



Studies of coordination compounds of Cu(II) with 3-(p-tolyl)-4 phenyl-1, 2, 4- triazole-5-thione at different pH

Rajkamal Sahu*

University Department Of Chemistry, T.M.B.U

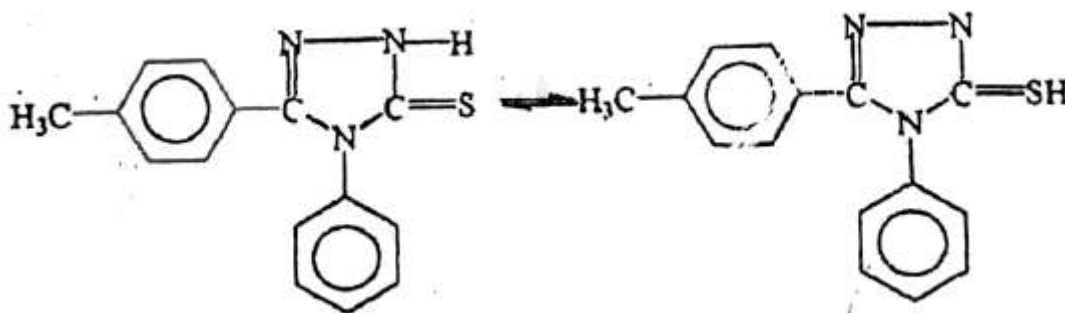
Abstract : Coordination compounds of Cu (II) with 3-(p-tolyl)-4-phenyl-1,2,4-triazole-5-thione (LH) such as [Cu(LH)₂Cl₂], [Cu(LH) (H₂O)/Cl], and [Cu(L) (H₂O)_n] have been synthesized and characterized on the basis of elemental analyses molecular mass determination, molar Conductance (conductance and magnetic moment measurements, IR, UV and ¹H NMR spectral studies. A hexacoordinated octahedral geometry has been proposed for all these coordination compounds. [Cu(LH)₂Cl₂] and [Cu(L)₂(H₂O)] are found to be non-electrolytic in nature while [Cu(LH) (4,0)]. Cl₂ has been of 1:2 electrolytic character.

(Key words: Triazole, Molar conductance, Magnetic moment, Ground term, Spectral bands)

Introduction

In continuation of our earlier communication¹, we report the synthesis and characterization of coordination compounds of Cu (II) with 3-(p-tolyl)-4-phenyl-1, 2, 4-triazole-5-thione at different pH. Triazole and its derivatives are found to be starting materials for the preparation of a wide range of heterocyclic compounds which are of immense importance in Medicinal chemistry? Mercaptotriazoles are associated with anti-bacterial, anti-fungal, anti-viral and schistosomicidal activities. As triazole and its derivatives have wide range of applications, coordination compounds of Cu(II) with 3-(p-tolyl)-4-phenyl-1,2,4-triazole-5-thione have been synthesized in acidic, neutral and alkaline media and characterized. 3-(p-tolyl)-4-phenyl-1, 2,4-triazole-5-thione(LH) is an interesting ligand containing both N and S atoms.

potential donor sites. It contains a thioamide group $\text{C}=\text{S}$ and hence can exist in the -C-N- following thione-thiol tautomeric forms in dynamic equilibrium with each other:



The electronic spectra of coordination compounds of Cu (II) display one band for each in the range of 15400-16200 cm^{-1} indicating distorted octahedral geometry for the compounds under study. These bands may be reasonably assigned to E, T, electronic transition.

The nature of metal-ligand bonding was established by comparing the LR spectra of the ligand (LH) and its coordination compounds with Cu(II) prepared in acidic, neutral and alkaline media.

There is a band at 3370-305 cm^{-1} in the LR spectra of $[\text{Cu}(\text{LH}), \text{Cl}]$ and $[\text{Cu}(\text{LH}) (\text{H}_2\text{O})] \text{Cl}$, assignable to hydrogen bonded ν mode of vibrations. This band is present in the range of 3320-3280 cm^{-1} in the I.R. spectrum of ligand. The shifting of this ligand band towards higher frequency region supports the coordination of the ligand through nitrogen atom of $> \text{N-H}$ group in these coordination compounds,

The band in the range of 3320-3280 cm^{-1} in the spectrum of ligand is absent in the spectrum of $[\text{Cu}(\text{L})(\text{H}_2\text{O})]$ indicating the deprotonation of the ligand in alkaline medium. This fact is further supported by the disappearance of weak ligand band at 2500 cm^{-1} due to ν_{SH} mode of vibration from the spectrum of $[\text{Cu}(\text{L})(\text{H}_2\text{O})]$

The strong and doublet bands at 1600 cm^{-1} and 1585 cm^{-1} (thioamide band-I) in the spectrum of the ligand are red shifted to a strong band at 1593 cm^{-1} and a weak band at 1580 cm^{-1} in the spectrum of all coordination compounds of Cu (II). The red shifting of these bands supports the coordination of the ligand through nitrogen atom in the coordination compounds.

There is a weak band in the spectrum of the ligand at 650 cm^{-1} , assigned to $\nu_{\text{C-S}}$ mode of vibration designated as thioamide band IV. This band undergoes a small red shift by 10-15 cm^{-1} in the spectrum of $(\text{Cu}(\text{LH}), \text{Cl})$ and $(\text{Cu}(\text{LH}), (\text{H}_2\text{O}), \text{Cl})$, while a large red shift by 35 cm^{-1} in the spectrum of $(\text{Cu}(\text{L})(\text{H}_2\text{O}))$. A small shift in thioamide band-IV is indicative of the coordination of the ligand through the sulphur atom of the one group ($> \text{C}=\text{S}$) while a large shift in this band indicates coordination of the ligand through the sulphur atom of deprotonated thiol ($-\text{SH}$) group.

A broad band at 3470-3650 cm is observed in the spectra of [Cu (LH),(H₂O)] Cl, and [Cu(L)₂ (HO)]. This band is absent in the spectrum of ligand. This band is assigned to ν OH mode of vibration of coordinated water molecules in these coordination compounds.

The presence of coordinated water in these species is further supported by the appearance of a new band in their spectra round 830 cm⁻¹, assigned to wagging mode of vibration of coordinated water molecules. New bands in the I.R. spectra of coordination compounds at 610 cm⁻¹ may be assigned to mode of vibration. The bands at 220-240 cm⁻¹ in the I.R. spectra of coordination compounds may be assigned to ν Cu mode of vibration. In addition to these bands, [Cu (LH), Cl₂] has a new band at 350 cm⁻¹ which is assigned to ν Cu-Cl mode of vibration. A close look at H NMR spectral data (Table-4) of coordination compounds reveals that there is a singlet band at δ = 1.2-1.5 ppm in all of them. The integral indicates that this band corresponds to six methyl protons of two p-tolyl groups. Another small singlet band is [Cu(LH)(H₂O)]Cl, prepared at pH=7.0 (neutral medium) indicated its 1:2 electrolytic nature. The electrolytic nature of this coordination compound is due to the presence of two chloride ions outside the coordination sphere. It was further confirmed by the addition of AgNO₃ reagent to the coordination compound solution leading to the formation of two moles of white precipitate of AgCl per mole of coordination compound.

Table : 1

Microanalytical data of coordination compounds

Sl. No.	Coordination compounds	% Found (% Calculated)						Molecular mass found (Calculated)	M.P.
		C	H	N	S	Cl	Cu		
1	[Cu(LH) ₂ Cl ₂] Light Blue	53.71 (53.85)	3.92 (3.89)	12.44 (12.56)	9.68 (9.57)	10.75 (10.62)	9.62 (9.49)	670.4 (668.5)	193°C
2	[Cu(LH) ₂ (H ₂ O) ₂]Cl ₂ Deep Blue	51.38 (51.10)	4.16 (4.25)	11.87 (11.92)	9.25 (9.08)	10.32 (10.07)	9.22 (9.01)	701.2 (704.5)	196°C
3	[Cu(L) ₂ (H ₂ O) ₂] Greenish Yellow	56.88 (57.00)	4.39 (4.43)	13.46 (13.30)	10.24 (10.13)	-	10.31 (10.05)	628.4 (631.4)	206°C

Table : 2

Molar conductance (Δ_m) of coordination compounds in 10⁻³ M DMF at 30°C

Sl. No.	Coordination compounds	Solvent	Molar conductance, Δ_m (Ohm ⁻¹ cm ² mol ⁻¹)
1	[Cu(LH) ₂ Cl ₂]	DMF	15
2	[Cu(LH) ₂ (H ₂ O) ₂]Cl ₂	DMF	182
3	[Cu(L) ₂ (H ₂ O) ₂]	DMF	18

The values of Magnetic moment (Table-3) of the coordination compounds were obtained in the range of 1.90 to 2.0 B.M. suggesting the distorted octahedral nature of the compounds.

Table : 3**Magnetic moment values (μ_{eff}) of coordination compounds of Cu (II)**

Sl. No.	Coordination compounds	Observed magnetic moment (μ_{eff})	Magnetic behaviour
1	[Cu(LH) ₂ Cl ₂]	1.93 B.M.	Paramagnetic
2	[Cu(LH) ₂ (H ₂ O) ₂]Cl ₂	1.90 B.M.	Paramagnetic
3	[Cu(L) ₂ (H ₂ O) ₂]	2.00 B.M.	Paramagnetic

observed at $\delta = 2.1-2.5$ ppm corresponding to two protons in coordination compounds prepared in acidic and neutral media. This band may be assigned to the two > N-H protons of the two triazole rings.

A multiplet band at $\delta = 6.5-7.0$ ppm corresponding to 8 protons (aromatic) of the two benzene rings of p-tolylgroup(15). Another multiplet band centered at 7.5-8.0 ppm corresponding to 10 protons is observed in all the coordination compounds which accounts for 10 protons of the two phenyl rings attached to the nitrogen atom of triazole ring. The slight downfield shift is due to the deshielding of these protons by the nitrogen atom.

The coordination compounds in neutral and alkaline media are found to have singlet band at $\delta = 4.1-4.5$ ppm corresponding to 4 protons which may be assigned to the 4 protons of the two coordinated water molecules. The single band for the protons of two water molecules indicates that they are in the same environment and occupy the trans positions, rather than cis, in octahedral geometry.

The signal at $\delta = 3.4$ ppm corresponding to S-H proton present in the spectrum of the ligand is absent in the spectra of coordination compounds.

This thiocarbonyl group confirms the coordination of the ligand through the sulphur atom of the

Table : 4

H NMR spectral data of coordination compounds

SL. No.	Coordination compounds	Band Assignments
1	[Cu(LH) ₂ Cl ₂]	$\delta = 1.2 \text{ ppm}(s, 6H)$, $\delta = 2.4 \text{ ppm}(s, 2H)$, $\delta = 6.8 \text{ ppm}(m, 8H)$, $\delta = 7.7 \text{ ppm}(m, 10H)$,
2	[Cu(LH) ₂ (H ₂ O) ₂ Cl ₂]	$\delta = 1.4 \text{ ppm}(s, 6H)$, $\delta = 2.5 \text{ ppm}(s, 2H)$, $\delta = 4.3 \text{ ppm}(s, 4H)$, $\delta = 6.65 \text{ ppm}(m, 8H)$, $\delta = 7.6 \text{ ppm}(m, 8H)$,
3	[Cu(L) ₂ (H ₂ O) ₂]	$\delta = 1.3 \text{ ppm}(s, 6H)$, $\delta = 4.3 \text{ ppm}(s, 4H)$, $\delta = 6.8 \text{ ppm}(m, 8H)$, $\delta = 7.8 \text{ ppm}(m, 10H)$,

On the basis of the microanalytical data, measurement of molecular masses, magnetic susceptibility and molar conductance measurements, IR, U.V. and H NMR spectral investigations, the following structures for the synthesized coordination compounds have been proposed:

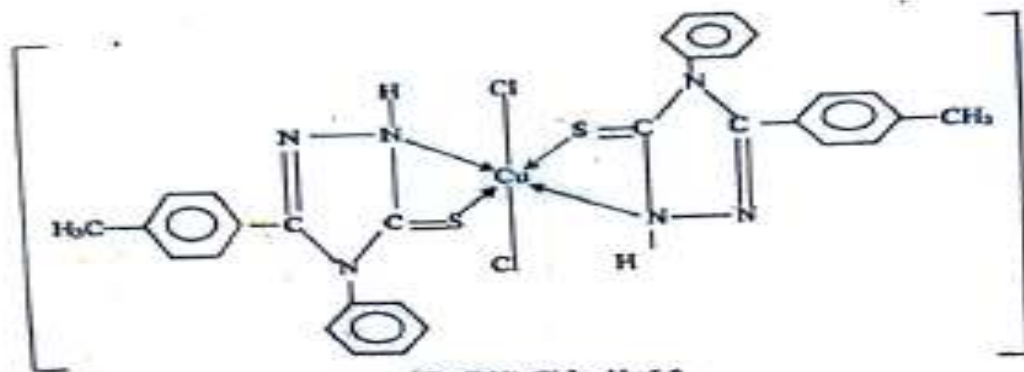


Fig. 2 (a)

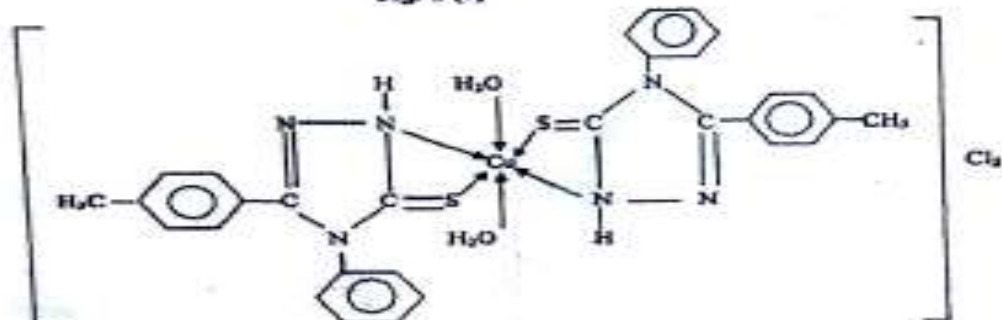


Fig.2 (b)

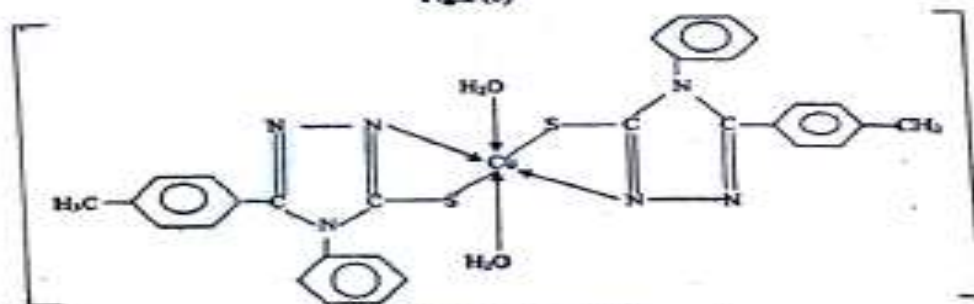


Fig. 2(c)

Conclusion

All the synthesized coordination compounds are monomeric with distorted octahedral geometry and all of them are paramagnetic in nature. $[\text{Cu}(\text{LH})_2\text{Cl}_2]$ and $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$ are non-electrolytic while $(\text{Cu}(\text{LH})_2(\text{H}_2\text{O})_2)\text{Cl}_2$ is 1:2 electrolytic in nature. The deprotonated ligand (L) has participated in coordination in alkaline medium where no deprotonation of the ligand has taken place in acidic and neutral media.

References

1. Sanjay Kumar and parmanand Singh: J. Chem. Tracks.; 17(2), 253 (2015)
A. Anjira et. al.: Oriental J. Chem., 29, 525 (2013)
2. A Saxema & R. Saxema: Oriental J. Chem., 29, 589 (2013).
3. R.N. Pandey, S.S.Kumar and R. Kumari: Oriental J. Chem., 29, 691 (2013)
4. A.R. Mishra, V. Srivastava and A. Sharma: Oriental J. Chem., 29, 1457 (2012)
5. S. Prasad, S.R.Kumar and K.K. Jha: J. Chem. Tracks, 14(1), 243 (2012).
6. V. Ravinder et al: Int. J. Chem. Tech. Res., 1(2), 369 (2009)
7. K.C. Satpathy et al.: J. Ind. Chem. Soc., 71, 593 (1994)
8. V.S Srivastava & G.C. Saxena: J. Ind. Chem Soc., 63,578 (1986)
9. B.B. Mahapatra, H. Sahu, B.K. Mahapatra & S. Guru: J. Ind. Chem. Soc., 55, 229 (1978)
10. Smt. H. Ranganathan, D. Ramaswamy and M. Santapara : Ind. J. Chem., 18A, 322 (1997)
11. S.P. Haremath, N.N. Gaudar and M.G. Purohit: Ibid, 19, 898 (1980)
12. Idem. : Ibid, p. 198 (Edit. 1981)
13. K.G. Srinivasanathy, N.M. Najegowda and G.K N Reddy : Ind. J. Chem., 18A, 322 (1979).
14. (1979).
15. J.N. Srivastava and J.D. Singh: J. Ind. Chem. Soc., 63, 1015 (1986)