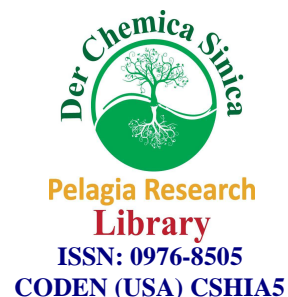




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### Synthesis and characterization of some biologically active mixed ligand complexes of transition metals such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)

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#### ABSTRACT

Present investigation deals with synthesis and characterization of Mixed ligand complexes of transition metals such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) using Schiff base prepared by condensing salicylaldehyde with ethylenediamine and 8-hydroxyquinoline. The Synthesized complexes have been characterized using conductivity measurements, room temperature magnetic properties and spectral methods such as IR, UV and NMR spectroscopy. The synthesized complexes were also screened for their biological activities such as antibacterial and antifungal. The studies made are indicating towards octahedral geometry for these complexes.

**Keywords:** Mixed ligand complexes, Transition metals, Spectral studies, Magnetic moments, Antimicrobial activity.

#### INTRODUCTION

The concept of mixed ligand complexes is always fascinating to the chemistry community. Interest in synthesis of mixed ligand complexes is because of their ease of synthesis and generally less time requirement for these reactions to occur than normal complex formation reaction using synthesized ligand and metal salt. These facts have prompted many researchers to publish their research work in this fascinating and interesting area of research [1-4].

8-hydroxyquinoline is used in many processes for the preparation of mixed ligand complexes from years [5-13]. Its ability to get bonded with metal with its phenolic oxygen and ring nitrogen results in forming stable chelates with metals in combination with some other ligands, thus producing stable mixed ligand complexes. Schiff bases are important in the area of research concerning to metal complex formation owing to their ease of preparation, binding ability, versatility they produce in the synthesized ligands by changing the reactants with substituted ones and various applications of the metal complexes synthesized using Schiff bases. Application of Schiff bases for the synthesis of mixed ligand complexes is known from many years. [14-18].

Present investigation deals with synthesis of mixed ligand complexes of transition metals such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) using Schiff base prepared by condensing salicylaldehyde with ethylenediamine and

8-hydroxyquinoline. The synthesized complexes have been characterized by molar conductance, room temperature magnetic properties and spectral methods such as IR, UV and NMR spectroscopy.

### MATERIALS AND METHODS

All the chemicals such as salicylaldehyde, ethylenediamine, 8-hydroxyquinoline, metal chlorides along with the solvents used in the present investigation were of good quality.

#### Analytical methods and measurements

The IR spectra were recorded as KBR pellets in the region 4000-200  $\text{cm}^{-1}$  on a THERMO NICOLET 380 spectrophotometer from Vishnu Chemicals pvt Ltd. Hyderabad. The  $^1\text{H-NMR}$  spectra was recorded in DMSO- $d_6$  on a bruker 300MHz using TMS as a reference from SAIF, Punjab University. Conductance measurements were performed in DMSO solutions using Equiptronics conductivity meter with inbuilt magnetic stirrer (Model Eq-664) at room temperature. Magnetic susceptibility values were measured at 25 $^{\circ}$ C by the Guoy's method using Copper (II) sulphate as calibrant. The complexes were soluble in DMSO and DMF but are insoluble in other common organic solvents and water.

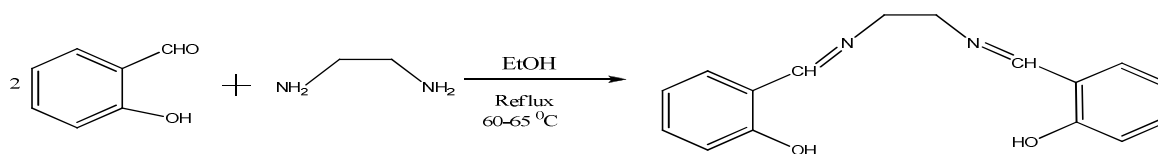
#### Antimicrobial assay of mixed ligand metal complexes:

Antimicrobial activity is determined using test microorganisms viz. *Candida albicans* (ATCC 14053), *Aspergillus niger* (MTCC 1781), *Staphylococcus aureus* (ATCC 10832) and *Escherichia coli* (ATCC 33684). The microbial cultures were purchased from National Collection of Industrial Microorganisms, NCL, Pune (India). The bacterial cultures were subcultured and maintained on Nutrient agar, whereas fungi on Potato dextrose agar medium.

The agar well diffusion method [23] was used to determine the antifungal and antibacterial activity of mixed ligand metal complexes. 0.1 ml of bacterial suspension ( $1.5 \times 10^8$  cfu/ml) of 24 hrs old activated culture of *S. aureus* and *E. coli* were swabbed separately on nutrient agar plate. Similarly 0.1 ml of activated fungal culture of *C. albicans* and *A. niger* spread on to each potato dextrose agar plates. After inoculation plates were incubated for 15 min for adsorption and wells were prepared into the seeded agar plates by using sterile cork borer (10 mm diameter). Wells were loaded with a 100  $\mu\text{l}$  (1000  $\mu\text{g/ml}$ ) of mixed ligand metal complexes, Schiff base and 8-hydroxyquinoline compound reconstituted DMSO. The standard Tetracycline (200  $\mu\text{g/ml}$ ) and Amphotericin B (200  $\mu\text{g/ml}$ ) was used to compare the antibacterial and antifungal activity respectively with mixed ligand metal complexes. The plates were incubated at 30 $^{\circ}$ C and measured the zone of inhibition around the well after 24-48 hrs for antibacterial assay and 48-72 hrs for antifungal activity. All experiments were performed in triplicate plates for each organism.

#### Preparation of Schiff base:

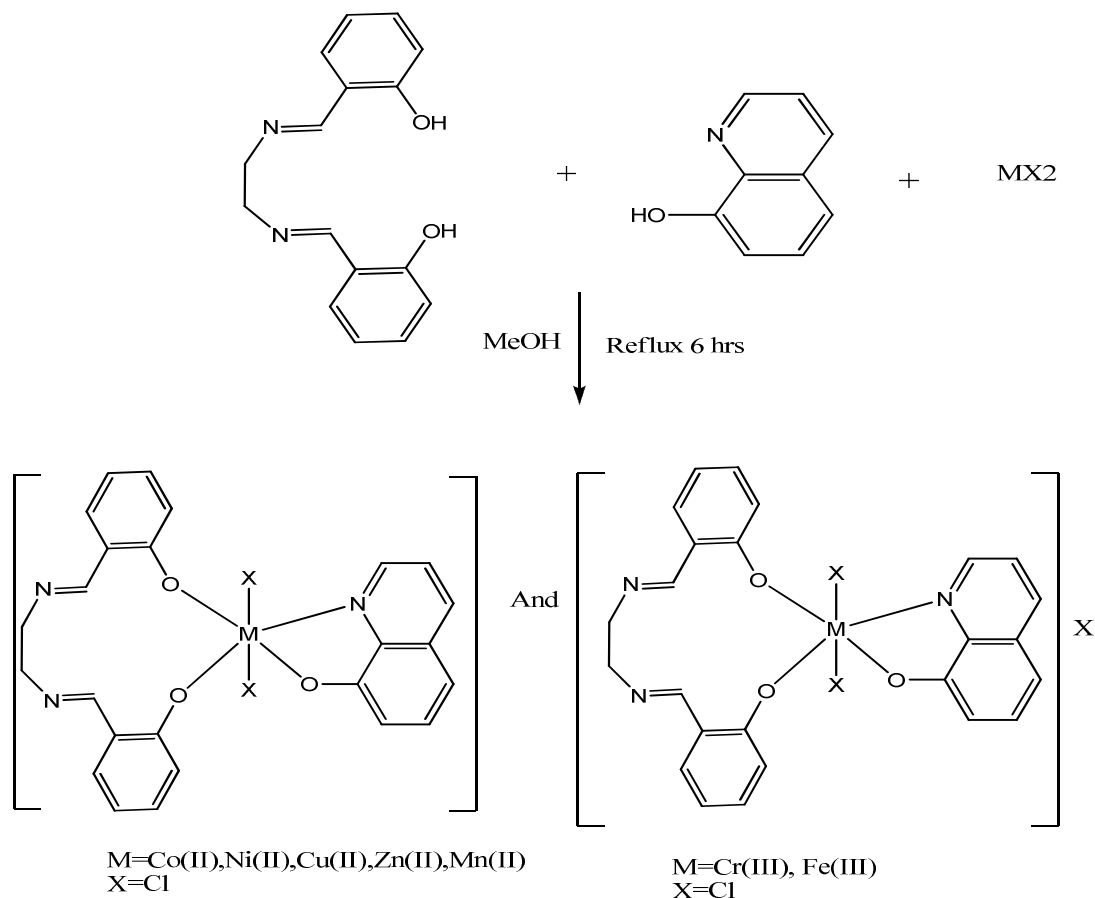
The Schiff base used in the present investigation was prepared by condensing two equivalents of salicylaldehyde with one equivalent of ethylenediamine by using the procedure reported earlier [19, 20].



Step 1: Preparation of Schiff base

#### Preparation of Mixed ligand metal complexes:

Hot methanolic solution (20 mL) of 8-Hydroxyquinoline (0.05 mmol) was added to a hot methanolic solution (20 mL) of schiff base (0.05 mmol) in two necked round bottom flask. Metal chloride solution (10 mL, 0.05 mmol) in methanol added dropwise to above reaction mixture. The resulting solution was refluxed with constant stirring for 6 hrs. The progress of the reaction was checked by thin layer chromatographic technique using solvent system 8:2 (Pet-ether + Ethyl acetate). After 6 hours refluxing was stopped, the reaction mixture was cooled to room temperature for about half an hour. The dark coloured precipitate appeared was then filtered, washed with methanol first then with acetone and dried in vacuum desiccator. The solid complex obtained was recrystallized from absolute ethanol.



## Step 2: Preparation of Mixed ligand complexes

## RESULTS AND DISCUSSION

All the mixed ligand complexes synthesized are coloured, non-hygroscopic and air stable solids. They are thermally stable indicating a strong metal-ligand bond. All the synthesized complexes are characterized using molar conductance, magnetic moments and spectral data. The physicochemical data collected for the complexes is shown in Table 1.

Table 1: Physico-chemical data of the mixed ligand metal complexes

Sr. No.	Complex Molecular formula	Colour	Melting Point (°C)	Yield %	Molar conductance 10 <sup>-3</sup> M	Magnetic moments $\mu_{eff}$ B. M.
1	C <sub>26</sub> H <sub>23</sub> Cl <sub>3</sub> CrN <sub>3</sub> O <sub>3</sub>	Dark black	>300	65	108.0	4.10
2	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> MnN <sub>3</sub> O <sub>3</sub>	Brown	280	72	22.0	5.91
3	C <sub>26</sub> H <sub>23</sub> Cl <sub>3</sub> FeN <sub>3</sub> O <sub>3</sub>	Dark green	275	68	134.0	5.90
4	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> CoN <sub>3</sub> O <sub>3</sub>	Green	260	75	20.0	4.72
5	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> NiN <sub>3</sub> O <sub>3</sub>	Light green	263	71	18.0	2.83
6	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> CuN <sub>3</sub> O <sub>3</sub>	Light green	270	62	12.0	1.95
7	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> ZnN <sub>3</sub> O <sub>3</sub>	Yellow	272	68	13.0	Diamagnetic

**Molar conductance measurements:**

Molar conductance values for all the synthesized complexes were measured in DMSO (10<sup>-3</sup> M) at room temperature. The low values of molar conductance obtained for synthesized mixed ligand complexes of divalent metal ions such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) indicate towards their nonelectrolytic behavior. The values obtained for Cr(III) & Fe(III) indicate towards 1:1 electrolytic nature.

**Thin layer chromatography:**

TLC of the all mixed ligand metal complexes was performed by using silica gel G in polar solvent system pet-ether and ethyl acetate (20%) and iodine vapors as the spray reagent. At the end of the reaction starting material was disappeared and all the complexes appeared as a single spot.

**Magnetic properties:**

All the complexes show magnetic moment values expected for octahedral geometry. The magnetic moment value for Cr(III) complex is 3.90 B. M. indicating towards three unpaired electrons close to spin only value, for Mn(II) and Fe (III) complexes the value is 5.91 and 5.90 B. M. respectively, which is close to that expected for high spin state indicating five unpaired electrons. For Co(II), Ni(II) and Cu(II) the values are 4.72, 2.83 and 1.95 B. M. indicating towards 2, 2, 1 unpaired electrons. Zinc complex is diamagnetic in nature.

**Solubility:**

Solubility of all the synthesized mixed ligand metal complexes along with 8-hydroxyquinoline was checked by using different solvents. The synthesized complexes are soluble in DMF, DMSO, partially soluble in MeOH, EtOH, Chloroform and insoluble in Acetone, Acetonitrile, and water except for few complexes being partially soluble. The solubility of all the synthesized complexes is represented in (Table 2).

**Table-2: Solubility of mixed ligand metal complexes**

Sr. No	Complexes	EtOH	MeOH	Acetone	Acetonitrile	Chloroform	Water	DMF	DMSO
1	C <sub>26</sub> H <sub>23</sub> Cl <sub>3</sub> CrN <sub>3</sub> O <sub>3</sub>	PS	PS	IS	IS	PS	IS	S	S
2	C <sub>26</sub> H <sub>23</sub> Cl <sub>3</sub> MnN <sub>3</sub> O <sub>3</sub>	PS	PS	IS	IS	PS	IS	S	S
3	C <sub>26</sub> H <sub>23</sub> Cl <sub>3</sub> FeN <sub>3</sub> O <sub>3</sub>	PS	PS	IS	IS	PS	IS	S	S
4	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> CoN <sub>3</sub> O <sub>3</sub>	PS	PS	PS	PS	PS	IS	S	S
5	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> NiN <sub>3</sub> O <sub>3</sub>	PS	PS	IS	IS	IS	IS	S	S
6	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> CuN <sub>3</sub> O <sub>3</sub>	PS	PS	PS	IS	PS	IS	S	S
7	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> ZnN <sub>3</sub> O <sub>3</sub>	PS	PS	PS	PS	PS	IS	S	S

\*I=Insoluble, PS= partially soluble, S= Soluble

**IR Spectra:**

The important infrared spectral bands and their assignments for the synthesized ligands and complexes were recorded as KBr discs and are presented in Table-3. The IR spectra for free ligands and its metal complexes were recorded within the IR range 4000-400 nm.

An important feature of infrared spectra of the metal complexes with 8-hydroxyquinoline is the absence of band at 3440 cm<sup>-1</sup> due to the O-H stretching vibration of the free O-H group of hydroxyquinoline [21]. This observation leads to the conclusion that complex formation takes place by the deprotonation of hydroxyl group of the hydroxyquinoline moiety.

Charles et. al [22], reported that for several metal complexes with HQ,  $\nu(\text{C-O})$  band is observed at 1120 cm<sup>-1</sup>. The position of this band undergoes variation depending on the metal complex under study. A strong  $\nu(\text{C-O})$  band is observed in the range 1103-1112 cm<sup>-1</sup> indicating the presence of oxine moiety in the complexes coordinating through its nitrogen and oxygen atoms as uninegative bidentate ligand.

**Table 3: IR Spectra of Synthesized complexes**

Sr. No.	Complex	$\nu(\text{C-H})_{\text{Ar}}$	$\nu(\text{C=C})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$
				For 8-hydroxyquinoline		
1	C <sub>26</sub> H <sub>23</sub> Cl <sub>3</sub> CrN <sub>3</sub> O <sub>3</sub>	3060	1467	1500	1109	529
2	C <sub>26</sub> H <sub>23</sub> Cl <sub>3</sub> MnN <sub>3</sub> O <sub>3</sub>	3080	1480	1500	1106	525
3	C <sub>26</sub> H <sub>23</sub> Cl <sub>3</sub> FeN <sub>3</sub> O <sub>3</sub>	2977	1467	1500	1103	524
4	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> CoN <sub>3</sub> O <sub>3</sub>	3047	1465	1499	1108	508
5	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> NiN <sub>3</sub> O <sub>3</sub>	3015	1460	1500	1106	599
6	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> CuN <sub>3</sub> O <sub>3</sub>	2977	1466	1502	1112	514
7	C <sub>26</sub> H <sub>23</sub> Cl <sub>2</sub> ZnN <sub>3</sub> O <sub>3</sub>	3048	1468	1499	1109	505

The  $\nu(\text{C=N})$  mode in oxine occurs at 1499-1502 cm<sup>-1</sup> in the spectra of metal complexes. This band is observed in the spectrum of the ligand in the higher region (1580 cm<sup>-1</sup>). A negative shift in this vibrational mode on complexation

indicates the coordination through tertiary nitrogen donor of HQ. The in plane and out of plane ring deformation modes are observed at 505 and 787  $\text{cm}^{-1}$  respectively, confirming coordination through the nitrogen atom of HQ with metal. The M-O stretching is observed in the range of 508-599  $\text{cm}^{-1}$ .

#### NMR Spectra:

The  $^1\text{H}$  NMR spectra of the complexes in DMSO  $d_6$  solvent gave well resolved multiplet at  $\delta$  7.00-7.5 ppm corresponding to 14 aromatic protons in mixed ligand metal complexes. The singlet at  $\delta$  8.2 ppm observed for two protons. In complexes the singlet observed at  $\delta$  3.0-3.7 ppm can be assigned to the proton of  $\text{CH}_2$  groups in Schiff base.

#### Electronic absorption spectra

The electronic spectra of the mixed ligand metal complexes have been measured in DMSO solution between in range 200-800 nm at room temperature. The spectral data of the mixed ligand metal complexes are tabulated in Table 4. In the spectra of the mixed ligand metal complex the absorption band observed at 270 nm were assigned to benzene  $\Pi \rightarrow \Pi^*$  transition and the band at 345-380 nm were assigned due to  $n \rightarrow \Pi^*$  transition associated with Schiff base azomethine moiety and new band observed at the 420-485 nm can be assigned to  $L \rightarrow M$  Charge transfer band. On the basis of spectral data octahedral geometry has been proposed for all mixed ligand complexes [17].

Table 4: Electronic spectra: UV visible spectra of mixed ligand metal complexes

Sr. No.	Compound	Electronic spectra (nm)		
		$\Pi \rightarrow \Pi^*$	$n \rightarrow \Pi^*$	$L \rightarrow M$
1	$\text{C}_{26}\text{H}_{23}\text{Cl}_3\text{CrN}_3\text{O}_3$	240	375	470
2	$\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{MnN}_3\text{O}_3$	230	380	430
3	$\text{C}_{26}\text{H}_{23}\text{Cl}_3\text{FeN}_3\text{O}_3$	280	345	485
4	$\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{CoN}_3\text{O}_3$	240	370	465
5	$\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{NiN}_3\text{O}_3$	235	385	450
6	$\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{CuN}_3\text{O}_3$	275	360	430
7	$\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{ZnN}_3\text{O}_3$	280	350	420

#### Antimicrobial activity of mixed ligand metal complexes:

8-Hydroxyquinoline, schiff base and their mixed ligand complexes of transition metals were screened for antibacterial and antifungal activity. The entire tested compound exhibited variable antibacterial activity and antifungal activity as shown in (Fig.3) Among mixed ligand metal complexes, the Cu complex ( $\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{CuN}_3\text{O}_3$ ) showed efficient antibacterial activity against *S. aureus* and *K. aerogene* with zone of inhibition 18 and 16 mm diameter respectively (Fig.3.A).

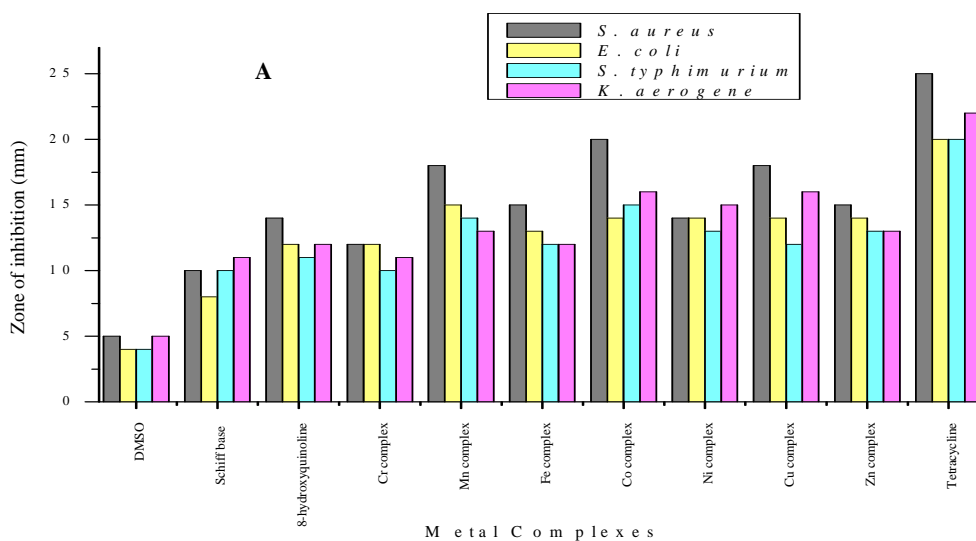
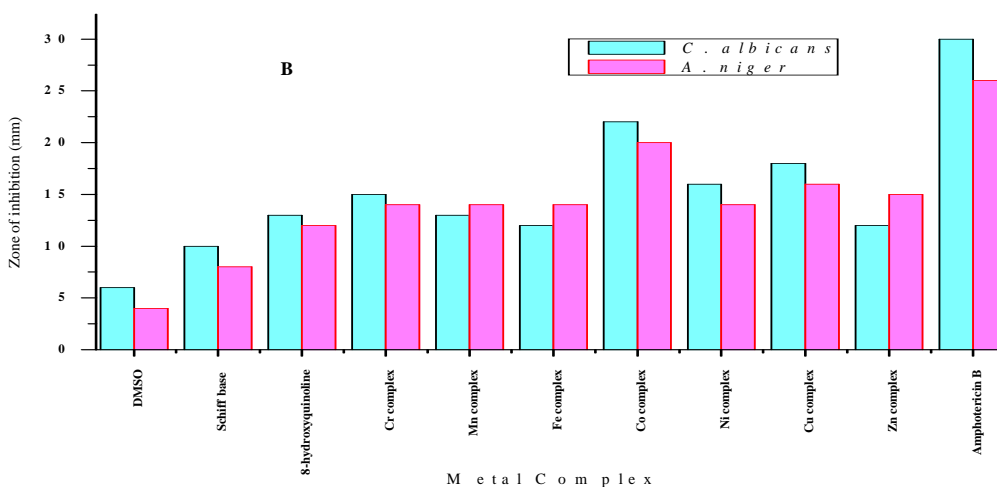


Figure 3: The antibacterial activity of mixed ligand complexes of transition metals against *S. aureus*, *E. coli*, *S. typhimurium* and *K. aerogene*

The Cu complex also exhibited good antifungal activity with zone of diameter 18 and 16 mm against *C. albicans* and *A. niger* respectively [13, 17] (Fig.3.B).



**Figure 3B:** The antifungal activity of mixed ligand complexes of transition metals against *C. albicans* and *A. niger*.

The Co complex ( $C_{26}H_{23}Cl_2CoN_3O_3$ ) also exhibited good antibacterial as well as antifungal activity with zone of diameter in the range of 14–20 mm against the tested bacterial and fungal pathogen as shown in (fig 3). Other metal complexes viz. Cr(III), Mn(II), Fe(III), Ni(II) and Zn(II) also exhibited moderate antibacterial and antifungal activity as shown in (fig 3). It was found that the negative control DMSO exhibited very limited antimicrobial activity against the bacterial and fungal microorganisms. The standard Tetracycline and Amphotericin B were used as positive control in order to compare the antimicrobial activity of mixed ligand metal complexes (fig 3). 8-Hydroxyquinoline and schiff base also exhibited antimicrobial activity but activity was found to be lower than the mixed ligand metal complexes as shown in (fig 3).

The antimicrobial activity of mixed ligand metal complexes indicated the strong antibacterial and antifungal activity than the 8-Hydroxyquinoline and schiff base. The pronounced antimicrobial activity of the metal complex compounds was may be due to the according to the overtone's concept and Tweedy's chelation theory.

## CONCLUSION

The complexes were obtained as colored powdered materials and were characterized using IR spectra,  $^1H$  NMR spectra electronic spectra and magnetic measurements conductance. The compounds were completely soluble in DMF and DMSO. From the *In vitro* antifungal and antibacterial activity data it is observed that the complexes exhibit higher activity than the ligands

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