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# THERMAL AND SPECTRAL PROPERTIES OF HALOGENOSALICYLATO-Cu(II) COMPLEXES

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## Abstract

This paper reports an investigation of thermal and spectral properties of the complexes $Cu_2(3,5\text{-}Cl_2sal)_4\cdot H_2O$ (**I**), $Cu(3,5\text{-}Br_2sal)_2\cdot 2H_2O$ (**II**), $Cu(3,5\text{-}I_2sal)_2\cdot 2H_2O$ (**III**) and $Cu(5\text{-}Isal)_2\cdot 2H_2O$ (**IV**), (where *sal*=salicylate). TG, DTG, DTA, IR, EPR and electronic spectra have been applied to investigate thermal and spectral properties of these complexes. The chemical composition of the complexes has been identified by means of elemental analysis and complexometric titration. Schemes of destruction of these complexes are suggested. Heating of these compounds first resulted in a release of water molecules. The thermal stability of these complexes can be ordered in the sequence: **IV**=**I**<**II**<**III**. The final product of the thermal decomposition was CuO in all cases. IR data suggested a unidentate coordination of carboxylates to Cu(II) in complexes **I**–**IV**.

**Keywords:** copper(II)-3,5-dihalogenosalicylate, copper(II)-5-iodosalicylate, DTA, EPR, IR, pyrolysis, TG, UV-VIS

## Introduction

The ability of salicylic acid and its derivatives to act as an oxygen donor and to form complexes with different metal ions is well known. Carboxylatocopper(II) complexes are of interest from both the chemical and biological points of view. Different possible coordination of the carboxyl group to the central atom lead to the existence of compounds with distinct crystal structures. Complexes having variously distorted octahedral coordination around the central atom are formed when the carboxyl group (Fig. 1) acts as a monodentate or as a chelating bidentate ligand [1, 2], however when the carboxyl group is coordinated through both oxygen atoms, complexes of binuclear [3, 4] or polymeric structure are formed [5].

The reveal of the relationship between the structure and thermal decomposition of metal carboxylate complexes, the study of the influence of metal and ligand nature on the process of thermal decomposition are of a certain interest. It is not surprising,

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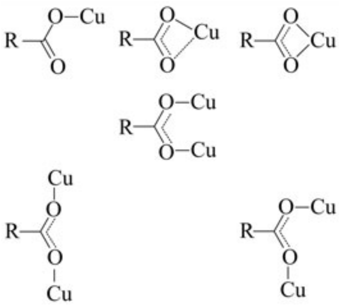

**Fig. 1** Different bonding modes of carboxylato group in copper(II) complexes

therefore, that many authors have investigated metal and ligand nature in coordination complexes of several central atoms and also examined their thermal properties [6–23]. In our previous papers we described the thermoanalytical properties of Mg(II), Cu(II) and Fe(III) complexes with pyridine and its derivatives [24–34]. Little data on structure and thermal decomposition of Cu(II) complexes with halogenosalicylic acids are available. Therefore, this paper describes the preparation of complexes formed by the halogenosalicylic acids with Cu(II), along with thermal analyses and spectral investigation of prepared complexes.

# Experimental

## *Preparation of the complexes*

In literature we found mostly used way to prepare copper(II) halogenosalicylates through preparing solution of Na(I) salts of halogenosalicylic acid. After preparing these solutions their pH was adjust to the value around 5 with sulfuric acid ($H_2SO_4$). The pH had adjusted before this solution was added to the solution of copper(II) sulfate. Due to the use of sodium hydroxide to form sodium salt solutions, we got the crude products which were recrystallized [35, 36]. We have decided to use copper(II) acetate instead of copper(II) sulfate and to use pure acids instead of their sodium salts. After this decision there was no need to adjust pH and byproduct of the reaction with acetic acid (weaker than all halogenosalicylic acids) because the equilibrium was sent to the side of products.

All compounds were prepared by addition a stoichiometric amount of halogenosalicylic acid to the solution of copper acetate in water. The reactions mixtures were stirred with the magnetic stirrer and the precipitation of different coloured products occurred. After several days the stable coloured products were filtered off, washed with water and dried in air.

## *Thermal analyses*

Thermal decompositions of the complexes were conducted using a T.A.I. SDT 2960 instrument. Measurements were carried out between room temperature and 1000°C in an atmosphere of dynamic air at a heating rate of 10°C $min^{-1}$, sample mass 10–20 mg.

### *Spectral measurements*

Electronic spectra in the region 200–1100 nm were measured with a Specord 200 spectrophotometer. IR spectra in the region 4000–200 $cm^{-1}$ were recorded by means of a Nicolet Magna 750 FTIR spectrometer. In both measurements the Nujol suspension technique was used. EPR spectra of powdered samples were recorded at room temperature by using a Brucker SRC-200D model of EPR spectrometer.

## Results and discussion

### *Chemical analysis of the compounds*

The contents of carbon and hydrogen were determined by elemental analysis and the contents of copper were determined by complexometric titration. The results given in Table 1 are in good agreement with theoretical expectations.

**Table 1** Chemical analyses data of the compounds

| Complex | Theoretical/% | | | Experimental/% | | |
|---|---|---|---|---|---|---|
| | C | H | Cu | C | H | Cu |
| $Cu(3,5\text{-}Cl_2sal)_2{\cdot}0.5H_2O$ | 34.70 | 1.46 | 13.11 | 34.45 | 1.68 | 13.15 |
| $Cu(3,5\text{-}Br_2sal)_2{\cdot}2H_2O$ | 26.05 | 1.20 | 9.47 | 26.01 | 1.41 | 9.41 |
| $Cu(3,5\text{-}I_2sal)_2{\cdot}2H_2O$ | 19.77 | 0.83 | 7.47 | 19.89 | 0.88 | 7.74 |
| $Cu(5\text{-}Isal)_2{\cdot}2H_2O$ | 26.88 | 1.93 | 10.16 | 26.14 | 1.74 | 10.11 |

### *Thermal decomposition of the complexes*

The thermal decomposition data of the complexes **I–IV** are collected in Table 2. The complexes **I–IV** are thermally relatively stable. Thermal decompositions of the compounds are multistage processes. The subsequent detachment of the ligands was observed. The final solid product was always identified as CuO.

The TG and DTA curves for the decomposition of $Cu_2(3,5\text{-}Cl_2sal)_4{\cdot}H_2O$ (**I**) are shown in Fig. 2. The TG curve indicates that it is thermally stable up to 105°C. Afterwards, the TG curve shows four mass loss steps. The first step between 105 and 175°C is accompanied by 1.75% mass loss (measured from the TG curve by TA instrument software), it is attributed to the dehydration process. The second step took place between 175 and 297°C and is accompanied by 29.00% mass loss. It is attributed, however, to the decomposition of the anhydrous complex to $Cu(sal)_2$. The third step took place between 297 and 405°C and is accompanied by 28.00% mass loss. It is attributed, however, to the decomposition of $Cu(sal)_2$ to Cu(sal’). The fourth step took place between 405 and 502°C and is accompanied by 25.00% mass loss. It is attributed, however, to the decomposition of Cu(sal’) to CuO as the final solid product. The thermal reaction of complex **I** can be represented as:

$$\mathrm{Cu_2(3,5\text{-}Cl_2sal)_4{\cdot}H_2O \xrightarrow{105-175°C} 2Cu(3,5\text{-}Cl_2sal)_2}$$

$$\mathrm{Cu(3,5\text{-}Cl_2sal)_2 \xrightarrow{175-297°C} Cu(sal)_2}$$

$$\mathrm{Cu(sal)_2 \xrightarrow{297-405°C} Cu(sal')}$$

$$\mathrm{Cu(sal') \xrightarrow{405-502°C} CuO}$$

**Table 2** Thermal decomposition data

| Complex | DTA results | | TG results | | |
|---|---|---|---|---|---|
| | $T_{peaks}$/°C | $T_{range}$/°C | Mass loss/% found (calc.) | Loss of | Composition of the residue found (calc.) |
| $Cu_2(3,5\text{-}Cl_2sal)_4{\cdot}H_2O$ | 132 endo | 105–175 | 1.75(1.86) | $H_2O$ | CuO |
| | 201 endo | 175–297 | 29.00(29.27) | $4Cl_2$ | 16.25(16.42) |
| | 320 exo | 297–405 | 28.00(28.50) | 2salH | |
| | 419 exo | 405–502 | 25.00(25.20) | decomposition of 2sal'* | |
| $Cu(3,5\text{-}Br_2sal)_2{\cdot}2H_2O$ | 163 endo | 132–187 | 5.00(5.09) | $2H_2O$ | |
| | 218 endo | 187–298 | 22.75(22.59) | $Br_2$ | Cu |
| | 331 exo | 298–443 | 31.00(30.69) | 5-BrsalH | 11.50(11.24) |
| | 469 exo | 443–564 | 28.25(28.13) | decomposition of 5-Brsal' | |
| $Cu(3,5\text{-}I_2sal)_2{\cdot}2H_2O$ | 172 endo | 140–206 | 4.00(4.10) | $2H_2O$ | |
| | 252 endo | 206–310 | 29.00(28.93) | $I_2$ | CuO |
| | 357 endo | 310–421 | 29.00(28.93) | $I_2$ | 9.00(9.26) |
| | 469 exo | 421–506 | 29.00(29.43) | decomposition of 2sal | |
| $Cu(5\text{-}Isal)_2{\cdot}2H_2O$ | 128 endo | 105–160 | 5.80(5.75) | $2H_2O$ | CuO |
| | 201 exo | 160–298 | 20.25(20.29) | HI** | 12.70(12.72) |
| | 343 exo | 298–407 | 20.25(20.29) | HI** | |
| | 471 exo | 407–497 | 41.00(40.96) | decomposition of 2sal | |

*sal'=Dianion of salicylic acid, **H is from atmosphere

The DTA curve for complex **I** (Fig. 2) shows two endothermic peaks at 132 and 201°C ascribed to the loss of $H_2O$ and $4Cl_2$, respectively and two intensive exothermic peaks maximized at 320 and 419°C ascribed to the loss of salH and decomposition of Cu(sal'), respectively, with the formation of CuO.

The TG and DTA curves for the decomposition of $Cu(3,5\text{-}Br_2sal)_2{\cdot}2H_2O$ (**II**) are shown in Fig. 3. The TG curve indicates that it is thermally stable up to 132°C. Afterwards, the TG curve shows four mass loss steps. The first step between 132 and 187°C is accompanied by 5.00% mass loss, it is attributed to the dehydration pro-

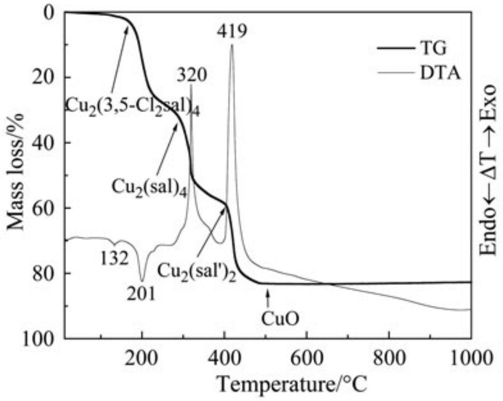

**Fig. 2** TG and DTA curves of $Cu_2(3,5\text{-}Cl_2sal)_4\cdot H_2O$ (**I**)

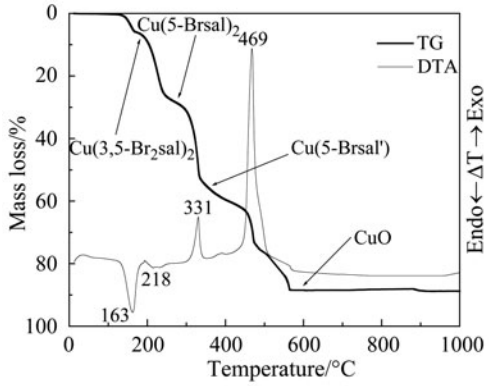

**Fig. 3** TG and DTA curves of $Cu(3,5\text{-}Br_2sal)_2\cdot 2H_2O$ (**II**)

cess. The second step between 187 and 298°C is accompanied by 22.75% mass loss. It is attributed, however, to the decomposition of the anhydrous complex to Cu(sal)(3,5-Brsal) or $Cu(5\text{-}Brsal)_2$. The third step between 298 and 443°C is accompanied by 31.00% mass loss. It is attributed, however, to the decomposition of the anhydrous complex to Cu(5-Brsal'). The fourth step took place between 443 and 564°C and is accompanied by 28.25% mass loss. It is attributed, however, to the decomposition of Cu(5-Brsal') to CuO as the final solid product. The thermal reaction of complex **II** can be represented as:

$$Cu(3,5\text{-}Br_2sal)_2\cdot 2H_2O \xrightarrow{132-187^\circ C} Cu(3,5\text{-}Br_2sal)_2$$

$$Cu(3,5\text{-}Br_2sal)_2 \xrightarrow{187-298^\circ C} Cu(sal)(3,5\text{-}Brsal)$$

$$Cu(sal)(3,5\text{-}Brsal) \xrightarrow{298-443^\circ C} Cu(5\text{-}Brsal')$$

$$Cu(5\text{-}Brsal') \xrightarrow{443-564^\circ C} CuO$$

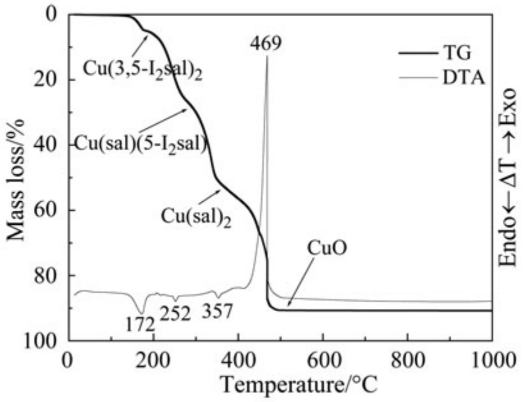

**Fig. 4** TG and DTA curves of $Cu(3,5\text{-}I_2sal)_2{\cdot}2H_2O$ (**III**)

The DTA curve for complex **II** (Fig. 3) shows two endothermic peaks at 163 and 218°C ascribed to the loss of $2H_2O$ and $Br_2$, respectively and two exothermic peaks maximized at 331 and 469°C ascribed to the loss of 5-BrsalH and decomposition reaction of Cu(5-Brsal'), respectively, with the formation of CuO.

The TG and DTA curves for the decomposition of $Cu(3,5\text{-}I_2sal)_2{\cdot}2H_2O$ (**III**) are shown in Fig. 4. The TG curve indicates that it is thermally stable up to 140°C. Afterwards, the TG curve shows four mass loss steps. The first step between 140 and 206°C is accompanied by 4.00% mass loss. It is attributed to the dehydration process. The second step between 206 and 310°C is accompanied by 29.00% mass loss. This step is attributed to the loss of $I_2$ and the residue could be assigned to $Cu(sal)(3,5\text{-}I_2sal)$ or $Cu(5\text{-}Isal)_2$. The third step took place between 310 and 421°C and is accompanied by 29.00% mass loss. It is attributed, however, to the loss of $I_2$ and to the decomposition of $Cu(5\text{-}Isal)_2$ to $Cu(sal)_2$. The fourth step took place between 421 and 506°C and is accompanied by 29.00% mass loss. It is attributed, however, to the decomposition of $Cu(sal)_2$ to CuO as the final solid product. The thermal reaction of complex **III** can be represented as:

$$Cu(3,5\text{-}I_2sal)_2{\cdot}2H_2O \xrightarrow{140\text{–}206°C} Cu(3,5\text{-}I_2sal)_2$$

$$Cu(3,5\text{-}I_2sal)_2 \xrightarrow{206\text{–}310°C} Cu(sal)(3,5\text{-}I_2sal)$$

$$Cu(sal)(3,5\text{-}I_2sal) \xrightarrow{310\text{–}421°C} Cu(sal)_2$$

$$Cu(sal)_2 \xrightarrow{421\text{–}506°C} CuO$$

The DTA curve for complex **III** (Fig. 4) shows three endothermic peaks at 172, 252 and 357°C ascribed to the loss of $2H_2O$, $I_2$ and $I_2$, respectively and an intensive exothermic peak maximized at 469°C ascribed to the decomposition reaction of salicylate with the formation of CuO.

To prove tentative intermediate decomposition products of **II** and **III** whether $Cu(sal)(3,5\text{-}I_2sal)$ or $Cu(5\text{-}Isal)_2$ the thermal decomposition of $Cu(5\text{-}Isal)_2{\cdot}2H_2O$ (**IV**)

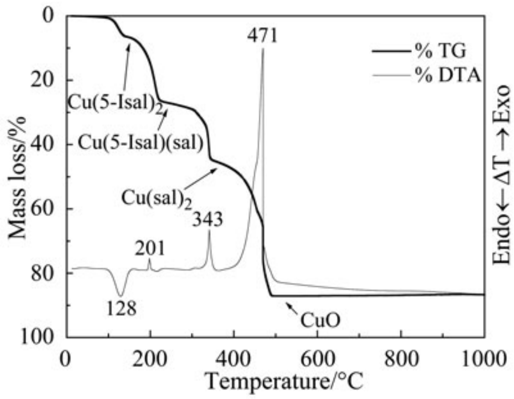

**Fig. 5** TG and DTA curves of $Cu(5\text{-}Isal)_2{\cdot}2H_2O$ (**IV**)

was studied. The TG and DTA curves for its decomposition are shown in Fig. 5. The TG curve indicates that it is thermally stable up to 105°C. Afterwards, the TG curve shows a mass loss step. This step between 105 and 160°C is accompanied by 5.80% mass loss. It is attributed to the dehydration process. The second step took place between 160 and 298°C and is accompanied by 20.25% mass loss. This step is attributed, however, to the decomposition of the anhydrous complex to Cu(sal)(5-Isal). The third step took place between 298 and 407°C and is accompanied by 20.25% mass loss. It is attributed, however, to the decomposition of the anhydrous complex to $Cu(sal)_2$. The fourth step took place between 407 and 497°C and is accompanied by 41.00% mass loss. It is attributed, however, to the decomposition of $Cu(sal)_2$ to CuO as the final solid product. The thermal decomposition of complex **IV** can be represented as:

$$Cu(5\text{-}Isal)_2{\cdot}2H_2O \xrightarrow{105-160^\circ C} Cu(5\text{-}Isal)_2$$

$$Cu(5\text{-}Isal)_2 \xrightarrow{160-298^\circ C} Cu(sal)(5\text{-}Isal)$$

$$Cu(sal)(5\text{-}Isal) \xrightarrow{298-407^\circ C} Cu(sal)_2$$

$$Cu(sal)_2 \xrightarrow{407-497^\circ C} CuO$$

The DTA curve for complex **IV** (Fig. 5) shows an endothermic peak at 128°C ascribed to the loss of $2H_2O$, followed by three exothermic peaks maximized at 201, 243 and 471°C. The first two exothermic peaks ascribed to the loss of Iodine and the third exothermic peak ascribed to the decomposition reaction of salicylate with the formation of CuO.

### *Electronic spectroscopy*

The UV absorptions of **I**–**IV** could be assigned to π–π* transitions of the aromatic system of salicylato anions bonded to copper(II) atom. All four compounds exhibit shoulders between 380–480 nm that could be assigned as charge–transfer and thus attributed to the characteristic bridging system with the antiferromagnetic interaction [37].

Visible spectrum of the dark brown $Cu_2(3,5\text{-}Cl_2sal)_4 \cdot H_2O$ (**I**) compound differs significantly (red shift of CT band and blue shift of *d*→*d* bands) from the spectra of three other ones and exhibit strong and well resolved shoulder at 472 nm (Table 3) followed by series of weak and unresolved shoulders at the lower energies up to 1100 nm without possibility to locate maximum of *d*→*d* transition. The light blue $Cu(3,5\text{-}Br_2sal)_2 \cdot 2H_2O$ (**II**) and turquoise-blue $Cu(3,5\text{-}I_2sal)_2 \cdot 2H_2O$ (**III**) compounds exhibit weak and very broad and asymmetrical *d*→*d* transition bands with maxima at 715 nm or 723 nm, respectively (Table 4). Both compounds exhibit weak and unresolved shoulders at lower energy side that are consistent with proposed pseudo–octahedral structure similar to $Cu(5\text{-}Clsal)_2 \cdot 2H_2O$ structure [36]. The electronic spectrum of light green $Cu(5\text{-}Isal)_2 \cdot 2H_2O$ (**IV**) exhibit similarly weak and broad *d*→*d* transition with maximum at 680 nm.

**Table 3** Selected electronic and EPR spectra data

| Compound | Electronic spectra[a] | $g_\perp$ | $g_{II}$ | $g_{av}$ | *G* |
|---|---|---|---|---|---|
| $Cu_2(3,5\text{-}Cl_2sal)_2 \cdot 0.5H_2O$ (**I**) | 472; 640sh, 820 sh | 2.040 | 2.270 | 2.117 | 6.8 |
| $Cu(3,5\text{-}Br_2sal)_2 \cdot 2H_2O$ (**II**) | cca 400sh; 715br | 2.040 | 2.320 | 2.133 | 8.0 |
| $Cu(3,5\text{-}I_2sal)_2 \cdot 2H_2O$ (**III**) | cca 400sh; 723br | 2.042 | 2.320 | 2.135 | 7.6 |
| $Cu(5\text{-}Isal)_2 \cdot 2H_2O$ (**IV**) | cca 400sh; 680br | 2.040 | 2.320 | 2.133 | 8.0 |

[a] CT band; *d*→*d* band(s), all values are in nm. sh – shoulder, br – broad

**Table 4** Infrared spectral data (4000–200 $cm^{-1}$) of complexes **I**–**IV**

| Assignments | **I** | **II** | **III** | **IV** |
|---|---|---|---|---|
| $\nu COO^-$ (as) | 1592, 1536 | $1555_{br}$, $1540_{sh}$ | 1553, 1532 | 1585, 1546 |
| $\nu COO^-$ (s) | 1487, 1453 | 1451, 1432 | 1441, 1421 | 1466, 1442 |
| $\Delta_{COO}$ | 105, 83 | 104, 108 | 112, 111 | 119, 104 |
| ν(OH) | 3538 | 3373 | 3471 | 3319, 3197 |
| ρ(HOH) | | 834, 807 | 823, 808 | 819, 808 |

as – antisymmetric and s – symmetric

### *IR spectroscopy*

The most important infrared spectral data of compounds **I**–**IV** are reported in Table 4. The IR spectra of compounds **I**–**IV** showed broad absorption bands between range 3586–3218 $cm^{-1}$. These frequencies correspond to the antisymmetric and symmetric OH stretching [38, 39]. These bands clearly confirm the presence of water in these compounds. Lower temperature of water evolution from $Cu_2(3,5\text{-}Cl_2sal)_4 \cdot H_2O$ (**I**) is in good agreement with infrared spectral data that suggested the presence of lattice water (HOH bending vibration at 1665 $cm^{-1}$) in comparison to compounds **II**–**IV** where coordinated water molecules are suggested (presence of ρ(HOH) bands (Table 4)).

Carboxylate ions can coordinate to metal ions in a number of ways such as unidentate, bidentate (chelating) or bridging. The analysis of $COO^-$ group bands allowed for the determination of the parameter $\Delta_{COO}=\nu COO^-(as)–COO^-(s)$. The magnitude of $\Delta_{COO}$ has been used by Nakamoto [40] as a criterion of the way by which carboxylate bind to metal ions. From the IR spectra, the calculated values of $\Delta_{COO}$ were close to 100 $cm^{-1}$. These values are in good agreement with the literature data for chelating mode of bonding salicylato anions [40], which are similar to those found for quasi-chelating bonding mode found in $Cu(5\text{-}Clsal)_2 \cdot 2H_2O$ structure [36]. The doublet structure of COO group bands is understandable on the $Cu(5\text{-}Clsal)_2 \cdot 2H_2O$ structure [36] data, where two non-equivalent salicylato anions were observed.

### *EPR spectroscopy*

EPR spectra of the compounds **I–IV** at room temperature showed the typical absorption bands of monomeric species and all of them are of axial symmetry. The spectra can be interpreted without hyperfine structure resolved. They can be interpreted by using a spin Hamiltonian for axial symmetry and the $g$ values ($g_\perp$, $g_{II}$ and $g_{av}$) are shown in Table 4 together with a $G$ parameter values. The $g$ values (the lowest value $g>2.04$ and the value of parameter $G>4$) are typical for a pseudo-octahedral coordination about Cu(II) atom with local tetragonal axes aligned parallel and with $d_{x^2-y^2}$ ground state.

## Conclusions

All complexes **I–IV** are hydrated and showed reasonable stability in air. They exhibit low solubility in water and were soluble in ethanol, methanol and dimethylsulfoxide. The decompositions of these compounds were initiated by elimination of water. Then decomposition of halogenosalicylato anions occurred (on the TG curves) in one or more steps. The thermal stability of the complexes can be ordered in the sequence: **I=IV<II<III**. The results revealed that CuO was left as residue at the end of the thermal degradation experiments of complexes **I–IV**. The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions and origin and preparation history [41, 42]. By means of spectral analyses the structure of the compounds have been studied. Infrared data suggested that one oxygen atom of carboxylate ions are used in coordination to Cu(II) and the other one is probably used in formation of asymmetrical hydrogen bond bridges similar to those found in $Cu(5\text{-}Clsal)_2 \cdot 2H_2O$ structure [38]. EPR data suggested a monomeric structure of all compounds and elongated axial symmetry of their coordination polyhedra. Without X-ray analysis, no definite structure can be described for the different components. However, spectroscopic and analytical data together with the thermal analyses techniques available enabled us to predict structures of these complexes.

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