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Original Research Article

STUDIES ON CHARACTERISATION OF MIXED METAL COMPLEXES OF COPPER (II) AND NICKEL (II) IONS WITH THIAZOLE DERIVATIVES AS LIGANDS

ANJANI KUMAR SHUKLA^{a1} AND NIDHI SRIVASTAVA^b

^aP.G. Department of Chemistry, R.D.S. College Muzaffarpur, Bihar, India

^bDepartment of Chemistry, B.R.A Bihar University, Muzaffarpur, Bihar, India

ABSTRACT

The ligands 1,2,3-trioxo-1-phenylamine-2-(thiazolehydrazono) butane H₂(L₁) and 1,2,3-trioxo-1-phenylamine-2-(4-methyl thiazolehydrazono) butane H₂ (L₂) were synthesized and used to prepare mixed Cu(II) /Ni(II) complexes. Characterisation of these synthesized complexes were carried out with the help of elemental analysis, magnetic moment data, IR, and UV- VIS spectral data.

KEYWORDS: Mixed Metal Complexes, Thiazoles IR, UV-VIS

The metal complexes containing two or more different metal ions in same moiety are of current interest for their physicochemical properties as a separate class. The discrete heteronuclear metal complexes with phenol based dinucleating macrocyclic ligands containing two different metal ligand binding sites have been developed (Prasad *et al.*, 1992). Several Earlier workers have also reported synthesis and characterisation of mixed metal complexes (Srivastava *et al.*, 2019; Shukla and Srivastava, 2021; Valery *et al.*, 2011). Such Mixed metal Complexes have been Identified as potential compounds in developing the Theoretical under founding of supermagnete In this paper, we describe the synthesis of mixed metal complexes containing Cu (II) and Ni (II) metal ions with multidentate ligands H₂(L₁) and H₂(L₂) having N,O donor atoms and the synthesized complexes were characterised with the help of elemental analysis, magnetic moment data IR, and UV-visible spectral studies.

EXPERIMENTAL

The Ligands H₂ (L₁) to H₂ (L₂) were Synthesised by the methods reported earlier [1,2,3,]. The Cu (II) complexes with ligands H₂ (L₁) to H₂ (L₂) were also prepared by the procedure described elsewhere.

The yellow complexes of Cu(II) with ligands as H₂ (L₁), and H₂ (L₂) was mixed with methanolic solution of NiCl₂.6H₂O, in 1:1 ratio the mixture was refluxed for 2 hours. The precipitate was filtered and washed with methanol for removal of unreacted NiCl₂.6H₂O. The obtained brown colour complexes were dried over fused calcium chloride and analysed for Cu, Ni, N and S.

RESULTS AND DISCUSSION

The physical characteristics of the complexes and elemental analysis for Cu, Ni, N, S are given in table 1. The complexes were found insoluble in water but soluble in organic solvents. On the basis of elemental analysis the molecular formula of complexes in were assigned as [Cu (L₁) Ac₂ (Ni) 3H₂O] and [Cu (L₂) Ac₂ (Ni) 3H₂O]. The insolubility of complexes in polar solvents clearly indicated the non electrolytic nature of complexes.

The Magnetic moment data of complexes were found in the range of 3.25 – 3.18 BM. which prompted that the three unpaired electron were present in the molecule and were suggestive of Cu (II) and Ni (II) both in +2 oxidation state and there is no antiferromagnetic coupling between the neighbouring metal ions. Magnetic moment data clearly indicated absence of Cu-Ni bond and further indicates the distorted octahedral geometry of Cu (II) ion.

I.R. spectra

The IR absorption bands of Cu (II), Ni (II) mixed metal complexes with ligands H₂L₁ to H₂L₂ are given in table 2.

The close examination of table 2 clearly indicated that no peak around 3200 cm⁻¹ was obtained in complexes which was present in ligands. The absence of this peak clearly indicated about deprotonation of N-H group in all ligands and also involvement of amino benzothiazolyl nitrogen atoms of ligand in coordination sphere. The absence of this peak clearly due to C-S-C cyclic group located around 832 cm⁻¹ in ligands remain approximately unchanged. This indicated that sulphur

¹Corresponding author

atom of the ligands is not Involved in coordination. A broad and strong peak in region $1630-1580\text{ cm}^{-1}$ indicated about either the involvement of carbonyl group in coordination or or presence of azo group in the ligands which remain unchanged. The occurrence of weak and medium peak around $3550-3480\text{ cm}^{-1}$ was indicative of presence of water molecule in coordination sphere. The absorption peak around 1410 cm^{-1} indicated about the presence of acetate group in complex. The complexes with ligands $H_2(L_1)$ to $H_2(L_2)$ the deprotonation of aminothiazolyl nitrogen and its participation in coordination have been evidenced. The involvement of O-atom of H-bonded carbonyl group and coordination of nitrogen atom of azomethine group was also confirmed. Deprotonation of azomethine nitrogen in mixed metal complexes indicated that Ni (II) was coordinated through nitrogen atom in the both complexes.

Electronic Spectra

The electronic spectral data of mixed metal complexes and their tentative assignments are given in Table 3.

The electronic spectral study of mixed metal complexes shows an intense band at 354 nm, a discernible shoulder near 440 nm and weak band at 747 nm. The former intense band is assigned to the $\pi \rightarrow \pi^*$ transition associated with the azomethine linkage [88\5] and the later transition to d-d transition due to ${}^2E_g \rightarrow {}^2T_{2g}$ approximately of Cu (II). The electronic spectral band near around 440 nm can be assigned to a charge transfer band from Cu (I) to Cu (II). The d-d transition bands arising from Ni (II) were not well resolved mixed with the above bands.

Table 1: Physical constant and analytical data of mixed metal complexes

Complex	Colour	% Yield	M.P. in °c	Magnetic Moment (BM)	Elemental Analysis			
					Cu	Ni	N	S
[Cu(L ₁)Ac ₂ (Ni) 3H ₂ O]	Brown	55	211	3.18	12.09 (12.07)	11.13 (11.08)	10.74 (10.70)	6.14 (6.09)
[Cu(L ₂)Ac ₂ (Ni) 3H ₂ O]	Brown	55	211	3.25	12.10 (12.08)	11.4 (11.04)	10.5 (10.1)	6.5 (6.10)

Table 2: I.R Spectral bands of mixed metal complexes

Complexes	I.R Spectral Bands (cm^{-1})			
	ν_{H_2O}	$\nu_{C=O}$	ν_{ac}	ν_{CSC}
[Cu(L ₁)Ac ₂ (Ni) 3H ₂ O]	3550-3440	1635-1580	1410	832
[Cu(L ₂)Ac ₂ (Ni) 3H ₂ O]	3550-3440	1635-1580	1410	832

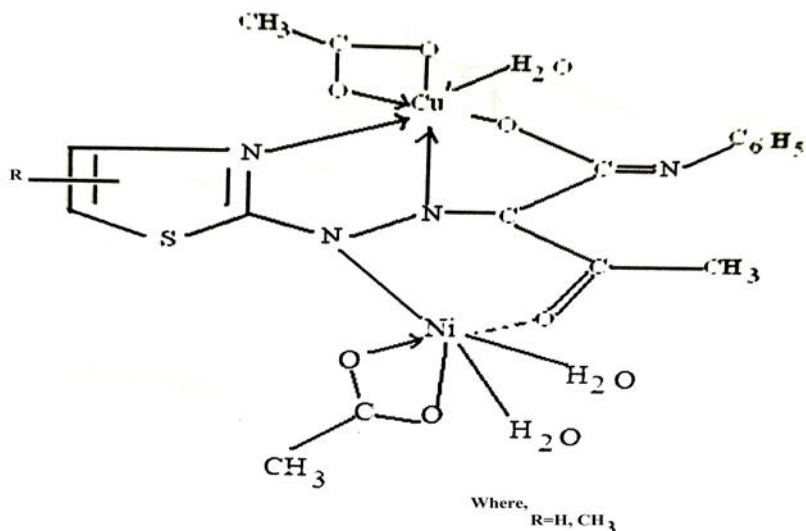
Table 3: Electronic spectral bands of mixed metal complexes

Complexes	${}^2E_g \rightarrow {}^2T_{2g}$	Cu (I) \rightarrow Cu (II)	$\pi \rightarrow \pi^*$
[Cu(L ₁)Ac ₂ (Ni) 3H ₂ O]	745 nm	440 nm	354 nm
[Cu(L ₂)Ac ₂ (Ni) 3H ₂ O]	745 nm	440 nm	354 nm

CONCLUSION

On the basis of IR studies. It was concluded that all complexes were aquo complex. No weight loss of complexes on increasing the temperature indicated that water molecules wear present in the coordination sphere.

It was further conclude that the ligand behave as tridentate donors. Thus ligands H_2L_1 and H_2L_2 wear O, N, S donors atom. The acetate ion in both complexes behaves as bidentate ion. On the basis of above observation the structures of synthesized coordination compounds wear proposed as:



Structure of synthesized coordination compound

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