



*Dedicated to Professor Eugen Segal
on the occasion of his 80th anniversary*

NOVEL TRIAZOLIC COPPER (II) COMPLEX: SYNTHESIS, THERMAL BEHAVIOUR AND KINETIC STUDY

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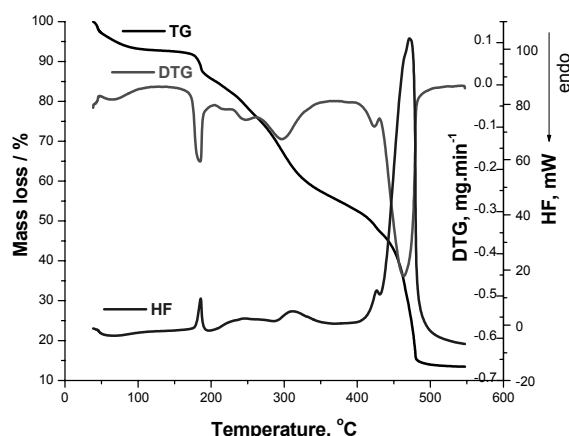
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Cu(II) complex with a triazolic ligand was synthesised and characterized. The stoichiometric composition of this complex was deduced from the thermal behaviour, FT-IR spectroscopy, complexometric titration and evolved gases analysis.

The kinetic analysis of the degradative process of the Cu(II) complex was investigated using the thermogravimetric data in air for the substance's decomposition in non-isothermal conditions. The kinetic parameters were obtained by means of different multi-heating rates methods (which are using five curves measured at different heating rates, $\beta=5, 7, 10, 12$ and $15 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$): isoconversional methods (model-free) Kissinger–Akahira–Sunose, Flynn–Wall–Ozawa and Friedman, respectively the non-parametric kinetics method (NPK), which allows a separation of the temperature, respective conversion dependence of the reaction rate. The values of the obtained kinetic parameters from the four applied methods are in a good agreement.



INTRODUCTION

Medicinal inorganic chemistry became an important research domain which is rapidly growing in the field of design and use of drugs and diagnostic agents. Studies on metal coordination compounds revealed that their biological activities led to the development of new chemotherapeutics which target specific physiological or pathological processes, especially for antitumor behavior. These studies involve both designed and natural products,

in association with essential metal ions such as copper or iron.¹

Copper is considered an essential element and has received considerable attention with regard to its presence in blood plasma and serum components. Cu(II) complexes with non-steroidal anti-inflammatory drugs (NSAID) are reported to possess an increased anti-inflammatory activity and a reduced gastrointestinal toxicity compared to the uncomplexed active substances. A variety of recent observations indicate that co-administration of

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Cu(II) with NSAIDs exhibit synergistic activity. Other pharmacological activities of copper complexes, and their potential as antiepileptic, anti-arthritic, antitumor, antiulcer, and anti-diabetic drugs were previously published.²⁻⁵

The chemistry of substituted 1,2,4-triazoles has known an intensive development in numerous scientific fields, such as medicine and pharmacy, agriculture, analytical chemistry and engineering. Studies have reported that substituted triazoles and their metal complexes are used as bioactive molecules (especially in the field of antifungal and antimicrobial formulations,⁶ as metal corrosion inhibitors,⁷ insecticides and pesticides,⁸ or plant growth regulators.⁹ Recent studies revealed that 1,2,4-triazole derivatives can be used as selective chemosensors for detection of metal ions.¹⁰ The importance of coordination compounds containing triazole-ligand moieties is suggested by the abundance of scientific papers published in this field, which reveals numerous uses of the metal complexes. In the last decades, several reviews have presented the synthetic paths for obtaining (porous) polymeric coordination materials, metal coordination complexes and spin-crossover complexes and their practical importance.¹¹⁻¹³

The versatility of coordinating capacity of 1,2,4-triazolic heterocycles resides in their structure: there are several binding modes due to the present of three nitrogens and the possibility of tautomerism.^{14,15} Previous studies had reported the structural properties of organotin derivatives of similar heterocyclic structures, and revealed supramolecular structures involving intermolecular Sn-S, N-H-S or S-S interactions.¹⁶

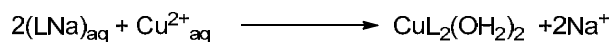
The coordinating capacity of triazoles can be modified via organic synthesis, different functional groups can be grafted on the triazolic nucleus.¹⁵ In our previous studies¹⁷⁻¹⁹ we set our goal in the synthesis of new acetic acid derivatives of 1,2,4-triazoles, compounds that possess and increased complexing capacities, as well as possible anti-inflammatory activity. 3-substituted 4*H*-4-amino-5-mercapto-1,2,4-triazoles are nitrogen and sulfur donor ligands and by their structure are polydentate, the potential coordinating sites are the sulfur atom, the endocyclic nitrogens as well by the exocyclic nitrogen from the amino group. By S-alkylation and the insertion of the -CH₂COOH moiety, the coordinating capacity is modified, a new coordinating site being the carboxylic oxygen.

Thermal analysis of substances with bio-pharmaceutical potential is the aim of many investigations,²⁰⁻²² which can be in the study of

purity, thermal stability and polymorphism evaluation and also a parameter in the studies of preformulation of drugs. In this context and as a continuation of our previous papers,²³⁻²⁴ which investigating thermal properties of some active compounds, the present work reports on synthesis, together with thermal and kinetic studies of Cu(II) complex with a triazolic ligand.

RESULTS AND DISCUSSION

The complex of Cu(II) was prepared from the sodium salt of 4*H*-4-amino-5-carboxymethylsulfanyl-3-phenyl-1,2,4-triazole (**1**) and was precipitated from aqueous solution by the interaction of the above mentioned triazole and an aqueous solution of CuCl₂·2H₂O according to the following equation:



Scheme 1

In order to elucidate the molecular formula for the metal complex, the Cu(II) content was determined by complexometric titration with EDTA. The experimental results are in good agreement with theoretical ones. The water content of the complex was determined by thermal analysis, and was calculated by the mass loss in the 40-100 °C range: the mass loss corresponds to a number of moles of water of approx. 2.06. The molar mass of the complex was also determined from thermogravimetric curve, being 600.31 g/mol. The molar mass was calculated by the means of the final decomposition product (after the thermal treatment of the complex at 550 °C), which was confirmed to be the Cu(II) oxide.

In our attempt to determine a possible melting point of the metal complex with the Boetius apparatus, in the 186-189 °C temperature range a change of colour was observed: the metal complex turned to brown. This decomposition was also sustained by the analysis of the TG curve.

Characterisation of CuL₂(OH)₂

Molecular formula: C₂₀H₂₂O₆N₈S₂Cu, *Molar mass:* 598.11 g/mol (calcd.); 600.31 g/mol (found); *Cu(II) content:* 10.62% (calcd.); 10.43±0.11 (found).

a) IR spectra

The IR spectra of the copper complex and the one for the acid form of the ligand are given in

Fig. 1. By the analysis of the FTIR spectra, it can be proven that characteristic vibration of the carboxylic OH no longer appears in the spectrum, suggesting that the formation of the metal complex occurs with the carboxylate anion. The presence of the coordinated water in the structure of the complex is suggested by the characteristic vibrations $\nu(\text{H}_2\text{O})$ as broad band in the 2500-3500 cm^{-1} range for chelated compounds.

According to literature,²⁵⁻²⁸ the COOH group is characterised by two major ways of vibrations: $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{OH})$, the latter being represented by two bands. Once the deprotonation of the -COOH group occurs, it is expected that the $-\text{COO}^-$ group adopts a C_{2v} symmetry, so $\nu^{\text{as}}(\text{COO})$ and $\nu^{\text{s}}(\text{COO})$ vibrations occurs. As expected, the analysis of the IR spectrum reveals that the deprotonation of the carboxyl group occurs in the metal complex, fact sustained by the shift of

$\nu(\text{C}=\text{O})$ from 1714 cm^{-1} (in the case of free ligand) to a low frequency (1617 cm^{-1}) in the case of the Cu(II) metal complex. The formation of the metal complex is sustained by the appearance of new bands in the 500-400 cm^{-1} region of the FTIR spectra, regions assigned to $\nu(\text{Cu}-\text{O})$ and $\nu(\text{Cu}-\text{N})$ respectively.²⁹

b) Thermal behaviour

The thermoanalytical curves of the Cu(II) complex obtained during heating at $\beta=15\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in air atmosphere exhibit four principal decomposition steps (Fig. 2). The first step in the temperature range 40-100 $^\circ\text{C}$ represents a dehydration step. The decomposition of the anhydrous complex commences in the temperature range 160-200 $^\circ\text{C}$, the final decomposition product was confirmed to be CuO.

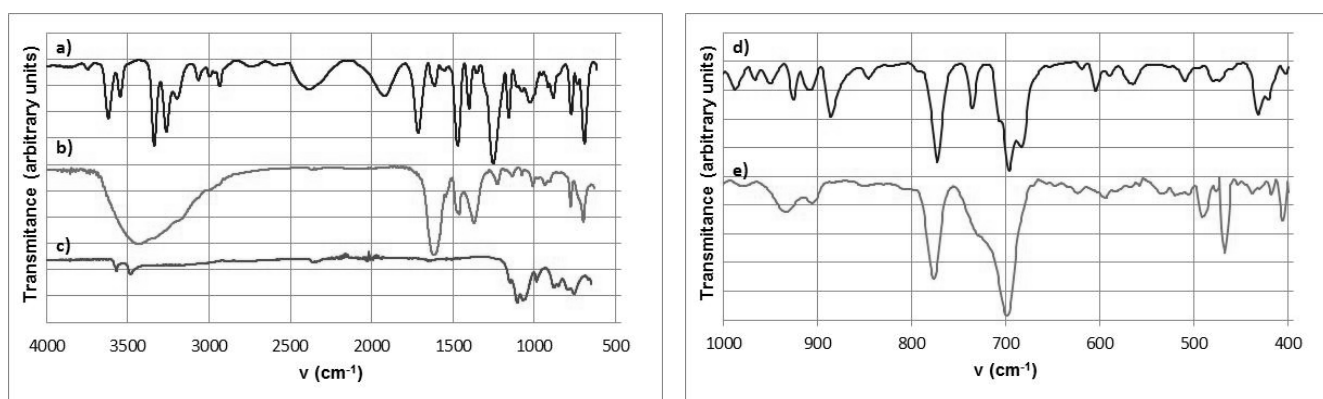


Fig. 1 – FTIR spectra of the ligand (a) and Cu(II) triazolic complex before (b) and after (c) heating at 550 $^\circ\text{C}$ on 4000-600 cm^{-1} ; respectively for the ligand (d) and Cu(II) triazolic complex (e) on 1000-400 cm^{-1} .

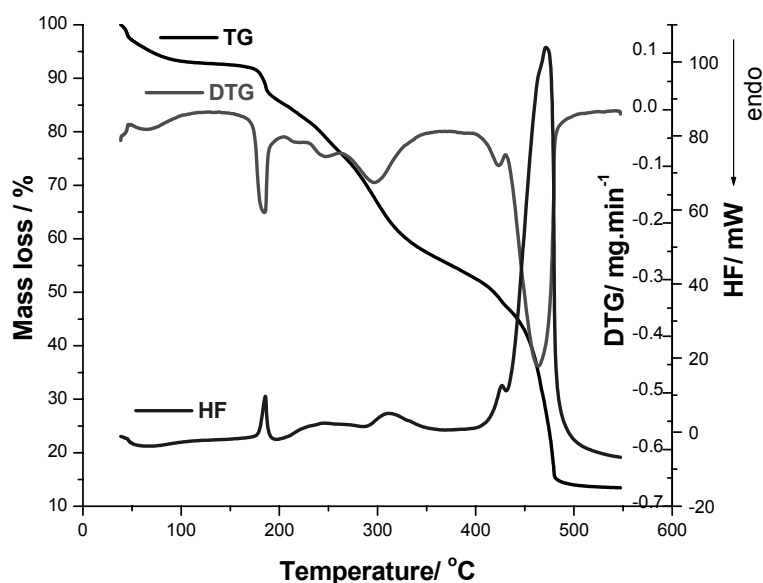


Fig. 2 – The thermoanalytical curves TG/DTG/HF obtained in air at $\beta=15\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ for the analysed Cu(II) complex.

Table 1

Thermoanalytical data of the analysed complex at different heating rate					
$\beta/^\circ\text{C}\cdot\text{min}^{-1}$	Process	$T_i(^\circ\text{C})$	$T_f(^\circ\text{C})$	$T_{\text{max DTG}}(^\circ\text{C})$	$T_{\text{max HF}}(^\circ\text{C})$
5	I	40	160	95	-
	II	160	200	175	176
	III	200	350	277	-
	IV	350	465	420	422
7	I	40	150	-	-
	II	150	200	180	179
	III	200	350	282	290
	IV	350	470	435	440
10	I	40	157	-	-
	II	157	202	182	179
	III	202	350	287	294
	IV	350	477	445	448
12	I	50	158	-	-
	II	158	206	185	187
	III	206	350	295	305
	IV	350	500	455	456
15	I	50	158	-	-
	II	158	206	185	187
	III	206	350	295	305
	IV	350	500	455	456

The DTG curve shows five overlapping maxima corresponding to overlapping steps in the thermogravimetric curve (TG). The first step (40–100 °C) corresponds to the liberation of two water molecules (calculated mass loss=6.02%, experimental mass loss=6.40%). The second step is a sharp endothermic event with $\text{DTG}_{\text{peak}}=180$ °C and $\text{HF}_{\text{peak}}=179$ °C. According to literature,²⁹ lattice water is removed at temperatures below 100 °C, whereas coordinated water could be eliminated within the 125–275 °C range. As a conclusion to this, the two water molecules correspond to the lattice water, not to coordination water (see Fig. 5).

After the water elimination, a decomposition process with a continuous mass loss takes place until 500 °C. The residue mass after the final decomposition is in agreement with formation of CuO (calculated mass loss=13.29%, experimental mass loss=13.45%).

The thermal analysis results of the new Cu(II) complex with the triazolic ligand, determined in non-isothermal conditions, at different heating rates, are summarized in Table 1.

c) EGA Analysis

From thermoanalytical curves recorded at a heating rate $\beta = 20^\circ\text{C}\cdot\text{min}^{-1}$, shown in Fig. 3, it is observed that the maximum peak occurs after about 10 minutes, the DTG curve's maximum was recorded at a temperature of 186 °C. Even if in that moment ($t=11.9$ min) the maximum concentration of the gases has not been met because the mass loss continues after the final temperature of the analysed process (200 °C), the EGA study confirmed that in

this degradative step, a compound with molar mass approx. 28 g/mol (calculated by the means of the thermogram) is released from the complex (Fig. 4). This fact suggests that the triazolic rings (by endocyclic nitrogen atoms) are not involved in the formation of the chelate, being liable to bond breaking. Even if the formation of the nitrogen molecule cannot be proven by IR spectroscopy, the breakdown of the triazolic moiety is sustained by the EGA of the gaseous mixture formed from ambient temperature up to 235.6 °C (corresponding time 11.88 min), when the process progress with the heterocyclic degradation, with carbon disulphide release. The main compounds that can be identified from the EGA spectra are water vapours ($\nu=3750\text{--}3500$ and $1900\text{--}1300$ cm^{-1}) from first mass loss and carbon disulphide ($\nu=2282\text{--}2050$ cm^{-1}) as a following process.

Because the evolved gas analysis was carried out on a temperature higher than the one of the studies process, in the IR spectra other bands were observed, as expected. This is another confirmation that the degradative process is continuous with the increase of the temperature.

A similar EGA profile was observed for the decomposition products on temperatures below 405.85 °C. With the increase of the temperature up to 491 °C, in the IR spectrum new bands appeared. The main compound that can be identified from the EGA spectrum is carbon dioxide ($\nu=2372$ cm^{-1}). The fact that the decarboxylation occurs at such a high temperature can be explained by the fact that the carboxyl group is involved in the coordinating bond, and that the lateral heterocyclic moiety is more susceptible to degradation.

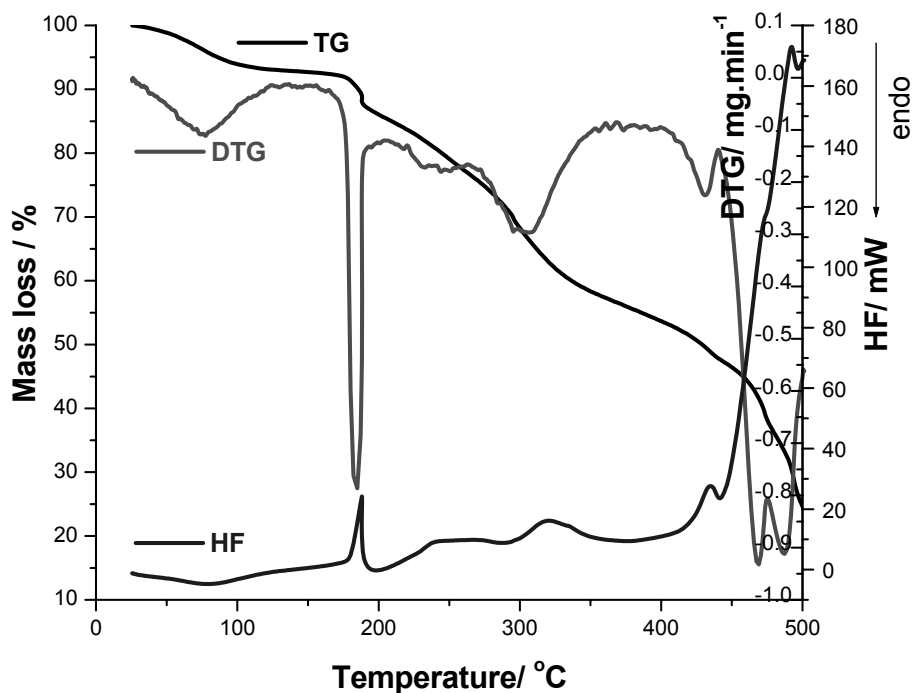


Fig. 3 – Thermoanalytical curves for Cu(II) triazolic complex at $\beta = 20^\circ\text{C}\cdot\text{min}^{-1}$.

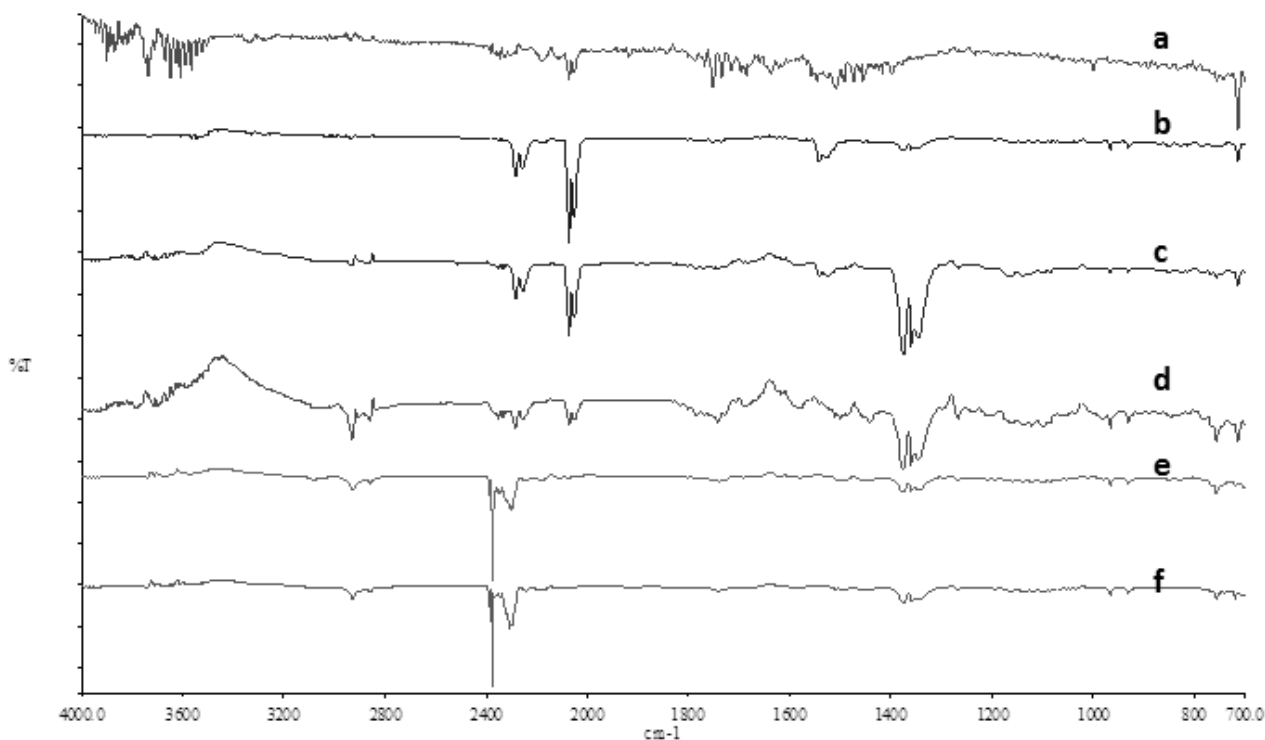


Fig. 4 – FTIR spectra of gaseous mixtures observed above metal complex in air at (a) $T = 235.6^\circ\text{C}$; (b) $T = 294.3^\circ\text{C}$; (c) $T = 334.4^\circ\text{C}$; (d) $T = 405.9^\circ\text{C}$; (e) $T = 491.9^\circ\text{C}$; (f) $T = 500^\circ\text{C}$ measured by the online TG-FTIR system (initial sample mass: 5.026 mg, heating rate: $20^\circ\text{C}\cdot\text{min}^{-1}$).

The products identified from the EGA spectra are according with the active substance's skeleton and are demonstrating a significant destruction of Cu(II) complex, namely of the triazolic ligands.

According to the experimental observations previously mentioned (FTIR spectroscopy, EGA and thermal analysis) a proposed structure for the metal complex is presented in Fig. 5.

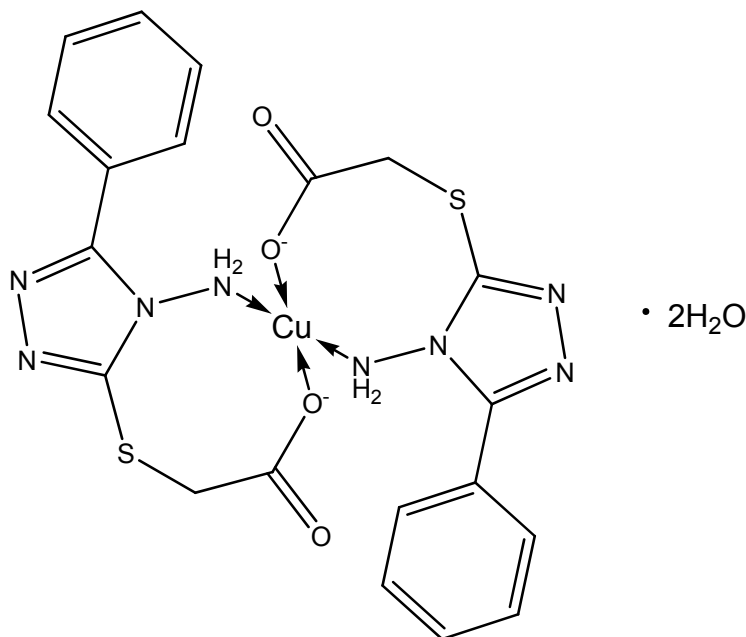


Fig. 5 – The proposed structure of the Cu(II) metal complex.

d) Kinetic Study

The kinetic investigation of Cu(II) triazolic complex's degradation was obtained from TG data by the use of two isoconversional integral methods: Kissinger–Akahira–Sunose and Flynn–Wall–Ozawa; one isoconversional differential method: Friedman and the non-parametric kinetics method (NPK).

By the use of *Flynn–Wall–Ozawa's method* (FWO),^{30,31} from the slope of the straight line $\log \beta$ vs. $1/T$, the activation energy of the analysed process was obtained, according with the Equation 1:

$$\ln \beta = \ln \frac{AE}{R \cdot g(\alpha)} - 5.331 - 1.052 \cdot \frac{E}{R \cdot T} \quad (1)$$

where $g(\alpha)$ is the integral conversion function. The FWO's method was applied to data obtained from the five thermogravimetric curves in order to determine the activation energy E_a for the main thermal decomposition step at around 150 °C to 200 °C. The values of the activation energy obtained by this method are presented in Table 2.

The Kissinger–Akahira–Sunose method (KAS)^{32,33} is a isoconversional integral method based on the following equation:

$$\ln \frac{\beta}{T^2} = \ln \frac{A \cdot R}{E \cdot g(\alpha)} - \frac{E}{R \cdot T} \quad (2)$$

Thus, for $\alpha = \text{constant}$, the plot of $\log(\beta/T^2)$ vs. $1/T$, obtained from different thermogravimetric

curves recorded at five heating rates, is a straight line and the slope of this can be used to evaluate the activation energy. The results obtained for this method are presented in Table 2.

Based on the basic Arrhenius equation, the third applied method, **Friedman** (FR),³⁴ which is an isoconversional differential method, provides the following expression for thermal degradation kinetics:

$$\ln \left(\beta \frac{d\alpha}{dT} \right) = \ln [A \cdot f(\alpha)] - \frac{E}{R \cdot T} \quad (3)$$

The plot of $\ln(\beta \frac{d\alpha}{dT})$ vs. $(1/T)$ gives the straight line with slope, E_a/R , from which E_a can be calculated and the obtained values are given in Table 2 for each degree of conversion $0.05 \leq \alpha \leq 0.95$.

Through application the two isoconversional integral methods, KAS and FWO, it was observed that the values of activation energy vary with the conversion degree, but this variation is lower than 10%. The small difference between E_{FWO} and E_{KAS} values can be assigned to different approximations of the temperature integral, which leads to a slight difference between the two equations, (1) and (2).

Regarding the dependence of E_a vs. α , according to Friedman method, this is an important one (~22%) and it is probably due to differential processing of the kinetic data.

Table 2

Activation energy's values obtained by the three isoconversional methods for the new metal triazolic complex

E_a kJ/mol	Conversion degree α																			$\overline{E_a}$ kJ/mol
	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.55	0.6	0.65	0.7	0.75	0.8	0.85	0.9	0.95	
FR	265.6 ±2.0	286.8 ±2.9	252.5 ±3.3	255.1 ±2.7	263.4 ±2.1	259.4 ±2.7	254.4 ±2.3	261.2 ±3.0	236.4 ±2.4	254.3 ±2.3	265.3 ±1.5	278.5 ±1.8	292.0 ±2.1	279.9 ±2.3	266.1 ±2.0	275.8 ±1.9	282.5 ±1.8	272.9 ±2.6	287.6 ±3.8	252.7 ±10.7
KAS	283.5 ±2.5	265.5 ±2.1	264.7 ±2.3	262.1 ±1.5	267.5 ±1.8	274.1 ±1.6	267.0 ±1.5	265.0 ±1.3	259.2 ±1.6	254.5 ±1.6	264.5 ±1.4	265.3 ±1.9	277.0 ±1.8	280.9 ±1.3	273.9 ±1.5	275.5 ±1.7	280.9 ±1.9	282.7 ±2.9	278.4 ±2.9	270.6 ±8.3
FWO	276.4 ±2.4	259.4 ±1.8	258.7 ±1.7	256.3 ±2.7	261.4 ±2.5	267.7 ±3.0	260.9 ±2.4	259.1 ±1.9	253.5 ±2.5	249.1 ±3.1	258.6 ±2.4	259.4 ±2.2	270.5 ±2.5	274.3 ±1.9	267.6 ±2.5	269.1 ±1.8	274.3 ±2.5	276.0 ±1.9	272.1 ±3.8	264.4 ±10.4

Table 3

Kinetic analysis for Cu(II) triazolic complex, the NPK method.

	Process	λ (%)	E (kJ·mol ⁻¹)	A (min ⁻¹)	n	m	Šestak-Berggren Equation ⁴⁰ $g(\alpha) = \alpha^m \cdot (1-\alpha)^n$
Cu(II) complex	1	91.2	251.6±12.1	8.16·10 ²⁷	1	–	(1- α)
	2	5.6	37.1±2.8	1.68·10 ⁴	1	2	$\alpha^2 \cdot (1-\alpha)$

The non-parametric kinetics method (NPK), developed^{35,36} and modified^{24,37,38} a few years ago, represents a special approach for processing the kinetic data. It is based on the single-step kinetics approximation, so that the basic relationship for the analysis of kinetic data represents Eq. 4, the general rate equation:

$$\frac{d\alpha}{dT} = k(T) \cdot f(\alpha) \quad (4)$$

The experimental values of reaction rates are arranged in a matrix which is expressed as a product of two vectors containing information on $k(T)$ and $f(\alpha)$. The most important feature of the method is that it enables to decouple the vectors related to the temperature and conversion functions without the need of any assumptions about their functionality. Validity of Eq. 4 is the only assumption made in the development of NPK method.

The experimental points obtained at different heating rates are interpolated as a continuous reaction rate surface. This surface is discretized into a square matrix M which is decomposed, using the singular value decomposition algorithm,³⁹ into the product of three matrixes:

$$M = U(\text{diag } S)V^T \quad (5)$$

The results of NPK analysis are systematized in Table 3. These data were obtained from the linearization of the vector v and of the vector u with different correlation functions to identify the reaction model.

It is noted that the main process is a first order chemical reaction ($n=1$) unaccompanied by any physical process ($m=0$). The secondary process requires a smaller activation energy comparative with the value required in the first process, but it contributes to the unit process in a small proportion (explained variance $\lambda = 0.056$). The secondary process is accompanied by a physical process ($m=2$).

The value of activation energy obtained from NPK method is $E_a = (251.6 \pm 12.1)$ kJ·mol⁻¹ (only the steps with $\lambda \geq 10\%$ are considered), which is in a

very good agreement with those obtained with the isoconversional methods (see Table 2).

EXPERIMENTAL

The synthesis of 4*H*-4-amino-5-carboxy-methylsulfanyl-3-phenyl-1,2,4-triazole (**1**) was previously reported by I. Ledeti *et al.*¹⁷ Other reagents were commercial products (Aldrich) and used as received. Decomposition/melting point of the metal complex was determined on a Bötius PHMK apparatus (Veb Analytik Dresden), and thin-layer chromatography was carried out on silica gel-coated plates 60 F₂₅₄ Merck using benzene:methanol 7:3, benzene:methanol 3:7 or benzene:ethyl acetate 1:1 (v/v) as eluants.

The Cu(II) content was determined by complexometric titration with EDTA, in buffer solution (NH₃/NH₄Cl) at pH ~ 8, in the presence of Murexid as indicator.

The thermoanalytical curves TG/DTG/HF for the Cu(II) complex were drawn up in an air atmosphere and under dynamic conditions at different heating rates using Perkin-Elmer DIAMOND equipment.

The TG/DTG/HF data were recorded under non-isothermal conditions. Samples of mass in the range of 3 to 7 mg were put into aluminium crucibles, at different heating rates β of 5, 7, 10, 12 and 15 °C·min⁻¹ up to 550 °C.

The evolved gas analysis (EGA) was carried out by a coupled TG/FTIR technique, using a Perkin Elmer SPECTRUM 100 device with an IR gas chamber connected by a transfer line to the exit of the DIAMOND furnace. The air flow of 100 mL·min⁻¹ and a heating rate of 20 °C·min⁻¹ were used. The FTIR spectra were processed by the Sadtler Gas Vapor Library.

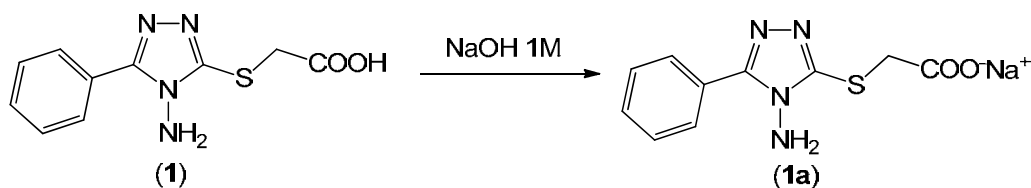
The FTIR spectra of different solid samples were obtained on the same spectrometer using the U-ATR technique.

Sodium salt of 4H-4-amino-5-carboxy-methylsulfanyl-3-phenyl-1,2,4-triazole (1)

The synthesis of the ligand (**1a**) was carried out in aqueous medium at 60 °C, by treating the stoichiometric amount of triazole (**1**) with NaOH 1M solution. The soluble sodium salt (**1a**) was purified while hot with active charcoal and the solvent was removed by distillation under reduced pressure (10 mm Hg). The purity of the sodium salt was verified by TLC using three eluting systems.

Synthesis of the Copper (II) metal complex

Copper (II) metal complex was prepared by dripping under intense stirring an aqueous solution of the triazolic ligand (**1a**) (20 mmol triazole in 5 mL distilled water) to an aqueous solution of CuCl₂·2H₂O (10 mmol in 2 mL of distilled water). After 2h of continuous stirring, an amorphous blue-green coloured solid metal complex was filtered off under vacuum, washed with distilled water (3x10 mL) and dried for 48h at 30 °C.



CONCLUSIONS

The Cu(II) complex with the sodium salt of 4H-4-amino-5-carboxy-methylsulfanyl-3-phenyl-1,2,4-triazole was synthesized and characterized. TG/DTG and HF traces reveal that the degradation of the complex begins at nearly 40 °C with a dehydration process and shows multi stage degradations.

The four stages of degradations occur in the temperature region of 40–160, 160–200, 200–350 and 350–465 °C. Using the TG curves obtained from the multiple heating measurements, the activation energy for the degradation of this complex was calculated using the Friedman, KAS and FWO methods, as well as the non-parametric kinetics method (NPK). The trend in the variation of activation energies calculated for the degradation of triazolic complex by employing KAS and FWO methods at each 5% conversion level for the various stages of degradations are similar. Regarding the dependence of E_a vs. α , according to Friedman method, this is an important one and it is probably due to differential processing of the kinetic data. The use of the NPK method led to evaluation of the kinetic parameters without any approximation. The application of isoconversional methods and NPK method led to the values of the activation energy which are all in a very good agreement.

By the use of the thermal analysis, IR spectroscopy, EGA and complexometric titration, a proposed structure for the metal complex was presented. The results show the importance of thermoanalytical methods in the structural identification as a complement to the already used methods.

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