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Spectroscopic studies of copper (II) complexes with some amino acids

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Copper-amino acids complexes in aqueous solution: $[Cu(\mathbf{L_1})_2]\cdot H_2O$ ($\mathbf{L_1}$=lysine), $[Cu(\mathbf{L_2})_2]\cdot H_2O$ ($\mathbf{L_2}$=glycine) and $[Cu(\mathbf{L_3})_2]\cdot H_2O$ ($\mathbf{L_3}$= leucine) were synthesized and analyzed by means of elemental analysis, thermogravimetric analysis, atomic absorption, FTIR, UV-VIS and EPR spectroscopies. The thermogravimetric analysis results are similar for all the complexes, the mass losses occurred in one or more steps until the complexes were destroyed and the copper oxide was formed. The atomic absorption spectroscopy and elemental analysis confirms the compounds stoichiometry. The FTIR spectra show that amino acids act as bidentate ligands with the coordination involving the carbonyl oxygen and the nitrogen atom of amino group. Powder EPR spectra at room temperature are typical for monomeric species with square-planar local symmetry around the metal ion, the principal values of the **g** tensor are: $g_{||}$=2.180, $g_{\perp}$= 2.100 for **1**, $g_{||}$=2.205, $g_{\perp}$= 2.090 for **2** and $g_{||}$=2.178, $g_{\perp}$= 2.112 for **3**. The EPR spectra of the Cu (II) - amino acids complexes in DMF solution display the copper hyperfine structure ($g_0 \approx 2.120$, $A_0 \approx 80$ G).

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Keywords: Amino acids, Cu (II) complexes, FTIR spectroscopy, UV-VIS spectroscopy, EPR spectroscopy

1. Introduction

In recent last years Cu (II) amino acids complexes have received much attention because of they proved to be useful as antitumor and antibacterial agents against *Staphylococcus aureus, Escherichia coli*, or nutritive supplies for human and animals, etc [1].

Twenty natural amino acids comprise the building blocks of proteins, which are chemical species indispensable to perform a huge number of biological functions, as exemplified by the role of enzymes [2]. From these twenty amino acids, eight are essential and cannot be produced by the human body.

Complexes of transition metals with amino acids in proteins and peptides are utilized in numerous biological processes, such as oxygen conveyer, electron transfer and oxidation. In these processes, the enzymatic active site, which is very specific, forms complexes with divalent metal ions [3].

Lysine (Fig. 1.a) is a charged polar amino acid with an extra amino group. It is an essential amino acid, and the human requirement is 1÷1.5 g daily, is important for proper growth and it plays an indispensable role in the production of carnitine, a nutrient responsible for converting fatty acids into energy and helping to lower cholesterol [4].

Glycine (Fig. 1.b) is the simplest amino acid in the body and the only protein amino acid that does not have optical isomers. Glycine consists of a single carbon molecule attached to an amino and a carboxyl group. Its small size helps it to function as a flexible link in proteins and allows for the formation of helices, an extracellular signaling molecule, recognition sites on cell membranes and enzymes, a modifier of molecular activity via conjugation and glycine extension of hormone precursors, and an osmoprotectant. There is substantial experimental evidence that free glycine may have a role in protecting tissues against insults such as ischemia, hypoxia, and reperfusion [5].

Leucine (Fig. 1.c) along with isoleucine and valine, are the branched-chain amino acids who represent about one-third of muscle protein. Leucine has been the most thoroughly investigated because its oxidation rate is higher than that of isoleucine or valine. Leucine also stimulates protein synthesis in muscle and is closely associated with the release of gluconeogenic precursors, such as alanine, from muscle [6].

In the globine from the hemoglobine leucine formes apreximative one third from the total amount of the amino acids.

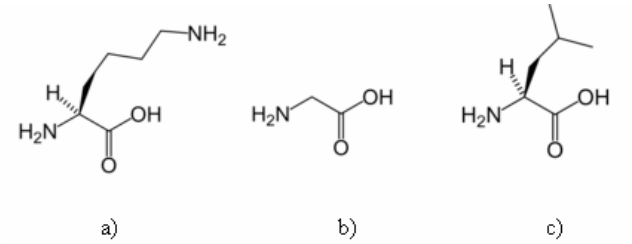


Fig. 1. Structure formulas for lysine (a), glycine (b), and leucine (c).

2. Experimental

2.1 Methods

The elemental analysis measurements were performed with a Vario EL device. The thermogravimetric analysis (TG) were carried out using a Q-1500 D derivatograph, in the temperature range of 20 ^{0}C to 500 ^{0}C, at a heating rate of 10 ^{0}C min^{-1}. The analyses were carried out over samples varying from 100 to 300 mg. Atomic absorption measurements were performed with an AAS-1 device at λ=320 nm wavelength. FT-IR spectra were taken with a Perkin-Elmer FTIR 1730 spectrophotometer over KBr solid samples in 4000-400 cm^{-1} range. UV and visible electronic spectra were recorded in the λ=190-800 nm range in aqueous solution, using a standard Jasco V-530 spectrophotometer. Powder EPR measurements were performed at room temperature at 9.4 GHz (X band) using a standard JEOL-JES-3B equipment.

2.2 Synthesis of copper amino acids complexes

The purpose of the study was to obtain neutral complexes of **$CuL_2 \cdot nH_2O$** type at pH=8-10, in the presence of a strong basis (NaOH) for deprotonation of the amino acid. The complexes were prepared following the procedure described in the literature [7]: 2 mmols of **L_1** (0.292g), **L_2** (0.150g) and **L_3** (262g) were dissolved in distilled water (5ml for **L_1**, 20ml for **L_2** and 131ml for**L_3**). For **L_2** and **L_3** dissolvation took place only with slow heating. For deprotonation of amino acids 0.33ml 30% NaOH was added. Then 1 mmol of metal salt (0.241g $Cu(NO_3)_2 \cdot 3H_2O$) was dissolved in 2ml of distilled water, and was added to the deprotonated amino acid solution under stirring it for several minutes. For all amino acids precipitation was instantenous, and were dark-blue for **L_1** (η=74.6%), intense blue for **L_2** (η=93.7%) and grey-green for **L_3** (η=69.6%). Melting points were recorded on an Electrothermal Analyser working in the temperature range of 20 ^{o}C and 370 ^{o}C.

3. Results and discussions

3.1 Elemental analysis

The Vario El device allows the quantitative determination of the carbon, nitrogen, hydrogen, sulphur, and oxygen in various operating modes. For the synthesised copper complexes the elemental analysis results confirm the 1:2 copper ion to ligand composition. Data of the elemental analysis for copper amino acids complexes are illustrated in Table 1.

Table 1. Elemental analysis results for copper amino acids complexes.

Complex	Molecular weight(g)	%C		%H		%N	
		Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
1	355	40.56	39.86	7.32	7.73	15.77	15.26
2	213.5	22.48	21.33	4.68	4.96	8.60	8.17
3	325.5	44.23	43.26	7.38	7.93	8.60	8.17

3.2 Thermogravimetric analysis

The weight loss profiles are analyzed the amount or percent of weight loss at any given temperature, and the temperature ranges of the degradation processes were determined [8, 9].

Complex **1**, starts to decompose around 90^{0}C and a 4.5% weight loss is observed (4.8% theoretical) in this step. The dehydration takes place and one molecule of crystallisation water is eliminated. The second step, starting at 140^{0}C shows a weight loss of 38% (theoretical 38.6%) corresponding to the -$(CH_2)_4$-NH_2 radical breaking from the lysine molecule. Around 220^{0}C a 33% (30.1% theoretical) mass loss appears due to the NH_2-CH-COO- radical breaking which remained from the amino acid. The constant stage was attributed to the rest of CuO, with 24.5% mass loss (26.5% theoretical). The purposed formula is [Cu-(**L_1**)$_2$]· H_2O (Fig. 2.a).

The decomposition of complex **2** (Fig. 2.b) and **3** starts around 120 ^{0}C respectively 110^{0}C with a recorded weight loss of 7.5% (6.35% theoretical) (2) and 4.65% weight loss (5, 23% theoretical) (**3**). Similar with the first complex, dehydration takes place and one molecule of crystallisation water was eliminated. For these complexes the second step took place around 190^{0}C respectively 260^0 with a massive weight loss of 70.50% (76.25% theoretical) (**2**) and 73% (76.16%) (**3**) corresponding to the deterioration of the amino acid molecul. The purposed formulae are [Cu-(**L_2**)2]·H_2O (Fig.2.b) and [Cu-(**L_3**)$_2$]·H_2O.

The thermogravimetric differential analysis results are similar for all the complexes, the mass lost occurred in one or two stages until the complex is destroyed and the copper oxide is formed.

Data of the thermal behaviour of the copper (II) amino acids complexes are presented in Table 2.

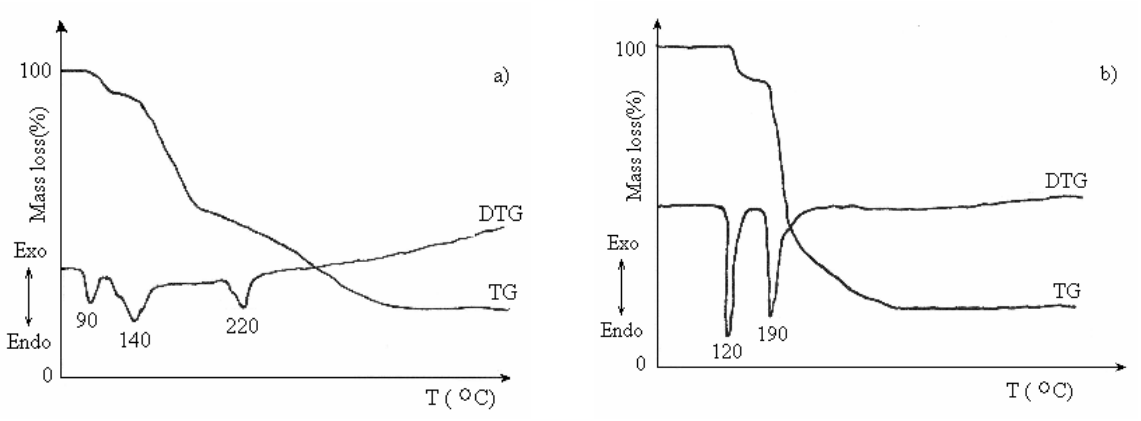


*Fig. 2. Derivatograms for **1** (a) and **2** (b) complexes.*

Table 2. Thermogravimetric data and purposed formulas for the synthesized complexes.

Complex	% Mass loss		T.max ^{0}C	Process	Atributed	Purposed Formula
	Calc.	Meas.				
1	4.8 38.6 30.1 26.5	4.5 38 33 24.5	90 140 220 >350	Endo Endo Endo Exo	$-(CH_2)_4-$ NH_2- $-NH_2-CH-$ COO- CuO	**$[Cu(L_1)_2]\cdot H_2O$**
2	6.35 76.25 17.65	7.25 70.50 22.35	120 190 >340	Endo Endo Exo	H_2O crist. Glycine CuO	**$[Cu(L_2)_2]\cdot H_2O$**
3	5.23 76.16 19.75	4.95 7.30 18.61	110 260 >360	Endo Endo Exo	H_2O crist. Leucine CuO	**$[Cu(L_3)_2]\cdot H_2O$**

3.3 Atomic absorption spectroscopy

The copper complexes theoretical concentrations have similar values with those of the synthesized complex, which demonstrates that complete reaction took place (Table 3).

Table 3. Copper concentrations obtained by means of atomic spectroscopy.

Complex	Copper complex concentration (%)	
	Synthesized	Theoretical
1	11.88	12.02
2	23.13	23.20
3	19.38	19.40

3.4 FT-IR spectroscopy

Information about the copper ion coordination was obtained by comparing the IR frequencies of the ligands with those of the copper complexes with amino acids as ligands.

In the figures (Figs. 3-5) the main parts of the IR spectra are presented and the most important absorption bands and their assignments are shown in Table 4.

In spectra of the ligands, the ν(N-H) stretching vibrations appear at 3118 cm^{-1} for $\mathbf{L_1}$, 3152 cm^{-1} for $\mathbf{L_2}$ and at 3052 cm^{-1} for $\mathbf{L_3}$. These bands appear shifted toward higher frequencies in the spectra of the complexes at 3283 cm^{-1} for **1**, 3159 for **2** and additional splitting appear in the spectrum of complex **3** at 3319 cm^{-1} and 3245cm^{-1}, proving the involvement of the aminic group in the complex formation [10].

The ν(C=O) stretching vibration is shifted toward higher frequencies in the spectra of the complexes with 20 cm^{-1} for **1**, 57cm^{-1} for **2** and 11 cm^{-1} for **3** which involves the carboxylic group in covalent bonding to the copper ion [11]. In the spectra of the ligands, the ν(O-H) stretching vibration could not be attributed, but in all three complexes this band appeared at similar frequencies, suggesting the presence of the crystallization water in this compound.

This involvement of $-NH_2$ group to the metal bonding formation was assigned to shifting of the δ(N-H) bending vibration toward higher frequencies in the complexes spectra.

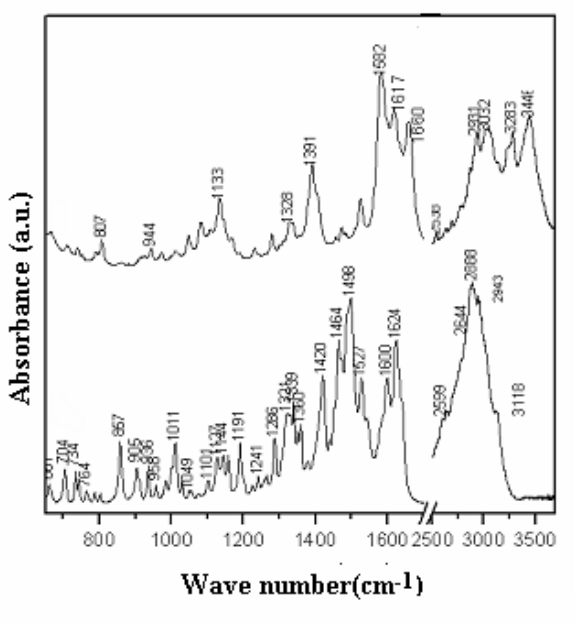


Fig. 3. FTIR Spectra of ***L₁*** *(up) and* ***1*** *(down).*

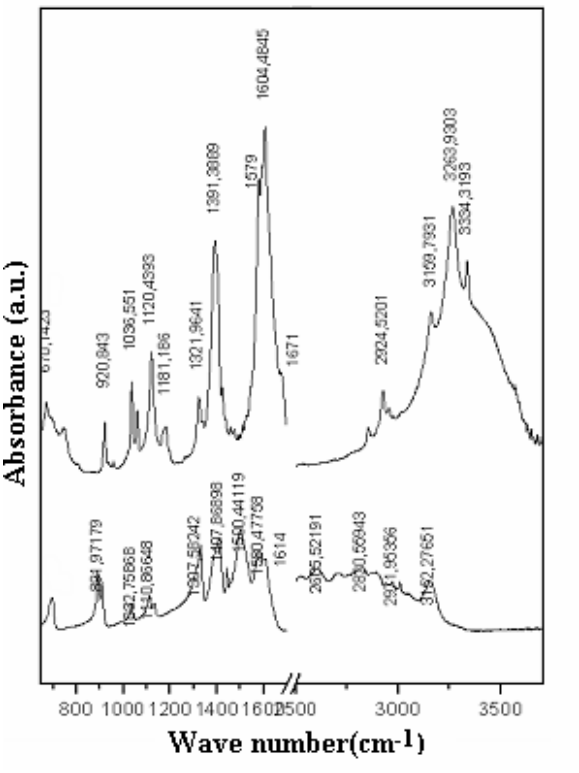


Fig. 4. FTIR Spectra of ***L₂*** *(up) and* ***2*** *(down).*

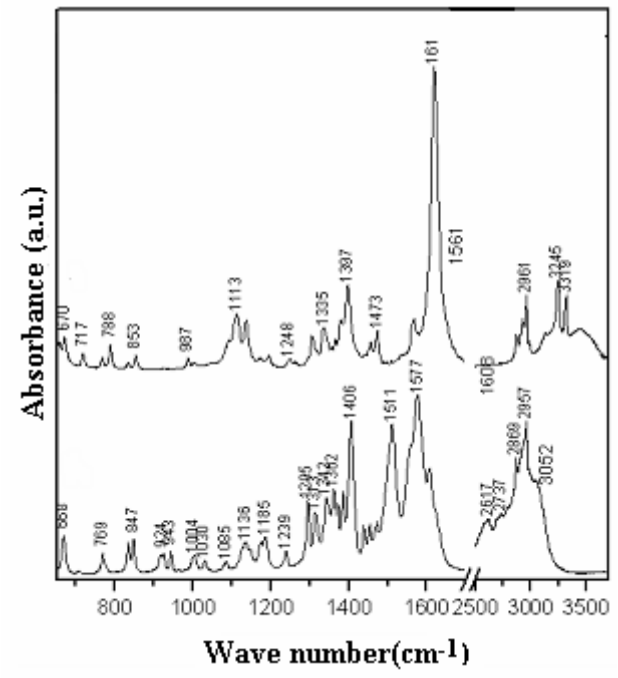


Fig. 5. FTIR Spectra of ***L₃*** *(up) and* ***3*** *(down).*

Table 4. FTIR spectral data (cm^{-1}).

Band	L_1	1	L_2	2	L_3	3
ν(N-H)	3118	3283	3152	3159	3052	3319 3245
ν(O-H)	-	3446	-	3334	-	3500
ν(C=O)	1640	1660	1614	1671	1608	1619
δ(N-H)	1600 1527	1617 1582	1580	1604 1579	1577 1511	1561

3.5 UV-VIS spectroscopy

The shift of n-π^* characteristic band in the UV spectra, attributed to the C=O bond (262nm for **L_1**, 270 nm for **L_2**, 277 nm for **L_3**, and 272 nm for **1**, 270 for **3**) is due to the involving of the non –bonding electron pairs of the oxygen in the metal-ligand bond formation (Figs. 6-8). The same transition could not be observed in the spectrum of complex **2** because of the high complex concentration [12].

The absorption spectra in the visible domain contain a wide band, centered at 639 nm for **1** and 620 for **2** and **3**, which can be observed only at higher concentrations of the complexes and was attributed to the d-d transition of the electrons which suggests a $^2T_{2g} \rightarrow {}^2E_g$ transition, specific for Cu (II) complexes with tetragonal distortion due to the Jahn-Teller effect.

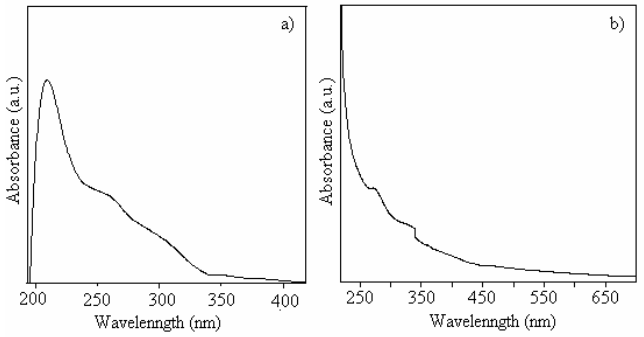


Fig. 6. UV spectra for $\mathbf{L_1}$ *(a) and* ***1*** *(b).*

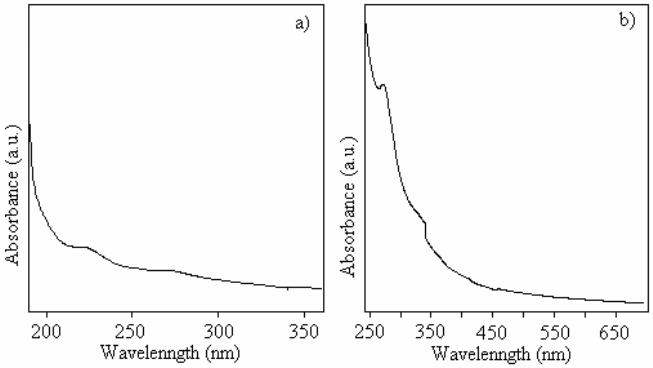


Fig. 7. UV spectra for $\mathbf{L_2}$ *(a) and* ***2*** *(b).*

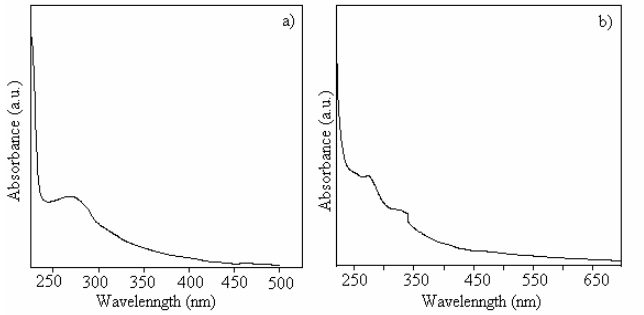


Fig. 8. UV spectra of $\mathbf{L_3}$ *(a),* ***3****(b) and* ***3*** *in DMSO (c).*

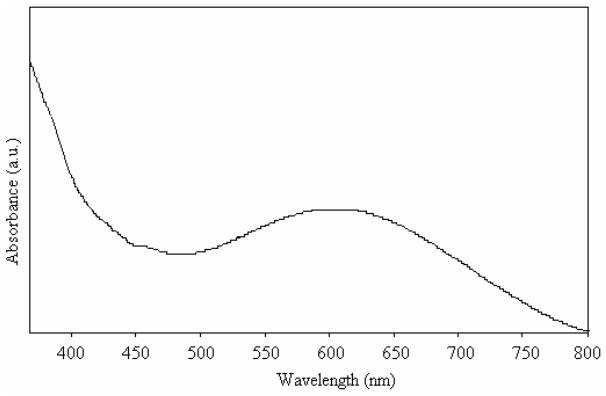


Fig. 9. VIS spectrum of ***2*** *in DMSO.*

3.6 EPR spectroscopy

Powder EPR spectra (Fig. 10.a,b,c) at room temperature are typically for monomeric species with square-planar local symmetry around the metallic ion, the principal values of the **g** tensor are: $g_{\|}$=2.180, $g_{\perp}$= 2.100 for **1**, $g_{\|}$=2.205, $g_{\perp}$= 2.090 for **2**, $g_{\|}$=2.178, $g_{\perp}$= 2.112 for **3** corresponding to a CuN_2O_2 cromophore.

The EPR spectra of the Cu(II)-amino acid complexes in DMF solution display the copper hyperfine structure g_0=2.120, A_0= 81G for **1**, g_0=2.122, A_0= 82G for **2**, g_0=2.121, A_0= 79G for **3** (Fig. 10.d)[14].

4. Conclusions

Three new copper amino acids complexes in aqueous solution were synthesized $[Cu(\mathbf{L_1})_2]\cdot H_2O$ ($\mathbf{L_1}$=lysine), $[Cu(\mathbf{L_2})_2]\cdot H_2O$ ($\mathbf{L_2}$=glycine) and $[Cu(\mathbf{L_3})_2]\cdot H_2O$ ($\mathbf{L_3}$= leucine) and analyzed by means of: elemental and thermogravimetric analysis, atomic absorption, FTIR, UV-VIS and EPR spectroscopies.

Elemental analysis and atomic absorption spectroscopy results revealed the formation of the three copper complexes. Thermal analysis allowed establishing the temperature at which the complexes decompositions begun, the weight loss allowed to estimate the decomposition stoichiometry and the amount of crystallisation or coordination water within the complexes. All complexes have similar thermal behaviour, showing one or two stages of degradation due to the decomposition of the amino acids molecules.

The IR spectra show that amino acids act as bidentate ligands with coordination involving the carbonyl oxygen and the nitrogen atom of amino group. The EPR spectra indicate pseudotetrahedral local symmetry for the copper ion.

The obtained structural data allow us to propose the structural formulas for the studied metal complexes as shown in Fig. 11.

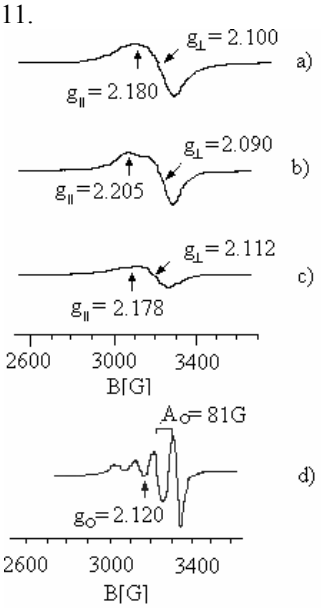
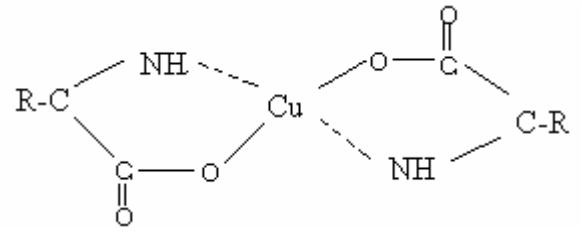


Fig. 10. Powder EPR spectra of ***1*** *(a),* ***2*** *(b),* ***3*** *(c) DMF solution of* ***1*** *(d).*



R= $-(CH_2)_4-NH_2$ for **1**
R= H for **2**
R= $-CH_2-CH(CH_3)-CH_3-$ for **3**

Fig. 11. Molecular formulas for the synthesized complexes.

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