

## II. CHEMISTRY

### Inorganic Chemistry

# MIXED LIGAND COMPLEXES OF BIS (SALICYLALDEHYDATO) COPPER(II) WITH THIOUREA AND SUBSTITUTED THIOUREAS

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The mixed ligand complexes of bis (salicylaldehydato) copper(II) with thioureas were prepared and characterized by magnetic, electronic and i.r. studies. All these studies indicate that the complexes have distorted octahedral stereochemistry.

**Keywords:** Copper ethylacetoacetate; Mixed ligand complexes

## INTRODUCTION

THE complexes of o-hydroxy aryl compounds closely resemble the  $\beta$ -diketonates. Therefore, the need arose to study the mixed ligand complexes of bis (salicylaldehydato) copper(II) with thiourea and substituted thioureas.

## EXPERIMENTAL

All the chemicals were of Analar grade. Ethylene thiourea was prepared as previously described by Allen *et al.* (1955). Copper chelate was prepared by reacting ethanolic solution of copper chloride dihydrate with salicylaldehyde in (1:2) ratio followed by dropwise addition of sodium acetate solution. The precipitated compound was washed with ethanol, ether and dried *in vacuo*. The complexes were prepared by suspending bis (salicylaldehydato) copper(II) in ethanol and a solution of thiourea or respectively substituted thiourea in ethanol was added in molar ratio 1:2. The mixture was refluxed till the colour of original compound changed from green to brown or blackish green. Then the content was cooled and filtered. Finally, it was washed with, ethanol — ether mixture and dried *in vacuo*.

The complexes were analysed for metal — nitrogen and sulphur by standard procedures. The analytical data are given in Table I.

### *Apparatus*

The infrared spectra of the samples were recorded in KBr pellet on Perkin Elmer-577 Spectrophotometer from 4000-400  $\text{cm}^{-1}$ . The electronic spectra recorded in pyridine solution with Carl-Zeiss Jena VSU-2 Spectrophotometer. Magnetic susceptibility measurements were made by using Gouy's method.

## RESULTS AND DISCUSSION

The complexes reported in the present investigation are of composition  $\text{Cu}(\text{sal})_2(\text{L})_2$  where sal, anion of salicylaldehyde and 'L' may be thiourea, allylthiourea, phenylthiourea N-N dephenylthiourea, or ethylenethiourea. The compounds have

TABLE I

Sl. No.	Complex and colour	Elemental Analysis			Electronic spectra (nm)		Infrared spectra	
		Copper* %	Sulphur* %	Nitrogen* %	$\nu_2$	$\nu_3$	$\nu(\text{C-N, N-H})^{**}$	$\nu(\text{C-S})^{**}$
1.	Cu(Sal) <sub>2</sub> (Tu) <sub>2</sub> Brown	13.9	13.7	12.1	735	810	—	(710)
		(13.87)	(14.00)	(12.33)			—	(730)
2.	Cu(Sa) <sub>2</sub> (Atu) <sub>2</sub> Dark brown	11.6	11.7	10.0	745	820	—	(762)
		(11.8)	(11.91)	(10.41)			(1540)	(740)
3.	Cu(Sal) <sub>2</sub> (Dptu) <sub>2</sub> Blackish green	8.4	8.3	7.1	785	850	(1580)	(610)
		(8.33)	(8.42)	(7.35)			(1560)	(630)
4.	Cu(Sal) <sub>2</sub> (Ptu) <sub>2</sub> Blackish green	10.8	9.4	8.9	770	845	(1530)	(612)
		(10.41)	(10.50)	(9.18)			(1515)	(638)
5.	Cu(Sal) <sub>2</sub> (Etu) <sub>2</sub> Blackish green	12.1	11.9	10.2	775	865	(1512)	(635)
		(12.35)	(12.47)	(10.80)			(1502)	(680)

\*calc. values are given in parentheses.

\*\*value for free ligands are given in parentheses.

where — Sal = anion of the salicylaldehyde.

Tu = thiourea; Atu = allyl thiourea; Dptu = N-N dephenylthiourea;

Ptu = phenylthiourea; Etu = ethylenethiourea.

low melting points and are sparingly soluble in ethanol, methanol and acetone, highly soluble in pyridine. Magnetic susceptibility measurements of copper(II) complexes show them to be paramagnetic (1.8–1.9 B.M.).

The absorption spectra of the complexes is characterized by two band maxima in the region 735–785 nm and 810–865 nm (Table I), which is also supported by the studies carried out by Bullock and Jones (1971) and Bhavé and Kharat (1979). The study of Agamber *et al.* (1969) on electronic spectra of Cu(II) indicates that the three transitions

$$2B_1 - 2A_1(\nu_1), 2B_1 - 2B_2(\nu_2), \text{ and } 2B_1 - 2E(\nu_3)$$

are found in close energy. In the present case, the third band may be diminished due to distortion caused by the non-identical nature of the coordinating atom.

In salicylaldehyde complexes most of the ligand absorption bands are shifted.  $\nu(\text{M-O})$  stretching vibration could not be recorded as it was beyond the range of instrument.  $\nu(\text{C}=\text{O})$  bond of salicylaldehyde is found to be in the range of 1620–1635  $\text{cm}^{-1}$  in the complexes. The characteristic band due to conjugated  $\text{C}=\text{O}$  group of salicylaldehyde is observed at about 1660  $\text{cm}^{-1}$  which shifts to lower frequency in copper chelate (1605  $\text{cm}^{-1}$ ) and again slightly shifts to higher frequency in the mixed ligand complexes.

The infrared spectrum of the parent compound has confirmed the presence of coordinated water molecules  $\sim 3,450 \text{ cm}^{-1}$ , while the complexes derived from thioureas do not show absorption in this region. This indicates that these mixed ligand complexes are anhydrous. The I.R. spectra of ligands and complexes show

a number of bands in the region 3400–3100  $\text{cm}^{-1}$  are attributed to the  $\nu(\text{N-H})$  vibration. According to Baily and Petesron (1968), the increase in frequencies of these band from 25 to 37  $\text{cm}^{-1}$  supported the sulphur coordination. In the present case, the increase ranging between 25 to 35  $\text{cm}^{-1}$  was observed.

Das and Ramana Rao (1973) observed substituted thioureas and respective complexes show a strong band near 1600  $\text{cm}^{-1}$  which is assigned to  $\text{NH}_2$  bending. This band remains unchanged on coordination showing that ligands are not bonded through nitrogen (except  $\text{Atu}$ ). In free thioureas, the strong bands observed near 1500  $\text{cm}^{-1}$  are attributed to the N-H deformation and C-N antisymmetric stretching vibrations. These bands are shifted to higher frequencies as expected for metal-sulphur bond. A band observed at 1540  $\text{cm}^{-1}$  in case of allyl thiourea disappeared on complexation indicating thereby the coordination through nitrogen. Swaminathan and Irving (1964) attributed the band near 750  $\text{cm}^{-1}$  as C-S stretching modes consistently shifted to lower frequencies on coordination (Table 1), thereby indicating weakening of double bond character of C-S. In case of allyl thiourea, there is a marked increase in frequency indicating the strengthening the double bond.

The above observations lead us to propose the distorted octahedral symmetry for the complexes studied during the present investigation.

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