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Synthesis antimicrobial and spectral characterization of Cu (II) metal complexes derived from heterocyclic Schiff bases

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ABSTRACT

Metal complexes of Cu (II) derived from heterocyclic Schiff bases of 2-Amino, 4,7-dimethyl benzothiazole and a) Resacetophenone b) Quaiacetophenone c) substituted salicylaldehyde (Iodo/ Bromo), d) Pyrrole-2-aldehyde e) Pyridine-2-aldehyde have been synthesized. The synthesized complexes have been characterized by IR, ^{1}H NMR, Electronic, ESR Spectra, TGA, XRD, Molar Conductance and their Magnetic moment. The spectral studies indicate square planar geometry for Cu (II) complexes. From XRD study, monoclinic, 'p' type crystal structure can be assigned to the synthesized complexes. The complexes were also screened for antifungal and antibacterial activities.

KEYWORDS

Shiff bases;
Benzothiazole;
Cu (II) metal complexes;
Antifungal and antibacterial activities.

INTRODUCTION

Schiff bases are the compounds containing –C=N- group (azomethine). These are the condensation products of O-hydroxyaldehydes and ketones with certain amines. Benzothiazole and its Schiff bases possess wide range of biological activity[1-3]. Several Schiff bases have been reported to possess remarkable antitumor[4] and antibacterial[5], antifungal[6], anticancer[7], anti-HIV[8] and anti-inflammatory[9] activities.

Cu (II) metal complexes of Schiff bases derived from 2-Amino, 4, 7-dimethyl benzothiazole have been screened for their antibacterial and antifungal activities. Synthesis and characterization of Cu (II) metal complexes of Schiff bases derived from a) Resacetophenone b) Quaiacetophenone c) substituted salicylaldehyde (Iodo/ Bromo), d) Pyrrole-2-aldehyde e) Pyridine-2-aldehyde with 2-Amino, 4,7-dimethyl benzothiazole have been reported.

EXPERIMENTAL

All the chemicals used for the synthetic work were of A.R. grade procured from Lancaster and Aldrich. The solvents used were purified by standard methods.

Synthesis of Schiff bases

Schiff bases were synthesized by taking equimolar ethanolic solutions of heterocyclic amine and respective hydroxyl aldehyde / ketone in 50 ml ethanol and refluxing the reaction mixture for 3-4 hours. Progress of the reaction was monitored by TLC. The reaction mixture was poured on crushed-ice or cold water and the separated solid was then filtered, washed with distilled water and dried and recrystallised from ethanol.

Synthesis of Cu (II) complexes

Cu (II) complexes were synthesized by adopting Raos method[10].

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To the ethanolic solution of respective Schiff bases, the ethanolic solution of Cu-acetate salt in stoichiometric ratio was added and refluxed for 3-4 hours. After cooling the reaction mixture, drop wise addition of alcoholic ammonia was done so as to raise the P^H up to 5 and to separate the solid. The precipated solid complexes filtered, washed and then dried over fused $CaCl_2$.

RESULT AND DISCUSSION

Synthesized Cu (II) complexes are soluble in ethanol, DMSO and DMF. The molar conductance's of the synthesized complexes determined in DMSO solvent at 10^{-4} M concentration and the molar conductance values are found to be in the range of 118-128 mhos cm^2 mol^{-1}which suggest that the complexes are non-electrolyte in nature[11].

The magnetic moment values for the complexes were calculated by Guoy Balance method. At the room temperature, magnetic moments exhibited by Cu (II) were found to be in the range of 1.77-1.84 B.M, suggesting paramagnetic nature and square planar geometry of the complexes.

TABLE 1 : Analytical data of Cu (II) complexes

Sr. No.	Mol. Formula	Mol. Wt.	M.P °C	Colour	Elemental Analysis (%)				X= Br/I (%)	Mol.Cond. Mhos cm2 mol-1
					C Found (cal)	H Found (cal)	Found (cal)N	Metal Found(cal)		
1	$(C_{17}H_{15}SN_2O_2)_2$ Cu	685	278	Gray	59.51(58.48)	4.37(3.18)	8.17(7.19)	9.26(8.67)	--	128
2	$(C_{17}H_{15}SN_2O_2)_2$ Cu	685	280	Green	59.51(58.41)	4.37(3.02)	8.71(7.78)	9.26(8.23)	--	128
3	$(C_{14}H_{12}SN_3)_2$ Cu	571	258	Dark Brown	58.80(58.02)	4.18(3.51)	14.68(14.00)	11.46(10.41)	--	126
4	$(C_{16}H_{11}SN_2I_2O)$ Cu	1127	219	Brick Red	34.04(32.07)	1.95(1.27)	4.96(3.67)	5.63(4.29)	I=45.04(44.40)	131
5	$(C_{16}H_{11}SN_2Br_2O)_2$Cu	939	240	Green	40.87(39.78)	2.34(1.85)	5.96(4.55)	6.75(5.29)	Br=34.06(33.01)	121
6	$(C_{17}H_{15}SN_2O)$ Cu	1035	268	Bottle Green	39.40(38.02)	2.70(1.65)	5.40(4.09)	6.13(5.22)	I=24.52(23.14)	130
7	$(C_{17}H_{14}SN_2O_2I)_2$ Cu	593	182	Dark Brown	60.66(59.32)	4.04(3.41)	14.15(13.87)	10.70(9.14)	--	118

The ESR spectral data[12] supports these very facts. The 'g' values calculated are less than 2.3 which suggest the sufficient covalent character of Cu (II) complexes, Cu $(L_1)_2$ to Cu $(L_8)_2$ respectively.

TABLE 2 : ESR spectral values of Cu (II) complexes

Complex Code	$g_?$	$g_?$	g_{av}	G Axial Symmetry Parameter	μ_{eff} BM From Gouy Balance
$Cu(L_4)_2$	1.80	1.91	1.87	2.27	1.73
$Cu(L_5)_2$	1.84	1.84	1.84	1.00	1.74
$Cu(L_6)_2$	1.84	1.85	1.85	1.05	1.73
$Cu(L_7)_2$	1.83	1.85	1.84	1.11	1.73
$Cu(L_5)_2$	1.79	1.92	1.88	2.58	1.76

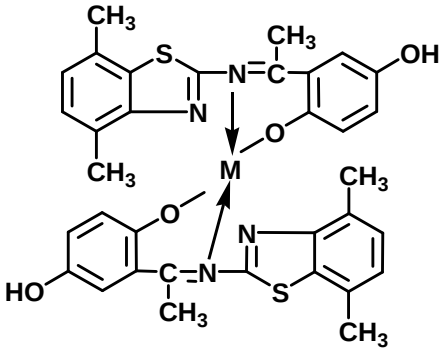
The electronic spectra showed bands in the range of 275-450 nm that is these spectral bands are observed near and above 30,000 cm^{-1} can be assigned to charge transfer transitions. The bands at 269 nm and 291 nm are typically characteristics for square-planar geometry for Cu (II) complexes[13-16].

The ^1H NMR spectra of complexes show broad signals due to presence of metal ion and the conformation of each signal is difficult due to complex pattern of splitiing.

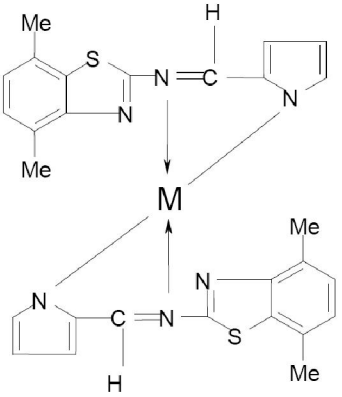
The IR spectra of ligands show characteristic azomethine (-C=N-) peak at1600-1627 cm^{-1}. These same bands show down word shifting in almost all Cu (II) complexes by about 8-10 cm^{-1}. Shifting of the band itself is the proof of involvement of azomethine 'N' in coordination with metal ion[17-19]. The constancy in the band value of 1554 cm^{-1} (-C=N-) ring suggests only the involvement of azomethine 'N' in coordination and lethargic nature of thiazole ring nitrogen. The band due to Ph-OH in ligands L_1 and L_2 shows significant shifting or it has disappeared on complexation which indicates deprotonation and involvement in coordination with Cu (II) metal ion. The presence of medium intensity band in 3356-3652 cm^{-1} range can be assigned due to –OH stretching due to presence of water of hydration[16-19]. This fact is well supported and confirmed by the thermal data analysis and their respective spectral figures. Thermo gravimetric analytical data suggest square plaar geometry for Cu (II) complexes.

Antimicrobial activity

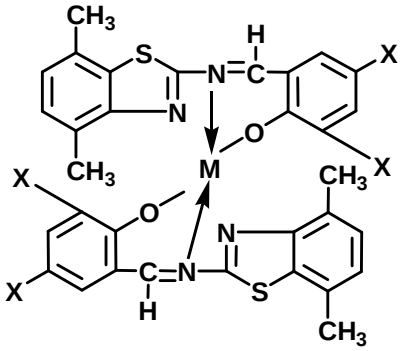
The synthesized complexes of Cu (II) were



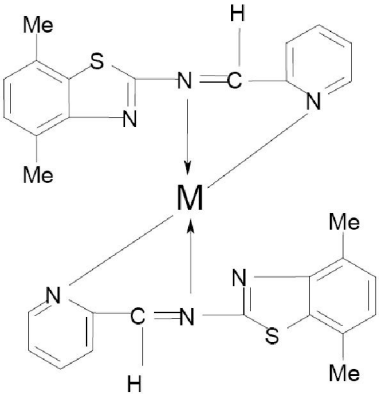
Structure of Cu (II) of L_2



Structure of Cu (II) of L_4



Structure of Cu (II) of L_5 and L_6



Structure of Cu (II) of L_8

Where X= I / Br

TABLE 3 : Antimicrobial activity of Cu (II) complexes

Sr.no.	Compound	Bacterial Strain				Fungal Strain			
		Ec	St	Sa	Bs	An	Pc	Fm	Af
1	Cu-L_1	RG	11	-ve	22	RG	-ve	-ve	RG
2	Cu-L_2	-ve	-ve	15	15	RG	-ve	-ve	RG
3	Cu-L_3	-ve	-ve	-ve	14	-ve	-ve	-ve	-ve
4	Cu-L_4	12	-ve	15	20	-ve	-ve	-ve	-ve
5	Cu-L_5	11	14	11	13	RG	-ve	-ve	-ve
6	Cu-L_6	13	-ve	17	21	-ve	-ve	-ve	-ve
7	Cu-L_7	12	-ve	15	24	-ve	-ve	-ve	-ve
8	Cu-L_8	13	12	13	15	+ve	-ve	-ve	RG
	Penicillin	13	18	36	18	NA	NA	NA	NA
	Grysofulvin	NA	NA	NA	NA	-ve	-ve	-ve	-ve

Ec-E.coli, St-S.typhi, Sa- S.aureus, Bs-B.subtilis; An-A.niger, Pc-P.chrysogenum, Fm-F.moneliformae, Ca-C.albicans:-ve: No growth of fungi,+ve; Growth of fungi, RG-Reduced growth, NA-Not Applicable, Zone of inhibition was measured in mm.

screened for antibacterial and antifungal activities. The antibacterial activity of the compounds was determined by agar diffusion method against various bacteria like E. coli, S. typhi, S. aureus, B. subtilis at various concentrations such as 20, 50 and 100 µg /ml. The zone of inhibition was measured in mm and DMSO was used as solvent. Sterile nutrient agar was seeded with test organism and layered in sterile petri plate. After solidification, agar cups were borered with cork borer 0.1 ml of the compound solution was added to the cup with the help of micropipettes, one cup in the plates was filled with solvent. Standard penicillin (10v/ml) was used as reference drug. The plates were kept at low temperature (4 °C) for 20 minute to allow diffusion of the compound. Then the plates were incubated at 37 °C for 24 hr. After proper incubation the plates were observed for zone of no growth (zone of inhibition of growth) around the cup. Similarly the same compounds were screened for the antifungal activity against different organisms like P. chrysogenum, A. niger, F. moniliformae, and A. flavus by using poison plate method[20]. The compound was mixed with sterile potato dextrose agar medium so as to get final concentration 2%. It was then poured in sterile petri plate and allowed to solidify. Spots of test organisms were placed on the agar surface. A plate without compound was prepared for control. The plates were incubated at room temperature for 48 hr. After proper incubation plates were observed for growth of the test organisms. The growth indicates that the compound is

not antifungal while inhibition of growth of test organism indicates antifungal activity. The antifungal activities of the compounds were compared with standard grysofulvin.

CONCLUSION

The analytical data shows 1:2 metal to ligand stoichiometry and the electronic spectral data suggest that all the Cu (II) complexes have square planar geometry. The molar conductivity data shows the non electrolytic nature of the cu (II) complexes.

The antimicrobial studies show that the complexes of the corresponding Schiff bases show more potent activity than their corresponding ligand.

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REFERENCES

[1] Q.Yu, R.Hu, L.Hong; Ziran Kexueban., **19**, 63-66 **(2001)**.
[2] S.Khan, M.K.Gupta, S.Varshney, A.K.Varshney; J.Inst.Chem., **76**, 125-129 **(2004)**.
[3] A.Kundu, N.A.Shakil, D.B.Saxena, P.Kumar, J.S.Walia; J.Envi.Sci.Health, **44**, 428-434 **(2009)**.
[4] S.Kato; Kokai Tokkyo Koho, 19 **(1985)**.
[5] E.N.Shlyakhov, L.E.Tomnatik, T.A.Burdenko, T.S.Chaika, U.I.Isapkov, N.M.Samus; Khimiko-Farmatseuticheskii 2. **23**, 186-189 **(1989)**.
[6] H.S.Hothi, A.Mattkar, J.R.Sharma, M.R.Manrao; Ind.J.Eri.Chem., **41**, 53-58 **(2008)**.
[7] V.E.Kuzmin, A.G.Artemenko, R.N.Lozytska, A.S.Fedtchouk, V.P.Lozitsky, E.N.Muratov, A.K.Meschriakov; SAR and QSAR in Envi.Res., **16**, 219-230 **(2005)**.
[8] S.K.Sridhar, S.N.Pandeya, E.Declereq; Boll.Chem. Farma., **140**, 302-305 **(2001)**.
[9] S.Bawa, S.Kumar; Ind.J.Chem., **48**, 142-145 **(2009)**.
[10] N.R.Rao, M.C.Ganorkar; Ind.J.Chem., **27A(52)**, 160, **(1998)**.
[11] N.R.Rao, P.R.Venkateshwar, G.V.Reddy, M.C.Genorkar; Ind.J.Chem., **26A(10)**, 887 **(1987)**.
[12] M.T.Geasy; Co-Ord.Chem.Rev., **81**, 7 **(1971)**.
[13] P.P.Maskar, R.M.Patil, M.M.Shaikh; Asian J.Chem., **19(6)**, 45-63 **(2007)**.
[14] N.Raman et al; Trans.Metal.Chem., **28**, 29-36 **(2003)**.
[15] M.Mokhlesh, Abd-Elzaher; J.Chinese Chem.Soc., **48**, 153-158 **(2001)**.
[16] A.S.El.Tabletal; Polish J.of Chem., **73**, 245-254 **(1999)**.
[17] D.R.Munde; Ph. D. Thesis-SRTMU-Nanded, **(2006)**.
[18] K.G.Karamunge; Ph. D. Thesis-SRTMU-Nanded, **(2006)**.
[19] Seema Habib; Ph. D. Thesis-SRTMU-Nanded, **(2011)**.
[20] S.K.Kalyani, A.S.R Murly, G.L.Tembe; JICS, **76**, 296-299 **(1999)**.
[21] R.J.Cruicksham, P.Duguid, R.R.Swain; Medical Micro., Churchill Livingstone, **1**, **(1998)**.