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Research Article

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Synthesis of metal based chemotherapeutic agents derived from chloro-acetic acid[1-(4-hydroxy-6-methyl-2-oxo-*2H*-pyran-3-yl)-ethylidene]-hydrazide

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ABSTRACT

Schiff base hydrazone chloro-acetic acid[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-ethylidene]-hydrazide (HL) and its transition metal(II) complexes of type ML_2 [where M= Co(II), Ni(II), Cu(II) and Zn(II)] have been synthesized and characterized on the basis of spectroscopic techniques (IR, NMR, electronic, ESR & mass) and magnetic susceptibility measurements. The physicochemical studies revealed that Schiff base hydrazone acted as monobasic tridentate ligand ONO coordinating through oxygen of hydroxyl group, azomethine nitrogen and carbonyl oxygen to divalent metal ion forming complexes with octahedral or distorted octahedral geometry. Schiff base ligand and its metal complexes have been tested for in vitro antimicrobial activity data against Gram positive bacteria Bacillus subtilis, Micrococcus luteus, Gram negative bacteria Pseudomonas aeruginosa, Pseudomonas mendocina and fungi Verticillum dahliae, Cladosporium herbarium, Trichophyton soudanense using different concentration of ligands and their complexes (25, 50, 100, 200 µg/mL). Streptomycin and Fluconazole were used as a standard drug for antibacterial and antifungal activity respectively. All synthesized compounds showed promising antimicrobial activities against tested organisms and complexes have enhanced activity as compared to the parent ligand.

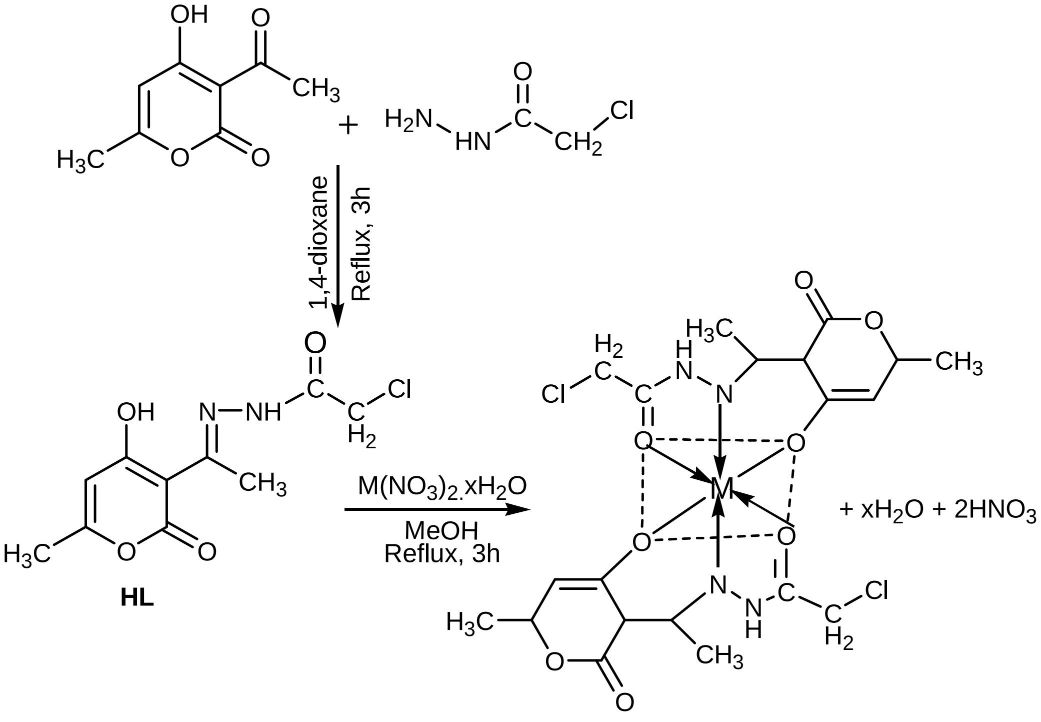
Keywords: Antimicrobial, octahedral, hydrazones, tridentate

INTRODUCTION

Schiff bases are mostly wide chelators due to their ease of preparation, structural variation [1], varied denticites and suitable steric, electronic control on their framework. The biocidal effect of Schiff bases and their transition metal complexes is of great interest due to their pharmacological activities [2-4]. Here 3-Acetyl-4-hydroxy-6-methyl-2H-pyran-2-one (dehydroacetic acid-DHA) has been used as one of the component for the preparation of Schiff base ligand which have been reported to act as potential biocides [5-7]. The implication of dehydroacetic acid as fungicide is owing to subsistence of several natural fungicides possessing structure analogous to 5,6-dihydro dehydroacetic acid like alternaic acid [8], podoblastins [9] and lachnellveoic [10]. It is however, noteworthy that the biological activity of dehydroacetic acid is enhanced on complexation to metal atom. It has been reported that many drugs possess modified pharmacological and toxicological potentials when given in the form of their metal complexes. Keeping the significance of metal complexes of dehydroacetic acid in mind, we have synthesized and characterized transition metal (II) complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff base hydrazone of dehydroacetic acid and studied the effect of complexation on their biocidal activity.

EXPERIMENTAL SECTION

All the chemicals used in synthesis were of analytical grade. Metal salts were used as nitrates obtained from Aldrich and used as such without any further purification. Elemental analysis of samples was carried out by using Perkin Elmer 2400 instrument. Metal contents were determined using standard gravimetric methods, cobalt as cobalt pyridine thiocyanate, nickel as nickel dimethylglyoximate, copper as cuperous thiocyanate and zinc as zinc ammonium phosphate. IR spectra were recorded on Shimadzu IR affinity-I 8000 FT-IR spectrometer using KBr disc. ^{1}H NMR and ^{13}C NMR were recorded on Bruker Avance II 300 MHz NMR spectrometer and all chemical shifts were reported in parts per million relative to TMS as internal standard in $CDCl_3$. UV spectra were recorded on UV-Vis-NIR Varian Cary-5000 spectrometer in DMF. Magnetic susceptibilities of complexes were measured by Gouy's method, using Hg $[Co(SCN)_4]$ as the calibrant at room temperature. Mass spectra were recorded on a API 2000 (Applied Biosystems) mass spectrometer equipped with an electrospray source and a Shimadzu Prominence LC.



M = Co (II), Ni(II), Cu(II) and Zn(II)
x = 1,6

Scheme - 1

Synthesis of Schiff base
Chloro-aceticacid[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-ethylidene]-hydrazide (HL)

A solution of chloroacetic acid hydrazide (2.16 g, 2 mmol) in 1,4-dioxane (10 mL) was added dropwise with stirring to solution of dehydroacetic acid (3.36 g, 2 mmol) in 1,4-dioxane (20 mL). The reaction mixture was refluxed for 3h and after cooling to room temperature, poured into beaker containing ice-cold water. The solid product formed was filtered and dried to give white compound, which was recrystallized from ethanol to get the desired Schiff base hydrazone.(Yield 75%)

Synthesis of cobalt(II) complex of chloro-aceticacid[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-ethylidene]-hydrazide

The methanolic solution of chloro-aceticacid[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-ethylidene]-hydrazide (HL) (2.58 g, 10 mmol) was added to the solution of metal salt $Co(NO_3)_2.6H_2O$ (1.45 g, 5 mmol) in methanol with constant stirring. The resulting solution was refluxed for 3h. On cooling to room temperature, the solid product separates out, filtered, washed with hot methanol or petroleum ether to remove unreacted metal nitrates and then dried in vacuum over anhydrous calcium chloride.

Similar procedure was adopted for the reactions of other hydrated metal nitrates $M(NO_3)_2$. xH_2O [M = Ni(II), Cu(II) and Zn(II)] with chloro-aceticacid[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-ethylidene]-hydrazide (HL) in 1:2 molar ratio **(*Scheme - 1*)**.

Pharmacology

Tested microorganisms

Microorganisms which was used for antibacterial and antifungal strains:

Gram positive bacteria *Bacillus subtilis* (MTCC No. 1790), *Micrococcus luteus* (MTCC No. 4821), Gram negative bacteria *Pseudomonas aeruginosa* (MTCC No. 9126), *Pseudomonas mendocina* (MTCC No. 7094) and fungi *Verticillum dahlia* (MTCC No. 2063), *Cladosporium herbarium* (MTCC No. 351), *Trichophyton soudanense* (MTCC No.7859). The bacteria and fungi were subcultured on Nutrient agar and Sabouraud dextrose agar respectively. The experimental values were compared with standard drugs *Streptomycin* for antibacterial activity and *Fluconazole* for antifungal activity.

Antibacterial activity assay

Stock solution for *in vitro* antibacterial activity was prepared by dissolving compound in minimum amount of DMSO. 15 mL of liquid nutrient agar for activation were prepared separately for tested target microorganism cultures. Inoculation was done with the help of micropipette with sterilized tips, 100 μL of activated strain was placed onto the surface of agar plate, spread over the whole surface and then two wells having diameter of 10 mm were dug in media. Sterilized stock solutions were used for the application in the well of inoculated agar plates. In this well of inoculated agar plates 100 μL of solution was poured and incubated at 37 °C for 48 h. Activity was determined by measuring the diameter of zone showing complete inhibition and has been expressed in mm.

Antifungal activity assay

For *in vitro* antifungal activity, the moulds were grown on sabouraud dextrose agar (SDA) at 25°C for 7 days and used as inoculate. 15 mL of molten SDA (45°C) was added to 100 μL volume of each compound having concentration of 100 μg/mL, reconstituted in the DMSO, poured into a sterile Petri plate and allowed to solidify at room temperature. The solidified poisoned agar plates were inoculated at the centre with fungal plugs 10 mm obtained from actively growing colony and incubated at 25°C for 7 days. Diameter of the fungal colonies was measured and expressed as percent mycelial inhibition using the following formula.

Inhibition of mycelial growth % = $(d_c - d_t)/d_c \times 100$

d_c, average diameter of fungal colony in negative control; d_t average diameter of fungal colony in experimental plates.

RESULTS AND DISCUSSION

All the metal complexes were obtained as colored solid, stable on prolonged exposure to air and insoluble in most of common organic solvents expect in DMF and DMSO. The molar conductivity of metal complexes in DMSO has low value 3.5-9.3 Ω^{-1} cm^2 mol^{-1} indicated non electrolytic nature of complexes. The purity of ligand and its metal complexes has been checked by TLC.

IR spectra

The mode of binding of Schiff base ligand to metal ion was elucidated by recording the IR spectra of complexes as compared with spectra of free ligands **(Table-1)**. A strong band observed at 3380 and 1675 cm^{-1} due to υ (N-H) and υ (C=O) group in the spectra of ligand were shifted to 3345-3365 cm^{-1} and 1635-1655 cm^{-1} respectively in complexes indicated that hydrazone ligand has coordinated to metal centre through carbonyl oxygen. The IR spectra of complexes have absorption bands at 1535-1555 cm^{-1} assigned to υ (C=N) stretching frequencies where as for free ligand these bands were observed at 1589 cm^{-1} which suggested the donation of the lone pair of electrons on azomethine nitrogen to metal centre [11]. Donation of lone pair of electron on nitrogen atom has also been strengthened by the shift of υ (N-N) band from 1014 cm^{-1} in free ligands to 1035-1045 cm^{-1} in complexes. In the spectrum of ligand the stretching vibration of υ (C=O, lactone) at 1726 cm^{-1} remains unaltered on complexation, indicated the non-involvement of this group in coordination. A characteristic band at 3420 cm^{-1} ascribed due to υ (OH), disappeared in spectra of metal complexes, confirmed deprotonation and coordination through oxygen [12]. Furthermore, the appearance of new bands of low frequency observed at 430-445 cm^{-1} and 490-510 cm^{-1} assigned to υ (M-O) and υ (M-N) vibrations respectively in complexes [13,14] also supports coordination.

Table-1: Infrared spectral characteristics (υ, cm^{-1}) of dehydroacetic acid hydrazone and its metal complexes

Ligands	**(N-H)**	**(N-N)**	**(C=O)**	**(C=N)**	**(M-O)**	**(M-N)**
HL	3380 m	1014 m	1675 s	1589 s	--	--
Co(L)$_2$	3345 m	1040 m	1640 s	1535 s	445 w	505 w
Ni(L)$_2$	3360 m	1035 m	1635 s	1555 s	430 m	495 m
Cu(L)$_2$	3354 m	1035 m	1655 s	1545 s	442 m	510 w
Zn(L)$_2$	3365 m	1045 m	1640 s	1550 s	435 w	490 m

^{1}H and ^{13}C NMR spectra

The NMR (^{1}H,^{13}C) spectra of compounds were recorded in $CDCl_3$ containing small amount of DMSO-d$_6$ with TMS as the internal reference (**Table-2**). On comparing ^{1}H NMR of Schiff base hydrazone and its zinc(II) complex Zn(L)$_2$, the absence of peak due to OH proton suggested the deprotonation of OH group and peak at δ 15.53 observed due to NH proton was almost same as that of free ligand showed coordination to metal ion through keto form. The signals due to proton of CH_2, CH (C_5), and CH_3 group (attached to C_6) remains almost unaltered on complexation except a slight shift in methyl protons attached to CH=N from δ 2.21 to δ 2.35, indicated involvement of azomethine nitrogen in bonding to metal ion. It was observed that DMSO has no coordinating effect in metal complexes.

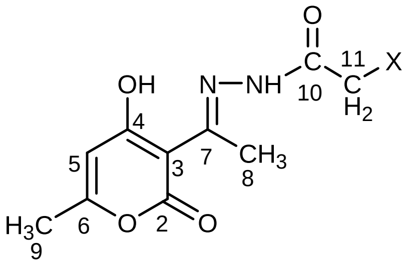


Fig.- I

Table-2: ^{1}H and ^{13}C NMR spectral characteristics (δ) of dehydroacetic acid hydrazone

Ligand/complex	**^{1}H NMR($CDCl_3$) δ in ppm**	**^{13}CNMR($CDCl_3$) δ in ppm**
HL	15.53 (s, 1H, NH), 11.24 (s, IH, OH), 5.90 (s, 1H, C_5-H), 2.21 (s, 3H, C_8-H), 2.58 (s, 3H, C_9-H), 3.50 (s, 2H, C_{11}-H)	63.97 (C_2), 97.43 (C_3), 189.53 (C_4), 106.72 (C_5), 156.51 (C_6), 162.04 (C_7), 12.70 (C_8), 18.52 (C_9), 181.34 (C_{10}), 35.02 (C_{11})
Zn(L)$_2$	15.63 (s, 1H, NH), 5.82 (s, 1H, C_5-H), 2.35 (s, 3H, C_8-H), 2.55 (s, 3H, C_9-H), 3.48 (s, 2H, C_{11}-H)	156.43 (C_2), 106.64 (C_3), 184.50 (C_4), 106.37 (C_5), 156.54 (C_6), 160.05 (C_7), 12.70 (C_8), 18.80 (C_9), 179.85 (C_{10}), 34.48 (C_{11})

In ^{13}C NMR of complex, the signals due to carbon (C_4) to which OH group is attached was shifted from δ 189.53 to δ 184.50, carbon of azomethine group (C_7) shifted from δ 162.04 to δ 160.05 and carbonyl carbon (C_{10}) shifted from δ 181.34 to δ 179.85. The other carbon atoms were observed in the range of δ 156.51-12.70 remain almost unaltered on complexation.

Mass Spectra

The LC-MS of ligand and its complexes were recorded which were in close agreement with molecular ion peak. Ligand HL ($C_{10}H_{11}N_2O_4Cl$) showed molecular ion peak at m/z = 258.66 and its corresponding cobalt(II) complex Co(L)$_2$ ($C_{20}H_{20}N_4O_8ClCo$), Ni(L)$_2$ ($C_{20}H_{20}N_4O_8ClNi$), Cu(L)$_2$ ($C_{20}H_{20}N_4O_8ClCu$), Zn(L)$_2$ ($C_{20}H_{20}N_4O_8ClZn$) showed a well-defined molecular ion peak at m/z 538.78, 538.54, 543.39, 545.24 respectively.

Electronic Spectra and Magnetic Susceptibility Measurements

The electronic spectral measurements were used for assigning the stereochemistry of metal ions in complexes based on positions and number of d-d transition peaks. The electronic spectra and magnetic moment data of compounds are summarized in **Table-3**. The electronic spectra of Co(II) complex showed three d-d bands at 8,750 cm^{-1}, 17,125 cm^{-1} and 24,930 cm^{-1} assignable to transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (υ_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (υ_2)and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (υ_3) respectively [15]. The energy ratio υ_2/υ_1 is 1.95 and was in the range of octahedral configuration. The ligand field parameters, racah interelectronic repulsion parameter B and nephelauxetic ratio β calculated for the Co(II) complex were found to be 632.00 cm^{-1} and 0.65, respectively. The Co(II) complex showed magnetic moment of 4.05 BM, corresponded to the presence of three unpaired electrons indicating a quartet ground state, which was orbitaly triply degenerate and caused an angular moment contribution to magnetic moment. These parameters along with the transitions indicated d^7 high spin system characteristics of octahedral geometry around Co(II). The electronic spectra of Ni(II) complex exhibited three bands at 9,250 cm^{-1}, 14,210 cm^{-1} and 24,825 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (υ_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (υ_2), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (υ_3) transitions respectively [16]. The energy ratio υ_2/υ_1 was found to be 1.53 which is in conformity with octahedral geometry. The parameter B, β calculated for the Ni(II) complex was found to be 752.33 cm^{-1}, 0.73, respectively. The B value for complex was found to be less than free ion value because of the decreased interelectronic repulsion from electron delocalization thereby suggested a weak covalent bond. The effective magnetic moment of Ni(II) complex was found to be 2.87 BM due to two unpaired electrons indicated a triplet ground state and have octahedral geometry around metal ion. For Cu(II) complex broad band at 15,890 cm^{-1} due to $^2E_g(D) \rightarrow {}^2T_{2g}(D)$ transition indicated the distortion from octahedral geometry, while another band at 24,450 cm^{-1} was due to charge transfer transition and have magnetic moment of 1.95 BM which corresponded to single unpaired electron with significant orbital contribution. This increase from spin only value might be due to orbital motion of electrons [17]. In the electronic spectrum of Zn(II) complex only one band at 22,330 cm^{-1} was observed due to LMCT transition and this complex was found to be diamagnetic as expected for d^{10} configuration.

Table-3: Electronic absorption spectral data and magnetic moment (μ) of transition metal(II) complexes of dehydroacetic acid hydrazone

Complexes	Absorption (cm^{-1})	Band assignment	B value (cm^{-1})	β value	Geometry	μ (BM)
$Co(L)_2$	24930 17125 8750	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	632.00	0.65	Octahedral	4.05
$Ni(L)_2$	24825 14210 9250	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	752.33	0.73	Octahedral	2.87
$Cu(L)_2$	24450 15890	π N→ Cu* $^2E_g(D) \rightarrow {}^2T_{2g}(D)$	--	--	Distorted Octahedral	1.95
$Zn(L)_2$	22320	LMCT	--	--	Octahedral	--

ESR spectra of copper(II) complex

The ESR spectra of polycrystalline sample of copper(II) complex was recorded at room temperature that possess a characteristic spectra having asymmetric bands with two g values ($g_\parallel$ and $g_\perp$). The values were computed from the spectrum using 'g' marker TCNE (g = 2.0023). The observed value for Cu(II) complex $Cu(L)_2$ was $g_\parallel = 2.38$ and $g_\perp = 2.10$. The anisotropic G value calculated comes out to be less than 4 (i:e 3.86) gave idea about some interaction between copper centers in Cu(II) complex. The trend $g_\parallel > g_\perp > 2.0023$ for this complex was in accordance with axially elongated octahedral geometry and showed that the unpaired electron is present in $d_{x^2-y^2}$ orbital of Cu(II) ion [18]. The $g_\parallel$ and $g_\perp$ values of six coordinated $Cu(L)_2$ complex was close to 2 and $g_\parallel > g_\perp$ suggested distortion from octahedral geometry in the complex. The value of $g_\parallel$ function is for indicating covalency, if $g_\parallel > 2.3$ it was characteristics of anionic environment and if $g_\parallel < 2.3$ it showed covalent environment in metal-ligand bonding. Since $g_\parallel$ in Cu(II) complex was less than 2.3 thus indicating covalent bonding in Cu(II) complex. The covalent character of M-L bond in the complex was further established by calculating spin orbital coupling constant λ (-754 cm^{-1}) which comes out to be less than Cu(II) free ion λ (-832cm^{-1}). The value of molecular orbital coefficients, in-plane σ bonding (α^2, 0.61) and in-plane π bonding (β^2, 0.97) indicated that there is substantial interaction in the in-plane σ bonding whereas the in-plane π bonding is almost ionic [19].

Antimicrobial activity

The *in vitro* antimicrobial activity of the dehydroacetic acid hydrazone and its transition metal (II) complexes at different concentrations (25, 50, 100, 200 μg/mL) are given in **Table-4, 5**. Antibacterial activity of ligand and its metal complexes were assessed against Gram positive bacteria *Bacillus subtilis, Micrococcus luteus* and Gram negative bacteria *Pseudomonas aeruginosa, Pseudomonas mendocina* using agar plate disc method and antifungal activity of ligand and its complexes were assessed against three fungi *viz. Verticillum dahliae*, *Cladosporium herbarium*, *Trichophyton soudanense*. *Streptomycin* and *Fluconazole* were used as the positive control to assess antibacterial and antifungal activity respectively.

In case of antibacterial activity, it was observed that ligand showed zone of inhibition ranging from 9-15 mm, with complexation with metal ion zone of inhibition increased ranging from 11-25 mm. Copper(II) complex showed highest activity against gram +ve bacteria at lower concentration (25μg/mL) almost near to standard drug *Streptomycin*.

In case of antifungal activity, it was observed that ligand showed 50% or less than 50% inhibition of mycelia growth against all the tested fungi, whereas all complexes showed more than 50% inhibition of mycelial growth and

Cu(II) complex was found to be more active showed more than 60% inhibition of mycelial growth. Cu(L)$_2$ was found to most active against *T. soudanense* and showed 70.7% mycelial growth inhibition.

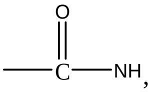
On comparing the bioactivity of ligand and their transition metal complexes, it was observed that the growth inhibition follows the trend: Cu > Zn > Ni > Co > HL. A marked enhancement was observed in the antimicrobial activity of ligand on coordination to metal ions under similar experimental conditions. Such increase in the activity of complexes was explained on the basis of chelation theory [20]. Besides chelation several other factors on which antimicrobial activity depends include the presence of toxophorically important group  $-C(=O)-NH$, which may invoke hydrogen bonding with active centres of cell constituents, there by resulting in interference with normal cell process [21]. The activity increased with increase in concentration of the test solution of the ligand and their complexes.

Table-4: The *in vitro* antibacterial activity of dehydroacetic acid hydrazones and its transition metal(II) complexes

Sr. No	**Compounds**	**Zone of Inhibition (mm)**															
		Gram +ve								**Gram –ve**							
		B. subtilis				***M. luteus***				***P. aeruginosa***				***P. mendocina***			
		25	**50**	**100**	**200**	**25**	**50**	**100**	**200**	**25**	**50**	**100**	**200**	**25**	**50**	**100**	**200**
1	**HL**	9	11	13	14	11	12	14	15	9	11	13	15	11	13	13	14
2	**Co(L)$_2$**	11	14	14	18	13	15	15	19	12	16	18	18	13	15	15	20
3	**Ni(L)$_2$**	14	16	17	19	15	16	17	19	14	16	16	19	15	17	17	20
4	**Cu(L)$_2$**	18	19	20	23	18	20	21	24	17	19	20	22	19	19	21	25
5	**Zn(L)$_2$**	16	18	18	20	15	17	19	21	16	18	18	20	18	18	20	23
6	***Streptomycin***	19	21	25	26	19	20	23	25	20	23	25	28	22	25	27	30

Table-5: The *in vitro* antifungal activity of dehydroacetic acid hydrazones and its transition metal(II) complexes

Sr. No	**Compounds**	**Mycelial growth Inhibition (%)**											
		V. dahliae				***C. herbarium***				***T. soudanense***			
		25	**50**	**100**	**200**	**25**	**50**	**100**	**200**	**25**	**50**	**100**	**200**
1	**HL**	45.8	46.4	47.2	48.3	44.2	45.9	46.4	47.3	47.2	49.4	50.1	51.2
2	**Co(L)$_2$**	54.2	54.8	58.7	58.7	53.8	55.6	57.4	59.2	53.1	54.3	54.9	56.2
3	**Ni(L)$_2$**	55.2	55.8	57.3	59.2	56.2	57.4	58.9	60.0	55.3	55.8	57.4	58.2
4	**Cu(L)$_2$**	60.2	61.4	63.3	64.5	60.4	62.2	62.8	63.4	64.4	66.2	67.8	70.7
5	**Zn(L)$_2$**	57.3	58.4	59.4	60.2	56.4	58.2	59.9	60.2	57.3	58.2	59.4	59.9
6	***Fluconazole***	76.2	79.4	79.8	81.2	75.8	77.2	78.3	81.9	74.1	76.4	79.6	83.3

CONCLUSION

Based on various physicochemical studies it revealed that Schiff base hydrazone acted as tridentate ligand ONO coordinating through oxygen of hydroxyl group, azomethine nitrogen and carbonyl oxygen to divalent metal ion forming complexes of type ML$_2$ with octahedral or distorted octahedral geometry. All synthesized compounds showed promising antimicrobial activities against tested organisms and complexes have better activity as compared to the parent ligand under identical experimental conditions.

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