Synthesis and ESR Spectroscopy Complexes of Copper(II) with Acyl- and Aroylhydrazones of Methyl Ester of 5,5-Dimethyl-2,4-Dioxohexanoic Acid

Tursunov Murod Amonovich¹, *, Sevinchova Dilobar Nematovna², Avezov Kuvondik Giyasovich¹, Umarov Bako Bafayevich¹, Ganiyev Bakhtiyor Shukurullayevich¹, Savriyeva Nigina Qahramon Qizi¹

¹Department of Chemistry, Bukhara State University, Bukhara City, Uzbekistan
²Department of Medical Chemistry, Bukhara State Medical Institute, Bukhara City, Uzbekistan

Email address:
tursunovma@mail.ru (T. M. Amonovich), h.ganiyev1990@gmail.com (G. B. Shukurullayevich)
*Corresponding author

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Abstract: The method of ESR is widely used for the investigation of electronic construction and the geometrical structure of the polynuclear complexes of the transition metals. The majority of the well-known experimental works had been done using monocrystals and polycrystalline examples. Construction of mononuclear complexes of the copper(II), the nature of antiferromagnetic exchange interaction, and its value was the object of the discussion by the scientists and that issue is being checked in the article. Complex compounds of copper(II) with 5,5-dimethyl-2,4-dioxohexane acid (\(\text{H}_2\text{L}_1\text{–H}_2\text{L}_{11}\)) methyl ether aroylhydrazones were synthesized and studied. The interaction of alcohol solutions of the \(\text{H}_2\text{L}_1\text{–H}_2\text{L}_{11}\) ligands with an aqueous ammonia solution of copper(II) acetate synthesized green fine-crystalline copper(II) complexes. Complexes investigation by the method of ESR spectroscopy, of the studying the magneto chemical properties of copper(II) complexes. If for the complex compound CuL\(_1\)• NH\(_3\), which has a cyclopentanone ring β-diketone fragment, the EPR parameters have the β substituent for \(\alpha^2=0.82\); value: \(g=2.099\), \(a_{\text{Cu}}=89.53\) e, \(a_{\text{N}}=12.81\) e, then for CuL\(_4\)• NH\(_3\) with a cyclohexane ring substituent these values are in the range: \(g=2.101\), \(a_{\text{Cu}}=87.48\) e, \(a_{\text{N}}=13.02\) e, \(\alpha^2=0.82\).

Keywords: Aroylhydrazone, Ethyl Ether of 5,5-dimethyl-2,4-dioxohexane Acid, Antiferromagnetic, Flat Square, Superposition

1. Introduction

In recent years, research in the field of coordination chemistry has been characterized by a stable tendency to shift the center of gravity from simple mononuclear compounds to more complex systems, which is primarily due to the search for new molecular materials and catalytic systems. These works, along with the consideration of their geometric and electronic structure, allow us to draw reasonable conclusions and predict the ways of directed synthesis of complex compounds with specified properties [1-3].

In contrast to Ni(II), the IR spectra of Cu(II) complexes similar in composition do not change noticeably when the complexes are dissolved in CCl\(_4\). They can be obtained by reacting an aqueous solution of copper(II) chloride–CuCl\(_2\)•2H\(_2\)O with an alcohol solution of the ligand with the subsequent addition of a dilute aqueous solution of ammonia or by mixing alcohol solutions of copper(II) acetate and the ligand. In the IR spectra of the obtained m(\(\text{HL}_2\)) complexes, an intense band is observed in the region of \(1735-1750\) cm\(^{-1}\), which should be attributed to the valence vibrations of the C=O bond of the uncoupled \(\text{COOC}_2\text{H}_5\) ester group. When the complex is formed due to nitrogen of the enhydrazone form, the bands of valence vibrations of this bond must show
a significant long-wave shift due to the inclusion of the C=O-
bond in the composition of the conjugated six-membered
chelated metal cycle.

According to the authors, as in the case of Nickel
complexes, copper(II) complexes arise by coordinating the
metal at the oxygen atom of the anion that corresponds to the
α-oxazine tautomeric form. The appearance of two intense
absorption bands at 1380 and 1550 cm⁻¹ due to fluctuations
in the NCO group is consistent with this structure of the
complexes [4].

Thus, the formation of a five-membered chelate cycle is
energetically more profitable than the formation of a six-
membered chelate cycle corresponding to the enhydrazone
form. Consequently, there is no coordination of the C=O-
energetically more profitable than the formation of a six-
membered chelate cycle.

2. Experimental

2.1. Materials and Reagents

All the chemicals and reagents used in the present study
were commercially available. These were purified by usual
methods of distillation (for liquids) and crystallization from
appropriate solvents (for solids). The organic solvents and
other agents used in the work were cleaned and dried
according to [11, 12]. Analysis of complex compounds for
metal content was performed according to [13, 14] and
atomic absorption method on the Perkin-Elmer 3030 V
spectrophotometer (USA), nitrogen was determined by the
Dumas method, carbon and hydrogen—by burning in the
oxygen current and on the Karlo-Erba-1106 element ana-
lyzer, the analysis data was calculated on the HEC-960 computer.

2.2. Methods of Analysis

ESR spectra of polycrystalline samples, liquid and frozen
solutions in toluene and other solvents were taken on a
Radiopan SE/X-2542 radio spectrometer with an operating
frequency of 9.4 GHz. The magnetic field was calibrated
using an NMR magnetometer. A stable radical, DPHG, was
used as the standard. Experimental spectra were transmitted
via a special interface to the SM-4 computer, which was used
for theoretical reconstruction of ESR spectra. The parameters
of the spectra were found by the method of the best
approximation between experimental and theoretical spectra
by minimizing the error functional according to the method
described in [15, 17].

The ESR spectra of all compounds were studied in
solutions pre-degassed in vacuum, toluene, chloroform,
DMSO and pyridine. This is done in order to remove oxygen
from solutions that widens the ESR lines. Toluene and
chloroform were chosen as an inert solvent. The concentra-
tion of solutions was 10·10⁻²·10⁻⁶ M. In some cases,
measurements of ESR spectra were performed on samples
with an isolate of ⁶³Cu up to 99.8%.

The static magnetic susceptibility of polycrystalline
samples in the range 77–300K was measured using the
Faraday and Gui method at the facilities described in [16].
the obtained values were corrected for temperature-
dependent Para magnetism and diamagnetism of ligands
calculated according to the Pascal scheme [15, 16]. the
reference sample was Co(Hg(CNS))₂.

Values of the MFF. monomer complexes were calculated
using the formula:

\[ M_{\text{eff}} = 2.83 \left( \gamma_{\text{L}} \cdot T \right)^{1/2} \]  

(1)

where \( \gamma_{\text{L}} = \gamma_{\text{dia}} - \gamma_{\text{dia}} \).

Values of the MFF. dimer complexes of copper(II) were
calculated using the formula:

\[ \mu_{\text{eff}} = 2.83 \left( \gamma_{\text{Cu}} \cdot T \right)^{1/2} \]  

(2)

where \( \gamma_{\text{Cu}} = 0.5 \gamma_{\text{dix}} \gamma_{\text{Mo}} \cdot \gamma_{\text{dix}} - 2\alpha \) (M is the molecular
weight of the monomer, \( \alpha \) is the impurity of the monomer).

Error in the definition of the MFF. was ±0.01 m.b.

2.3. General Procedure for Preparation of Copper(II)
Complexes with Methyl Hydrazones
5,5-dimethyl-2,4-dioxohexanoic Acid Ester

Aroylhydrazines were synthesized based on the methyl
esters of the corresponding acids and hydrzone hydrate using
well-known methods [18]. to obtain thiobenzylohydrazine, a
carboxymethyl ether of dithiobenzoic acid was previously
synthesized. Carboxymethyl ether of dithiobenzoic acid from
benzyl chloride. Then 8.5 g of dithiobenzoic acid and
8 ml of 50% hydrazine hydrate was added, while the solution
discoled.

After adding 10-15 ml of glacial acetic acid and
cooling with ice, hydrzone crystals fell out. The precipitate
was filtered out and recrystallized from benzene. The final
product was obtained with m. p. 70.5-71.5°C, yield (58%)
which is characterized by [19-24, 31].

Cul₁·NH₂. A hot solution of 1.25 g (0.005 mol) of
copper(II) acetate in 15 ml of concentrated ammonia was
added drop by drop to a solution of 1.52 g (0.005 mol) of
benzoyl hydrzone of methyl ether 5,5-dimethyl-2,4-
dioxohexanoic acid (H₂L₁) in 20 ml of ethanol. A green
solution is obtained, from which green crystals fall out after 5
minutes. The complex compound was filtered, repeatedly
washed with water, and then with alcohol and dried in a
vacuum desiccator over P₂O₅. Yields 0.95 g.

Similarly, other copper(II) ammonia complexes were
synthesized with the ligands $H_2L^1$–$H_2L^{11}$ and $H_2L^5$–$H_2L^9$, respectively (table 1).

**Table 1. Yields and results of elemental analysis of complex copper(II) compounds based on acyl- and aroyl-hydrazones of methyl and ethyl ether of 2,4-dioxocarboxylic acids.**

| Complex | Yield, % | Found, % | Brutto-formule | Calculated, % |
|---------|---------|----------|----------------|---------------|
| CuL\(^{1}\)NH\(_{3}\) | 75 | 17,88 47,34 4,78 11,91 | Cu\(_{11}\)H\(_7\)N\(_2\)O\(_4\) | 17,91 47,39 4,83 11,84 |
| CuL\(^{2}\)NH\(_{3}\) | 66 | 15,82 41,96 4,01 14,08 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\) | 15,89 42,05 4,03 14,01 |
| CuL\(^{3}\)NH\(_{3}\) | 49 | 14,82 47,78 5,39 13,19 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\) | 14,88 47,83 5,43 13,12 |
| CuL\(^{5}\)Py | 81 | 13,33 55,39 5,27 8,89 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\) | 13,38 55,63 5,30 8,85 |
| CuL\(^{6}\)N\(_{3}\) | 53 | 15,97 51,38 5,79 10,64 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\) | 16,01 51,44 5,84 10,59 |
| CuL\(^{7}\)Py | 78 | 13,79 57,51 5,44 9,21 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\) | 13,84 57,57 5,49 9,15 |
| Cu\(_{11}\)N\(_{3}\)=H\(_{7}\)O\(_{2}\)Br | 77 | 13,71 41,57 4,33 9,17 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\)Br | 13,76 41,61 4,37 9,10 |
| CuL\(^{2}\)Py | 70 | 12,06 48,08 4,18 8,13 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\)Br | 12,13 48,15 4,23 8,02 |
| CuL\(^{3}\)NH\(_{3}\) | 57 | 14,39 51,81 6,37 12,77 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\) | 14,44 51,86 6,41 12,73 |
| CuL\(^{6}\)N\(_{3}\) | 61 | 14,82 50,59 5,86 9,90 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\)Br | 14,88 50,64 5,90 9,84 |
| CuL\(^{8}\)N\(_{3}\) | 70 | 15,97 51,38 5,79 10,54 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\)Br | 16,01 51,44 5,84 10,59 |
| CuL\(^{10}\)Py | 73 | 13,79 57,53 5,42 9,23 | Cu\(_{12}\)H\(_{10}\)N\(_2\)O\(_5\)Br | 13,84 57,57 5,49 9,15 |

The interaction of alcohol solutions of the $H_2L^1$–$H_2L^{11}$ ligands with an aqueous ammonia solution of copper(II) acetate synthesized green fine-crystalline copper(II) complexes.

![Figure 1. Compound of the acyl- and aroylhydrazones ligands.](image1.png)

**Figure 1. Compound of the acyl- and aroylhydrazones ligands.**

\[ R=CH_2X-n, \ X=N(CH_3)_2 \ (CuL^{11}NH_3), OCH_3 \ (CuL^{10}NH_3), CH_3 \ (CuL^{9}NH_3), H \ (CuL^{8}NH_3), Br \ (CuL^{7}NH_3), NO_2 \ (CuL^{6}NH_3), R=H \ (CuL^{5}NH_3), CH_3 \ (CuL^{4}NH_3), C_2H_5 \ (CuL^{3}NH_3), izo-C_3H_7 \ (Cu^{10}NH_3), \text{tret.-}C_6H_5 \ (CuL^{11}NH_3). \]

3. Result and Discussion

The obtained copper(II) copper oxides obtained from ESR spectra in a chloroform solution and toluene have a flat-square structure. The ESR spectra are similar to the spectra of the previously studied compounds and represent a superposition of spectra from $^{65}$Cu and $^{65}$Cu nuclei (I$_{Cu}$=3/2). All this unequivocally testifies to the flat-square structure of the coordinating node of Copper(II) with trans-located atoms [N$_2$O$_2$]. The different widths of the STS lines for nuclear spin projections are explained by the McConnell relaxation mechanism, the parameters of which are given in Table 2.

\[ H=g\beta H_0 S + <a_0>S + a_0H_0 S \]

\[ H=\alpha + \beta m_1 + \gamma m_2^2 \]

**Figure 2. ESR spectrum of complex compound CuL\(^{2}\)NH\(_{3}\) in solid form.**

The spectra of all copper(II) complex compounds are described by an isotropic spin Hamiltonian (SH) of the form (1), where $g$ is the measure of the effective magnetic moment of the electron, the dimensionless $g$-factor, that is, the ratio of the magnetic moment of the electron to its total angular momentum Landau (for a free electron $g=2.002322$), is the Bohr magneton, $S=1/2$, $I=3/2$ is the spin of the nucleus of $\beta$ the copper atom, In is the spin of the nucleus of the nitrogen atom.
The width of the ESR spectra for complex copper(II) compounds is described by equation (4) [27], where it is taken into account that $m$ is the projection of the nuclear spin of the copper atom in the direction of the external magnetic field, $\alpha$, $\beta$, $\gamma$—are the coefficients due to various contributions to the relaxation mechanisms. In the copper(II) compounds studied, the unpaired electron is located on a molecular orbitals of the B1g type. According to this equation, $\alpha^2$ and $(\alpha')^2$—are the coefficients for the atomic orbitals of copper $(d_{x^2-y^2})$ and the atoms of the ligands $(\sigma_i)$, respectively. The semantic value of the coefficient $\alpha$ in equation (5) can be expressed in terms of its square as the probability density of finding an unpaired electron on the orbital $|d_{x^2-y^2}>$. Then the quantity $(\alpha')^2$, of course, determines the degree of delocalization of the unpaired electron on the orbitals of the ligand atoms. If $\alpha^2$ and $(\alpha')^2$ are equal to 0.5, then the metal-ligand bond in the complexes is covalent. In the case, if $\alpha^2=0$ and $(\alpha')^2=0$, the nature of the bond will be purely ionic. These coefficients $\alpha$ and $\alpha'$ are related to each other by the normalization equation (6), where $S$ is the overlap integral. The energy of the isotropic hyperfine interaction of the unpaired electron with the ligand nuclei is expressed by the equation (6) [28, 29], in this equation $\gamma_N$—is the gyromagnetic ratio of the nitrogen atom, $\beta_N$—is the magnetic moment of the ligand, $\rho_S(0)$—is the density 2s-orbitals on the nucleus of the nitrogen atom. It should be noted that when $(\alpha')^2=0$, the unpaired electron is not on the ligand atoms and the DHFS disappears.

$$\alpha^2 + (\alpha')^2 \geq \alpha \cdot \alpha' \cdot S = 1 \quad (5)$$

$$<a_N>=\frac{4}{9} \pi \cdot \gamma_N \cdot \beta_N \cdot (\alpha')^2 \cdot |\rho_S(0)|^2 \cdot S \cdot I_Z \quad (6)$$

If for the complex compound CuL·NH$_3$, which has a cyclopentanone ring $\beta$-diketone fragment, the ESR parameters have the $\beta$ substituent for the $\alpha^2=0.82$; value: $g^\prime=2.099$, $a_{\alpha N}=89.53$ e, $a_{\alpha N}=12.81$ e, then for CuL·NH$_3$ with a cyclohexane ring substituent these values are in the range: $g^\prime=2.101$, $a_{\alpha N}=87.48$ e, $a_{\alpha N}=13.02$ e, $\alpha^2=0.82$ (Figure 2, Table 2). Such a slight change in the parameters of the ESR spectra indicates that an increase in the number of carbon atoms in cycloalkanones does not significantly affect the parameters of the ESR spectra as compared with $\beta$-diketone fragment of the ligand $\beta$ the perfluoroalkyl substituent of the molecule. Confirmation of the conclusions on the flat-square structure of copper(II) complexes in solutions of chloroform and toluene at room temperature, the value of the covalence degree of the copper-ligand bond calculated from the isotropic ESR parameters by formula (7):

$$\alpha^2 = \frac{1}{0.43} (\frac{\alpha_{\alpha N}}{0.036} + g - 2) + 0.02 \quad (7)$$

In the most intense fourth component of the HFS of the ESR spectrum of the complexes, the DHFS from nine lines from the nuclei of two non-equilibrated nitrogen atoms of the chelating ligand and the ammonia molecule should be resolved. According to theory, the cleavage constant from the nitrogen atom of the chelating ligand should be twice the splitting constant from the nitrogen atom of ammonia. The poor resolution of the DHFS from two non-equivalent nitrogen atoms (Figures 1, 2, Table 2) is apparently explained by the strong broadening of the DHFS lines under the influence of the electronegative ester radical adjacent to the metallocycle of the copper(II) ion [30, 31].

![Figure 3. ESR spectrum of the complex compound CuL·NH$_3$ in a solution of chloroform at room temperature.](image)

| Compounds | $g^\prime \pm 0.001$ | $a_{\alpha N} \pm 0.01$ | $a_{\alpha N} \pm 0.01$ | $\alpha^2$ |
|-----------|----------------------|------------------------|------------------------|-----------|
| CuL·NH$_3$ | 2.0967 | 91.09 | 15.8/7.9 | 0.82 |
| CuL·NH$_3$ | 2.099 | 86.08 | 12.17 | 0.90 |
| CuL·NH$_3$ | 2.095 | 89.84 | 12.8 | 0.82 |
| CuL·NH$_3$ | 2.0961 | 93.19 | 13.5 | 0.82 |
| CuL·Pipe | 2.095 | 92.35 | 15.9/7.8 | 0.84 |
| CuL·Py | 2.093 | 90.56 | 16.0/8.0 | 0.81 |
| CuL·NH$_3$ | 2.118 | 93 | 16.0/8.03 | 0.84 |
| CuL·NH$_3$ | 2.0964 | 89.32 | 15.7/7.9 | 0.83 |
| CuL·NH$_3$ | 2.0956 | 91.47 | 16.0/8.0 | 0.83 |
| CuL·NH$_3$ | 2.097 | 89.94 | 15.8/7.8 | 0.84 |
| CuL·NH$_3$ | 2.09 | 89 | 15.7/7.8 | 0.84 |

4. Conclusion

Thus, by the method of ESR spectroscopy, by studying the magneto chemical properties of copper(II) complexes, it was established that these compounds in the solid state and in a solution of nonpolar solvents have a planar-square structure with a trans $\cdot$-N$_2$-O$_2$ coordination sphere that passes to the octahedral through square-pyramidal when choosing highly polar solvents. The complexes synthesized by us made it possible to create drugs that accelerate the convergence of seeds, the growth of cotton plants and protect it from wilt disease. The analysis of these parameters shows that the introduction of electronic or electron-acceptor groups into the para-position of the benzene of the hydrazide fragment has negligible influence on the nature of the ESR spectra of copper complexes.

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References

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