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COPPER(II) OXALATE OBTAINED THROUGH THE REACTION OF 1,2-ETHANEDIOL WITH $Cu(NO_3)_2 \cdot 3H_2O$
Structural investigations and thermal analysis

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The paper presents the experimental results of the structural investigations and thermal analysis of copper(II) oxalate, a polynuclear coordination compound, obtained by a new method, through the reaction of 1,2-ethanediol with $Cu(NO_3)_2 \cdot 3H_2O$.

The reaction between 1,2-ethanediol and $Cu(NO_3)_2 \cdot 3H_2O$ occurs, under some working conditions, with the oxidation of 1,2-ethanediol to the oxalate anion (L). The synthesized polynuclear coordination compound, $[CuL \cdot 0.3H_2O]_n$, was characterized by chemical analysis, electronic and vibrational spectra and thermal analysis. The thermal properties of the polynuclear coordination compound have been investigated by TG, DTG and DSC. The obtained decomposition product is CuO.

Powder XRD (X-ray diffraction), IR spectroscopy and TEM (transmission electron microscopy) were used to characterize the composition, the crystalline structure and the surface morphology of the copper oxide obtained through thermolysis. The thermal conversion product, copper(II) oxide, has a microporous structure with a large specific area.

Keywords: *copper(II) oxalate, 1,2-ethanediol, homopolynuclear coordination compound, nitrate, thermal analysis*

Introduction

Knetsch and Groeneveld [1–3] have synthesized and studied a number of complexes with diols as ligands.

In our previous papers [4–13] we have reported the results of the studies of the oxidation reactions between 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol and some metallic nitrates.

The coordination compounds synthesized in this way contain glyoxylate anion, lactate anion, malonate anion and 3-hydroxypropionate anion as ligands.

The reaction between 1,2-ethanediol and $Cu(NO_3)_2 \cdot 3H_2O$ occurs with the oxidation of 1,2-ethanediol to glyoxylate anion [4, 13] or oxalate anion, depending the working conditions.

The thermal conversion of homo- and hetero-polynuclear complexes with anions of carboxylic acids as ligands have been carried out to oxide systems with irreductible structure and properties, required by the modern technology in various fields [14–27].

These compounds decompose at relatively low temperatures, forming simple or mixed oxides and volatile products (CO, CO_2, H_2O).

The determination of the forming conditions of non-stoichiometric oxides of Ni and Co led to an original method for obtaining anodes with electrocatalytically active films for the oxygen evolution at the electrolysis of alkaline solutions [28].

This paper presents the results obtained at the investigation of 1,2-ethanediol oxidation with $Cu(NO_3)_2 \cdot 3H_2O$, in an acid medium (pH~1.5). The obtained coordination compound was investigated from the standpoint of the composition and physical-chemical properties. It will be shown that it can be a precursor for copper oxide, which is obtained at relatively low temperatures.

Experimental

Materials

Chemicals

For the synthesis of the coordination compound, $Cu(NO_3)_2 \cdot 3H_2O$, ‘Reactivul’, Bucharest, with minimal purity of 99%, 1,2-ethanediol, ‘Reactivul’, Bucharest, with purity of 99% and nitric acid solution 1 M ($F=1.000 \pm 0.002$) were used. The impurities from the reagents do not influence the synthesis and purity of the obtained compound as they are removed in the subsequent purification step.

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Synthesis of the coordination compound

The elaborated method of the synthesis of the complex compound is based on the oxidation reaction of 1,2-ethanediol in an alcohol–water system by copper nitrate and nitric acid and the simultaneous isolation of the complex compound from the reaction system.

A solution of water+diol+$Cu(NO_3)_2 \cdot 3H_2O$+nitric acid in the molar ratio: 1,2-ethanediol: $Cu(NO_3)_2 \cdot 3H_2O:HNO_3=1.5:1.5:1$ was prepared. This mixture was heated in a water bath. The reaction was considered completed when no more gas evolution was observed.

The solid reaction product was purified by refluxing from an acetone–water mixture.

The solution was filtered and the solid blue-green product was washed with acetone and finally maintained in air until constant mass. The reaction yield was nearly quantitative.

Methods

TG, DTG and DSC curves (in the range 25–1000°C) corresponding to the decomposition of the coordination compound were recorded on a Simultaneous TG-DTA/DSC Apparatus 409PC produced by Netzsch GERATEBAU GMBH–Germania, in static air atmosphere at a heating rate of 10°C min^{-1}.

The coordination compound was also characterized by the following methods: chemical analyses, IR spectroscopy and electronic spectroscopy (diffuse reflectance technique).

The IR spectrum (KBr pellets) was recorded on a Jasco FT-IR Spectrophotometer, in the range 400–4000 cm^{-1}.

The electronic spectrum was recorded by diffuse reflectance technique using a spectrophotometer SPEKOL 10 Carl Zeiss Jena and MgO as a reference material.

The characterization of the copper oxide obtained by thermal decomposition of polynuclear coordination compound copper(II) oxalate was performed by elemental analysis, IR spectroscopy and X-ray diffraction (XRD). The crystal structure of the copper oxide was evaluated by X-ray diffraction, and his microstructure was examined by transmission electron microscopy (TEM).

Powder X-ray diffraction patterns of the samples were recorded on a BRUKER D8 Advance diffractometer with graphite monochromator on the diffracted beam, using CuK_α radiation (λ=1.54056 Å). The X-ray power was 40 kV and 30 mA.

The powder samples were grounded in order to reduce the granulation (when necessary) and then pressed in the specimen holder.

The patterns were recorded over a range of 2θ angles from 30 to 95° and crystalline phases were identified using the Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD) files. The data were collected and processed with the DIFFRAC plus program package.

The TEM images were obtained using a JEOL 1010 electron microscope with CCD camera.

Results and discussion

The evolution of the reaction between 1,2-ethanediol and $Cu(NO_3)_2 \cdot 3H_2O$ was investigated by IR spectroscopy. As the reaction advances the bands due to the nitrate ion decreases in intensity, proving that the nitrate ion is consumed in the reaction [29]. At the same time, the appearance and the increase of the band intensity in the range of 1580–1680 cm^{-1} ($\nu_{asym(COO^-)}$) is observed, which is specific to the ligands of the complex compounds which contain at least two oxygen atoms as donors such as the carboxylic anions of the acids [30].

The elemental analysis results (Table 1) as well as the IR investigation have indicated that the synthesized coordination compound has the following empirical chemical formula: $CuL \cdot 0.3\ H_2O$, where L is oxalate anion.

In order to separate and identify the ligand, the complex has been treated with R–H cationite (Purolite C-100). After the retention of the metal cations, the resulted oxalic acid has been identified by specific reactions: reaction with $KMnO_4$ solution (precipitate MnO_2), the reaction with resorcin in sulphuric acid medium (a blue ring appear), the reaction with CH_3COONa and then with $CaCl_2$ solution (it is deposited a very fine white precipitate of calcium oxalate), the reaction with H_2SO_4 concentrate (the carbon oxide that is generated during the reaction burns with a characteristic blue flame).

The physical properties (white solid, rhombic-pyramidal crystals, highly soluble in water, ethylic alcohol, strongly acid ($HO_2C \cdot CO_2H \cdot 2H_2O$))

Table 1 Composition and elemental analysis data

Compound (composition formula)	Cu(II)%		C%		H%	
	calc.	exp.	calc.	exp.	calc.	exp.
$CuL \cdot 0.3H_2O$	40.48	40.54	15.29	14.98	0.38	0.46

Table 2 Characteristic absorption bands in IR [cm^{-1}] for the oxalic acid and the corresponding assignments

ν_{OH}, ν_{H_2O}	$\nu_{as(COO)}$	$\nu_{sim(CO)}+\delta_{OCO}$	$\nu_{C\text{–}OH}$	δ_{OCO}	δ_{CCO}
3425 vs,b	1686 vs	1262 vs	1125 m	725 s	481 s

s – strong (v - very); b – broad; m – medium

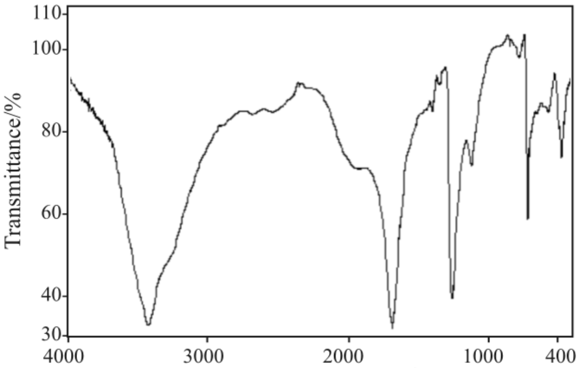


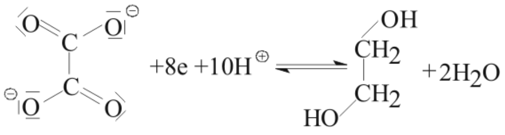
Fig. 1 IR vibrational spectrum of the oxalic acid

[31], the IR spectrum of oxalic acid (Fig. 1) are in good agreement with those from the literature [32, 33].

Table 2 shows the characteristic bands in IR [cm^{-1}] for the oxalic acid and the corresponding assignments.

These results as well as those previously reported [4, 13] concerning the oxidation of 1,2-ethanediol with metallic nitrates suggest that the oxidation of the 1,2-ethanediol with $Cu(NO_3)_2\cdot3H_2O$ occurs, in some working conditions, to oxalate anion, coordinated to Cu(II).

Consequently, we suggest the following mechanism for the reaction between 1,2-ethanediol and $Cu(NO_3)_2$ in an acid medium:



(1)

$$NO_3^{\ominus}+3e+4H^{\oplus} \Leftrightarrow NO+2H_2O \quad (2)$$

$$3C_2H_4(OH)_2+8NO_3^{\ominus}+2H^{\oplus} \Leftrightarrow \\ \Leftrightarrow 3C_2O_4^{2\ominus}+8NO+10H_2O \quad (3)$$

$$[Cu(H_2O)_4]^{2\oplus}+C_2O_4^{2\ominus} \rightarrow \\ \rightarrow Cu(C_2O_4)(H_2O)\cdot xH_2O+(3-x)H_2O \quad (4)$$

$$NO+1/2O_2 \rightarrow NO_2 \quad (5)$$

The oxidation of the 1,2-ethanediol occurring simultaneously with the coordination of the oxidation product by the complex generator determines the shifting of the equilibrium towards oxidation, leading thus to the formation of the polynuclear coordination product.

The suggested formula of the coordination compound as well as information concerning its structure are going to be confirmed by the results which will be presented in the following.

Diffuse reflectance spectrum of Cu(II)-oxalate

The diffuse reflectance spectrum of the coordination compound shows the presence of the characteristic bands of the Cu(II) hexacoordinated ion in a (pseudo)octahedral environment (Fig. 2).

In the electronic spectrum of the complex compound $[CuL\cdot0.3H_2O]_n$ one may distinguish a single band assigned to the transition *d–d* ($t_{2g}^6 e_g^3 \rightarrow t_{2g}^5 e_g^4$):

$$^2T_{2g} \leftarrow {}^2E_g$$

The presence in the electronic spectrum of an asymmetrical large band is due to the lowering of the symmetry by elongation of octahedron in order to suppress the orbital degeneration. The maximum at ~13.333 cm^{-1} (λ~760) and the blue-green intense colour plead for an octahedral distorted geometry. Elongation of the axial bonds can determine the passing from the octahedral symmetry to the tetragonal pyramid or square-planar coordination. The fundamental term is ^2E_g (the double orbital degeneration of the fundamental state is imposed by the two disposal possibilities of the unpaired electron on e_g orbitals d_z^2 and $d_{x^2-y^2}$). The Cu(II) ion, having the electronic configuration d^9, exhibits distortions from octahedral symmetry (the Jahn–Teller effect). His orbital degeneration in O_h symmetry occurs due to the possibility of the disposal

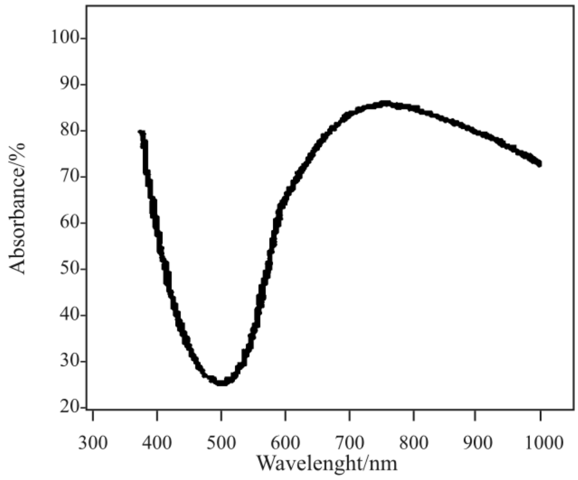


Fig. 2 Diffuse reflectance spectrum of the coordinative homopolynuclear compound $[CuL\cdot0.3H_2O]_n$

of unpaired electron in both orbitals e_g (d_z^2 and $d_{x^2-y^2}$), the fundamental state being ^2E_g.

In the electronic spectra of the Cu(II) complex compounds, instead of a single absorption band due to $^2T_{2g}\leftarrow{}^2E_g$, as a rule one may observe more bands or a large unsymmetrical band solvable in more components (the lowering of symmetry, achieved by elongation of the octahedron, in order to suppress orbital degeneration, has as result that instead of a single transition there are usually three). This fact explains the presence of a large asymmetric band in the electronic spectra.

If the octahedron is distorted by stretching along *z*-axis (the lowering of $O_h\rightarrow D_{4h}$ symmetry), the ligands placed on *z*-axis (H_2) will interact more weakly with the orbitals having *z* – component: d_z^2, d_{xz}, d_{yz}. These orbitals, in accord with the crystal field theory, are stabilized supplementary. At the same time, by conserving the energy centre, the $d_{x^2-y^2}$ and d_{yz} orbitals will be suitable unstabilized. The unpaired electron will be placed in d_z^2 orbital, which determines an energy gain.

According to angular overlap model, in the case of complex compounds tetragonally distorted by elongation of the octahedron, the antibonding character of the $d_{x^2-y^2}$ orbital increases and the energy of the antibonding orbital $(d_z^2)^*$ decreases, having as a result a supplementary stabilization of the investigated complex compound, according to Jahn–Teller theorem.

Elongation of the bonds from the axial position can determine the passing from symmetry to the tetragonal or plane-square pyramid one [34, 35].

IR vibrational spectrum of Cu(II)-oxalate

In order to obtain information regarding the structure of synthesized compound and the ligand coordination, the IR spectrum was recorded within the range 400–4000 cm^{-1} (Fig. 3).

Table 3 shows the characteristic bands in IR (cm^{-1}) for the solid and blue-green coloured complex and the corresponding assignments.

The broad band in the range 3200–3600 cm^{-1} with a maximum at 3427 cm^{-1} is assigned to the formation of the hydrogen bonds between water molecules and the carboxylate group [36].

The intense band at 1627 cm^{-1} is assigned to asymmetrical vibration of the carboxylate ion and the value shows that the resonance from carboxylate group is maintained during complex formation, the metal-carboxylate bond being prevailing with respect to the ionic one [30].

The band at 1379 cm^{-1} is assigned to the symmetric vibration $\nu_{sym(COO^-)}$. These values, beside δ_{OCO} found at 821 cm^{-1}, are in agreement with the position of corresponding absorptions in oxalate-bridged copper(II) complex [30, 37, 38].

In accordance with Nagase *et al.* [39], the 501 cm^{-1} band, obtained for the investigated complex can be attributed to the group of vibrations $\nu_{Cu\text{–}O}+\nu_{C\text{–}C}$.

The band at 418 cm^{-1} is attributed to the group of vibrations $\nu_{Cu\text{–}O}+\delta_{OCO}$.

The obtained compound is insoluble in water, ethanol and ether. It can be destroyed only by concentrated solutions of HCl or H_2SO_4. These statements as well as the above mentioned data suggest a polynuclear structure which corresponds to the following formula:

$$[CuL\cdot 0.3H_2O]_n$$

Thermal conversion of Cu(II)-oxalate

In order to confirm the composition and the structure of the coordination compound $[CuL\cdot 0.3H_2O]_n$ as well

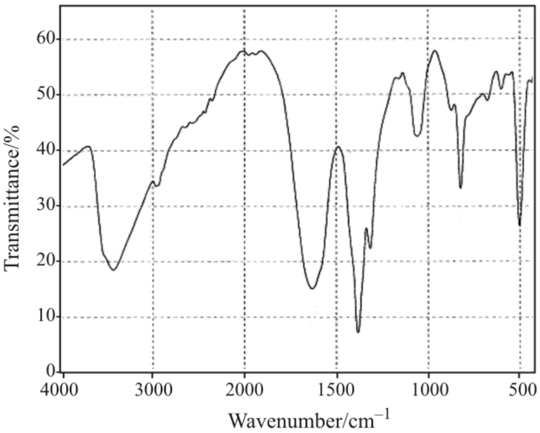


Fig. 3 IR vibrational spectrum of the homopolynuclear coordination compound $[CuL\cdot 0.3H_2O]_n$

Table 3 Characteristic absorption bands in IR for Cu(II)-oxalate and the corresponding assignments

Wavenumber/cm^{-1}	Assignment	Wavenumber/cm^{-1}	Assignment
3427 s,b	$\nu_{asym(OH)}+\nu_{sym(OH)}$ or hydrogen bonding	821 m	δ_{OCO}
1627 vs	$\nu_{asym(COO^-)}$	668 w	coordinated water
1379 vs	$\nu_{sym(COO^-)}$	501 s	$\nu_{Cu\text{-}O}+\nu_{C\text{-}C}$
1315 s	$\nu_{sym(CO)}+\delta_{OCO}$	418 w	$\nu_{Cu\text{-}O}+\delta_{OCO}$

s – strong (v – very); b – broad; m – medium; w – weak

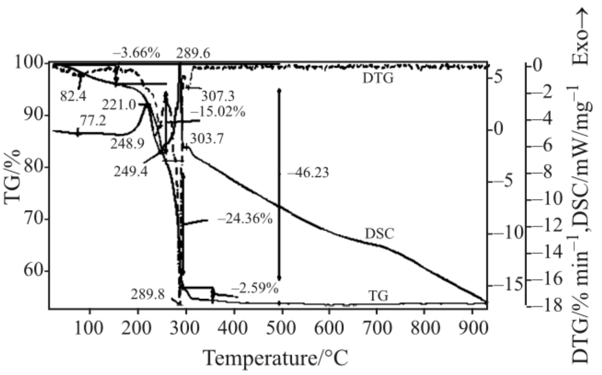


Fig. 4 Thermal analytical curves (TG, DTG and DSC) for the coordination compound decomposition at the heating rate of 10°C min^{-1}

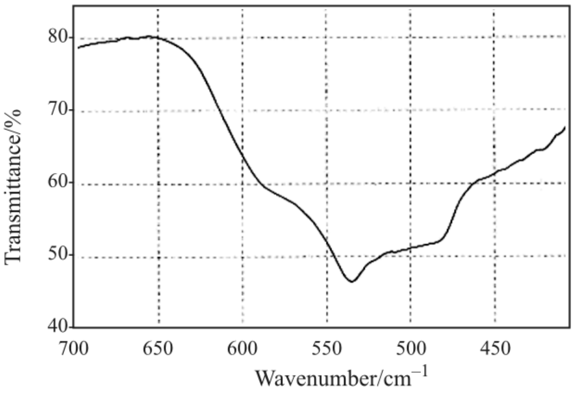


Fig. 5 IR vibrational spectrum of copper(II) oxide

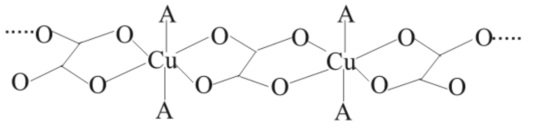
as to establish the steps of the conversion to copper(II) oxide, the thermal analytical methods (TG, DTG, DSC) have been used [40, 41].

The obtained TG, DTG and DSC curves, showed in Fig. 4, suggest three steps which occur at the progressive heating of the coordination compound.

In the temperature range 25–165°C, $[CuL\cdot 0.3H_2O]_n$ display an endothermic dehydration DSC peak (broad). TG mass losses correspond to $0.3H_2O$. DSC curve also shows endothermic mass loss process with peak maxima at 249.4°C. This peak is assigned to complex decomposition as indicated from TG mass loss in the temperature range 165–260°C. The exothermic peak, maximum 289.6°C, could be ascribed to the oxidation of copper(I) oxide (cuprite) and copper formed, probably, in tiny amounts in the second step [42, 43].

Copper(II) oxide, obtained at 1000°C, was the only component of the conversion of the complex compound.

It is also seen that the onset temperature of decomposition of copper(II) oxalate (about 80°C) is lower. This can be explained in terms of the electronegativity of the central metal ion Cu^{2+} [44, 45].



According to Kitagawa *et al.* [46], the copper(II) oxalate can take the following polynuclear polymeric structure:

A is axial ligand (H_2O) or vacant

Because the final product of thermal analysis is copper(II) oxide, the rupture of the C–O bond is the first step in the decomposition.

The higher interaction between Cu and O (due to the higher electronegativity of copper) results in a strong Cu–O bond and therefore a week C–O bond. Therefore, the copper oxalate shows a lower onset temperature of decomposition (a lower thermal stability) [44, 47].

The composition of a residual sample determined by elemental analysis (Cu: 79.9% and O: 20.1%) corresponds to the CuO. The residue was identified by IR and XRD.

The IR spectrum (Fig. 5) of the conversion product obtained at 1000°C exhibits only the bands characteristic for copper(II) oxide (534.28 and 420.48 cm^{-1}) being in agreement with the literature data [33].

The X-ray diffraction patterns (Fig. 6) shows the presence of the characteristic peaks for CuO (tenorite), in accordance with JCPDS 48-1548.

As can be seen, the sample is relatively well crystallized. Figure 7 shows the TEM images of the copper(II) oxide particles.

The TEM images show that the thermal decomposition product has a microporous structure with a large specific area. These TEM pictures are useful for examining the morphology of particles obtained by thermal decomposition of the complex. Ultrafine copper(II) oxide particles, mainly 10–50 nm,

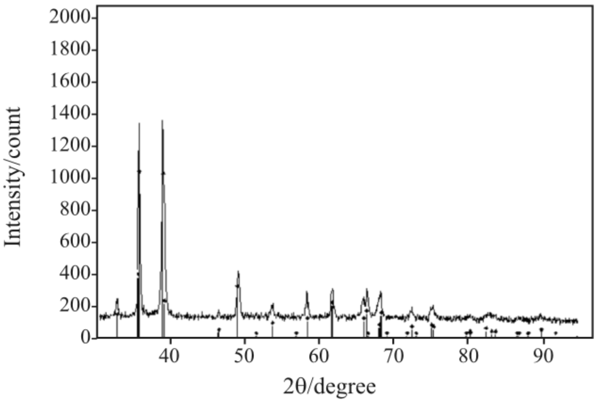


Fig. 6 The XRD of the solid product obtained by thermal conversion in air of the polynuclear coordination compound $[CuL\cdot 0.3H_2O]_n$ (sample of CuO, continuous line; the lines from JCPDS 48-1548, short dashes)

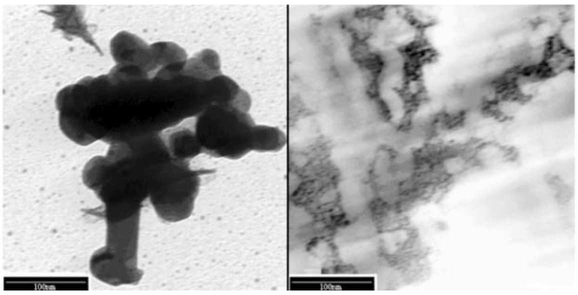


Fig. 7 TEM images for copper(II) oxide obtained by thermal decomposition of polynuclear coordination compound copper(II) oxalate. The magnification is the same for the two images (100 nm scale bar)

were obtained, together with a smaller number of submicrometer-sized spherical aggregates.

Conclusions

A new elaborated method of synthesis of the complex compound having oxalate anion as ligand is based on the oxidation reaction of 1,2-ethanediol in an alcohol–water system by copper nitrate and nitric acid and the simultaneous isolation of the complex compound in the reaction system.

The coordination compound synthesized by this new method is a homopolynuclear combination with the formula $[CuL\cdot 0.3H_2O]_n$; this complex has been investigated by elemental analysis, thermal analysis (TG, DTG and DSC), electronic and IR spectroscopy. All the experimental investigations lead to the conclusion that the complex is characterized by a (pseudo)octahedral configuration of the copper(II) ion.

The thermal conversion product obtained at 1000°C is CuO. The TEM images show that the copper(II) oxide has a microporous structure with a large specific area.

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