

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

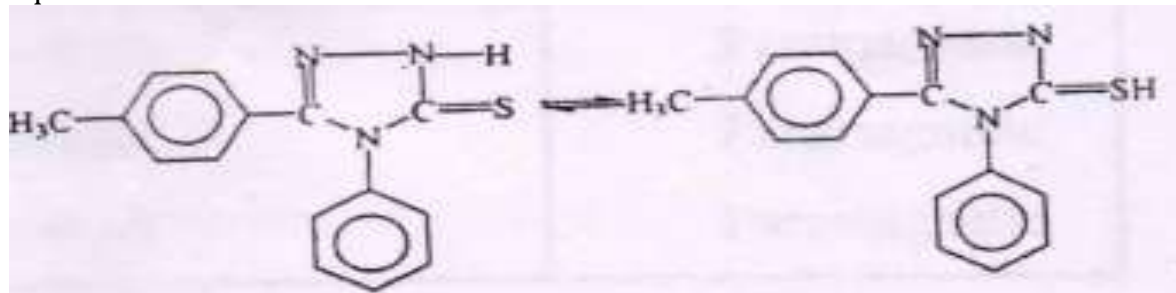
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Abstract: Coordination compounds of Cu(II) with 3-(p-tolyl)-4-phenyl-1,2,4-triazole-5-thione(LH) I (p-tolyl)-4-phenyl-1,2,4-triazole-5-thione(LH) such an interesting ligand containing both N and S as as [Cu(LH),Cl]. [Cu(LH),(H₂O),Cl], and potential donor sites .It contains a thioamide [Cu(L),(H₂O),] have been synthesised and characterised on the basis of elemental analyses group and hence can exist in the molccular mass detemination, molar conductance and magnetic moment measurements, IR,UV and ¹H NMR following thione-thioltautomeric forms in dynamic spectral studies. A hexacoordinated octahedral geometry has been proposed for all these coordination compounds. [Cu(LH),Cl] and [Cu(L),(H₂O),] are found to be non-electrolytic in nature while H₂C [Cu(LH),(H₂O),Cl], has been of 1:2 clectrolytic character,

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

Introduction

In continuation of our earlier communication, we report the synthesis and characterisation of coordination compounds of Cu (1) 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 chemistry². Mercaptotriazoles are associated with anti-bacterial, anti-fungalt,anti- viral and schistosomicial activities. As triazole and its derivatives have wide range of applications, coordination compounds of Cu (11) with 3-(p-tolyl)-4-phenyl-1,2,4-triazole-5-thione have been synthesised in acidic, neutral and alkaline media and characterised 3-p-tolyl)-4-pheny-1,2,4-triazole-5-thione(LHH) is an interesting ligand containing both N and S as potential donor sites .It contains a thioamide group and hence can exist in the following thione-thioltautomeric forms in dynamic equilibrium with each other:



Due to tautomeric forms of the ligand, it has several donor sites for coordination to the

metal ions. It can function as a monodentate ligand coordinating either through nitrogen atom of N- H group or through sulphur atom of $C = S$ group. It can also act as bidentate ligand coordinating through both nitrogen and sulphur atoms. Deprotonated thiol sulphur may also participate in coordination. In view of the interesting structural and biochemical features, coordination compounds of 3-(p-tolyl)-4-phenyl-1,2,4-triazole-5-thiohe with Cu (II) have been prepared and investigated.

Experimental

The ligand and its coordination compounds with Cu (II) ion in acidic, alkaline and neutral media in the pH range of 6-7-10 were prepared. The stoichiometry and structure of

Table-2

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

Sl. No.	Coordination compounds	Solvent	Molar conductance, Δ_m ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
1	$[\text{Cu}(\text{LH})_2\text{Cl}_2]$	DMF	15
2	$[\text{Cu}(\text{LH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	DMF	182
3	$[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$	DMF	18

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

Sl. No.	Coordination compounds	Observed magnetic moment (μ_{eff})	Magnetic behaviour
1	$[\text{Cu}(\text{LH})_2\text{Cl}_2]$	1.93 B.M.	Paramagnetic
2	$[\text{Cu}(\text{LH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	1.90 B.M.	Paramagnetic
3	$[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$	2.00 B.M.	Paramagnetic

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 ET electronic

transition. The nature of metal-ligand bonding was established by comparing the I.R. spectra of the ligand (LH) and its coordination compounds with Cu(1) prepared in acidic, neutral and alkaline media.

There is a band at 3370-3050 cm⁻¹ in the I.R. spectra of [Cu (LH), Cl] and [Cu (LH),(H₂O)]Cl, assignable to hydrogen bonded ν N mode of vibrations. This band is present in the range of 3320-3280 cm⁻¹ in the IR. spectrum of ligand. The shifting of this ligand band towards higher frequency region supports the coordination of the ligand through nitrogen atom of > N-H group in these coordination compounds.

The band in the range of 3320-3280 cm⁻¹ compounds of Cu (1) display one band for each in the spectrum of ligand is absent in the spectrum

in the range of 15400-16200 cm⁻¹ indicating of [Cu(L),(A,O),] indicating the deprotonation of

distorted octahedral geometry for the compounds the ligand in alkaline medium. This fact is further

under study. These bands may be reasonably supported by the disappearance of weak ligand

band at 2500 cm⁻¹ due to ν SH mode of vibration assigned to ET, electronic transition. from the spectrum of [Cu (L),(H₂O),]

The strong and doublet bands at 1600 cm⁻¹ ligand (LH) and its coordination compounds with cm and 1585 cm⁻¹ (thioamide band-I) in the Cu(1) prepared in acidic, neutral and alkaline 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 the ligand through nitrogen atom in these coordination compounds.

There is a weak band in the spectrum of shifting of this ligand band towards higher the ligand at 650 cm⁻¹, assigned to ν mode of frequency region supports the coordination of vibration designated as thioamide band-IV. This the ligand through nitrogen atom of > N-H group band undergoes a small red shift by 10-15 cm⁻¹ in the spectrum of [Cu (LH),Cl], and [Cu LHD,HLO],Cl, while a large red shift by 35 cm⁻¹ in the spectrum of [Cu (L),HO,IA] small shift in thioamide band-IV is indicative of the coordination of the ligand through the sulphur atom of thione group (C-S) while a large shift in this band indicates coordination of the ligand through the sulphur atom of deprotonated thiol (-SH) group.

A broad band at 3470-3650 cm⁻¹ is observed in the spectra of [Cu (LH),(H₂O)]Cl, and [Cu(L)₂(H₂O)]. This band is absent in the spectrum of ligand. This band is assigned to ν H 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 around 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 ν ce mode' of vibration. The bands at 220-240 cm⁻¹ in the I.R.

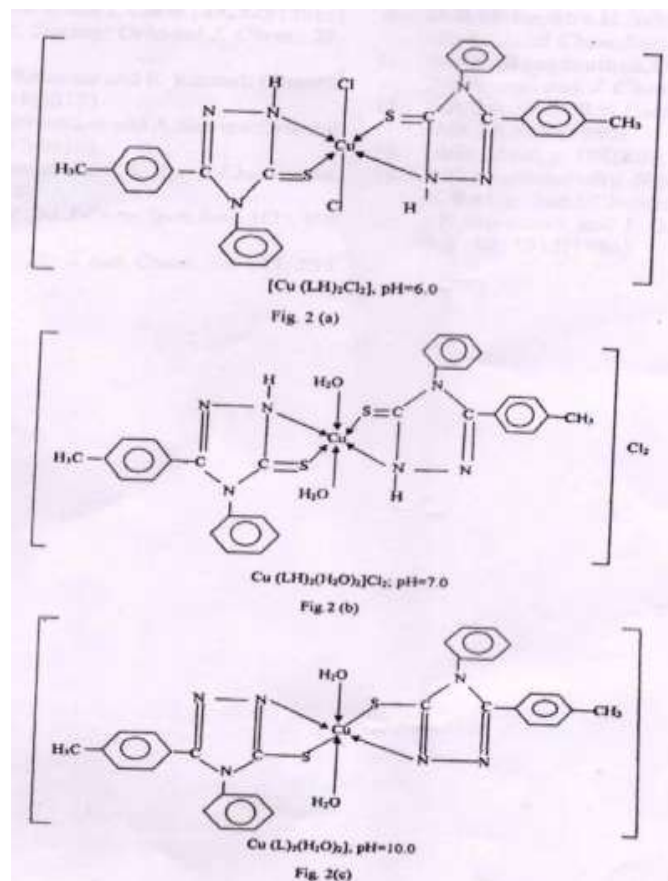
spectra of coordination compounds may be assigned to veus model of vibration. In addition to these bands, [Cu (LH), CL] has a new band at 350 cm which is assigned toV cu mode of vibration.

A close look at 'H NMR spectral data (Table-4) of coordination compounds reveals that there is a singlet band at $\delta=1.2-1.5$ ppm in all of them. The integral indicates that this band corresponds to six methyl protons', 7 of two p-tolyl groups. Another small singlet band is observed at $-2.1-2.5$ 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-tolyl groups, 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 the 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 a singlet band at $6-4,1-4.5$ 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 -3.4 ppm corresponding to S-H proton present in the spectrum of the ligand is absent in the spectra of coordination compounds. This confirms the coordination of the ligand through the sulphur atom of the thiocarbonyl group.

Table-4
'H NMR spectral data of coordination compounds

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

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



Conclusion

All the synthesised coordination $[Cu(LH)_2Cl_2]$, is 1:2 electrolytic in nature. compounds are monomeric with distorted octahedral geometry and all of them are coordination in alkaline medium where as no paramagnetic in nature. $[Cu(LH)_2Cl_2]$ and deprotonation of the ligand has taken place in $[Cu(L)_2(H_2O)_2]$ are non-electrolytic while acidic and neutral media.

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