

Spectral Investigations of the Copper Complexes of 3,3'-Dimethoxyl-4,4'-Bisphenyl-Bis(Allyl Thiourea)

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Mass, IR and electronic spectral studies of the Cu(I) and Cu(II) complexes of 3,3'-dimethoxyl-4,4'-bisphenylene-bis(allyl thiourea) (DMBPBATU) have been reported. From the studies it was concluded that DMBPBATU is linked quadridentatively to Cu(I) and Cu(II) compounds forming their tetragonal complexes coordinated through its S and N atoms.

Key Words: Spectral studies, Copper complexes, 3,3'-dimethoxyl-4,4'-bisphenyl-bis(allyl thiourea).

INTRODUCTION

Numerous complexes of substituted thiourea derivatives, such as N-methyl-N-phenyl thiourea (MPTU), phenyl thiourea (PTU), N'-naphthyl-N-phenyl thiourea (NPTU), N-cyclohexyl-N'-phenyl thiourea (CPTU), N-benzyl-N-phenyl thiourea (BPTU), etc., with some transition elements, have been reported¹⁻⁵. The new derivative of thiourea, 3,3'-dimethoxyl-4,4'-bisphenyl-bis(allyl thiourea) (DMBPBATU) has not been used to prepare its complexes. Therefore, the synthesis and spectral investigations of the complexes of DMBPBATU with Cu(I) and Cu(II) are presented in the present work.

EXPERIMENTAL

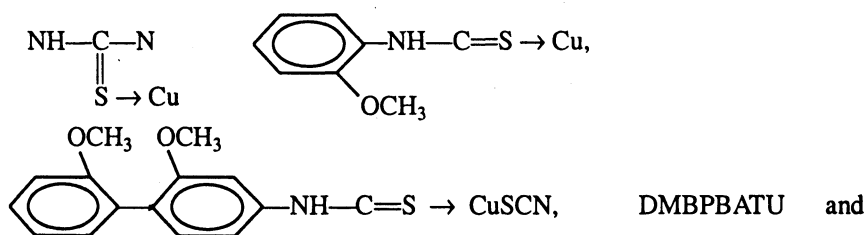
AnalaR grade chemicals were used throughout the present work. The ligand, DMBPBATU, was synthesized by the reported methods^{6, 7}. To prepare its complexes with Cu(I) and Cu(II) compounds, equimolar weights of CuSCN and CuSO₄·5H₂O mixed with DMBPBATU subsequently and separately and dissolved in DMF, were refluxed for 12 h till the products were formed. The resultant masses were separated, washed with DMF followed by ethanol and ether, dried and stored in vacuum desiccator over fused CaCl₂.

The quantitative estimations for the constituent elements were done by well known procedures⁸. The molecular mass was determined by Rast's method, while spectral analyses of the complexes were performed, consequently, on JEOL-SX-102 (FAB) mass spectrometer, IR on Perkin Elmer RXI (4000-450 cm⁻¹) and UV/V is on Perkin-Elmer Lambda-15 (800-200 nm) spectrometers at room temperature from CDRI Lucknow.

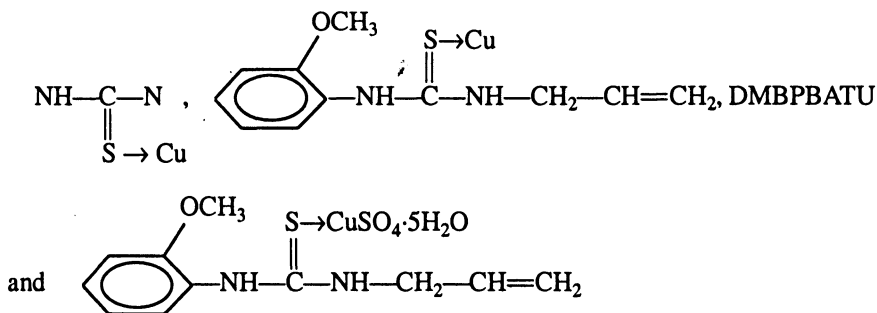
RESULTS AND DISCUSSION

Both complexes are soluble in DMSO and decompose on heating above 300°C. The chemical data of the complex, Cu(I) DMBPBATU: % found (calcd.): C = 49.10 (49.02), H = 4.60 (4.62), N = 12.04 (12.40), S = 17.0 (17.10), Cu = 11.37 (11.28) and m.w. 558 (563) assign it as DMBPBATU·CuSCN; the analytical data of the complex DMBPBATU·CuSO₄·5H₂O: % found (calcd.), C = 38.10 (38.18), H = 5.25 (5.20), N = 8.17 (8.09), S = 14.0 (13.87), Cu = 9.26 (9.18) and its m.w. 685.5 (692) formulate it as DMBPBATU·CuSO₄·5H₂O.

The prominent mass lines at (m/z) 136, 229, 391, 442 and 560 subsequently for



DMBPBATU → CuSCN fragments are observed in the mass spectrum of the complex, Cu(I)-DMBPBATU; while the fragments,



at mass lines (m/z) 136, 273, 443(M - 1) and 473(M + 2) are found in the mass spectrum of the complex Cu(II)-DMBPBATU, inferring that one mol of DMBPBATU has linked to one mol of each CuSCN and CuSO₄·5H₂O.

The IR spectra (Table-1) of the complexes, recorded, are compared to that of ligand, DMBPBATU and it is observed that the frequency at 536 cm⁻¹ for S=C—N band in the ligand has shifted to higher region with the broadness and in doublet form, indicating the coordination as S=C—N→M. The vibration for C=S in lower region has also collocated due to L→M coordination through its S atoms. The other assignments in their IR spectra remain unchanged as that of DMBPBATU, showing no linkage of its other groups to copper atoms. Hence, from these IR spectral results, it is inferred that two NH—CS—NH group of DMBPBATU have coordinated to copper atoms quadridentatively through its S and N atoms as explained by their array (Figs. 1 and 2).

TABLE-1
IR SPECTRAL DATA OF THE COMPLEXES

S. No.	Cu(I) DMBPBATU		Cu(II) DMBPBATU	
	Vibrations (cm ⁻¹)	Bands	Vibrations (cm ⁻¹)	Bands
1.	563 (b, d)	S=C-N→M	618 (b, d)	S=C-N→M
2.	776 (b, d)	C=S-N→M	777 (b, d)	C=S-N→M
3.	851 (s)	C=S	—	—
4.	951	C ₆ H ₄ -NH	—	—
5.	1024 (s)	CH ₂ -NH	1104 (s)	CH ₂ -NH
6.	1232 (s)	CH ₂ -NH	1400 (s)	CH ₂ -NH
7.	1386 (s)	-O-CH ₃	1344 (s)	-O-CH ₃ -
8.	1599 (s)	>C=C<	1629 (s)	>C=C<
9.	2368	δ(N-H)	2364 (s)	δ(N-H)
10.	3366 (b)	δ(N→H)	3136 (b)	δ(N-H)
11.	37588 (s)	δ(N-H)	3200-3500 (b)	O-H

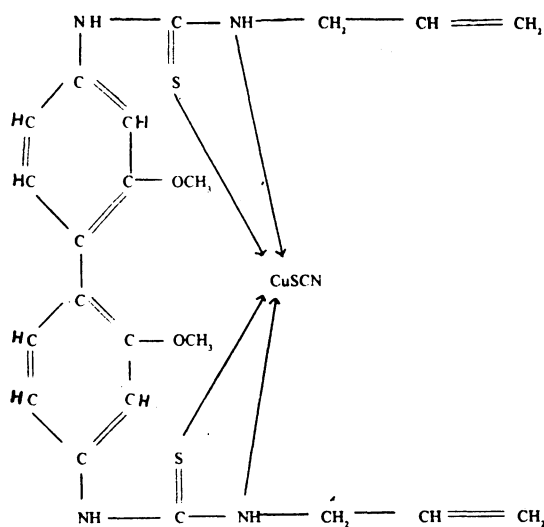


Fig. 1 Proposed structure of the complex, DMBPBATU·CuSCN

This view is supported by their electronic spectra. Two peaks are observed in each UV spectrum of ligand and Cu(II)-DMBPBATU. These assignments in ligand are according to $\pi \rightarrow \pi^*$ (strong) and $n \rightarrow \pi^*$ (weak) transitions, while in the electronic spectrum of the complex Cu(II), the former vibration at 34770 cm^{-1} due to charge transfer transition caused by Cu^{2+} ion and lower band at 25906 cm^{-1} for ${}^2T_{2g} \leftarrow {}^2E_g$ transition have occurred.

Three bands at 274, 284 and 597 nm have appeared in the electronic spectrum of the complex Cu(I). DMBPBATU, out of which the former peak at 36496 cm^{-1} (274 nm) is due to charge transfer transition, expressing the presence of Cu^+ ion in the complex. Both the remaining vibrations are for $\pi \rightarrow \pi^*$ (strong) and $n \rightarrow \pi^*$

(weak) transitions on account of various groups of DMBPBATU in the complex. The values of frequency ratio $\nu_1/\nu_2 < 2$ and oscillator strength 'f' of the order of 10^{-5} for Spin-Allowed Laporte-Forbidden (spin-orbital coupling) transition, expound $L \rightarrow M$ coordination. The values, determined for band gap energy ($\Delta E_g = 0.439-1.039$ eV) and number of conducting electrons ($n_c = 2.05-8.73 \times 10^{-2}$) indicate that both the complexes are semi-conductive in nature.

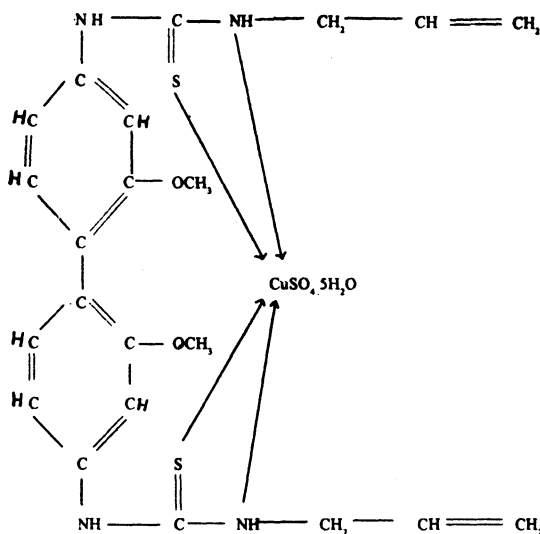


Fig. 2 Proposed structure of the complex, DMBPBATU·CuSO₄·5H₂O

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