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SYNTHESIS AND CHARACTERIZATION OF A NEW COORDINATIVE COMPOUND OF Cu(II) WITH 1-(3 BROMO, 2 HYDROXY, 4 METHYL-PHENYL)-2-(4 BROMO-PHENYL-SULPHANYL)-ETANONE

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Abstract: Continuing the research in the field of complex compounds, the authors present in this paper the synthesis and characterization of a new compound of Cu(II) with the ligand 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulphanyl)-etanone. Different methods were used, such as chemical elemental analysis, thermal-gravimetry, infrared absorption spectroscopy and electronic spin resonance (ESR). From chemical analysis resulted that the combination ratio ligand-central atom is 2:1. The new compound can also be used for gravimetric determination of Cu(II).

Keywords*: 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-ethanone, Cu(II), gravimetric determination*

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Introduction

The new resulted compound from the interaction of Cu(II) with 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulphanyl)-etanone is of the same type with the coordination compounds presenting coordinative bonds with the groups $\rangle C = O$ şi O(H) present as substituent in α position of the benzene ring.

The synthesis and characterization of related compounds[1-3] reported in literature are important for practical use in gravimetric determination of metallic ions. The compound presented in this paper is important for gravimetric determination of Cu(II).[4-6]

The paper presents the synthesis and study of the solid complex compound resulted from the reaction between 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-ethanone with Cu(II) in the combination ratio ligand:metal of 2:1. The obtained reaction product was studied by the following methods: chemical analysis, infrared absorption spectroscopy, thermal-gravimetry and electronic spin resonance (ESR).[7]

Experimental

For experimental determinations, solutions of 10^{-1} M $CuCl_2 \cdot 2H_2O$ (Merck) and ligand 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-ethanone were used.[8,9]

The synthesis of the coordination compound presented in this paper was accomplished following a method described in literature,[10,11] using as solvent a mixture 1:1 (in volumes) ethanol (98%) and water for the inorganic salt. For the ligand 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-ethanone (noted HL), di-methyl formamide (DMF) was used for solving.

The preparing process consisted in mixing and stirring at room temperature for 75 minutes a mixture of 100 mL $CuCl_2 \cdot 2H_2O$ 10^{-1} M and 200 mL ligand 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-ethanone of the same concentration. The precipitate was filtered and washed at vacuum and then dried in an oven at 105°C until constant weight.

In the specified conditions, an obtaining yield of 100% was accomplished. The reaction is:

$$CuCl_2 + 2(C_{15}H_{12}O_2SBr_2) + 2H_2O \rightarrow Cu(C_{15}H_{11}O_2SBr_2)_2 \cdot 2\,H_2O + 2HCl$$

For the synthesized compound the content of C, H, S, Br and Cu(II) was determined based on literature indications[11,12] specific for these elements.

The thermal stability of the synthesized compound was determined with a Q 1500 D MOM Budapest derivatograph, by simultaneously registering weight loss (TG), derivate of weight loss (DTG) and temperature variation (T).[13]

A 100 mg sample of the synthesized compound was introduced in a ceramic crucible and then heated until a temperature of 1000 °C with a heating speed of 10 °C/min.

The registration sensitivities were fixed for the values: TG-500μV, DTG-2.5mV and T-500μV. Al_2O_3 freshly submitted to a calcination process at 1200 °C was used as standard reference substance. The reaction orders and activation energies were calculated.[14-16]

The IR absorption spectrum of the compound was registered in the domain 400-4000 cm^{-1} with a FTIR 660 Plus Spectrometer, using KBr pellets method.[17]

The ESR spectrum of the studied complex compound was registered on solid samples with an IFA Bucuresti Spectrometer, using as standard

substance diphenylpicrylhydrazyl (DPPH) and the magnetic field of intensity 3216.9 Gauss and frequency 9030 MHz.

From the ESR spectrum of the compound, following literature indications,[18,19] the g-factor and the number of unpaired electrons corresponding to one central coordinated atom respectively, were calculated applying the method of double graphical integration and the mathematical relation:

$$N_x = N_e \cdot \frac{A_x}{A_e}$$

where N_x is the number of unpaired electrons of the sample; $N_e = 2.81 \cdot 10^{19}$ unpaired electrons/mL for the standard substance; A_x and A_e are the ESR spectrum areas for the sample and for the standard substance respectively.

From the relation $g = g_e \cdot H_e/H_x$, g-factor (spectroscopic splitting factor) was calculated in which $g_e = 2.0055$ for the standard substance and H_x şi $H_e = 3216.9$ Gauss represent the magnetic field values corresponding to the analyzed sample and to the standard substance respectively.

These mathematical relations can be applied only when both graph curves (for standard substance and for the sample) are of the same type, Gauss or Lorentz.

Results and discussions

The synthesis reactions and the chemical analysis of the studied compound indicated that for the central atom Cu(II) correspond two anions of the ligand 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-ethanone (Figure 1).

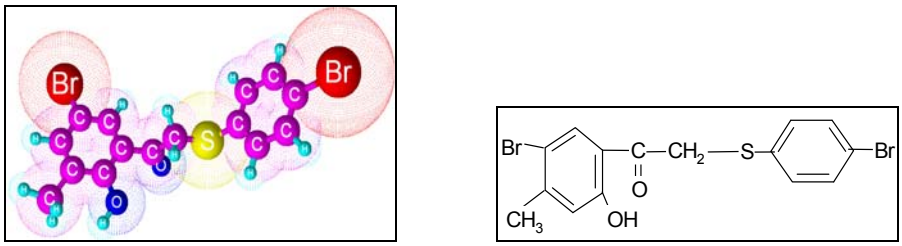

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Figure 1. a) 3D structure of the ligand 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-etanone;
b) structure of the ligand
1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-etanone.

The elemental composition of the studied compound was determined with an error of maximum ± 0.28% and is presented in Table 1, corresponding to the chemical formula: $Cu(C_{15}H_{12}O_2SBr_2)_2$ or more simply denoted $CuL_2{\cdot}2H_2O$.

Table 1. Elemental composition of the studied compound (%).

Element	% (calculated)	% (experimental)
C	40.3	40.12
H	2.46	2.59
S	7.16	7.26
Br	35.78	35.59
Cu	7.11	7.22
Molecular Mass	893.14	819.2

The characteristic temperatures for the thermal decomposition reactions of the studied compound are presented in Table 2.

For reaction order and activation energies calculations the Freeman-Carroll[13] method were used.

Table 2. The characteristic temperatures for the thermal decomposition stages of the studied compound

CuL2	Step I	Step II	Step III
Initial temperature (°C)	190	270	420
Final temperature (°C)	260	410	620

In Table 3, the values for the reaction order and activation energy characteristic for the thermal decomposition reactions of the compound $CuL_2 \cdot 2H_2O$[13,14,18,19] are presented.

For the thermal decomposition of the coordination compound presented in this paper the reaction order has the values between 0.4 and 1.5 (Table 3), in accordance with the results reported in literature.[19]

Table 3. The values of the reaction order and of the activation energy for the studied compound

	Stage I	Stage II	Stage III
Reaction order	0.8	0.6	1.6
Activation energy (kJ / mol)	13601	14142	29505

The fractional values for the reaction order are due to the fact that chemical reaction is influenced by the volatile compounds transport through the solid layer, to the inter-phase phenomenon or to „vaporizing" the volatile component at the surface of the solid compound.[3,11-13,17,18]

For the thermal decomposition reaction of the studied compound that takes place in steps, the increase of the dispersion degree is accomplished by the volatile compounds evaporation that lead to a reduced layer that has to be passed.[11,15,16]

The IR absorption spectra of the studied compound give important information on chemical bonding of the central atom Cu(II) with some

donor atoms of the ligand.[20] In the infrared absorption spectra, some characteristic peaks for the bonds: $\rangle C=O\rightarrow Cu^{2+}$, $Cu^{2+}-O-C\langle$ and $Cu^{2+} \leftarrow OH_2$ were important to be observed due to the interaction between functional groups: $\rangle C-OH$ and $\rangle C=O$ of the ligand and of the coordination water with the metal ion (Figure 2).

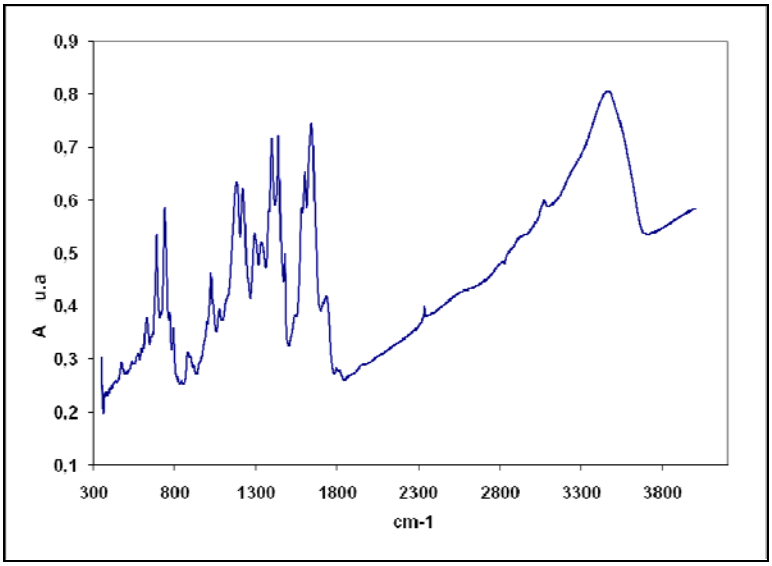
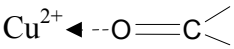


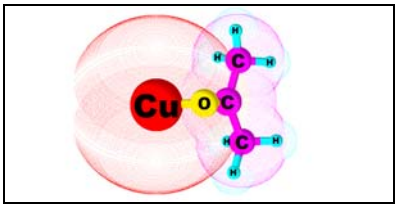
Figure 2. The infrared absorption spectra of the complex $CuL_2 \cdot 2H_2O$.

For the low frequencies of the IR spectrum (400–1500 cm^{-1}), some bands characteristic for the valence vibrations of the simple bonds C–C, C–O, Cu–O and also distortion vibrations of different bonds appear. The characteristic C–O vibration bands observed for the ligand in the field 1257-1277 cm^{-1} are displaced to higher wavelength values and become less intense in the spectra of the studied coordination compound.[19-22]

The valence stretching vibrations of the carbonyl group that appear in the ligand at 1605 cm^{-1} are displaced for the complex compound $CuL_2 \cdot$

$2H_2O$ at a value of 1636 cm^{-1}, that is an argument for the coordination bond between the central atom Cu(II) with the oxygen of the carbonyl group.





The IR absorption spectra of the complex $CuL_2 \cdot 2H_2O$ is presented in Figure 2. The characteristic peak for the phenol (from orto position) group absorption at 3267-3265 cm^{-1} is no longer observed in the studied compound.

For phenol groups,[15,17,21] the most important absorption frequency is at 1147-1237 cm^{-1} ($\nu_{C\text{-}OH}$) and is no longer present in the complex due to the substitution of the hydrogen atom with Cu(II). From the IR spectra it is deduced that every central atom Cu(II) is bonded to oxygen atoms from the phenol group after the substitution of hydrogen.

The electronic spin resonance spectra of the studied compound show that the central atom Cu(II) is paramagnetic. The spectroscopic splitting factor g, calculated based on literature indications[1,2,3,6,23-25] has the value 2.0288, higher than 2.0023 characteristic for the free electron. This is due to the contribution of the orbital moment and to the covalence degree of the bonds between central atom Cu(II) (Table 4) and other donor atoms from the ligand. This observation is in accordance with other studies reported[26,27] referring to the same central atom and the same type of ligand (Figure 3).

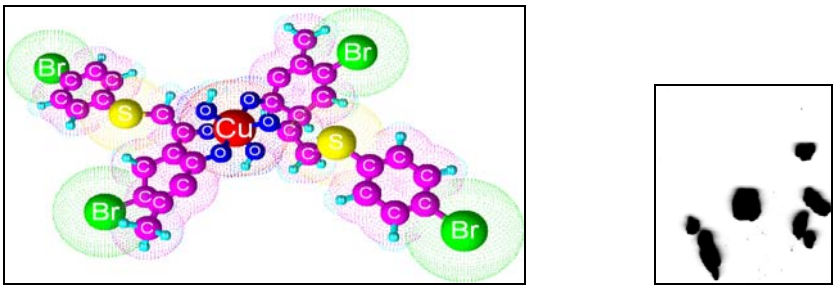


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Figure 3. a) 3D structure of the complex $CuL_2 \cdot 2H_2O$;
b) The complex CuL_2 crystals.

The value of the g-factor of unpaired electrons decreases with the increase of stability of the studied complex $CuL_2 \cdot 2H_2O$ (Table 4).[26-28]

Table 4. The values of the g-spectroscopic number attributed to the intensity of the magnetic field corresponding to the center of the spectrum of the analyzed sample, H_x (Gauss) and the number of uncoupled electrons for each central atom (n) from the studied compound.

	g	Hx	n
CuL2	2.0288	3254.2	0.91

The chemical analysis, IR absorption spectroscopy, derivatographic thermal analysis and electronic spin resonance (ESR) indicated that the central atom Cu(II) presents a paramagnetic behavior, in accordance with other results reported in the literature.[29,30] The experimental data and the interpretations are similar with results presented by other authors.[31,32]

Conclusions

A new compound of Cu(II) with the ligand 1-(3 bromo, 2 hydroxy, 4 methyl-phenyl)-2-(4 bromo-phenyl-sulfanyl)-etanone in molar ratio central atom: ligand as 1:2 was synthesized and studied.

The studied complex combination was characterized by modern chemical methods: elemental chemical analysis, thermal derivatography, infrared absorption spectroscopy and electronic spin resonance (ESR).

From the studies resulted that the central atom Cu(II) is coordinated to the oxygen atoms from the groups $\rangle C = O$ and O-(H) of the ligand: $C_{15}H_{12}O_2SBr_2$. The studied coordinative compound presents a relatively high thermal stability as it starts to decompose at a temperature close to 200 ºC.

This compound can be used for quantitative determination of the metallic ion, the method presenting the advantage that all the reactions take place in normal conditions and with a yield of 100%. Also, the precipitate obtained can be easily separated by filtration.

From the ESR spectra resulted that the new studied compound presents as central atom Cu(II) and a coordination number of six.

The present study presents practical importance that consists of using the obtaining reaction of the compound as a dosage method for Cu(II) ion by gravimetric measurements with a maxim error of ±0.29%.

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