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TRANSITION METAL COMPLEXES OF THE FORMYL VANILLINE DERIVATIVES LIGAND FAMILY

Tudor ROSU*, Angela KRIZA*, Viorel CARCU*, Anca NICOLAE**

*Dept. of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest, 23 Dumbrava Rosie st., Bucharest, Romania

**Dept. of Organic Chemistry, Faculty of Chemistry, University of Bucharest, Romania

ABSTRACT

Divalent 3d metal complexes with formyl-vanilline derivatives, of the type ML_2 or ML_2X_2 (M = Cu(II), Co(II); X = Cl), were sythesized by reaction of the corresponding metal(II) chlorides with 1-[3'-formyl-4'-methoxy-6'-hidroxybenzilydene]-2-phenazinoylhydrazine, (FBFH), 1-benzilydene-2-phenazinoylhydrazine, (BFH), and 3'-formyl-5',6'-dihydroxybenzilydene-2-nitro-4-methylaniline, (FBAH). The novel complexes were characterized by ESR, IR, electronic spectroscopy, molar electric conductibility measurements and magnetic studies. These compounds appear to be hexacoordinated.

RESUMO

Complexos divalentes de metais 3d com derivados de formilvanilina foram sintetizados através da reação do cloreto de metal(II) correspondente com 1-(3'-formil-4'-metoxi-6'-hidroxibenzilideno)-2-fenazinoilhidrazina, (FBFH), 1-benzildeno-2-fenazinoilhidrazina, (BFH), e 3'formil-5',6'-dihidroxibenzilideno-2-nitro-1-metilanilina, (FBAH). Os complexos tem a estrutura geral ML_2 ou ML_2X_2 (M=Cu(II), Co(II); X=Cl). Os novos complexos foram caratcerizados usando técnicas de RSE, infravermelho, condutibilidade molar elétrica e estudos magnéticos. Estes complexos parecem ser hexacoordenados.

KEYWORDS : phenazinoylhydrazine, copper(II), cobalt(II), hydroxybenzilydene, IR spectra

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INTRODUCTION

In coordinative chemistry an important part in the coordination process is played by the ligands characterized by the presence of several donor groups. Thus the derivatives resulting from 3-formyl-5,6-dihydroxybenzilidene or 2-formyl-4-methoxy-benzilidene with phenazinoilhydrazine can favour the coordination of the metal ions by several chromophore groups. In 1979, Mihaceva L.H. and co-workers[1] synthetized and characterized by means of X-Ray spectrum studies the Co(II) and Cu(II) complexes with ligands, derived from the amide of the nicotinic acid. The structural data point to an octahedral geometry of the metal ions and their coordination with the amide nitrogen atom.

Hughes M.N. and co-workers[2], Nonoyama M. and co-workers[3] have shown that in the Co(II) and Cu(II) complexes with amides derivated from hydrazine, the metal ion has an octahedral geometry. Thus, the occurence of the absorption band fairly intensive at 1550 cm^{-1} can be assigned to the vibration frequency of the amide group, $\nu_{>C=O}$, and the sharp bands specific to the complexes that occur at 1595 cm^{-1} and 1630 cm^{-1} are characteristic of the $\nu_{>C=N}$ groups.

EXPERIMENTAL PART

The work has aimed at the synthesis and the solid-phase characterization of the Co(II) and Cu(II) complexes with 1-[3'-formyl-4'-methoxy-6'-hidroxybenzilydene]-2-phenazinoilhydrazine, (FBFH), 1-benzilydene-2-phenazinoilhydrazine, (BFH), and 3'-formyl-5',6'-dihydroxybenzilydene-2-nitro-4-methylaniline, (FBAH).

In order to obtain the Co(II) and Cu(II) complexes with the above-mentioned ligands the methanol solutions of $CuCl_2.2H_2O$ and $CoCl_2.6H_2O$ have been prepared the methanol solutions of the above-mentioned ligands have been prepared separately. The thus prepared solutions have been mixed so that the combination ratio M:L should be around 1:2 (Cu(II):FBFH = 1:2; Cu(II):FBH = 1:2; Co(II):FBFH = 1:2; Co(II):FBH = 1:2 and Cu(II):FBAH = 1:2). After some 45 minutes refluxing the solutions were cooled to get a differently coloured precipitates. After philtering, methanol washing and drying, the precipitates were subject to elementary analysis, thus determining C%, N%, O%, Cl% and M(II)%, respectively (Carlo Erba LA 1108 analyser and AAS 1N Carl Zeiss Jena atomic absorption spectrophotometer). To characterize the prepared complexes the IR spectra in the KBr pellet for the 4000-200 cm^{-1} (Specord M-80 Carl Zeiss Jena), the electronic spectra in diffuse reflectance by using MgO has a dilution matrix (VSU-2P Carl Zeiss Jena spectrophotometer), the electronic spectra in solution (Shimadzu 310 PS spectrophotometer), the ESR spectra (Varian E-9 spectrophotometer at room temperature on pouwder); conductivity measurements using dimethylformamide as a solvent (HACH TDS-meter conductometer) have been performed. The magnetic measurements have been performed by the Faraday method at room temperature, using $Hg[Co(SCN)_4]$ as a blank test.

RESULTS AND DISCUSSION

The synthesized complexes occur under the form of microcrystalline, differently coloured, water insoluble, sparingly soluble in tetrahydrofuran and soluble in dimethylformamide powders. The elementary analysis led to the results presented in Table 1.

Table 1

As one can easily conclude from the above presented data, the combination ratio M:L for all the prepared complexes is 1:2.

With a view of determining the coordination pattern of the ligands with the metal ions Cu(II) and Co(II) the IR spectra for the 4000-200 cm^{-1} range heve been determined. From the data presented in Tables 2-4 it has been ascertained that the absorption bands specific to the vibration frequencies of the groups non-involved in the formation of the chemical bonds with the metal ions, Cu(II) and Co(II), remain unchanged. In Table 2 the IR spectra for the Cu(II) and Co(II) complexes with the FBFH ligand are presented.

Table 2

The absorption band from 1670 cm^{-1} with an increased intensity in the ligand spectrum specific to the stretching vibration frequency $\nu_{C=O}$ (amide I) shifts towards smaller wave numbers and it splits into absorption bands of average intensity:
1652 cm^{-1}, 1638 cm^{-1} for the complex of the Cu(II) ion and 1660 cm^{-1}, 1643 cm^{-1} respectively, for the complex of the Co(II) ion. This behaviour can be assigned to the formation of the chemical bond of the ligand with the metal ion M(II) via the >C=O group. Likewise, the 1620 cm^{-1} absorption band specific to the frequency of the $\nu_{C=N}$ valency vibration (the chemical bond >C=N was formed as a result of the condensation of formyl-vanillin with phenazinoilhydrazine) shifts with about 20 cm^{-1} towards smaller wave numbers, to 1603 cm^{-1} for the Cu(II) complex and 1605 cm^{-1} respectively for the Co(II) complex, confirming the coordination of nitrogen atom to the respective metal ions. The 1160 cm^{-1} absorption band, very strong and sharp, specific to the frequency of $\nu_{Ar\text{-}OH}$ valency vibration shifts towards wave numbers that are about 15 cm^{-1} smaller and it diminishes its intensity. In the IR spectrum of the two complexes this band lies at 1145 cm^{-1} for the Cu(II) complex and at 1148 cm^{-1} for the Co(II) one, respectively.

Similarly, in the IR spectra of the two complexes there occur absorption bands of low intensity located at 505, 475, 329 cm^{-1} and at 520, 393, 308 cm^{-1} respectively, that are assigned to the vibration frequencies $\nu_{M\text{-}O}$ and $\nu_{M\text{-}N}$, $\delta_{N\text{-}M\text{-}N}$, respectively. This order of the frequencies of the vibrations $\nu_{M\text{-}O}$, $\nu_{M\text{-}N}$, respectively corresponds to the values presented by Nonoyama[3], Anagnostopoulos[4], Nakamoto[5]. The IR spectra for the Cu(II) and Co(II) complexes with the BFH ligand are presented in Table 3.

Table 3

As in the previous case it has been ascertained that the absorption band from 1680 cm^{-1} in the ligand spectrum, specific to the vibration frequency $\nu_{C=O}$ (amide I) shifts, within the spectrum of the complexes, towards smaller wave numbers and splits in to two bands pointing to a coordination of the oxygen atom from the >C=O group to the corresponding metal ions. Similarly, the absorption band from 1625 cm^{-1} typical of the $\nu_{C=N}$ stretching vibration frequency shifts within the spectrum of the complexes towards wave numbers that are about 20 cm^{-1} smaller. This behaviour points out the coordination of the nitrogen atom with the Cu(II) and Co(II) metal ions.

Table 1. Elementary chemical analysis for the prepared complexes

Compound	C %		N %		O %		Cl %		M %	
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
$Cu(FBFH)_2$	61.28	60.74	13.15	12.33	14.85	14.07	-	-	7.37	6.85
$Cu(FBAHCl)_2$	61.26	60.89	14.29	13.98	3.82	3.17	8.93	8.21	8.10	7.83
$Co(BFH)_2$	61.61	60.32	13.06	12.62	14.93	15.35	-	-	6.88	6.11
$Co(BFHCl)_2$	61.53	60.81	14.35	13.82	3.85	3.20	9.10	8.69	7.57	7.18
$Cu(BFAHCl)_2$	48.97	48.17	7.62	7.11	21.76	20.92	9.65	8.87	8.70	8.25

Table 2. IR bands of the $MC_{44}N_8O_8H_{30}$ complexes and the $C_{22}N_4O_4H_{16}$ ligand (cm^{-1})

$C_{22}N_4O_4H_{16}$	$CuC_{44}N_8O_8H_{30}$	$CoC_{44}N_8O_8H_{30}$	Assignment
3018 (m)	3018 (m)	3018 (m)	ν_{CH} (Ar)
1460 (m)	1460 (m)	1462 (m)	$\nu_{C=C}$ (Ar)
2850 (m) 1282 (s) 1070 (s)	2850 (m) 1280 (s) 1070 (s)	2852 (m) 1282 (s) 1069 (s)	ν ($-OCH_3$)
2720 (m) 1695 (s)	2718 (m) 1693 (s)	2722 (m) 1697 (s)	ν_{Ar-CHO}
1620 (s)	1603 (m)	1605 (m)	$\nu_{C=N}$
1670 (s)	1652 (m) 1638 (m)	1660 (m) 1643 (w)	$\nu_{C=O}$ amida I
1580 (s)	1580 (s)	1579 (s)	ν_{C-N} amida II
1044 (m)	1056 (m)	1054 (m)	ν_{N-N}
1160 (s)	1145 (m)	1148 (m)	ν_{Ar-OH}
	505 (m) 475 (w) 329 (w)	520 (m) 393 (w) 308 (w)	ν_{M-O} ν_{M-N} δ_{N-M-N}

s - strong; m - medium; w - weak

Table 3. IR bands of the $MC_{40}N_8O_2H_{28}Cl_2$ complex and the $C_{20}N_4OH_{14}$ ligand (cm^{-1}

$C_{20}N_4OH_{14}$	$CuC_{40}N_8O_2H_{28}Cl_2$	$CoC_{40}N_8O_2H_{28}Cl_2$	Assignment
3o10 (m)	3010 (m)	3012 (m)	ν_{CH} (Ar)
1880 (w)	1888 (w)	1892 (w)	δ_{CH} (Ar)
1450 (m)	1450 (m)	1452 (m)	$\nu_{C=C}$ (Ar)
1625 (s)	1608 (m)	1605 (m)	$\nu_{C=N}$
1680 (s)	1662 (m)	1668 (m)	$\nu_{C=O}$
	1647 (w)	1651 (w)	(amida I)
1595 (s)	1592 (s)	1596 (s)	ν_{C-N}
			(amida II)
1037 (m)	1051 (m)	1050 (m)	ν_{N-N}
	512 (w)	535 (w)	ν_{M-O}
	493 (w)	415 (w)	ν_{M-N}
	309 (w)	328 (w)	δ_{N-M-N}
	276 (w)	294 (w)	ν_{M-Cl}

s- strong; m - medium; w - weak

Table 4. Ir bands of the $CuC_{30}N_4O_{10}H_{24}Cl_2$ complex of the $C_{15}N_2O_5H_{12}$ ligand (cm^{-1})

$C_{15}N_2O_5H_{12}$	$CuC_{30}N_4O_{10}H_{24}Cl_2$	Assignment
2962 (s)	2962 (s)	ν (CH_3) as
2870 (m)	2870 (m)	ν (CH_3) sim
1o35 (m)	1038 (m)	ν_{CH} (Ar)
1490 (s)	1492 (s)	$\nu_{C=C}$ (Ar)
1560 (s)	1562 (s)	ν (NO_2) as
1370 (s)	1370 (s)	ν (NO_2) sim
875 (m)	878 (m)	ν_{C-N}
2720 (m)	2718 (m)	ν_{Ar-CHO}
1690 (s)	1690 (s)	
1173 (s)	1170 (w)	ν_{Ar-OH}
	1138 (m)	
1635 (s)	1620 (m)	$\nu_{C=N}$
	573 (m)	ν_{Cu-O}
	437 (w)	ν_{Cu-N}
	320 (w)	δ_{N-Cu-N}
	265 (m)	ν_{Cu-Cl}
3402 (m)	3380 (w)	ν ($Ar-NH_2$)
810 (s)	758 (m)	

s- strong; m - medium; w - weak

The analysis of the IR spectra for both complexes in the range of the small wave numbers has rendered evident the presence of some new bands of low intensity, ranging between 270 cm^{-1} and 540 cm^{-1}. These absorption bands were assigned to the $\nu_{M\text{-}O}$ and $\nu_{M\text{-}N}$, vibration frequencies whose values are in accordance with observations made by the Nakamoto[5] for complexes endowed with an octahedral geometry. The absorption bands from 276 cm^{-1} and 294 cm^{-1}, respectively, were assigned to the $\nu_{M\text{-}Cl}$ valency vibration frequencies[6,7]. From the Tables 2 and 3 one can notice that for FBFH and BFH ligands the absorption bands occur at 1044 cm^{-1} and 1037 cm^{-1} respectively, typical of the $\nu_{M\text{-}N}$ stretching vibration frequencies. In the IR spectra of the four complexes of the Cu(II) and Co(II) ions, these bands shift with 10-15 cm^{-1} towards bigger wave numbers, confirming in this way the coordination of the sp^2 hybridized nitrogen atom with the metal ions[8]. In Table 4 the IR absorption bands of the $CuC_{30}N_4O_{10}H_{24}Cl_2$ complex and of FBAH ligand are presented.

Table 4

The vibration frequencies specific to the groups involved in the formation of the chemical bonds with Cu(II) ion ($\nu_{Ar\text{-}OH}$ = 1173 cm^{-1}, $\nu_{Ar\text{-}NH}$ = 810 cm^{-1}) shifted towards smaller wave numbers with in IR spectrum of the complex. The new absorption bands that occured in the IR spectrum of the complex in the range of the small wave numbers of low intensity at 573 cm^{-1} and 320 cm^{-1} are assigned to the vibrations of $\nu_{Cu\text{-}O}$ and $\nu_{Cu\text{-}N}$ valency and to the deformation vibration $\delta_{N\text{-}Cu\text{-}N}$[3,5]. The absorption band from 265 cm^{-1} was assigned to the frequency of $\nu_{Cu\text{-}Cl}$ valency vibration frequencies[6,7].

The bands corresponding to the electronic transitions and assigned to these ones for the prepared complexes and the ligands are presented in Table 5.

Table 5

As it can easily ascertained from the data presented in the table, the absorption bands specific to the chromophore group of the ligands are included in the 30770-38815 cm^{-1} range. As for the complexes, the above mentioned absorption bands are found again in the spectrum, but they shifted towards the lower frequencies and there occur further bands due to the d-d transitions. The assignment of the electronic transitions of the Co(II) complexes has been performed by using a splitting diagram in accordance with the data presented by Meredith P.L. and co-workers[9].

Driessen W.L. and co-workers[10] and for the Cu(II) complexes a splitting diagram for a distorted octahedral geometry was used[11,12].

The frequencies of the electronic transitions for all the complexes point to a distorted octahedral geometry with a stronger distorsion for the $CuC_{30}N_4O_{10}H_{24}Cl_2$ complex. This statement is in accordance with the values of the electron parameters of the ligand field (Table 6) for the Co(II) complexes.

Table 6

The different values of the Δt and Δs splitting parameters of the two complexes of Co(II) point to the presence of the chlorine ions within the coordination area of Co(II). Similarly, the value of the β parameter suggests the fact that the chemical bond in the $CoC_{40}N_8O_2H_{22}Cl_2$ combination has a stronger ionic nature than the $CoC_{44}N_8O_8H_{30}$ combination. The values of the experimental magnetic moments (Table 7) both for the Co(II) complexes and for the Cu(II) ones confirm the distorted octahedral geometry[13,14].

Table 7

Table 5. Electronic spectra and the assignment of the transitions (cm^{-1})

Compound	ν, cm^{-1}	Assignment
$C_{22}N_4O_4H_{16}$	35715	$\pi \rightarrow \pi^*$
	30770	$n \rightarrow \pi^*$
$CoC_{44}N_8O_8H_{30}$	33200	$\pi \rightarrow \pi^*$
	29020	$n \rightarrow \pi^*$
	21100	$^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)$
	16540	$^4T_{1g}(^4F) \rightarrow {}^4A_{2g}(^4F)$
	9120	$^4T_{1g}(^4F) \rightarrow {}^4T_{2g}(^4F)$
$CuC_{44}N_8O_8H_{30}$	34278	$\pi \rightarrow \pi^*$
	29435	$n \rightarrow \pi^*$
	15420	$z^2 \rightarrow x^2\text{-}y^2$
	10250	$xz,yz,xy \rightarrow x^2\text{-}y^2$
$C_{20}N_4OH_{14}$	35210	$\pi \rightarrow \pi^*$
	32430	$n \rightarrow \pi^*$
$CoC_{40}N_8O_2H_{22}Cl_2$	34015	$\pi \rightarrow \pi^*$
	31210	$n \rightarrow \pi^*$
	22840	$^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)$
	17415	$^4T_{1g}(^4F) \rightarrow {}^4A_{2g}(^4F)$
	9260	$^4T_{1g}(^4F) \rightarrow {}^4T_{2g}(^4F)$
$CuC_{40}N_8O_2H_{28}Cl_2$	33890	$\pi \rightarrow \pi^*$
	31075	$n \rightarrow \pi^*$
	15940	$z^2 \rightarrow x^2\text{-}y^2$
	9850	$xz,yz,xy \rightarrow x^2\text{-}y^2$
$C_{15}N_2O_5H_{12}$	38315	$\pi \rightarrow \pi^*$
	35720	$n \rightarrow \pi^*$
$CuC_{30}N_4O_{10}H_{24}Cl_2$	36500	$\pi \rightarrow \pi^*$
	33720	$n \rightarrow \pi^*$
	16400	$x^2\text{-}y^2 \rightarrow xy$
	18250	$z^2 \rightarrow xy$

Table 6. Electronic parameters of the ligand field for the Co(II) complexes (cm^{-1})

Parameters	$CoC_{44}N_8O_8H_{30}$	$CoC_{40}N_8O_2H_{22}Cl_2$
10Dq	7420	8155
B	690	820
β	0,710	0,844
Δ_t	390	647
Δ_s	652	548

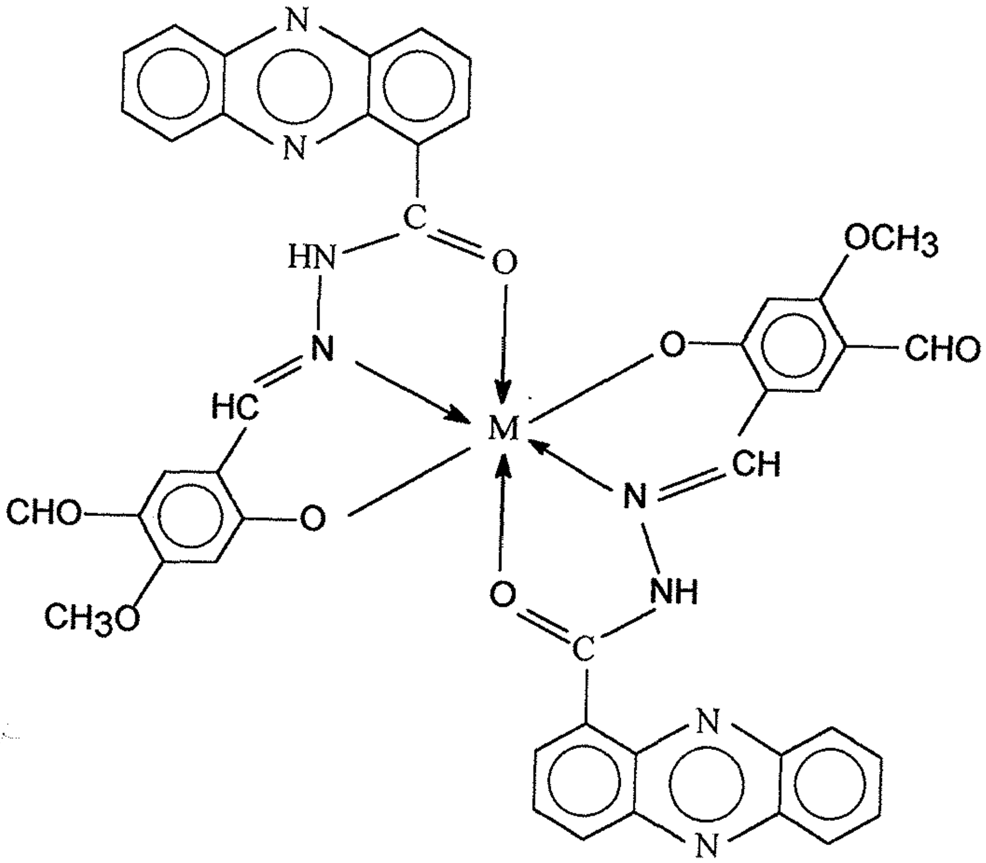
Table 7. The molar electric conductibilies, Λ_M ($\Omega^{-1}cm^2mol^{-1}$), and the experimental magnetic moments, μ_{exp} (MB), for the prepared complexes

Compound	Λ_M ($\Omega^{-1}cm^2mol^{-1}$)	μ_{exp} (MB)
$CoC_{44}N_8O_8H_{30}$	36	5,17
$CoC_{40}N_8O_2H_{22}Cl_2$	24	5,04
$CuC_{44}N_8O_8H_{30}$	19	1,92
$CuC_{40}N_8O_2H_{22}Cl_2$	27	2,10
$CuC_{30}N_4O_{10}H_{24}Cl_2$	13	2,05

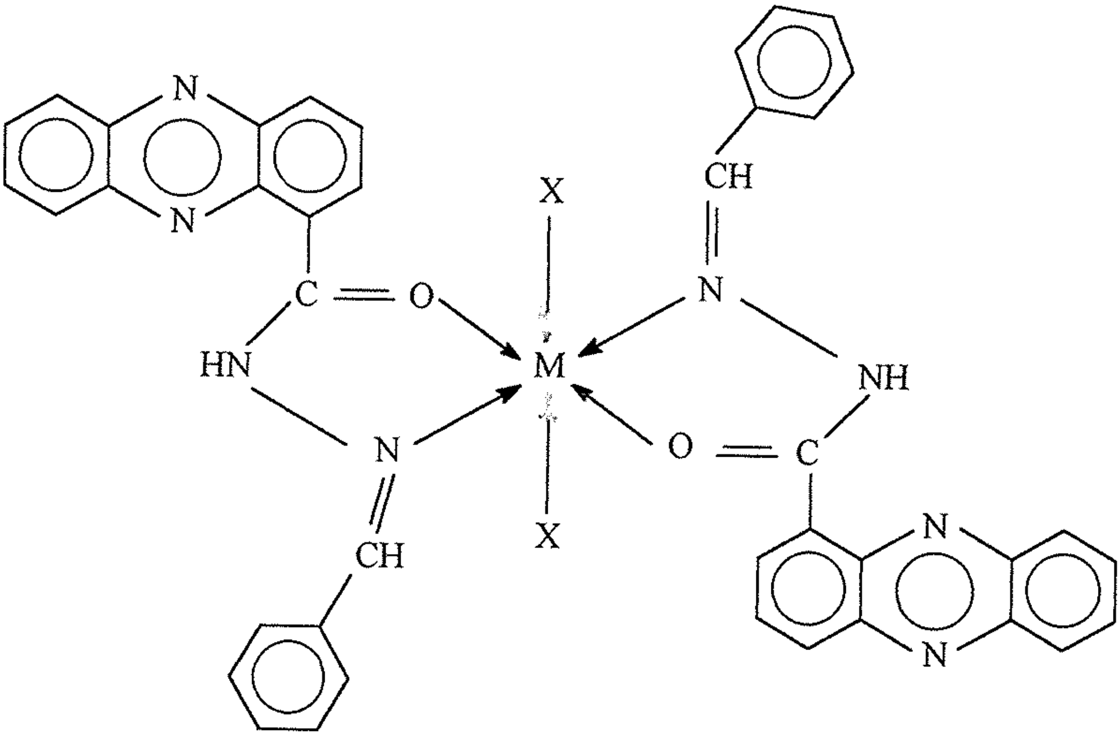
Table 8. The values of the splitting parameter, g, for the Cu(II) complexes

Parameter {g}	$CuC_{44}N_8O_8H_{30}$	$CuC_{40}N_8O_2H_{28}Cl_2$	$CuC_{30}N_4O_{10}H_{22}Cl_2$
g_x	2,077	2,005	2,015
g_v	2,142	2,204	2,198
g_z	2,266	2,175	2,112

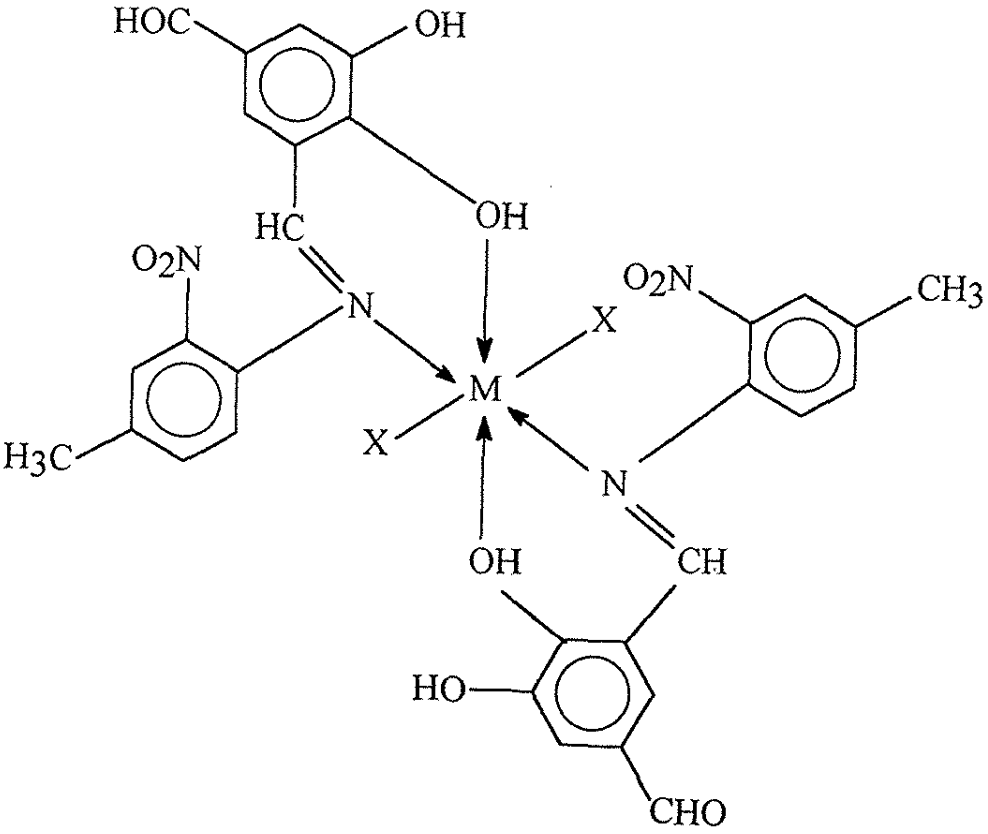
Ⓐ M (II) = Cu (II); Co (II)



Ⓑ M (II) = Cu (II); Co (II)
X = Cl



Ⓒ M (II) = Cu (II)
X = Cl



The molar electric conductibilities of the solutions of 10^{-3}M concentration, in DMF, for all the prepared complexes, have values lower than 65 $\Omega^{-1}mol^{2}cm^{-1}$ (Table 7) establishing in this way the non-electrolyte nature of these ones. The values of the tensor {g} obtained from the ESR spectra for the Cu(II) complexes are mentioned in Table 8.

Table 8

The intensity of the bands and the anizotropy of the g_x and g_y parameters from the equatorial plane may result from the different interactions with the ligands which cause a rather strong distorsion[15]. Correlating the values of the experimental determinations one can hold that all the prepared complexes belong to the distorted octahedral simmetry group (Figures a,b,c).

CONCLUSIONS

New complexes with derivatives of phenazinoilhydrazine have been synthetised;.

Spectral and magnetic estimations on microcrystalline powders of the prepared complexes have been performed;

The Co(II) and Cu(II) complexes belong to the distorted O_h symmetry group.

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