

Synthesis and Spectral Studies of Cu(II) Complexes of 4[N-(2-Hydroxy-1-naphthalidene) Amino] Antipyrine Thiosemicarbazone

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A series of five complexes of Cu(II) with 4[N-(2-hydroxy-1-naphthalidene) amino] antipyrine thiosemicarbazone (HNAAPT) have been reported. Characterisation of these complexes were made on the basis of elemental analysis, molecular weight, magnetic moment, conductivity measurements, infrared and electronic spectra. In all the complexes HNAAPT behaves as tridentate (N, N, S) ligand. Thermal properties of these complexes were also investigated.

INTRODUCTION

Thiosemicarbazones are known to exhibit antiviral¹, antitubercular², fungicidal¹, antitumour^{3,4} and pharmacological⁵ behaviour. Thiosemicarbazones are amongst the widely studied nitrogen and sulphur donor ligands⁶. They are capable of acting as neutral or charged moieties. Renewed interest has been shown in these compounds because of their metal complexes also possess a wide spectrum of medicinal properties⁷⁻¹⁰. Recently a number of papers have come forward describing the synthesis and characterisation of Co(II), Ni(II) and UO₂(VI) complexes of thiosemicarbazones¹¹⁻¹³. In the present study a series of five Cu(II) complexes of 4[N-(2-hydroxy-1-naphthalidene) amino] antipyrine thiosemicarbazone (HNAAPT) are reported.

EXPERIMENTAL

$\text{MX}_2 \cdot n\text{H}_2\text{O}$ (M = Cu, X = Cl⁻, Br⁻, NO₃⁻ or CH₃COO⁻) were obtained from BDH and used as such. Cu(SCN)₂ was prepared by mixing metal chloride (in ethanol) and the ethanolic solution of potassium thiocyanate in 1 : 2 molar ratio. Precipitated KCl was filtered off and the filtrate having respective metal thiocyanate was used immediately for complex formation. The ligand HNAAPT was prepared as reported earlier¹⁴.

The Cu(II) salt and the ligand were dissolved in ethanol and the mixture boiled under reflux for 4 h. On cooling and filtration, a microcrystalline complex separated out; the crystals were washed with ethanol and anhydrous diethyl ether and kept in a desiccator over fused CaCl₂.

All the physico-chemical analyses were performed according to the reported method¹⁵.

RESULTS AND DISCUSSION

The reaction of Cu(II) salts with HNAAPT resulted in the formation of the complexes $\text{CuX}_2 \cdot (\text{HNAAPT}) \cdot \text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-$, Br^- , NO_3^- , NCS^- or CH_3COO^-). The analytical data of these complexes are presented in Table-1. All the complexes are quite stable and can be stored for months without any appreciable change. The complexes do not have sharp melting points and decompose on heating beyond 270°C. The electrical conductance of the complexes in nitrobenzene is presented in Table-1. The molar conductance of all Cu(II) complexes (Table-1) are too low to account for any dissociation; therefore they are non-electrolytes. Magnetic moments of Cu(II) complexes have one unpaired electron. The observed magnetic moments of the Cu(II) complexes (Table-1) lie in the range 1.80–1.90 B.M. The observed magnetic moments of the complexes are inconsistent with the presence of a single unpaired electron.

A study and comparison of IR spectra of HNAAPT and its complexes with Cu(II) imply that the ligand behaves as a neutral tridentate and the metal is coordinated through N and N of two azomethine groups and S of thioketo group. A strong band observed at 3300–3200 cm^{-1} region in free ligand has been assigned to $\nu(\text{NH})$ vibration. Practically no effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorption at *ca.* 1610 cm^{-1} in the free ligand is attributed to $\nu(\text{C}=\text{N})$ of imine nitrogen, which is in agreement with the observations of previous workers^{11, 16}. On complexation, these frequencies were observed to be shifted to lower wavenumbers (Table-2). In the spectra of present ligand, the bands observed in 1300–1125 cm^{-1} region, 1120–1095 cm^{-1} and 840–730 cm^{-1} regions are assigned to [$\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})$], $\delta(\text{N}-\text{C}-\text{S}) + \delta(\text{C}=\text{S})$ and $\nu(\text{C}=\text{S})$ respectively, following the reports of Irving *et al.*¹⁷ Coordination of sulphur with the metal ion would result in the displacement of electrons towards the latter, thus resulting in the weakening of (C=S) bond. Hence on complexation $\nu(\text{C}=\text{S})$ stretching vibrations should decrease and that of $\nu(\text{CN})$ should increase. In the present Cu(II) complexes of HNAAPT, the frequency in the range 1300–1125 cm^{-1} gets increased by nearly 50–60 cm^{-1} ; similarly bending modes of (N—C—S) and (C=S) also get increase but in lesser amount. On the other hand, on complexation the frequencies in 840–730 cm^{-1} are shifted to lower wavenumbers and intensities of the bands are also reduced. The possibility of thione-thiol tautomerism ($\text{H}-\text{N}-\text{C}=\text{S}) \rightleftharpoons (\text{C}=\text{N}-\text{SH})$ in this ligand is ruled out for no band around 2700–2500 cm^{-1} , characteristic of the thiol group displaced in the infrared absorption^{18, 19}. In the far infrared region $\nu(\text{Cu}-\text{N})/\nu(\text{Cu}-\text{S})$ bands have also been identified (Table-2). The presence of coordinated water was suggested by the very broad absorption band centred around 3450 cm^{-1} in the infrared spectrum. Bands at *ca.* 930 and 770 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water²⁰. In the infrared spectra of thiocyanate complexes the three fundamentals absorption

TABLE-1
ANALYTICAL, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC MOMENT DATA OF Cu(II) COMPLEXES OF HNAAPT

Complex	% Analysis, found (calcd)			m.w. found (calcd.)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	μ_{eff} (B.M.)
	Cu	N	Anion			
CuCl ₂ (H ₂ O)(HNAAPT)	10.79 (10.90)	14.29 (14.42)	5.40 (5.49)	576 (582.5)	2.3	1.82
CuBr ₂ (H ₂ O)(HNAAPT)	9.38 (9.45)	12.37 (12.50)	4.63 (4.76)	666 (671.5)	3.1	1.90
Cu(NO ₃) ₂ (H ₂ O)(HNAAPT)	9.89 (9.99)	17.47 (17.62)	4.97 (5.03)	629 (635.5)	2.9	1.80
Cu(NCS) ₂ (H ₂ O)(HNAAPT)	10.00 (10.11)	17.67 (17.84)	5.14 (5.29)	623 (627.5)	3.3	1.83
Cu(CH ₃ COO) ₂ (H ₂ O)(HNAAPT)	9.93 (10.08)	13.22 (13.34)	4.97 (5.08)	624 (629.5)	2.7	1.87

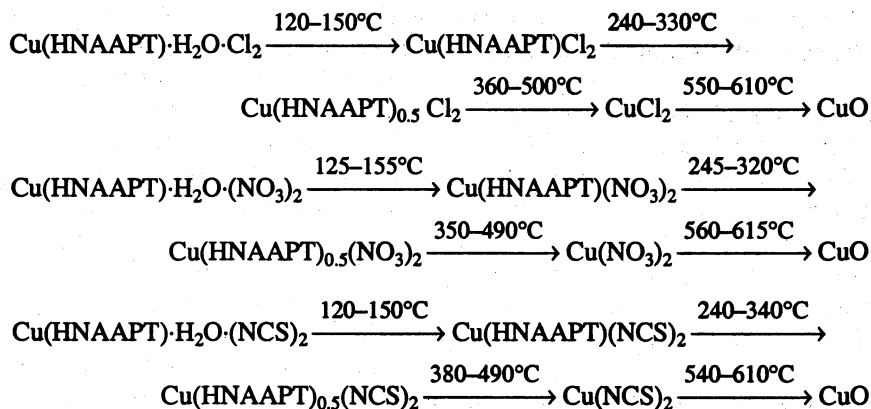
TABLE-2
KEY INFRARED BANDS (cm⁻¹) OF Cu(II) COMPLEXES OF HNAAPT

Compounds	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})$	$\delta(\text{NCS}) + (\text{CS})$ bending	$\nu(\text{N}-\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{Cu}-\text{N})/$ $\nu(\text{Cu}-\text{S})$
HNAAPT	3300 s	1610 vs	1290 s	1130 m	1045 m	840 s	-
	3200 s		1250 m	1070 m		765 s	-
CuCl ₂ (HNAAPT)(H ₂ O)	3320 m	1555 m	1370 s	1180 m	1070 m	790 s	445 m
	3205 m		1330 m	1140 m		755 s	332 w
CuBr ₂ (HNAAPT)(H ₂ O)	3315 s	1565 m	1365 m	1175 m	1068 m	795 m	440 m
	3202 m		1325 m	1135 m		750 m	335 w
Cu(NO ₃) ₂ (HNAAPT)(H ₂ O)	3315 s	1572 s	1375 m	1170 m	1072 m	792 s	442 m
	3205 m		1335 m	1130 m		745 s	325 w
Cu(NCS) ₂ (HNAAPT)(H ₂ O)	3312 s	1570 s	1360 m	1172 m	1075 m	780 m	445 m
	3200 m		1330 m	1125 m		748 m	330 w
Cu(CH ₃ COO) ₂ (HNAAPT)(H ₂ O)	3315 s	1570 m	1355 m	1170 m	1070 m	795 m	430 m
	3205 m		1320 m	1130 m		50 s	340 w

(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 ions²¹. The absence of ν_3 band of ionic nitrate (D_{3h}) at *ca.* 1360 cm^{-1} and the occurrence of two strong bands at *ca.* 1560–1490 cm^{-1} and 1300–1280 cm^{-1} region suggest the covalent nature of NO_3^- . The presence of ν_2 , ν_6 , ν_3 and ν_5 bands in all these complexes further confirms the covalency of NO_3^- ions in these complexes. By applying Lever separation method²², the monodentate nature of nitrate ions in these complexes is suggested. In acetate complexes two bands have been observed at *ca.* 1630 and 1390 cm^{-1} which may be assigned to antisymmetric and symmetric (COO^-) stretching vibrations²³ respectively.

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 band of the central ion, *i.e.*, an electronic transition mainly localised on Cu(II). Ligand field parameter *ca.* 10 Dq has been estimated from the equation suggested by Lever *et al.* These data are in good agreement with those reported for other D_{4h} symmetry complexes.

Thermal properties of these complexes were studied by thermogravimetric analysis. The t.g. data indicate that the complexes contain one mole of coordinated water, which is evident by loss of weight at *ca.* 150°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 solvent, the remaining 0.5 mole of ligand is removed from the coordination sphere at *ca.* 500°C. Finally, at 610°C, CuO is formed. Thermal changes are represented as follows:



The overall experimental results predict that the Cu(II) ions display a coordination number six in these complexes.

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