SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 7, N° 8, 1999

COORDINATION COMPOUNDS OF Cu(II) AND Ni(II) WITH SCHIFF BASES DERIVED FROM FORMYLMENTHONE AND *o*-, *m*-, *p*-TOLUIDINE

Adalgiza Ciobanu*, Florica Zălaru**, D.Albinescu*, Christina Zălaru*

* Faculty of Chemistry, Organic Chemistry Dept., University of Bucharest, 90-92 Panduri Road, Romania
** Faculty of Chemistry, Inorganic Chemistry Dept., University of Bucharest, 23 Dumbrava Rosie, Romania

ABSTRACT

The Schiff bases obtained from formylmenthone and o-, m-, p-toluidine behave as bidentate ligands with O and N donor atoms in Ni(II) and Cu(II) complexes by the type NiL_2 and $CuL_2.(H_2O)_2$. The donor atoms and the possible geometry for the complexes were assigned by means of chemical, thermodifferential analyses and electronic, EPR and IR spectra.

RESUMO

As bases de Schiff obtidas de o,m, e p-toluidina e formilmentona agem com ligantes bidentados com átomos doadores de O e N e reagem com Ni(II) e Cu(II) formando complexos do tipo NiL_2 e $CuL_2(H_2O)_2$. A natureza dos átomos doadores e a geometria e estrutura dos complexos foi determinada usando análise química e termodiferencial e métodos de espectroscopia eletrônica, infravermelha e de REP.

KEYWORDS: Coordination compounds of Cu(II) and Ni(II), Schiff bases derived from formylmenthone

DOI: 10.48141/SBJCHEM.v7.n8.1999.95_1999.pdf

INTRODUCTION

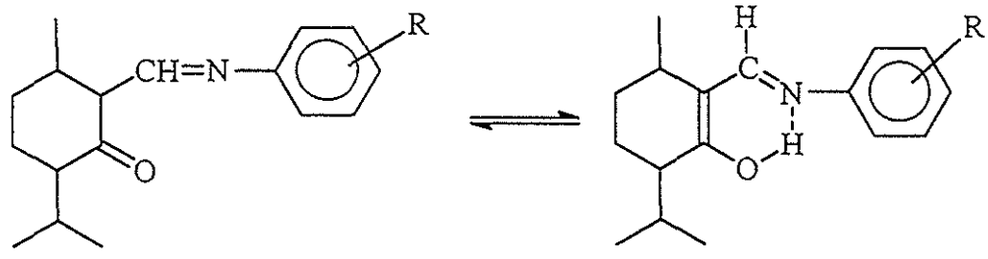
Our previous paper[1] has reported the preparation and characterisation of the coordination compounds of some "3d" metals with Schiff bases derived from 3-formylcarvone and *o*-, *m*-, *p*-toluidine. The position of the methyl substituent on the benzene ring has determined the type of the complex and monodentate or bidentate coordination of the ligands. It seemed desirable to investigate the coordination ability of the Schiff bases derived from 2-formylmenthone and *o*-, *m*-, *p*-toluidine on the same "3d" metals, for purposes of comparison (scheme 1).

Three new ligands able to generate complexes have been synthesized:

6 – isopropyl – 3 – methyl – 2 - [(2'-methylphenylamino) methylen] cyclohexan - 1 – one, (*ortho* – L);

6 – isopropyl – 3 – methyl – 2 - [(3'-methylphenylamino) methylen] cyclohexan - 1 – one, (*meta* – L);

6 – isopropyl – 3 – methyl – 2 - [(4'-methylphenylamino) methylen] cyclohexan - 1 – one, (*para* – L);



1a 1b

Scheme 1

where R = *o*-, *m*-, *p*- methyl.

The presence of the >C=O and >C=N – groups lying in *ortho*-position with respect to each other favours keto-enolic tautomerism (Scheme 1). This tautomerism has been attributed to an intramolecular hydrogen bond and might explain their chelating ability. NMR studies have shown that such Schiff bases with the carbonyl and azomethine groups lying in the *ortho*-position exist in solution as the enolic tautomer (1b) and that the tautomer distribution was solvent dependent[2,3].

EXPERIMENTAL

The ligands were prepared according to the literature and $Cu(CH_3COO)_2.H_2O$ and $Ni(CH_3COO)_2.4H_2O$ p.a. Merck were used.

The complexes were prepared by mixing warm aqueous methanol solution (50%) of metal acetate (1 mmol) and ligands (2 mmols). The resulting precipitates were filtered and washed with aqueous methanol solution (50%) and dried at room temperature. The metal content was obtained gravimetrically.

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

EPR spectra were recorded at room temperature on polycrystalline powders, on ART-5-IFA Spectrograph.

The klystron frequency was 9060 MHz and modulation of the magnetic field 100 KHz. The EPR spectral parameters were calculated against a Mn(II) standard.

Thermodifferential analyses were carried out with a Paulik-Paulik-Erdey Derivatograph Q 1500-D MOM. Conditions of measurements: temperature range up 1000°C, heating program: 10 degree/min., sensitivity DTA = 1/10, m_4 = 0.0180 g, S = 20 and m_5 = 0.0372 g, S = 50; atmosphere over sample air.

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

RESULTS AND DISCUSSION

Characteristic data for the Cu(II) and Ni(II) complexes are presented in Table 1. The elemental and thermodifferential analyses are consistent with their formulation as anhydrous, monomeric Schiff bases chelates (NiL_2) or hydrated, monomeric complexes ($CuL_2.(H_2O)_2$) with water molecules either as coordinated or as crystalline water. All the metal chelates are brownish-red, readily soluble in organic solvents (chloroform, acetone, methanol), but sparingly soluble in water.

Thermodifferential analysis curves for compounds Cu(*para*-L)$_2$.$(H_2O)_2$ and Ni(*para*-L)$_2$ are shown in detail in Figures 1a and 1b.

Table I. Elementary analysis results for the complexes studied

No	Compound	Cu% Found/Calcd.	Ni% Found/Calcd.	H_2O% Found/Calcd.
1.	Cu(*ortho*-L)$_2$.(H_2O)$_2$	10.37/9.94	-	7.03/5.63
2.	Cu(*meta*-L)$_2$.(H_2O)$_2$	9.64/9.94	-	6.80/5.63
3.	Ni(*meta*-L)$_2$	-	10.14/9.80	-
4.	Cu(*para*-L)$_2$ (H_2O)$_2$	10.09/9.94	-	6.91/5.63
5.	Ni(*para*-L)$_2$	-	10.50/9.80	-

For compound Cu(*para*-L)$_2$.(H_2O)$_2$ (Fig.1a) the mass loss observed within 60-215°C range in the TG curve corresponds to the loss of two water molecules per molecule of each copper compound. The TG curve shows that the water molecules are liberated in two steps (weight loss at 170°C, found: 2.98%, calcd., for H_2O: 2.88%; weight loss at 215°C, found: 7.03%, calcd., for $2H_2O$: 5.76%). Hence, the two water molecules are present as coordinated water, in Cu(II) complexes.

The results indicate that compound Ni(*para*-L)$_2$ (Fig.1b) is stable up to 150°C, but rapidly looses ligands at 565°C (weight loss at 565°C, found: 88.86%, calcd., for 2L: 90.14%).

The electronic diffuse reflectance spectra of the complexes are given in Fig.2 and 3.

The spectra of the Ni(II) complexes (3 and 5, Fig.2) are similar and are consistent with tetrahedral Ni(II) complexes[4]. The spectra present the band ν_3 (660 nm) assignable to the $^3T_1(P) \leftarrow {}^3T_1$ transition weak band (760 nm, compound Ni(*meta*-L)$_2$) or the shoulder (760 nm, compound Ni(*para*-L)$_2$) are assigned as spin forbidden transitions to components of ^1D levels[4]. The band ν_1 assignable $^3T_2 \leftarrow {}^3T_1$ transition (near 500 nm) is covered by a broad and intense band due to the ligands (500 nm). It is present in the spectra of the copper complexes, also. The spectra of the copper complexes

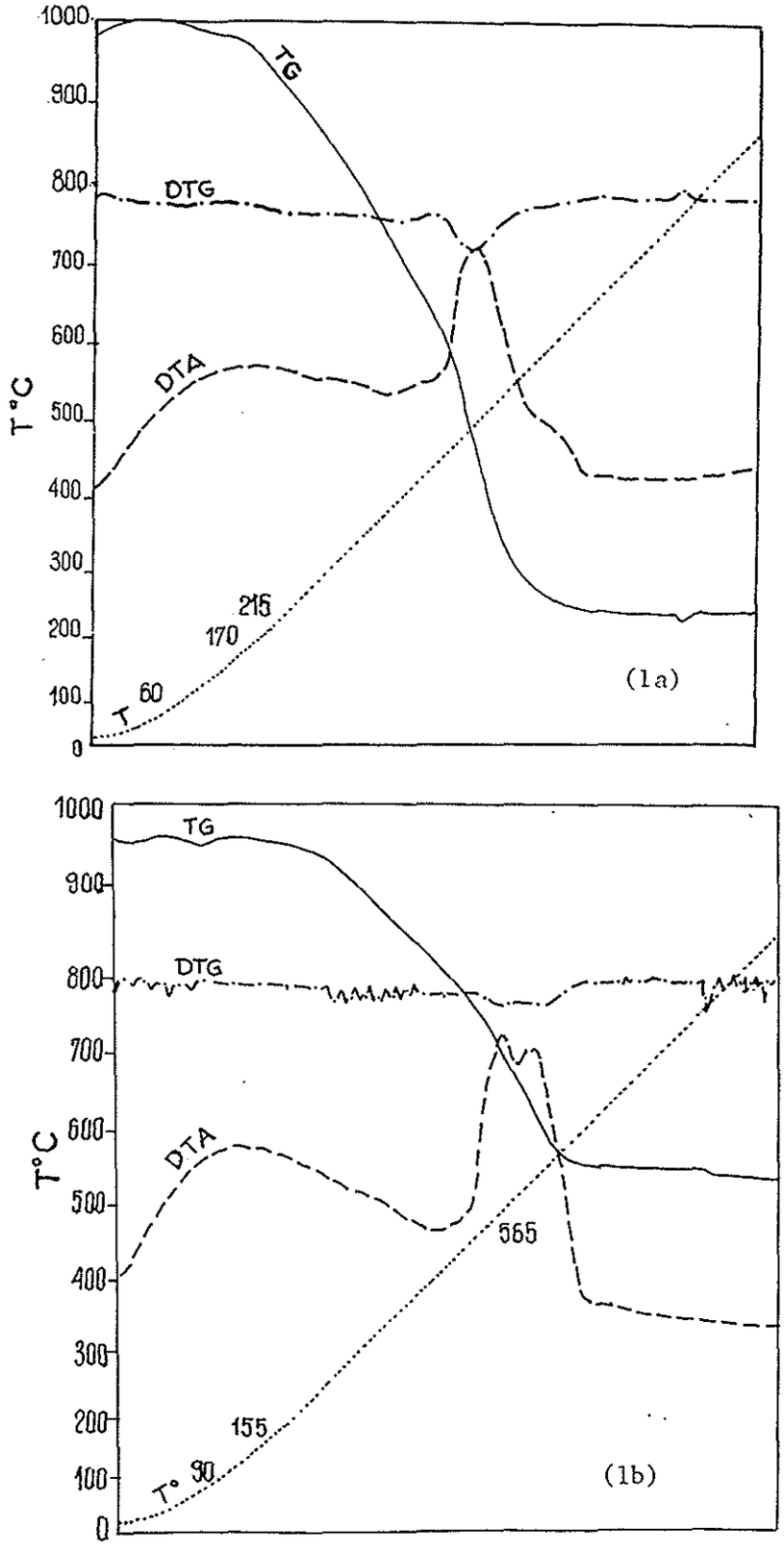


Fig. 1. Thermodifferential curve of Cu(*para*-L)$_2$ 2H$_2$O (1a) and Ni(*para*-L)$_2$ (1b)

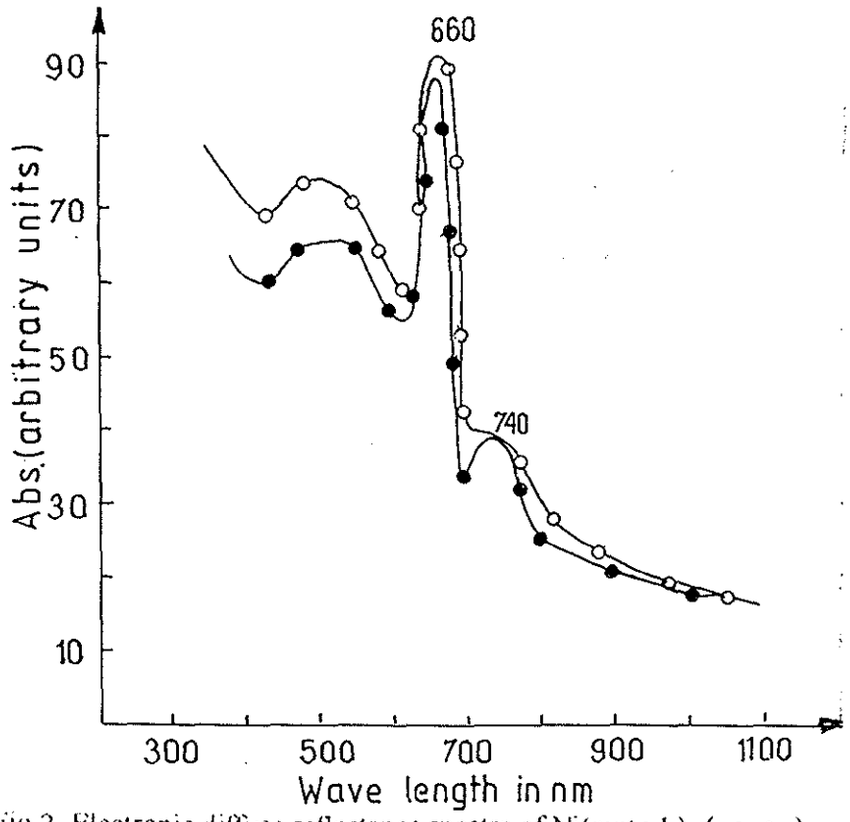


Fig.2. Electronic diffuse reflectance spectra of Ni(*meta*-L.)$_2$ (-•-•-) and Ni(*para*-L.)$_2$ (-o-o-)

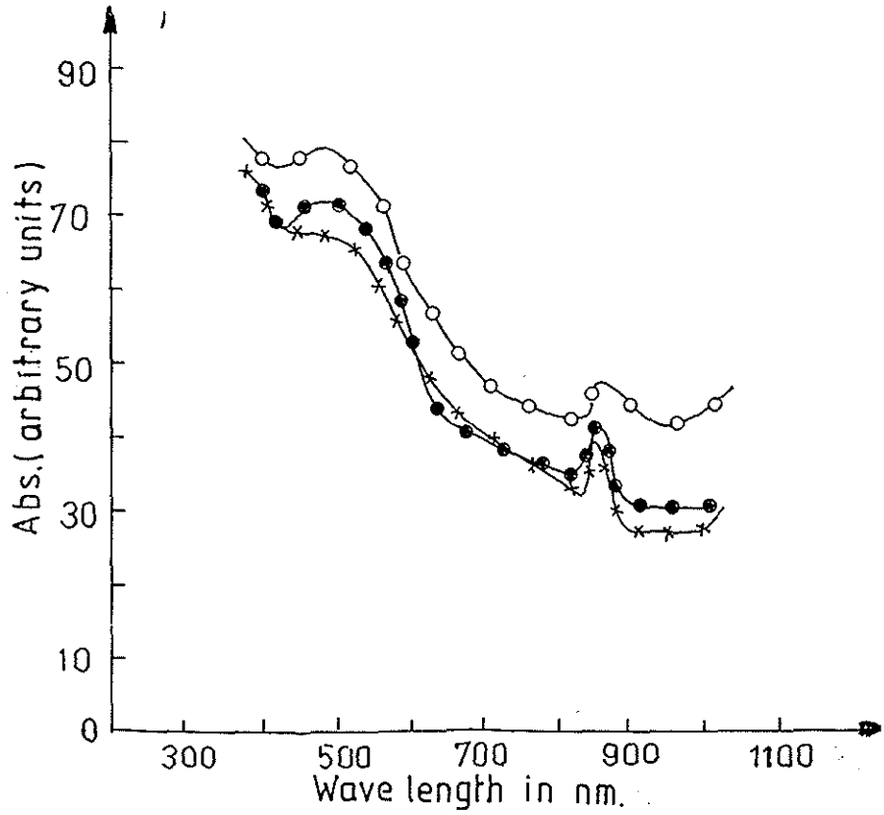
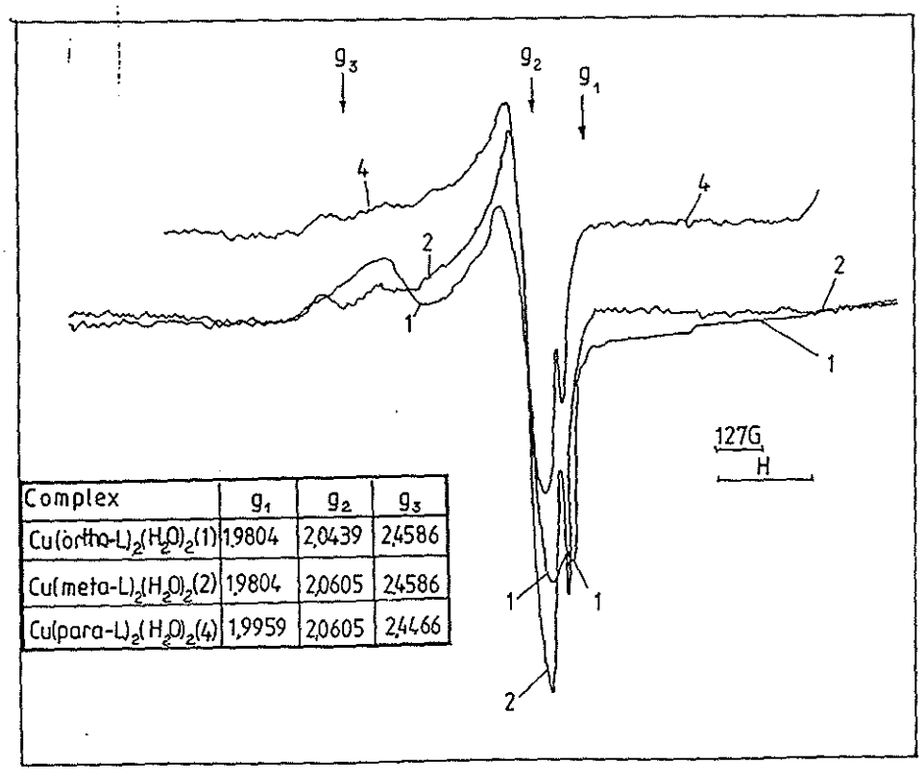


Fig.3. Electronic diffuse reflectance spectra of:
Cu(*ortho*-L.)$_2$.(H$_2$O)$_2$ (-x-x-);
Cu(*meta*-L.)$_2$.(H$_2$O)$_2$ (-• • -);
Cu(*para*-L.)$_2$.(H$_2$O)$_2$ (-o-o-)

(Cu(*ortho*-L)$_2$.(H$_2$O)$_2$, Cu(*meta*-L)$_2$.(H$_2$O)$_2$, Cu(*para*-L)$_2$.(H$_2$O)$_2$) in Fig.3 are similar and present a band at 800 nm that could be assigned to a *d-d* transition associated with a distorted octahedron[5-7]. EPR spectra of the three copper complexes recorded at room temperature on polycrystalline samples present a similar intense EPR signal characteristic monomeric species of Cu(II) ion with a third order anisotropy for the factor *g* resulting from distortion of octahedral geometry (Fig.4).

This anisotropy is compatible with Cu(II) ion in a compressed rhombic-octahedral geometry[6,7] with R > 1 and supports the electronic spectra. In a three *g* value spectrum with $g_1 < g_2 < g_3$, the value of $R = (g_2 - g_1)/(g_3 - g_2)$ may be significant[8]: if R > 1, a predominant dz^2 ground state is present and would be consistent with compressed axial or rhombic symmetry with slight misalignment of the axex. If R < 1, a predominant $dx^2 - y^2$ ground state is present[6-8].

The main IR bands and their assignments for the free ligands and the complexes are shown in Table 2.



Complex	g_1	g_2	g_3
Cu(ortho-L)$_2$(H$_2$O)$_2$(1)	1,9804	2,0439	2,4586
Cu(meta-L)$_2$(H$_2$O)$_2$(2)	1,9804	2,0605	2,4586
Cu(para-L)$_2$(H$_2$O)$_2$(4)	1,9959	2,0605	2,4466

Fig.4. EPR spectra and SPR spectral parameters of:
Cu(*ortho*-L)$_2$.(H$_2$O)$_2$ (1);
Cu(*meta*-L)$_2$.(H$_2$O)$_2$ (2);
Cu(*para*-L)$_2$.(H$_2$O)$_2$ (4).

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

No.	L/compound	ν_{OH}	$\nu_{C=O}$	$\nu_{C=N}$	H_2O coord.
	Ortho-L	3200-3320m	1700sh	1550, 1590, 1630vs	-
1.	Cu(*ortho*-L)$_2$.(H$_2$O)$_2$	3423s	-	1558, 1615vs	1111w
	Meta-L	3310, 3450m	1700vw	1560, 1620, 1640s	-
2.	Cu(*meta*-L)$_2$.(H$_2$O)$_2$	3395m	-	1557s, 1610vs	1094w
3.	Ni(*meta*-L)$_2$	3398m	-	1543s, 1510vs, 1635s	-
	Para-L	3300, 3400m	1700vw	1520, 1580, 1630s	-
4.	Cu(*para*-L)$_2$.(H$_2$O)$_2$	3399m	-	1514vs, 1545s, 1613s	1111w
5.	Ni(*para*-L)$_2$	3422m	-	1510, 1543, 1558m	-

s – strong; m – medium; w – weak; sh – shoulder; v – very

The keto-enolic tautomerism is supported by presence of the bands due to ν_{OH} and $\nu_{C=O}$. The band due to $\nu_{C=O}$ (1700 cm^{-1}) occurs as a very weak band or a shoulder. The band due to ν_{OH} occurs as a broad band (3200-3600 cm^{-1} range) with two unresolved peaks. The band due to $\nu_{C=N}$ occurs as a broad band (1500-1600 cm^{-1} range) with three unresolved peaks. A comparison of the position of the bands in spectra of the complexes with their position in the IR spectra of free ligands shows changes of the bands due to ν_{OH} and $\nu_{C=N}$. Upon coordination, the stretching frequencies, $\nu_{C=N}$ are shifted to lower values and stretching frequencies ν_{OH} are shifted to higher values. These changes are generally noticed upon coordination of the Schiff bases containing an N and O donor atoms, by the both donor atoms[9]. The new band near 1111 cm^{-1} occurring in the IR spectra of the three copper complexes only could be assigned to the coordinated water molecules in agreement with Fujita[10] and is be consistent with the results of the thermodifferential analysis.

On the basis of elemental, differential analyses and spectral measurements, we conclude that Cu(II) ion is hexacoordinated in a compressed rhombic geometry, while Ni(II) ion is tetracoordinated in a tetrahedral geometry.

The ligands acted bidentately with both O and N donor atoms by deprotonation of the OH group making evident the participation of the ligands in the enolic tautomeric form.

Cu(II) coordinates by atom donors, N and O in a plane and by shorter bonds to axial water molecules in a compressed rhombic geometry (Fig.5).

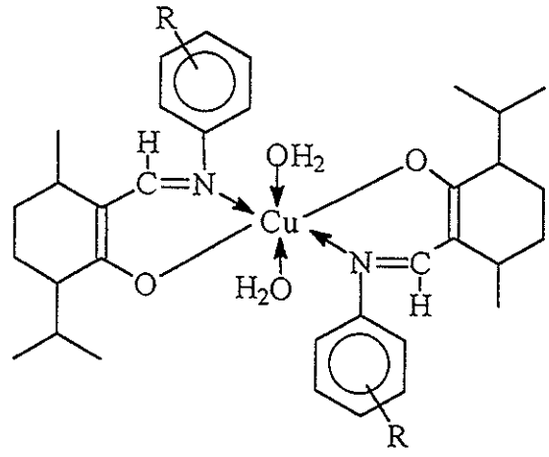


Fig.5. Structural formula proposed for the Cu(II) complexes

The tetrahedral environment of the Ni(II) ion suggested by electronic spectra is obtained by both donor atoms, N and O.

We may conclude that the metallic ion determines the type of the new complexes.

The arguments for the structure of the new chelates were fully supported by the spectral data (electronic, EPR and IR spectra).

REFERENCES

1. P.Grandclaudon, F.Zălaru, D.Albinescu, A.Ciobanu and A.Meghea, *An.Univ.Bucharest, 6, 11* (1997)
2. G.O.Dudek, *J.Am.Chem.Soc., 85*, 694 (1963)
3. G.O.Dudek and G.P.Volpp, *J.Am.Chem.Soc., 86*, 2697 (1964)
4. A.B.Lever, *"Inorganic Electronic Spectroscopy"*, Elsevier, Amsterdam, 182, 1968
5. B.J.Hathaway, *J.Chem.Soc.,* 1196 (1972)
6. B.J.Hathaway and D.E.Billing, *Coord.Chem.Rev., 143* (1970)
7. B.J.Hathaway, *Structure and Bonding, 57*, 85, 109 (1984)
8. D.E.Billing, R.J.Dudley, B.J.Hathaway and A.Tomlinson, *J.Chem. Soc.(A),* 691 (1971)
9. G.C.Percy and D.A.Thortnton, *J.Inorg.Nucl.Chem., 34*, 3357 (1972)
10. J.Fujita, K.Nakamato and M.Kobayshi, *J.Am.Chem.Soc., 78*, 3963 (1956)