COORDINATION COMPOUNDS OF Cu(II) WITH SCHIFF BASES DERIVED FROM FORMYLMENTHONE AND AROMATIC AMINES

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Abstract

The Schiff bases obtained from formylmenthone and some aromatic amines behave as bidentate ligands with O and N donor atoms in Cu(II) complexes of the type $CuL_2(CH_3OH)_2$, CuL_2, $(CuLCH_3COO)_2$ or as monodentate ligand, $CuL_4(CH_3COO)_2$. The donor atoms and the possible geometry of the complexes were assigned by means of chemical analyses, electronic, EPR and IR spectra and conductivity measurements.

Introduction

Schiff bases represent a versatile series of ligands, the metal complexes of which have been widely studied. The interest in the study of the reactivity of some substances originating from plants (dill, mint, caraway) such as menthone and carvone and their derivatives might be explained by the numerous applications of these natural compounds and their derivatives (in medicine, industry of odorant products, additives in food industry).

Our previous papers[1-3] have reported the synthesis and characterization of the coordination compounds of some 3d metals with formylated derivatives of carvone and menthone[1] and with Schiff bases derived from formylcarvone or formylmenthone and aromatic amines.[2,3] It seemed desirable to investigate the coordination ability of the Schiff bases derived from 2-formylmenthone with aromatic amines, for comparison purpose.

Three new Schiff bases able to generate complex compounds have been synthesized: 6-isopropyl-3-methyl-2-[(2'-nitro-4'-methoxy-phenylamino)-methylene]cyclohexan-1-one (**A**), 6-isopropyl-3-methyl-2-[(4'-carboxyphenylamino)-methylene]-cyclohexan-1-one (**B**), and 6-isopropyl-3-methyl-2-[(2'-carboxyphenylamino)-methylene]-cyclohexan-1-one (**C**).

The nature of the substituent on the N atom of azomethine group could influence the coordination ability of these Schiff bases. In addition, the presence of the >C=O and >C=N- groups lying in vicinal position with respect to each other favors keto-enolic-enamine tautomerism (Scheme 1).
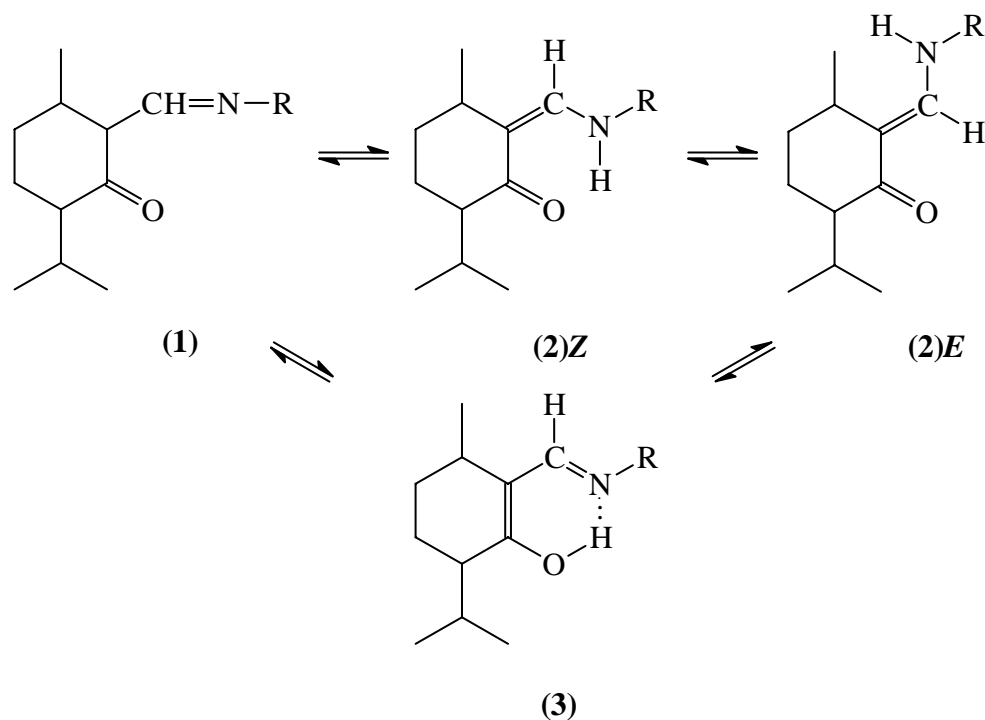
Scheme 1

NMR studies have shown that some Schiff bases exist in solution as the enol tautomer (**3**) and that tautomer distribution is solvent dependent.[4-6]

Results and discussion

The Schiff bases (**A–C**) have been characterized by ^{1}H NMR and ^{13}C NMR spectra in CDCl$_3$.

The spectra suggest that in CDCl$_3$ solution these Schiff bases exist in both tautomeric forms (**1**)–(**2**). The fact that methine protons and deuterable protons (NH) appear as doublets is a good proof of an enamine structure. However the results of NMR analysis did not provide sufficient data to differentiate between the two stereoisomers *E*, *Z* of the enamine form.

Synthesis was performed in methanolic medium in a molar ratio Cu:L = 1:2. The new complex compounds were obtained by interaction of the methanolic ligand solution with methanolic Cu(II) acetate solution. Two different complexes of the same Schiff base noted **B**, were obtained: (Cu**B**CH$_3$COO)$_2$ and [Cu**B**$_4$](CH$_3$COO)$_2$. Characteristic data for the Cu(II) complexes are presented in Table 1.

Table 1. Analytical and physical data and molar conductivity, λ (Ω^{-1}cm^{2}mol^{-1}).

| No.	Ligand	Compound	Empirical formula	Color	mp (°C)	λ
1	**A**	Cu**A**$_2$(CH$_3$OH)$_2$	CuC$_{38}$H$_{54}$O$_{10}$N$_4$	Red	105–107	12
2	**B**	(Cu**B**CH$_3$COO)$_2$	Cu$_2$C$_{40}$H$_{50}$O$_{10}$N$_2$	Khaki	230–232	-
3	**B**	[Cu**B**$_4$](CH$_3$COO)$_2$	CuC$_{76}$H$_{98}$O$_{16}$N$_4$	Light green	153–155	136
4	**C**	Cu**C**$_2$	CuC$_{36}$H$_{44}$O$_6$N$_2$	Brick	238–240	19

Analytical results for Cu, C, H, N were within ± 0.4% of calculated values for all the synthesized compounds.

The complexes are sparingly soluble in water, but soluble in organic solvents, except (Cu**B**CH$_3$COO)$_2$.

All the complexes have been characterized by electronic, EPR, IR spectra, and conductivity measurements. The conductivity measurements supported the electrolytic character 1:2 of [Cu**B**$_4$](CH$_3$COO)$_2$ compound and the non-electrolytic nature of the others.[7]

Electronic spectra. Diffuse reflectance electronic spectra of the complex compounds (Table 2) are similar and they present one broad absorption band (600–800 nm range) with λ_{max} differently centered, which was assigned to a d-d transition expected for Cu(II) complex compounds in a distorted tetragonal octahedron with various degrees of axial distortion.[8-10] In addition the spectrum of compound **4** presents a shoulder (520 nm), which could be assigned to the ligand **C**.

The EPR spectra recorded at room temperature on polycrystalline samples present EPR signals characteristic to a monomeric species of Cu(II) with various degrees of axial distortion for the complex compounds **1**, **3** and **4** only (Table 2, Figure 1).
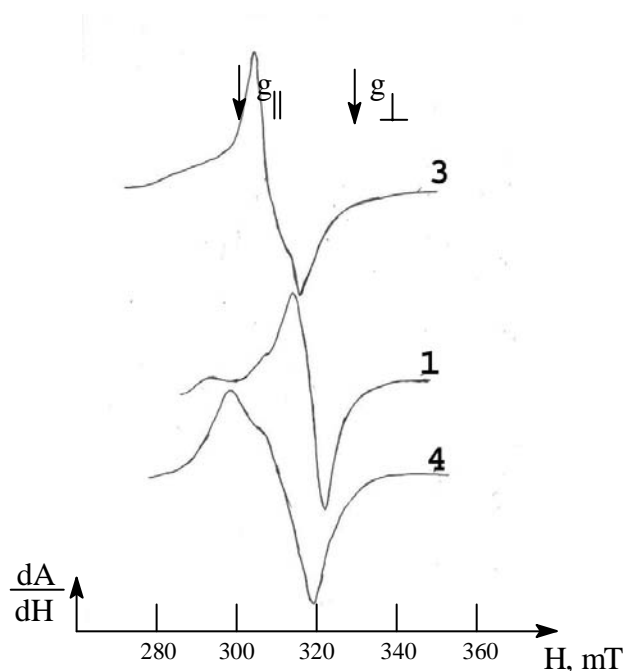
Figure 1. EPR spectra of the compounds **1**, **3** and **4**.

The shape of the line is in agreement with the geometry of the elongated axial octahedron with $g_\parallel > g_\perp$ (compounds **1** and **4**), in agreement with the assignment given on the basis of the electronic spectra.[8] The EPR signal of $[CuB_4](CH_3COO)_2$ compound has a third order anisotropy for the factor g, which is compatible with Cu(II) ion in a rhombic distorted geometry, axially elongated.[8-10] The EPR spectrum of $(CuBCH_3COO)_2$ does not present signal. This is probably due to the increase in the exchange interactions enabling some dimer structure and it is proved by its insolubility and thermal stability (mp 230 °C).

Table 2. Electronic spectral data and EPR spectral parameters.

No.	Compound	λ_{max}	g_1	$g_\perp = g_2$	$g_\parallel = g_3$
1	$CuA_2(CH_3OH)_2$	750	-	2.0647	2.1430
2	$(CuBCH_3COO)_2$	730	-	-	-
3	$[CuB_4](CH_3COO)_2$	700	2.0689	2.1118	2.1566
4	CuC_2	520sh; 740	-	2.1295	2.2273

IR spectra. The positions of some infrared absorption bands within the 400-4000 cm^{-1} are listed in Table 3. The band assignments are based on the infrared spectra of the free ligands.

Table 3. The main absorption bands and their assignments in IR spectra (cm^{-1}).

No.	Ligand / compound	$\nu_{OH\ assoc.}$	ν_{NH}	$\nu_{C=O}$	$\nu_{C=N}$ $\nu_{C=C}$	ν_{COOH} assym/sym	$\nu(NO_2)$ assym/sym
	A	3482w	3368w	1675vw	1642m 1579m	-	1523vs 1336vs
1	CuA$_2$(CH$_3$OH)$_2$	3500br	-	-	1615vw 1587m	-	1525vs 1368vs
	B	-	3300sh	1674vs	1642m 1600vs 1553s	1276vs 1155vs	-
2	(CuBCH$_3$COO)$_2$	3410br	-	-	1639m 1601s	1278m 1167m	-
3	[CuB$_4$](CH$_3$COO)$_2$	3422br	-	1693m	1642s 1604vs 1559s	1276s 1171s	-
	C	3425br	-	1700vw	1639vw 1601vw 1590vw	1280vw 1250vw	-
4	CuC$_2$	3500br	-	-	1630sh 1601vw 1590vw	1280vw 1230vw	-

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

The keto-enolic-enamine tautomerism (Scheme 1) is supported by the presence in IR spectra of free ligands of the bands due to: $\nu_{C=O}$, ν_{OH}, ν_{NH}, $\nu_{C=N}$ and by the splitting of some bands. The nature, number and position of the groups substituted on the benzene ring could explain the differences occurring in the shape, intensity and position of these bands. Thus, for ligand **A**, the band 3482 cm^{-1} can be assigned to ν_{OH} characteristic to the OH group associated through an intramolecular hydrogen bond, O-H…N (Scheme 1), but the band 3368 cm^{-1} is rather due to ν_{NH}. The spectrum of ligand **C** presents a broad band with four peaks, but the spectrum of ligand **B** presents a shoulder at 3300 cm^{-1} in this range. For ligands **B** and **C** this band could be the result of overlapping of the bands due to ν_{OH} and ν_{NH} with ν_{COOH} band characteristic to aryl-COOH group. The band due to $\nu_{C=O}$ (1674-1700 cm^{-1} range) occurs as a very weak (ligands **A** and **C**) or a

very strong band (ligand **B**). The band due to $\nu_{C=N}$ occurs as a broad one with some peaks (ligands **B** and **C**), or as a band with two peaks (ligand **A**); only the higher frequency band has been empirically assigned to $\nu_{C=N}$. This assignment is supported by its sensitivity to metal ion complexation.[6] The IR spectrum of $CuA_2(CH_3OH)_2$ shows that the $\nu_{C=N}$ (1642 cm^{-1}) band is shifted to lower value (1615 cm^{-1}) and the ν_{OH} band is shifted to higher value (3500 cm^{-1}). These changes are generally noticed upon coordination of the Schiff bases containing N and O donor atoms, through both donor atoms making chelate structure.[6] The ligand **A** acts bidentately through both O and N donor atoms by deprotonation of the OH group making evident the participation of the ligand in the enolic tautomeric form. The $\nu_{C=O}$ (1675 cm^{-1}) disappeared. The six-coordinated surrounding of the Cu(II) is due to axially bound methanol molecules (Figure 2). The IR spectrum of CuC_2 compound shows the same changes, suggesting the same chelate structure. If its formula is correlated with electronic spectrum data, Cu(II) ion would be tetracoordinated in a distorted square-planar geometry.[10] Nevertheless, we must not exclude the possibility of a six-coordinated surrounding of the Cu(II) ion, due to the O donor atom from COOH group in ortho -position on the benzene ring, which supports the EPR spectrum of the compound.

For $(CuBCH_3COO)_2$, almost all characteristic bands of ligand **B** are changed (number, position, intensity), but these changes involve the ν_{OH} and $\nu_{C=N}$ stretching too, suggesting for ligand **B** the same coordination as for ligands **A** and **C**. These changes, correlated with the information given by the electronic and EPR spectra and its insolubility could suggest that Cu(II) ion is tetracoordinated in a dimer structure through both N and O donor atoms with acetate ion as a bidentate bridge (Figure 3a). The assignment of the bands due to ν_{COOH} (1574 cm^{-1} asymm. and 1414 cm^{-1} sym.) of the acetate ion or when it serves as bidentate bridge (1603 cm^{-1}, 1418 cm^{-1} respectively)[11] was not possible, because of their overlapping with other bands in this range.

The IR spectrum of $[CuB_4](CH_3COO)_2$ compound shows that the very strong band ($\nu_{C=O}$, 1674 cm^{-1}) is shifted to a higher value (1693 cm^{-1}), while the others are not changed. This might suggest the involvement of the carbonyl group in coordination, thus making evident the participation of ligand **B** in the keto tautomeric form (**1**). The ligand acts monodentately. The six-coordination surrounding of Cu(II) ion could be achieved by oxygen atoms of the carbonyl group in a plane and by longer bonds to axial acetate ion
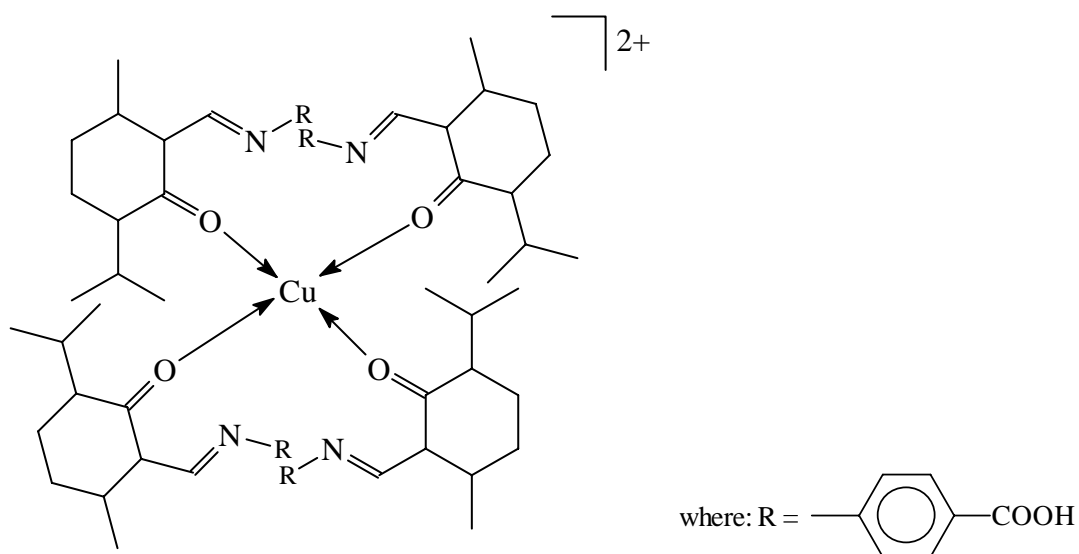
in a distorted elongated rhombic geometry. This is supported by its EPR and electronic spectra (Figure 3b).
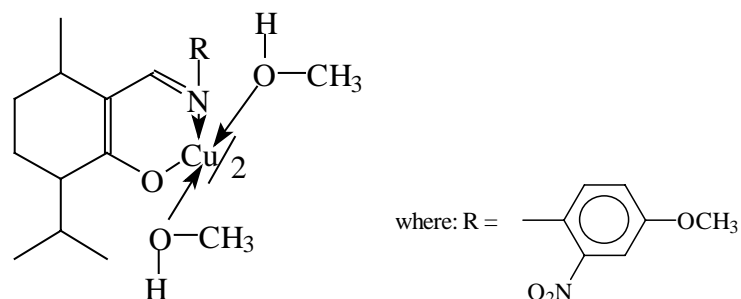
Figure 2. Suggested structural formula for $CuA_2(CH_3OH)_2$.
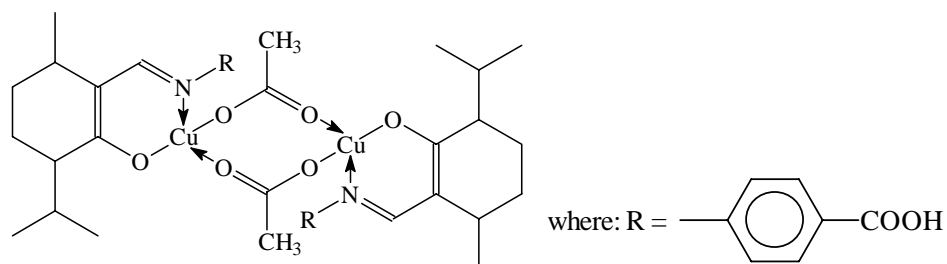
Figure 3a. Suggested structural formula for $Cu(BCH_3COO)_2$.

Figure 3b. Suggested structural formula for $[CuB_4](CH_3COO)_2$.

Conclusions

The nature, number and position of the substituents on the benzene ring determine the type of the coordination compounds and the bidentate or monodentate behavior of the ligands upon coordination.

The arguments for proposed structures of the complexes were fully supported by the spectral data (electronic, EPR, IR spectra).

The electronic and steric effects of the carboxyl substituent at the p-position in the benzene ring may be transmitted to affect the strength of hydrogen bond O-H…N, making possible the participation of ligand **B** in different tautomeric forms upon coordination.

Experimental

The ligands were prepared according to the literature.[12]

Ligand **A** ^{1}H NMR (CDCl$_3$) δ 7.95 (d, 1H, *J* 12.9 Hz, -CH=N-), 7.97 (d, 1H, *J* 11.4 Hz, -CH=N-), 9.93 (d, 1H, *J* 12.9 Hz, >NH), 9.95 (d, 1H, *J* 11.4 Hz, >NH), 0.82 and 0.85 (2d, 6H, *J* 6.8 Hz, -CH$_3$ 9(10)), 0.96 and 0.98 (2d, 6H, *J* 6.8 Hz, -CH$_3$ 9(10)), 1.18 and 1.22 (2d, 6H, *J* 6.6, 7.0 Hz, -CH$_3$ 7). ^{13}C NMR (CDCl$_3$) δ 136.6, 139.8 (-CH=N-), 202.8 (>C=O).

Ligand **B** ^{1}H NMR (CDCl$_3$) δ 7.16 (d, 1H, *J* 11.8 Hz, -CH=N-) 50%, 7.24 (d, 1H, *J* 11.7 Hz, -CH=N-) 50%, 12.06 (d, 1H, *J* 11.8 Hz, >NH) 50%, 12.20 (d, 1H, *J* 11.7 Hz, >NH) 50%, 0.82 and 0.85 (2d, 6H, *J* 6.8 Hz, -CH$_3$ 9(10)), 0.97 and 0.99 (2d, 6H, *J* 6.8 Hz, -CH$_3$ 9(10)), 1.18 and 1.22 (2d, 6H, *J* 6.6, 7.0 Hz, -CH$_3$ 7), ^{13}C NMR (CDCl$_3$) δ 139.8, 139.5 (-CH=N-), 203.7 (>C=O), 171.1 (-COOH).

Ligand **C** ^{1}H NMR (CDCl$_3$) δ 8.01 (d, 1H, *J* 14.7 Hz, -CH=N-) 30%, 8.18 (d, 1H, *J* 13.6 Hz, -CH=N-) 70%, 10.42 (d, 1H, *J* 14.7 Hz, >NH) 30%, 10.48 (d, 1H, *J* 13.4 Hz, >NH) 70%, 0.81 and 0.84 (2d, 6H, *J* 6.8 Hz, -CH$_3$ 9(10)), 0.96 and 0.98 (2d, 6H, *J* 6.8 Hz, -CH$_3$ 9(10)), 1.19 and 1.23 (2d, 6H, *J* 7.0, 6.6 Hz, -CH$_3$ 7), ^{13}C NMR (CDCl$_3$) δ 138.2, 139.0 (-CH=N-), 202.8 (>C=O), 170.3 (-COOH).

Cu(CH$_3$COO)$_2$.H$_2$O p.a. Merck was used. The copper content in products was determined by gravimetric analysis. The carbon, hydrogen and nitrogen content was determined by microcombustion.

Syntheses:

1. CuA$_2$(CH$_3$OH)$_2$. To a warm methanolic solution (~40 °C) of ligand **A** (2 mmol) a warm methanolic solution (40 °C) of Cu(II) acetate (1 mmol) was added. The microcrystalline, red colored, sparingly soluble product was filtered off with suction, washed with methanol and air-dried. Anal. Calcd for CuC$_{38}$H$_{54}$O$_{10}$N$_4$: Cu 8.03, C 57.73, H 6.88, N 7.12. Found: Cu 7.90, C 57.96, H 7.02, N 7.35.

2. (CuBCH$_3$COO)$_2$. To a warm methanolic solution (~40 °C) of ligand **B** (2 mmol) a warm methanolic solution (40 °C) of Cu(II) acetate (1 mmol) was added. The microcrystalline, khaki colored, sparingly soluble product was filtered off with suction, washed with methanol and air-dried. Anal. Calcd for Cu$_2$C$_{40}$H$_{50}$O$_{10}$N$_2$: 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. [CuB$_4$](CH$_3$COO)$_2$. To the remaining light-green filtrate from the synthesis of the compound **2**, 10 ml of water were added; a microcrystalline light-green colored product precipitated immediately. This was filtered off, washed with water and air-dried. Anal. Calcd for CuC$_{76}$H$_{98}$O$_{16}$N$_4$: 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 methanolic filtrate without addition of water.

4. CuC$_2$. This complex was obtained in the same way as compound **1**. Anal. Calcd for CuC$_{36}$H$_{44}$O$_6$N$_2$: Cu 9.56, C 65.08, H 6.68, N 4.23. Found: Cu 9.33, C 65.20, H 6.34, N 4.02.

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 (^{1}H NMR) and 75 MHz (^{13}C NMR) respectively, in CDCl$_3$. 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.

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Povzetek

Članek opisuje koordinacijske spojine bakrovega(II) iona in različnih Schiffovih baz pripravljenih iz formilmentona in nekaterih aromatskih aminov. Ugotovljeno je bilo da se uporabljeni ligandi lahko koordinirajo bidentatno preko kisikovih in dušikovih ligandov, ali pa tudi monodentatno. Predpostavljene geometrije in vezavna mesta so bila določena na osnovi rezultatov kemijskih analiz, spektroskopije (elektronska, EPR, IR) in meritev prevodnosti.