

SYNTHESIS OF SOME N,N,O / N,N,S DONOR LIGANDS AND THEIR METAL COMPLEXES

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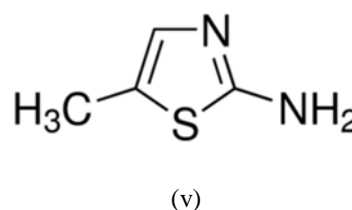
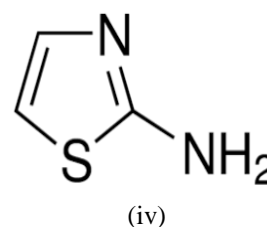
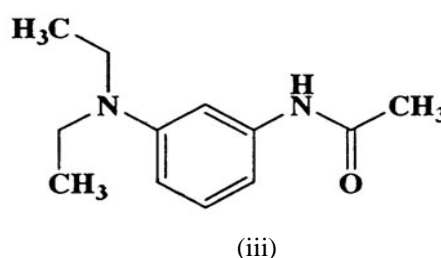
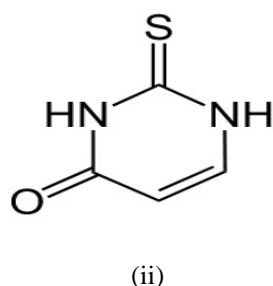
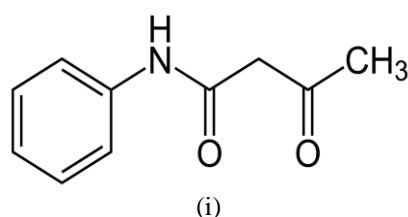
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ABSTRACT

The paper describes the synthesis of six ligands derived by the reaction of diazotized solution of aminothiazole and its methyl derivatives with acetoacetanilide, thiouracil and, 3-acetyl-amino-N, N-diethylaniline. These ligands were used to synthesise their copper (II) complexes which were characterised with the help of elemental analysis, magnetic moment, IR and uv-visible spectral analysis. A geometry and structure was also proposed for such complexes.

KEYWORDS: Complexes, Magnetic Moments, IR, UV-Visible Spectra

The compounds containing sulphur and nitrogen atoms have been found their uses in medicinal chemistry as antituberculous, Hypotics, local anaesthetics, antispasmodics. The hypoglycemic activities have also been reported in some derivatives of the series of similar compounds (Prasad *et al.*, 1992) (Srivastava, 1990). The incorporation of transition metal ions have been found to enhance such activities in several cases. With this view, the attempts were made to synthesise and characterise Cu (II) complexes with six ligands obtained by the reaction of acetoacetanilide (I) thiouracil (II) and 3-acetyl-amino-N,N- diethyl aniline (III) with diazotised solution of 2-aminothiazole (IV) and its methyl derivatives (V). Their characterisation was done with the help of elemental analysis magnetic moment measurement, uv-visible spectral and IR spectral studies.



EXPERIMENTAL

2-aminothiazole (0.1 mole) and 4-methyl-2-aminothiazole (0.1 mole) were dissolved in dil HCl (25 ml), cooled to 0°C and saturated sodium nitrate was added dropwise in it. The diazotised solution was treated with the aqueous ethanolic solution of acetoacetanilide (0.1 mole), thiouracil (0.1 mole) 3-acetyl-amino-N,N-diethyl aniline solution separately. The precipitates were filtered out and crystallized by ethanol to obtain the

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crystalline ligands. The ligands were insoluble in water but soluble in organic solvents like chloroform, acetone, acetic acid etc.

The Cu (II) complexes of the above ligands were synthesized by refluxing methanolic solution of Copper (II) acetate dehydrate (0.1 mole) and the ligands (0.1 mole) for 4-5 hours and the pale brown precipitate obtained, were filtered out (Srivastava *et al.*, 2019) (Srivastava and Srivastava, 1994) (Srivastava *et al.*, 2014). The precipitates were repeatedly washed with

aqueous methanol to remove the unreacted ligand. The complexes were insoluble in water and organic solvents.

RESULTS AND DISCUSSION

Characterisation of Ligands

The elemental analysis and other physical constants along with the major, IR and UV-vis spectral bands of ligands were tabulated and presented in the table 1 and 2.

Table 1: Physical and Analytical Data of Ligands

Name of Ligands	Abbr.	Colour	Yields (%)	Percentage		M.P °c
				N	S	
1,2,3-trioxo-1-phenylamine-2-(thiazolyhydrazono) butane	H ₂ (L ₁)	Yellow	75	19.30 (19.44)	11.04 (11.12)	145
1,2,3-trioxo-1-phenylamine-2-(4-methylthiazolyhydrazono) butane	H ₂ (L ₂)	Yellow	76	18.56 (18.61)	10.52 (10.61)	149
5-(2-thiazolylazo) thiouracil	H ₂ (L ₃)	Radish Violet	75	29.00 (29.04)	13.10 (13.27)	128
5-(4-methyl) (2-thiazolylazo)thiouracil	H ₂ (L ₄)	Radish Violet	78	27.41 (27.48)	25.06 (25.10)	132
3-(acetylamino)-4-(2-thiazolylazo) N,N-diethylaniline	H(L ₅)	Deep Yellow	80	22.00 (22.11)	9.90 (10.13)	160
3-(3-acetylamino)-4-(4-methyl-2-thiazolylazo) N,N-diethylaniline	H(L ₆)	Deep Yellow	75	22.00 (22.11)	9.96 (10.13)	165

Table 2: Characteristics I.R and UV spectral bands of Ligands

Ligands	R Spectral Bands (cm ⁻¹)						UV-Visible Spectral Bands (nm)
	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-S-C}}$	$\nu_{\text{N=N}}$	$\nu_{\text{C=S}}$	
H ₂ (L ₁)	3175(b)	1630(s),1530(s)	1580(s)	873	-----	-----	204,1234,367
H ₂ (L ₂)	3170(b)	1635(s),1575(s)	1525(s)	870(m)	-----	-----	205,235,365
H ₂ (L ₃)	3185(b),3164(b)	1630(s)	1580(s)	870	1540	1137	234,367
H ₂ (L ₄)	3180(b),3160(b)	1635(s)	1580(s)	870(m)	1540(s)	1137(m)	235,365
H(L ₅)	3190(b)	1635(s)	1580(s)	875(m)	1580	-----	234,367,523
H(L ₆)	3185(b)	1640(b)	1575(s)	870(m)	1585(s)	-----	235,365,525

Thus it is observed that all the ligands display a characteristic band of medium intensity at around $3260 \pm 20 \text{ cm}^{-1}$. This band is assigned to N-H stretching vibration which indicated that during coupling reaction, the nitrogen atom of amino group of thiazolyl ring retains hydrogen. The occurrence of two strong and sharp peak at 1630 cm^{-1} and 1530 cm^{-1} in ligands H₂ (L₁) and H₂ (L₂) clearly indicated the presence of two types of carbonyl groups in ligands. It was reasonable to conclude that one carbonyl group is hydrogen bonded while the other is free. However the occurrence of only one strong and

sharp peak at 1630 cm^{-1} in ligands H(L₃) to H(L₆) indicated that there was only one free carbonyl group in these ligand. The presence of IR spectral band at about 1580 cm^{-1} which was very strong and sharp clearly suggested that the all ligands were containing C=N group. The presence of medium to strong peak at around 850 cm^{-1} was assigned to the C-S-C stretching frequency which further confirmed the presence of thiazolyl moiety in all the molecule.

The above discussions indicated that in ligands H₂(L₁) and H₂(L₂), the active methylene group undergoes

condensation with the diazo group while in the remaining group, the phenyl or thiouracil part has directly been condensed with the diazo group.

The uv-visible spectra band also supports the above observation i.e. band around 367 nm indicative of $\pi \rightarrow \pi^*$ transition arises due to N=N/N=C group in the molecule and band around 204 nm is assigned due to hydrazono group present in ligands H₂ (L₁) and H₂

(L₂). The strong band around 234 nm were assigned due to $n \rightarrow \pi^*$ transition of hydrazono group. The adsorption at 523 nm in ligands H(L₅) and H(L₆) may be -N(C₂H₅)₂ group.

Characterisation of Complexes

The characteristic physical constants of the complexes were tabulated and presented in table 3.

Table 3: Physical and analytical data of complexes

Complexes	Colour	Yield	M.P °c	Magnetic Moment (BM)	Elemental Analysis (%)		
					Cu	N	S
Cu (HL ₁) (AC) H ₂ O	Pale Brown	60	240	1.98	17.06 (17.23)	15.17 (15.19)	8.52 (8.68)
Cu (HL ₂) (AC) H ₂ O	Pale Brown	65	245	1.83	16.09 (17.01)	15.01 (15.5)	8.02 (8.4)
Cu L ₃ H ₂ O	Pale Brown	50	182	1.75	19.7 (19.81)	21.25 (21.84)	9.95 (9.98)
Cu L ₄ H ₂ O	Pale Brown	51	188	1.75	18.17 (18.81)	20.75 (20.84)	8.85 (8.98)
Cu (L ₅) ₂	Pale Brown	70	200	1.80	8.92 (9.19)	9.91 (10.06)	4.60 (4.68)
Cu (L ₆) ₂	Pale Brown	70	205	1.72	8.52 (9.00)	9.61 (1.96)	4.40 (4.28)

The elemental analysis conforms to the composition of complexes mentioned in the table.

The magnetic moment value of copper complexes were in the range 1.73-2.20 BM, which is

characteristic of octahedral or square planar Cu (II) complexes.

I.R absorption bands of Cu (II) complexes with ligands H₂ (L₁) to H(L₆) are given in table 4.

Table 4: Characteristics I.R spectral bands of Cu (II) complexes

Complexes	I.R Spectral Bands (cm ⁻¹)					
	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{C=O}}$	ν_{ac}	$\nu_{\text{N=N}}$	ν_{CSC}	$\nu_{\text{N=C}}$
Cu (HL ₁) (AC) H ₂ O	3550-3440	1635-1580	1410	—	835	—
Cu (HL ₂) (AC) H ₂ O	3555-3436	1680-1585	—	1440	832	—
Cu L ₃ H ₂ O	3490-3460	1635-1585	—	1415	880	—
Cu L ₄ H ₂ O	3500-3465	1630-1585	1415	—	832	—
Cu (L ₅) ₂	—	1580	—	1525	835	—
Cu (L ₆) ₂	—	1580	—	1520	835	—

As evident from the table, the peak around 3200 cm⁻¹ in I R spectra (which was characteristic of NH group) was not present in complexes while they were present in all ligands. The absence of this peak in complexes clearly indicated about deprotonation of NH group in all ligands during complexation and involvement of the amino thiazolyl nitrogen in coordination. The absorption peak due to C-S-C cyclic group located around 850 cm⁻¹ in ligands remain almost unchanged. It indicated

that sulphur atom of the ligands was not involved in coordination in the Cu (II) complexes. A broad and strong peak in complexes 1630-1580 cm⁻¹ suggested about either the involvement of carbonyl group in coordination or presence of azo group in the ligand which remain unchanged. The occurrence of weak and medium peak around 3550-3480 cm⁻¹ are indicative of presence of water molecule in coordination sphere of Cu (II) ion and which was not observed in complexes with ligands H(L₅)

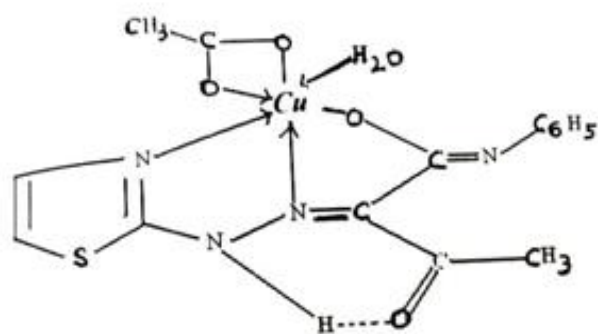
and H(L₆) indicating that the coordinated water molecules were absent in such complexes. The absorption peak around 1410±5 cm⁻¹ in complexes with ligands H₂ (L₁) and H₂ (L₂) indicated that free acetato group was also present in such complexes. The absence of peak around 1540 cm⁻¹ in these complexes, indicated that in complexes with ligands H₂ (L₁) and H₂ (L₂) the azo group was absent but the same was present in all other complexes.

The band position of complexes have been presented in table 5. The tentative assignments of bands were made by assuming pseudooctahedral geometry for complexes with ligands H₂ (L₁), H₂ (L₂), H(L₅) and H(L₆) where as pseudotetrahedral geometry for ligands H₂ (L₃) and H₂ (L₄).

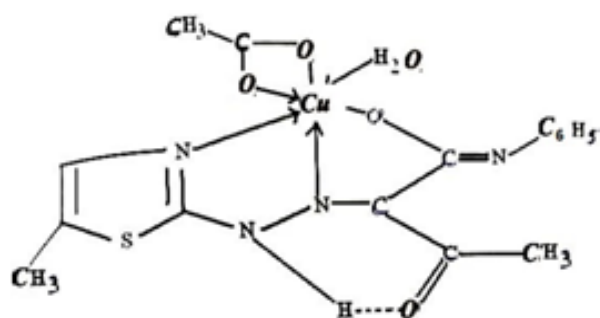
Table 5: Electronic spectral bands of copper (II) complexes in nm

Complexes	² B _{1g} → ² A _{1g}	² B _{1g} → ² B _{1g}	² B _{1g} → ² E _g	A ₁ → T ₂	B ₁ → T ₂
Cu (HL ₁) (AC) H ₂ O	790	650	440	—	—
Cu (HL ₂) (AC) H ₂ O	795	655	435	—	—
Cu L ₃ H ₂ O	—	—	—	790	590
Cu L ₄ H ₂ O	—	—	—	796	596
Cu (L ₅) ₂	800	650	435	—	—
Cu (L ₆) ₂	790	655	435	—	—

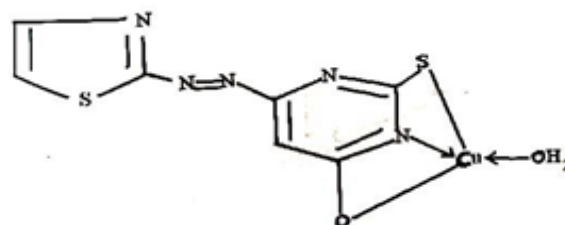
STRUCTURES



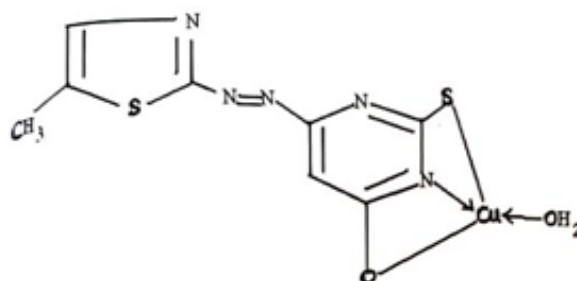
[Cu(HL₁)(Ac)H₂O]



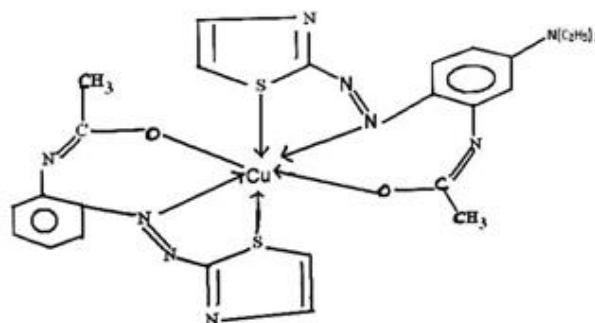
[Cu(HL₂)(Ac)H₂O]



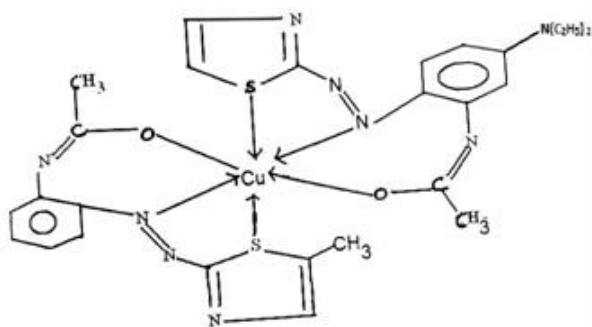
[Cu(L₃)H₂O]



[Cu(L₄)H₂O]



[Cu(L₅)₂]



[Cu(L₆)₂]

CONCLUSION

The structure of the synthesized coordination compounds were assigned on the basis of observations recorded above.

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