at 942 cm^{-1} in the free ligand due to υ(N-N) shifted to higher wave numbers by about 10-15 cm^{-1} in all coordination complexes which was an additional evidence for coordination of azomethine nitrogens .

Many workers have reported medium intensity bands for υ(C-O-C) of furan ring vibrations in the region 1020- 1250 cm^{-1} . In present case υ(C-O-C) stretch was observed at 1247 cm^{-1} in free ligand, L. This band remains unaltered in all complexes indicating non participation of the furan O- atom in bonding with metal ions.

Metal ligand vibrations are generally observed in far IR region and usually give valuable information regarding the bonding of ligands to the metal ions . In the present case appearance of new bands in the spectra of complexes in the regions 500-550 cm^{-1} and 421-460 cm^{-1} were assigned to υ(M-O) and υ(M-N) vibrations [20]. The bands appearing in the regions 1480-1440 cm^{-1} , 1100-1064 cm^{-1} and 805- 740 cm^{-1} were usual modes of phenyl ring vibration.

In spectra of all complexes a strong band appeared at 1506 cm^{-1} which is typical of DMF with oxygen atom coordinated to metal ion [21]. In addition spectra of all complexes also showed bands at ~ 1380 cm^{-1} and ~ 1600 cm^{-1} due to υ_{asy} (COO) and υ_{sym} (COO) vibrations of coordinated acetate ions. These bands with separation of $\Delta \upsilon = 220$ cm^{-1} adequately support monodentate coordination by acetate ions [22].

Table 2: IR spectral data of Schiff base ligand (L) and its coordination complexes (cm^{-1}).

Compound	υ(C=N)	υ(C=O)	υ(N-N)	υ(M-O)	υ(M-N)	phenyl ring vibrations
L	1604	1660	935	-	-	1480,1146,752
[$Co_2L(DMF)_4(CH_3COO)_4$]	1590	1600	948	502	450	1461,1069,668
[$Ni_2L(DMF)_4(CH_3COO)_4$]	1580	1630	950	509	458	1462,1073,745
[$Cu_2L(DMF)_4(CH_3COO)_4$]	1592	1614	945	530	460	1440,1078,765
[$Zn_2L(DMF)_4(CH_3COO)_4$]	1590	1641	942	528	438	1471,1105,750

3.2. ^{1}H NMR Spectra

The ^{1}H NMR spectrum of ligand, L shows signals at 11.92 ppm (s, 2H) due to (CONH) amide protons and at 8.46 ppm due to (-H-C=N-, 2H) azomethine protons. The aromatic protons of furan and benzene are in the region 6.71 ppm-7.95 ppm. In the ^{1}H NMR spectrum of Zn(II) complex the signals due to –CONH- and –N=CH- protons show a downfield shift of 0.02 ppm and 0.30 ppm, respectively, thereby suggesting the involvement of oxygen and nitrogen atoms in bonding with metal ion. ^{1}H NMR spectrum of complex also show three singlets centred at 6.78, 1.96 and 1.73 ppm due to HCO and CH_3 protons of coordinated DMF. In addition spectrum of complex also shows singlet at 1.11 ppm due to CH_3 protons of acetate ions [23].

3.3. Electronic spectra and magnetic moments

In electronic spectra of Co(II) complexes appeared two absorption bands at 16628 cm^{-1} and 21154 cm^{-1}. These bands are assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions, respectively, in an octahedral environment [24].

The six coordinate Ni(II) complexes exhibited bands at 15342 cm^{-1} and 25810 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively. The high energy band in the region 29000–30000 cm^{-1} is assigned to charge transfer in the case of Co(II) and Ni(II) complexes. The light green Cu(II) complexes exhibited a single broad asymmetric band at 16206 cm−1. The broadness of the band indicated the three transitions, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$, and $^2B_{1g} \rightarrow {}^2Eg$, which are similar in energy and give rise to only one broad band. The high intensity band observed at 28,800 cm−1 was assigned to charge transfer [25]. The broadness of the band may be due to dynamic John-Teller distortion. All of these data suggest a distorted octahedral geometry around Cu(II).

Room temperature magnetic susceptibility measurements indicated paramagnetic nature for Co, Cu, and Ni complexes. The six-coordinate Co(II) complex exhibited magnetic moments of 4.86 B.M., suggesting octahedral geometry for Co(II) [26]. Ni(II) complex showed magnetic moment value of 2.95 B.M., slightly higher than the spin only (2.83 B.M.) value, indicating an octahedral environment around Ni(II) ion [27]. The observed magnetic moments for Cu(II) complex is 1.78 B.M., suggesting a distorted octahedral geometry around Cu(II).

3.4. EPR Spectroscopy

The ESR spectrum of Cu(II) complex in polycrystalline state had been recorded at room temperature. $g_{\parallel}$ and $g_{\perp}$ values had been found to be 2.44 and 2.05 respectively. The g_{av} values was calculated to be 2.18. Neiman and Kivelson [28] have reported $g_{\parallel}$ value less than 2.3 for covalent character and greater than 2.3 for ionic character of metal ligand bond in complexes. In the present case $g_{\parallel}$ value is slightly higher than 2.3 suggesting a small amount of ionic character of metal ligand bond. The trend $g_{\parallel}$ (2.302) > $g_{\perp}$ (2.048) > ge (2.0023) observed for the copper complex suggests that the unpaired electron is localized in the dx^2-y^2 orbital of the copper ion. The g_{av} value greater than 2 for this complex indicated the presence of covalent character of metal ligand bond [29]. The axial symmetry parameter (G) value for the complex was calculated to be 9.17 which was greater than 4 suggesting no interaction between copper centres.

3.5. Mass Spectroscopy

The mass spectrum of Schiff base ligand, L shows a molecular ion peak $[M]^+$ at m/z 350.3574 which corresponds to its proposed molecular formula. The molecular ion peak for Schiff base complex, $[Zn_2 L (DMF)_4 (CH_3 COO)_4]$ appear at m/z – 985.7321 consistent with the proposed molecular formula of the complex .

3.5. Pharmacology results

The microbial results of Schiff base and its Zn(II) complex are systematized in Tables 3,4,5 and 6.

Table 3. Antibacterial activity of L and its Zn(II) complex

Compounds	Diameter of zone of inhibition (mm).				
	Gram positive bacteria		Gram negative bacteria		
	S. Pyogenes	*MRSA**	*P. aeruginosa*	*K. pneumoniae*	*E. coli*
Zn(II) complex	18.4±0.4	18.4±0. 4	25.3±0.4	13.6±0.2	17.7±0.4
L	17.2±0.2	16.2±0.2	23.2±0.2	12.1±0.4	15.5±0.2
Standard	22.5±0.4	21.5±0.4	31.0±0.2	19.0±0.2	27.0±0.4
DMSO	-	-	-	-	-

*Positive control (standard); ciprofloxacin and negative control (DMSO) measured by the Halo Zone Test (Unit, mm). * Methicillin resistant Staphylococcus aureus (MRSA +Ve), Zn(II) complex = $[Zn_2L (DMF)_4 (CH_3 COO)_4]$*

Table 4. MIC and MBC results of L and its Zn(II) complex

Compounds	Gram positive bacteria				Gram negative bacteria					
	S. Pyogenes		*MRSA**		*P. aeruginosa*		*K. pneumoniae*		*E. coli*	
	MIC	MBC	MIC	MBC	MIC	MBC	MIC	MBC	MIC	MBC
Zn(II)complex	25	50	25	50	50	100	25	100	25	50
L	25	100	25	100	50	100	25	100	50	100
Standard	6.25	12.5	6.25	12.5	12.5	25	6.25	25	6.25	25

MIC (µg/ml) = minimum inhibitory concentration, i.e the lowest concentration of the compound to inhibit the growth of bacteria completely; MBC (µg/ml) = minimum bacterial concentration, i.e., the lowest concentration of the compound for killing the bacteria completely.

Table 5. Antifungal activity of L and its Zn(II) complex. Positive control (greseofulvin) and negative control (DMSO) measured by the Halo Zone Test (Unit, mm). Diameter of zone of inhibition (mm)

Compounds	CA	AF	TM	PM
Zn(II)complex	19.4±0.2	17.9±0.3	14.2±0.2	11.5±0.4
L	17.2±0.4	14.4±0.2	11.3±0.4	9.2±0.2
Standard	30.0 ±0.2	25.5±0.2	24.5±0.3	20.5±0.5
DMSO	-	-	-	-

CA; *Candida albicans*, AF; *Aspergillus fumigatus*, TM; *Trichophyton mentagrophytes,* PM; *Penicillium marneffei.*

Table 6. MIC and MFC of L and its Zn(II) complex

Comp.	CA		AF		TM		PM	
	MIC	MFC	MIC	MFC	MIC	MFC	MIC	MFC
Zn(II)complex	25	50	50	100	12.5	25	50	100
L	25	100	50	100	20	100	50	100
Standard	6.25	25	12.5	25	6.25	25	12.5	25

CA; Candida albicans, AF; Aspergillus fumigatus, TM; Trichophyton mentagrophytes, PM; Penicillium marneffei. MIC (µg/ml) = minimum inhibitory concentration, i.e the lowest concentration of the compound to inhibit the growth of fungus completely; MFC (µg/mm)minimum fungicidal concentration, i.e., the lowest concentration of the compound for killing the fungus completely.

The investigation of antibacterial screening data revealed that Schiff base ligand, L and its Zn(II) complex showed moderate to good bacterial inhibition against all bacterial strains. Both compounds showed good inhibition against *S. pyogenes*, *S. aurues* and *E. coli*. The antifungal screening data for both of these compounds also showed moderate to good activity against all fungal strains. Both compounds showed good activity against *C. albicans, A. fumigates* and P. *marneffei*. The MBC and MFC of these compounds were found to be two or four times higher than corresponding MIC results. The biological activity of the Schiff base exhibited a considerable enhancement on coordination with the metal ion against all bacterial and fungal strains. This enhancement in the activity may be rationalized on the basis that its structure mainly possess an additional >C=N bond. It has been suggested that Schiff base with nitrogen and oxygen donor systems inhibit enzyme activity, since the enzymes which require these groups for their activity appear to be especially more susceptible to deactivation by metal ions on coordination. Moreover, coordination reduces the polarity [30,31] of the metal ion mainly because of the partial sharing of its positive charge with the donor groups [32,33] within the chelate ring system formed during coordination. This process, in turn, increases the lipophilic nature of the central metal atom, which favours its permeation more efficiently through the lipid layer of the microorganism [34-36] thus destroying them more aggressively.

Some important factors such as the nature of the metal ion, nature of the ligand, coordinating sites, geometry of complex, concentration, hydrophilicity, lipophilicity and presence of co-ligands have considerable influence on antibacterial activity. Certainly, steric and pharmacokinetic factors also play a decisive role in deciding the potency of an antimicrobial agent. Apart from this , the mode of action of these compounds may also invoke hydrogen bond through the >C=N-N=CH- group with the active centres and thus interfere with normal cell process. The presence of lipophilic and polar substituent is expected to enhance antibacterial activity. Heterocyclic ligands with multifunctionality have greater chance of interaction either with nucleoside bases (even after complexation with metal ion) or with biologically essential metal ions present in the bio system and be promising candidates as bactericides since they always tend to interact especially with some enzymatic functional groups, in order to achieve higher coordination numbers [37]. Thus antibacterial property of metal complexes cannot be ascribed to chelation alone, but it is an intricate blend of several contributions.

CONCLUSION

Binuclear complexes of type, $[M_2 L (DMF)_4(CH_3 COO)_4]$ [M = Co(II), Ni(II), Cu(II) and Zn(II)] of Schiff base ligand, Furo-(phenyldimethine)-carbohydrazone, L were synthesized and characterized by various physico-chemical and spectroscopic methods. The bonding modes of L via two azomethine nitrogens and two carbonyl oxygens have been deduced by FT-IR, ^{1}H NMR spectral findings. The overall geometry around respective metal ions has been drawn on the basis of electronic spectral findings and magnetic moment values. The comparative antimicrobial activity on the ligand and its Zn(II) complex has shown that complex possess higher activity than free Schiff base, L.

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