

## COPPER (II), NICKEL (II) AND COBALT (II) COMPLEXES OF ACYLHYDRAZINE SCHIFF BASES

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## ABSTRACT

Cu<sup>II</sup>, Ni<sup>II</sup> and Co<sup>II</sup> complexes of Schiff bases, derived from O-amino benzoylhydrazine, salicylaldehyde and benzaldehyde (1:1:1) and O-amino benzoylhydrazine and O-hydroxyacetophenone (1:2) were prepared from aqueous and ethanolic media and characterized by analytical, spectroscopic and magnetic data. The complexes are coloured, insoluble in common organic solvents, melt or decompose above 200° and adopt planar or octahedral stereochemistry.

## INTRODUCTION

SCHIFF bases derived from acylhydrazines act as multidentate ligands and react in their keto-enol forms<sup>1-5</sup>. In view of this we presently report Cu<sup>II</sup>, Ni<sup>II</sup> and Co<sup>II</sup> complexes with a Schiff base (H<sub>2</sub>J) derived from O-aminobenzoyl hydrazine and O-hydroxyacetophenone (1:2) and a mixed Schiff base (HL) from O-aminobenzoylhydrazine, salicylaldehyde and benzaldehyde (1:1:1) which is different from the disalicylalimine reported earlier<sup>2</sup>.

## EXPERIMENTAL

## Preparation of the Ligands

The ligand H<sub>2</sub>J and HL were prepared by reacting O-aminobenzoylhydrazide<sup>6</sup> (m.p. 120°, Lit. 121°) and O-hydroxyacetophenone (1:2) and salicylaldehyde plus benzaldehyde (1:1:1) respectively. The products were purified by recrystallization.

## Preparation of the Complexes

The metal salts of BDH, AR grade were used for preparation of the complexes which were obtained by refluxing the ligands with the metal salts in 1:1 molar ratio either in alcoholic or aqueous medium keeping metal salts slightly in excess. The products were washed with either ethanol or water and dried over anhydrous calcium chloride.

## Analysis

Metal part in the complexes was analyzed by following literature procedures after destroying the organic moiety. The ligands were estimated volumetrically<sup>2</sup>, while chloride was determined gravimetrically and nitrogen microanalytically using a Coleman nitrogen analyzer. Analytical and some general characteristics of the complexes are given in Table I.

TABLE I  
Analytical, electronic and magnetic moment data of Cu<sup>II</sup>, Ni<sup>II</sup> and Co<sup>II</sup> complexes of Acylhydrazine Schiff bases H<sub>2</sub>J and HL

Sl. No.	Complex and colour	Dec. pt.	Analysis (%)				Magnetic moment $\mu_{\text{eff}}$ B.M.	Electronic bands $\lambda_{\text{max}}$ nm		
			Metal	Nitrogen	Ligand	Chloride				
(a)	Cu (HJ) Cl Green	>250	12.6 (13.1)	9.0 (8.6)	80.4 (79.6)	6.9 (7.3)	1.9	255, 325, 342, 360, 380, 410, 625.		
(b)	Cu (HJ) <sub>2</sub> Green	>250	7.3 (7.6)	9.8 (10.0)	91.32 (92.4)	Nil	1.2	225, 255, 300, 395, 625.		
(c)	NiJ Red	>250	13.7 13.2	9.8 9.4	87.2 86.7	Nil	diamagnetic	250, 285, 356, 388.		
(d)	CuLCl Green	200 m	14.0 (14.4)	9.3 (9.5)	76.9 (77.6)	7.9 (8.0)	2.0	210, 273, 290, 405, 685.		
(e)	NiLCl.H <sub>2</sub> O Green	>250	13.6 (13.0)	9.5 (9.2)	76.1 (75.2)	8.0 (7.8)	3.1	250, 295, 310, 430, 950.		
(f)	CoLCl.H <sub>2</sub> O Reddish Brown	>250	12.8 (13.0)	8.8 (9.2)	75.8 (75.2)	7.5 (7.8)	4.7	250, 290, 435, 565, 1175.		

m = melts.

tallization. (H<sub>2</sub>J, m.p. 191. Found C, 70.41; H, 5.32; N, 10.43; C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub> Reqd. C, 71.32; H, 5.42; N, 10.85%) (HL, m.p. 200°. Found: C, 74.10; H, 5.13; N, 12.02; C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub> Reqd. C, 73.47; H, 4.96; N, 12.24%).

I.r. and electronic spectra, in nujol, were recorded on a Perkin-Elmer 621 and a Cary 14 respectively. Magnetic measurements were carried out on a Faraday balance using Hg[Co(NCS)<sub>4</sub>] as the calibrant. Diamagnetic corrections were

applied using Pascal's constants. Some important, and octahedral stereochemistry respectively like i.r. bands are given in Table II. salicylaldimine complexes<sup>1</sup>. Similarly Co<sup>II</sup> com-

TABLE II  
Some important i.r. bands of  $H_2J$ ,  $HL$  and their  $Cu^{II}$ ,  $Ni^{II}$ ,  $Co^{II}$  complexes

Sl. No.	Complexes	$\nu(OH) + \nu(NH)$	$\nu(C=O)$	$\nu(C=N)$	Amide II + $\nu(C-O)$ Phenyl	Amide III
	$H_2J$	3490 3380 3220	1625	1610	1584 1548	1365
(a)	$Cu(HJ)Cl$	3315 3125 3100	1610	1610	1584 1540	1400 1373
(b)	$Cu(HJ)_2$	3490 3375 3210	1623	1605	1569 1545	1375
(c)	$NiJ$	3260 3195 3070	..	1602 1590	1570 1525	1385 1365 1355
	$HL$	3376 3316	1642	1614 1600	1542	1371
(d)	$CuLCl$	3458 3436 3216 3084	1616	1604	1570	1392
(e)	$NiLCl \cdot H_2O$	3360 3240	1617	1600	1570 1544	1390
(f)	$CoLCl \cdot H_2O$	3250 3066 2974	1617	1596	1667 1542	1390

#### RESULTS AND DISCUSSION

$Cu^{II}$  forms 1:1 complexes with both the ligands in ethanol but 1:2  $Cu(HJ)_2$  in aqueous medium.  $Ni^{II}$  and  $Co^{II}$  yield 1:1 complexes in ethanol but fail to react in aqueous medium.

The complexes prepared in the ethanolic medium carry one chloride ion. The complexes are coloured and insoluble in common organic solvents and decompose above 250° except the  $Cu^{II}$  complex (d) which melts at 200°. A broad band in 3600–3400  $cm^{-1}$  region indicates the presence of water molecules in some of the complexes.

Electronic absorption bands of  $H_2J$  at 222, 245, 295 and 375 nm and those of  $HL$  at 238, 305 and 325 nm, considerably shift towards red in the metal complexes due to metal-ligand bonding. The complexes (a, b, d) absorb at 625, 625 and 685 nm respectively like other planar complexes<sup>7</sup>. The colour, absorption bands and magnetic data of  $Ni^{II}$  complexes (c and e) correspond to planar

plex (f) appears to have mixed planar and octahedral stereochemistry in solid state.

Broad, i.r., bands centred at 3490, 3380, 3220  $cm^{-1}$  in  $H_2J$  and 3370, 3316  $cm^{-1}$  in  $HL$  due primarily to  $\nu(OH) + \nu(NH)$  show the presence of strong intramolecular hydrogen bonding. The presence of these bands in the complexes suggest the presence of H-bonded residues in complexes. Bonding through  $>C=O$  is, however, evident from the negative shift in  $\nu(C=O)$ . Similar, but small, negative shift in  $\nu(C=N)$  may be due to coordination of one  $>C=N$  group. Amide II (1550  $cm^{-1}$ ) bands in the ligands split and show positive as well as negative shifts confirming, indirectly, the coordination of  $>C=O$  group.  $\nu(C-O)$  (1250  $cm^{-1}$ ) also shifts to higher frequency on chelation.

In  $NiJ$  (c), however,  $\nu(C=O)$  (1625  $cm^{-1}$ ) of ligand is replaced by a doublet around 1600  $cm^{-1}$  indicating the absence of  $>C=O$  group due to



enolization. Bonding through  $\text{NCO}^-$  group<sup>5</sup> is evident from a strong band around  $1525\text{ cm}^{-1}$ .

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### CONTRIBUTION TO THE INDIAN CAPNODIACEAE

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#### INTRODUCTION

**D**URING the fungal survey of some of the forests of Western Ghats the authors collected a number of plants infected with sooty moulds. Critical study revealed that they belong to the genus *Capnodium* Mont. Batista and Cifferi<sup>1</sup> (1963) have recognised 13 species of this genus distributed throughout the world, based on the morphology of perithecia, asci and ascospores. From India 12 species are recorded (Butler and Bisby<sup>2</sup>, 1931 and 1962), but their identity is doubtful. It is therefore worthwhile to revise the Indian species of *Capnodium*, in the light of Batista and Cifferi's work (1963).

The authors made intensive collection of the species of *Capnodium* and the specimens have been deposited in the mycological herbarium of the Botany Department, Shivaji University. This paper deals with two new species of *Capnodium* Mont, collected during their studies.

#### (1) *Capnodium batistae* sp. nov.

Mycelium moniliform, septate with subglobose cells  $8.5\text{--}10 \times 4.5\text{--}8\ \mu$ , usually dark brown, forms subiculum on the leaves.

Pycnidia flasklike, occasionally round, when flasklike often branched, narrow at the upper part and swollen at the middle part, dark brown,  $400\text{--}520\ \mu$  in height,  $32\text{--}40\ \mu$  in breadth at the middle part and  $16\text{--}18\ \mu$  in breadth at the upper part. Pycnidiospores hyaline  $1\text{--}1.5\ \mu$ , round.

Perithecia dark brown,  $80\text{--}96 \times 75\text{--}85\ \mu$ , oval to round, but slightly narrow at the tip and arise usually from the base of the pycnidia. Perithecial wall made up of polygonal cells  $4.7\text{--}4.5 \times 6\text{--}6.5\ \mu$ . Asci elliptical, bitunicate and 8-spored,  $24\text{--}28 \times$

$10\text{--}11.5\ \mu$ , sessile, apophysate. Ascospores elliptical to elongate, with 2 transverse septa but without vertical septa, hyaline, slightly pointed at the tips,  $8\text{--}9 \times 1\text{--}1.5\ \mu$ .

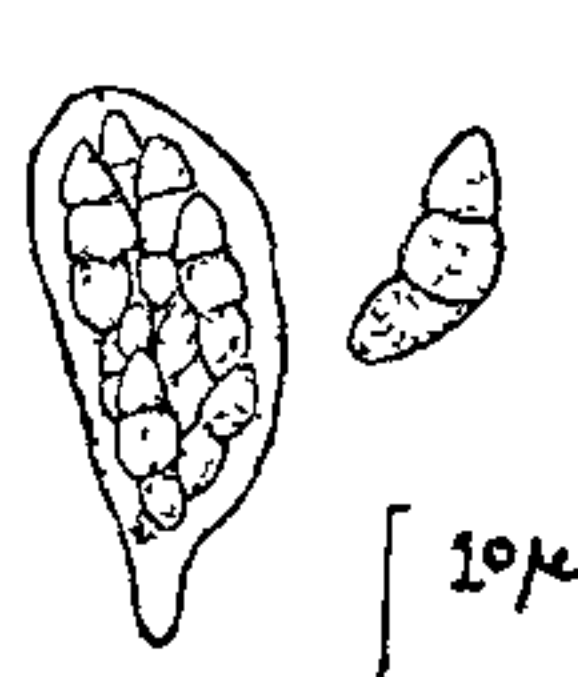


FIG. 1

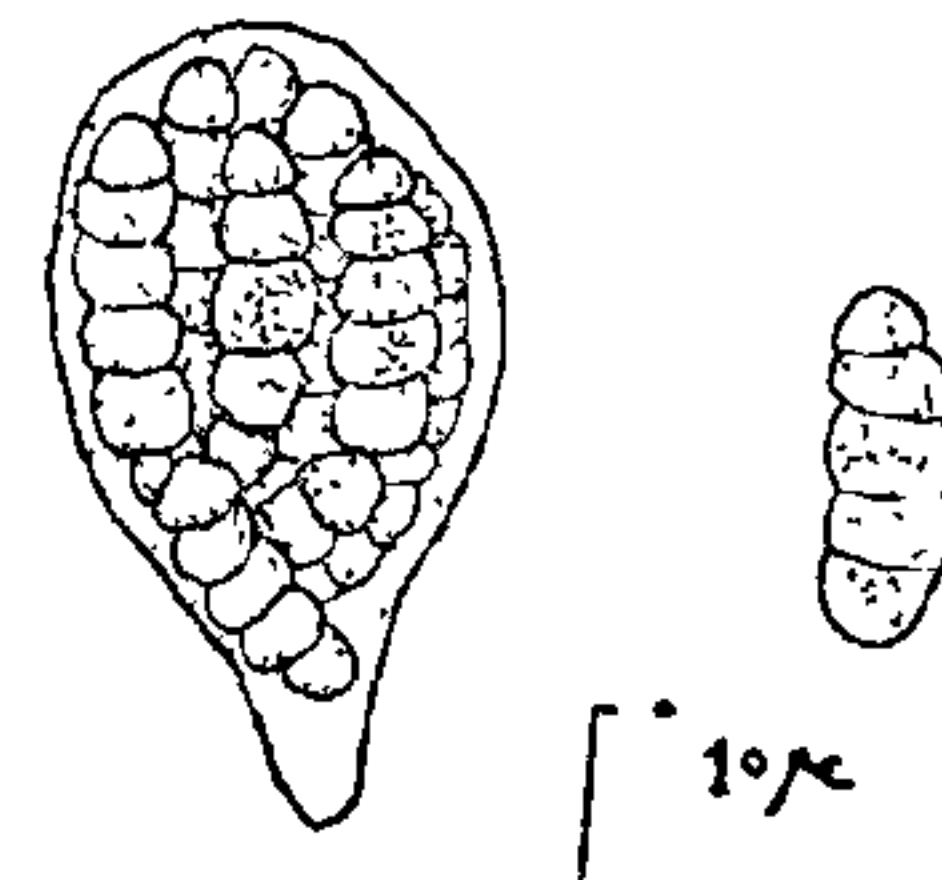


FIG. 2

FIGS. 1-2. Fig. 1. Ascus and ascospore of *Capnodium batistae*. Fig. 2. Ascus and ascospore of *Capnodium kamatii*.

On the leaves of *Ficus carica* L. (Urticaceae) Agri. College Campus, Kolhapur, collected by D. K. Kulkarni on 7-7-1976. Maintained under reference number Cap. No. 1 (Holotype).

Table I clearly shows the difference between new species on *F. carica*, L. and *C. anonae* Pat. which is reported on *F. glomerata*, L., *F. bengalensis*, L., *F. retusa*, L. and *F. bengamina*.

**Latin diagnosis.**—Mycelium moniliformae septatae cellulis subglobosae, magnit  $8.5\text{--}10\ \mu \times 4.5\text{--}8\ \mu$ , plerumque atro-brunneis, subiculum formentibus in foliis.

Pycnidia ampuliformiae, raro sphaerica, ubi ampuliformia seape ramasae, angustatae ad apicem, et inflata, bulbosa, ad median; atro-brunneis  $400\text{--}520\ \mu$  alta,  $32\text{--}40\ \mu$  lata ad median,  $16\text{--}18\ \mu$  lata ad apicem. Pycnidiosporae hyalinae, globosae  $1\text{--}1.5\ \mu$  in diam.