

SYNTHESIS AND STRUCTURAL STUDIES ON COPPER(II) COMPLEXES OF SEMICARBAZONE AND THIOSEMICARBAZONES OF 2,4-DIHYDROXY ACETOPHENONE

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Some copper(II) complexes of the type $CuLX$ (where $L = DAPS$ and $DAPT$ and $X = Cl, NO_3, CH_3COO^-$ and NCS) have been prepared with 2,4-dihydroxyacetophenone semicarbazone ($DAPS$) and 2,4-dihydroxyacetophenone thiosemicarbazone ($DAPT$) and characterised by conventional chemical and physical measurements. The infrared spectra ($4000-180\text{ cm}^{-1}$) reveal that both $DAPS$ and $DAPT$ act as tridentate ligands while nitrate/acetate and thiocyanato groups are coordinated through oxygen and nitrogen atoms respectively. The $M-N$, $M-S$, $M-O$ and $M-X$ frequencies have been located in their far infrared spectra and assigned. The polycrystalline ESR spectra suggest distorted square planar environment in metal complexes (except $CuLOAC$ complexes). Thermogravimetric analysis indicates that all the chelates are anhydrous. All the complexes are found to be non-electrolytes in dimethylformamide.

Key Words : Copper (II); 2,4-Dihydroxyacetophenone semicarbazone; 2,4-Dihydroxyacetophenone thiosemicarbazone

INTRODUCTION

THE chelating properties of thiosemicarbazones containing ONS donor sequence are well established.¹ However, the ligational behaviour of semicarbazones containing ONO donor sequence are infrequently studied and compared. The analytical properties of semicarbazones and thiosemicarbazones are compared in our recent papers.²⁻⁵ The present communication describes a number of copper(II) complexes derived from 2,4-dihydroxyacetophenone semicarbazone ($DAPS$) and 2,4-dihydroxyacetophenone thiosemicarbazone ($DAPT$).

EXPERIMENTAL

General Procedure

Equimolar ($1 \times 10^{-2}M$) Copper salt solution (50 ml) and reagent ($DAPS$ or $DAPT$) solutions (50 ml) were taken in 250 ml round bottom flask containing 50 ml of sodium acetate-acetic acid buffer ($pH, 5.0$) solution. The reaction mixture was refluxed for 1 hour and cooled. The solid that separated was filtered, washed with hot water and then with hot ethanol. The solid complexes were dried at $110^\circ C$ in an electric oven.

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Copper (L) Thiocyanato Complexes

To the green colour solution obtained as a result of mixing of copper(II) chloride with ligand as above, an ethanolic solution of ammonium thiocyanate (1.0g) was added. The colour of this solution immediately turned to brownish red and precipitate of ammonium chloride settled down after stirring for about 20 minutes. This was filtered and filtrate was refluxed for 1 hour, whereby a dark red coloured precipitate was obtained. It was filtered off washed with hot water and hot ethanol and finally dried at 110 °C. The ligands were synthesized as described earlier.²

Physical Measurements

The details of the physical measurements and elemental analysis (Table I) were the same as described earlier.⁶ All ESR spectra were recorded on a Varian Spectrometer in the solid state as poly crystalline sample using DPPH as a reference material at room temperature.

TABLE I
Analytical data of copper complexes

Complex	Percentage of				
	C found (calcd)	H found (calcd)	N found (calcd)	Cu found (calcd)	Cl found (calcd)
Cu (C ₉ H ₁₀ N ₃ O ₃ Cl) Cl	34.50 (35.18)	3.20 (3.25)	13.70 (13.60)	20.90 (20.70)	11.65 (11.54)
Cu (C ₉ H ₁₀ N ₃ O ₃) NO ₂	33.50 (32.38)	3.10 (2.99)	16.45 (16.79)	19.15 (19.05)	
Cu (C ₉ H ₁₀ N ₃ O ₃) CH ₃ COO	40.10 (39.93)	4.05 (3.93)	12.50 (12.68)	19.10 (19.22)	
Cu (C ₉ H ₁₀ N ₃ O ₃) NCS	35.90 (36.41)	2.90 (3.03)	71.20 (16.99)	19.50 (19.28)	
Cu (C ₉ H ₁₀ N ₃ O ₂ S) Cl	33.50 (33.43)	3.20 (3.09)	12.70 (13.00)	18.90 (19.67)	11.10 (10.97)
Cu (C ₉ H ₁₀ N ₃ O ₂ S) NO ₂	31.20 (30.89)	2.90 (2.86)	16.00 (16.02)	18.50 (18.18)	
Cu (C ₉ H ₁₀ N ₃ O ₂ S) CH ₃ COO	38.10 (38.09)	3.70 (3.75)	12.10 (12.12)	18.30 (18.34)	
Cu (C ₉ H ₁₀ N ₂ O ₂ S) NCS	35.10 (34.72)	3.90 (2.89)	16.10 (16.20)	18.10 (18.39)	

RESULTS AND DISCUSSION

The interaction of DAPS and DAPT with copper(II) ions yields complexes corresponding to the general formula CuLX (where L = DAPS or DAPT and

$X = \text{Cl}, \text{NO}_3, \text{CH}_3\text{COO}$ and NCS). All the complexes as expected for a ONS and ONO donor sets are sparingly soluble in non-polar solvents and possess no sharp melting point. All the complexes are non-electrolytes. They do however decompose on heating above 260°C . The magnetic moments of all these complexes at room temperature have been found in the range $1.74 - 1.82 \text{ B.M.}$, which are very close to spin only for one unpaired electron and are in range normally observed for copper(II) complexes having an orbitally non-degenerate B_{1g} ground state, thereby indicating no metal interaction. In fact, no significant conclusion can be drawn from the magnetic data regarding the stereochemistry of copper complexes.

The electronic spectra of $\text{CuL CH}_3\text{COO}$ complexes showed absorption peaks at 12900cm^{-1} region and are assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition. The bands observed for $\text{CuL CH}_3\text{COO}$ around 18350cm^{-1} are attributed to ${}^2B_{1g} \rightarrow {}^2E_g$ transition (Table I). The electronic spectra of all complexes exhibits broad and intense peaks assignable to $L \rightarrow M$ charge transfer (Table I).

ESR powder spectra usually do not yield accurate molecular g values but in most cases it is possible to distinguish unambiguously between $d_{x^2-y^2}$ or d_{xy} ground state on one hand and d_{z^2} ground state on the other hand. Thus $d_{x^2-y^2}$ (or d_{xy}) ground state gives a spectrum $g_{\parallel} > g_{\perp} > 2.04$ and in most cases whilst a d_{z^2} ground term usually gives a spectrum with $g_{\perp} > g_{\parallel} \approx 2.00$. For the present copper complexes $g_{\perp} = 1.871 - 1.895$; $g_{\parallel} = 2.015 - 2.032$. The lowest g value is not greater than 2.04. The g value suggest the presence of copper(II) ion in axial symmetry with all the principal axes aligned parallel and is consistent with the absence of square planar structure. The g values for $\text{CuL CH}_3\text{COO}$ complexes may suggest the presence of approximately square planar geometry (Table II). A typical X-band ESR spectrum of $\text{Cu (DAPS) CH}_3\text{COO}$ is presented in Fig. 1.

Infrared Spectral Studies

Band assignments for semicarbazone and thiosemicarbazone complexes are difficult to arrive at because of the extensive mixing of internal modes of the ligands,

TABLE II

Magnetic, esr and electronic spectronic spectral data of copper complexes of DAPS and DAPT

Complex	$\mu_{\text{eff}}(\text{M}\cdot\text{B})$	g_{\parallel}	g_{\perp}	$L \rightarrow M$ cm^{-1}	${}^2B_{1g} \rightarrow {}^2A_{1g}$ cm^{-1}	${}^2B_{1g} \rightarrow {}^2E_g$ cm^{-1}
$\text{Cu (C}_9\text{H}_{10}\text{N}_3\text{O}_3) \text{Cl}$	1.81	2.019	1.863	28980		
$\text{Cu (C}_9\text{H}_{10}\text{N}_3\text{O}_3) \text{NO}_3$	1.76	2.032	1.858	28960		
$\text{Cu (C}_9\text{H}_{10}\text{N}_3\text{O}_3) \text{CH}_3\text{COO}$	1.78	2.135	1.985	28990	12850	18350
$\text{Cu (C}_9\text{H}_{10}\text{N}_3\text{O}_3) \text{NCS}$	1.74	2.015	1.866	28950		
$\text{Cu (C}_9\text{H}_{10}\text{N}_3\text{O}_2\text{S) Cl}$	1.82	2.026	1.871	27780		
$\text{Cu (C}_9\text{H}_{10}\text{N}_3\text{O}_2\text{S) NO}_3$	1.78	2.021	1.895	27760		
$\text{Cu (C}_9\text{H}_{10}\text{N}_3\text{O}_2\text{S) CH}_3\text{COO}$	1.78	2.126	1.981	27750	12950	18400
$\text{Cu (C}_9\text{H}_{10}\text{N}_3\text{O}_2\text{S) NCS}$	1.80	2.016	1.879	27760		

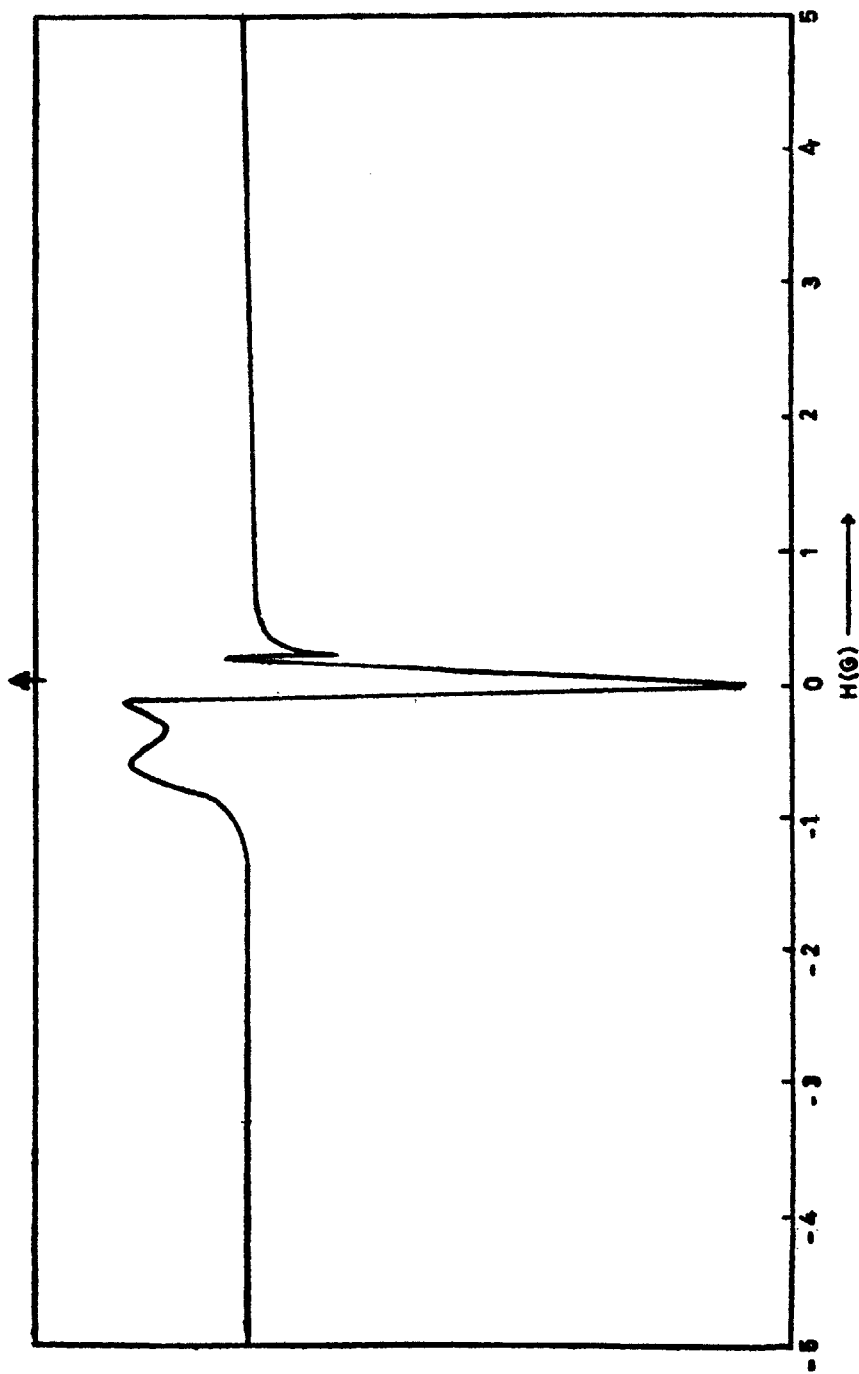


FIG 1 A typical X-band ESR spectrum of [Cu (DAPS) CH₃COO] complex

e.g., deformation modes involving $-\text{NH}_2$ are mixed with skeletal bending and stretching modes. The absorption bands in the region $3348, 3260\text{cm}^{-1}$ (DAPS) and $3300, 3168\text{cm}^{-1}$ (DAPT) in the ligands have been assigned to the NH_2 and NH frequencies⁷. The frequencies do not undergo any appreciable shift on complex formation indicating non-participation of terminal $-\text{NH}_2$ group in coordination. In IR spectra of ligands bands are observed at 3485 (DAPS) and 3488 (DAPT) usually associated with stretching vibrations of phenolic groups. The intensity of these bands decreased considerably indicating the loss of *ortho* phenolic proton on chelation and formation of bond between copper and oxygen.⁸

A strong band at 1627 DAPS and 1630cm^{-1} (DAPT) in the spectra of ligands have been observed due to $> \text{C} = \text{N}$ mode of azomethine linkage. In the spectra of complexes this band is shifted to lower frequency (around 1600cm^{-1}) which suggest that unsaturated nitrogen of the azomethine linkage is coordinated to copper.⁹

Amide bands for DAPS are observed at 1679 (Amide I); 1594 (Amide II); $1376, 1289$ and 1252cm^{-1} (Amide III). These bands are shifted to lower frequencies around $1650, 1530, 1349, 1242$ and 1203cm^{-1} due to coordination of amido oxygen ($> \text{C} = \text{O}$) in chelation.¹⁰ The infrared spectrum of DAPT shows an intense strong band at 842cm^{-1} and no band due to $\nu \text{S} - \text{H}$ near 2570cm^{-1} indicate that the ligand remain in thione form in the solid state¹¹. The downward shift ($\sim 35\text{cm}^{-1}$) of $> \text{C} = \text{S}$ band in the spectra of copper complexes suggests the coordination of the metal ion through sulphur atom of the $> \text{C} = \text{S}$ group.⁶

The facts are further substantiated by the presence of bands in far infrared regions. The bands around 540 and 570cm^{-1} may be assigned to $\text{Cu}-\text{N}$ in copper complexes of DAPS and DAPT respectively. Similarly, $\nu \text{Cu}-\text{O}$ and $\nu \text{Cu}-\text{S}$ bands are observed around 340 and 330cm^{-1} in DAPS and DAPT complexes of copper respectively. In the spectra of complexes $\nu \text{Cu}-\text{X}$ bands at 275 ($\text{Cu}-\text{Cl}$): 1740 ($\text{Cu}-\text{NO}_3$): $2080, 290$ (w) $\text{Cu}-\text{NCS}$)¹² are observed.

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