

# COORDINATION COMPOUNDS OF Cu(II) WITH SCHIFF BASES DERIVED FROM 3-FORMYLCAMPHOR AND AROMATIC AMINES

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Copper(II) complexes employing the Schiff bases derived from formylcamphor and aromatic amines as ligands have been prepared. The complex compounds  $\text{CuL}_4(\text{CH}_3\text{COO})_2$  have been characterized by chemical analysis, electronic, IR, EPR spectra, differential thermal analysis and conductivity measurements. The ligands were prepared and characterized by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra.

## Introduction

Our previous papers [1,2] have reported the preparation and characterization of the coordination compounds of some “3d” metals with Schiff bases derived from 3-formylcarvone and 2-formylmenthone with aromatic amines. It seemed desirable to investigate the coordination ability of the Schiff bases derived from 3-formylcamphor and aromatic amines on the Cu(II), for purpose of comparison. Four new ligands able to generate complexes have been synthesized and characterized by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra:

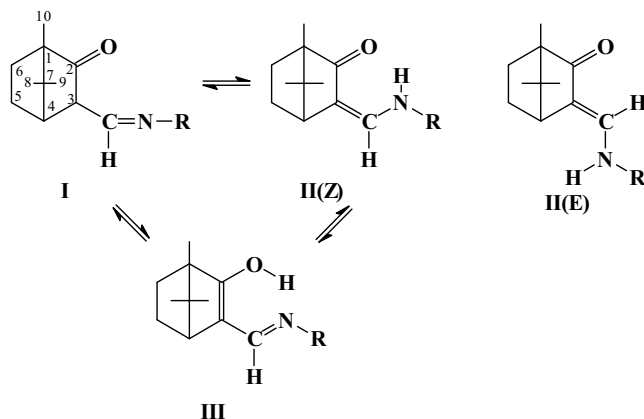
- 3-[(3',4'-dimethylphenylamino)methylen]bornan-2-one (A)
- 3-[(2'-pyridylamino)methylen]bornan-2-one (B)
- 3-[(1'-naphthylamino)methylen]bornan-2-one (C)
- 3-[(4'-chlorophenylamino)methylen]bornan-2-one (D)

The presence of the  $>\text{C}=\text{O}$  and  $>\text{C}=\text{N}$ - groups lying in *ortho* position with respect to each other favours keto-enolic-enamine tautomerism (I – III). The forms I-III may be present in tautomeric equilibrium in solid or in solution.

NMR studies have shown that some Schiff bases with N, O donor atom set exist in solution as enolic tautomer and that the tautomer distribution was solvent dependent [3], but other Schiff bases exist as ketoamine [4-6], the form II being preferred over the form I and III. Knorr and Ruf [7] have shown that the nature of R-substituent brings strong differences in their tautomeric equilibria. In addition, they have shown by NMR-studies, the presence of E/Z isomerism of the form II.

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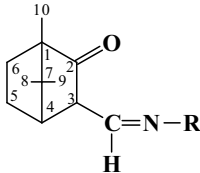
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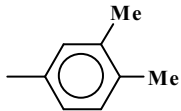
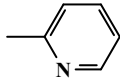
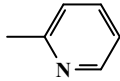
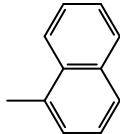
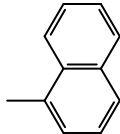
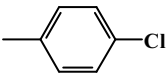
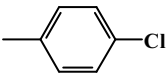


Scheme 1.

Our Schiff bases (A – D) have been characterized by  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  (Table 1).

Table 1.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  chemical shifts (ppm) for ligands A-D in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$



R	$^1\text{H-NMR}$	Assignments	$^{13}\text{C-NMR}$
	6.15-6.1 dH	-CH=N- >C=O	130.57 207
	0.85; 0.95; 0.97	$\text{CH}_3$ -camphor	$\text{C}_{10}$ $\text{C}_9$ $\text{C}_8$ 9.3 18.81 20.36
	2.18; 2.22 S3H 6.07	$\text{CH}_3$ ring -CH=N- >C=O	138 203
	9.98 0.99; 0.85; 0.71	NH $\text{CH}_3$ camphor	$\text{C}_{10}$ $\text{C}_9$ $\text{C}_8$ 9.0 18.5 20.2
	7.2; d; 11.4	-CH=N- >C=O	132 209.14
	9.75 0.89; 0.94; 1.04 S3H	NH $\text{CH}_3$ camphor	$\text{C}_{10}$ $\text{C}_9$ $\text{C}_8$ 9.07 19.0 20.3
	7.1 6.83-6.9 10.77	-CH=N- >C=O NH	131.53 209.14
	0.84; 0.92; 0.97 S3H	$\text{CH}_3$ camphor	$\text{C}_{10}$ $\text{C}_9$ $\text{C}_8$ 9.02 18.94 20.48

The spectra suggest that in  $\text{CDCl}_3$  solution these Schiff bases are tautomerised into both I-II forms.

## Experimental

The ligands were prepared according to literature and  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  p.a. Merck was used.

The coordination compounds,  $\text{CuL}_4(\text{CH}_3\text{COO})_2$  have been obtained following the same general procedure. In a typical experiment to a methanolic solution of ligand (2 mmol) was added a methanolic solution of Cu(II) acetate (1 mmol). To this reaction mixture, 10 ml of water were added. The precipitate obtained were filtered off, washed with water and air-dried.

The copper contents were determined by gravimetrically analyses. The nitrogen contents were determined by microcombustion.

IR spectra (KBr, pellets) were measured on a BIO-RAD FTS-135 Spectrometer.

EPR spectra were recorded at room temperature in polycrystalline powders on ART-5-IFA Spectrograph. The clystron frequency was 9060 MHz. The EPR spectral parameters were calculated against a Mn(II) standard.

The electronic diffuse spectra within 300-1100 nm range were obtained with VSU-2P Zeiss-Jena Spectrophotometer, using MgO as a standard.

NMR spectra-all spectra were recorded on a Varian Gemini 300 Spectrometer operating at 300 MHz ( $^1\text{H}$ -NMR) and 75 MHz ( $^{13}\text{C}$ -NMR) respectively, in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$ . The chemical shifts were referred to tetramethylsilane (TMS) as the internal standard.

Conductivity measurements were performed in methanol solution  $10^{-3}$  M on a Radelkis OK 102/1 Conductometer.

Thermodifferential analyses were carried out with a Paulik-Paulik-Erdey Derivatograph Q-1500 D MOM. Conditions of measurements: temperature range at  $1000^\circ\text{C}$ ; heating program: 10 degree /min; sensivity DTA = 1/10; m = 0.0190 g; S = 20 mg; atmosphere over sample air.

## Results and Discussion

Synthesis complex compounds were performed in methanolic medium from the ligands (A-D) and Cu(II) acetate monohydrate in a molar ratio Cu:L = 1:2, but the complex compounds having the general formula  $\text{CuL}_4(\text{CH}_3\text{COO})_2$  were obtained only, when 10 ml water are added to the mixture reaction (Table 2).

The complex compounds are sparingly soluble in water and soluble in organic solvents (methanol, ethanol, chloroform).

Conductivity measurement has shown their non-electrolyte character [8] supporting their formulation on the bases of the chemical analysis.

Diffuse reflectance electronic spectra of the complex compounds are similar (Table 3).

These spectra are consistent with a elongated tetragonal octahedral stereochemistry. The spectra of our complex compounds yield only one broad absorption band. It is known, that

the absorption band, owing to d-d transition expected for Cu(II) ion in a elongated tetragonal octahedron within the 550÷700 nm range, is shifted towards the near UV range when the Cu(II) ion is in a distorted octahedron towards square-planar [9÷12].

**Table 2. Results of the elemental analyses and molar conductivity in methanolic solution  $10^{-3}$  M.**

No.	Molar ratio Cu:L	Complex	Colour	Cu%		N%		$\lambda_M$ $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$
				Found/calcd	Found/calcd	Found/calcd	Found/calcd	
1	1:2 and 1:4	$\text{CuA}_4(\text{CH}_3\text{COO})_2$	Light-green	4.08/4.83	4.50/4.26	67		
2	1:2 and 1:4	$\text{CuB}_4(\text{CH}_3\text{COO})_2$	Light-green	5.31/5.27	11.66/9.29	57		
3	1:2 and 1:4	$\text{CuC}_4(\text{CH}_3\text{COO})_2$	Brown	3.26/4.53	4.85/3.79	71		
4	1:2 and 1:4	$\text{CuD}_4(\text{CH}_3\text{COO})_2$	Light-green	6.12/5.45	4.48/4.18	7		

**Table 3. Electronic spectral data and EPR spectral parameters**

No.	Compound	$\lambda_{\text{max}}$ (nm)	$g_{\perp}$	$g_{\parallel}$
1	$\text{CuA}_4(\text{CH}_3\text{COO})_2$	720	2.0745	2.166
2	$\text{CuB}_4(\text{CH}_3\text{COO})_2$	708	-	-
3	$\text{CuC}_4(\text{CH}_3\text{COO})_2$	500	2.05	2.2250
4	$\text{CuD}_4(\text{CH}_3\text{COO})_2$	500	-	-

The EPR spectra recorded at room temperature on polycrystalline samples presents EPR signals characteristic of a monomeric species of Cu(II) with varied degrees of axial distortion for complex compound 1 and 3 only (Table 3) and Fig. 1. The shape of the line is in agreement with the geometry of the elongated axial octahedron with  $g_{\parallel} > g_{\perp}$ .

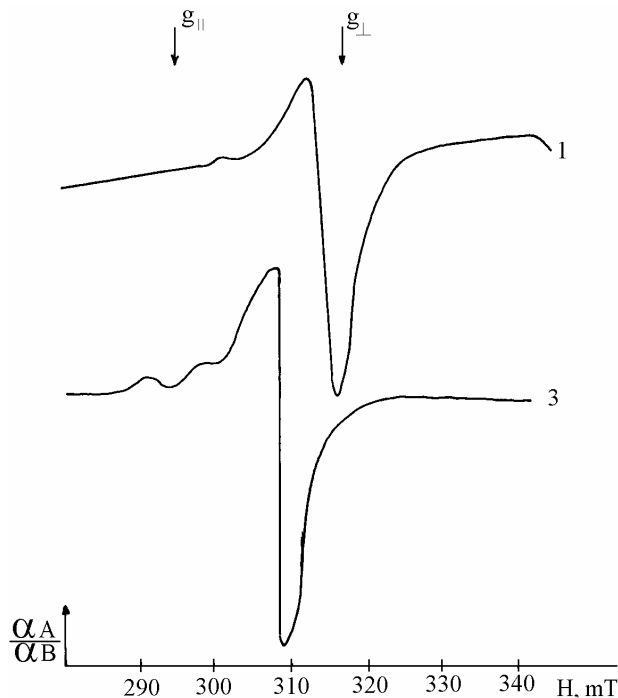


Fig. 1: EPR Spectra of the compounds 1 and 3.

Thermodifferential analysis curves for the complex compounds are similar. In Fig. 2 is shown in detail thermodifferential curve for  $\text{CuA}_4(\text{CH}_3\text{COO})_2$ . The results indicate that the compound is stable up to  $175^\circ\text{C}$ , but rapidly loses ligands, up to  $360^\circ\text{C}$  (weight loss at  $360^\circ\text{C}$ , found: 54.10%, calcd: for  $2\text{L}(\text{CH}_3\text{COO}) = 52.2\%$ ); the weight loss continues up to  $550^\circ\text{C}$  when it begins an oxidation process.

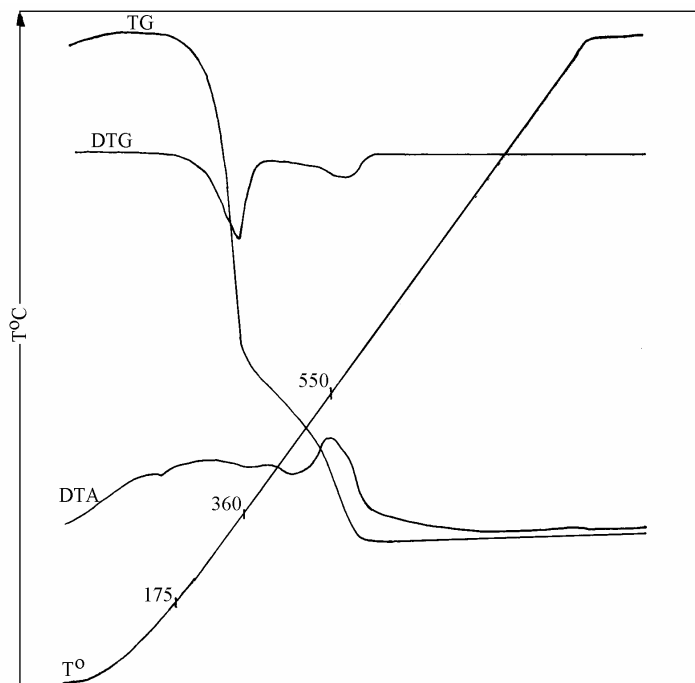


Fig. 2: Thermodifferential curve of  $\text{CuA}_4(\text{CH}_3\text{COO})_2$  compound.

IR spectra. The positions of some infrared absorption bands within the  $700\text{--}4000\text{ cm}^{-1}$  range are listed in Table 4. The band's assignments are based on the infrared spectra of the free ligands.

It has been concluded from infrared evidence, that these ligands are tautomerised into both I and II forms. This tautomerism is supported by the presence of the bands  $\nu_{\text{C=N}}$ ,  $\nu_{\text{C=O}}$  and  $\nu_{\text{NH}}$  and by the splitting of some bands, supporting their NMR spectra. The differences observed in the shape, intensity and position of these bands in the IR spectra of the free ligands could be explained by the nature of the R-substituent on N atom.

The sharp band which occurs in  $3278\text{--}3331\text{ cm}^{-1}$  range is rather due to  $\nu_{\text{NH}}$  than  $\nu_{\text{OH}}$  non-associated which appears near  $3600\text{ cm}^{-1}$ . The band due to  $\nu_{\text{C=O}}$  ( $1695\text{--}1706\text{ cm}^{-1}$ ) appears as a sharp and very strong or medium one and the band due to  $\nu_{\text{C=N}}$  ( $1629\text{--}1632\text{ cm}^{-1}$ ) appears as very strong band with two or three peaks.

The examination of the complex compound spectra shows some remarks:

- the band due to  $\nu_{\text{C=N}}$  is shifted to higher values ( $1611\text{ cm}^{-1}$ ) for compound 2, only;

- the band due to  $\nu_{C=O}$  appears as a very strong one and is shifted to lower values ( $1682\text{ cm}^{-1}$ ) for compound 3, only, this consists as an argument for the coordination of ligand C by O atom donor;
- for this compound the bands due to  $\nu_{NH}$  and  $\nu_{C=N}$  are not changed or changed little;
- the band due to  $\nu_{NH}$  is less intense and is shifted little to higher values. For compounds 1 and 4 appears a new broad band centered at  $3434\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  respectively. This new band could indicate the formation intramolecular hydrogen bond as in form II(Z) (Scheme 1) by the coordination to Cu(II) ion;
- the assignment of the bands due to  $\nu_{COO^- \text{ asym}}$  ( $1574\text{ cm}^{-1}$ ) and  $\nu_{COO^- \text{ sym}}$  ( $1414\text{ cm}^{-1}$ ) characteristic for acetate ion was not possible because of their overlapping with the bands present within range.

**Table 4. The main absorption bands in the IR spectra ( $\text{cm}^{-1}$ ) and their assignments**

Ligand/Compound	$\nu_{NH}$	$\nu_{C=O}$	$\nu_{C=N}$
A	3298w	1695m	1594s
$\text{CuA}_4(\text{CH}_3\text{COO})_2$	3300w	1694m	1581vs
	3434w br		1595vs
			1581s
B	3312vw 3281vw	1706vs	1604vs
$\text{CuB}_4(\text{CH}_3\text{COO})_2$	3312m 3282m	1703vs	1573vs
			1482vs
			1611vs
			1571vs
			1478s
C	3278w	1697m	1632s
$\text{CuC}_4(\text{CH}_3\text{COO})_2$	3283vw	1679m	1611vs
		1682vs	1572s
			1633s
			1612vs
			1578s
D	3280m	1703s	1611s
$\text{CuD}_4(\text{CH}_3\text{COO})_2$	3295w 3400br	1703m	1580vs
			1614vs
			1590s

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; br = broad

All these changes could suggest possibility of coordination of this ligands to Cu(II) ion by either O atom donor (compound 3) or N atom donor (the other ones), the ligands acting monodentately forming compounds of the  $\text{ML}_4(\text{CH}_3\text{COO})_2$  type. The six coordinated surrounding of the Cu(II) ion is due to axially binded acetate ion.

Based on the above data the following structural formula is suggested for  $\text{CuA}_4(\text{CH}_3\text{COO})_2$  compound (Fig. 3).

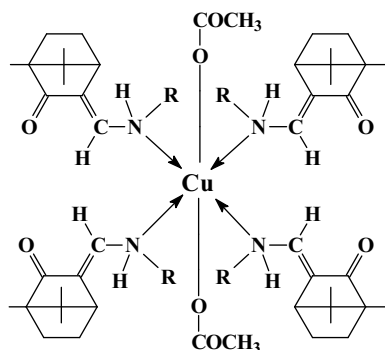


Fig. 3: Structural formula proposed for the  $\text{CuA}_4(\text{CH}_3\text{COO})_2$  compound.

## Conclusions

In the new obtained complexes, the Cu(II) is hexacoordinated.

The ligands A-D act monodentately in the tautomeric form (II) by the N atom donor (ligands A, B, D) and by the O atom donor (ligand C with a bulky R-substituent on the N atom).

The two acetate anions are axially bounded.

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