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ORIGINAL RESEARCH PAPER

# Two new Cu(II) and Zn(II) schiff base complexes: Synthesis, characterization and their biological activity

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**ABSTRACT:** New two nano- sized Schiff base complexes [M(L)], where L= 2, 2'-((1E, 1E')-(1, 2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) and M=Cu or Zn, (a, b complexes) were synthesized by ultrasonic irradiation. These complexes were characterized by elemental analysis, molar conductivity, FT-IR, fluorescence emission, $^1$H NMR, field emission scanning electron spectroscopy (FESEM) and UV-Vis spectroscopy. The UV-Vis spectroscopic data and fluorescence emission bands of these nano-sized Schiff base complexes show a shift in comparison with the bulk sample analogue, due to the reduction in particle size to nano scale. In vitro antimicrobial activities of the title compounds against some Gram-positive (*Staphylococcus aureus, Micrococcus luteus, Bacillus cereus, Eterococcus faecalis)* and Gram-negative bacteria (*Pseudomonas aeruginosa, Escherichia coli, Klebsiella sp, Pscudomonas sp)* and fungus strain *(Candida albicans)* were investigated *and compared with each other*. It was found that Cu (II) complex showed higher antibacterial activity than the Zn (II) complex.

**Keywords:** *Antimicrobial effect; FESEM; Fluorescence emission; Nano scale; Schiff base complex*

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## INTRODUCTION

Transition metal complexes with salen-type Schiff base ligands have played essential role in efficient catalysts [1], antimicrobial and anticancer drugs [2,3], sensors [4], nonlinear optic [5] and DNA cleavage performance fields [6]. Hence synthesis and characterization of Schiff base complexes have been widely investigated in coordination chemistry.

Among these complexes, copper and zinc Schiff base complexes have been receiving considerable attention for their fascinating applications [7-9]. Copper Schiff base complexes have been synthesized for studying of the non-enzymatic oxygenation reactions to the understand the oxygenase-catalyzed reactions [10-11].

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Furthermore, copper complexes have been synthesized as models of metalloproteins for a better understanding of biological systems [12-14]. Zinc Schiff base complexes are a new class of luminescent compounds which showed photoluminescence properties [15]. Also, because of their catalytic properties, they are used as use as models of biological significance [16-18]. As in recent years, synthesis of materials in nano scale has been increasing based on the fact that the reduction in particle size to nanometer scale results in high surface to volume ratio, change in electronic structure of materials that shows fascinating physical and chemical properties that are different from the bulk materials such as the mechanical, optical, and magnetic properties [19, 20]. For these reasons, we wish to report on the prepartion a new nano copper

and zinc Schiff base complexes based on salen type ligand, where ligand= 2, 2'-((1E, 1E')-(1, 2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolat). The structure and morphology of synthesized complexes were investigated by means of Fourier transformed infra-red (FT-IR), nuclear magnetic resonance ($^1$H NMR), field emission scanning electron microscopy (FESEM) as well as electronic and fluorescence property measurements.

## EXPERIMENTAL

### *Materials and instrumentation*

All the chemicals and solvents were purchased from Merck Company and used without further purification. Microanalysis for C, H and N were determined on a Thermo Finnegan Flash Elemental Analyzer 1112EA. Melting points were measured on an Electrothermal Apparatus-9100. The FT-IR spectra were recorded on a Bruker-Tensor 27 spectrometer (4000-400 $cm^{-1}$) in KBr pellets. Molar conductance measurements were made by means of a Metrohm 712 conductometer in EtOH. $^1$ H NMR spectra were acquired on a Bruker Avance III 300 spectrophotometer operating at 400 MHz in DMSO-d6 as a solvent. The UV-Vis spectra of the title complexes were run in methanol solution on a Cary 50 UV-Vis spectrophotometer in the range of 200-800 nm at room temperature (25°C). An ultrasonic bath (WUC AOZH, 50-60 HZ, and 0.14 kW) was used for the ultrasonic irradiation. The samples were characterized with a field emission scanning electron microscope (FESEM) (Hitachi S-4160) with gold coating. Fluorescence emission spectra were recorded on a Cary Eclipse Spectro fluorometer from 300-700 nm at room temperature (25°C).

### *Synthesis of 2, 2'-((1E, 1E')-(1, 2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenol) ($H_2L$)*

$H_2L$ was prepared according to the literature with a little modification of the methodology reported previously [21]. 1, 2-Diaminobanzene (0.1 g, 1 m mol) was added to a 10-ml ethanolic solution of 5-bromo-2 hydroxy benzaldehyde (0.4 g, 2 m mol) and the reaction mixture was stirred for 15 min at room temperature. The formed precipitate was separated after filtration, washed with cold ethanol, and dried in desiccator over anhydrous CaCl2. Yield: 85%. m.p.: 190 °C. Anal. Calc. for $C_{20}H_{14}Br_2N_2O_2$ (474.15 g $mol^{-1}$): C, 50.66; H, 2.98; N, 5.91. Found: C, 50.53; H, 2.90; N, 5.88%. FT-IR (KBr), cm-1: ν(OH) 3629, ν(NH) 2941, ν(C=O) 1734, ν(C=N) 1628, ν(C=$C_{ring}$) 1455, ν(C-O) 1363, δoopb(OH) 778, ν(CBr) 537.1H-NMR (400 5 MHz, DMSO-*d*6, 25 °C, ppm): $\delta$ = 12.9 (*s*, 1H; OH), 10.9 (*s*, 1H; NH), 10.1 (*s*, 1H; =CH-NH), 8.9 (*s*, 1H; CH=N), 6.6-7.9 (*m*, 10H, rings). UV/Vis (MeOH) $\lambda_{max}$, nm (log$\varepsilon$, L $mol^{-1}$ $cm^{-1}$): 244 (4.21), 275 (4.01), 345 (3.87).

### *Synthesis of polyaniline*

To prepare the nano- sized of 2, 2'-((1E, 1E')-(1, 2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) Cu (II) complex, a reaction flask containing $H_2L$ (0.2 g, 0.4 mmol) in methanol (10 ml) was placed in an ultrasonic bath with output power of 0.14 kW. The solution was exposed to ultrasonic irradiation at room temperature, then 10 ml methanolic solution of Cu $(CH_3COO)_2$. $4H_2O$ (0.08 g, 0.4 mmol) was added to the mixture in a dropwise manner for15 min (The reaction was completed after15 min). The dark green precipitate was filtered off, washed with cold methanol and diethyl ether, and dried under vacuum over anhydrous $CaCl_2$. Yield: 80%; m.p.: >300°C. Molar conductance ($10^{-3}$ M, DMSO) 19 $ohm^{-1}$ $cm^2$ $mol^{-1}$, (Fig. 1).

### *Synthesis of nano- sized of 2, 2'-((1E, 1E')-(1, 2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) Zn (II) complex*

The method of preparation of nano- sized of 2, 2'-((1E, 1E') - (1, 2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) Zn (II) complex, was the same as mentioned above. To methanolic solution of $H_2L$ (0.2 g, 0.4 mmol) was added 10 ml methanolic solution of Zn $(CH_3COO)_2$. $4H_2O$ (0.09 g, 0.4 mmol) in a drop wise manner for 15 min (The reaction was completed after 15 min). The dark yellow precipitate is filtered off, washed with cold methanol and diethyl ether, and dried under vacuum over anhydrous $CaCl_2$. Yield: 85%; m.p.: >300 °C. Molar conductance ($10^{-3}$ M, DMSO) 21 $ohm^{-1}$ $cm^2$ $mol^{-1}$, (Fig. 1).

### *FT-IR study*

The infrared spectra of the copper (II), (a) and zinc (II), (b) Schiff base complexes are shown in Fig. 2. In both spectra, the strongest bonds in 1614 $cm^{-1}$ are assigned to the vibrations of azomethine groups $\nu_{(C=N)}$. The bands at 2916 and 2926 $cm^{-1}$ were assigned to the alphabetic C-H bonds of the azomethine group

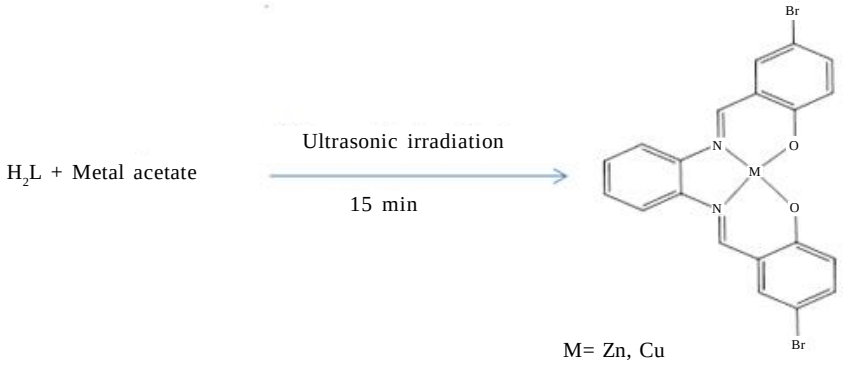


Fig. 1: The process of preparation of nano-sized Cu(II) and Zn(II) Schiff base complexes.

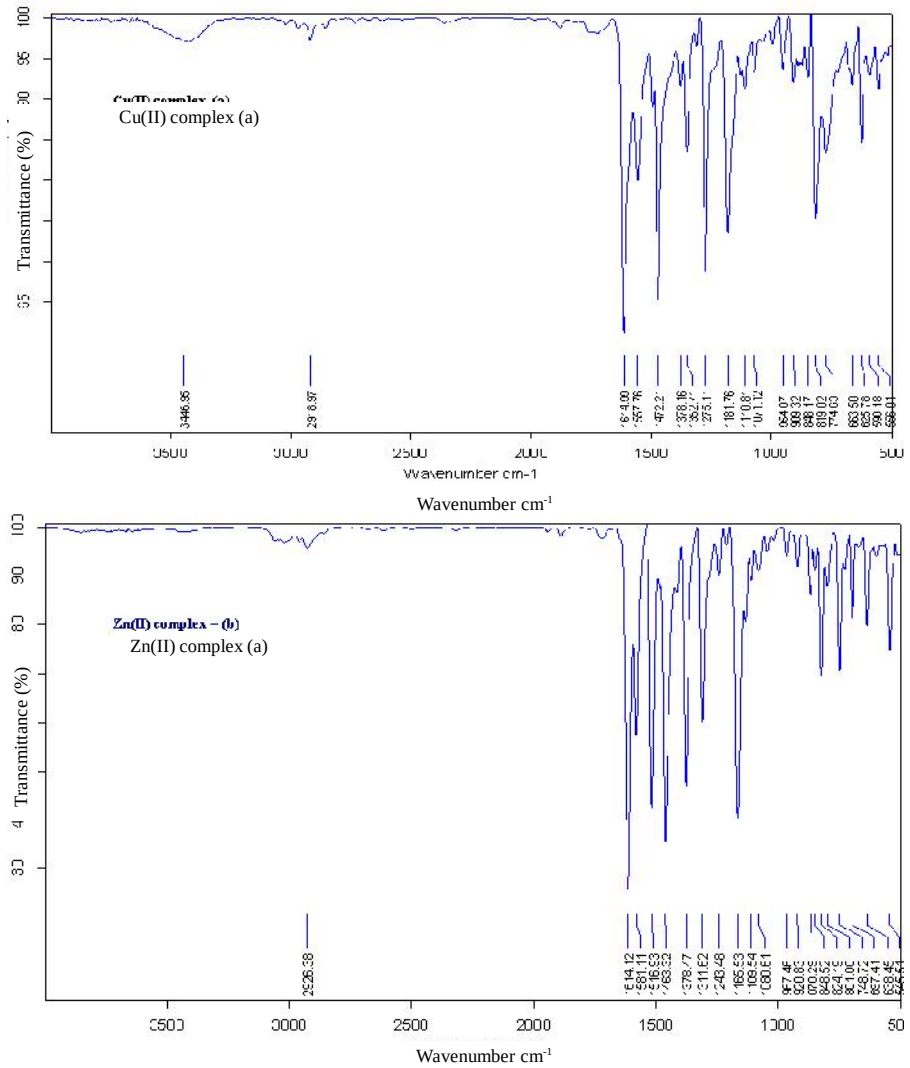


Fig. 2: The infrared spectra of the (a) nano-sized copper (II), (b) and zinc (II) Schiff base complexes

for copper and zinc Schiff base complexes respectively [22, 23]. The aromatic C=C bond was demonstrated by the stretching vibration at 1516 $cm^{-1}$ for copper complex, whereas these bonds are observed at 1472 $cm^{-1}$ for zinc complex.

The phenolic C-O bonds were suggested to appear by the bands at 1352 $cm^{-1}$ for copper and 1352 $cm^{-1}$ for zinc complex respectively. In addition, the M-N bands of copper and zinc complexes were also predicated by the bands observed at 656 $cm^{-1}$ and 545 $cm^{-1}$, respectively. The M-O bands of copper and zinc complexes were also predicated by the bands observed at 690 $cm^{-1}$ and 638 $cm^{-1}$, respectively.

***$^1$HNMR study of Zn (II) complex***

The 1H NMR spectra of the synthesized compounds were recorded in DMSO-d6 (Fig. 3). $^1$HNMR spectrum of Zn (II) complex showed disappearance of the phenolic proton signals which were assigned at 12.40 ppm compared with the $^1$H-NMR spectrum of $H_2L$ ligand due to the deprotonating of the phenolic groups and subsequently the replacement of the protons by Zn metal. The signals of Zn (II) complex shift (with downfield shielding) comparing to $H_2L$ ligand complexation of the Zn (II) ion by the azomethine groups. The azomethine proton exhibited a singlet at 9.001 ppm, the aromatic protons of the phenyl group revealed a multiple within the region 6.64 -7.87 ppm. Because of DMSO is coordinated to the central zinc ($^1$HNMR spectrum of complex monitored in DMSO-d6 solvent), the peaks corresponding to DMSO are observed at 2.48 -3.33 ppm.

***UV-Vis spectra***

The UV-Vis spectra of the compounds were obtained in methanol at room temperature. In the UV-Vis spectrum of $H_2L$ (Fig. 4a), the intense band at 375 nm is attributed to $\pi$-$\pi$* transition of the aromatic rings and other bands are correlated to azomethine $\pi$-$\pi$* and n-$\pi$* transitions. The UV-Vis spectra of nano sized copper (II) (Fig. 4b) and zinc (II) (Fig. 4c) Schiff base complexes (in EtOH) consists, the bands below 400 nm, are attributable to intra-ligand (ILCT) $\pi$-$\pi$* and n-$\pi$* transitions of the benzene ring and the azomethine group respectively [23, 24]. The band at 438 nm (Fig. 4b) is assigned to the $^2B_1g$ ---> $^2Eg$ transition that suggesting a square-planar geometry of the copper (II) Schiff base complex[25]. A band at 410 nm (Fig. 4c) can be assigned to spin-allowed metal-to-ligand charge transfer (MLCT) transition to zinc (II) complex [26].

***Fluorescence emission study***

The fluorescence emission studies of $H_2L$ ligand and its nan-sized Cu (II) and Zn (II) Schiff base complexes were investigated at room temperature (25°C). The fluorescence emission spectrums of the ligand in EtOH are shown in Fig. 5.

When excited at 290 nm, the ligand shows an emission band at 500 nm, which is correlated to intraligand transitions. The fluorescence emission properties of the nano-sized of copper (II) and zinc (II) Schiff base complexes were investigated at room temperature (25°C) in EtOH. The fluorescence emission spectra of the complexes are shown in Fig. 5. The emission bands are located at 520, 512 nm for the copper (II) and zinc (II) complexes respectively. The shift of emission bands was due to complexation. The emission bands are assigned as intraligand fluorescence (ILCT charge transfer). These bands are a duo to energy transfer between the HOMO ($\pi$, bonding) and LUMO ($\pi$*, antibonding) of the ligand. Comparing the absorption and emission bands of copper (II) and zinc (II) complexes in bulk scale and nano complexes analog, revealing nano complexes have more intensity with a shift due to the reduction particle size to nano scale [27].

***Morphology and particle size distribution study***

The morphology and particle size distribution of nano-sized of copper (II) and zinc (II) Schiff base complexes were investigated by the field emission scanining electron spectroscopy (FESEM). The FESEM micrographs of the copper (II) Schiff base complex in Fig. 6a and Fig. 6c clearly shows that the morphology of the complex is spherical shape with the particle size distribution of about 40-50 nm (Fig. 6a). Fig. 6c and 6d gives an overall view of the zinc (II) Schiff base complex, revealing its morphology is nano grains with the particle size distribution of about 80-90 nm (Fig. 6b).

The particle size distribution of complex is shown in Fig. 7, for nano-sized copper (II) Schiff base complex in (Fig. 7a) and for nano-sized zinc (II) complex in (Fig. 7b).

***Biological part***

*Antimicrobial activity:* Strains of bacteria and yeast were obtained from PTCC (Persian Type Culture Collection, Tehran). Antimicrobial activity of $H_2L$ and its metal complexes (Cu (II) and Zn (II)) against 5

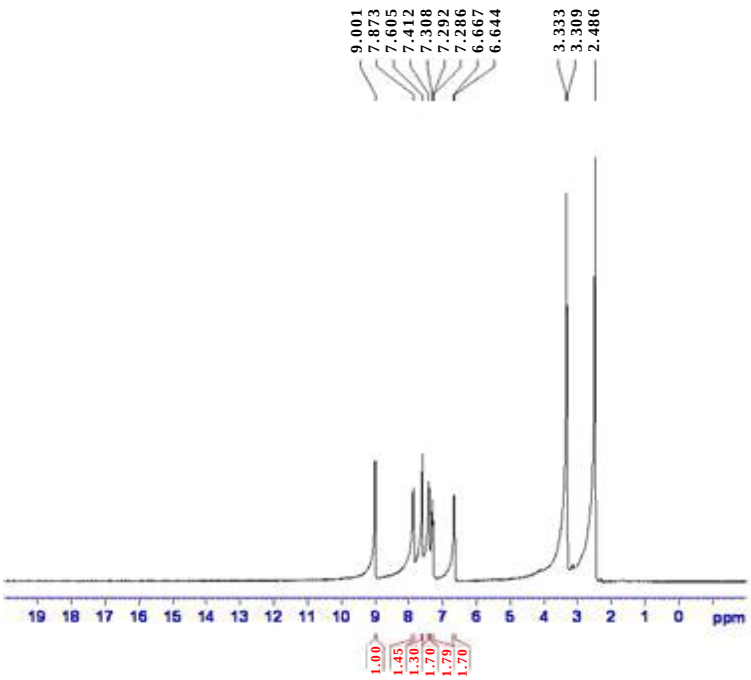


Fig. 3: [1]HNMR spectrum of Zn (II) complex in DMSO as a solvent.

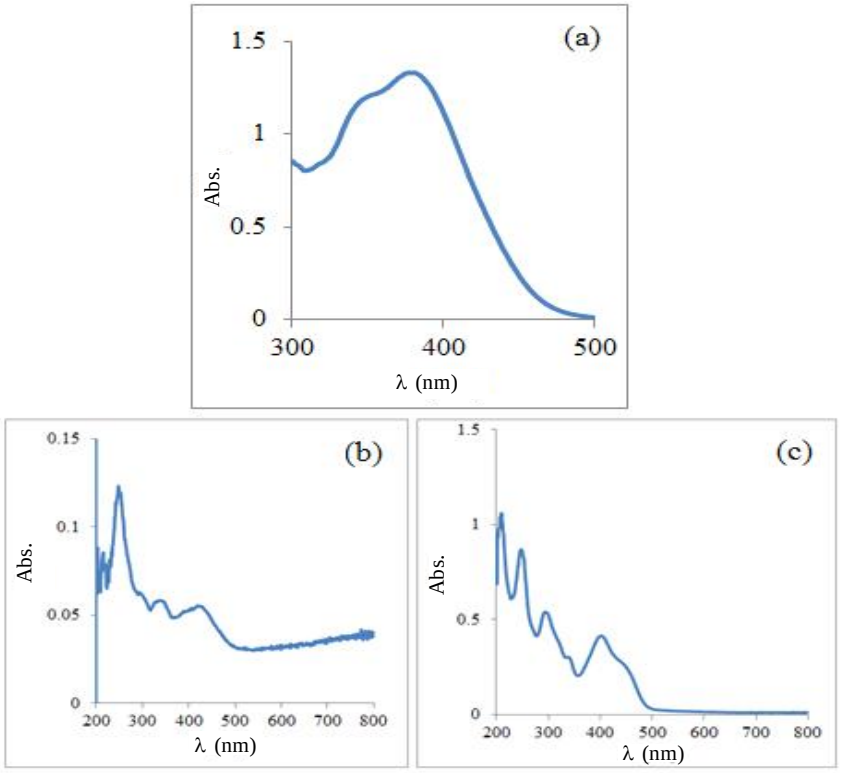


Fig. 4: UV-Vis spectra of $H_2L$ ligand(4a), nano sized copper(II) complex(4b) and nano sized zinc(II) complex (4c) in MeOH

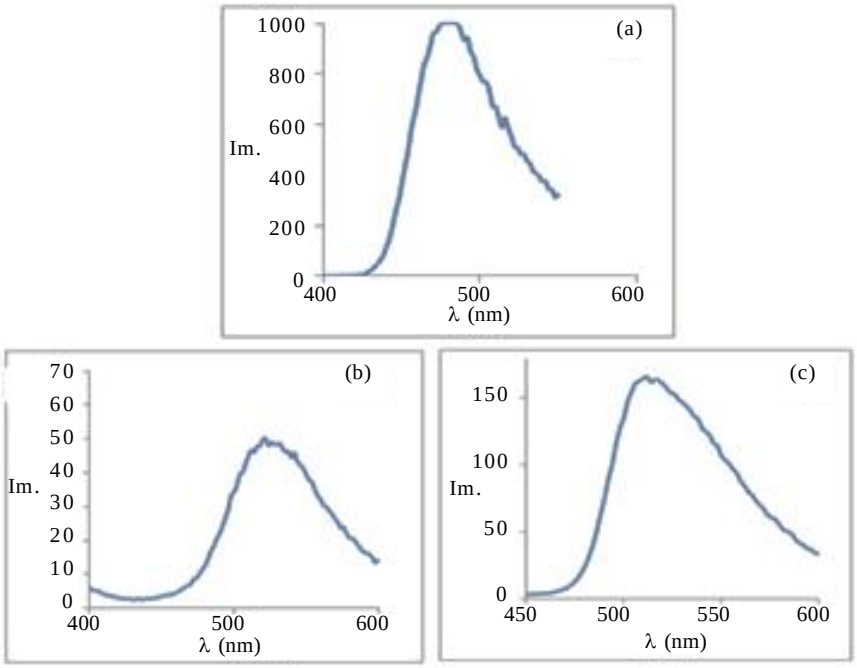


Fig. 5: Fluorescence emission spectra of $H_2L$ (5a), nano copper(II) complex (5b)and nano zinc(II) complex (5c) in EtOH

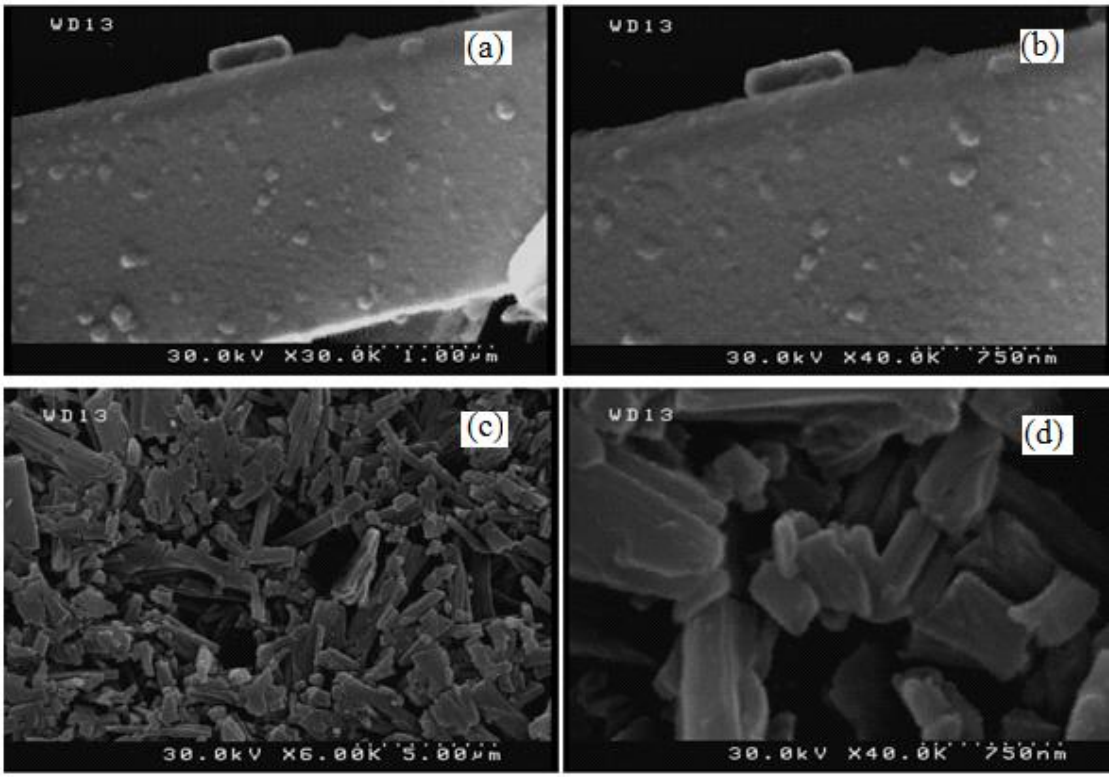


Fig. 6: FESEM images of copper (II) Schiff base complex (6a, 6c) and the FESEM images of zinc (II) Schiff base complex (6b, 6d) in different magnification

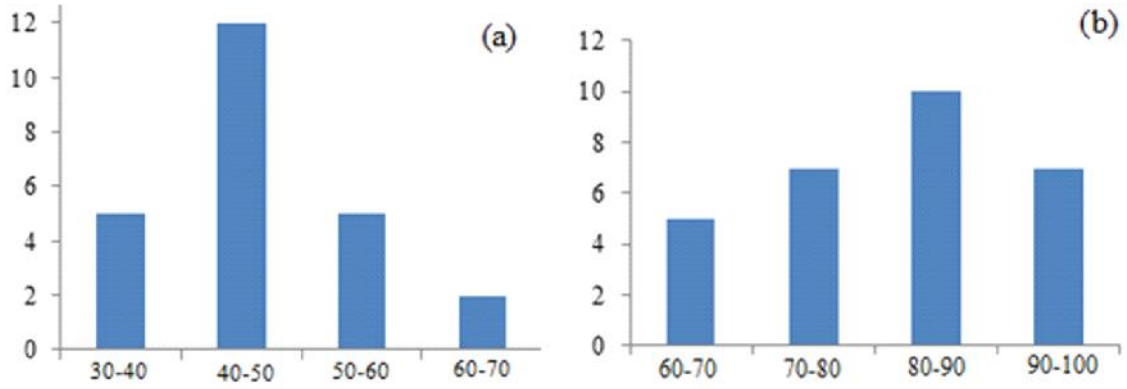


Fig. 7: Particle size distribution of nano-sized copper (II) Schiff base complex (7a) and nano-sized zinc (II) Schiff base complex (7b).

reference strains (*Pseudomonas aeruginosa* PTCC 1214, *Staphylococcus aureus* PTCC 1112, *Micrococcus luteus* PTCC 1110, *Bacillus cereus* PTCC 1015, *Escherichia coli* PTCC 1330), 3 clinical strains (*Pseudomonas sp, Klebsiella sp*, *Eterococcus faecalis*) , and one yeast (*Candida albicans* PTCC 5027) were studied. The species of bacteria were grown in Mueller Hinton Agar/Broth (Merck). Brain Heart Infusion Agar/Broth (Merck) was used for culturing of *Eterococcus faecalis*. *Candida albicans* PTCC 5027 was grown in Sabouraud Dextrose Agar/Broth (Merck). The concentrations of microbial suspensions were adjusted to $10^8$ cells/ mL.

For assay antimicrobial effect of $H_2L$ and its metal complex (Cu (II) complex and Zn (II) complex), the agar well diffusion method was used for the antimicrobial screening [28]. An overnight culture of each bacterium and yeast strains (18-24h) adjusted to a turbidity equivalent to a 0.5 Mc Farland standard [29]. The inoculums suspension of the microbial stains was swabbed on the entire surface of agar media. Wells were cut and 50 ìl of the compound (30 mg/ml; DMSO was used as solvent) were added. The plates were incubated at 37°C for 24- 48 hours. The antimicrobial activity was assayed by measuring the diameter of the inhibition zone formed around the well. The diameter of the zone of inhibitions was measured by measuring scale in millimeter (mm). DMSO as a solvent was used as a negative control, whereas media with ciprofloxacin (standard antibiotic) and fluconazole (standard antifungal drug) were used as the positive controls. The experiments were performed in triplicate.

*Biofilm formation assessment:*

In order to assay of anti-biofilm effect of $H_2L$ and its metal complex (Cu(II) and Zn(II), the microliter plate adhesion assay was employed, described by Kubota [30]. In this study, a culture of the bacteria and yeast were grown overnight in the broth media. Then, the overnight cultures were diluted 1:100 into fresh medium for biofilm assays. 100 µl of the dilution was added on well in a 96 well dish. For quantitative assays, we typically use 4-8 replicate wells for each treatment. The microliter plate was incubated for 24 h at 37°C. After incubation, 25 µl of 1% Crystal Violet was added to each well, shaking the plates three times to help the colorant to get the bottom of the well. After 15 minutes at room temperature, each well was washed with 200 µl sterile PBS to remove the planktonic cells and stain not adhered to the wall. This process was repeated three times. Only the adhered bacteria forming the biofilm were kept on the surface of the wall. The Crystal violet bound to the biofilm was extracted later with two washes of 200 µl of ethyl alcohol. The liquid washing, alcohol was transferred to a glass tube containing 1.2 ml of alcohol and agitated. To determine the degree of biofilm formation, the absorbance was determined at 540 nm in a UV spectrophotometer. Controls were performed with Crystal Violet binding to the wells exposed only to the culture medium without bacteria. Data for biofilm formation of all strains were compared with the data for the negative control.In the result, the antibacterial activity of against $H_2L$ and its metal complex Cu (II) and Zn(II) reference strains (*Pseudomonas aeruginosa* PTCC 1214, *Staphylococcus aureus* PTCC 1112,

Table 1: In vitro antimicrobial activity of $H_2L$ Schiff base ligand and its metal complexe with (Cu(II) ion, 30 mg/ml (IZ)

| Microorganism | Flucnazol dia. | Ciprofloxacin dia. | Cu(II) complex of clear zone(nm) | Zn(II) complex dia. | $H_2L$ dia. |
|---|---|---|---|---|---|
| *P. aeruginosa* PTCC 1214 | 0 | 22 | 11 | 0 | 0 |
| *S. aureus* PTCC 1112 | 0 | 25 | 10 | 0 | 10 |
| *M. luteus* PTCC 1110 | 0 | 31 | 12 | 0 | 12 |
| *B. cereus* PTCC 1015 | 0 | 24 | 15 | 0 | 9 |
| *E. coli* PTCC 1330 | 0 | 27 | 9 | 0 | 0 |
| *Seudom*onas sp* | 0 | 0 | 0 | 0 | 0 |
| E. faecalis* | 0 | 0 | 0 | 8.5 | 0 |
| *C. albicans* PTCC 5027 | 35 | 0 | 11 | 0 | 0 |

*Clinical bacteria

*Micrococcus luteus* PTCC 1110, *Bacillus cereus* PTCC 1015, *Escherichia coli* PTCC 1330), 3 clinical strains (*Pseudomonas sp, Klebsiella sp*, *Eterococcus faecalis*), and one yeast (*Candida albicans* PTCC 5027) were assessed by evaluating the presence of inhibition zone (IZ), MIC and MBC values. The results show that $H_2L$ has an antimicrobial effect and it is only effective against gram positive bacteria (*S. aureus* PTCC 1112 *and M. luteus* PTCC 1110) but, it seems that it has no antimicrobial effect against gram negative strain and *Candida albicans* PTCC 5027 (Table 1). However, according the results, the bacteria which isolated from clinical samples were resistant to $H_2L$ and antibiotic (Ciprofloxacin) (Table 1). The antibacterial activity of Cu(II) complex and Zn(II) complex against five references strains (*Pseudomonas aeruginosa* PTCC 1214, *Staphylococcus aureus* PTCC 1112*, Micrococcus luteus* PTCC 1110, *Bacillus cereus* PTCC 1015, *Escherichia coli* PTCC 1330), 3 clinical strains (*Pseudomonas sp, Klebsiella sp*, *Eterococcus faecalis*), and one yeast (*Candida albicans* PTCC 5027) were assessed by evaluating the presence of inhibition zone (I Z), MIC and MBC values. In this study, we found that Cu (II) complex is effective against gram positive and negative bacteria. Also, it has an antifungal effect against *Candida albicans* PTCC 5027 (Table 1). In addition, according the results, the bacteria which isolated from clinical samples were resistant to antibiotic (Ciprofloxacin) but two resistant strains (*Klebsiella sp* and *Eterococcus faecalis*) were sensitive to Cu(II) complex (Table 1). It seems that Zn(II) complex does not show antimicrobial effect (Data not shown).

The MIC and MBC values for $H_2L$ were in the range of 30 mg/ml to 0.118 mg/ml. The results of our study showed that $H_2L$ compound was effective on gram positive bacteria. It not only inhibited the growth of *S.aureus* PTCC 1112 and *M.luteus* PTCC 1110 but also killed them (Table 2). But this compound had only bacteriostatic effect on *B. cereus* PTCC 1015 (Table 2). According the biofilm formation results, we found that $H_2L$ repressed biofilm formation in *S. aureus* PTCC 1112 (0.235 mg/ml) and *M .luteus* PTCC 1110 (0.235 mg/ml). The results show that the stop of biofilm formation by $H_2L$ has occurred before minimum lethal and inhibitory concentration (Table 2). But this compound could not stop biofilm formation in *B. cereus* PTCC 1015 before minimum inhibitory concentration (MIC).

The MIC and MBC values for Cu(II) were in the range of 30 mg/ml to 0.118 mg/ml. The results of our study showed that Cu(II) complex was effective on all microorganisms except *Pseudomonas sp* which isolated from clinical samples. It not only inhibited the growth of *Pseudomonas aeruginosa* PTCC 1214, *Staphylococcus aureus* PTCC 1112*, Micrococcus luteus* PTCC 1110, *Bacillus cereus* PTCC 1015, *Escherichia coli* PTCC 1330, *Klebsiella sp* and *Candida albicans* PTCC 5027 but also killed them (Table 2). It means that it has both bacteriostatic and bactericidal effects. However, this compound had an only bacteriostatic effect on *E. faecalis* (Table 2).

According the biofilm formation results, we found that Cu(II) complex repressed biofilm formation in *Pseudomonas aeruginosa* PTCC 1214 (0.235 mg/ml),

Table 2: Comparison of Anti-biofilm formation effect, MIC and MBC of H2L Schiff base ligand and its metal complex with (Cu(II) ion, (mg/ml)

| Microorganisms | Cu (II) Schiff base complex | | | $H_2L$ ligand | | |
|---|---|---|---|---|---|---|
| | MBC | MIC | ABF* | MBC | MIC | ABF* |
| *S. aureus* PTCC1112 | 0.938 | 0.465 | 0.235 | 0.938 | 0.465 | 0.235 |
| *M. luteus* PTCC1110 | 0.938 | 0.465 | 0.235 | ND** | ND** | ND** |
| *B. cereus* PTCC1015 | 1.875 | 0.938 | ND** | 0.938 | 0.465 | 0.235 |
| *E. coli* PTCC1330 | 1.875 | 0.938 | 0.465 | ND** | 1.875 | ND** |
| *Pseudomonas sp** | 0.938 | 0.465 | 0.235 | ND** | ND** | ND** |
| *Klebsiella sp** | 1.875 | 0.938 | ND** | ND** | ND** | ND** |
| *E. faecalis** | ND** | 1.875 | ND** | ND** | ND** | ND** |
| *C. albicans* PTCC5027 | 0.465 | 0.235 | ND** | ND** | ND** | ND** |

*Anti-biofilm formation effect; **Not determined

*Staphylococcus aureus* PTCC 1112 (0.235 mg/ml), *Bacillus cereus* PTCC 1015 (0.465 mg/ml) and *Escherichia coli* PTCC 1330 (0.235 mg/ml). The results show that the stop of biofilm formation by Cu (II) complex has occurred before minimum lethal and inhibitory concentration (Table 2). But this compound could not stop biofilm formation in *Micrococcus luteus* PTCC 1110, *Klebsiella sp, Enterococcus faecalis* and *Candida albicans* PTCC 5027 before minimum inhibitory concentration (MIC).

## RESULTS AND DISCUSSION

Schiff base ligand 2, 2'-((1E, 1E')-((4- methyl-1, 2 phenylen) bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) ($H_2L$) synthesized in a short time with improved yields. New nano-structured of 2, 2'-((1E, 1E')-(1, 2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) metal (II) Schiff base complexes, [M (L)], where M=Cu, Zn, were synthesized in mild conditions by ultrasonic method in short time with improved yields (Fig. 1). The title complexes are stable in air and soluble in some common solvents such as DMF, DMSO, MeOH, EtOH but insoluble in n-hexane. From the result of these analyses the geometry of copper and zinc (II) Schiff base complexes were suggested a square-planar geometry. Ultrasonic method is simple, safe, low-cost, and fast. We expect this method can be extended in coordination chemistry to synthesize various complexes in nano- scale. Our study shows, that the $H_2L$ Schiff base ligand and its Cu (II) complex are a good candidate as anti-bacterial compounds and Zn (II) complex has not any antibacterial activity. So, this Cu (II) complex has a good antibacterial activity like our previous work[31].

## CONCLUSION

A tetradentate Schiff base ligand 2, 2'-((1E, 1E')-((4- methyl-1, 2 phenylen) bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) ($H_2L$) and its metal complexes Cu(II) and Zn (II) as nano sized were synthesized in our laboratory with improved yields. Moreover, the metal complexes synthesized products were tested for antimicrobial activities and the results obtained were promising.

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