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SYNTHESIS, CHARACTERISATION AND THERMAL BEHAVIOUR OF SOME THIOSULFATO- AND SULFATO COPPER(II) COMPLEXES

Antibacterial activity

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The investigation concerning the synthesis, spectrochemical and biological properties as well as thermal stability of some tiosulfato- and sulfato copper(II) complexes of type [Cuphen(S_2O_3)(H_2O)$_n$]·mH_2O (phen: 1,10-phenanthroline; **(1)**: *n*=2, *m*=0; **(2)**: *n*=2, *m*=0.5) and respectively [Cuphen(OSO_3)(H_2O)$_n$] (**(3)**: *n*=0; **(4)**: *n*=2) are presented in this paper. The bonding and stereochemistry of the complexes have been characterised by IR and electronic studies. The *in vitro* qualitative and quantitative assays of the antimicrobial activity of the tested compounds *vs.* planktonic and adherent Gram negative bacterial strains isolated from different surfaces in the hospital environment demonstrated that all compounds exhibited very good antimicrobial activity *vs. Escherichia coli*, *Klebsiella sp.* and *Enterobacter sp.* with very low M.I.C. values.

The thermal analysis has evidenced the thermal intervals of stability and also the thermodynamics effects that accompany them both in synthetic air and argon. The thermal behaviour is complex according to DTG and DSC curves including dehydration as well as thiosulfate and phenanthroline decomposition.

Keywords: *biological activity, 1,10-phenanthroline, sulfato copper(II) complex, thermal stability, thiosulfato copper(II) complex*

Introduction

In small quantities thiosulfate anion occurs naturally in hot springs and geysers and also is produced by certain microorganisms. Together with sulfate, this species plays also an important role in the *L*-cysteine biosynthesis and some cells produce it either by elemental sulphur oxidation or by *L*-cysteine degradation [1, 2].

Thiosulfate derivatives have found uses as fungicide, fixative in photoprocessing activity, whitening agents for paper, screening agents for gold allergies [3] as well as antirheumatic drugs [4].

Even if there are a rather small number of complexes with thiosulfate only or thiosulfate and amine as ligands full characterised, it was evidenced a versatile coordination mode for this anion. The studies evidenced that it could coordinate as unidentate through sulfur atoms [5–8], as (O,S) chelate [8–10], as bridge through (S) [11, 12], (O) [13], (O,S) [14–16] or simultaneous through (S) and (S,O) [17]. An unusual mode evidenced is one containing bridging thiosulfate group bound by both sulfur atoms [18]. The main directions of these studies concerned structure determination of these complexes.

Recently it was shown that complexes of transition metals with mixed ligands (thiosulfate and aromatic amines) behave as antibacterials [19]. Regarding the thermal behaviour of this kind of complexes there are rather few information [20–22].

On the basis of these considerations the investigation concerning the synthesis, spectral data, biological behavior as well as thermal stability of some copper(II) complexes with mixed ligands (thiosulfate/sulfate and 1,10-phenanthroline) are presented. The bonding and stereochemistry of the complexes have been characterised by IR and electronic spectra. The results showed that all compounds exhibited antimicrobial activity *vs.* Gram-negative bacterial strains such as *Escherichia coli*, *Klebsiella spp.* and *Enterobacter sp.*.

Experimental

All reagents were of commercial analytical quality and have been used without further purification. Chemical analysis of carbon, nitrogen, sulfur and

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hydrogen has been performed using an EA 1110 analyzer. Copper was determined volumetrically using the thiosulfate method.

Synthesis of complexes

Complex [Cu(phen)$S_2O_3(OH_2)_2$] **(1)**

An aqueous solution containing 5 mmoles (0.998 g) copper acetate monohydrate, 5 mmoles (0.992 g) phenanthroline monohydrate and 5 mmoles (1.240 g) sodium thiosulfate pentahydrate in 130 mL water (pH of the solution 5.5) was magnetically stirred at room temperature for 7 days, until the green sparingly soluble species initially obtained turns in light blue. The precipitate was filtered off, washed with water (until to negative reaction for thiosulfate anion) and air-dried. Analysis found: Cu, 16.15; C, 36.71; H, 3.31; N, 7.12; S, 16.22; required for $CuC_{12}H_{12}N_2O_5S_2$: Cu, 16.21; C, 36.77; H, 3.09; N, 7.15; S, 16.36.

Complex [Cu(phen)$S_2O_3(OH_2)_2$]·$0.5H_2O$ **(2)**

The mixture obtained by dissolving a 5 mmoles (0.998 g) copper acetate monohydrate, 5 mmoles (0.992 g) phenanthroline monohydrate and 5 mmoles (1.240 g) sodium thiosulfate pentahydrate in 140 mL boiling water (pH of the solution 5.5) was magnetically stirred at room temperature for 7 days, until a sparingly soluble species, green coloured was formed. The precipitate was filtered off, washed with water (until to negative reaction for thiosulfate anion) and air-dried. Analysis found: Cu, 15.65; C, 35.83; H, 3.31; N, 6.41; S, 15.82; required for $CuC_{12}H_{13}N_2O_{5.5}S_2$: Cu, 15.85; C, 35.95; H, 3.26; N, 6.99; S, 16.00.

Complex [Cu(phen)SO_4] **(3)**

To a solution of copper acetate monohydrate (0.998 g, 5 mmoles) in water (120 mL) was added in small portion 25 mmoles (6.250 g) sodium thiosulfate until the solution turns light yellow, and (also in small portion) 5 mmoles (0.992 g) phenanthroline monohydrate. The reaction mixture was then magnetically stirred at room temperature for 7 days, until a sparingly soluble species, brown coloured was formed. The precipitate was filtered off, washed with water (until negative reactions for thiosulfate and sulfate anion) and air-dried. Analysis found: Cu, 18.74; C, 42.52; H, 2.31; N, 8.40; S, 9.62%, required for $CuC_{12}H_8N_2O_4S$: Cu, 18.70; C, 42.41; H, 2.36; N, 8.25; S, 9.42%.

Complex [Cu(phen)$SO_4(OH_2)_2$] **(4)**

The mixture obtained by dissolving 2.5 mmoles (0.499 g) copper acetate monohydrate, 2.5 mmoles (0.496 g) phenanthroline monohydrate and 15 mmoles (3.720 g) sodium thiosulfate pentahydrate in 60 mL water (pH of the solution 5.5) was magnetically stirred at room temperature for 7 days, until a sparingly soluble species, light green coloured was formed. The precipitate was filtered off, washed with water (until to negative reactions for thiosulfate and sulfate anion) and air-dried. The same species was obtained for a molar ratio of reactants of 1:1:2 and 1:1:5 using both or boiling water. Analysis found: Cu, 17.38; C, 38.40; H, 3.00; N, 7.30; S, 8.58%, required for $CuC_{12}H_{12}N_2O_6S$: Cu, 16.91; C, 38.35; H, 3.19; N, 7.46; S, 8.52%.

Methods

IR spectra were recorded in KBr pellets with a Bio-Rad FTIR 135 spectrometer in the range 400–4000 cm^{-1}. Electronic spectra by diffuse reflectance technique, with MgO standard, were recorded in the range 380–1100 nm, on a VSU 2P-Zeiss Jena spectrometer.

The qualitative screening of the susceptibility spectra of different microbial strains to the complexes was performed by adapted diffusion techniques: paper filter disk impregnation with the tested substances solutions, the disposal of tested solutions in agar wells and the spotting of tested solutions on microbial inoculums seeded medium, while the quantitative assay for the establishment of the minimal inhibitory concentration (M.I.C., $\mu g/cm^3$) value was based on liquid medium serial dilutions [23]. The compounds were dissolved in DMF to a final concentration of 1 mg mL^{-1}. The *in vitro* biological screening effects were tested against a bacterial inoculum ($1.5\cdot10^8$ UFC/cm^3) represented by 82 Gram negative, *Enterobacteriaceae* strains isolated from different surfaces in the hospital environment (*Escherichia coli*, *Klebsiella spp.* and *Enterobacter sp.*). For the M.I.C. assay, stock solutions were prepared by dissolving the compounds in DMF and serial binary dilutions were performed in nutrient broth distributed in 96-multiwell plates, further inoculated with a standard inoculum of bacterial strains. The plates were incubated at 37°C for 24 h. The lowest concentration that inhibited the visible microbial growth was considered the MIC value for the tested compound.

For the assessment of adherent bacteria susceptibility to the tested compounds, a simple model for the development of *in vitro* monospecific biofilms was used, consisting of cultivating the

Table 1 Absorption maxima (cm^{-1}) and assignments for anionic thiosulfate, 1,10-phenanthroline and complexes **(1)**–**(4)**

$Na_2S_2O_3$	phen	**(1)**	**(2)**	**(3)**	**(4)**	Assignments
494w	–	417w	425w	–	484m	$\nu(SS)/\nu_2(SO_4)$
552m	–	500m 525m	525w 608m	590w 625s	529m 582s 642m	$\delta_{as}(SO)/\nu_4(SO_4)$
665s	–	606s	614s	–	–	$\delta_s(SO)$
–	722vs	722s	721m	718s	721s	$\rho(CH)$
1000vs	–	1013vs	1014m	1003s	928m 1007s	$\nu_s(SO)/\nu_1(SO)_4$
1134vs	–	1212vs 1243vs	1113vs 1142s	1161m 1202s 1255m	1045m 1227vs 1241s	$\nu_{as}(SO)/\nu_3(SO_4)$
–	1445vs 1580vs	1429m 1518m 1583w	1424m 1513m 1590w	1425m 1509w 1580w	1428s 1517m 1584m	$\nu(C{=}C)+\nu(C{=}N)$
		1621w	1630m	–	1625m	$\delta(OH)$
3409vs	–	3428s	3454vs	–	3442s 3531m	$\nu(OH)$

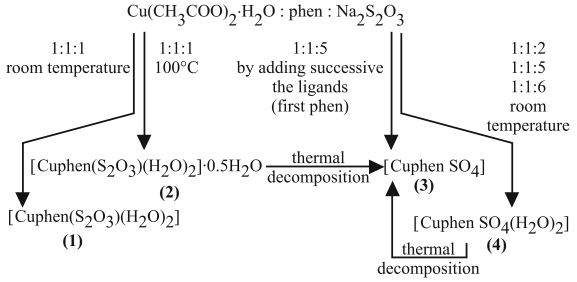
microbial strains in 60 multi-well plates, in nutrient broth and incubated at 37°C for 72 h. At the end of experiment, the wells were emptied, washed 3 times with PBS (phosphate buffered saline), fixed with cold methanol and stained with violet crystal solution 1% for 30 min. The biofilm formed on plastic wells was suspended again in acetic acid 30% and the intensity of the colored suspension was assayed by measuring the absorbance at 490 nm.

The thermochemical investigations were carried out under dynamic air atmosphere (15 cm^3 min^{-1}), with sample mass about 40 mg at heating rates of 5–20 K min^{-1}. DSC measurements were performed on a Netzsch Thermobalance STA 409CC/PG/PC type, while the thermogravimetry/mass spectrometry on a STA 409 C one. The crystalline phases in the calcinated powders were identified by XRD powder methods using a Philips Xpert X-ray diffractometer (CuK_α radiation).

Results and discussion

Synthesis and physico-chemical characterization of the complexes

In this paper, we report the synthesis, physico-chemical and biological characterisation of some Cu(II) complexes with 1,10-phenanthroline and thiosulfate or sulfate as ligands. The major goal of this paper was the study of the thermal behaviour of these complexes that present also *in vitro* antibacterial activity. The complexes are of type $[Cuphen(S_2O_3)(H_2O)_n]\cdot mH_2O$ ((**1**): n=2, m=0; (**2**): n=2, m=0.5) and respectively $[Cuphen(OSO_3)(H_2O)_n]$ ((**3**): n=0; (**4**): n=2). These species have been obtained as it is shown in Scheme 1. The study evidenced that at 1:1 molar ratio the obtained species are hydrated complexes with coordinated thiosulfate while by using an excess of thiosulfate some sulfate complexes were formed.



Scheme 1

The major IR spectral features of complexes, sodium thiosulfate and 1,10-phenanthroline are presented in Table 1.

As it can be observed, in all spectra appear the characteristic bands of the coordinated phenanthroline [24]. As for the bands corresponding to the vibration modes of the thiosulfate these are significantly split and shifted in the spectra of the complexes. In the characteristic range for the $\nu_{as}(SO)$ vibrations, the spectra of the complexes **(1)** and **(2)** display two components, both shifted towards higher wavenumbers. In the same mode are shifted the bands associated to $\nu_s(SO)$ while those associated with $\delta_s(SO)$, $\delta_{as}(SO)$ and respectively $\nu(SS)$ are shifted towards lower wavenumbers. All these modifications indicate the involvement of the SSO_3 groups in coordination through the sulphur atom in the case of complex **(1)** [25, 26] and both oxygen and sulphur in case of complex **(2)** [27]. For complex **(1)** the difference between ν_{as}(SO) and ν_s(SO) of 31 cm^{-1} indicate a small distortion of the thiosulfate from C_{3v} symmetry upon coordination.

In the case of complexes **(3)** and **(4)** the spectra show more signals assigned to ν_3 and ν_4 vibration modes in the characteristic ranges for sulfate. The position and intensity of these bands indicate that the sulfate in the complex **(3)** acts as chelate while in compound **(4)** is involved in coordination as bridge [28].

The water presence, except for complex **(3)**, generates the appearance of a large band at about 3400 cm^{-1} assigned to ν(OH) stretching vibrations and a weak one at about 1625 cm^{-1} assigned to δ(OH) vibration mode [24].

The diffuse-reflectance spectra of complexes show a single broad band as is usually observed for copper(II) ion in complexes with different ligands [29]. The absorption maximum for complex **(1)** is found at 680 nm and a shoulder is observed at lower values. The position of the absorption maximum and the general aspect of the spectrum are in agreement with a square-pyramidal stereochemistry. The spectrum for complex **(2)** displays an absorption band above 1100 nm aspect characteristic for complexes with cis-octahedral stereochemistry. The narrow band with the absorption maximum at 480 nm indicates a square-planar stereochemistry for complex **(3)**. The absorption maximum at 670 nm for the complex **(4)** is in agreement with an octahedral coordination [29].

Biological activity

It was evidenced that Gram-negative bacteria are inherently resistant to many hydrophobic antibiotics behaviour associated with the activity of multidrug resistance (MDR) efflux pumps. Moreover, in recent years, it was observed that in nature most bacteria form complex surface-attached (sessile) communities called biofilms. The pathogenicity of biofilms, even of those formed by opportunistic microorganisms is magnified by two biofilm characteristics, namely the increased resistance or tolerance to antimicrobials and the inability of the host's defence mechanisms (phagocytes, antibodies) to be efficient against the bacterial cells of biofilm community [30]. Taking into account that the physiology and antibiotic sensitivity of biofilm growing microorganisms are completely different from planktonic, we comparatively studied the susceptibility to the new complexes of planktonic, as well as biofilm growing bacterial cells.

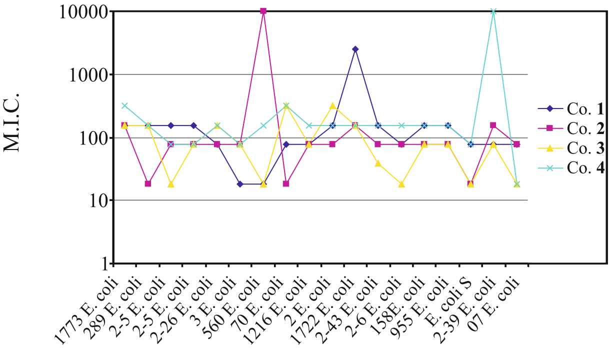


Fig. 1 The antimicrobial activity of the tested compounds *vs. E. coli* strains

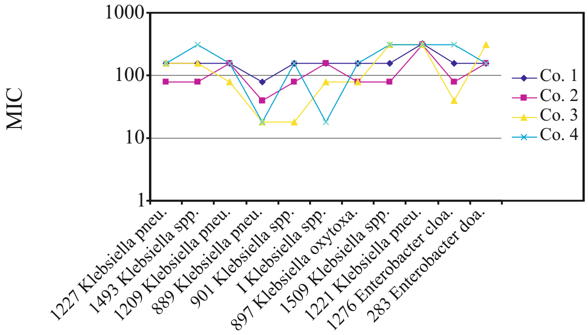


Fig. 2 The antimicrobial activity of the tested compounds *vs. Klebsiella sp.* and *Enterobacter cloacae* strains

As concerning the susceptibility of planktonic bacteria, all complexes exhibited antimicrobial activity *vs.* the majority of the tested strains. Concerning the quantitative testing assays, the tested compounds exhibited very good antimicrobial activity with low M.I.C. values (18–156 μg mL^{-1}) *vs. E. coli* (Fig. 1), as well as *Klebsiella spp.* and *Enterobacter spp.* (Fig. 2). While for *E. coli* strains the compound **(3)** was seemingly the most constantly active on all tested strains, in case of *Klebsiella spp.* and *Enterobacter spp.* all compounds exhibited comparative levels of the antimicrobial activity.

The tested compounds also inhibited the ability of the tested strains to develop biofilms on inert substrata, as exemplified for one *Klebsiella pneumoniae* strain in Fig. 3, demonstrating that, beside their bactericidal activity, these compounds also possess, especially at subinhibitory concentrations, some anti-pathogenic features, by blocking the microbial adhesins' synthesis. These results are accounting for the potential contribution of these compounds to the development of new antimicrobial agents directed against adherent bacteria, known to produce chronic, persistent and difficult to treat infections.

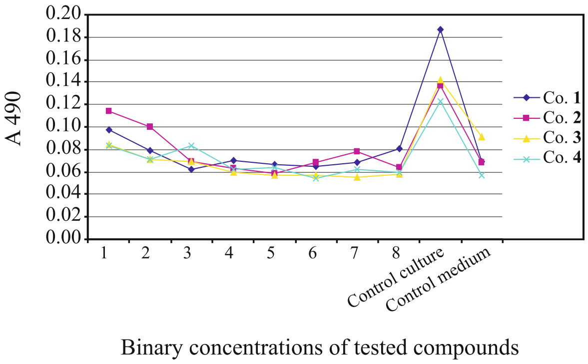


Fig. 3 The ability of *Klebsiella pneumoniae* strain to develop biofilms (quantified by measuring the A 490 nm) in the presence of different compounds solutions concentrations

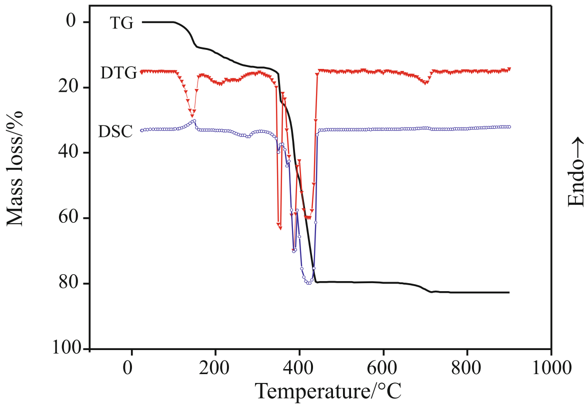


Fig. 4 TG, DTG and DSC curves of complex **(1)** in air atmosphere

Thermal behaviour of the complexes

The TG, DTG and DSC curves corresponding to the complex **(1)** heating under a flow of synthetic air are presented in Fig. 4.

The thermal decomposition occurs in four steps in air while in argon only three steps are observed. According to the mass losses, the following degradation scheme might be proposed for complex **(1)** in synthetic air:

$$[Cu(phen)S_2O_3(OH_2)_2] \rightarrow [Cu(phen)S_2O_3] \rightarrow$$

$$[Cu(phen)SO_4] \rightarrow CuSO_4{\cdot}5CuO \rightarrow CuO$$

The observed mass variation (found air/argon: 9.19/9.14%; calcd: 9.20%) during the first step corresponds to the loss of two water molecules. This process occurs in 104–164/109–173°C range (air/argon) accompanied by an endothermic effect. The higher temperature of dehydration is an indicative of the coordinative nature of water molecules. The second step, exothermic, corresponds to anhydrous thiosulfate complex decomposition between 179–294°C. This process, in air, leads to a sulfate complex as chemical analysis and spectral data indicate. The intermediate isolated at 250°C presents all spectral features of complex **(3)**. Unlike the Zn(II) and Cd(II) complexes [22, 23] for **(1)** a complex sulfide stabilisation was not observed in this temperature range. By temperature increasing the sulfate complex suffers at least four exothermic transformations leading to $CuSO_4{\cdot}5CuO$. These processes occur in a complex step and cannot be delimited. In the final step, the remaining sulfate decomposes exothermally in 634–714°C range to give CuO as final residue (found/calcd. overall mass loss: 79.63/79.71).

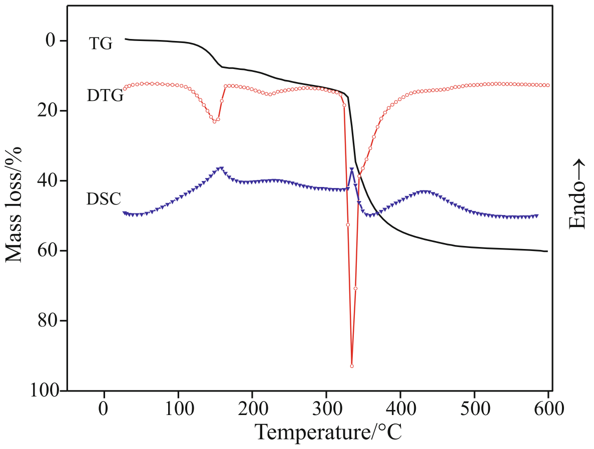


Fig. 5 TG, DTG and DSC curves of complex **(1)** in argon

After water elimination the thiosulfate decomposition is observed in the argon flow also in the second step (Fig. 5).

Several evolved species such as S (32 *m*/*z*), SO_2 (64 *m*/*z*) and SO_3 (80 *m*/*z*) respectively were identified by mass spectroscopic investigations in the 174–294°C range. The benzene fragments (76 *m*/*z*) were also observed in this range indicating that the phenanthroline decomposition starts also. Last step is an overlapping of at least two processes. The remaining thiosulfate elimination generates peaks for S, SO, SO_2 and SO_3 species in the mass spectrum. The phenanthroline is released also in this step with or without fragmentation (*m*/*z*: 76, 154, 179). The final residue in inert atmosphere is copper (ASTM-040836) with Cu_4S_7 (ASTM 72-0617) traces as XRD indicates.

For complex **(2)** within the temperature interval 68–175/64–183°C (air/argon) the water molecules are lost in two well definite, endothermic steps. The temperature range corresponding to the last two water molecules elimination (119–175/104–183°C) indicates their coordination nature. This behaviour supports for this compound the formulation $[Cu(phen)S_2O_3(OH_2)_2]{\cdot}0.5H_2O$. The next steps are

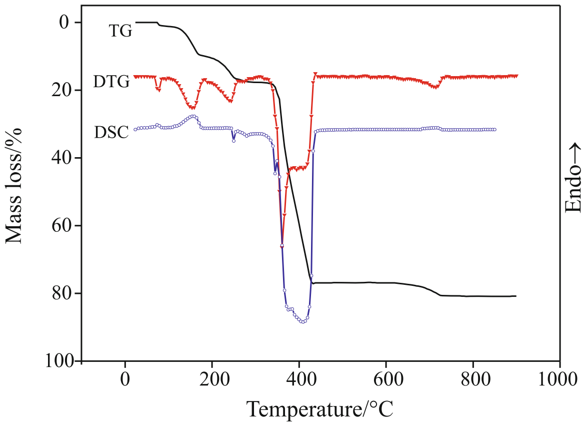


Fig. 6 TG, DTG and DSC curves of complex **(2)** in air atmosphere

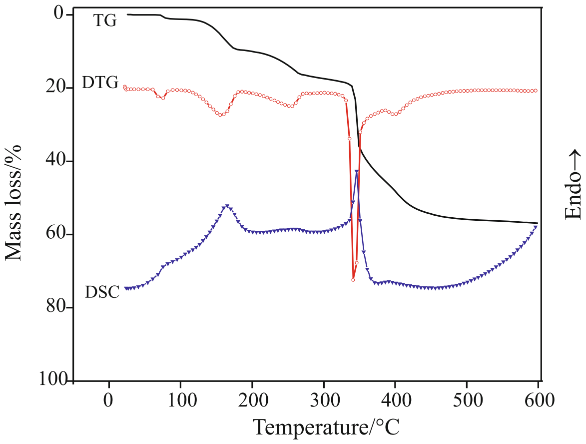


Fig. 7 TG, DTG and DSC curves of complex **(2)** in argon

similar with those observed for complex **(1)** both in air and argon and comprise thiosulfate as well as phenanthroline transformation and elimination (Figs 6 and 7).

The thermal decomposition of complex **(4)** follows four steps both in air and inert atmosphere. First step corresponds to the water elimination with an endothermic effect. The higher temperatures corresponding to this process (90–180/85–175°C) support also the water presence as ligand. Next two steps, also endothermic, are associated with the coordinated phenanthroline elimination. Last step is a very complex one being composed by at least four exothermic processes that can be associated with the stepwise decomposition of $CuSO_4$. The products of these transformations are copper(II) oxide (in air) and metallic copper (in inert atmosphere) respectively.

Conclusions

The copper(II) complexes with mixed ligands (1,10-phenanthroline and thiosulfate/sulfate) have been synthesised and characterised as new effective antimicrobial agents.

The spectroscopic studies revealed two coordination modes both for thiosulfate and sulfate anions respectively. The electronic spectra revealed different surroundings for Cu(II) such as square-pyramidal (for **(1)**) octahedral (for **(2)** and **(4)**) and square-planar (for **(3)**) respectively.

The *in vitro* qualitative and quantitative antimicrobial activity assays showed that the complexes exhibited a very good antimicrobial activity against Gram-negative planktonic and adherent bacterial strains, representing potential candidates for the development of new antimicrobial agents directed *vs.* multiresistant Gram-negative, strains as well as adherent bacteria, known to produce chronic, persistent and difficult to treat infections.

The thermal behaviour of these derivatives was investigated by thermal analysis (TG, DTG, DSC) both in synthetic air and argon. Except for the water elimination, a similar behaviour for complexes **(1)** and **(2)** both in air and inert atmosphere was evidenced. The final residues were the copper oxide (in air) and metallic copper in inert atmosphere as X-ray diffraction indicates.

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