

Synthesis and Magneto-spectral Studies of Cu(II) Coordination Compounds of 4[N-(*p*-Dimethylamino benzalidene)amino]antipyrinesemicarbazone

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A series of five coordination compounds of copper(II) with 4[N-(*p*-dimethylamino benzalidene)amino]antipyrinesemicarbazone (DABAAPS) have been described in this work. Characterization of these coordination compounds was made on the basis of elemental analysis, molecular weight, magnetic moment, conductivity measurements, infrared and electronic spectra. In all the coordination compounds DABAAPS behaves as tridentate (N, N, O) ligand. Thermal properties of these compounds were also investigated.

Key Words: Synthesis, Magnetic, Spectral, Copper(II), Complexes, Semicarbazone.

INTRODUCTION

In continuation of our work on bio-active metal coordination compounds of biologically active ligands¹⁻⁴, the synthesis and characterization of five coordination compounds of copper(II) with 4[N-(*p*-dimethylamino benzalidene) amino] antipyrine semicarbazone (DABAAPS) have been reported.

EXPERIMENTAL

All the solvents and reagents used were of AnalaR grade, the ligand DABAAPS was synthesized in the laboratory by reported method^{5,6}.

Copper(II) salts were obtained from BDH and used as such, Cu(SCN)₂ was prepared by mixing copper(II) chloride (in ethanol) and the ethanolic solution of potassium thiocyanate in 1 : 2 molar ratio. Precipitated KCl was filtered off and the filtrate having Cu(SCN)₂ was used immediately for complex formation.

All the coordination compounds were synthesized by following the general method. The corresponding copper(II) salt (1 mmol) and DABAAPS (1 mmol) were dissolved separately in ethanol and mixed drop by drop. The reaction mixture was refluxed on a water bath for *ca.* 2 h. On cooling and filtration, a

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microcrystalline compound separated out; the crystals were washed with ethanol and diethyl ether and kept in a desiccator over fused CaCl_2 .

All the physico-chemical analyses were performed according to the reported method^{7,8}.

RESULTS AND DISCUSSION

The reaction of Cu(II) salts with DABAAPS resulted in the formation of the coordination compounds $[\text{Cu}(\text{DABAAPS})\text{X}\cdot\text{H}_2\text{O}]\text{X}$ ($\text{X} = \text{Cl}^-$, Br^- , NO_3^- , NCS^- or CH_3COO^-). The analytical data of these compounds are presented in Table-1. All the coordination compounds do not have sharp melting points but decomposed beyond 245°C . They are quite stable and can be stored for months without any appreciable change. The molar conductance values of the complexes in nitrobenzene (Table-1) indicate that they are 1 : 1 electrolytes. The molecular weights in freezing nitrobenzene are in broad agreement with conductance data (Table-1). Magnetic measurements of the Cu(II) compounds (Table-1) show that all the complexes are paramagnetic and have one unpaired electron. The observed magnetic moments of the present compounds (Table-1) lie in the range 1.72–1.85 B.M. The observed magnetic moments of the complexes are inconsistent with the presence of a single unpaired electron.

TABLE-1
ANALYTICAL, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC
MOMENT DATA OF COPPER(II) COORDINATION COMPOUNDS OF DABAAPS

Complex	%Analysis: found (calcd.)			m.w.: found (calcd.)	Ω_m ($\text{ohm}^{-1}\text{cm}^2$ mol^{-1})	μ_{eff} (B.M.)
	Cu	N	Anion			
$\text{CuCl}_2(\text{DABAAPS})\cdot(\text{H}_2\text{O})$	11.57 (11.68)	17.77 (18.03)	12.89 (13.06)	270 (543.5)	23.3	1.72
$\text{CuBr}_2(\text{DABAAPS})\cdot(\text{H}_2\text{O})$	9.86 (10.00)	15.29 (15.44)	24.68 (25.53)	316 (634.5)	22.2	1.76
$\text{Cu}(\text{NO}_3)_2(\text{DABAAPS})\cdot(\text{H}_2\text{O})$	10.51 (10.64)	20.94 (21.12)	—	297 (596.5)	25.4	1.82
$\text{Cu}(\text{NCS})_2(\text{DABAAPS})\cdot(\text{H}_2\text{O})$	10.54 (11.47)	21.25 (21.41)	19.49 (19.71)	293 (588.5)	25.8	1.81
$\text{Cu}(\text{CH}_3\text{COO})_2(\text{DABAAPS})\cdot(\text{H}_2\text{O})$	10.50 (10.25)	16.45 (16.59)	—	294 (590.5)	26.8	1.84

Infrared Spectra: A study and comparison of IR spectra of DABAAPS and its coordination compounds with copper(II) imply that the ligand behaves as a neutral tridentate coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms. The key infrared bands (cm^{-1}) of these coordination compounds are presented in Table-2. The characteristic absorption of the carbonyl group in free DABAAPS is observed⁹ at *ca.* 1705 cm^{-1} (amide-I band). In all the coordination compounds, this band is shifted toward lower energy in $1655\text{--}1645\text{ cm}^{-1}$ region. The amide-II band in DABAAPS has been observed at 1570 cm^{-1} . In all the present coordination compounds, this band is also shifted towards lower

wavenumbers by 30–25 cm^{-1} . This observation suggests coordination through the carbonyl oxygen atom⁹. The strong band at *ca.* 1605 cm^{-1} in free DABAAPS apparently has a large contribution from the $\nu(\text{C}=\text{N})$ mode of semicarbazone moiety¹⁰. This has been observed as a blue shift in the position of the (C=N) band in all the complexes as compared to the free ligand. Another strong band was observed at *ca.* 1620 cm^{-1} due to azomethinic (C=N) absorption. On complexation, this band is shifted towards the lower frequency region which is suggestive of the coordination through the azomethinic N-atom¹¹. In far infrared spectra $\nu(\text{Cu}-\text{N})/\nu(\text{Cu}-\text{O})$ bands have also been identified¹². The presence of coordinated water was suggested by the broad adsorption band centred around 3445 cm^{-1} in the infrared spectra. Bands at *ca.* 932 and 772 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water¹². In the infrared spectra of thiocyanate complex, the three fundamental absorptions (C—N) stretch (ν_1), (C—S) stretch (ν_3) and (N—C—S) bending (ν_2) are identified, which are associated with the terminal N-bonded isothiocyanate ions¹³. The absence of ν_3 band of ionic nitrate (D_{3h}) at *ca.* 1365 cm^{-1} and the occurrence of two strong bands at 1525 and 1305 cm^{-1} suggests the covalency of NO_3^- in $\text{Cu}(\text{NO}_3)_2(\text{DABAAPS})(\text{H}_2\text{O})$. By applying lever separation method¹⁴, the monodentate nature of NO_3^- in this complexes is suggested. In acetate complex, two bands have been observed at *ca.* 1632 and 1390 cm^{-1} which may be assigned to antisymmetric and symmetric (COO^-) stretching vibrations respectively¹⁵.

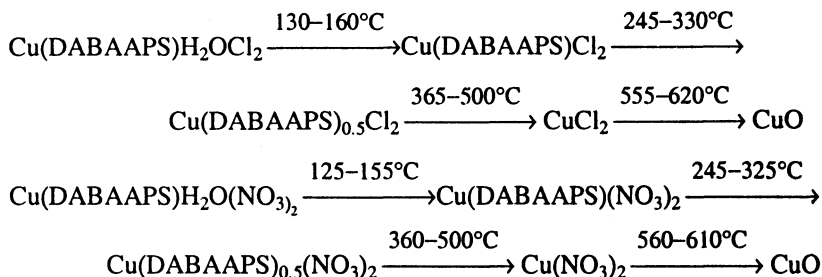
TABLE-2
KEY INFRARED BANDS (cm^{-1}) OF COPPER(II) COORDINATION
COMPOUNDS OF DABAAPS²

Compounds	$\nu(\text{C}=\text{N})$ (azomethinic)	$\nu(\text{C}=\text{N})$ (Hydrazinic)	$\nu(\text{C}=\text{O})$			$\nu(\text{Cu}-\text{N})/$ $\nu(\text{Cu}=\text{O})$
			I	II	III	
DABAAPS	1620 s	1605 s	1705 s	1570 m	1350 m	—
$\text{CuCl}_2(\text{DABAAPS})(\text{H}_2\text{O})$	1580 s	1630 m	1655 s	1532 m	1330 m	462 m, 390 w
$\text{CuBr}_2(\text{DABAAPS})(\text{H}_2\text{O})$	1592 s	1635 m	1645 s	1535 m	1338 m	452 m, 386 w
$\text{Cu}(\text{NO}_3)_2(\text{DABAAPS})$ (H_2O)	1585 s	1620 s	1640 s	1535 m	1332 m	455 m, 390 w
$\text{Cu}(\text{NCS})_2(\text{DABAAPS})$ (H_2O)	1590 s	1632 s	1650 s	1542 m	1336 m	445 m, 380 w
$\text{Cu}(\text{CH}_3\text{COO})_2(\text{DABAAPS})$ (H_2O)	1595 s	1625 s	1648 s	1538 m	1335 m	448 m, 381 w

The electronic spectra of Cu(II) complexes consist of a broad band in (16000 \pm 200) cm^{-1} range of medium intensity in the visible region which can be identified as a *d-d* of the central ion, *i.e.*, an electronic transition mainly localized on Cu(II). Ligand field parameter *ca.* 10 Dq has been estimated from the equation suggested by Lever *et al.*¹⁶ These data are in good agreement with those reported for other D_{4h} symmetry complexes.

Thermal properties of these complexes were studied by T.G.A. The T.G. data indicate that the complexes contain one mole of coordinated water, which is evident

by loss of weight at *ca.* 160°C. There is no change up to *ca.* 250°C, after which there is a break in the curves due to evaporation of 0.5 mole of organic ligand; the remaining 0.5 mole of ligand is removed from the coordination sphere at *ca.* 500°C. Finally at *ca.* 620°C, CuO is formed. Thermal equations are shown as below:



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