

COORDINATION COMPOUNDS OF Cu (II) WITH AZOMETHINE

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abstract: Cu (II) complexes employing the Schiff bases derived from 3-formylcarvone, 2-formylmenthone and 3-formylcamphor and *p*-aminobenzoic acid have been prepared. The complex compounds $\text{CuL}_2 \cdot 2\text{H}_2\text{O}$, $(\text{CuLCH}_3\text{COO})_2$, $[\text{CuL}_4](\text{CH}_3\text{COO})_2$ and CuL_2 have been characterized by chemical analysis, electronic, IR, EPR spectra, thermodifferential analysis, and conductivity measurements.

Introduction

The present interest in the study of the reactivity of some substances existing in plants (caraway, dill, mint) such as carvone, menthone and their derivatives might be explained by the numerous applications (in medicine, industry of odorant products, additives in food industry).

Our previous papers [1,2] has reported the synthesis and characterization of the coordination compounds of some “3d” metals with Schiff bases derived from 3-formylcarvone, 3-formylcamphor and 2-formylmenthone and *o*-, *m*-, *p*-toluidine. The position of the methyl substituent on the benzene ring has determined the type of the complex compound and monodentate and bidentate coordination of the ligand.

It seemed desirable to investigate, for purpose of comparison, how the different nature of the formyl-derivatives could influence the coordination ability of these Schiff bases.

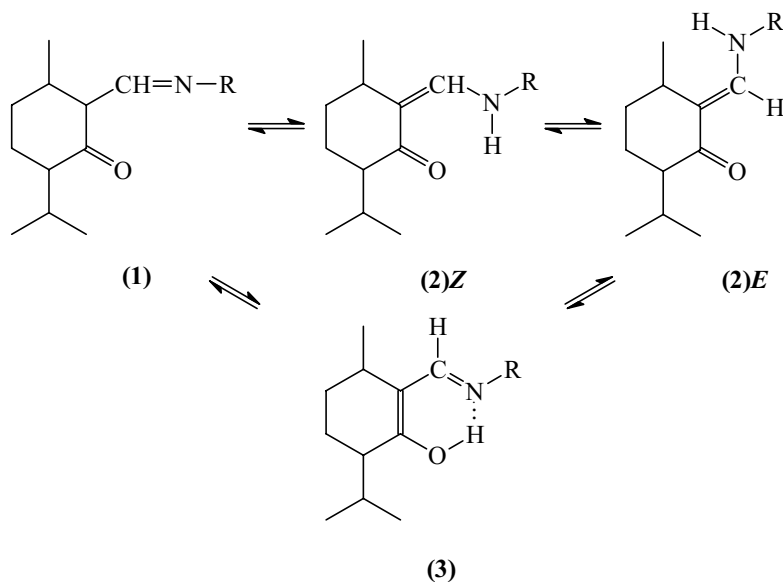
This paper describes the coordination ability of the three Schiff bases derived from the formylmenthone, formylcarvone and formylcamphor and the same aminoacid, *p*-aminobenzoic acid. The presence of the $>\text{C}=\text{O}$ and $>\text{C}=\text{N}$ - groups lying in vicinal position with respect to each other favours keto-enolic-enamine tautomerism (Scheme 1). NMR studies have shown that some Schiff bases exist in solution as enolic tautomer (3) and that tautomer distribution was solvent dependent [3].

Three ligands able to generate complexes have been synthesized:

- 4-isopropenyl-1-methyl-3-[(phenylamino)-methylene]-1-ciclohexene-2-one-4'-carboxylic acid noted A;

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- 4-isopropyl-1-methyl-2-[(phenylamino)-methylene]-cyclohexan-3-one-4'-carboxylic acid noted B;
- 3-[(phenylamino)-methylene]-bornan-2-one-4'-carboxylic acid noted C.



Scheme 1.

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 copper contents were determined by the gravimetric analyses. The carbon, hydrogen contents were determined by microcombustion.

Syntheses:

1. $\text{CuA}_2 \cdot 2\text{H}_2\text{O}$; The complex compound was prepared by mixing warm methanol solutions 50% of Cu (II) acetate (1 mmole) and ligand (2 mmoles). The resulting precipitate was filtered off in vacuum and washed with aqueous methanol solution 50% and air-dried. Analysis for: $\text{C}_{36}\text{H}_{36}\text{O}_7\text{N}_2$ calculated: Cu, 9.24; C, 62.83; H, 5.24; found: Cu, 8.95; C, 63.02; H, 4.84.

2. $(\text{CuBCH}_3\text{COO})_2$; To a warm methanol solution ($\sim 40^\circ\text{C}$) of ligand **B** (2 mmoles) it was added a warm methanol solution (40°C) of Cu (II) acetate (1 mmole). The microcrystalline khaki colored sparingly soluble product was filtered off in vacuum, washed with methanol and air-dried. Analysis: $\text{Cu}_2\text{C}_{40}\text{H}_{50}\text{O}_{10}\text{N}_2$ % calculated: Cu, 15.02; C, 56.79; H, 5.96; N, 3.33; % found: Cu, 15.17; C, 56.55; H, 5.73; N, 3.62.

3. $[\text{CuB}_4](\text{CH}_3\text{COO})_2$; To the remaining light green filtrate from the synthesis of the compound **2**, 10 ml of water were added; immediately a microcrystalline light-green

colored product precipitated. This was filtered off, washed with water and air-dried. Analysis: $\text{CuC}_{76}\text{H}_{98}\text{O}_{16}\text{N}_4$ % calculated Cu, 4.58; C, 65.79; H, 7.12; N, 4.05; % found: Cu, 4.39; C, 65.52; H, 7.01; N, 4.15. The same compound was isolated by crystallization of the remaining methanol filtrate without addition of water.

4. CuC_2 ; To a warm methanol solution ($\sim 40^\circ\text{C}$) of ligand was added a warm methanol solution of Cu (II) acetate (1 mmole). The microcrystalline light-green colored sparingly soluble, product was filtered off in vacuum and washed with methanol. Analysis for $\text{CuC}_{36}\text{H}_{40}\text{O}_6\text{N}_2$ calculated: Cu, 9.63; C, 65.50; H, 6.06; found: Cu, 9.24; C, 65.21; H, 7.18;

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 were recorded on a Varian Gemini 300 Spectrometer operating at 300 MHz (^1H -NMR) and 75 MHz (^{13}C -NMR) respectively, in CDCl_3 or $\text{DMSO}-d_6$. The chemical shifts were referred to tetramethylsilane (TMS) as the internal standard.

Thermodifferential analysis was carried out with a Paulik-Paulik-Erdey Derivatograph Q-1500 D MOM. Conditions of measurements: temperature range at 1000°C ; heating program 10 degree /min; sensitivity DTA = 1 /10; $m_1 = 0.0180$ g; S = 50 mg; atmosphere over sample air.

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

Results and Discussion

Our Schiff bases A – C have been characterised by ^1H – and ^{13}C – NMR spectra in CDCl_3 and $\text{DMSO}-d_6$ respectively. These spectra put in evidence the presence of keto – enolic – enamine tautomerism. In addition, the spectra have shown that in $\text{DMSO}-d_6$ and CDCl_3 solutions, the ligands B and C exist as enamine tautomer in both *Z/E* diastereoisomers:

Ligand B: ^1H – NMR (CDCl_3 , δ ppm, J_{Hz}): -NH = 9.10 (d, 1H, 12.7, $E = 85\%$); 9.80 (d, 1H, 12.0, $Z = 15\%$); ^{13}C – NMR (CDCl_3 , δ ppm): >CO = 205.3 (*E*); 204.4 (*Z*).

Ligand C: ^1H – NMR ($\text{DMSO}-d_6$, δ ppm, J_{Hz}): -NH = 12.06 (d, 1H, 11.8, $E = 50\%$); 12.20 (d, 1H, 11.7, $Z = 50\%$); ^{13}C – NMR (CDCl_3 , δ ppm): >CO = 203.7.

Synthesis was performed in methanol medium in a molar ratio Cu:L = 1:2 for the ligand B and C and in water – methanol mixture 1:1 for the ligand A. Two different compounds were obtained with the ligand B (Table 1).

The thermodifferential analysis has confirmed the formula of the compound $\text{CuA}_2 \cdot \text{H}_2\text{O}$. The mass loss observed within 120-190 $^\circ\text{C}$ range on TG curve corresponds to the loss of two water molecules per molecule (found: 4.95%, calculated: 5.23%). Hence, the two water

molecules are present as coordinated water. The electrolytic character 1:2 of the $[\text{CuB}_4](\text{CH}_3\text{COO})_2$ compound is showed by the conductivity measurements [4]. Except compound **2**, the others are soluble in organic solvents.

Table 1. Analytical, physical data and molar conductivity, $\lambda(\Omega^{-1}\text{cm}^2\text{mole}^{-1})$

No	Ligand	Complex	Empirical formula	Color	M.p. ($^{\circ}\text{C}$)	λ
1	A	$\text{CuA}_2 \cdot 2\text{H}_2\text{O}$	$\text{C}_{36}\text{H}_{36}\text{O}_7\text{N}_2$	Light-brown	172-174	10
2	B	$(\text{CuBCH}_3\text{COO})_2$	$\text{Cu}_2\text{C}_{40}\text{H}_{50}\text{O}_{10}\text{N}_2$	Khaki	230-232	-
3	B	$[\text{CuB}_4](\text{CH}_3\text{COO})_2$	$\text{CuC}_{76}\text{H}_{98}\text{O}_{16}\text{N}_4$	Light-green	153-155	136
4	C	CuC_2	$\text{CuC}_{36}\text{H}_{40}\text{O}_6\text{N}_2$	Light-green	270-272	15

The diffuse reflectance electronic spectra of the complex compounds are similar; the broad band with a maximum 600÷750 nm range can be assigned to a d-d transition. This band can be associated with a distorted elongated tetragonal octahedron with various degrees of axial distortion up to square planar [5,6] The strong absorption which occurs at ~ 400 nm is assigned to the ligand A. Its “tails off” goes to strongly into the visible range that could explain its colour.

The EPR spectra of the compounds **1** and **4** are similar. The spectra present a EPR signal with two g factors (with $g_{\parallel} > g_{\perp}$) characteristic for the elongated tetragonal octahedral stereochemistry supporting the electronic spectra (Table 2) [5,6]. EPR signal of the compound **3** has a third order anisotropy for the g factor which is compatible with Cu (II) ion in a rhombic distorted geometry, axially elongated⁵. The EPR spectra of compound **2** does not present signal.

Table 2. Electronic spectral data and EPR spectral parameters.

No.	Complex	λ_{max} (nm)	$g_{\parallel} = g_3$	$g_{\perp} = g_2$	g_1
1	$\text{CuA}_2 \cdot 2\text{H}_2\text{O}$	400;600	2.2439	2.036	-
2	$(\text{CuBCH}_3\text{COO})_2$	730	-	-	-
3	$[\text{CuB}_4](\text{CH}_3\text{COO})_2$	700	2.0689	2.1118	2.1566
4	CuC_2	750	2.2320	2.065	-

The most relevant absorption bands in IR spectra of the free ligands and their complex compounds are shown in Table 3.

The keto-enolic-enamine tautomerism is supported by the presence of the bands due to ν_{OH} , ν_{NH} , $\nu_{\text{C=O}}$ and $\nu_{\text{C=N}}$. The different nature of the ring of the ligands A-C could explain the differences occurring in the shape, intensity and position of these bands (Table 3).

IR spectrum of the compounds **1,2** and **4** presents the changes that involve the ν_{OH} and $\nu_{\text{C=N}}$ stretching frequencies suggesting the same donor atoms. The band due to $\nu_{\text{C=N}}$ is shifted to lower values and ν_{OH} band is shifted to higher values (compounds **1** and **2**) or keeping its broad character (compound **4**). Schiff bases containing an N, O, donor atom set, upon coordination to metal ion through both O and N, a decrease of the $\nu_{\text{C=N}}$ frequency and a increase of the ν_{OH} are generally noticed [3]. These changes could suggest that ligands A, C and B in the compound **2** act bidentately by both the O and N donor atoms through the deprotonation of the OH groups making evident the participation of these ligands in enolic

tautomeric form. Cu (II) coordinates with four strong bond N and O donor atoms in a plane and with weaker bond to two axial molecules of water for the compound **1**, only, while in the chelate, CuC₂, Cu (II) ion would be tetracoordinated in a square planar geometry distorted to tetrahedron [6] (Figs. 1 and 2).

Table 3. The main absorption bands in the IR spectra (cm⁻¹) and their assignments.

Ligand/ complex	ν_{OH}	ν_{NH}	$\nu_{C=O}$	$\nu_{C=N}$
A	3405 m	-	1700 m	1680 s
1	3410 s	-	1700 w	1650 sh
B	-	3300 sh	1674 vs	1642 m
2	3410 br	-	-	1639 m
3	3422 br	-	1693 m	1642 s
C	3540-3300 br,s	-	1740 vs	1610 vs
4	3440-3200 m	-	1740 vs	1600m

vs – very strong, s – strong, m – medium, w – weak, vw – very weak, br - broad, sh - shoulder

The IR spectrum of [CuB₄](CH₃COO)₂ compounds shows that the band due to $\nu_{C=O}$ (1674 cm⁻¹) is shifted to higher values (1693 cm⁻¹), while the others did not change. This might suggest the involvement of the carbonyl group upon coordination making evident the participation of ligand B in the keto-tautomeric form, the ligand acted monodentately. The six – coordination surrounding of Cu (II) ion could be achieved by oxygen atoms of the carbonyl in a plane and by longer bonds to axial acetate ion in a distorted elongated rhombic geometry supporting its EPR spectrum.

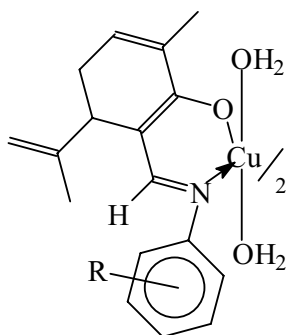


Fig. 1: Structural formula proposed for the CuA₂ 2H₂O compound.

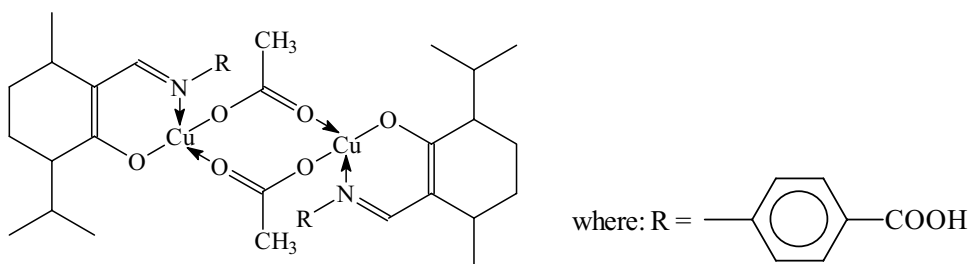


Fig. 2: Structural formula proposed for the $(\text{CuBCH}_3\text{COO})_2$ compound.

Conclusions

The ligands B and C exist in CDCl_3 or $\text{DMSO}-d_6$ solutions as enamino – tautomer forms in both the *Z/E* diastereoisomers, but in methanol solution it is possible to exist as enolic - tautomer forms.

With the ligands A and C the chelates $\text{CuA}_2 \cdot 2\text{H}_2\text{O}$ and CuC_2 were obtained. The ligands act bidentately in enolic - tautomer form.

With the ligand B two compounds: $(\text{CuBCH}_3\text{COO})_2$ and $[\text{CuB}_4](\text{CH}_3\text{COO})_2$ were obtained. The ligand acts bidentately in former in the enolic - tautomer form and monodentately in a latter in the keto – tautomer form.

Some complexes adopted a distorted octahedral stereochemistry and others adopted a square planar geometry distorted up to tetrahedron.

Three complexes were formulated as mononuclear species on the basis of chemical analysis, molar conductivity, thermal behaviour, electronic, IR and EPR spectra, while one was formulated as a binuclear compound.

These differences in the coordination ability of the three Schiff bases could be explained through different nature of the formyl - derivatives (formylcarvone, formylmenthone, formylcamphor).

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