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NOTE

Synthesis and Spectral Properties of Copper(II) Complexes of 4[N-(3′-Nitrobenzylidene) Amino] Antipyrine

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The interaction of 4[N-(3′-nitrobenzylidene) amino] antipyrine (3′-NO_2BAAP) with Cu^{2+} salts in non-aqueous solvent resulted in the coordination complexes with the general composition $CuX_2 \cdot 2$(3′-NO_2BAAP). These complexes were characterized through elemental analyses, electrical conductance, infrared and electronic spectra.

4-Aminoantipyrine is known as a potential ligand for various metal ions[1-3]. Comparatively very little is known about the N-substituted 4-aminoantipyrine complexes of 3d-metal ions[4, 5]. In view of this, in the present work, the authors wish to report some new complexes of Cu^{2+} ion with 4[N-(3′-nitrobenzylidene) amino] antipyrine. VO^{2+} and UO_2^{2+} complexes of this ligand have already been reported[5, 6].

Hydrated copper(II) salts were obtained from BDH (AR grade). $Cu(NCS)_2$ was prepared by reaction of methanolic solution of $Cu(NO_3)_2$ and KCNS. The ligand 3′-NO_2BAAP was synthesized in the laboratory by reported method[7]. All the complexes were synthesized by the following general method. Copper(II) salt (1 mmol) was dissolved in acetone and 2,2′-dimethoxypropane and the solution was refluxed for 30 min. The ligand (2.1 mmol) was dissolved in minimum amount of hot ethanol. These solutions were mixed together and the reaction mixture refluxed in a water bath for *ca.* 2 h. The reaction mixture was allowed to cool slowly. In some cases, the precipitate was obtained immediately and in some cases gradual precipitation took place. The complexes were then filtered, washed thoroughly with ethamol and ether and then kept under vacuum over P_4O_{10}.

All the physico-chemical analyses of these complexes were performed, as reported earlier[8].

The interaction of Cu(II) salts with 3′-NO_2BAAP in ethanol resulted in the formation of the complexes with the general composition $CuX_2 \cdot 2$(3′-NO_2BAAP)

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($X = Cl^-$, Br^-, NCS^-, NO_3^- or CH_3COO^-). The analytical data are presented in Table-1. All the complexes are quite stable and could be stored for weeks without any appreciable change. The molar conductance values of these complexes in nitrobenzene are in 2.3–3.9 ohm^{-1} cm^2 $mole^{-1}$ range suggest that all the complexes are non-electrolytes[9]. The magnetic moment values of Cu(II) complexes lie in the range 1.81–1.92 B.M. Although the observed magnetic moments are consistent with the presence of a single unpaired electron they yield no stereochemical information[10, 11]

TABLE-1
ANALYTICAL, CONDUCTIVITY AND MOLECULAR WEIGHT DATA OF Cu^{2+} COMPLEXES OF 3′-NO_2BAAP

Complexes	Found (Calcd.) %			Mol. wt. Found (Calcd.)
	Cu	N	Anion	
$CuCl_2 \cdot 2(3'\text{-}NO_2BAAP)$	7.79	13.76	8.62	798
	(7.89)	(13.88)	(8.80)	(806.5)
$CuBr_2 \cdot 2(3'\text{-}NO_2BAAP)$	7.00	12.38	17.59	887
	(7.09)	(12.50)	(17.86)	(895.5)
$Cu(NO_3)_2 \cdot 2(3'\text{-}NO_2BAAP)$	7.31	16.12	—	851
	(7.38)	(16.28)	—	(859.5)
$Cu(NCS)_2 \cdot 2(3'\text{-}NO_2BAAP)$	7.36	16.27	13.43	846
	(7.45)	(16.44)	(13.62)	(851.5)
$Cu(CH_3COO)_2 \cdot 2(3'\text{-}NO_2BAAP)$	7.33	13.01	—	848
	(7.43)	(13.12)	—	(853.5)

The infrared spectra of all the complexes show a considerable negative shift in carbonyl (pyrazolone) absorption $\Delta\nu(C{=}O)$ 45–40 cm^{-1} indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the oxygen atom of the free base (Table-2). It is well known[12] that as a result of coordination through the carbonyl oxygen the double bond character between the carbon and oxygen is reduced. The decrease in the bond character causes a bathochromic effect in the carbonyl stretching frequency. The C=O stretching frequency occurring at *ca.* 1642 cm^{-1} in the free ligand has been observed in the region 1602–1598 cm^{-1} in all the complexes[13, 14]. Another important band occurring at *ca.* 1590 cm^{-1} is attributed to $\nu(C{=}N)$ mode[13, 14]. In spectra of all the complexes this band is shifted to lower wave-number and appears at 1565–1560 cm^{-1} indicating the involvement of N-atom of the azomethine group in coordination[13, 14]. Other absorption bands of the ligand do not show any significant change on complexation. In the far IR region $\nu(Cu{-}O)/\nu(Cu{-}N)$ is assigned in 460–345 cm^{-1} range[8].

In nitrato complex the absence of the ionic nitrate ν_3 band (D_{3h}) at *ca.* 1360 cm^{-1} and the presence of 1500 and 1308 cm^{-1} due to splitting of ν_3 mode indicate the lower symmetry of coordinated nitrato group[15, 16]. Distinction between mono and bidentate nitrate groups on the basis of infrared evidence is usually difficult but on the basis of the separation in combination bands ($\nu_1 + \nu_4$) in 1800–1700 cm^{-1} region the monodentate groups are concluded[15, 16]. In $Cu(NCS)_2 \cdot 2(3'\text{-}NO_2BAAP)$

complex, the three fundamental absorptions C—N stretch (ν_1), C—S stretch (ν_3) and N—C—S bending (ν_2) are identified at *ca.* 2040, 830 and 465 cm^{-1} respectively suggesting the terminal N-bonded isothiocyanate ions in this complex[17]. In acetato complex the bands around 1508, 1455, 1340 and 715 cm^{-1} which can be assigned to ν_{asym}(COO), ν_{sym}(COO), δ(CH$_3$) and δ(OCO) vibrations respectively indicating the presence of acetate ion in the coordination sphere[18]. In chloro complex the band around 380 cm^{-1} region is assigned to ν(Cu—Cl) mode.

TABLE-2

KEY IR BANDS (cm^{-1}) OF CuX$_2$·2(3'-NO$_2$BAAP) COMPLEXES

Compound	ν(C=O)	ν(C=N)	ν(Cu—O)/ν(Cu—N)
3'-NO$_2$BAAP	1642 s	1590 s	—
CuCl$_2$·2(3'-NO$_2$BAAP)	1602 s	1562 s	450 m, 340 w
CuBr$_2$·2(3'-NO$_2$BAAP)	1600 s	1560 s	460 m, 350 m
Cu(NO$_3$)$_2$·2(3'-NO$_2$BAAP)	1595 s	1565 s	445 m, 355 w
Cu(NCS)$_2$·2(3'-NO$_2$BAAP)	1598 s	1562 s	450 w, 360 w
Cu(OAc)$_2$·2(3'-NO$_2$BAAP)	1600 s	1565 s	450 m, 362 w

The electronic spectra of these complexes consist of a broad band (15800–16300 cm^{-1}) of medium intensity in the visible range which can be identified as a d-d band of the central ion, *i.e.*, an electronic transition mainly localized in Cu(II) and a series of at least two more bands also in the visible region, which can be assigned to a charge-transfer mechanism operating from the anions to Cu(II) ion. An inspection of the electronic spectra of these complexes immediately rules out the possibility of a tetrahedral structure. The spectra of tetragonally distorted octahedral complexes involve three transitions, *viz.*, $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$, and $^2B_{1g} \rightarrow {}^2A_{1g}$, but bands due to these transitions usually overlap to give one broad absorption spectrum. The complexes under investigation show one such band in the region 16300–15800 cm^{-1}. The appearance of a single band in these complexes is not expected because of the steric hindrance caused by the bulky ligand molecule. Thus these complexes have approximately D_{4h} symmetry. An approximate value of 10 D_q has been calculated and is given in Table-3.

TABLE-3

ELECTRONIC SPECTRAL BANDS (cm^{-1}) OF Cu(II) COMPLEXES OF 3'-NO$_2$BAAP

Complexes	(d–d) bands	CT-bands		10 D_q
CuCl$_2$·2(3'-NO$_2$BAAP)	15800	23080	28770	7900
CuBr$_2$·2(3'-NO$_2$BAAP)	16000	23000	28750	8000
Cu(NO$_3$)$_2$·2(3'-NO$_2$BAAP)	16060	23100	28770	8030
Cu(NCS)$_2$·2(3'-NO$_2$BAAP)	16300	23000	28800	8150
Cu(OAc)$_2$·2(3'-NO$_2$BAAP)	16250	23500	28600	8125

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