RESEARCH ARTICLE OPEN ACCESS

Synthesis, spectral, thermal and biological studies of Cu(II) complexes of triazole-Derived Schiff Bases

*Mallikarjun S.Yadawe and Sangamesh A.Patil.
*S.B.Arts and K.C.P.Science college Bijapur-586103, India
P.G.Department of Chemistry, Karnataka University, Dharawad-580003, India

ABSTRACT
A series of copper(II) complexes of Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl have been synthesized and characterized on the basis of analytical and spectroscopic studies. The elemental analysis agrees well with the 1:1 stiochiometry of the type M.L.(H_2O), with L coordination via the two imine nitrogen and two thiolato sulphurs in an overall octahedral geometry. Some of the complexes were screened for their antibacterial and antifungal activity and one representative Cu(II) complex was evaluated for oxytosic activity.
Key words-Synthesis, spectral study, antibacterial and antifungal study and elemental analysis

Date of Submission: 14-12-2017 Date of acceptance: 03-01-2018

I. INTRODUCTION

Several complexes of various transition metals with 3-substituted-4-amino-5-mercapto-1,2,4-triazole ligands have been reported from our laboratory[1-7]. 3-substituted-4-amino-5-mercapto-1,2,4-triazoles are sulphur and nitrogen donor ligands and are potentially multidentate. The potential coordinating sites are (i) sulphur of thiol group (ii) nitrogen of the primary amino group and (iii) two nitrogen almost at positions 1 and 2 in triazole ring systems. Thus these ligands can be polydentate. There has been considerable interest in the study of organic ligands containing two or more different donor atoms because such ligands throw light on the nature of metal ligand bonding. Many quantitative studies have confirmed that metal chelates are more stable than those of related unidentate ligands.

Metal complexes with biacetyl bis(sulphanylphenylazine) have been described[8]. Because of their flexible ligating capacity, hydrazones derived from biacetyl have attracted the attention of many investigators[9].Substituted triazoles are biologically active as bactericides, pesticides and fungicides. The triazole derivatives have been reported to act as systemic protectant fungicides against leaf rust for both spring and winter wheat. In our pursuit of our new ligands for metal complexes, we have synthesized a new series of organic compounds[10],via the condensation of 3-substituted-4-amino-5-mercapto-1,2,4-triazole with glyoxal/biacetyl/benzyl (fig 1). The ligands have four donor sites, with the SNNS sequence and varied bonding and stereo chemical behavior in complexes with different metal ions. This potential aroused our interest elucidating the structures of copper(II) complexes with these Schiff bases and in studying their biological properties. In this paper we report the synthesis, spectral characterization of copper(II) complexes with these ligands.

II. EXPERIMENTAL

All the chemicals used were of reagent grade. The 3-substituted-4-amino-5-mercapto-1,2,4-triazoles were prepared the reported methods[11].

Fig.1 Structure of Schiff bases

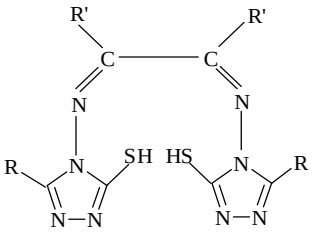


Table 1

Schiff base	R’	R
I	H	H
II	H	CH_3
III	H	C_2H_5
IV	H	C_3H_7
V	CH_3	H

VI	CH_3	CH_3
VII	CH_3	C_2H_5
VIII	CH_3	C_3H_7
IX	C_6H_5	H
X	C_6H_5	CH_3
XI	C_6H_5	C_2H_5
XII	C_6H_5	C_3H_7

Synthesis of copper(II) complexes

Copper sulphate (0.01mol) in the minimum amount of water was added to Schiff base(0.01mol) in an ethanolic medium. The reaction mixture was refluxed for an hour. Then to reaction mixture 2mmol of sodium acetate was added and reflection was continued for about 2hrs and the precipitation of the complex was initiated by adding water to the reaction mixture. The precipitated complex was filtered, washed with water containing alcohol and dried under vacuum over fused calcium chloride.

Elemental analysis

Copper and sulphur were analyzed by a gravimetric method[12]. Nitrogen was estimated by Dumas method.

Physical measurement

Magnetic susceptibility at room temperature were measured with a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant. Electronic spectra (Nuzol mull) were recorded on a DMR spectrophotometer in the 350-1500nm region. Solution spectra were recorded in DMF on a HITACHI model 200-20 spectrophotometer in the 200-900nm region. I.r. spectra were recorded on a Hitachi model 270-IR spectrophotometer in the 4000-200cm^{-1} region in Nuzol mulls.

III. RESULTS AND DISCUSSION

Copper(II) complexes are dark green in colour. All the complexes are insoluble in most of common organic solvents, but reasonably soluble in DMF, DMSO and pyridine.

All the complexes analyse for 1:1 stoichiometry of the type $M.L.2H_2O$ where l stands for a doubly deprotonated ligand (Table.1)

Conductivity measurements (10^{-3}mol solution in DMF) indicated that the complexes are non-electrolytes in DMF.

To know whether the water molecules are held loosely or coordinated to the metal ion, a weighed sample of the complex was dried over P_2O_5 in vacuum for about an hour and weighed again. There was no loss in the weight of the complex. Then the same complex was heated for about 2 hrs at 105^0C, could indicate no loss in weight. These observations suggest that, the water molecules present in the complexes are coordinated to metal(II) ion.

Table 2: Analytical and Molar Conductance Data of Copper(III) complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl

Complex. No	Empirical formula	M% Cald Obtd	N% Cald Obtd	S% Cald Obtd	Molar conductance $Ohm^{-1}cm^2mole^{-1}$
1	$(C_6H_4N_8S_2)Cu.2H_2O$	18.07 18.02	31.85 31.87	18.20 18.23	32.31
2	$(C_8H_8N_8S_2)$ $Cu.2H_2O$	16.74 16.74	29.50 29.52	16.86 16.88	17.17
3	$(C_{10}H_{12}N_8S_2)$ $Cu.2H_2O$	15.59 15.60	27.48 27.50	15.70 15.64	19.26
4	$(C_{12}H_{16}N_8S_2)$ $Cu.2H_2O$	14.59 14.55	25.71 25.72	14.69 14.65	23.42
5	$(C_8H_8N_8S_2)$ $Cu.2H_2O$	16.74 16.72	29.50 29.47	16.86 16.84	18.90
6	$(C_{10}H_{12}N_8S_2)$ $Cu.2H_2O$	15.59 15.55	27.48 27.45	15.70 15.67	12.67
7	$(C_{12}H_{16}N_8S_2)$ $Cu.2H_2O$	14.59 14.57	25.71 25.73	14.69 14.72	14.60
8	$(C_{14}H_{20}N_8S_2)$ $Cu.2H_2O$	13.70 13.72	24.16 24.12	13.80 13.77	12.34
9	$(C_{18}H_{12}N_8S_2)$ $Cu.2H_2O$	12.62 12.59	22.24 24.29	12.70 12.73	27.43
10	$(C_{20}H_{16}N_8S_2)$ $Cu.2H_2O$	11.95 11.89	21.07 21.10	12.04 12.09	34.99
11	$(C_{22}H_{20}N_8S_2)$ $Cu.2H_2O$	11.35 11.29	20.01 20.06	11.43 11.46	35.97
12	$(C_{24}H_{24}N_8S_2)$ $Cu.2H_2O$	10.81 10.84	19.06 19.01	10.89 10.77	28.93

I.r spectra

The free Schiff bases appear to exist in both thiol and thione tautomeric forms, suggested by a broad band in the 3200-3100cm^{-1} region assigned to ν(NH) and also a broad band medium intensity at ca.2400cm-1 assigned to ν(SH).

Thus these ligands exhibit thiol-thione tautomerism. The high intensity band around 1615+5cm-1 are assigned to ν(C=N) in view of

previous assignments[13]. The ligands also exhibit a medium intensity band around 740cm^{-1} has been attributed to ν(C=S)[14].

In comparison with spectra of the Schiff bases, all the Cu(II) complexes exhibited the band of ν(HC=N) in the region of around 1608-1607cm^{-1} showing the shift of band to lower wave numbers indicating that the azomethine nitrogen atom is coordinated to the metal ion[15].

Table 3: Important Infrared Frequencies(in cm^{-1}) of Copper(III) complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases along with their assignments.

Complex .No	ν (OH)	ν C=N)	Thiamide I	Thiamide II	Thiamide III	Thiamide IV	ν (M-N)	ν (M-S)
1	3420br	1620s	1595s	1320m	1040m	675m	560m 410m	335m
2	3400w	1615s	1590m	1355m	1040s	675m	540m 465m	345m
3	3405w	1615s	1590m	1355m	1040m	670m	540m 465m	240m
4	3415w	1620s	1590s	1360s	1060sm	680m	535m 465m	245m
5	3400br	1610s	1595s	1360s	1065s	680m	545m 410m	345m
6	3405w	1615s	1595s	1320m	1070m	670m	560m 410w	380m
7	3415w	1615s	1595s	1325m	1045m	675m	565m 415w	375m
8	3420w	1610s	1590s	1325s	1045m	670m	555m 465w	380m
9	3420brs	1610s	1595m 1570s	1380s	1050m	680m	550m 440w	350m
10	3415m	1610s	1595s 1570m	1360s	1040m	675m	560m 465m	385m
11	3415m	1615s	1590s 1565s	1355s	1070m	680m	560m 435m	340m
12	3410m	1620s	1595s 1570s	1345s	1065s	670m	555m 405w	355m

Magnetic data

The magnetic moments of copper(II) complexes fall in the range of 1.68-1.85 B.M, which correspond to one unpaired electron. The magnetic moments of the regular octahedral copper(II) complexes are expected to follow the relationship

$$\mu_{eff} = \mu_{spin\ only}\ (1\text{-}2\ \Lambda^{1/}10Dq)$$

where Λ=spin orbit coupling constant.

The μ_{spin} only and Λ^{1} values for free copper(II) ion 1.73 B.M and -830cm^{-1} respectively. The calculated μ_{eff} values are in the range of 1.69-1.92 B.M. for the copper(II) complexes. The tetragonally distorted octahedral copper(II) complexes are normally expected to have lower magnetic moments as compared to the octahedral ones due to larger separation in interaction terms.

The observed μ_{eff} values are in the range of 1.68 to1.85 B.M. Thus the copper(II) complexes under investigation may be considered to have tetragonally distorted octahedral structure, with planar arrangement of ligand molecule around copper(II) and two water at an axial positions. This is further proved by electronic spectral data.

Electronic spectra

The electronic spectra of copper(II) complexes exhibit bands in the region ca 11345-17243 cm^{-1} in the visible region assigned to $^{2}Eg \rightarrow {}^{2}T_{2g}$ (Table-3). It corresponds to the combination of three possible transitions as expected for Copper(II) tetragonal symmetry. The broadness of the band due to John-Teller effect. In addition to this band the other band is in the region 23584-26890 cm^{-1} has been assigned to charge transfer band. The band separation in the spectra is of the order of 2500 cm^{-1} consistent with the proposed geometry[17]. The electronic spectra of these copper(II) complexes have also been taken in DMF,

which exhibit only one broad band in the 15854-13842 cm^{-1}. Which is characteristic of distorted octahedral environment. This data suggests that, there is no gross deviation in stereochemistry of these complexes occurs in the solid and solution phases. The electronic spectral parameters Dq and LFSE have been calculated. The ß[1] and β values could not be determined as there is no interelectronic repulsion in a d^9 system.

Table 4: Electronic spectral bands and ligand field parameters of the copper(II) complexes with 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases

Complex.No	State	Transitions(cm^{-1})	Dq cm^{-1}	LFSE K.cal/mole	μ_{eff} B.M
1	Nujol DMF C.T	16983-12934 14924 25458	1495.85	25.64	1.92
2	Nujol DMF C.T	16998-11345 13884 25316	1417.15	24.29	1.93
3	Nujol DMF C.T	17243-12510 14324 24989	1487.65	25.50	1.92
4	Nujol DMF C.T	16680-11895 14833 23584	1428.75	24.49	1.93
5	Nujol DMF C.T	17200-12830 13888 23809	1501.50	25.74	1.92
6	Nujol DMF C.T	16666-12501 15854 25458	1458.30	24.99	1.92
7	Nujol DMF C.T	17084-13851 14825 25080	1546.75	26.51	1.91
8	Nujol DMF C.T	16734-10850 14342 24964	1379.20	23.64	1.93
9	Nujol DMF C.T	16342-12934 15834 24390	1463.80	25.09	1.92
10	Nujol DMF C.T	16342-12934 15834 24390	1463.80	25.09	1.92
11	Nujol DMF C.T	17010-12152 13842 25160	1458.10	24.99	1.92
12	Nujol DMF C.T	17000-13010 13940 24935	1501.50	25.74	1.92

Thermal studies

Thermal decomposition of Cu(II) complexes has been studied as a function of temperature (table 5) by TGA/DTG.

For the copper(II) complexes 2,5 and 10 decomposition from50-350,60-190^{0}C and 7-210^{0}C correspond to loss of coordinated water molecules. There is a gradual decrease in weight up to 470^{0}C, 375^{0}C and 335^{0}C may be ascribed to decomposition of the complex. After 470,375 and 350^{0}C, this is due to oxidation of organic matter.

Table 5: Thermogravimetric data of copper(II) complexes

S.NO	Complex. No	Empirical formula	Decomposition temperature	% weight loss Ods cald	Inferences	Order of reaction	Energy of activation
1	2	$(C_8H_8N_8S_2)$ Cu.$2H_2O$	185 165 690	9.45 9.44 7.00 6.80 66.00 67.09	Loss of water molecule Loss of glyoxal residue Loss of triazole residue	0.65	25.45
2	5	$(C_8H_8N_8S_2)$ Cu.$2H_2O$	230 265 690	9.50 9.48 14.30 14.22 60.00 60.07	Loss of water molecule Loss of biacetyl residue Loss of triazole residue	0.65	29.99
3	10	$(C_{20}H_{16}N_8S_2)$ Cu.$2H_2O$	165 268 338	6.80 6.77 33.50 33.48 48.00 48.16	Loss of water molecule Loss of benzyl residue Loss of triazole residue	1.5	25.59

Kinetic study

The Freeman and Corroll procedure[18] , was used to evaluate the kinetic parameters such as order of reaction and energy of activation from a single experimental curve(fig 2) from the plot of $\frac{\Delta \log dw/dt}{\Delta \log W_r}$ Vs $\frac{\Delta T^{-1}}{\Delta \log W_r}\times 10^3 K^{-1}$

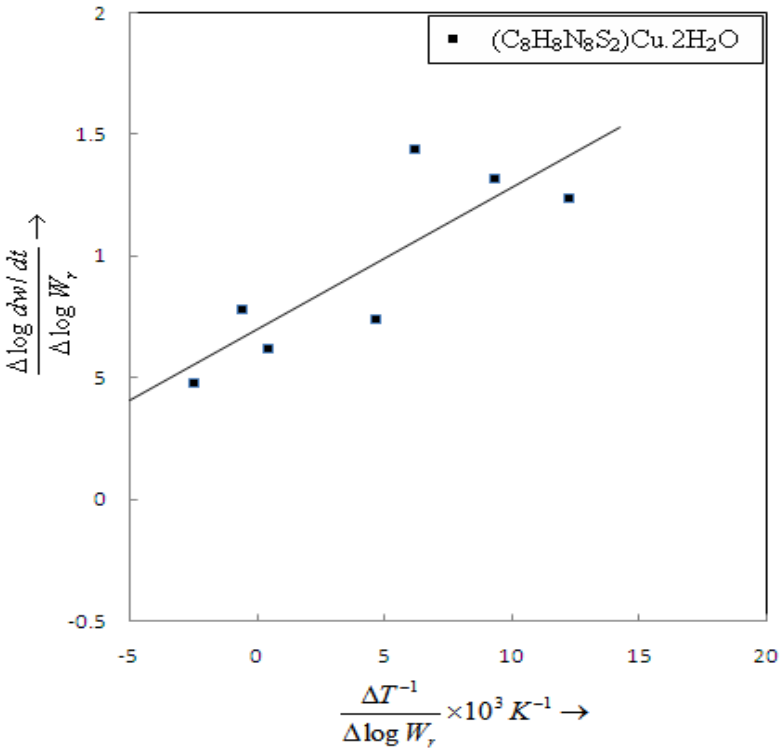


Fig.2

The determined order of reaction and energy of activation are plotted in Table.6.

Table.6.

S.NO	Complex.NO	Empirical formula	$\frac{\Delta \log dw/dt}{\Delta \log W_r}$	$\frac{\Delta T^{-1}}{\Delta \log W_r}\times 10^3 K^{-1}$
1	2	$(C_8H_8N_8S_2)$ Cu.$2H_2O$	0.74 1.44 1.24 0.78 1.32 0.62 0.48	4.66 6.21 12.25 -0.60 9.35 0.43 -2.48

Biological activity

Triazoles and their derivatives have been proved to be effective bactericides[19], pesticides[20], fingicides[21], and insecticides[22]. The antimicrobial activities of some triazole derivatives and their metal complexes of thiocarbohydrazones have been reported from our laboratory[23,24,25,26].We have screened most of the Schiff bases and complexes reported in this study for antibacterial and antifungal activity. Also, one of the copper(II) complexes has been evaluated with respect to its oxytocic activity.
From the table 7, it can be concluded that, copper(II) complexes are more active than the free Schiff bases.

Table 7: Biological Results of 3-Substituted-4-amino-5-mercapto-1,2,4 triazole Schiff bases and lanthanum(III) complexes

Ligand.No	R	R`	Activity Against*			
			Bacteria B.cirrafigellosus	Bacteria E.coli	Fungi C.albicans	Fungi A.niger
I	H	H	13	12	18	13
II	CH_3	H	15	13	20	13
III	C_2H_5	H	15	13	16	13
IV	C_3H_7	H	14	14	19	12
V	H	CH_3	15	17	13	17
VI	CH_3	CH_3	14	13	14	21
VII	C_2H_5	CH_3	16	14	16	19
VIII	C_3H_7	CH_3	17	15	18	19

Metal complexes of copper(III) complexes

Ligand.NO	Complex.No	Activity Against*			
		Bacteria B.cirrafigellosus	Bacteria E.coli	Fungi C.albicans	Fungi A.niger
I	1	12	16	19	15
II	2	11	15	20	16
III	3	12	14	18	20
IV	5	22	17	14	23
V	6	24	22	16	16
VIII	7	25	25	17	25
VIII	8	23	24	15	22

***Zone of inhibition in mm**

DMF 0.1ml solvent control	11	11	11	11
Sulphomethoxozole(20mcg)	20	20	-	-
Gentamycin (10 mcg)	24	24	-	-
Nystatin(50 IU	-	-	23	25

Key for interpretation

Less than13	Inactive
13-16	weakly active
17-20	moderately active
More than 25	highly active

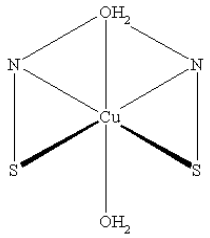
These observations suggest that, the copper(II) complexes exhibit highest (24,25) antibacterial and antifungal activity. The enhanced antibacterial and antifungal activity in copper(II) complexes of the ligands may be due to the presence of methyl groups (biacetyl residue) instead of glyoxal residue in the ligands. Furthermore, complex No.5 was found to exhibit the oxytocic activity of oxytocin on isolated rat uterus (Table 8).
Data showing the oxytocic activity of copper(II) complex.5.

Table 8

Volume of test solution added(cm^{-1})	Peak height(cm)	Oxytocic activity
0.1(Std.oxytocic)	3.1	88.57
0.2(Std.oxytocic)	3.5	100.00
0.3(Std.oxytocic)	3.4	100.00

$(C_8H_8N_8S_2)$ $Cu.2H_2O$ + $0.3cm^3$ Std oxytocic		97.15 (2.85 Inhibition)

The analytical, magnetic and spectral data lead us to propose the general structure shown in fig 2 for these complexes.



ACKNOWLEDGEMENTS

The authors are thankful to President B.L.D.E Association Bijapur, Principal, Head of chemistry S.B.Arts and K.C.P.Science college Bijapur. Special thanks to Dr.S.A.Patil Dept of Chemistry, Karnataka University Dharawad for valuable guidance.

REFERENCES

[1]. S.A.Patil,B.M.Badiger,S.M.Kudari and V.H.Kulkarni.,Transition Metal Chem.,8,238 (1983).
[2]. B.M.Badiger, S.A.Patil, S.M.Kudari and V.H.Kulkarni Rev,Roum,Chim.,31, 849 (1986).
[3]. A.Y.Naik, S.D.Angadi and V.H.Kulkarni, Oriental J.Chem., 10,23(1994).
[4]. M.S.Yadawe and S.A.Patil ,Transition,Met.Chem.,22, 220 (1997).
[5]. Prakash Gouda Avagi, B.Nagaraj reddy and Sangamesh A.Patil., Transition Met. Chem., 31,842-848 (2006).
[6]. Mallikarjun S.Yadawe and Sangamesh A.Patil.,Asian J.Research Chem 3(2), (2010).
[7]. Kulkarni.A.D and Patil.S.A., Med Chem Res, 2010
[8]. Mukharjee.G,Poddar.S.M and Dey.K., Transition Metal Chem.,12,323 (1987)
[9]. K.Dey,S.Ray, P.K.Bhattacharya,A.Gangophyaay,K.K.Bhasin and R.D.verma, J Indian Chem Soc.,62,809 (1985) and refs cited therein.
[10]. M.S.Yadawe and S.A.Patil, Indian J.Heterocycl.Chem.,2,41 (1992).
[11]. K.S.Dhaka, Jagmohan.V.K, Chadha and H.K.Pujari., Indian J Chem.,12B,288 (1974).
[12]. N.S.Biradar and V.H.Kulkarni., Rev.Roum.Chim;16,1203 (1971);18,63(1973)
[13]. P.R.Shukle, V.K.Singh and J.Bhargava, J.Indian.Chem.Soc.,59,620(1082)
[14]. R.V.Gadag and M.R.Gajendragad, Talanta,25,418 (1978)
[15]. Azza Abu-Hassan A A, Adel Emara A.A (2004) Metal Complexes of some thiocarbohydrazone ligands:Synthesis and structure, J Coord Chem 57(11):973-987.
[16]. B.K.Patel, M.M.Patel., Ind J Chem., 29,90 (1990)
[17]. A.Y.Naik, S.D.Angadi, V.H.Kulkarni., Oriental J Chem, 10,23 (1984).
[18]. E.S.Freeman and Corroll, J.Phys.Chem.,62,394(1958)
[19]. A.K.Sengupta, O.P.Bajaj and U.Chandra., J.Indian Chem Soc.,55,962(1978)
[20]. H.Singh, L.D.S.Yadav and R.K.Bhattacharya., J.Indian Chem.Soc.,56,1013 (1979) and refs cited therein.
[21]. S.Giri,H.Singh, L.D.S.Yadav andR.K.Khare, J.India Chem.Soc, 55,168(1978)
[22]. G.Tanara, Jpn, Kokai,973,7495 (1974);Chem.Abstr,82,15630h(1975)
[23]. S.A.Patil,B.M.Badiger,S.M.Kudari and V.H.Kulkarni J.Indian Chem.Soc.,61,713(1984)
[24]. S.A.Patil and V.H.Kulkarni .,ActaChim.hungary,118,3(1985).
[25]. M.S.Yadawe and S.A.Patil., Transition Metal.Chem.,22,220-224(1997).
[26]. G.B.Bagihalli,P.G.Avaji,P.S.Badami and S.A.Patil., Journal of Coordination Chemistry,vol.61,17,2793-2806(2008).

International Journal of Engineering Research and Applications (IJERA) is **UGC approved** Journal with Sl. No. 4525, Journal no. 47088. Indexed in Cross Ref, Index Copernicus (ICV 80.82), NASA, Ads, Researcher Id Thomson Reuters, DOAJ.

Mallikarjun S.Yadawe "Synthesis, spectral, thermal and biological studies of Cu(II) complexes of triazole-Derived Schiff Bases." International Journal of Engineering Research and Applications (IJERA) , vol. 7, no. 12, 2017, pp. 65-71.