

Synthesis and Spectral Properties of Cu(I), Ag(I) and Hg(I) Complexes ligated with Thioamide Ligand

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Abstract

Some bi-coordinated four membered ring chelates of composition ML [M = Cu(I)/Hg(1); LH = 1-benzyl tetrazoline-5-thione] have been prepared and investigated using elemental analysis, magnetic, IR, UV-vis and ¹H NMR spectral data. The thioamide ligand acts as mononegative bidentate (N,S) and no disproportionation of Hg(1) and Cu(1) occurs during complex formation.

Key words: Metal-Metal bond, Thioamide, Spectral studies.

Introduction

In continuation of our earlier work¹⁻³ on complexes of 1-substituted tetrazoline-5-thione, the present paper reports some bicoordinated four membered ring chelates of Cu(I) Ag(I) and Hg(I). The structural elucidation are reported on the basis of spectroscopic and analytical data. Of special interest is the mercurous ion and cuprous ion which display disproportionation during complex formation. It is failed to occur in the present case and almost quantitative yield of complexes is obtained.

Experimental

All the chemicals were of AR-grade or CP-grade. 1-Benzyl tetrazoline-5-thione was prepared by the method of Lieber *et al.*⁴. Copper(I)⁵ and Mercury(I)⁶ complexes were prepared following our previous method. Silver(I) complexes were prepared using a general method. An aqueous silver nitrate and methanolic solution of ligand were mixed in equimolar ratio and the mixture was refluxed for 30 min. It was then acidified with dil. nitric acid (pH=6.8), precipitated complex were filtered, washed first with methanol then with large volume of water and dried under vacuum

over anhydrous CaCl_2 .

C, H, N were determined by micro-analytical method. IR Spectra of ligand and complexes were recorded on a Perkin-Elmer model- 577 spectrophotometer in the range of $4000\text{--}2000\text{ cm}^{-1}$ as KBr Pellets. Magnetic measurements were made on Gouy balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The electronic spectra were recorded with zies (Jena) model of automatic recording system.

Results and Discussion

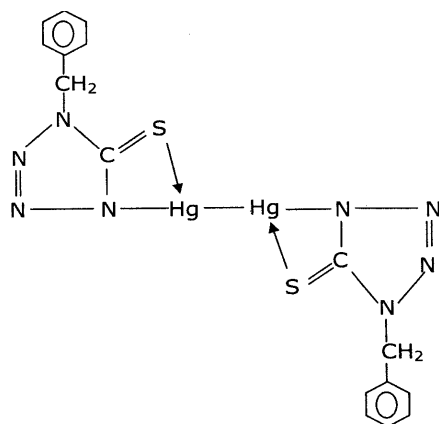
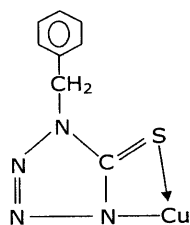
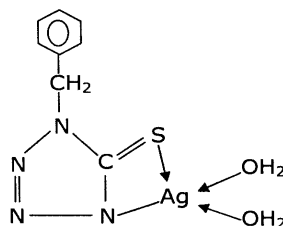
Elemental analysis of complexes correspond to the stoichiometry of Cu(I) and Hg(I) complexes is ML while that of Ag(I) complexes in $[\text{ML}(\text{H}_2\text{O})_2]$ (Table 1). The ligands act as mononegative bidentate anion and deprotonation of imino hydrogen atom was assumed on complexation. All products were stable solid and diamagnetic. The diamagnetic nature of Hg(I) complexes indicated the

Table 1. Analytical data of complexes

complex/ (MF)	Colour	Analysis % : Found/ Calculated			
		Metal	N	C	H
Cu(1Bt5T) ($\text{CuC}_8\text{H}_7\text{N}_4\text{S}$)	light green	25.01 (24.96)	22.12 (21.99)	37.68 (37.71)	3.24 (3.14)
[Ag(1Bt5T)(H_2O) ₂] ($\text{AgC}_8\text{H}_{11}\text{N}_4\text{O}_2\text{S}$)	Light Yellow	32.33 (32.21)	16.69 (16.72)	28.60 (28.66)	3.30 (3.28)
[Hg(1Bt5T)] ($\text{HgC}_8\text{H}_7\text{N}_4\text{S}$)	White	50.98 (51.22)	14.32 (14.30)	24.49 (24.51)	2.14 (2.04)

Table 2. Major spectral data of ligand and complexes

comps	IR(cm^{-1}) : Thioamide Bands				¹ H NMR (PPM)	
	Band I	Band II	Band III	Band IV	Imino proton	Phenyl protons
1Bt5TH (ligand)	1510 (s)	1290 (m)	1050 (m)	810 (m)	1.54	7.85
Cu(I) Complex	1485 (m)	1310 (ms)	1030 (m)	770 (m)	-	7.86 7.88
Ag(I) Complex	1480 (m)	1312 (m)	1025 (m)	780 (m)	-	7.88
Hg(I) complex	1485 (m)	1315 (m)	1030 (m)	785 (m)	-	7.86

**Str. - I****Str. - II****Str. - III**

presence of Hg_2^{++} species. The two electron each from $Hg^+(5d^{10}6s^1)$ in σ -bonding molecular orbital are paired forming Hg_2^{++} in metal-metal bond by 6s-6s overlapping⁷. The diamagnetism of Hg(I) and Cu(I) were as expected for d^{10} -configuration. The electronic spectra of Ag(I) complexes exhibit strong absorption between 31270 - 30000 cm^{-1} and Cu(I) complexes display two strong bands around 32775 cm^{-1} and 38465 cm^{-1} due to charge transfer agreement with previous assignments in literature⁷.

The two distinct absorption bands in

IR spectrum at 3175 cm^{-1} and 3060 cm^{-1} in the spectrum of ligand are assigned to superimposed bands of νNH and νCH vibrations. These bands are observed as single band at 3045 cm^{-1} probably due to replacement of imino nitrogen by monovalent cations and formation of Metal-N-bond. Sola⁸ *et al.* and Okamamoto and co-workers⁹ have reported that secondary thioamides are easily deprotonated to give their thionate anionic form which enhances the donor capability of sulphur atom via the N- to -S backbone. The simultaneous formation of M-N and M-S bond was assumed considering

the red shift of thioamide band I, band III and band IV and blue shift of thioamide band II on complexation¹⁰. This is also supported by the presence of new bands of medium to weak intensities in the region 330-450 cm⁻¹ which are not present in the spectrum of ligand. The new bands occur either a broad or split bands which may be inter-and /or intermolecular interaction of M-N and M-S bands in the solid structure¹¹.

All metal(I) chelates were insoluble in water and common organic solvents and in view of this polymeric or dimeric bicoordinated structure may be proposed for them considering previous observations¹¹. Many thioamide complexes are known to form stable four membered ring including metal ion¹². Cartwright *et al.*¹³ have reported considerable stability of four membered chelates of thioamide ligands using X-Rays crystallographic studies. The four membered ring of ML stoichiometry may contain both Metal-N and Metal-S bond in assigned structure (Str. I, II and III). The stability of chelates are attributed due to back bonding to vacant d-orbitals of sulphur.

All chelates display broad multiplet in the region δ 7.55-7.67 PPM due to phenyl protons in ¹H NMR spectra. The broad nature of peak may be due to large quadrupole resonance broadening effect of tetrazole nitrogen atoms¹⁴. The resonances due to imino proton of the ligand observed at δ 1.26 PPM is absent in the spectra of complexes suggesting formation of Metal- N bond and deprotonation of N-H group on complexation. This observation is consistent with results of IR spectra. Thus, the ligand acts as mono negative bidentate anion

in all metal chelates.

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