

ISOLATION AND STRUCTURAL STUDIES ON THE COMPLEX OF COPPER (II)
WITH IMPRAMINE HYDROCHLORIDE

H. SANKE GOWDA AND JAYARAMA

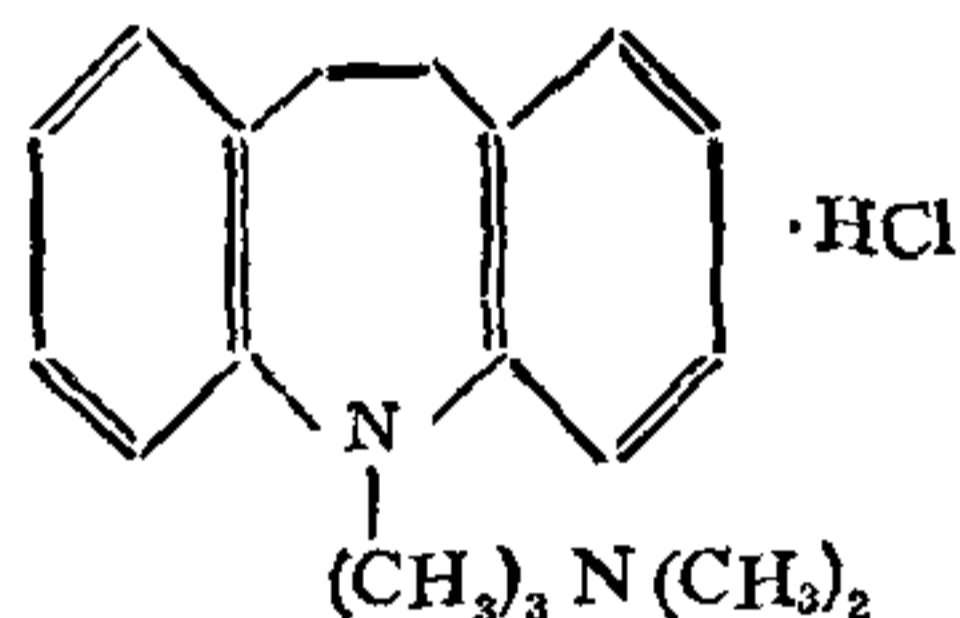
Department of Post-Graduate Studies and Research in Chemistry, Manasagangothri, University of Mysore
Mysore 570 006, India

ABSTRACT

Copper(II) complex of imipramine hydrochloride has been isolated and characterized by elemental analysis, magnetic moment, electronic, infrared and e.s.r. spectral studies. Thermogravimetric studies on the complex have been included.

INTRODUCTION

IMPRAMINE HYDROCHLORIDE (IPH) is analogous to phenothiazines which are good coordinating agents¹⁻⁵. The present communication reports on the interaction of Cu(II) with IPH. IPH has the following structure:



EXPERIMENTAL

Solutions (10^{-4} – 10^{-3} M) of Cu-IPH complex in methanol were used for recording UV and visible spectra. KBr pellet technique was used for IR spectra. ESR spectrum was made on polycrystalline powder sample using DPPH as calibrant. Conductance measurements were carried out with 10^{-4} M solutions of the complex. T. G. A. was made on Stanton Thermo balance Model HT-SM at a heating rate of $6^\circ\text{C}/\text{min}$. Magnetic measurements were made at 27°C using Gouy balance. Chemical analysis was carried out by conventional methods.

Isolation and purification of the complex

The complex was prepared by mixing equimolar solutions of the ligand and the metal ion in acetone in the ratio of 1 : 1 and concentrating at 60°C with an equal volume of benzene in which the complex is insoluble. The solid separated was washed with ether and recrystallised from benzene and dried *in vacuo*.

RESULTS AND DISCUSSION

The Cu(II)-IPH complex (m.p. 155°C) is brown in colour soluble in water, acetone, methanol, ethanol and DMF and almost insoluble in benzene and toluene. The molar conductance of the complex was $82\ \text{ohm}^{-1}\ \text{mole}^{-1}\ \text{cm}^2$ showing it to be an electrolyte in DMF. Analytical data are:

Calculated for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{CuCl}_2\text{H}_2\text{O}$: C, 51.88%; H, 6.37%; Cl, 15.93%; N, 6.37%; Cu, 12.16%. Found: C, 51.63%; H, 6.02%; Cl, 15.87%; N, 6.28%; Cu, 12.24%.

The magnetic moment of the complex was normal (2.01 B.M.).

Electronic spectrum of Cu-IPH was characterized by the presence of three bands respectively at 630 ($\epsilon = 818$), 520 ($\epsilon = 700$) and 430 nm ($\epsilon = 1180$). These bands clearly show that stereochemistry around Cu(II) is distorted octahedral in methanol solutions.

The ESR spectrum of the complex is characteristic of an octahedral geometry and compares well with powder ESR^{6,7} of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. The two g values obtained were $g_{\parallel} = 2.247$ and $g_{\perp} = 2.046$ which correspond to a species belonging to an elongated tetragonal or distorted octahedral symmetry since $g_{\parallel} > g_{\perp}$. Further, $G = (g_{\parallel} - 2)/(g_{\perp} - 2) > 4$ suggesting the absence of any spin exchange interactions in the solid state.

Infrared spectral studies on the free ligand and its complex revealed that IPH acts as a bidentate ligand by coordinating through its heterocyclic nitrogen atom and the tertiary nitrogen atom in the side chain. A new band around $3250\ \text{cm}^{-1}$ in the IR spectrum of the complex shows the presence of coordinated water molecules.

TGA of the complex demonstrated that two coordinated water molecules escape at the temperature range $200 - 220^\circ\text{C}$. The weight loss constancy is attained at about 710°C and the black residue obtained was characterized as CuO by x-ray diffraction.

In the light of the foregoing evidence, we propose the six coordinated structure for the Cu-IPH complex having distorted octahedral geometry.

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SYNTHESIS OF SOME α -NAPHTHOL DERIVATIVES: DYE INTERMEDIATE

ASHUTOSH, N. D. PANDEY AND J. K. MEHROTRA

Chemical Laboratories, M.N.R. Engineering College, Allahabad 211 004, India

ABSTRACT

6 (or 7 or 8) acetylamino-2-(ω -sarcosino)-3 (or/and 6) sulpho (or disulpho)-1-naphthols were prepared by condensation of 6 (or 7 or 8) acetylamino-3-(or/and 6)-sulpho (or disulpho)-1-naphthols, glycine, formaldehyde in presence of sodium acetate in acetic acid medium.

NAPHTHOLS and their derivatives are well known as important intermediates in dye-industries¹⁻⁶. Mannich type of reaction (as described below) was carried out with 6 (or 7 or 8)-amino-3 (or/and 6)-sulpho (or disulpho)-1-naphthols to introduce sarcosino group. However, free $-\text{NH}_2$ groups of these naphthols interfere in this reaction. Therefore, equimolecular amounts of *N*-acetyl⁶ derivatives of these naphthols, glycine, sodium acetate and formaldehyde in excess of acetic acid at 60–80° were heated for the preparation of 6 (or 7 or 8)-acetylamino-2-(ω -sarcosino)-3 (or/and 6)-sulpho (or disulpho)-1-naphthols (I). The acetyl group was removed by hydrolysis to yield 6 (or 7 or 8) amino-2-(ω -sarcosino)-3 (or/and 6)-sulpho (or disulpho)-1-naphthols (II). The structure of I was established by degradative methods,

as well as from their ir spectra. II was diazotised and refluxed gently in presence of ethyl alcohol and sulphuric acid to give 2-(ω -sarcosino)-1-naphthols⁸ (III), III was oxidised with alkaline potassium permanganate to yield phthalonic acid (IV), formation of which shows that the sarcosino group is substituted in the ring which possesses the phenolic group. III on fusion with KOH, followed by acidification of the resulting product, gave 1-hydroxy-2-naphthylmethanol (V) (m.p. 152°; lit.⁹ 152; yield 40%) with the expulsion of methylamine. V on heating with zinc dust yielded 2-naphthyl methanol (VI) (m.p. 80°; lit.⁷ 80.5°), which indicates that the sarcosino group takes the available β -position. Reactions taking place are shown in the Structure.

The ir spectra (KBr disc) of I (Table I, compound numbers 1, 2 and 3) showed absorption bands at 3300–3330 cm^{-1} (α -naphtholic-OH); 3130–3134 cm^{-1} , 1565–1580 cm^{-1} ($-\text{CH}_2\text{NHCH}_2-$); 1700–1705 cm^{-1} ($-\text{COOH}$); 1200–1210 cm^{-1} , 1035–1055 cm^{-1} (SO_3^-); 1680–1695 cm^{-1} and 3255–3270 cm^{-1} ($-\text{NHCO}-$).

EXPERIMENTAL

Preparation of 6 (or 7 or 8) acetylamino-2-(ω -sarcosino)-3-(or/and 6) sulpho (or disulpho)-1-naphthol (I)

Pure 6 (or 7 or 8) acetylamino-3 (or/and 6) sulpho (or disulpho)-1-naphthol (0.1 mole), glycine (7.5 g, 0.1 mole) and crystalline sodium acetate (13.6 g, 0.1 mole) were taken in 100 ml of acetic acid and dissolved with slight heating (40°) on a water-bath. The resulting mixture was cooled to room temperature and formalin (36% aqueous solution of formaldehyde; 9 ml, 0.1 mole) was added to it dropwise with thorough stirring. The temperature rose to 45° during the course of addition of formalin. The contents of the beaker were heated at 60° for four hours, and the temperature was then raised to 80°. Heating was continued at this temperature for further four hours, the reaction product cooled and poured in 300 ml of absolute alcohol dropwise with continuous stirring.

