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Research Article

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Schiff base complexes of Copper (II) ions : Synthesis, Characterization and Antimicrobial studies

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ABSTRACT

*Two new Cu(II) Schiff base complexes have been synthesized and characterized by elemental analysis, infrared, electronic spectra, thermal analyses, and magnetic susceptibility measurements. From the analytical data the molecular formula of the complexes are proposed as $[Cu(II)(4\text{-}Pmpbs)_2](CH3COO)_2.4H_2O$ (**1**) and $[Cu(II)(2\text{-}Hbbig)_2H_2O](CH_3COO)_2$ (**2**) where, 4-Pmpbs = 4-(pyridin-2-yl)methanimino-N-pyrimidin-2-yl-benzenesulphonamide and 2-Hbbig =(2-hydroxybenzylidine)-3-(H-benzo)imidazol-2-yl(guanidine)]. Complex (**1**) was found to be distorted square planar whereas complex (**2**) as distorted square pyramidal geometry acting the Schiff base ligands as a bidentate chelate. Antimicrobial activity against several microbes have been tested and found both complexes exhibited potent antibacterial activity with the reference standard ciprofloxacin.*

Keywords: Schiff base, Cu(II) complex, antimicrobial study.

INTRODUCTION

In recent years, Schiff-base metal complexes have become interested in bioinorganic chemistry because of many of these complexes provide biological models in understanding the structure of biomolecules and biological processes [1]. Naturally occurring dioxygen carriers and storage proteins contain a transition metal ion to which dioxygen can reversibly bind, e.g., iron (haemoglobin) and copper (haemocyanin). Such systems have been modelled by a number of Schiff-base complexes [2-4]. Some cobalt(II) Schiff-base complexes are also able to bind reversible dioxygen and they have been used as simplified models in the study of reversible binding of dioxygen by its natural transporters [2–4]. Schiff base always have proven themselves as useful chelators because of their preparational accessibilities, structural varieties and varied denticities [5]. So, transition metal Schiff base complexes still have been the most well-known resources in the scope of heterogeneous catalysis, molecular electronics, single molecule based magnetism and, above all, photochemistry[6]. Hence, significant contemporary interests have grown gradually in this field to explore their physical, magnetic, optical and electronic properties through the variation of transition metal ions like nickel(II), copper(II), iron(II/III) and manganese(II/III) in different co-ordination environments with organic co-ligands with suitable bridging units [7-11]. This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning the metal centered electronic factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts. The flexibility of disposition of different donor sites is the secret behind their successful performance in mimicking peculiar geometries around the metal centers, leading to very interesting spectroscopic properties with varied magnetic activities [12]. Among all the transition metal complexes, Cu (II) Schiff base complexes with pseudohalides are well known for their preparational accessibilities, exhibiting the flexibility of the coordination geometry around the metal center [13, 14]. The coordination number usually varies from four to six depending upon the donor site geometry around the metal and above all the steric constraints imposed by the ligand itself. It is well known that some drugs have greater activities when administered as metal

complexes than as free organic ligands only [15]. A large number of reports are available on the biochemistry and the microbial activities of transition metal complexes containing O, N and S, N donor atoms. The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural lability and are sensitive to molecular environment [15]. In the present work we report the synthesis of the two new Schiff base ligand complexes, characterisation and their antimicrobial study with different microbes/ bacteria.

EXPERIMENTAL SECTION

All the chemicals were analytical grade and used as received without further purification.

Synthesis of complexes [$Cu(II)(4\text{-}Pmpbs)_2](CH3COO)_2.4H_2O$ **(1)**
Sulfadiazine (0.50g, 2 mmol) in 25 ml of ethanol was added to pyridine-2-carboxaldehyde (0.18 g, 2 mmol) in 15 ml of ethanol with constant stirring for 30 min. The solution mixture was filtered and the filtrate was refluxed for 4 hr. While refluxing the yellow solution mixture changes into red in colored. To the red color solution mixture, 0.5 g of sodium acetate was added as buffering agent followed by addition of 1mmol (0.199 g) of Cu-acetate monohydrate. The solution mixture was continued to reflux half an hour. The solution was then cooled at room temperature; crystalline precipitate was obtained and collected by filtration, dried in vacuum desiccators over anhydrous $CaCl_2$. Analytical data (Calc. value): C(%), 51.78(51.74); H(%), 3.51(3.47); N(%), 18.87(18.84). Molecular formula: $C_{34}H_{36}CuN_{10}O_{12}S_2$

Complexes $[Cu(II)(2\text{-}Hbbig)_2H_2O](CH_3COO)_2$ **(2)**
2-hydroxyacetophenone (0.272 g, 2 mmol) in 20 ml of methanol was added to 2-guanidinobenzimidazole (0.350 g, 2 mmol) in 10 ml of methanol. The resulting solution was stirred for an hour at 60^{o}C. The yellow coloured solution was then refluxed for about 3 hours till the solution changes into red. To the red coloured solution, copper acetate monohydrate (1 mmol, 0.199 g) in 15 ml methanol was added dropwise with constant stirring. The resulting solution was stirred magnetically at 60^{o}C for two hours. The solution was then cooled at room temperature; crystalline precipitate was obtained and collected by filtration, dried in vacuum desiccators over anhydrous $CaCl_2$. Analytical data (Calc. value): C(%), 54.40 (55.42); H(%), 6.66(6.63); N(%), 18.16(18.19). Molecular formula: $C_{33}H_{26}CuN_{10}O_7$.

Physical measurements
Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin - Elmer 2400 – II elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrum 400 in the range of 4000 – 400 cm^{-1} using KBr pellets. The absorption spectroscopy measurements were performed using a SHIMADZU UV-VISIBLE 2450 Spectrophotometer. Magnetic susceptibility measurements were performed using a Sherwood magnetic susceptibility balance (M.S.D) using copper sulphate pentahydrate as standard substance at room temperature and diamagnetic corrections were made using Pascal's constants. TGA and DTA were performed using a Perkin Elmer STA 6000 Simultaneous Thermal Analyzer.

Antimicrobial activity
The antimicrobial activity of the two complexes (**1** and **2**) were examined against different gram- positive (EF= *Entrobacter facealis*, SA= *Staphytococcus aureus*); gram-negative (PA= *Pseudomonas auriginosa*, EC= *Escherichia coli*, ST= *Salmonella typhi*) by using disc diffusion method [16]. Petriplates (100 mm) was prepared with 20 ml of sterile nutrient agar (NA) for testing the bacterial. The test cultures were swabbed on the top of the solidified media and allowed to dry for 10 min. Stock solutions of each compounds were diluted in DMSO to produce 2000 µg/ml. The dilutions of the compounds were deposited on 4 mm diameter sterile filters paper discs (10 µl per disc) which were subsequently placed on the inoculated petriplates and left for 10 min at room temperature for compound diffusion. Negative control was prepared using DMSO. Ciprofloxacin (5µg/disc) for bacteria were served as positive control. The plates were inoculated with bacteria were incubated at 37°C for 24 hrs. The experiment was repeated thrice and the average results were recorded. MIC was defined as the lowest concentration of extract that inhibited visible growth on agar.

RESULTS AND DISCUSSION

Infrared Spectroscopy
The FTIR spectra of the synthesized complexes were recorded within 4000-400 cm^{-1}. Complex (**1**) shows broad absorption bands at 3504 - 3338 cm^{-1} which may be assigned for ν(O-H) stretching frequency, showing the presence of lattice water molecules. The strong bands at 1631 and 1591 cm^{-1} is attributed to the imines ν(C=N) vibration of the azomethine and pyrimidine ring [17, 18]. The two absorption bands found at 1362 and 1151 cm^{-1} are assigned to the ν_{asy} and ν_{sym} of the SO_2 group [17, 18]. Strong absorption bands at 547 and 420 cm^{-1} may assigned for the ν(Cu-O) and ν(Cu-N) coordination respectively[19]. The two broad absorption bands at 3400 - 3317 and 3201 cm^{-1} for

the complex (**2**) are attributed to ν(OH) vibrations. The strong absorption bands at 1674 cm^{-1} are assigned to the imine(azomethine) ν(C=N) stretching vibration. Strong and sharp absorption band at 744 cm^{-1} are assigned for the imidazole, as results of coordination [20, 21, 22]. The presence of coordinated water molecules has confirmed by the presence of IR absorption bands at 823 cm^{-1} for [ρ_r(HOH)] , 686 cm^{-1} for [δ_w(HOH)] [23,24]. Strong absorption bands at 441 and 349 cm^{-1} may assigned for the ν(Cu-N) of guanidine nitrogen and ν(Cu-N) of imidazole nitrogen coordination respectively[25,26].

UV-Vis spectra

The electronic spectra of the complex(**1**) in methanol shows an absorption band at 15,432 cm^{-1} corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition supporting distorted Cu(II) square planar structure of the complex [27, 28] and the complex (**2**) in methanol shows an broad absorption band at 16,920 cm^{-1} corresponding to $^2B_1 \rightarrow {}^2E$ transition supporting distorted Cu(II) square pyramidal structure of the complex[27, 28].

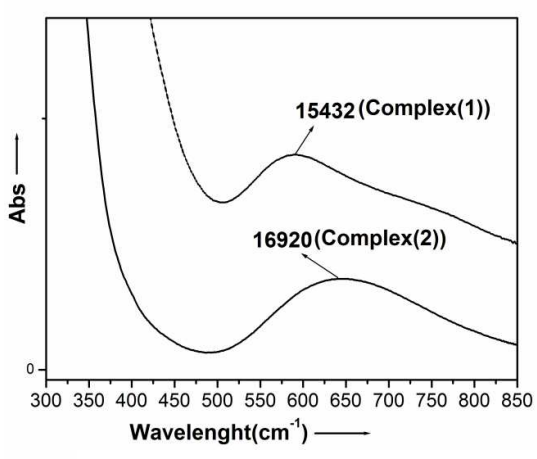

Figure: 1 Electronic spectra of the complexes (1 and 2).

Magnetic susceptibility measurements

The magnetic susceptibility measurement of the complexes (**1**) and (**2**) at room temperature was found to be 1.92 and 1.81 B.M respectively [27,28].

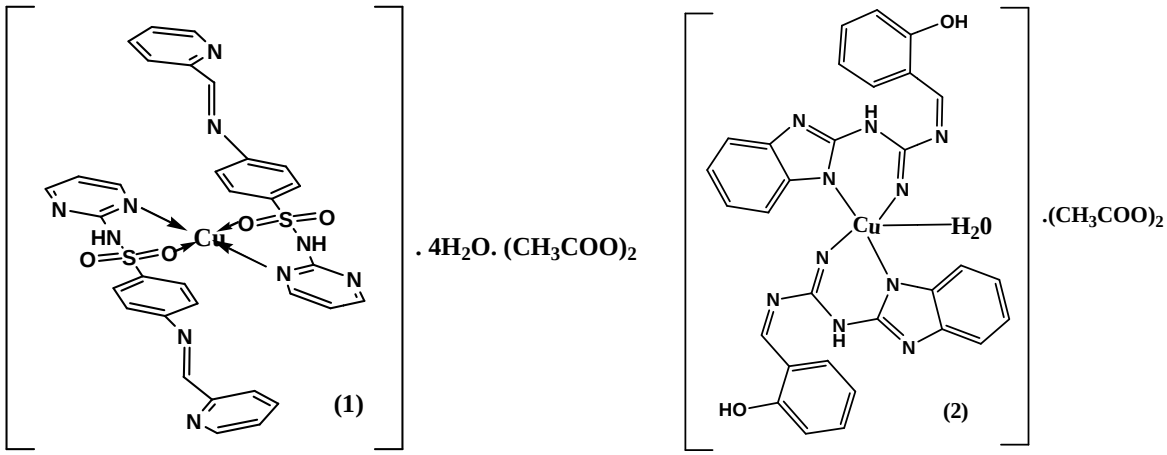

Figure: 2 Molecular structures of complex(1) and (2)

Thermal analyses

TG and DTA curves of the complexes (**1**) and (**2**) are given in the figure 3. Dehydration and decomposition pattern of the complexes shows that the molecular formula are in good agreement with the analytical data. TG curve of the complex (**1**) shows a dehydration curve of four lattice molecules in the temperature range of 110-132^oC, showing an endothermic DTA peak at 115^oC followed by loss of two molecules of the Schiff base ligand in the temperature range of 283-331^oC and decomposition of two molecules of acetate in the temperature range 332-417^oC, showing an exothermic peak at 347^oC [29,30,31]. Similarly, on heating, complex (**2**) shows a dehydration of one molecule of coordinated water in the temperature range of 114-245^oC. After the loss of one molecule of coordinated water, the

complex decomposes into copper oxide in two steps which corresponds to one molecule of the ligand in the second step and one molecule of ligand with two acetate molecules in the third step in the temperature ranges of 245 – 315 and 319 - 520°C, showing exothermic peaks at 309 and 458°C respectively as reflected in TGA and DTA curves [29, 30, 31].

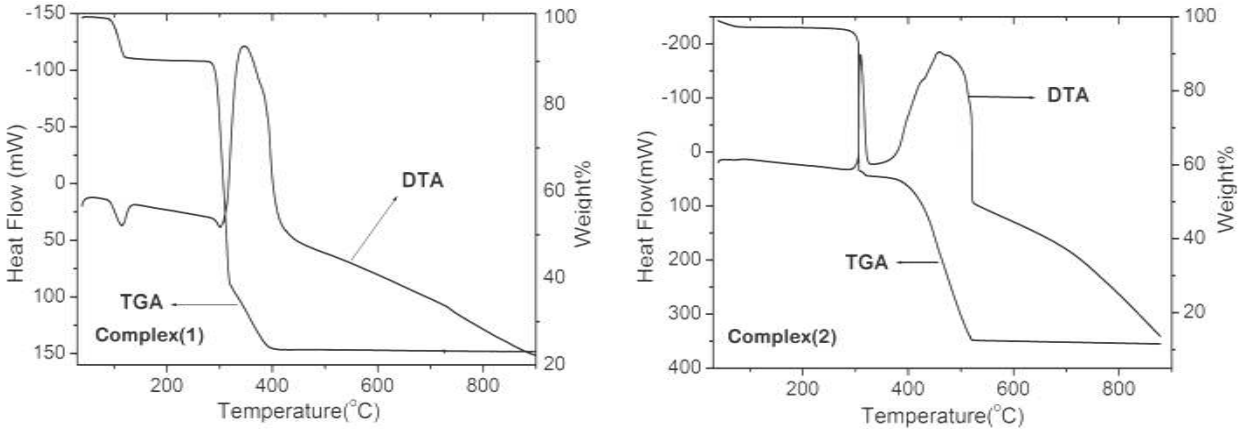

Figure: 3 TGA and DTA plot of complex (1) and (2).

Antimicrobial activity and minimum inhibitory concentration, MIC

The tests were carried for concentrations of 125, 250, 5×10^2, 1×10^3 DMSO solutions of the two complexes. The inhibition zones caused by the various complexes on the different microorganisms were examined. The results of the preliminary screening test are listed in table 1. It has been observed from the activity data of the complexes and compared with the activity of a standard Ciprofloxacin (Cip). The antibacterial results showed very good activity against some bacteria (*E. Faecalis, S. Aureus, P. Auriginosa, E. Coli,* and *S. Typhi*) in comparison with the standard drug ciprofloxacin (Cip). The complex (**1**) showed very good activity against EF, SA, PA, EC and ST at a concentration of 5×10^2 and 1×10^3. A similar type of activity was shown by complex (**2**) also very good activity against EF, SA, PA, EC and ST with the concentration of 250, 5×10^2 and 1×10^3.

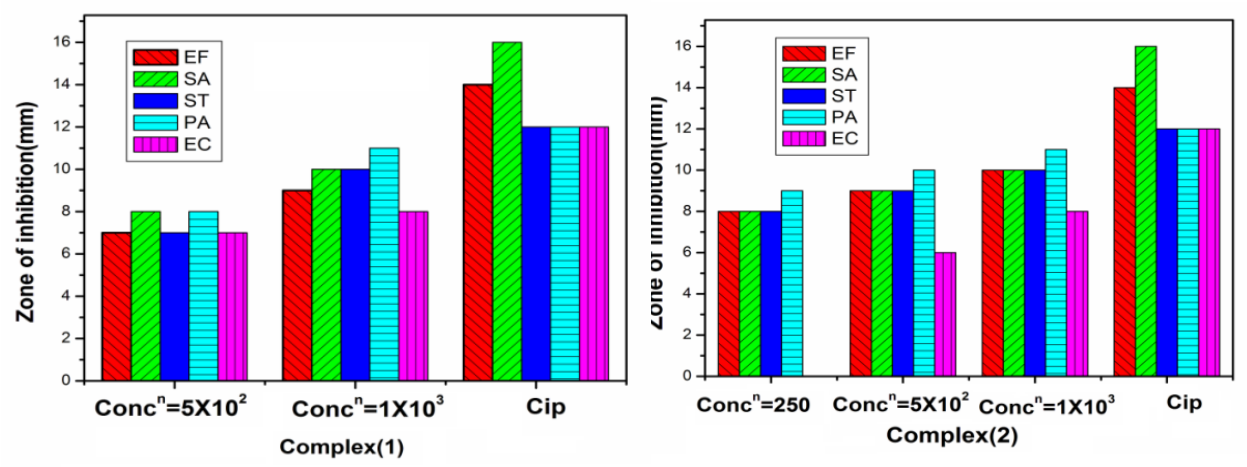

Figure: 4 Zone of inhibition (mm) at 250, $5x10^2$ and $1x10^3$ concentrations of complexes (1 and 2).

Table 1: Antibacterial activity (inhibition zone)

Name of the compound	Name of micro-organism	Inhibition (mm) (Different conc. of each comp. (µg/disc)					
		$1x10^3$	$5x10^2$	250	125	Cip.	MIC(µg)
Complex(**1**)	EF	9	7	-	-	14	125
	SA	10	8	-	-	16	125
	ST	10	7	-	-	14	125
	PA	11	8	-	-	12	125
	EC	8	7	-	-	12	125
Complex(**2**)	EF	10	9	8	-	14	62.5
	SA	10	9	8	-	16	62.5
	ST	10	9	8	-	14	62.5
	PA	11	10	9	-	12	31.25
	EC	8	6	-	-	12	125

Gram-positive= EF - Enterobacter faecalis; SA- Staphytococcus aureus.
Gram-negative= PA - Pseudomonas auriginosa; EC - Escherichia coli; ST – Salmonella typhi.
Standard= Cip – Ciprofloxacin

CONCLUSION

In the present work we have synthesised two new Cu(II) Schiff base complexes and characterized by different analytical techniques and found that the complexes are inconsistence with our expected structures and revealed distorted square planar and square pyramidal geometry around metal ions; where the ligand act as bidentate chelate with NO and NN donor sites forming six- membered chelate rings. Antimicrobial activity of the synthesised complexes was done in comparison with Ciprofloxacin as standard to reveal the potency of the synthesized complexes. In all the five selected strains *E. Faecalis, S. Aureus, P. Auriginosa, E.Coli* and *S. Typhi* showed sensitivity to all complexes at higher concentrations (250, 500 and 1000 µg/ml) and no sensitivity at lower concentrations.

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