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Synthesis, characterization and biological activity of mixed ligand metal (II) complexes derived from benzofuran-2-carbohydrazide schiff base and malonyldihydrazide

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ABSTRACT

The mixed ligand complexes of the type $[M(L)(L^{'})Cl_2]$ *, where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), L = primary ligand derived from reaction between benzofuran-2-carbohydrazide and 3, 4, 5-trimethoxybenzaldehyde (TMeOBFC) and* $L^{'}$ *= secondary ligand, malonyldihydrazide (mdhz) have been synthesized. The structures of the complexes have been proposed in the light of analytical data, IR, UV-Vis,* ^{1}*H NMR, DART-MS, ESR spectra, and magnetic studies. The antibacterial and antifungal activities of the ligands and their metal complexes have been screened against bacteria E. coli and S. aureus and fungi A. niger and A. flavus.*

Keywords: Benzofuran, Schiff base, Mixed ligand complexes, Spectral studies, Biological activity.

INTRODUCTION

Schiff base ligands are of significant interest not only for their pharmacological properties as antibacterial, antifungal, and anticancer agents [1, 2], but also for their capacity for chemical recognition of anions and metals of biochemical and environmental importance [3, 4]. Schiff base complexes of transition metals are of particular interest to inorganic chemists because their structural, spectral, and chemical properties are often strongly dependent on the nature of the ligand structure [5 – 8]. The coordination chemistry of transition metal complexes with mixed ligands are of current interest because they can provide new materials with useful properties such as magnetic exchange[9, 10], electrical conductivity [11], photoluminescence [12], nonlinear optical property [13], and antimicrobial activity [14]. The biological importance of mixed ligand complexes is that they are sometimes more effective than the free ligands [15]. Mixed-ligand complexes containing nitrogen and oxygen donors are important owing to their antifungal, antibacterial, and anticancer activities [16].

The aim of the present work is to synthesize and characterize the Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) mixed ligand metal complexes with primary ligand derived from benzofuran-2-carbohydrazide and 3, 4, 5-trimethoxybenzaldehyde (TMeOBFC) and secondary ligand as malonyldihydrazide (mdhz). The Schiff base and their metal complexes were screened for their antibacterial and antifungal activities.

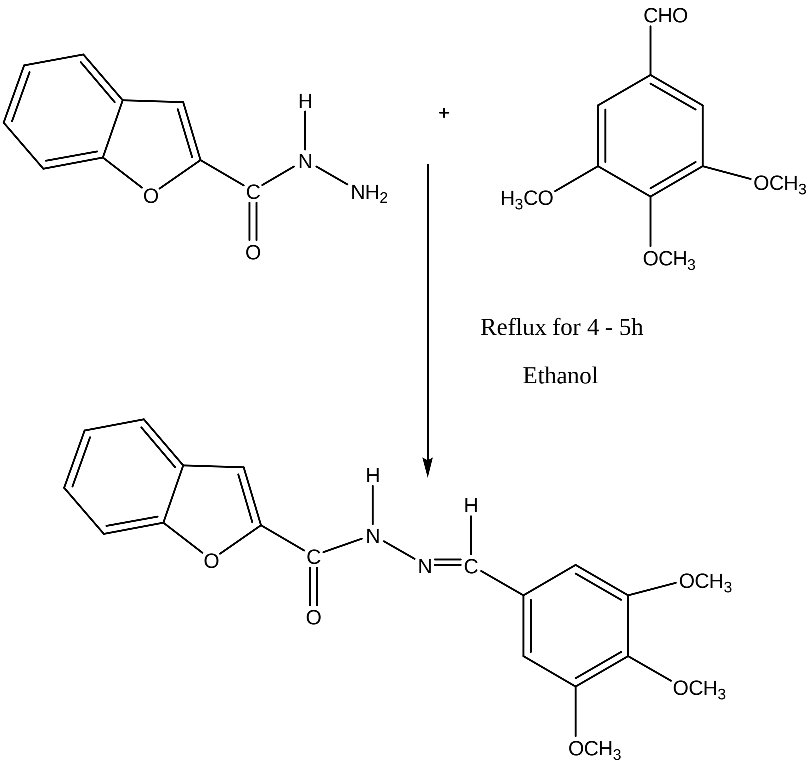
MATERIALS AND METHODS

Experimental

All the chemicals used were of analytical reagent grade (AR) and of highest purity available. Benzofuran-2-carbohydrazide and malonyldihydrazide were synthesized according to the literature procedures [17, 18]. The metal and chloride contents were determined as per Vogel's procedure [19]. Carbon, Hydrogen and Nitrogen analysis were carried out micro analytically on a Perkin Elmer 240C model at the Central Drug Research Institute (CDRI) Lucknow. The IR spectra of the Schiff's base and their mixed ligand complexes were recorded in KBr pellets in the region 4000-350 cm^{-1} on a Perkin Elmer 783 FT-IR spectrophotometer. The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes were recorded on an Elico-SL-164 double beam UV-visible spectrophotometer in the range 200-1100 nm in DMF (10^{-3} M) solution. The ^1H NMR spectra were recorded in DMSO-d_6 on a Bruker 300 MHz spectrophotometer using TMS as an internal standard. The ESR spectrum of the Cu(II) complex in polycrystalline state was recorded on a Varian-E-4X band EPR spectrophotometer using TCNE as 'g' marker (g=2.00277) at room temperature. DART-mass spectra were recorded on a JEOL-AccuTOF JMS-T100LC Mass spectrometer having a DART (Direct Analysis in Real Time) source. Dry Helium was used with 4 LPM flow rate for ionization at 350 ^{O}C, the orifice 1 set at 28 V. Molar conductivity measurements were recorded on a Elico CM-180 conductivity bridge in DMF (10^{-3} M) solution using a dip-type conductivity cell fitted with a platinum electrode and the magnetic susceptibility measurements were made at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant.

Synthesis of (E)-N′-(3, 4, 5-trimethoxybenzylidene)benzofuran-2-carbohydrazide [TMeOBFC]

A solution of benzofuran-2-carbohydrazide (1.76 g, 0.01 mol) in ethanol (25 mL) was added to 3, 4, 5-trimethoxybenzaldehyde (1.96 g, 0.01 mol) in ethanol (20 mL). The reaction mixture was refluxed on a water bath for 4-5 h. The Schiff base separated on partial removal of the solvent and cooling to room temperature as light yellowish crystalline solid, which was filtered, washed with ethanol and recrystallised from ethanol. The synthesis of Schiff base is shown in Scheme-1.



Scheme-1. Synthesis of Schiff base [TMeOBFC]

$C_{19}H_{18}O_5N_2$ [TMeOBFC]: Mol. Wt = 354, m.p = 233 ^{O}C, Yield = 72 %

Synthesis of Metal(II) Mixed Ligand Complexes

An ethanolic solution (20 mL, 0.01 mol) of the appropriate metal chloride, MCl_2, (M = Co, 2.378 g; M = Ni, 2.377 g; M = Cu, 1.705 g; M = Zn, 1.363 g; M = Cd, 2.013 g; M = Hg, 2.715 g) was added to an ethanolic solution (30 mL) of the Schiff base, primary ligand [TMeOBFC] (3.54 g, 0.01 mol). An ethanolic solution (20 mL, 0.01 mol) of the secondary ligand malonyldihydrazide (1.32 g) was added to the previous solution and the reaction mixture was refluxed for about 3 h on a water bath and then aqueous alcoholic solution of sodium acetate was added to the mixture to adjust the pH 6 to 7 and further refluxed for about an hour. The complexes precipitated were filtered and washed with distilled water, then with alcohol and finally dried in vacuum over fused calcium chloride (Yield = 56 – 62 %).

Biological activities

The Schiff base ligand and its Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes have been studied for their antibacterial and antifungal activities by agar diffusion method respectively in DMF solvent against *Escherichia coli* and *Staphylococcus aureus* bacterial species using agar nutrient as the medium and gentamycin as the standard drug and against *Aspergillus niger* and *Aspergillus flavus* fungi species using potato dextrose agar as the medium and fluconazole as the standard drug [20, 21]. The stock solution (10 mg / 10 mL) was prepared by dissolving the compounds in DMF. A circular well was made at the center of each petri dish with a sterilized steel borer. Then, 0.1 mL of each test solution was added to the well using a micropipette and the plate was incubated, 24 h for bacteria and 48 h for fungi at 37 ^oC and the diameter of inhibition zone were noted.

Table-1 Elemental analysis, molar conductance and magnetic susceptibility data for Schiff base [TMeOBFC] and their mixed ligand metal complexes

Molecular formula of Schiff base / Complexes	Mol. weight	C%		H%		N%		M%		Cl%		$\Lambda_M{}^*$	μ_{eff} (BM)
		found	calcd	found	calcd	found	calcd	found	calcd	found	calcd		
$C_{19}H_{18}O_5N_2$ TMeOBFC (L)	354	64.21	64.41	4.82	5.08	7.76	7.91	-	-	-	-	-	-
$[Co(L)(L^{'})Cl_2]$	616.32	42.62	42.87	4.02	4.25	13.38	13.64	9.23	9.56	11.21	11.50	18.29	4.88
$[Ni(L)(L^{'})Cl_2]$	616.07	42.65	42.89	4.01	4.25	13.36	13.64	9.21	9.53	11.23	11.51	16.27	2.99
$[Cu(L)(L^{'})Cl_2]$	620.93	42.23	42.55	3.92	4.22	13.21	13.53	10.02	10.23	11.18	11.42	12.23	1.79
$[Zn(L)(L^{'})Cl_2]$	622.77	42.21	42.43	3.89	4.21	13.18	13.49	10.23	10.50	11.13	11.39	21.55	-
$[Cd(L)(L^{'})Cl_2]$	669.79	39.23	39.45	3.75	3.91	12.23	12.55	16.45	16.78	10.23	10.59	19.17	-
$[Hg(L)(L^{'})Cl_2]$	757.97	34.69	34.86	3.21	3.46	10.82	11.09	26.21	26.46	9.08	9.35	20.35	-

* *Molar conductance values in ohm^{-1}cm^{2}mole^{-1}.*

RESULTS AND DISCUSSION

The analytical data shows that all of the complexes have 1:1:1(metal : primary ligand : secondary ligand) stoichiometry (Table-1). The molar conductance values (12.23 – 21.55 ohm^{-1}cm^{2}mole^{-1}) are too low to account for any dissociation of the complexes in DMF, indicating non-electrolytic nature of the complexes [22]. All the complexes are light in color, stable and non-hygroscopic in nature and possess high melting points. The complexes are insoluble in common organic solvents but soluble in DMF and DMSO.

Magnetic Properties

Magnetic susceptibility measurements at room temperature exhibit paramagnetism for Co(II), Ni(II) and Cu(II) complexes and μ_{eff} values are listed in Table-1. Cobalt(II) complexes in an octahedral field are orbitally degenerate which causes an orbital angular momentum contribution to the magnetic moment and the experimental magnetic moment values lie between spin-only, $\mu_{SO} = [4S(S + 1)]^{1/2} = 3.88$ BM and $\mu_{SL} = [4S(S + 1) + L(L + 1)]^{1/2} = 5.2$ BM values. The obtained magnetic moment (μ_{eff}) value for the complex is 4.88 BM lying in the range between μ_{SO} and μ_{SL} indicating an octahedral geometry around Cobalt(II) [23, 24]. The Ni(II) complex shows magnetic moment value of 2.99 BM indicating an octahedral environment around Ni(II) ion [25, 26]. The observed magnetic moment for the Cu(II) complex is 1.79 BM suggesting a distorted octahedral geometry for Cu(II) complex [27].

Electronic spectra

The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes were recorded for freshly prepared solution in DMF(10^{-3} M) at room temperature and their data are produced in Table-2. The electronic spectra of Co(II) complex show two bands at 15923 and 19894 cm^{-1}. These two bands are assignable to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow$

$^4T_{2g}$ (P) (ν_3) transitions respectively in an octahedral environment [28]. The ν_1 band was calculated using an equation suggested by Underhill and Billing [29].

The Ni(II) complex exhibit two bands at 15223 and 26221 cm^{-1} assignable to $^3A_{2g}$ (F) → $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) (ν_3) transitions respectively in an octahedral environment. The lowest band ν_1 could not be observed due to limited range of the instrument used. However, it is calculated by using band fitting procedure [29].

The Cu(II) complex exhibit a single broad asymmetric band in the region 13056 – 17535 cm^{-1}. The broadness of the band indicates that the expected three transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), $^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_2) and $^2B_{1g} \rightarrow {}^2E_g$ (ν_3) are similar in energy and give rise to only one broad band. The broadness of the band may be due to dynamic Jahn – Teller distortion. All of these data suggest a distorted octahedral geometry around Cu(II).

The octahedral geometry [30] for Co(II), Ni(II) and Cu(II) mixed ligand complexes is further supported by the values of ligand field parameters such as Racah inter-electronic repulsion parameter (B'), ligand field splitting energy (10 Dq), covalency factor (β) and ligand field stabilization energy (LFSE) [31]. The B' values for the complexes were lower than free ion values, which is an indication of orbital overlap and delocalization of d – orbitals. The β values obtained are less than unity suggesting a considerable amount of covalent character for the metal – ligand bonds. The β value for Ni(II) complex is less than the Co(II) complex, indicating more covalency of M – L bond [32].

Table-2 Electronic spectral bands and ligand field parameters of the Co(II), Ni(II) and Cu(II) complexes in DMF (10^{-3} M) solution.

Complexes	Transitions in cm^{-1}			Dq (cm^{-1})	B' (cm^{-1})	β	β%	ν_2 / ν_1	LFSE (k.cal)
	$\nu_1{}^a$	ν_2	ν_3						
$[Co(L)(L')Cl_2]$	7413	15923	19894	851	906	0.933	6.694	2.148	14.589
$[Ni(L)(L')Cl_2]$	9250	15223	26221	925	912	0.877	12.308	1.646	31.714
$[Cu(L)(L')Cl_2]$	13056 - 17535			1530	-	-	-	-	26.228

^{a} *calculated values*

IR spectra

Due to the complex nature of the IR spectra of the mixed ligand metal complexes with varying intensities it is very difficult to assign all the bands, attempts, however, have been made to assign some of the important vibrational stretching bands on the basis of the reports available in the literature.

The Schiff base TMeOBFC shows medium broad bands at 3448 cm^{-1} and at 3216 cm^{-1} due to ν (NH) stretch of hydrazine residue. These bands are assigned to ν_{asym} and ν_{sym} stretching vibrations of secondary amide. These bands shift to higher wave numbers by about 8–16 cm^{-1} in the complexes, this shows clearly that the non-involvement of 'N' of NH group in bonding with metal ions [33]. The strong intensity bands appearing at 1695 cm^{-1} and at 1626 cm^{-1} are assigned to ν (C=O) and ν (C=N) stretching vibrations respectively in free ligand. These bands shift to lower wave numbers by about 27–56 cm^{-1} in the spectra of metal complexes indicating that ligand coordinate to metal ion through oxygen of C=O group and nitrogen of –N=CH- group [34, 35]. The band observed at 1031 cm^{-1} is assigned to ν (N-N) stretch of hydrazine residue, this band shifts to higher wave numbers by about 10-16 cm^{-1} in the metal complexes, confirming the bonding through one of the nitrogen atom of hydrazine moiety [36].

The secondary ligand malonyldihydrazide shows a pair of bands corresponding to ν (NH_2) at 3306 and 3295 cm^{-1} [37]. These bands are assigned to ν_{asym} and ν_{sym} stretching vibrations of primary amine and shift to a lower wavenumber side in all the metal complexes, indicating the involvement of nitrogen of primary amine in bonding with metal ion.

Metal-ligand vibrations are generally observed in the far-IR region and usually give valuable information regarding the bonding of ligands to metal ions. However, non-ligand new bands appearing in the region 530–518 cm^{-1} and 460–411 cm^{-1} were assigned to ν (M-O) and ν (M-N) stretching vibrations [38 – 40]. The weak intensity bands appearing in the region 390–362 cm^{-1} are assigned to ν (M-Cl) stretching vibrations.

^{1}H NMR spectra

^{1}H NMR spectra of [TMeOBFC] and their Zn(II) and Cd(II) complexes were recorded in DMSO-d_6.

The signal at δ (12.13) (s, 1H) is assigned to amide proton (-CONH-) and the signal at δ (8.44) (s, 1H) is assigned to azomethine proton (-N=CH-) in [TMeOBFC]. The signals due to (-CONH-) are shifted to downfield in the spectra of Zn(II) δ (12.56) (s, 1H) and Cd(II) δ (12.47) (s, 1H) complexes, indicating coordination of oxygen of –CONH- with metal ions. The azomethine protons shifts downfield in the spectra δ (8.65, 8.71) (s, 1H) supporting coordination of 'N' of the –N=CH- group with the metal ions. The aromatic protons at δ (6.94 – 7.83) shift downfield in the complexes. The signals at δ (3.29) (s, 3H, $-OCH_3$), δ (3.67) (s, 3H, $-OCH_3$) and δ (3.91) (s, 3H, $-OCH_3$) are due to the protons of three $-OCH_3$ groups present on the phenyl ring. Thus ^1H NMR observations supplement the assigned geometry.

Mass spectra

The DART-mass spectrum of the Schiff's base [TMeOBFC] has showed a molecular ion peak at m/z 355, which is one mass unit more than that of the molecular weight of the Schiff's base. The DART-mass spectrum of the $[Ni(L)(L')Cl_2]$ showed a molecular ion peak at m/z 616 which is same as that of the molecular weight of the complex. Thus Mass studies support the proposed composition.

ESR spectrum of Cu(II) complex

The ESR spectra of Copper(II) complex in a polycrystalline state has been recorded at room temperature. The $g_{\|}$ and $g_{\perp}$ values have been found to be 2.286 and 2.059 respectively. The g_{av} was calculated to be 2.138. The spectra have asymmetric bands with $g_{\|} > g_{\perp} > 2.00277$ (TCNE) observed, indicating the unpaired electrons lie predominantly in the d_{x2-y2} orbital with possibly mixing of d_{z2} because of low symmetry [41]. Appreciable difference between the $g_{\|}$ and $g_{\perp}$ values indicates a high degree of Jahn-Teller distortion around Copper(II). The axial symmetry parameter 'G' is determined as $G = (g_{\|} - 2.00277) / (g_{\perp} - 2.00277) = 4.962$ is found to be more than 4 [42].

Antibacterial and antifungal activities

The investigated compounds were tested for their activity against two bacteria *E. coli* and *S. aureus* and against two fungi *A. niger* and *A. flavus* by agar diffusion method. The results were summarized in Table-3 along with standards. A comparative study of the ligands and their complexes indicates that complexes exhibit higher antimicrobial activity than the free ligands [43, 44]. From the Table-3 and figs 1 and 2, it is clear that Co(II), Cu(II) and Cd(II) complexes are found to be more potent than other investigated complexes. A marked enhancement of activity was exhibited in all the complexes against all the bacterial / fungal strains. It was evident from the data that the antimicrobial activity of all the compounds was increased on coordination. Increased activity on metal chelation can be explained on the basis of chelation theory. The factors capable of increasing lipophilic nature are expected to enhance the antimicrobial property. While chelation is not the only criterion for antimicrobial activity, it is an intricate blend of several contributions such as the nature of the metal ion and the ligand, the geometry of the metal complex, the lipophilicity, the steric, and the pharmacokinetic factors [45].

Table-3 Antimicrobial activity of the ligands and their mixed ligand metal complexes.

Schiff base / Complexes	Zone of inhibition in mm			
	Bacteria		Fungi	
	E. coli	*S. aureus*	*A. niger*	*A. flavus*
TMeOBFC (L)	11	12	14	16
mdhz (L$'$)	13	15	16	15
$[Co(L)(L')Cl_2]$	18	19	19	21
$[Ni(L)(L')Cl_2]$	14	15	17	16
$[Cu(L)(L')Cl_2]$	18	20	20	21
$[Zn(L)(L')Cl_2]$	15	16	16	17
$[Cd(L)(L')Cl_2]$	19	18	19	20
$[Hg(L)(L')Cl_2]$	16	17	15	16
Gentamycine	20	22	--	--
Fluconazole	--	--	22	23

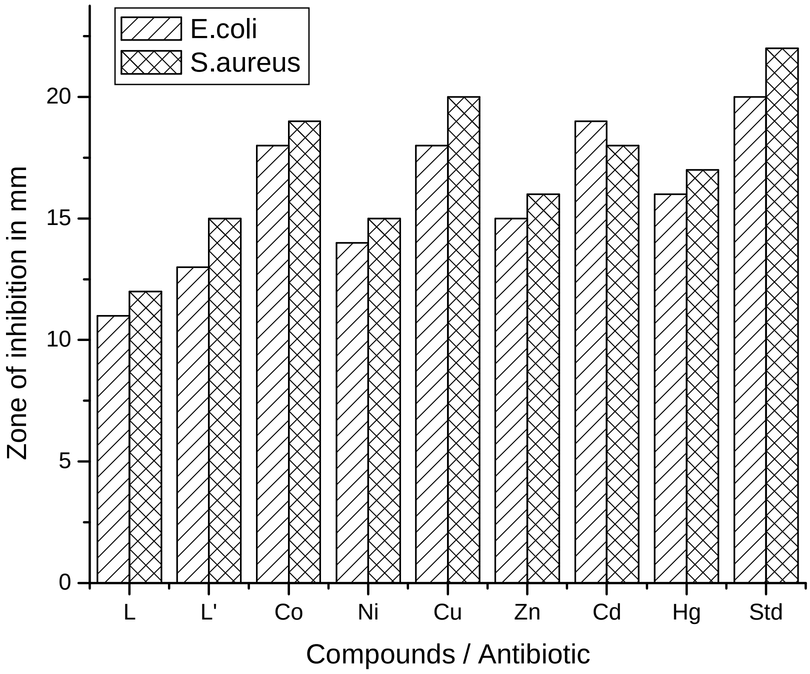


Figure-1. Antibacterial results of Schiff base [TMeOBFC] (L), malonyldihydrazide (L′), mixed ligand metal (II) complexes and Gentamycin (Std) at 1 mg /mL concentration.

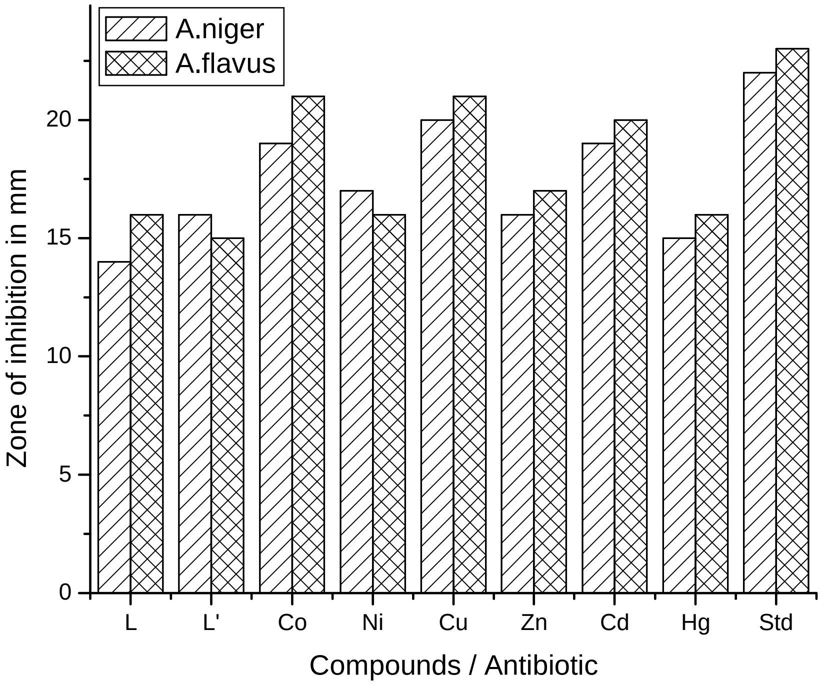
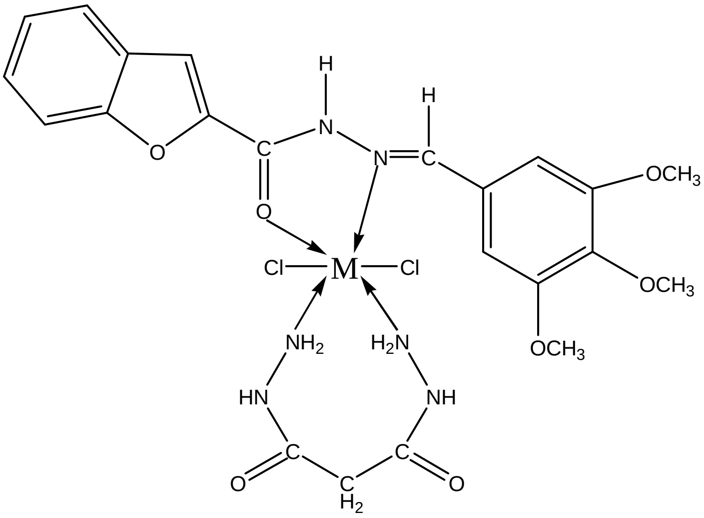


Figure-2. Antifungal results of Schiff base [TMeOBFC] (L), malonyldihydrazide (L′), mixed ligand metal (II) complexes and Fluconazole (Std) at 1 mg / mL concentration

CONCLUSION

In this paper, we report new mixed ligand complexes of the type $[M(L)(L^{'})Cl_2]$, where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), L = primary ligand (TMeOBFC) and $L^{'}$ = secondary ligand (mdhz) were synthesized. The Schiff base TMeOBFC acts as neutral bidentate by coordinating through azomethine 'N' and 'O' of –CONH- group to the metal ions, whereas mdhz coordinate through amino groups. Based on analytical data and spectroscopic studies we propose octahedral structures (Fig-3) to all the complexes. Biological activity results shows that metal complexes are more active compared to parent ligands.



Where M= Co(II), Ni(II), Cu(II), Zn(II), Cd(II) or Hg(II)

Figure-3. Suggested structures of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) or Hg(II) complexes

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