

**SYNTHESIS AND STRUCTURAL CHARACTERIZATION
OF N - (2' - HYDROXY - 1' - NAPHTHALEN METHIN) - 2 -
AMINOANILINE COMPLEXES**

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ABSTRACT

N - (2' - hydroxy - 1 - naphthalen methin) - 2 - aminoaniline (HL) forms stable complexes with chromium(III), of the type $[CrL_2]Cl$, nickel(II) and copper(II), of the type $[ML_2]$ ($M = Cu, Ni$).

Their structures have been characterized on the basis of elemental analysis, magnetic moment determinations, IR, electronic and EPR spectral studies. Chromium(III) and copper(II) form distorted octahedral complexes, while nickel(II) forms typically a square-planar complex. Ligand field parameters have been calculated for these complexes.

KEYWORDS: Schiff bases; chromium(III), copper(II), nickel(II) complex compounds

RESUMO

N-(hidroxi-1-naftalen metin) -2 aminoanilina (HL) forma complexos estáveis com cromo (II) do tipo $(CrL_2)Cl$ e com cobre (II) do tipo (ML_2) , ($M=Cu, Ni$).

A estrutura destes complexos foi determinada usando análise elementar, determinações de momento magnético, e métodos de espectroscopia no infravermelho, ultravioleta-visível e RPE. Cromo (III) e cobre (II) formam complexos octaédricos distorcidos e o níquel (II) forma um complexo típico quadrado-planar. Parâmetros correspondentes ao campo ligante foram calculados para estes complexos.

1. INTRODUCTION

Although many investigations have been performed on transition metal complexes with Schiff's bases derived from *o* - hydroxy -naphthaldehyde with amines ¹⁻⁴, no studies have been made on the ligand field parameters in such complexes .

The present paper describes the synthesis and the characterization of Cr (III), Ni (II) and Cu (II) complexes with N - (2' - hydroxy - 1' - naphthalen methin) - 2 - aminoaniline (HL). The ligand contains azomethine N and amine N, and one OH phenolic group, capable of coordination with various metal ions.

A noteworthy point here is that the amine N is not coordinated in the nickel (II) complex, but it is coordinated in the chromium (III) and copper (II) complexes.

2. EXPERIMENTAL

All the chemicals used were of analytical reagent grade. The Schiff base was synthesized by refluxing 2-hydroxy naphthaldehyde and *o*-phenylene diamine in ethylene glycol in 1:1 ratio, for 4h. The yellow product obtained was filtered and washed successively with ethylene glycol and ethanol. It was recrystallized from a mixture ethylene glycol/ethanol.

Preparation of metal complexes:

Hot ethanolic solutions of ligand (0,01 mol) and metal chlorides (0,005 mol) were mixed with continuous stirring. The resulting solutions were refluxed on a water-bath for 2h.

After concentrating and cooling, coloured solids resulted. These were filtered, washed with ethanol and air dried.

The purity of Schiff base and its complexes was determined by C, H and N analyses. Metal content was determined by standard procedures ⁵.

Infrared spectra (in KBr pellets) were recorded on a Spekord M-80 Carl Zeiss Jena spectrophotometer, in the range of 4000-400 cm^{-1} . Diffuse reflectance spectra were measured on Spekord M-40 spectrophotometer in the range of 200-900 nm.

Molar conductance was measured in DMF (10^{-3}M), using a Phillips PR 9500 conductivity meter, at room temperature.

Thermogravimetric analysis was carried out in static air atmosphere, at a heating rate of 10^0 C/min, using a MOM Q-1500 derivatograph.

Magnetic susceptibility measurements were performed by the Faraday method, at room temperature, using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant.

3. RESULTS AND DISCUSSION

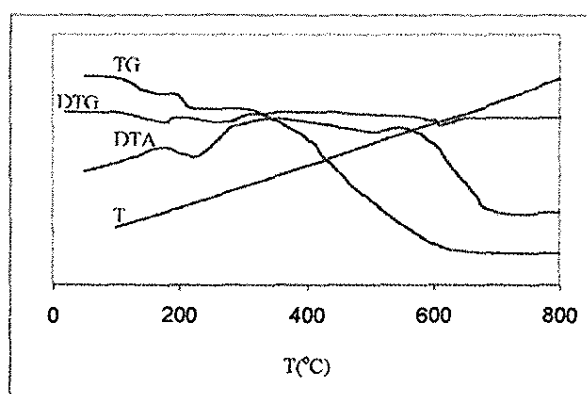
The results of elemental analysis (Table 1) reveal that the complexes have 1:2 (M:L) stoichiometry.

The thermal stability data (Figure 1) show that the decomposition of Cr(III) complex starts at 220^0C , corresponding to the removal of anionic chloride ⁶. The broad exothermic peak in the range of $350-600^0\text{C}$ for all the complexes corresponds to the loss of the organic ligand ^{6,7}.

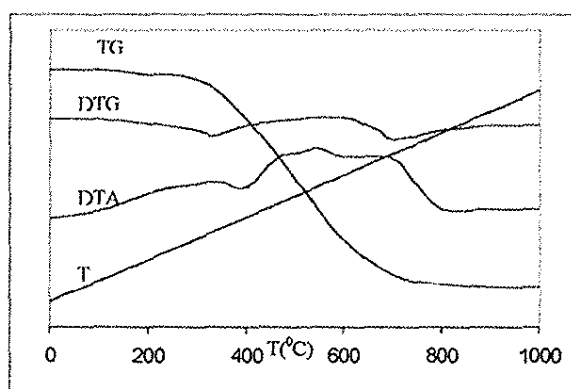
The significant bands (cm^{-1}) observed in the infrared spectra of the Schiff base and its metal complexes are listed in Table 2.

Table 1. Analytical Data for the Complexes Studied

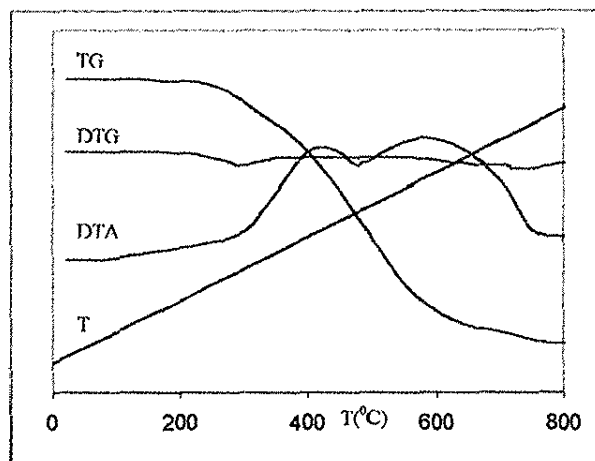
Complex	Colour	C% Calc/exp	N% Calc/exp	Metal% Calc/exp	$\lambda(\text{DMF})$ $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
[CrL ₂]Cl	Brown	66,90	9,18	8,53	66
		66,07	8,34	7,96	
[NiL ₂]	Red	69,98	9,60	10,36	34
		69,60	9,34	10,22	
[CuL ₂]	Orange	69,62	9,55	10,92	27
		68,92	8,92	10,34	



(a)



(b)



(c)

Figure 1. Thermogravimetric curves of Cr(III) (a), Ni(II) (b) and Cu(II) (c) complexes

Table 2. Characteristic Bands in the IR Spectra of the Ligand and its Complexes ($\nu_{\max}$, cm^{-1})

HL	[CrL ₂]Cl	[NiL ₂]	[CuL ₂]	Assignments
3410 ms	3380 ms	3408 ms	3382 ms	$\nu_{\text{as}}(\text{NH}) \text{NH}_2$
3320 m	3305 m	3320 m	3302 m	$\nu_{\text{sim}}(\text{NH}) \text{NH}_2$
2970 ms	-	-	-	ν_{OH} chelatic
1620 s	1595 s	1600 s	1585 s	$\nu_{\text{C=N}}$
1620 s	1610 s	1620 s	1600 s	$\delta(\text{NH}_2)$
1490 ms	1460 ms	1480 m	1480 m	$\nu_{\text{sim}} \text{C-N}$
1320 s	1350 s	1365 s	1365 s	$\nu_{\text{C-O}}$ phenolic
-	570 w	560 w	630 w	$\nu_{\text{M-O}}$
-	505 w	500 w	520 w	$\nu_{\text{M-N}}$ azomethinic
-	450 w	-	500 w	$\nu_{\text{M-N}}$ aminic

The strong absorption band in the infrared spectrum of the ligand, appearing at 1620 cm^{-1} , was assigned to the stretching vibration of >C=N group ($\nu_{\text{C=N}}$) and to the deformation in the plane vibration of the amine group (δ_{NH})⁸⁻¹¹. In the IR spectra of all the complexes this band splits into two components.

In the spectra of Cr(III) and Cu(II) complexes, these two bands appear at lower wave numbers, indicating the coordination of the nitrogen atom of the azomethine group and the nitrogen atom of amine group to the metal ion.

The bands assigned to asymmetric and symmetric N-H stretching mode of NH_2 group are also lowered, which confirms the coordination of the ligand through the amine group to the metal ion¹².

In the IR spectrum of Ni(II) complex, only one component of the band at 1620 cm^{-1} appears at lower wave number. No shift is observed for the bands due to asymmetric and symmetric N-H stretching modes of NH_2 . It is therefore concluded that in the Ni(II) complex the coordination takes place through the nitrogen atom of the azomethine group, but NH_2 group is not involved in the complexation^{12,13}.

The band due to the intramolecularly bonded phenolic group is not observed in the case of the metal complexes, indicating that the deprotonation of the phenolic group has taken place during the complexation. The positive shift in $\nu_{\text{C-O}}(\text{phenolic})$ is also in agreement with the coordination of the ligand through the phenolic oxygen¹³⁻¹⁵.

At lower frequencies, the complexes exhibit new bands with low intensity, at $570\text{--}630\text{ cm}^{-1}$ and $460\text{--}500\text{ cm}^{-1}$, which are assigned to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$, respectively^{9,10,16,17}.

The IR spectral data indicate clearly that the coordination of the ligand takes place through the azomethine and the amine nitrogen and the phenolic oxygen in Cr(III) and Cu(II) complexes and through the azomethine and the phenolic oxygen in Ni(II) complex.

Magnetic and electronic spectral data .

The nickel(II) complex was found to be diamagnetic, suggesting square planar geometry. This conclusion is further supported by the electronic spectrum of the complex (Figure 2), which exhibits three strong bands: at 19758 cm^{-1} ($^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$), 22321 cm^{-1} ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) and 25201 cm^{-1} ($^1\text{A}_{1g} \rightarrow ^1\text{E}_g$).

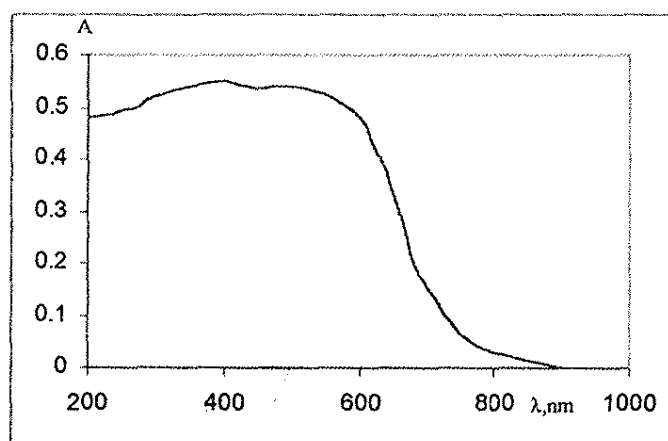


Figure 2. Diffuse-reflection electronic spectrum of the Ni(II) complex

The observation of a spin-forbidden $d-d$ transition at 15220 cm^{-1} (${}^1A_{1g} \rightarrow {}^3A_{2g}$) permitted the calculation of the strong field parameters Δ_1 , Δ_2 and Δ_3 (we assumed the $C/B=4$)¹⁸. The following values of the spectral parameters were determined:

$$\Delta_1 = 22027\text{ cm}^{-1}$$

$$\Delta_2 = 4831\text{ cm}^{-1}$$

$$\Delta_3 = 2313\text{ cm}^{-1}$$

$$B = 567\text{ cm}^{-1}$$

Therefore, the sequence of the d antibonding molecular orbitals is:

$$a_{1g}(d_{z^2}) < e_g(d_{xz}, d_{yz}) < b_{2g}(d_{xy}) < b_{1g}(d_{x^2-y^2})$$

These results are in agreement with those obtained by Goyal and Lal⁸.

The magnetic moment of the chromium(III) complex, 3.84 M.B., is very close to spin-only value in octahedral stereochemistry.

The electronic spectrum (Figure 3.) shows six spin allowed transitions, in agreement with an octahedral symmetry, with tetragonal distortion¹⁹. The transition with low intensity, appearing at 14925 cm^{-1} , is a spin-forbidden transition, due to ${}^4A_{2g} \rightarrow {}^2A_{1g}, {}^2B_{1g}, {}^2A_{2g}, {}^2E_g$.

Due to low energy of first spin-allowed transition, its assignment is difficult and the correlation of the electronic spectral data with the results of Electronic Paramagnetic Resonance (EPR) Spectroscopy is absolutely necessary.

The chromium(III) complex shows an axial Electronic Paramagnetic Resonance spectrum, with $g_{||} > g_{\perp}$ (Figure 4.)

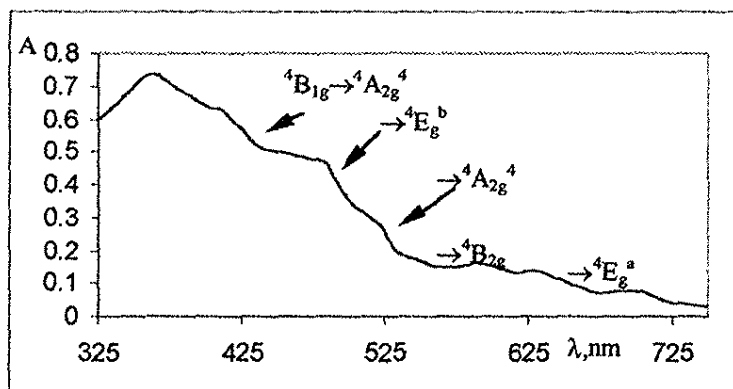


Figure 3. Diffuse-reflection electronic spectrum of the Cr(III) complex

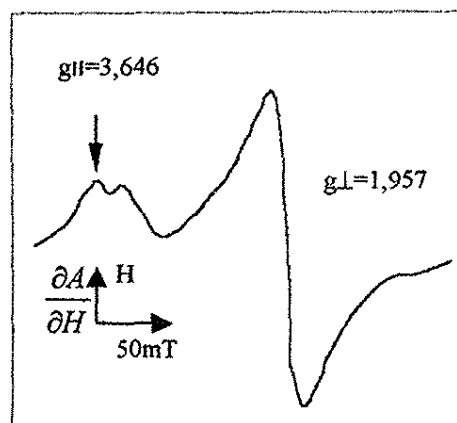


Figure 4. Electronic Paramagnetic Resonance powdered spectrum (X band) of the Cr(III) complex

This is in accordance with a higher energy of ${}^4B_{2g}$ level than that of ${}^4E_g^a$ level, suggesting an octahedral symmetry distorted by elongation along z axis.

On the basis of these observations, the UV-VIS absorption bands may be assigned to the following transitions (Table 3):

Table 3. Electronic Transitions for the Cr(III) complex

Observed bands (ν_{max} , cm^{-1})	Assignments
14925	${}^4B_{1g} \rightarrow {}^2A_{1g}, {}^2B_{1g}, {}^2A_{2g}, {}^2E_g$
15151	${}^4B_{1g} \rightarrow {}^4E_g^a$
16890	${}^4B_{1g} \rightarrow {}^4B_{2g}$
19607	${}^4B_{1g} \rightarrow {}^4A_{2g}^a$
20920	${}^4B_{1g} \rightarrow {}^4E_g^b$
25640	${}^4B_{1g} \rightarrow {}^4A_{2g}^b$
28571	${}^4B_{1g} \rightarrow {}^4E_g^c$

The observation of all the six spin-allowed transitions permitted the calculation of the ligand field parameters, in terms of the Crystal Field Theory and the Angular Overlap Model.

Two approaches were utilised for the analysis of the electronic spectrum:

1. the weak field approach and
2. the strong field approach¹⁹.

In the weak field approach, the splitting of the lowest energy quadruplet term gives the value of the D_t parameter¹⁹⁻²¹:

$$D_t = 4/7 (Dq_{xy} - Dq_z) \text{ (for } D_{4h} \text{ symmetry) ;}$$

$Dq_{xy} = Dq_L$ = in-plane (xy) ligand field strength ;

Dq_z = out-of plane (z) ligand field strength.

The value of D_s was determined using the splitting of the second "octahedral" band :

$$-6D_s + 5/4 D_t = E(^4A_{2g}^a) - E(^4E_g^b)$$

The values of the ligand field parameters calculated with this approach are given in Table 4.

Table 4. Ligand Field Parameters of the Cr(III) complex (cm⁻¹)

Parameter	Weak field method	Strong field method
Dq_L	1689	1689
Dq_z	1340	935
D_t	199	431
D_s	-177	-257
$d\sigma$	-107	-423
$d\pi$	763	1465
Δ_1	-1526	-2931
Δ_3	287	1128
$e'_\sigma(L)$	6591	5075
$e'_\sigma(Z)$	6447	4511
$e'_\pi(L)$	721	19
$e'_\pi(Z)$	1484	1484
B_{55}	710	710
B_{35}	335	773
B_{33}	156	833

The positive value of D_t corresponds to an octahedron elongated along the z-axis.

The signs of $d\sigma$ and $d\pi$ parameters suggest that the phenolic oxygen is a poorer σ donor, but a better π donor toward chromium(III) than nitrogen. As a consequence of the sign of $d\pi$, Δ_1 is negative, indicating that the d_{xy} level is lower than d_{xz} and d_{yz} levels.

In order to use the relations proposed by Lever for the determination of AOM parameters¹⁹, we assigned $e'_\pi(z) = 1484\text{cm}^{-1}$, value determined for the phenolic oxygen²².

Because in xy plane we have azomethinic nitrogen and amine nitrogen and $e'_\sigma(N)$ azomethinic = 7682cm^{-1} ²², we have determined $e'_\sigma(N)_{\text{aminic}} = 5500\text{cm}^{-1}$.

Thus, the primary aromatic amine nitrogen is a poorer σ -donor towards Cr(III) than the aliphatic amine nitrogen (for which e'_σ varies between $6700\text{-}7300\text{cm}^{-1}$)²³.

The value of e'_σ (L) comprises only the contribution of the azomethinic nitrogen, since the amines do not possess any orbitals capable of a π -interaction with the metal ion.

In the strong field approach, the energy of the states is expressed in terms of the $\Delta_1, \Delta_2, \Delta_3$ and B parameters¹⁹. The results of this method are also given in Table 4 (column 3).

The agreement between the two sets of data may be considered good.

In both approaches, Δ_1 is negative and Δ_3 is positive, which implies the following sequence of energy levels:

$$d_{xy} < d_{xz}, d_{yz} < d_{z^2} < d_{x^2-y^2}$$

If we express the distortion of the octahedral symmetry by DS, DT and DQ parameters²⁴, we obtain:

Weak field approach

$$DS = 1239\text{cm}^{-1}$$

$$DT = 2698\text{cm}^{-1}$$

$$DQ = 43248\text{cm}^{-1}$$

$$DT/DQ = 0,06$$

Strong field approach

$$DS = 1799\text{cm}^{-1}$$

$$DT = 5842\text{cm}^{-1}$$

$$DQ = 39527\text{cm}^{-1}$$

$$DT/DQ = 0,14$$

The magnitude of DT/DQ ratio is a measure of the degree of tetragonal distortion and one observes that the strong field approach indicates a stronger distortion from octahedral symmetry than the weak field approach.

The X-band EPR spectrum of the powdered complex (Figure 4.) has been used to complete the informations on the metal-ligand bond.

The spin Hamiltonian parameters have the following values:

$$g_{\parallel} = 3,646 \quad g_{\perp} = 1,957$$

$$D = 785\text{G} (0,072\text{cm}^{-1})$$

$$E = 200\text{G} (0,018\text{cm}^{-1})$$

The anisotropy of the g factor is consistent with an axial distortion, but its values give little information on distortions in the crystal field. McGarvey showed that the g factor is not very sensitive to the distortions in the crystal field, but it is very sensitive to the nature of the molecular orbitals²⁵. The g factor can be greater than 2,0023 for the complexes in which the ligand atoms have large values for the spin-orbit interaction parameter and possess considerable σ and π bonding capability.

Because the parallel g shift depends on interactions involving the bonding in xy plane, a great value of $g_{\parallel}$ may be correlated with a high degree of overlap between the nitrogen atomic orbitals and the $d_{x^2-y^2}$ and d_{xy} orbitals.

The axial zero-field parameter, D , is related both to the square of spin-orbit coupling constant and the splitting of the first excited state. Thus, the small value of D for our complex indicates a small axial distortion, in agreement with the results of electronic spectroscopy. The small rhombic distortion ($E = 0,018\text{cm}^{-1}$) is due to the existence of two types of nitrogen atoms in the equatorial plane.

Using the equation ²⁶ :

$$2D = 8/9 \xi^2 \frac{E(^4B_{2g}) - E(^4E_g^a)}{\Delta^2}$$

which neglects the contribution of the doublet states of the spin-orbit coupling constant value, we obtained $\xi = 163\text{cm}^{-1}$ ($\lambda = 54\text{cm}^{-1}$). This small value is due to the radial expansion of *d* orbitals through the ligand orbitals, a direct result of this process being the reduction of interelectronic repulsion parameter.

Garrett and DeArmond ²⁶ found a direct relation between the spin-orbit coupling constant and the F_2 parameter (or B parameter). Thus, the small value of ξ is in agreement with the small value determined for B.

The electronic spectrum of the copper(II) complex shows a broad band at 16129 cm^{-1} and another at 19700 cm^{-1} , which are in agreement with a distorted octahedral symmetry (Figure 5.).

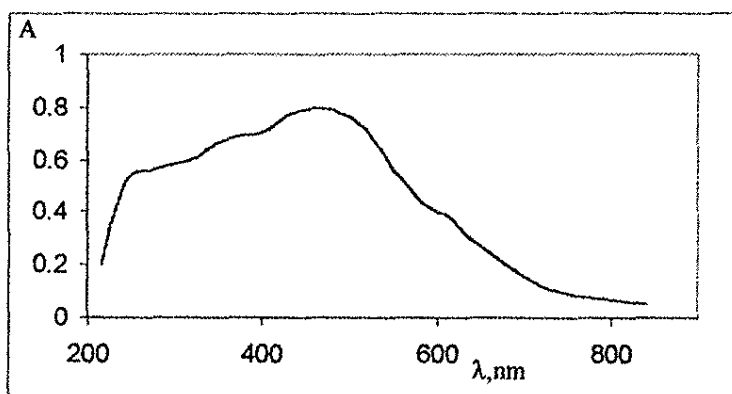


Figure 5. Diffuse-reflection electronic spectrum of the Cu(II) complex

The magnetic moment (1,89 MB) is normal for the d^9 system with one unpaired electron. The EPR spectrum (Figure 6.) gives the following values for the g factor :

$$g_{\parallel} = 2,193 \text{ and } g_{\perp} = 2,060.$$

Since $g_{\parallel} > g_{\perp} > g_e$, the unpaired electron will be in the $d_{x^2-y^2}$ orbital and the octahedron will be along the z' axis ²⁷⁻²⁹.

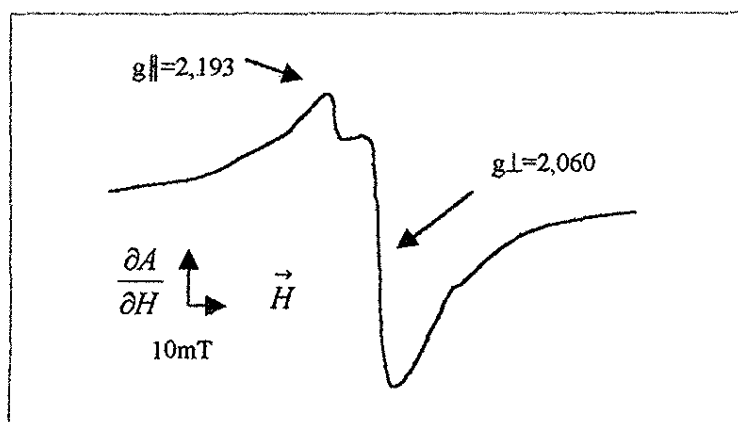
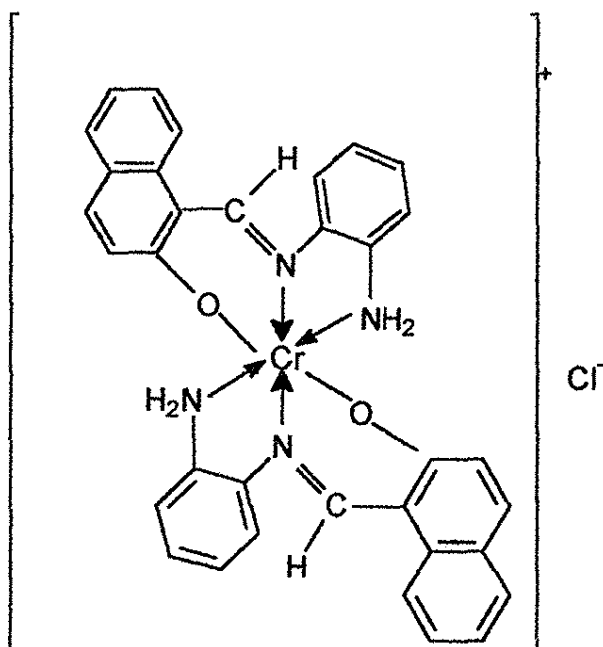


Figure 6. Electronic Paramagnetic Resonance powdered spectrum (X band) of the Cu(II) complex

Thus, the two bands observed in UV-VIS may be assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. Using the energy of the transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$ (Δ_0) and $g_{||}$ value²⁷, we obtained for the spin-orbit coupling constant the value: $\lambda = -348\text{cm}^{-1}$. The magnitude of $\lambda/\lambda_0 = 0,46$ ratio indicates an important covalent character of the metal-ligand bond.

On the basis of the results of physico-chemical analyses, the following structures may be assigned for the complexes obtained (Figure 7.):



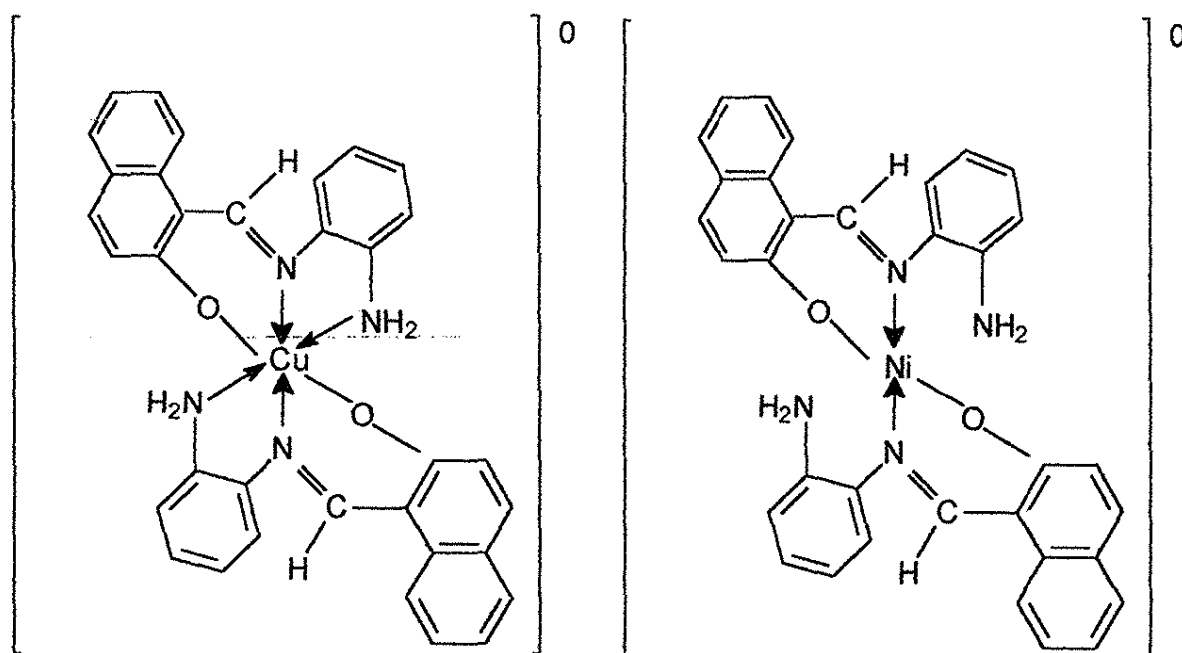


Figure 7. Structures of the Complexes Studied

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