

The symmetric and antisymmetric [ν (C = C) + ν (C — N)] vibrations of the pyridine ring of 'APT' are shifted to higher wave numbers on complexation, implying pyridinic nitrogen-metal bond. The absorption bands at 1333 and 1308 cm^{-1} assigned to [ν (C = C) + ν (C = N) + ν (CN)] show the upward shift of frequencies while the band at 760 cm^{-1} (in the free ligand) assigned to ν (C = S) shows a considerable decrease in frequency ($\sim 75 \text{ cm}^{-1}$), indicating the sulphur coordination to the metal¹⁰. In cyano and nitrate complexes, the band at 2210 cm^{-1} may be assigned to the cyano group frequency indicating the coordination through nitrogen, while the medium intensity absorption peaks at 1530 and 1270 cm^{-1} are assigned to the ν (Cu-NO₃) vibrations¹¹.

The medium intensity bands observed in the far-i.r. region 454–425 cm^{-1} and 315–280 cm^{-1} are assigned to ν (Cu-S) and ν (Cu-Py. N) vibrations respectively, while in the complexes (1 and 2), ν (Cu-Cl) and ν (Cu-Br) are observed at 320 and 225 cm^{-1} respectively supporting sq. planar geometry around the copper (II) ion. In complexes (5 and 6) ClO₃ and BrO₃ are coordinated to the metal through the oxygen as -O-ClO₂ and -O-BrO₂ respectively as the ν (Cu-

Cl/Br) band is not observed. In the complex 7, CH₃COO is coordinated through ketonic oxygen. Metal ligand stretching force constants (K-values) for ν (Cu-S), ν (Cu-Cl/Br) and ν (Cu-Py. N) are given in Table I.

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COMPLEXES OF Cu(II), Ni(II) AND Co(II) WITH SCHIFF BASE DERIVED FROM 2-AMINO-5-METHYLPYRIDINE AND SALICYLALDEHYDE

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ABSTRACT

Complexes of Cu(II), Ni(II) and Co(II) with a Schiff base derived from 2-amino-5-methylpyridine and salicylaldehyde have been prepared and characterised. Based on elemental analysis, infrared and electronic absorption spectra, a square planar structure for Cu(II) complex and tetrahedral structures for Ni(II) and Co(II) have been proposed.

INTRODUCTION

A VARIETY of Schiff base complexes of transition metal ions have received considerable attention¹ and some have been shown to exhibit reversible oxygenation behaviour². Since the geometrical arrangements play a significant part in their spectroscopic, magnetic, substitution and redox³ properties, the Schiff base derived from 2-amino-5-methylpyridine and salicylaldehyde and the geometrical arrangements of its complexes with Cu(II), Ni(II) and Co(II) have been reported in this study.

EXPERIMENTAL

The free ligand was prepared by refluxing equimolar quantities of 2-amino-methylpyridine and salicylaldehyde in ethanol for 30 min. and keeping the reaction mixture stirred at ca. 20° C for ca. 6 h. The recrystallisation from ethanol of the deep yellow crystals gave the ligand in the pure form.

The bis-salicylaldehydato complexes of the metal ions were prepared according to literature methods⁴ and 0.005 mole of the complexes was refluxed in methanol or chloroform (50 ml) for 1 h. While

hot, 0.01 mole of 2-amino-5-methylpyridine dissolved in methanol (10 ml) was added and the mixture was refluxed for a further period of 2-3 h in the case of Ni(II) and Cu(II) and 30 min. in the case of Co(II). The solid obtained was washed with cold methanol and ether recrystallised from methanol.

The Schiff base complexes of Cu(II) and Co(II) were freely soluble in methanol, chloroform and benzene whereas the Ni(II) complex was only slightly soluble. The analytical and spectroscopic data are tabulated in Table I.

(viz., benzylidene aniline) is reported⁷ to be obscured by $\pi-\pi^*$ transition, indirectly the $n-\pi^*$ transition in this system has been located at about 360 nm⁸.

The complexation of this Schiff base to Cu(II), Co(II) and Ni(II) leads to shift of 2 nm in the positions of B bands and 0-5 nm in the $n-\pi^*$ transition at 305 nm as shown in Table I. However, the complexation leads to a shift (7 ± 1 nm) and intensification of the absorption peak at 348 nm suggesting the involvement of $-C=N-$ linkage in the co-ordination to the metal ions. Complexation leads to a

TABLE I
Analytical and Spectral Data

Compound	Colour	M. Pt. (°C)	Nitrogen		Metal		Electronic λ_{max} (nm)	Spectra data IR (stretching) bands			
			Calc. (%)	Found (%)	Calc. (%)	Found (%)		C=N	C-O (cm ⁻¹)	M-N	M-O
Ligand	Bright yellow	101	13.21	13.02	238, 270 305, 348	1610 (s)	1280 (m)
Cu (II) Complex	deep brown	207	11.53	11.28	13.07	12.88	238, 272 306, 355 400, 680-690 ^b	1620 (s)	1315 (m)	535	505
Ni(II) Complex	Orange > 260 Yellow		11.64	11.55	12.21	11.91	238, 272 305, 354 390	1615 (s)	1315 (m)	530	490
Co (II) Complex	Bright > 260 red		11.60	11.36	12.17	11.91	238, 272 310, 356 395	1601 (s)	1313 (m)	530	490

(s) = sharp, (m) = medium, ^b = broad.

RESULTS AND DISCUSSION

The electronic absorption spectrum of the Schiff base exhibits four absorption bands at 238 nm, 270 nm, 305 nm and 348 nm in methanol. Aryl groups are known to exhibit two absorption bands in the u.v. region, viz., 200-220 nm and 240-270 nm which are assigned to $\pi-\pi^*$ transitions and are termed as K and B bands respectively^{5,6}. Substituents in the benzene nucleus, however, are known to give rise to shift of K band to the benzoid B region, while B band is displaced to 270-285 nm, similar to that observed for the Schiff base reported in this study. The absorption bands at 305 nm and 348 nm are attributable to $n-\pi^*$ transitions arising from $-OH$ and $-C=N-$ in an extensively conjugated π -electron system. The band at 348 nm is also sensitive to the polarity of the solvent. Although the $n-\pi^*$ band in a related molecule

highly intense absorption in the 400 nm region for the Cu(II) ($\epsilon=12,170$ M⁻¹ cm⁻¹) complex and much weaker absorptions for Ni(II) ($\epsilon=794$ M⁻¹ cm⁻¹) and Co(II) ($\epsilon=812$ M⁻¹ cm⁻¹) complexes. The Schiff base complex of Cu(II) alone exhibits a weak band (broad) at 680-690 nm indicating that the Cu(II) is in a square planar environment since truly tetrahedral complexes are reported⁹ to show no absorption peak between 500 and 800 nm. As contrasted to the Cu(II) complex, cobalt and nickel complexes do not exhibit any absorption peak suggesting tetrahedral environment in the latter cases.

The infrared spectra of the complexes also show that the $(-C=N-)$ band at 1610 cm⁻¹ in the free ligand is shifted to 1615 cm⁻¹, 1620 cm⁻¹ and 1601 cm⁻¹ for Cu(II), Ni(II) and Co(II) complexes respectively and thus providing further evidence for

$-C\equiv N-$ co-ordination to the metal ions¹⁰. Further, the i.r. spectra of the salicylaldehydato-metal complexes differ from those of the corresponding Schiff base complexes on account of the absence of $(C=O)$ and of the presence of $(-C\equiv N-)$. The shift in $C-O$ stretching frequency observed in the free ligand at 1280 cm^{-1} to higher frequencies, viz., $1310-1315\text{ cm}^{-1}$ in the complexes is indicative of the co-ordination of phenolic $-OH$ ¹¹. The infrared absorption bands observed in the region of $490-510\text{ cm}^{-1}$ and $520-535\text{ cm}^{-1}$ for various complexes can be attributed to the $M-O$ and $M-N$ stretching frequencies respectively. Thus, the electronic absorption and i.r. spectra along with elemental analysis suggest that pyridine nitrogen is not involved in the co-ordination and ideal geometries of Cu(II) (square planar) Ni(II) and Co(II) (tetrahedral) are preserved in the new Schiff base complexes at room temperature (25°C).

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