



SYNTHESIS AND CHARACTERIZATION OF THE COMPLEXES OF 1–4, PHENYLENE–BIS–ALLYL–THIOUREA (PBATU) WITH Cu (I) AND Cu (II) COMPOUNDS

PRATIBHA and R. C. DWIVEDI

Department of Chemistry, J. M. V. Ajitmal, ETAWAH (U.P.) INDIA

and S. P. S. JADON*

Department of Chemistry, S. V. College, ALIGARH–202001 (U.P.) INDIA

ABSTRACT

The mass, I.R., electronic and ^1H NMR spectral investigations of the complexes of PBATU with Cu (I) and Cu (II) along with quantitative estimations, formulate them as, Cu CSN.PBATU and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \cdot \text{PBATU}$. A quadridentative coordination of PBATU to Cu (I) and Cu (II) has been suggested through S and N atoms of NH – C – NH group.



Key words : Copper, 1,4–Phenylene bis allyl thiourea, Coordination

INTRODUCTION

Thiourea and its derivatives have S and N atoms, which have the tendency to donate the electron pairs to metal atom or ions forming their complexes. The complex of tetramethyl thiourea with platinum chloride has been reported¹. The other complexes of thiourea derivatives with copper, gold and palladium have been studied crystallographically^{2,3}. The complexes of some thiourea derivatives such as BPTU, DMPTU, PMTU and PPTU etc. with palladium, rhodium and iridium chlorides have been reported^{4,5}. The complexes of PBATU with Cu (I) and Cu (II) were prepared and investigated in the present investigations.

EXPERIMENTAL

All chemicals used were of AnalaR grade and doubly distilled. PBATU, a substituted derivative of thiourea was prepared by refluxing ethanolic solution of both p–phenylenediamine with allylthiocyanate for 4 hours till a brown product was formed. The brown mass was separated, washed with alcohol and ether successively, dried and stored in a dry desiccator. To prepare the complexes, PBATU ligand was mixed with copper thiocyanate and copper sulphate separately in DMF and refluxed for six hours. The resultant products were separated, washed with DMF followed by alcohol and ether, dried and stored in vacuum.

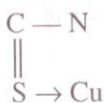
*For correspondence

Gravimetric methods⁶ were adopted for elemental analysis. Mass, IR, U.V. and ¹H NMR spectra of the complexes were recorded on a JEOL SX 102 (FAB), Perkin Elmer RXI (450–4000 cm⁻¹), Perkin–Elmer–Lambda 15(200 to 800 mm,) and Burker ¹HNMR PRX–300 spectrometers at room temperature at CDRI, Lucknow.

RESULTS AND DISCUSSION

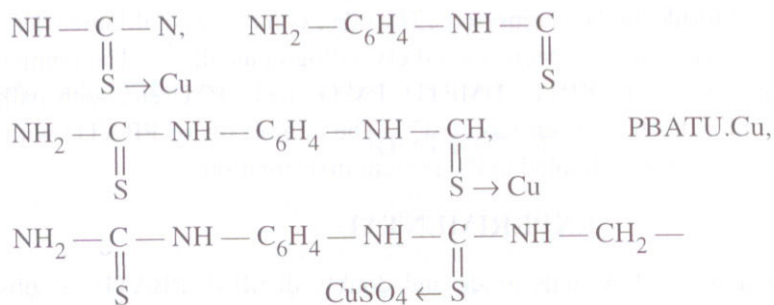
The complex of PBATU with copper thiocyanate is black while its complex with copper sulphate is dark blue in colour. Both complexes on heating decomposed above 300°C. These are soluble in DMSO. The complexes are termed as C₁ and C₂. The analytical data of complex C₁; % found (cal); C 40.01 (39.32), H 3.80 (4.21), N 16.65 (16.35), S 23.52 (22.48), Cu 15.12 (14.87), mol. wt. 420 (427.0) and for complex C₂ % found (cal); C30.08 (230.32), H 5.00 (5.05), N 10.10 (10.10), S 17.24 (17.32), O 25.99 (25.75) and Cu 11.50 (11.46) mol wt. 556 (554.), assigned them as CuSCN.PBATU and CuSO₄.5H₂O, PBATU, respectively.

These molecular formulae of the complexes C₁ and C₂ were ascertained by their mass spectral data. In the mass spectrum of complex C₁, the prominent mass peaks at m/z 136, 307, 369 and 429 are due to



PBATU, PBATU → Cu and PBATU → Cu SCN fragments, confirming the molecular formula of C₁ as PBATU.CuSCN.

The important mass peaks in mass spectrum of the complex C₂ at (m/z) 136, 154, 273, 369, 401, 460, 560 are due to



fragments, supporting the molecular formula of complex C₂ as PBATU.CuSO₄.5H₂O.

The IR spectra of the complex are compared to that of ligand (Table 1). The vibrations observed in the IR spectrum of ligand in the lower region have shifted expressing the coordination of ligand with Cu (I) and Cu (II) ions through its two N and two S atoms quadridentatively forming the tetragonal complexes of PBATU with copper thiocyanate and

copper sulphate. The vibrations for other groups present in ligand remain unchanged, suggesting no linkage of other groups of the ligand with Cu (I) and Cu (II) ions. The S and N atoms of only NH — C — NH group have donated the electron pairs shifting their positions.



The frequency of NH group linked with benzene rings remains the same. It means that this NH group has not coordinated to the metal ions. Hence, the geometrical array of the complex C_1 and C_2 may be represented as in Fig. 1 and 2. The electronic spectrum of complex C_1 consists of 3 peaks, out of which former peak at 38051.75 cm^{-1} is due to charge transfer transition caused by copper ions while the remaining bands 34818.94 and 22163.12 cm^{-1} are according to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition in complex C_1 . Two peaks, observed, in U.V. spectrum of complex C_2 at 33557.05 and 23877.75 cm^{-1} are for charge transfer and ${}^2T_{2g} \leftarrow {}^2E_g$ transitions. The values determined for the other tansers such as oscillator strength (f) of the order $3-9 \times 10^{-5}$ and frequency ratio $\nu_1/\nu_2 < 2$ suggests the occurrence of spin allowed Laporte forbidden transitions indicating coordination of $L \rightarrow M$. The values of band gap energy, $\Delta E_g = 0.6 - 1.0 \text{ eV}$ and number of conducting electrons, $n_c = 2-6 \times 10^{-2}$ suggests the semiconductivity of the complexes.

Table 1. I.R. spectral data of the complexes

S.No.	Complex PBATU. Cu (I)		Complex PBATU.Cu (II)	
	Vibration (cm^{-1})	Bands	Vibrations (cm^{-1})	Bands
1.	504.0 (b)	S = C - N \rightarrow M	561.5(b)	S = C - N \rightarrow M
2.	608 (b)	C = S \rightarrow M	650.0	C = S \rightarrow M
3.	837.5 (s)	C = S	799.3	C = S \rightarrow M
4.	950 (b)	C ₆ H ₅ - NH	857.9(s)	C = S
5.	1094 (b)	CH ₂ - NH	925.2(s)	C ₆ H ₅ - NH
6.	1235 (s)	CH ₂ - NH	1014-1225	CH ₂ - NH
7.	1309	C = S	1294.3	C = S
8.	1388.6	-CH ₂ -	1382.7	-CH ₂ -
9.	1550.8 (s)	\diagdown C=C \diagup	1522.43	\diagdown C=C \diagup
10.	2366.6	δ N - H	2342-64(b)	δ N - N
11.	3195.0	HN \rightarrow M	3177.0	HN \rightarrow M
12.	3754.1	δ N - H	3350.4	O - H

The ${}^1\text{H}$ NMR spectra of the complexes C_1 and C_2 have a quartet in the range of $\delta = 4.97$ to 5.20 for the C₆H₄ groups as aromatic ring attached with NH groups to both its sides having a set

of the singlet and doublet peaks due to the different number of protons linked with various atoms of PBATU molecule as shown by their structures.

The appearance of symmetrical peaks on the both of benzene rings explain the symmetrical linkage of thiourea substituted groups; thus, as given in confirming the geometrical array Fig. 1 and 2 of both complexes C_1 and C_2 .

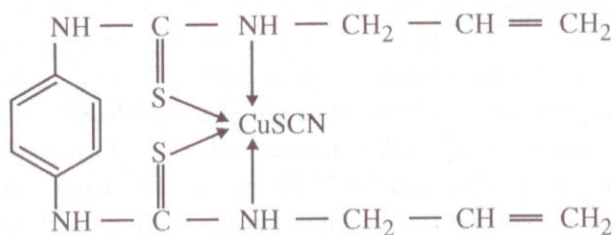


Fig. 1. Structure of the Complex, CuSCN.PBATU

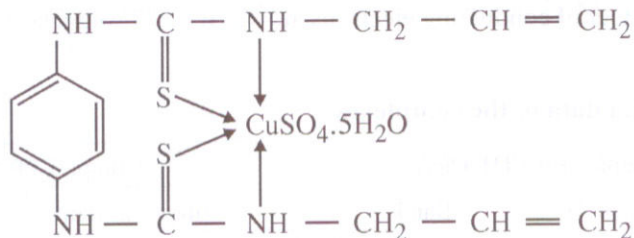


Fig. 2. Structure of the Complex, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O.PBATU}$

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