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Research Article

Synthesis, Characterisation, Crystal Structure, and Antimicrobial and Larvicidal Studies of $[Cu(2,2'\text{-bipy})_2SO_4]\cdot 3CH_4N_2O\cdot 2H_2O$

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A pentacoordinated mononuclear copper(II) complex, namely, bis(2,2′-bipyridine)sulphatecopper(II) urea trisolvate dihydrate, has been synthesised and characterised by molar conductance and UV-Vis and FTIR spectra. The structure of the complex was unambiguously confirmed by single crystal XRD. The complex crystallizes in monoclinic system, space group *C2/c*, with the values $a = 20.155(4)$, $b = 20.858(4)$, and $c = 14.425(3)$ Å; $\alpha = 90.00^\circ$, $\beta = 96.51^\circ$, and $\gamma = 90.00^\circ$; $V = 6025(2)$ Å^3 and $Z = 8$. The Cu(II) ion is coordinated to four nitrogen atoms of two bidentate 2,2′-bipyridine ligands (bipy) and by one oxygen atom of the sulphate group and displays distorted trigonal bipyramidal geometry. The crystal packing is stabilized by inter- and intramolecular hydrogen bonding. The Cu(II) complex was screened for antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumonia*, *Aspergillus niger*, *Aspergillus flavus*, and *Candida albicans*. Larvicidal activity of the synthesized copper(II) complex was carried out against larvae of *Culex quinquefasciatus* and *Anopheles subpictus*.

1. Introduction

The coordination chemistry of copper has been connected to diverse fields like industry, electronics, and medicine. Adducts of metal complexes act as very good model systems for investigations in the area of molecular recognition and molecular association [1, 2]. Due to the interaction of the metal ions with Lewis bases, the metal complexes increase their coordination number, which takes place by either intermolecular association or adduct formation with the solvents or ligands possessing good ligating ability [3]. The ligands with various donor features show different types of molecular associations.

Aromatic nitrogen heterocycles are important class of ligands in coordination chemistry. Among them bidentate chelating agent like 2,2′-bipyridine and its analogues readily form stable complexes with most of the transition metal ions and have been extensively used due to their applications in various fields like catalysis, preparative coordination chemistry, electrochemistry, and biochemistry [4].

Human beings suffer extensively due to insects especially mosquito bites. Some mosquitoes are vectors for diseases, which means that they can transmit diseases from one human or animal to another. According to the World Health Organization, mosquito bites result in the deaths of more than 1 million people every year. The majority of these deaths are due to malaria. The World Health Organization estimates that between 300 and 500 million cases of malaria occur each year and a child dies from malaria every 30 seconds. Recent estimates indicate that 90% of the 1.5–3 million deaths due to malaria occur in Africa [5] and over one-third of the 146 million people infected with lymphatic filariasis are from this continent [6]. Mosquitoes are the major vector of transmitting harmful diseases such as malaria, yellow fever, filariasis, and dengue fever. *Culex quinquefasciatus*, the southern house mosquito, transmits diseases such as lymphatic filariasis and malaria [7, 8]. Hence, we made an attempt to study the larvicidal activity of the Cu(II) complex. Herein, we report the synthesis and spectroscopic and crystal

structure of Cu(II) complex and its antibacterial, antifungal, and larvicidal activities.

2. Experimental

2.1. Materials and Physical Measurements. All the reagents and chemicals were procured from commercial sources and were used without purification. $CuSO_4 \cdot 5H_2O$ was purchased from S.D. Fine Chemicals, Mumbai (India), and 2,2′-bipyridine was purchased from Central Drug House (P) Ltd., Mumbai (India).

Molar conductance of the complex was measured in DMSO (10^{-3} M) solution using a direct digital conductivity meter. FTIR spectra of solid complex were recorded using KBr pellet in the region of 4000–400 cm^{-1} on AVATAR 330 spectrophotometer. A UV-Vis spectrum of the complex was recorded in the region of 200–800 nm using a Hitachi U-2800 spectrophotometer in DMSO.

2.2. Synthesis. An aqueous solution of copper(II) sulphate (1 mmol, 0.253 g) was added to an aqueous solution of urea (1 mmol, 0.061 g) and the solution was stirred for 30 min at 343 K. Then, an ethanolic solution of 2,2′-bipyridine (1 mmol, 0.158 g) was added in drops and the solution was stirred for additional 3 h at the same temperature. The resultant blue-coloured solution was filtered and kept at room temperature. Blue-coloured crystals obtained by slow evaporation of the mother liquor were collected and dried.

2.3. X-Ray Crystallography. For the determination of crystal structure, single crystal of the complex was used for data collection on Bruker single crystal Kappa Apex II diffractometer. The crystal of the Cu(II) complex with the crystal size of 0.23 × 0.19 × 0.15 mm^3 was mounted on a glass fibre and used for data collection. Crystal data were collected using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å).

The structure was solved by direct method using SHELXS-97 and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [9, 10]. All the nonhydrogen atoms were refined anisotropically. A summary of pertinent crystal data along with further details of structure determination and refinement are given in Table 1.

2.4. Antimicrobial Activity. The Cu(II) complex was screened for antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus*, and *Klebsiella pneumoniae* by the well-agar diffusion method [11]. Stock solutions were prepared by dissolving 1 mg of the sample per mL of DMSO solution. In a typical procedure, a well was made on the agar medium inoculated with the microorganism. The well was filled with the test solution using a micropipette and the plate was incubated at 35°C for 24 h. The antifungal activity was also evaluated against *Aspergillus flavus, Aspergillus niger*, and *Candida albicans*. DMSO was used as negative control whereas ampicillin and polymyxin B sulphate were used as positive control against bacteria and fungi, respectively. The antimicrobial activity was evaluated by measuring the zone of inhibition in mm.

Table 1: Crystal data and structure refinement for the complex $Cu(2,2'\text{-bipy})_2SO_4]\cdot 3CH_4N_2O\cdot 2H_2O$.

Empirical formula	$C_{23}H_{32}CuN_{10}O_9S$
Formula weight	688.19
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	C2/c
a/Å	20.155(4)
b/Å	20.858(4)
c/Å	14.425(3)
α/°	90.00
β/°	96.51(3)
γ/°	90.00
Volume/$Å^3$	6025(2)
Z	8
ρ_{calc} mg/mm^3	1.517
m/mm^{-1}	0.861
$F(000)$	2856.0
Crystal size/mm^3	0.23 × 0.19 × 0.15
2Θ range for data collection	3.84 to 56.62°
Index ranges	$-25 \le h \le 19$, $-27 \le k \le 27$, and $-19 \le l \le 12$
Reflections collected	21903
Independent reflections	6624 [R(int) = 0.0310]
Data/restraints/parameters	6624/0/461
Goodness of fit on F^2	1.031
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0360, wR_2 = 0.0878
Final R indexes [all data]	R_1 = 0.0642, wR_2 = 0.0990
Largest diff. peak/hole/e $Å^{-3}$	0.32/−0.34

2.5. Larvicidal Activity. The egg and egg rafts of *Culex quinquefasciatus* and *Anopheles subpictus* were procured from Zonal Entomological Research Centre, Vellore, Tamil Nadu, to start the colony and larvae were kept in plastic trays containing dechlorinated water. They were maintained at 27 ± 2°C and 75–85% relative humidity under 14 : 10 light and dark cycles. Larvae were fed with powdered nutrient broth once in a day. Pupae were transferred from the trays into plastic bottles containing dechlorinated water where the adults emerged. After 4 days the hatched larvae turned into larvae in early fourth stage and were subjected to experimentation.

Larvicidal Bioassay. From the stock solution, 1000 ppm was prepared with dechlorinated tap water. The larvicidal activity was assessed [12, 13] using the procedure reported by Rahuman et al. [14]. For the bioassay test, larvae were taken in three batches of 20 in 200 mL of water and 1.0 mL of the Cu(II) complex. The control was set up with polysorbate 80. The numbers of dead larvae were counted after 24 h of exposure, and the percentage mortality was reported from the average of triplicates. The experimental media, in which 100% mortality of larvae occurs alone, were selected for dose-response bioassay.

Dose-Response Bioassay. From the stock solution, different concentrations ranging from 5 to 500 mg/L were prepared. Based on the preliminary screening results, Cu(II) complex was subjected to dose-response bioassay against the larvae of *Culex quinquefasciatus* and *Anopheles subpictus*. The numbers of dead larvae were counted after 24 h of exposure, and the percentage mortality was reported from the average of triplicates [15].

3. Results and Discussion

The copper(II) complex is found to be stable at room temperature and soluble in ethanol, DMF, and DMSO. The lower molar conductivity value of 5 Ω^{-1} cm^2 mol^{-1} in DMSO supports the nonelectrolytic nature of the complex [16].

3.1. Spectroscopic Characterisation. The UV-Vis spectra of the Cu(II) complex displayed $\pi \rightarrow \pi^*$ transition of benzene ring at 283 nm and the band which appeared at 388 nm corresponds to $n \rightarrow \pi^*$ transition. The broad band which appeared at 635 nm corresponds to d-d transition of the copper(II) ion.

The FTIR spectra of the Cu(II) complex show a broad and intense band at 3388 cm^{-1}, due to strong hydrogen bonds including urea and water molecules [17, 18]. The C=N stretching frequency of 2,2′-bipyridine appears at 1603 cm^{-1}. The free sulphate ion is highly symmetric. Upon coordination, the symmetry of the sulphate group is lowered. Medium bands which appeared at 485 and 990 cm^{-1} correspond to υ_1 and υ_2 modes of vibrations, respectively. The monodentate sulphate ion displayed sharp bands at 1097 and 1124 cm^{-1} which correspond to υ_3 the symmetric stretching and the bands which appeared at 612 cm^{-1} correspond to υ_4 the asymmetric bending vibrations. Cu–O and Cu–N linkages are confirmed by weak bands observed at 412 and 553 cm^{-1}, respectively [19].

3.2. Crystal Structure. The selected bond lengths and bond angles of the synthesized Cu(II) complex are listed in Table 2. An ORTEP [20] view of the Cu(II) complex along with the atom numbering scheme is depicted in Figure 1. The complex crystallizes in monoclinic system, space group *C2/c*.

In the present work, we made an attempt to synthesize an adduct of urea and 2,2′-bipyridine with copper(II) ion. But urea molecules remain uncoordinated with the metal ion. The complex crystallizes with three urea molecules and two water molecules which remain uncoordinated with the Cu(II) ion. The Cu(II) ion is pentacoordinated via the nitrogen atoms of 2,2′-bipyridine and oxygen atom of sulphate group. Five-coordination is common for Cu(II) with either trigonal bipyramidal (tbp) or square pyramidal geometry. For distinguishing between tbp and square pyramidal geometry in case of five-coordinated metal complexes, Addison et al. [21] have introduced index of trigonality τ (where $\tau = (\beta - \alpha)/60$, in which α and β are the two largest coordination angles). In general, $\tau = 0$ for an ideal square pyramidal and $\tau = 1$ for ideal tbp geometry. In the present case, by taking N2-Cu-N4 as β (174.42°) and N3-Cu-O1 as α (136.04°), the τ value is calculated as 0.64. This value is intermediate between square pyramidal and tbp and the τ value is slightly closer to the later one (ideal tau = 1) [22, 23]. This indicates that the complex exhibits distorted tbp geometry and the distortion may be due to the presence of bulky groups like 2,2′-bipyridine.

The basal plane is occupied by N1-Cu, N3-Cu, and O1-Cu with the bond distances 2.121(2), 2.070(2), and 2.031(2) Å, respectively. The equatorial plane is occupied by N2-Cu and N4-Cu with the bond distances being 1.977(2) and 1.969(2) Å, respectively. The bond angle N2-Cu-N4 is 174.42(7)°. Using the bond angles N1-Cu-N3 (107.84(7)°), N3-Cu-O1 (136.04(7)°), and O1-Cu-N1 (116.03(6)°), the sum of the bond angles around Cu(II) is calculated as 359.91° which is very close to 360°. This confirms the presence of Cu(II) ion with very slight deviation from the basal plane. Three molecules of urea and two molecules of water remain uncoordinated with the Cu(II) ion, whereas these involve

Table 2: Selected bond lengths [Å] and bond angles [deg.] for the complex $[Cu(2,2'\text{-bipy})_2SO_4]\cdot 3CH_4N_2O\cdot 2H_2O$.

Bond lengths			
Cu–N1	2.1210(18)	N1–C5	1.346(3)
Cu–N2	1.9775(17)	N1–C1	1.341(3)
Cu–N3	2.0697(19)	N3–C11	1.341(3)
Cu–N4	1.9694(17)	N4–C16	1.343(3)
Cu–O1	2.0307(16)	N4–C20	1.339(3)
O1–S1	1.4930(16)	N3–C15	1.347(3)
N2–C10	1.340(3)	C15–C16	1.473(3)
N2–C6	1.342(3)	C5–C6	1.478(3)
Bond angles			
N2–Cu–N1	79.42(7)	N4–Cu–N2	174.42(7)
N2–Cu–N3	100.72(8)	N4–Cu–N3	80.62(8)
N2–Cu–O1	90.06(7)	N4–Cu–O1	92.69(7)
N3–Cu–N1	107.84(7)	O1–Cu–N1	116.03(7)
N4–Cu–N1	95.00(7)	O1–Cu–N3	136.04(7)

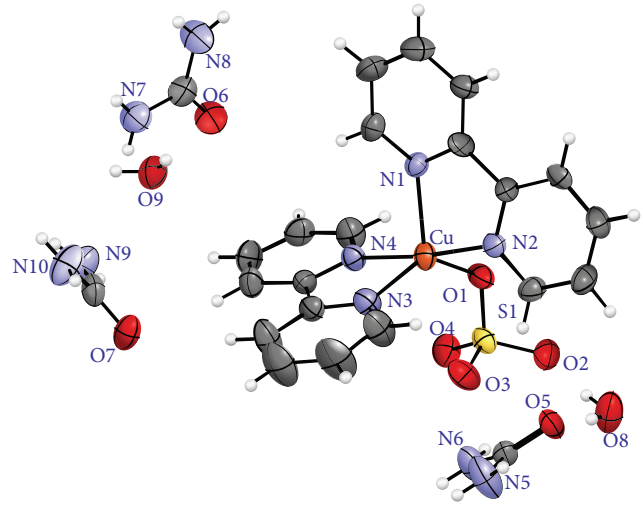

Figure 1: An ORTEP view of Cu(II) complex with the numbering scheme.

Table 3: Hydrogen bond lengths (Å) and bond angles (°) for $[Cu(2,2'\text{-bipy})_2SO_4]\cdot 3CH_4N_2O\cdot 2H_2O$.

D–H ⋯ A	*d* (D–H)	*d* (H ⋯ A)	*d* (D ⋯ A)	∠DHA
C17–H17 ⋯ O7	0.930	2.47	3.393	171
C18–H18 ⋯ O9	0.930	2.55	3.238	131
C14–H14 ⋯ O7	0.929	2.45	3.374	172
C10–H10 ⋯ O5	0.929	2.60	3.230	135
C7–H7 ⋯ O1	0.929	32.41	3.234	148
N6–H6B–O3[a]	0.79	2.13	2.919	142
O8–H8Y ⋯ O3	0.912	2.78	3.440	129
O8–H8Y ⋯ S1	0.912	2.87	3.739	158
O8–H8Y ⋯ O2	0.912	1.99	2.898	172
O9–H9X ⋯ O6	0.796	2.026	2.807	166
N7–H7B ⋯ O2[b]	0.82	2.16	2.974	172(3)
N8–H8A ⋯ O4[b]	0.80	2.06	2.848	167
N8–H8B ⋯ O4[b]	0.80	2.06	2.848	173

Symmetry codes: (a) $1 - x, y, 1/2 - z$; (b) $x, 1 - y, 1/2 + z$.

Table 4: Antimicrobial data of Cu(II) complex.

Compound	*S. aureus*	*E. coli*	*K. pneumoniae*	*A. niger*	*A. flavus*	*C. albicans*
Cu(II) complex	22	16	12	<10	<10	<10
Bipy	<10	14	11	<10	<10	<10
Urea	<10	<10	<10	<10	<10	<10
Ampicillin	30	16	33			
Polymyxin B sulphate				11	11	11

Table 5: LC_{50}, LC_{90} and other statistical analyses of Cu(II) complex against the larvae of *Culex quinquefasciatus* and *Anopheles subpictus*.

Species	LC_{50} ± SE (ppm)	UCL–LCL	LC_{90} ± SE (ppm)	UCL–LCL	χ^2 (df = 4)
Culex quinquefasciatus	58.21 ± 4.21	66.46–49.95	285.70 ± 34.18	352.70–218.70	8.31
Anopheles subpictus	28.95 ± 2.22	33.312–2.60	168.05 ± 23.56	360.79–245.61	8.88

LC_{50}: lethal concentration that kills 50% of the exposed larvae.
LC_{90}: lethal concentration that kills 90% of the exposed larvae.
UCL: upper confidence limit; LCL: lower confidence limit; χ^2: chi-square.
df: degree of freedom significant at $P < 0.05$ level.

intermolecular hydrogen bonding. The crystal packing is mainly stabilized by inter- and intramolecular hydrogen bonding. These interactions are depicted in Figure 2 and the corresponding data are given in Table 3.

3.3. Antimicrobial Activity. The zone of inhibition exhibited by Cu(II) complex against the bacteria and fungi under study is summarized in Table 4. The results revealed that the Cu(II) complex is found to be resistant to the fungi under study, whereas it shows moderate activity against the bacteria showing zone of inhibition 22 mm, 16 mm, and 12 mm against *S. aureus, E. coli*,and *K. pneumoniae*, respectively. The antibacterial activity exhibited by the Cu(II) complex is comparatively greater than the corresponding chelating agents like bipy and urea.

3.4. Larvicidal Activity. The results of larvicidal activity of the Cu(II) complex (Table 5) showed higher mortality value

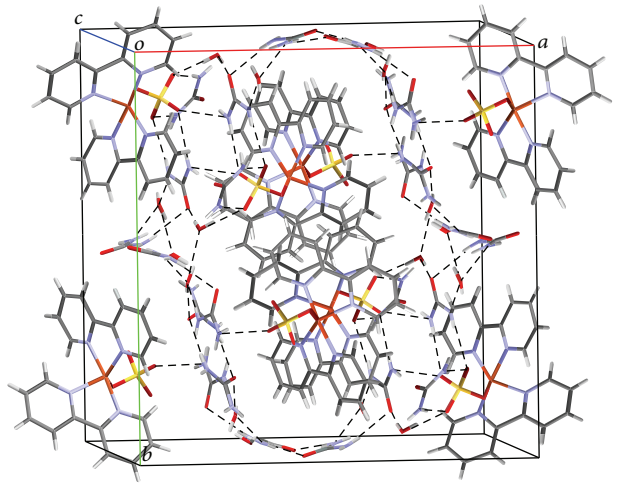

Figure 2: The molecular packing diagram of Cu(II) complex. Hydrogen bonds are shown as dashes.

of 85 ± 2.44% and 61 ± 2.74% against the larvae *Culex quinquefasciatus* and *Anopheles subpictus*, respectively.

The average larval mortality data were subjected to probit analysis for calculating LC_{50}, LC_{90} and other statistics at 95% fiducial limits of upper confidence limit and lower confidence limit, and chi-square values were calculated. Results with $P < 0.05$ were considered to be statistically significant.

4. Conclusions

The titled complex was characterized by UV-Vis, FTIR, and X-ray crystallography. The structural analysis revealed that the Cu(II) complex exhibited distorted trigonal bipyramidal geometry around Cu(II) ion. The antimicrobial studies suggested that the Cu(II) complex exhibited moderate antibacterial activity against *S. aureus, E. coli*, and *K. pneumoniae* and resistance to the fungi under investigation. The Cu(II) complex exhibited good larvicidal activity against *Culex quinquefasciatus* and *Anopheles subpictus*.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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