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Synthesis, Characterization and Biological Evaluation of Mixed Ligand Complexes of Co(II) and Cu(II)

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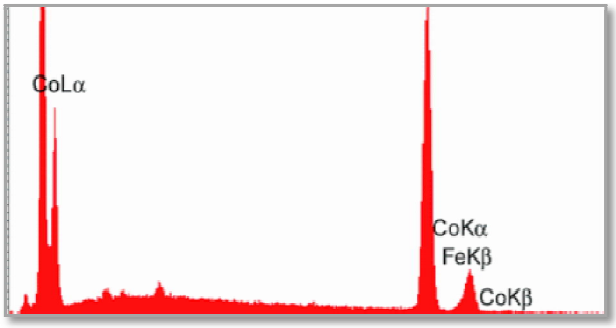
ABSTRACT

The Schiff base prepared from condensation between (3,4,5-Trimethoxy benzaldehyde) and 4-Amino antipyrine.[4-(3,4,5-Trimethoxy-benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one] (TMBAAP) is taken as primary ligand and an amino acid L-Tryptophan is added as Co-ligand through refluxation to form mixed ligand metal complex. The mixed ligand complexes [M(TMBAAP)(Try)(H_2O)$_2$] where (M= Co, Cu metal ions) were characterized employing elemental analysis, UV-visible, FTIR, and SEM spectral techniques. The characterization elucidates structural features and suggested octahedral geometry with respect to the obtained metal complexes. The invitro antibacterial and antifungal assay of mixed ligand was evaluated. The details of results pertaining to Synthesis, Characterization and Biological evaluation of Mixed Ligand Complexes of Co(II) and Cu(II) are well presented in the present research investigation.

Graphical Abstract



EDAX graph of Cobalt mixed ligand complex
[Co(TMBAAP)(Try)(H_2O)$_2$]

Keywords: Schiff base, Mixed ligand metal complex, SEM-EDAX, Anti-bacterial, Anti-fungal assay.

INTRODUCTION

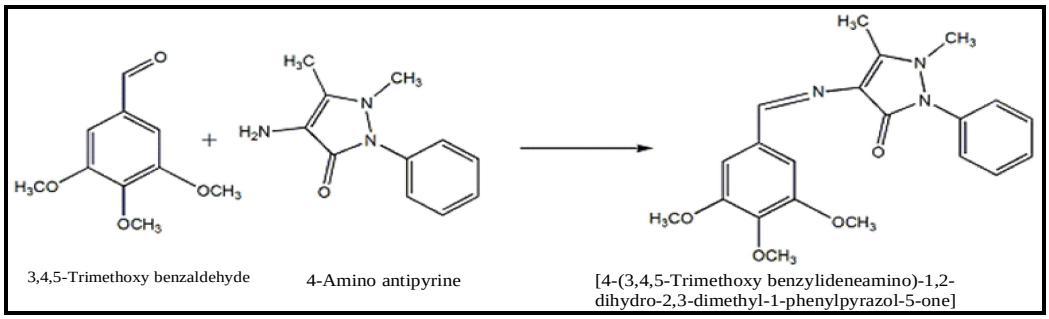
Schiff base and its metal complexes are accomodatable composites produce by precipitating an primary amine and carbonyl group (aldehyde or ketone). A contemplation in review of literature

divulges that azomethine or Schiff base complexes or and imines exhibits genius inducement exploit illustrated in substantial reactions. The manipulation is intermittently embellished by output, insight the properties in twain of ligands and metals necessists in chelation, which drives in generating of tremdously aggressive conglomerated molecules [**1-2**]. The percussion of metal ions on biological endeavour of Schiff base and its queer chemical consideration has induced a notable augmentation in development of their co-ordination behavior. Mixed ligand or accomodated complexes are an crucial classification of co-ordinated molecules and have enchanting protuberant courteonous and are also known as azo-methines and imines [**3-6**]. It is conceivable to synthesize a broad variety of mixed ligand complexes with one metal ion, and massive numerals of compounds can be synthesized by mixing variety of metal ions and could be consolidated. This embellishes an estimable scope for the investigation of compound structure and accompanied with interdependent relations. A enormous numerals of such complexes are consolidated and examined. Beyond them, assorted ligands with complexes derived from tryptophan displays anti microbial assay [**7, 8**]. Azo dyes pigments of 4-Amino antipyrine are well-known multidentate ligands that co-ordinate in neutral and ionic form. 4-amino antipyrine is important in a variety of fields, including anti-cancer therapy. Anti-inflammatory, anti-oxidant, and anti-HIV properties have previously been revealed-tryptophan is a rare amino acid due to the complexity of its catabolism, and the wide variety of diseases is complicated in medical practices [**9, 10**]. As a result, the authors focused on the advancement of mixed ligand complexes [4-(3,4,5-Trimethoxy benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one] (TMBAAP) with metals Co(II),Cu(II), and L-Tryptophan an amino acid as a Co-ligand in this study. The antibacterial and antifungal assays of derived complexes were investigated in vitro.

MATERIALS AND METHODS

All synthetic compounds were obtained from business sources and used without being cleansed. IR spectra recorded on potassium bromide (KBr) pellet using a Bruker Fourier Transform Infrared (FT-IR) spectrometer in the wavenumber range 4000-400 cm^{-1}. The Ultra Violet (UV-Visible) 1800 series was used for electronic phantom research, with a frequency range of 200-400 nm. Graphical SEM images are obtained using a filtering electron magnifying instrument. Instrument FLEX-SEM 1000 along with EDAX Graphs.

Synthesis of Primary Ligand: The selected aldehyde in preparation of primary ligand is 3,4,5-Trimethoxy benzaldehyde (2g) (0.1M) was taken and solvated in 50 mL of methanol. The 4-Amino antipyrine (2.2g) (0.1M) was disintegrated in 50 mL of refined water .These arrangements were blended in a sanitized 250 mL round base flagon and mixed with an attractive stirrer. This response combination was invigorated in water shower by refluxing for 60 min. On cooling and slow vanishing at room temperature, yellow hued accelerate was framed. The strong result was disconnected by refiner and washed ordinarily with high temp water. Then, at that point, it was dissipated in vacuum. The level of yield is 85%. Methanol was used to recrystallize the compound. Formation of Schiff base primary ligand (TMBAAP) with the elimination of water molecule was shown in scheme 1 as given below.



Scheme 1. Synthesis of primary ligand [TMBAAP].

Synthesis of Mixed Ligand metal complex [Co(TMBAAP)(Try)(H_2O)$_2$]: A warm methanolic solution of 10 mL [4-(3,4,5-Trimethoxy benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenyl pyrazol-5-one] (0.1M) was added as a primary ligand to a warm methanol suspension of cobalt chloride (0.88g)(0.05M). After 40 minutes, a methanolic solution of L-Tryptophan (2.2g) (0.1M) amino acid was added as a secondary ligand in the amount of 5ml. The mixture was vigorously agitated. The solution was then refluenced for about 2 h. The precipitate that formed changed from yellow to dark purple crystals. The crystals were strained, purified with warm water, and vacuum dried. The yield percentage was 72 percent. The formation of cobalt mixed ligand metal complex was given in scheme 2 as given below.

$Cocl_2.2H_2O$ + TMBAAP → [Co(TMBAAP)(H_2O)$_2$] + Try → [Co(TMBAAP)(Try)(H_2O)$_2$

Scheme 2. Synthesis of mixed ligand metal complex [Co(TMBAAP)(Try)(H_2O)$_2$].

Synthesis of Mixed Ligand metal complex [Cu(TMBAAP)(Try)(H_2O)$_2$]:. To a warm methanolic solution of 10 ml [4-(3,4,5-Trimethoxy benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one] (0.1M) as a primary ligand, a warm methanol suspension of Copper chloride (0.72g)(0.05M) was added. After 40 minutes, a methanolic solution of L-Tryptophan (2.2g) (0.1M) amino acid was added as a Co- ligand in the amount of 5ml. The mixture was vigorously agitated. The solution was then refluenced for about 2 hours. The precipitate produced changed the colour of the crystals from yellow to dark green. The crystals were strained, purified with warm water, and vacuum dried. The yield percentage was 78 percent in copper mixed ligand metal formation.

$Cucl_2.2H_2O$ + TMBAAP → [Cu(TMBAAP)(H_2O)$_2$] + Try → [Cu(TMBAAP)(Try)(H_2O)$_2$]

Scheme 3. Synthesis of mixed ligand metal complex [Ni(TMBAAP)(Try)(H_2O)$_2$].

RESULTS AND DISCUSSION

Infrared Spectral Studies: The FTIR spectrum of the primary ligand (TMBAAP) showed distinctive bands at 1648 cm^{-1} and 1598 cm^{-1}, which were associated to (C=O) and (C=N) respectively. The band at 1648 cm^{-1} corresponds to the (C=O) expended trembling of the azomethine ligand and is transmitted to the substituted province at 1594cm^{-1} to 1579 cm^{-1}, distinguishing coordination of oxygen from the carbonyl group towards the metal ion. The spectrum shows accurate fine peaks at (3431-3080) that are attributed to the carboxyl component (O-H) and indole moiety's (N-OH). There was a modification in frequency with change in contour and intensity on co-ordination with metal ion at (1648-1899cm^{-1}) noticing that antipyrine's carbonyl oxygen was involved in chelation. There are two more frequencies observed in the IR spectra of Cu(II) complex at 549 cm^{-1} and 431 cm^{-1} determinated to (M-N) and (M-O) stretching vibration. The FTIR spectra of Schiff base and mixed ligand metal complexes were illustrated (Figure 1-3).The FTIR spectral data of Schiff base and metal complexes were given table 1.

Table 1. IR absorption bands (cm^{-1}) of ligand and its metal complexes

Ligand \ Metal complexes	C=O	C=N	C=C	C-N	C-O	M-N	M-O
(TMBAAP)	1698	1598	1553	1355	1295	–	–
[Co(TMBAAP) (Try)(H_2O)$_2$]	1684	1572	1556	1381	1228	549	477
[Cu(TMBAAP) (Try)(H_2O)$_2$]	1683	1574	1550	1336	1231	549	431

Electronic Spectral studies: The electronic spectral bands of Schiff base and its mixed ligand metal complexes with initial values are described in the table 2 as given below. Two bands appeared at 298 nm and 326 nm in the UV-Visible spectrum of Schiff base may be attributed to ($n\rightarrow\pi^*$) transitions within aromatic rings and azo-methine group. The electronic spectra of the mixed ligand complex [Co(TMBAAP)(Try)(H_2O)$_2$] a band near 23,529 cm^{-1} can be assigned to d-d transition suggesting the

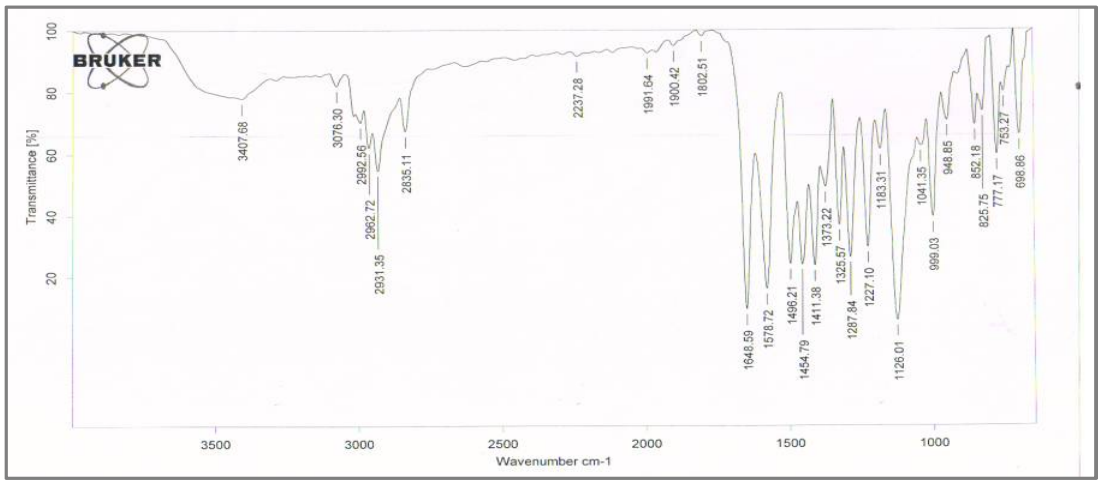


Figure 1. FTIR spectra of Schiff's base (TMBAAP).

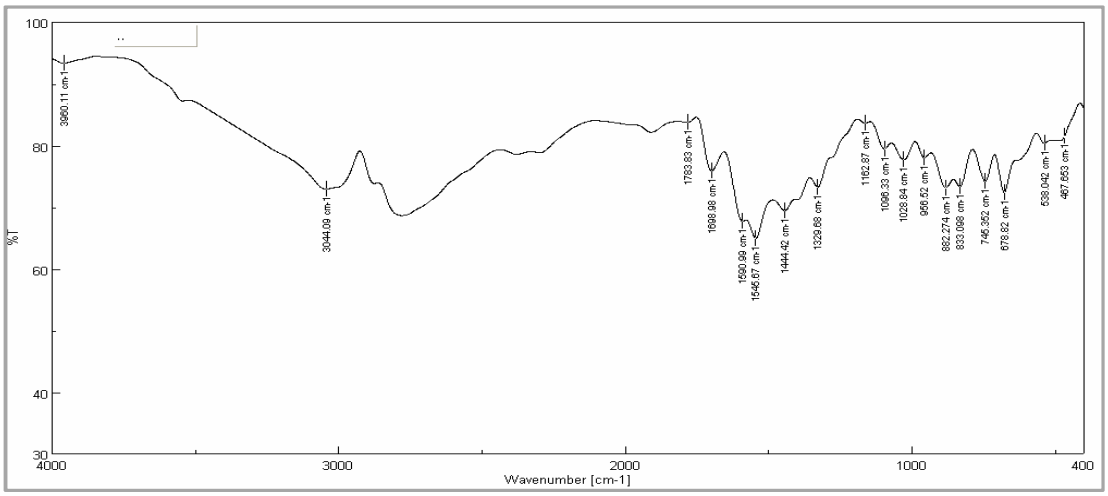


Figure 2. FTIR Spectra of cobalt mixed ligand complex.

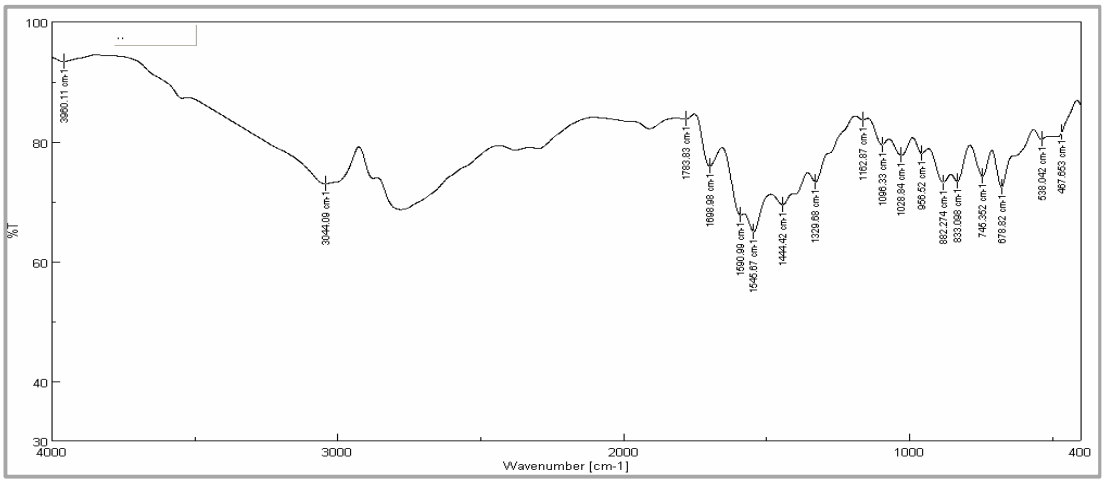


Figure 3. FTIR Spectra of Copper mixed ligand complex.

octahedral geometry around cobalt ion. The Ultra violet spectral data of mixed ligand complex $[Cu(TMBAAP)(Try)(H_2O)_2]$ exhibited a broad absorption band at 18,181 cm^{-1} ,due to d-d transition suggesting the octahedral geometry around copper ion.

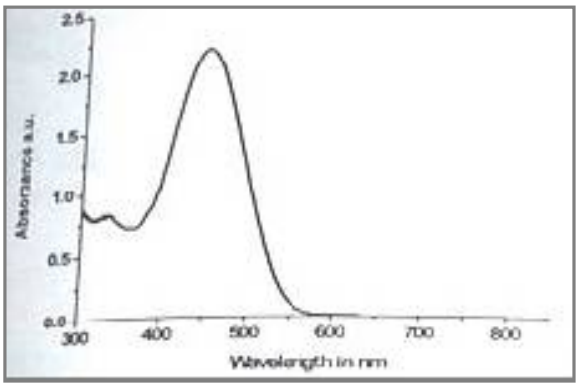


Figure 4. Electronic spectra of cobalt mixed ligand complex.

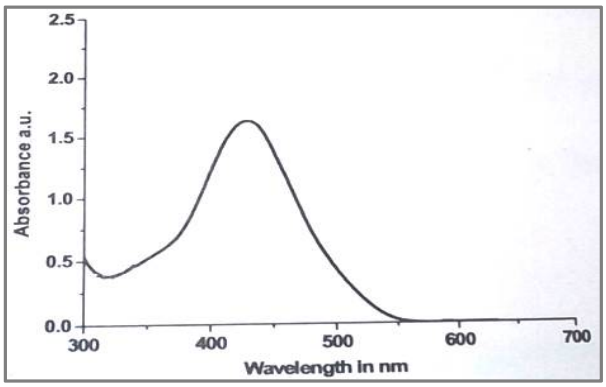


Figure 5. Electronic spectra of Copper mixed ligand complex.

Table 2. Physico-chemical and electronic spectral data of Schiff base and mixed ligand complexes

Compound	Molecular weight (gm mole^{-1})	Colour	(Yield %)	UV data (Assignments)
[TMBAAP]	461.45	Yellow	85	n-π^* (Transition)
[Co(TMBAAP)(Try)(H_2O)$_2$	820.67	Purple	72	d-d (Transition)
[Cu(TMBAAP)(Try)(H_2O)$_2$]	825.28	Green	76	d-d (Transition)

Scanning Electronic Microscope: Scanning electron micrographs (SEM) reveal the skeleton containing Co(II) and Cu(II) complexes. The SEM graphical images were captured at a excited conduction of 15 kV, and the amplification was adjusted to meet the needs of the experiment, ranging from 150 xs to 3000x. Perceptual stage partitions in opaque layers were detected in SEM images. Territory sizes of 10µm in cobalt complexes and 20 µm in copper complexes were discovered. It was clear that there were significant changes in Schiff's morphology based on complexation, the shape, and the size. of nano particles are spherical of some aggregation. The Energy dispersive X-ray analysis of mixed ligand complexes [M(TMBAAP)(Try)(H_2O_2)] were taken. The sample was coated on the platinum plates at room temperature. The EDAX investigations on mixed ligand metal complexes show compositions of the nano structured complexes. The complexes have nano structures with array of different shapes in which array, the oxygen gets adsorbed and percentage of oxygen gets elevated. The EDAX spectrum is shown along with SEM image and graph as given below.

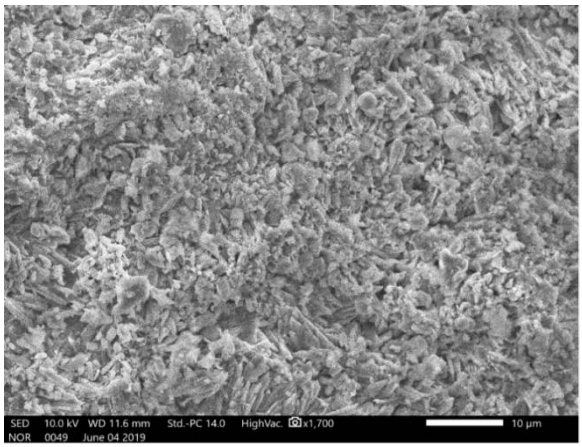


Figure 6. SEM image of Cobalt mixed ligand complex.

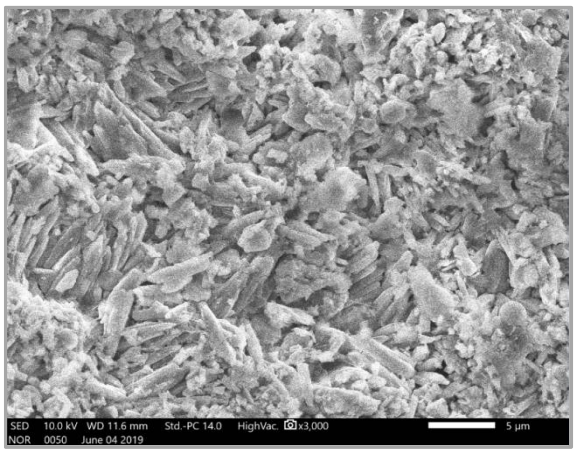


Figure 7. SEM image of Copper mixed ligand complex.

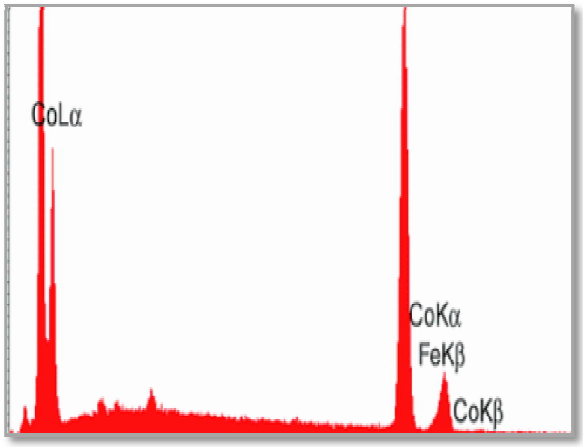


Figure 8. EDAX graph of Cobalt mixed ligand complex.

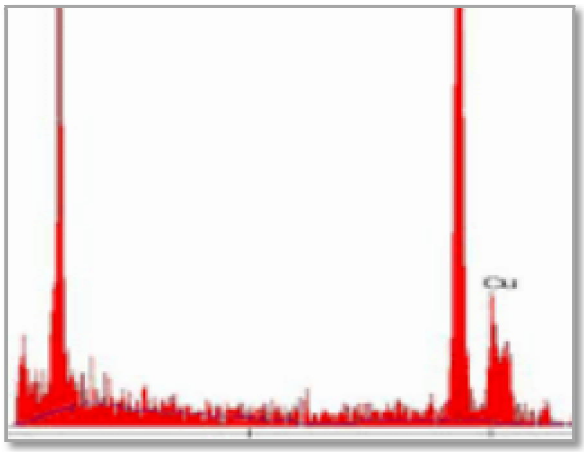


Figure 9. EDAX graph of Copper mixed ligand complex.

APPLICATION

Anti-Microbial Assay

Method employed: The technique utilized for testing the action of the mixed ligand alongside metal complexes against microbes is paper plate methodology utilized by Gananamanickam *et.al*. Petri plates of same size, hot air oven, Autoclave, disinfected pipettes and filter paper. All of the necessary equipment was sterilized before usage, and each sensitive safety provision was taken to avade contagion all through the progression**.**

Strategy of Experimenting microbial Assay: Disinfected supplement agar 15-20 mL was filled plates of same size under aseptic conditions. The plate doused with the individual solvents of test arrangement is utilized as control. Accordingly the bacterial and parasitic development in the test Petri plates is contrasted and the development in controls. The zone of hindrance of microbes and contagious development in the Petri plates under assessment is estimated. The prepared Mixed ligand complexes Cobalt and Copper were tested in contrast to the subsequent micro-organisms, the two bacterial species *Staphylococcus aureus* and *K.pneumonia* and two fungal species *Aspergillus niger* and *Trycophyton rubrum*. A competitive consideration of the values of Schiff base ligand (TMBAAP) and mixed ligand complexes illustrates potential anti-microbial assay as shown in the table 3 below.

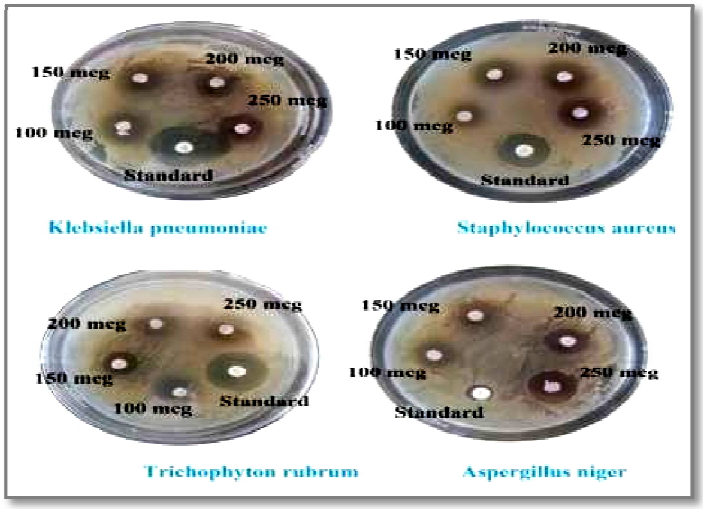


Figure 10. Antimicrobial activity of mixed ligand metal complexes [M(TMBAAP)(Try)$(H_2O)_2$] done by using Disc diffusion method.

Table 3. Zone of inhibition

Compound	Bacteria		Fungi	
	Staphylococcus aureus	*K.pneumonia*	*Aspergillus niger*	*Trycophyton rubrum*
[TMBAAP]	8(mm)	8(mm)	11(mm)	9(mm)
[Co(TMBAAP)(Try)(H_2O)$_2$]	18(mm)	24(mm)	25(mm)	17(mm)
[Cu(TMBAAP)(Try)(H_2O)$_2$]	18(mm)	26(mm)	25 (mm)	18(mm)

CONCLUSION

The author stated the synthesis of a mixed ligand complex containing [M (TMBAAP) (Try)(H_2O)$_2$], where M represents Co(II) and Cu(II) metal ions. The Schiff's base and its complexes are solvable in water and DMSO (Dimethyl sulfoxide), and they have an octahedral geometry. The anti-fungal and anti-bacterial veiling assignments were checked for Staphylococcus aureus, *Klebsiella pneumoniae*, *Trycophyton rubrum*, and *Aspergillus niger*. The results showed that the mixed ligand complex had potential activity in contrast to the pathogens tested, which we hope will aid in the development of new drugs to control anti-bacterial and anti-fungal diseases.

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Conflict of Interest: The authors declare no conflicts of interest.

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