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SYNTHESIS, SPECTRAL, CYCLIC VOLTAMMETRIC AND BIOLOGICAL STUDIES OF COPPER (II) COMPLEXES WITH N, N', N"-TRIS-(BENZIMIDAZOLYL) METHANE LIGAND

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ABSTRACT

The tripodal ligand N, N', N''-tris-(Benzimidazolyl)-methane (TBM) containing benzimidazole as pendant groups has been synthesized and utilized to prepare Cu (II) complexes of general composition [Cu (TBM) X_2]. n H_2O. Where X is an exogenous anionic ligand (X = Cl^-, NO_3^-, CH_3COO^- and $HCOO^-$). Complexes of 1 : 1 stochiometry form with the ligands in methanol and were characterized by elemental analysis, EPR, IR, UV-VIS spectroscopic and other analytical techniques. X-band EPR spectra of the above complexes indicate a typical axial spectra with severe distortion of the N_2X_2 basal plane. The cyclic voltammograms of the complexes were taken in DMSO. Cyclic Voltammetric measurement of the complexes display quasi reversible redox wave. The –ve reduction potential values reveal the strong binding of anionic donors stabilizing the Cu (II) oxidation state. The magnetic moment data reveal the monomeric nature. The IR spectral data reveal unidentate mode of binding of the benzimidazole and anionic donors to the copper site. The UV spectra reveal that the UV bands are all blue shifted upon coordination and in general in enhance in intensity. The large molar extinction coefficients reveal that the copper site in the complexes is of low symmetry.

Key words: TBM [N, N′, N″-tris-(Benzimidazolyl) methane], Tridentate, Benzimidazolyl, Exogenous, Ligand, *E. coli.*

INTRODUCTION

Besides the biological importance copper compounds are amongst the most useful and versatile oxidation catalysts known[1,2]. A natural process of considerable industrial importance is the copper catalyzed oxidative coupling of 2, 6-Xylenol to form an aromatic polyether[3-5]. They bind and transport dioxygen[6] leading to extensive efforts by bioinorganic chemists to learn about the structures and mechanism of action of the protein active site[7]. This approach involves the synthesis and characterization of low molecular weight

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compounds that can duplicate either the physiochemical properties of the protein active site and/or mimic their functional attributes[7,8]. The finding that biological copper exists in distorted tetrahedral/distorted square pyramidal environments and that imidazole residue of the Histidine is a bridging/terminal ligand to copper centres, has prompted the synthesis and characterization of small molecule mimics of copper active sites. The present study is aimed at generating Cu (II) sites in low symmetry environments utilizing tridentate, N, N′, N″-tris-(Benzimidazolyl) methane as the ligand that has been scarcely used earlier[9-18]. These copper (II) complexes with distorted geometries may have potential relevance in copper containing enzymes such as Superoxide Dismutase (SOD) and Laccases.

EXPERIMENTAL

Materials and methods

All the solvents were dried over molecular sieves. IR spectra were taken on a Shimadzu IR-435 spectrophotometer, X-band EPR spectra on a Jeol JES-PE 3XG EPR spectrometer with a variable temperature liquid nitrogen cryostat, ^{1}H NMR spectra on 90 MHz Perkin-Elmer at USIC, University of Delhi, Delhi-7. Magnetic Susceptibility was determined by the using a CAHN-2000 balance in the solid state. The cyclic voltammograms were taken in Dayalbagh University, Agra. UV-VIS spectra were taken on a Thermo Spectronic-Vision 32 Spectrophotometer in St. Johns College, Agra.

Preparation of the ligand

The ligand was synthesized as described before[18]. A mixture of 24 mmoles of benzimidazole, 120 millimoles of anhydrous K_2CO_3 and 1.2 millimoles of tetrabutylammonium hydrogen sulphate were vigorously stirred and refluxed in dry chloroform (25 mL) overnight. Then the mixture was filtered and the residue washed with hot chloroform (2 x 25 mL). The organic solution was evaporated and the crude product purified by crystallization (EtOH-H_2O), while crystals were obtained with good yield (60%). The common formula of the ligand is $C_{22}H_{16}N_6$. The ligand was characterized by C, H, N; IR, ^{1}H NMR and ^{13}C NMR. TBM: ^{1}H NMR (DMSO- d_6) (rel. intensity in ppm) : 7.0 (m, 9H); 7.76 (s, 3H); 7.8-8.0 (m, 3H); 8.76 (s, H) : ^{13}C NMR (DMSO- d_6) (rel. intensity in ppm) : 142.1(s) ; 138.2(s) ; 121.95(s) ; 115.4 (s).

Preparation of the complex

$[Cu\ (L)\ X_2]$:

($X = Cl^-$ and NO_3^-)

$CuX_2.yH_2O$ (1 mmol) and the appropriate ligand were dissolved in 10 mL of methanol, respectively. Both the solutions were mixed. The solution was stirred for about three hours and then solvent was stripped off on a rotatory evaporator (Ca.45^oC). The residue was treated with dry ethanol and filtered. To the filtrate, ether was added (1 : 7). Upon standing a parrot green the precipitate was obtained. The precipitate was then centrifuged and recrystallized with Ethanol-ether (1 : 5) mixture.

[Cu (L) X_2]:

(X= $HCOO^-$ and CH_3COO^-)

1 mmol of copper (II) chloride in 10 mL of methanol was treated with a solution of sodium hydroxide in methanol. The copper (II) hydroxide precipitate was filtered off. This was then resuspended in methanol (10 mL) and acetic acid / formic Acid solution added to it dropwise directly reacted with ligand (1 mmol) in MeOH. The reaction mixture was stirred for about four to five hours. Then the solution was reduced to a small volume on a rotatory evaporator. The solution was created with excess of diethyl-ether. The greenish-blue precipitate formed was filtered off. It was then washed with methanol-ether mixture (1 : 5) and was dried over P_2O_5 in vacuum.

Table 1: Elemental analysis: Found (Calculated):

Complex	% C (Cal.)	% H (Cal.)	%N (Cal.)	% Cu (Cal.)
[Cu (TBM) Cl].Cl_2H_2O	49.9 (49.4)	3.1 (3.7)	15.2 (15.7)	11.1 (11.9)
[Cu (TBM) $(NO_3)_2$].H_2O	47.1 (46.4)	2.8 (3.2)	19.0 (19.7)	10.7 (11.2)
[Cu (TBM) $(HCOO)_2$].H_2O	54.9 (53.8)	3.5 (3.9)	17.0 (15.7)	11.9 (11.9)
[Cu (TBM) $(OAc)_2$].CH_3OH	56.0 (56.1)	3.8 (4.3)	14.6 (14.5)	11.4 (11.0)

RESULTS AND DISCUSSION

Electronic spectroscopy

The ligand and their copper complexes show characteristic UV spectra of the benzimidazolyl group. Their absorption band and extinction coefficients are reported in Table 2. The UV bands are all blue shifted upon co-ordination and is general enhanced in intensity as evidenced by bands and their extinction coefficients. These bands in all

probability could be assigned to the π- π* transition within the benzimidazole nucleus. This includes the band at 242 nm in TBM ligand which is associated with imidazole ring showing clear evidence of (-C=N-) coordination to the Copper centre in these complexes. Additionally a weaker band is observed at about 300 nm. Since the binding of copper (II) ion occurs through the nitrogen of the imidazole, it may be justified to utilize and compare the charge transfer spectra of the chromophores with our system.

Tetragonal Cu (II) complex with imidazole as ligand have absorption maxima in a wide range between 550 to 850 nm.[19] All the copper complexes exhibit one major absorption band in the range 680-840 nm. The large molar extinction coefficients of these complexes ranging from 100-500 LM^{-1} cm^{-1} indicate that the Copper site in the complexes is of low symmetry. Utilizing the energy ranges covered by the d-d transition of CuN_{4-6} chromophores of different stereochemistry[20], it is concluded that the present complexes fall in the class of a compressed tetrahedron or distorted square based pyramidal. The distortion being towards a tetrahedral arrangement of the basal plane. Upon comparing the analogous complexes with Cl^-, NO_3^-, $HCOO^-$ and OAc^- exogenous ligands it is found that acetate provides a weaker and formate provides stronger equatorial ligand field as evidenced by the respective λ_{max} in the visible region.

Table 2: Optical bands (nm) of Copper (II) complexes and their extinction coefficients

Complex	Solvent	λ_{max}	Log Є
[Cu (TBM) Cl].Cl_2H_2O	MeOH	242, 268, 275, 755	5.08, 5.06, 5.01, 1.94
[Cu (TBM) $(NO_3)_2$].H_2O	DMF	273, 279, 700	4.85, 4.83, 1.85
[Cu (TBM) (HCOO)].H_2O	DMSO	272, 280, 680	4.93, 4.90, 1.87
[Cu (TBM) $(OAc)_2$].CH_3OH	DMSO	274, 280, 304, 770	4.32, 4.32, 3.97, 1.85

IR Spectroscopy

IR spectra were taken in Schimadzu IR-435 spectrophotometer. In the free ligand a strong band is found around 1460 cm^{-1}. The 1460 cm^{-1} band is attributed to stretching mode for (-C=N-C=C-) while the other one is an overtone or combination band[21].

The copper complexes containing acetate and formate show bands at 1620-1630 cm^{-1} and 1370-1390 cm^{-1}, respectively. These suggest the presence of coordinated acetate / formate and are assigned to a unidentate of acetate / formate group[22]. In our nitrato complexes band

are found in the same region as for unidentate NO_3^-, Hence, it is likely that we have a monodentate NO_3^- band to copper in the copper complexes. The data of ligand and complexes are in the following Table 3.

Table 3: IR frequencies (cm^{-1}) and proposed modes of assignments for the Copper (II) Complexes

Complexes	Assignments
[Cu (TBM) Cl]. Cl. $2H_2O$	
1620 (w)	$\upsilon_{(-C=N-)}$
1450 (s)	$\upsilon_{(-C=N-C=C-)}$
1370 (m)	L
740 (s)	L
[Cu (TBM) $(NO_3)_2$]. H_2O	
1620 (m)	$\upsilon_{(-C=N-)}$
1450 (sh)	$\upsilon_{(-C=N-C=C-)}$
1430 (sh, w)	$\upsilon_{a(NO_2)}$
1300 (s)	$\upsilon_{s(NO_2)}$
1000 (m)	$\upsilon_{s(NO)}$
740 (s)	L
[Cu (TBM) $(HCOO)_2$].H_2O	
1630 (w)	$\upsilon_{(-C=N-)}$ and $\upsilon_{(-C=O)}$ Stretching of Unidentate formate
1460 (s)	$\upsilon_{(-C=N-C=C-)}$
1380 (m)	Unidentate formate mode
740 (s)	L

Cyclic voltammetry

The cyclic voltammogram of complexes were recorded in DMSO solution and has been shown in Table 4. A three electrode configuration composed of Pt-disk working electrode, a Pt-wire counter electrode and $Ag/AgNO_3$ reference electrode was used for measurement. The cyclic voltammogram of the complexes are shown in Fig. 2a-2d. A

reduction wave can be observed at 0.185, 0.017, 0.017 and -0.531 volts vs. $Ag/AgNO_3$ for the following complexes [Cu (TBM) Cl] $Cl_2.H_2O$, [Cu (TBM) $(NO_3)_2$]. H_2O, [Cu (TBM) $(HCOO)_2$].H_2O and [Cu (TBM) $(OAc)_2$].CH_3OH, respectively. This wave corresponds to a one electron-reduction of Cu (II) to Cu (I). The –ve reduction potential indicates that Cu (II) in these complexes is stabilized with respect to the Cu (I) oxidation state. Such a stabilization is expected with a strongly anionic donor like the one employed in the above series.

Table 4: Cyclic Voltammetry of metal complexes

Complexes	Scan rate (mV/Sec.)	Supporting electrolyte	Solvent	Oxidation potential (Volt)	Reduction potential (Volt)
[Cu (TBM) Cl].Cl.2H_2O	100	$Ag/AgNO_3$	DMSO	0.429	0.185
[Cu (TBM) $(NO_3)_2$].H_2O	100	$Ag/AgNO_3$	DMSO	0.254	0.017
[Cu (TBM) $(HCOO)_2$].H_2O	100	$Ag/AgNO_3$	DMSO	0.432	0.017
[Cu (TBM) $(OAc)_2$].CH_3OH	100	$Ag/AgNO_3$	DMSO	0.054	-0.531

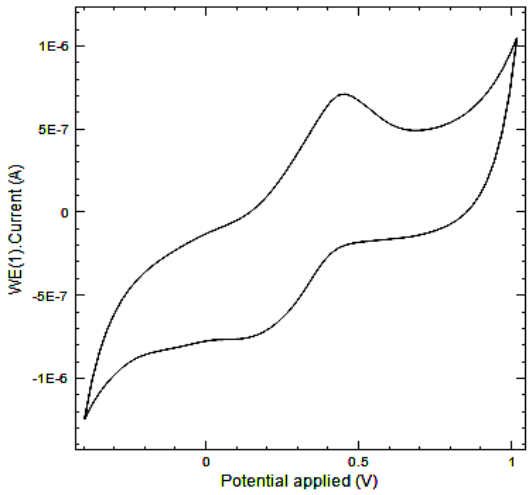


Fig. 2a: Cyclic voltammogram of [Cu(TBM) Cl] Cl.2H_2O in DMSO Scan rate 100 mV/Sec

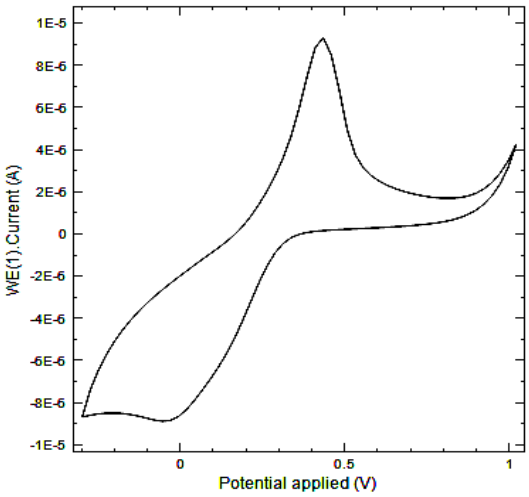


Fig. 2b: Cyclic voltammogram of [Cu(TBM)$(NO_3)_2$].H_2O in DMSO Scan rate 100 mV/Sec.

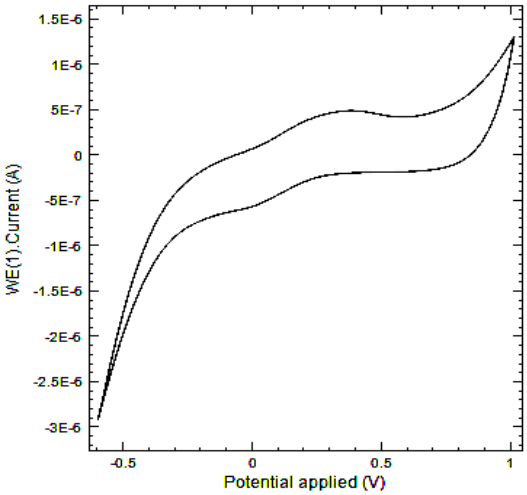


Fig. 2c: Cyclic voltammogram of [Cu(TBM) $(HCOO)_2$].H_2O in DMSO Scan rate 100 mV/ Sec.

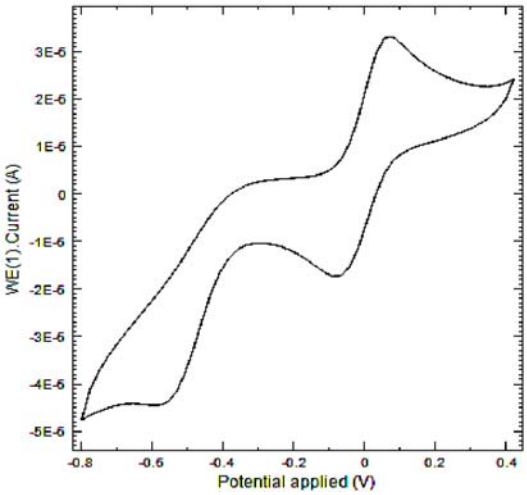


Fig. 2d: Cyclic voltammogram of [Cu(TBM) $(OAc)_2$].CH_3OH in DMSO Scan rate 100 mV/ Sec.

EPR Spectroscopy

Fig. 3a represents the X-band of [Cu (TBM) Cl].C1.2H_2O at 153 K (-120^{o}C), examined as a frozen Dimethyl formamide solution. The EPR spectrum reveals the presence of the distorted tetragonal site in the complex. This is evident from the $g_\parallel$ and $g_\perp$ value which shows $g_\parallel > g_\perp > 2.0$. The above spectrum is in accordance with that expected for Cu (II) ion found in a tetragonal environment with four strongly bound equatorial ligands and one or two weakly bound axial ligands.

The unique feature of the EPR spectrum of [Cu (TBM) Cl].C1.2H_2O complex is the low value of $A_\parallel$ which is close to 80 gauss. Such a low value has been reported only for complexes in near tetrahedral environment[23]. We believe that a similar pseudo tetrahedral structure exists for this complex. The quotient $g_\parallel$ / $A_\parallel$ also support our presumption as its value is very high. On this basis we tend to formulate it as [Cu (TBM) Cl].C1.2H_2O.

Fig. 3b and 3c represent the X-band epr spectrum of some of the copper (II) complexes in the solid state diluted in ligand/ZnO at room temperature. The [Cu (TBM) $(HCOO)_2$] and Cu (TBM) (NO_3)].H_2O, show broad one line spectra with peak to peak line width of 700 and 150 gauss, respectively and the corresponding g_1 values are 1.99 and 2.04, respectively. The unusually broad single line width of 700 gauss in the case of [Cu (TBM) $(HCOO)_2$] is due to dipolar effects. The single g value has been interpreted to arise from a

complex containing a grossly misaligned tetragonal axes as in [Cu (II) $(dien)_2$ $(NO_3)_2$ (X_1)][24]. This situation is probably the most common reason for the observation of an isotropic epr spectrum.

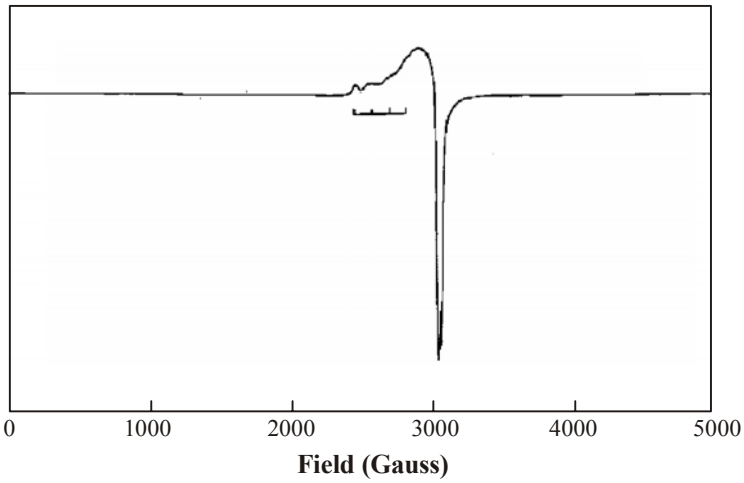


Fig. 3a: 5000 G Scan of [Cu (TBM) Cl] Cl.2H_2o frozen in DMF at X-band. Microwave power 5 mw: Microwave frequency 9.196 GHz; Modulation Amplitude 2 x 10G; Receiver gain 0.63 x 10^2; Temp = 153 K

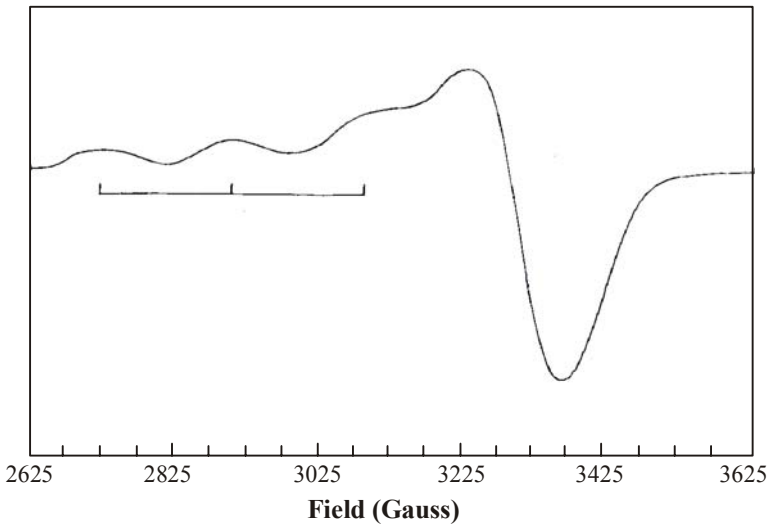


Fig. 3b: 1000 G Scan of [Cu (TBM) $(OAc)_2$] centered at 3000 G at X-band. Microwave power 10 mw; Microwave frequency 9.19 GHz; Modulation amplitude 2 x 1G; Receiver Gain 3.2 x 10^2

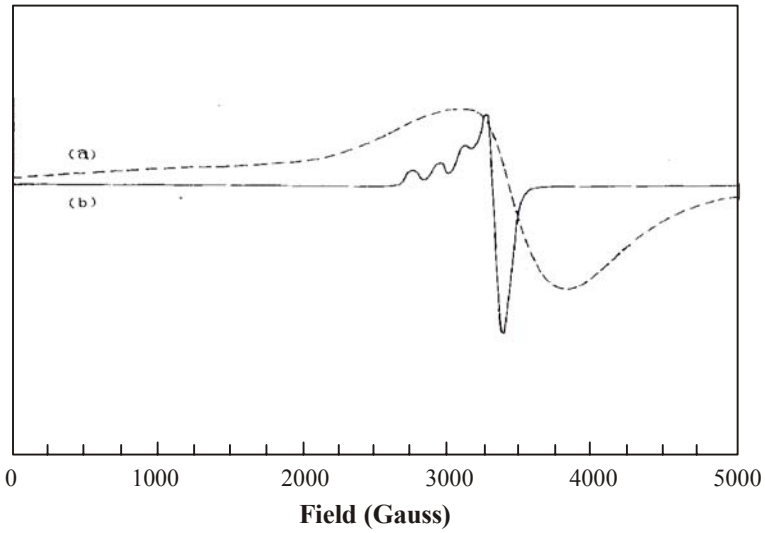


Fig. 3c: 5000 G Scan of (a) [Cu (TBM) $(NO_3)_2$] at X-band, Microwave power 10 Mw; Microwave frequency 9.45 GHz; Modulation Amplitude 0.63 x 1G; Receiver gain 0.5 x 10^2 (Solid Line); (b) [Cu (TBM) $(HCOO)_2$].H_2O at X-band. Microwave power 10 mw; Microwave frequency 9.44 GHz; Modulation Amplitude 0.63 x 1G; Receiver gain 1 x 10^2 (……dotted line)

The [Cu (TBM) $(OAc)_2$] complex in the solid state shows resolution of $g_\parallel$ component with an $A_\parallel$ = 185 gauss. Based on the $A_\parallel$ data we have depicted the remaining two $g_\parallel$ components by the stick diagram. Thus, the solid state spectrum of this complex is in keeping with a tetragonal geometry. A calculation of the ratio g_2-2/g_1-2 indicates that the ratio is more than 4 indicating slight misalignment of axis[24]. [Cu (TBM) $(NO_3)_2$] complex in the solid state shows a two g-value spectrum with g_1 = 2.08 and g_2 = 2.26. These values have been calculated according to Knebuhl's method[25], and are in keeping with an axial spectrum. The lowest g value is greater than 2.04 indicating that it has a distorted square pyramidal geometry. This result is also supported by electronic spectroscopy in solution. Thus, in this case the solution and solid state geometry are the same.

Magnetic susceptibility

The magnetic susceptibilities of copper (II) complexes the room temperature were determined by using a CAHN 2000 balance. The solid state magnetic moments at room temperatures for the above complexes are found to lie in the range of 1.63 to 1.99 B.M. as shown in Table 5.

Table 5: Magnetic Susceptibilities of metal complexes at room temperature

Complexes	μ_{eff} (B.M)
[Cu (TBM) Cl]. Cl. $2H_2O$	1.76
[Cu (TBM) $(NO_3)_2$]. H_2O	1.73
[Cu (TBM) $(HCOO)_2$]. H_2O	1.88
[Cu (TBM) $(OAc)_2$].CH_3OH	1.94

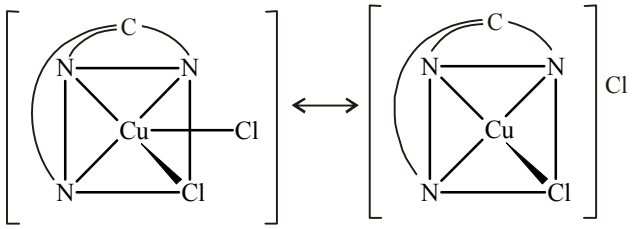
Biological activities

All the complexes were screened *in-vitro* for their antimicrobial activity against bacteria and fungi. All the complexes inhibit the growth of bacteria and fungi. To check the inhibition activities 40 ug/mL in methanol of each complex was used. Only qualitative study of zone of inhibition was performed for each complex. The copper complexes show antibacterial activity similar to earlier synthesized complexes[26-27]. Antibacterial activities of our complexes against some bacteria are shown in Table 6.

Table 6: Antibacterial activities of metal complexes against some bacteria

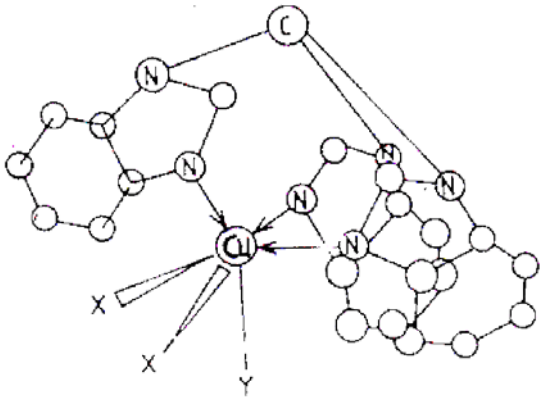
Complexes	*S. aureus*	*E. coli*	*E. aeruginosa*
[Cu (TBM) Cl].Cl.$2H_2O$	+	+	-
[Cu (TBM) $(NO_3)_2$].H_2O	+	+	+
[Cu (TBM) $(HCOO)_2$].H_2O	+	+	-
[Cu (TBM) $(OAc)_2$].CH_3OH	+	-	-

On the basis of above studies, the proposed structure of Cu (II) Complexes are depicted in Fig. 4 below:



(a) Solid (b) Solution

(i)



(ii)

Fig. 4: Proposed structures of (i) [Cu (TBM)Cl_2] complex in (a) solid (b) solution (ii) [Cu(TBM)X_2] complexes (Where X = Cl^-, NO_3^-, $HCOO^-$ and OAc^-)

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REFERENCES

1. H. Gampp and A. D. Zuberbuhler, J. Mol. Catal., **7**, 8188 (1980).
2. W. G. Nigh, Oxidation in Organic Chemistry, Part B, W. S. Trahnowsky (Ed.), Academic, New York (1973) pp. 1-96.
3. G. W. Parshell, Homogeneous Catalysis, Interscience, New York (1980).
4. H. L. Finkbeiner, A. S. Hay and D. M. White, Polymerization and I. Skeist, Ed., Interscience, New York (1973) pp. 537-581.
5. A. S. Hay, Polym. Eng. Sci., **16**, 1 (1976).
6. K. D. Karlin and J. Zubieta, (Eds.), Copper Coordination Chemistry: Biochemical and Inorganic Perspective, Adenine, Guilderland, New York (1983).
7. K. D. Karlin and Y. Gultnech, J. Chem. Educ., **62**, 983-990 (1985).

8. E. I. Solomon, Copper Coordination Chemistry: Biochemical and Inorganic Perspectives, K. D. Karlin and J. Zubieta (Eds), Adenine, Guilderland, New York (1983) pp. 1-22.

9. S. Trofimenko, J. Am. Chem. Soc., **89**, 6288 (1967).

10. J. P. Jesson, S. Trofimenko and D., R. Eaton, J. Am. Chem. Soc., **89**, 3148 (1967).

11. S. Trofimenko, J. Am. Chem. Soc., **89**, 3170 (1967).

12. S. Trofimenko, J. Am. Chem. Soc., **91**, 58 (1967).

13. S. Trofimenko, J. Am. Chem. Soc., **92**, 17 (1970).

14. S. Trofimenko, J. Am. Chem. Soc., **92**, 5118 (1970).

15. S. Trofimenko, J. Am. Chem. Soc., **91**, 3183 (1969).

16. J. P. Jesson, J. Chem. Phys., **45**, 1045 (1966).

17. J. P. Jesson, J. Chem. Phys., **43**, 1049-1056 (1966).

18. Julia M[a]del Mazo, Avila and Elguero, Organic Preparation and Procedures Int., **16(5)**, 299-307 (1984).

19. D. L. McFadden, J. Chem. Soc. Dalton Trans., **47** (1976).

20. E. I. Solomon, The Binuclear Copper Active Site Hemocynin, Tyrosinase and Type 3 Copper Oxidase, Chapter 2.

21. T. J. Lane, I. Makagawa and C. A. Reed, Inorg. Chem., **24**, 2914 (1985).

22. M. R. Rosenthal, J. Chem. Edu., **50**, 331 (1973).

23. E. G. See Bauer, E. P. Duliba, D. A. Scogen, R. B. Gennis and R. L. Belford, J. Am. Chem. Soc., **105**, 4926 (1983).

24. B. J. Hathaway, M. J. Bew and D. E. Billing, J. Chem. Soc.(A), 1090 (1969).

25. F. K. Knebuhl, J. Chem. Phys., **33**, 1074 (1960).

26. Magan Prasad and Yogesh Kumar Sharma, Int. J. Chem. Sci., **10(1)**, 509-518 (2012).

27. H. T. Michels, J. O. Noyce and C. W. Keevil, Letter in Applied Microbiology, **49**, 191-195 (2009).

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