Synthesis and Solid - state Characterization of a Cobalt(II) Triazolic Complex

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A new metal complex containing Co(II) as central ion and an S-alkylated triazolic ligand was synthesised and characterized by elemental analysis, FTIR spectroscopy, thermal analysis and evolved gases analysis. The degradation of the complex architecture was evaluated by the use of kinetic analysis using thermogravimetric data in air under non-isothermal conditions. The kinetic parameters were evaluated by using five different heating rates, β=5, 7, 10, 12 and 15 °C·min⁻¹ and applying isoconversional methods such as Kissinger–Akahira–Sunose, Flynn-Wall-Ozawa and Friedman, respectively the non-parametric kinetics method (NPK). The obtained values of the kinetic parameters from the above-described methods are in a good agreement.

Keywords: alkylated 1,2,4-triazole; cobalt complex; thermal analysis; kinetic study

In the last century, a great attention was granted to the importance of mineral elements in the living systems, from microorganism to humans. Nowadays, cobalt is considered an essential "ultratrace" element, for all animals. The major constituent containing a source of cobalt is the water-soluble vitamin cobalamin, which plays an essential role in the formation of blood and in the normal activity of the nervous system and brain[1-2].

It was revealed that the presence of cobalt in soils is necessary so it can assure the recommended amount for grazing animals, namely a daily uptake of 0.2 mg/kg , assuring in this way the source for central ion in the synthesis of vitamin B12.[3]

In the field of medicinal chemistry, a separate research field developed, namely the one involved in the study and evaluation of diagnostic agents and drugs consisting in metal coordination compounds, or so called metal complexes. Numerous published studies [4-6] proved that complexes containing metals as central ions and different functionalized ligands can be incorporated in new pharmaceutical formulations and chemotherapeutic agents that can target specific pathological or physiological processes, including antineoplastic ones. Metal coordination compounds containing central ions of transitional metals such as cobalt, iron, rhodium, copper and zinc have all been used in medicine [7]. More recently, a review was published regarding the actual importance of bioactivities of Co(III) complexes [8].

Co(II) complexes with ligands derived from aspirin, namely [2-acetoxy-(2-propynyl)benzoate] hexacarbonyl-dicobalt and hexacarbonyl[μ-(2-ethylphenyl)methanol] dicobalt (Co-EPM) were investigated on antiproliferative activity on pleural mesothelioma (MPM) cell lines, having

an epithelioid or a sarcomatoid phenotype and the results showed that can be considered an antitumor drug candidate [9]. Sanatkar et al. reported the synthesis and characterization of two neutral mononuclear complexes of Co(II) and Zn(II) with the non-steroidal anti-inflammatory drug meloxicam[10]. Even if is not studied so widely as other transitional ions, Co(II) was used as complex generator in a series of complexes of meloxicam, along with other trace ions, such as nickel(II), zinc(II) and cadmium(II).[11]

Literature data reveals that heterocyclic derivatives, such as functionalized 1,2,4-triazoles and their supramolecular structures possess various activities such as pesticides and insecticides [12], growing regulating agents for plants [13], antifungal and antimicrobial [14].

Metal complexes of Co(II) with functionalized triazoles as ligands are presented in literature [15-16], and biological evaluations were carried out: for antibacterial activity towards both planktonic and biofilm-embedded cells and cytotoxic activities [17] and strong urease inhibition activities [18].

Triazolic nucleus can be variously functionalized, different functional groups can be grafted in different positions, leding to numerous derivatives that can act as ligands [19]. In previous studies [20-22] we described the synthetic protocol followed in order to prepare S-alkylated 1,2,4-triazoles that contain thioacetic moiety and exocyclic amino group, acting as a bidentate ligand. As previously stated [23], 3-substituted 4*H*-4-amino-5-mercapto-1,2,4-triazoles can act as polydentate ligands by the presence of nitrogens and sulfur. The S-functionalisation realized by the grafting of the –CH₂COOH moiety determined the apparition of a new coordinating point, the carboxylic oxygen.

Thermal-induced degradation of chemical entities, including bioactive molecules reveals important aspects about the stability and the mechanisms of decomposition [24-26] which can be successfully used in the study of stability, purity and preformulation of active pharmaceutical ingredients. Following previous studies [27-37], this paper describe the synthesis, thermal and kinetic studies of a metal complex with triazolic ligand of Co(II) transitional ion.

Experimental part
Materials and methods

The synthesis of 4*H*-4-amino-5-carboxy-methylsulfanyl-3-phenyl-1,2,4-triazole (**1**) was previously reported by I. Ledeţi et al.[21]. Other reagents were commercial products (Aldrich) and used as received. Decomposition/melting point of the metal complex was determined on a Böetius PHMK apparatus (Veb Analytik Dresden), and thin-layer chromatography was carried out on silica gel-coated plates 60 F$_{254}$ Merck using benzene:methanol 7:3, benzene:methanol 3:7 or benzene:ethyl acetate 1:1 (v/v) as eluants.

The Co(II) content was determined by complexo-nometric titration by an indirect method, using a standard analytical procedure, after dezagregation, using KSCN as indicator.

The thermoanalytical curves TG/DTG/HF for the Co(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.

The synthesis and purification of the ligand was carried out in aqueous medium and was previously reported [23]. The purity of the sodium salt was confirmed by the means of thin layer chromatography using three different eluting systems. The structure of the ligand is presented in figure 1.
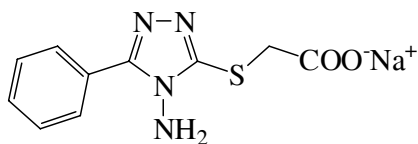

Fig. 1. The structure of ligand

Co(II) coordination compound was obtained by dripping under intense magnetic stirring an aqueous solution of the triazolic ligand (1.090g, 40 mmol in 10 mL of distilled water) to an aqueous solution of CoCl$_2$· 6H$_2$O (0.476g, 20 mmol in 5 mL of distilled water). After 2h of continuous intense stirring, an amorphous pale-pink coloured solid metal complex was filtered off under vacuum, washed with distilled water (3x10 mL) and dried for 72h at room temperature.

Results and discussions

The Co(II) complex was prepared from the sodium salt of 4*H*-4-amino-5-carboxy-methylsulfanyl-3-phenyl-1,2,4-triazole (LNa) (fig. 1) by the interaction in aqueous medium of the ligand with the solution of CoCl$_2$· 6H$_2$O according to scheme 1:

$$2(LNa)_{aq} + Co^{2+}_{aq} \xrightarrow[\text{2h}]{\text{intense stirring/r.t.}}$$
$$CoL_2(OH_2)_2 \cdot 4H_2O + 2Na^+$$

Scheme 1
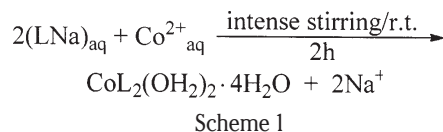
Molecular formula of the metal complex was evaluated by both thermal analysis and complexometric titration. The Co(II) content was determined in the presence of an excess of EDTA at *p*H ~5 in the presence of CH$_3$COONH$_4$ 3M. The obtained results are in good agreement with the ones obtained by theoretical means. The water content of the complex was determined by the use of thermal analysis, being represented by the mass loss observed in the 45-95 °C temperature range: the corresponding mass loss to one mole of complex correspond to a number of moles of water of approx. 6.18. The molar mass of the complex was also determined from thermogravimetrical curve, being 665.56 g·mol^{-1}. The molar mass was estimated by the means of the final decomposition product (after the thermal treatment of the complex at 550 °C), which was confirmed to be the Co(II) oxide, CoO.

Characterisation of CoL$_2$(OH$_2$)$_2$·4H$_2$O

Molecular formula: C$_{20}$H$_{30}$O$_{10}$N$_8$S$_2$Co;
Molar mass: 665.56 g/mol (calcd.); 670.30 g/mol (found);
Co(II) content: 8.85% (calcd.); 8.76±0.23 (found).

FTIR spectroscopy

The UATR-FTIR recorded spectra for the Co(II) complex and the one for the acid form of the ligand are presented comparatively in figure 2. By the analysis of the FTIR spectra, it can be proven that characteristic vibration of the carboxylic OH from alkylated triazole that was used as ligand are no longer present as bands in the spectrum, suggesting that in the case of metal complex, the sodium salt of ligands remains non-protonated. The presence of the coordinated/lattice water in the structure of the complex is suggested by the characteristic vibrations ν(H$_2$O) as broad band in the 2600-3700 cm^{-1} spectral range for chelated compounds.

Literature [38-41] indicates that carboxyl group -COOH is characterised by two major ways of vibrations: ν(C=O) and ν(C-OH), the last one being represented by two distinct bands. Once the deprotonation of the -COOH group took
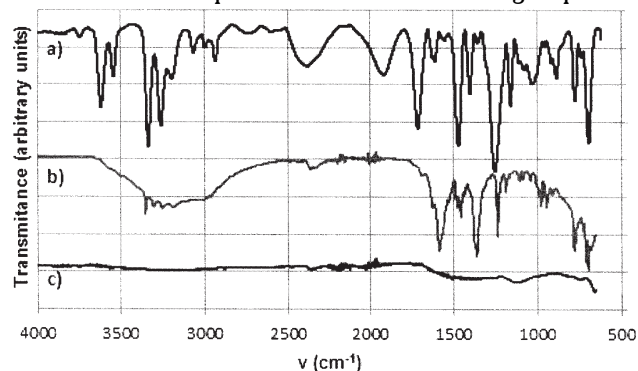

Fig. 2. UATR-FTIR spectra on 4000-600 cm^{-1} spectral range for the ligand (a) and Co(II) metal complex before (b) and after (c) thermal treatment at 550ºC
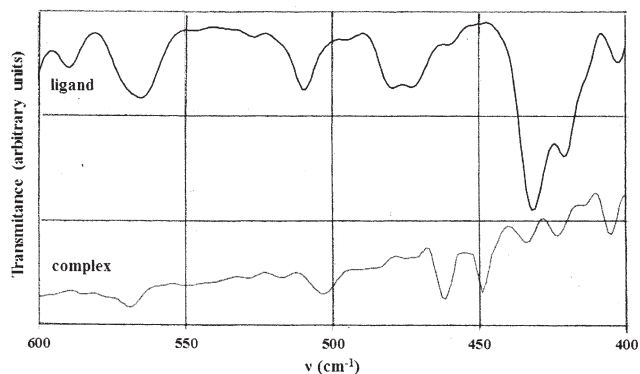
Fig. 3. FTIR spectra on 600-400 cm^{-1} spectral range for the ligand and Co(II) metal complex

Fig. 4. The TA curves TG / DTG / HF obtained in air at β = 5°C min^{-1} for the analysed Co(II) complex

place, the deprotonated carboxylate group -COO$^-$ adopts a C$_{2v}$ symmetry, so two distinctive vibrations occur, namely ν^{as}(COO) and ν^s(COO). According to this, FTIR spectroscopy reveals the deprotonation of the carboxyl in the case of Co(II) complex, by the shift of ν(C=O) from 1714 cm^{-1} (in the case of free ligand) to a considerable lower frequency (1590 cm^{-1}) in the case of the Co(II) coordination compound. The formation of the metal complex is sustained by the appearance of new bands in the 500-400 cm^{-1} spectral range (at 462 cm^{-1} and 448 cm^{-1}, respectively) of the FTIR spectra, regions assigned to ν(Co→O) and ν(Co→N) respectively (fig. 3) [42].

Thermal behaviour

In our attempt to determine the melting point of the metal complex with the Böetius apparatus, at 200 °C, the pale-pink solid turns into colourless needle crystals, which at 228-230 °C turn into intense violet needles. These decomposition events are sustained by the analysis of the TG/DTG/HF curves, where an endothermal process that occurs with mass loss is reveled. The event observed on Böetius at 228-230 °C is also revealed by DTG curve as a maximum for the decomposition process that starts at 187 °C (DTG$_{peak}$=230 °C).

The TA curves obtained at the analysis of the Co(II) complex at a heating rate of β=5 °C·min^{-1} in air atmosphere exhibit multistadial decomposition steps, that can be associated with different overlapping eight individual steps (fig. 4). Due to the fact that the dehydration step involves three mass losses that occur in a narrow interval of temperature, we named this process as process I in table 1. The first step in the temperature range 42-92 °C represents a dehydration step. The decomposition of the anhydrous complex begins at 187 °C and is continuous up to 550°C, the final decomposition product was confirmed to be CoO.

In the temperature range corresponding to dehydration step, DTG curve shows three peaks that can be associated with the loss of different type of water molecules. Even if literature [42] mentions that lattice water is removed first and at temperatures under 100°C, while coordinated water is eliminated over 100 °C, the well individualised peaks on the DTG curve suggest that the water loss could be associated with both lattice and coordination water. According to these observations we can conclude that DTG$_{peak}$ =44 °C and DTG$_{peak}$ = 55°C are associated with the removal of 4 molecules of water (4.02 molecules of water, Δm=10.86%). Another process with mass loss and with a DTG$_{peak}$ = 86 °C can be associated with the removal of 2 more molecules of water (calculated 2.19 molecules of water, Δm=5.94%). These results lead to the conclusion
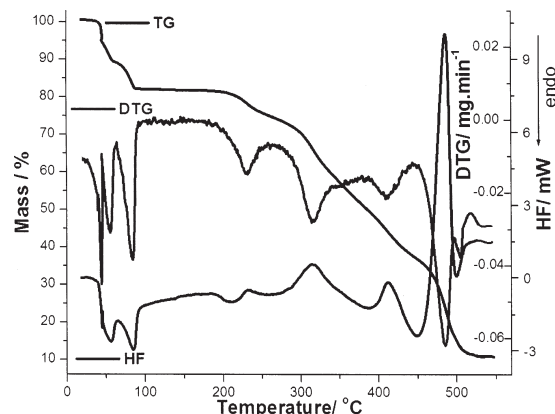
that in the structure of Co(II) complex, there are both molecules of water corresponding to lattice and as well coordination water (fig. 5). An interesting aspect that can be mentioned can be associated with the individual steps of water elimination from the structure of the coordinative compound and can be tentatively associated with the macroscopic observations made during heating on the Böetius plate. The loss of water from the structure can be associated with the modification of geometry of anhydrous complex vs. hydrated form(s).

After the complete water elimination corresponding to the six molecules of water, the decomposition of the anhydrous complex occurs with a continuous mass loss up to 550 °C. The residue mass after the final decomposition is in agreement with formation of CoO (calculated final mass=11.18%, experimental final mass =11.29%). The thermal analysis results of the new Co(II) complex with the triazolic ligand, determined in non-isothermal conditions, at different heating rates, are summarized in table 1.

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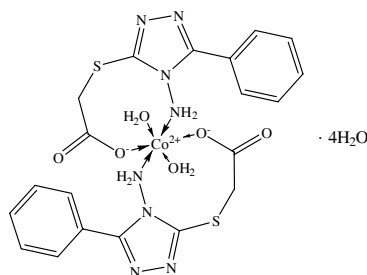

Fig. 5. The proposed structure of the Co(II) metal complex

Kinetic Study

The studied decomposition step was the thermal-induced degradation that took place at temperature between 150 - 200 °C. This process was evaluated by the application of four kinetic methods: Kissinger–Akahira–Sunose and Flynn-Wall-Ozawa (isoconversional integral methods), Friedman (isoconversional differential methods) and the non-parametric kinetics method (NPK).

The kinetic analysis was obtained from DTG data and has been done in order to calculate the kinetic parameters (activation energy E_a; pre-exponential factor A) by the use of five applied heating rates β: 5, 7, 10, 12 and 15 °C·min^{-1} and the decomposed fraction α from 0.05 to 0.95.

The first applied method was Flynn-Wall-Ozawa's method (FWO) [43]. For this method, the activation energy can be calculated from the plots of logarithm of the heating

Table 1
THERMOANALYTICAL DATA OF THE ANALYSED COMPLEX AT DIFFERENT HEATING RATE

β (°C·min⁻¹)	Process	T_i(°C)	T_f(°C)	$T_{max\ DTG}$ (°C)	$T_{max\ HF}$ (°C)
	I	42	92	44; 55; 86	55; 86
	II	187	261	230	213
5	III	261	378	315	315
	IV	378	444	411	412
	V	444	497	484	486
	VI	497	550	505	500
	I	42	99	45;67;93	68;96
	II	190	269	244	247
7	III	269	370	329	328
	IV	370	475	429	437
	V	475	508	505	505
	VI	508	550	521	520
	I	47	99	48; 61;88	61;89
	II	191	270	232	236
10	III	270	370	318	319
	IV	370	463	421	423
	V	463	514	504	505
	VI	514	550	517	519
	I	48	103	50;63;88	63;90
	II	193	277	240	245
12	III	277	362	327	327
	IV	362	475	427	434
	V	475	517	510	511
	VI	517	550	517	519
	I	49	108	50;68;95	68;96
	II	193	278	247	248
15	III	278	363	331	328
	IV	363	478	432	431
	V	478	520	512	514
	VI	520	550	524	525

rate β versus the inverse of the absolute temperature at different conversion degree. By applying the equation 1, from the slope of the straight line $\log\beta$ vs. $1/T$ (fig. 6) the activation energy (E_a) of the analysed process was obtained:

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

where $g(\alpha)$ is the integral conversion function. For all the conversion levels, nearly parallel straight lines are observed. All resulted values of the activation energy are summarized in table 2.

The next utilised method is a model-free integral too, Kissinger–Akahira–Sunose method (KAS) [44-45] which permitted the evaluation of the activation energy (E_a) from Kissinger plot of $\log(\beta/T^2)$ against $1/T$ based on the following equation:

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

Thus, for α = constant, the plot of $\log(\beta/T^2)$ vs. $1/T$, obtained from different thermogravimetrical curves recorded at five heating rates, is a straight line and the slope of this can be used to evaluate the activation energy (E_a). The KAS plots are depicted in figure 7. It can be observed that for all conversion levels, an accurate correlation was obtained. The results obtained for this method are presented in table 2.

The third applied method, Friedman (FR) [46] derives from the basic Arrhenius equation where the logarithm of the reaction rate at constant degree of conversion versus $1/T$ gives a straight line of slope $(-E_a/R)$. The basic equation used is eq. (3):

$$\ln(\beta\frac{d\alpha}{dT}) = \ln[A \cdot f(\alpha)] - \frac{E_a}{R \cdot T} \qquad (3)$$

The Friedman plot $\ln(\beta\frac{d\alpha}{dT})$ against $1/T$ for the calculation of E_a/R at each 0.5 conversion degree of the new metal complex is presented in figure 8.

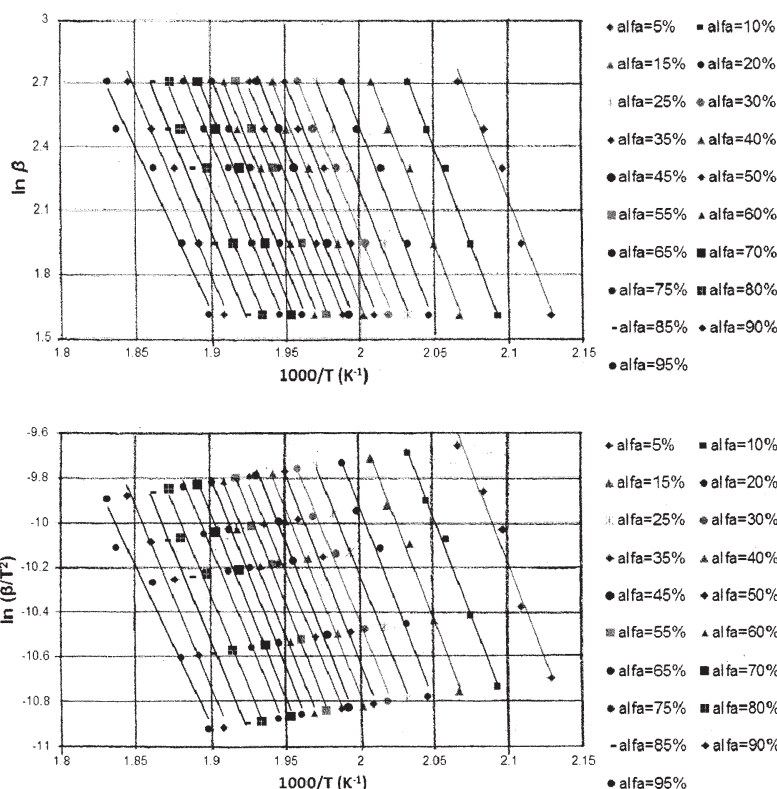Evaluating the data from table 2, obtained by the three isoconversional methods, KAS, FWO and FR, it was

Fig. 6. The plot $\ln\beta$ vs. 1000/T for the Flynn-Wall-Ozawa method

Fig. 7. The plot $\log(\beta/T^2)$ vs. 1/T for the Kissinger–Akahira–Sunose method
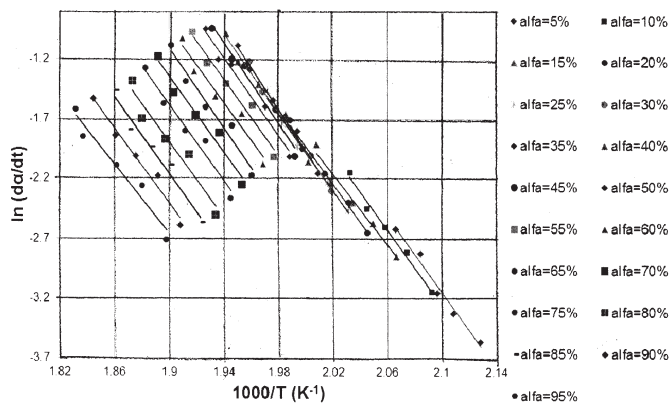
Fig. 8. The plot $\ln(\beta\frac{d\alpha}{dT})$ vs. 1/T for the Friedman method

Table 2.
ACTIVATION ENERGY VALUES OBTAINED BY THE THREE ISOCONVERSIONAL METHODS FOR THE NEW METAL TRIAZOLIC COMPLEX.

E_a	Conversion degree α																			$\overline{E_a}$ kJ/mol
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	133.3	132.2	134.2	130.9	134.1	145	144.8	138.8	140.1	135.0	133.2	131.1	138.8	132.5	133.8	133.5	134.4	130.5	124.8	134.8±1.1
KAS	144.7	145.6	145	146	139.9	138.5	141.0	139.5	140.2	135.1	141.4	139.4	142.0	138.5	137.6	136.4	137.3	136.3	118.7	139.1±1.4
FWO	145.0	146.1	145.6	146.6	140.9	139.6	142.0	140.6	141.4	136.5	142.6	140.7	143.1	139.9	139.0	138.0	138.9	138.0	121.3	140.3±1.2

Table 3
KINETIC ANALYSIS FOR Co TRIAZOLIC COMPLEX, THE NPK METHOD

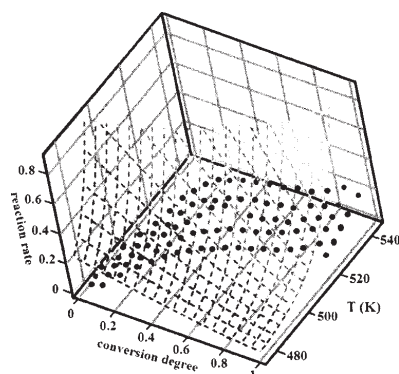|	Process	λ (%)	E (kJ·mol⁻¹)	A (min⁻¹)	n	m	Šestak-Berggren Eq. $g(\alpha)=(1-\alpha)^n\cdot\alpha^m$	λ·E (kJ·mol⁻¹)
Co(II) complex	1	68.6	139.4±12.1	$7.03\cdot10^{14}$	4/3	-	$(1-\alpha)^{4/3}$	140.5±7.7
	2	30.6	146.4±5.7	$5.55\cdot10^{14}$	-	1	α	

Fig. 9. The reaction rate surface obtained by the NPK method

observed that the differential Friedman and integral KAS and FWO methods yields similar trend of variation of the activation energy values with the conversion degree, but this variation is lower than 10%.

The small difference between the E_a values between differential and integral methods can be assigned to a systematic error caused to the different approximations of the temperature integral, employed in the development of these isoconversional methods.

The non-parametric kinetics method (NPK) is a method developed by Sempere et al. [47-48] and modified by Vlase et al. [49-50] a few years ago, which is based on the general rate equation and used only a single-step kinetics approximation (the validity of the eq. 4):

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

At different heating rates, the experimental points obtained are interpolated as a continuous reaction rate surface (fig. 9). The results of NPK analysis are presented in table 3.

It is noted that the main process is a chemical reaction with reaction order n=4/3 accompanied by a physical process (m=1). The secondary process requires a similar activation energy comparative with the value required in the first process, but it contributes to the unit process in a small proportion (explained variance λ= 30.6 %). In the

case of the degradation process which was analysed, there were identified two parallel processes, with 68.6% and 30.6% contribution to the observed thermal behaviour.

The value of activation energy obtained from NPK method is E_a= (140.5±7.7) kJ·mol⁻¹ is very similar with those obtained with the isoconversional methods (table 2).

Conclusions

A Co(II) complex with heterocyclic ligand (4H-4-amino-5-carboxy-methylsulfanyl-3-phenyl-1,2,4-triazole) was synthesized and characterised. Thermal analysis showed that the crystallised coordination compound is stable with six molecules of water at room temperature and up to 42 °C, when the loss of water occurs progressively up to 92 °C. The anhydrous complex is stable up to a considerable temperature (187 °C), when it starts decomposing as a continuous multistadial process.

The kinetic triplet for the degradation of Co(II) complex was calculated using the Friedman, KAS and FWO methods, as well as the non-parametric kinetics method (NPK). 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 corroboration of information obtained by thermal behaviour, FTIR spectroscopy and complexometric titration, we tentatively proposed a structure for the Co(II) complex. It was shown that metal complex contains two coordinated water molecules to central Co(II) ion and 4 water molecules in the crystalline lattice.

References

1. VOGIATZOGLOU, A., REFSUM, H., JOHNSTON, C., et al., Neurology, **71**, no. 11, 2008, p. 826

2. CRACAN, V., BANERJEE, R., Chapter 10: Cobalt and Corrinoid Transport and Biochemistry, in BANCI, L. (editor), Metallomics and the Cell. Metal Ions in Life Sciences 12, Springer, 2013.

3. SCHWARZ, F. J., KIRCHGESSNER, M., STANGL, G. I., J. Anim. Phys. Anim. Nutrit. **83**, no. 3, 2000 p. 121.

4. MANIKANDAN, R., VISWANATHAMURTHI, P., VELMURUGAN, K., NANDHAKUMAR, R., HASHIMOTO, T., ENDO, A., J. Photochem. Photobiol. B: Biol., **130**, no. 5, 2014, p. 205

5. BEFANI, C., MYLONIS, I., GKOTINAKOU, I.M., GEORGOULIAS, P., HU, C.J. SIMOS, G., LIAKOS, P., Int. J. of Biochem. Cell Biol., **45**, no. 11, 2013, p. 2359

6. SIMONSEN, L.O., HARBAK, H., BENNEKOU, P., Sci. Tot. Environ., **432**, 2012, p. 210

7. BERTINI, I., GRAY, H.B., STIEFEL, E.I., VALENTINE, J.S., Biological Inorganic Chemistry: Structure and Reactivity, University Science Books: Sausalito, CA, USA, 2007.

8. CHANG, E.L., SIMMERS, C., KNIGHT, D.A., Pharmaceuticals, **3**, 2010, p. 1711

9. ZANELLATO, I., BONARRIGO, I., RAVERA, M., GABANO, E, GUST, R., OSELLA, D., Metallomics, **5**, no. 12, 2013, p. 1604

10. SANATKAR, T.H., HADADZADEH, H., SIMPSON, J., JANNESARI, Z., J. Mol. Struct., **1049**, 2013, p. 336

11. DEFAZIO, S., CINI, R., J. Chem. Soc., Dalton Transactions **9**, 2002, p. 1888

12. PRAKASH, G.A., SANGAMESH, A.P., Transition Met. Chem., **33**, 2008, p. 275

13. YE, X.-X., CHEN, Z.-F., ZHANG, AN-J., ZHANG, L.-X., Molecules, **12**, 2007, p. 1202.

14. SUMRRA, S.H., CHOHAN, Z.H., Spectrochim. Acta A, **98**, 2012, p. 53

15. WU, X., YANG, P., DING, B., DU, G.X., WANG, Y., Synth. React. Inorg. Met. Org. Chem. **44**, no. 7, p. 1034.

16. ERFANTALAB, M., KHANMOHAMMADI, H., Spectrochim. Acta A, **125**, 2014, p. 345

17. BADEA, M., CALU, L., CHIFIRIUC, M.C., BLEOTU, C., MARIN, A., ION, S., IONIŢÍ, G., STANICÍ, N., MÍRUŢESCU, L., LAZÍR, V., MARINESCU, D., OLAR, R., J. Therm. Anal. Calorim., 2014, DOI: 10.1007/s10973-014-3821-4

18. QIN, J., LEI, N., ZHU, H.-L., J. Coordin. Chem., **67**, no. 7, p. 1279

19. BERCEAN, V.N., CREANGĂ, A.-A., BADEA, V., DELEANU, C., CSUNDERLIK, C., Rev. Chim.(Bucharest), **62**, no. 1, 2011, p. 47.

20. BERCEAN V.N., LEDEŢI I.V., BADEA V., BĂLAN, M., CSUNDERLIK C., Rev. Chim.(Bucharest), **61**, no.11, 2010, p. 1028

21. LEDEŢI I.V., BERCEAN V.N., BADEA V., BĂLAN M., CSUNDERLIK C., Rev. Chim.(Bucharest), **61**, no.9, 2010, p.833

22. LEDEŢI I.V., BERCEAN V.N., TĂNASE, I.M., CREANGĂ, A.A., BADEA V., CSUNDERLIK C., Rev. Chim.(Bucharest), **61**, no. 10, 2010, p. 935

23. LEDEŢI I., FULIAŞ, A., VLASE, G., VLASE, T., DOCA, N., Rev. Roum. Chim., **58**, no. 4-5, p. 441

24. NETO, H.S., NOVÁK, C., MATOS, J.R., J. Therm. Anal. Calorim., **97**, 2009, p. 367.

25. NUNES, R.S., SEMAAN, F.S., RIGA, A.T., CAVALHEIRO, E.T.G., J. Therm. Anal. Calorim., **97**, 2009, p. 349

26. DREBUSHCHAK, V.A., SHAKHTSHNEIDER, T.P, APENINA, S.A., DREBUSHCHAK, T.N., MEDVEDEVA, A.S., SAFRONOVA, L.P, BOLDYREV, V.V., J. Therm. Anal. Calorim., **84**, 2006, p.643

27. VLASE, T., VLASE, G., DOCA, N., ILIA, G., FULIAS, A., J. Therm. Anal. Calorim., **97**, no.1, 2009, p.467

28. FULIAS, A., VLASE, G., VLASE, T., SOICA, C., HEGHES, A., CRAINA, M., LEDETI, I., Chem. Cent. J., **7**, article no. 70, 2013, p.1

29. FULIAS, A., VLASE, G., GRIGORIE, C., LEDETI, I., ALBU, P, BILANIN, M., VLASE, T., J. Therm. Anal. Calorim., **113**, no.1, 2013, p.265

30. SUTA, M.-L., VLAIA, L., FULIAS, A., LEDETI, I., HADARUGA, D., MIRCIOIU, C., Rev. Chim (Bucharest), **64**, no. 11, 2013, p. 1279

31. NODITI, G., LEDETI, I., SIMU, G., SUTA, M.-L., ONETIU, D., FULIAS, A., Rev. Chim (Bucharest), **65**, no. 1, 2014, p. 65

32. LEDEŢI, I., FULIAŞ, A., VLASE, G., VLASE, T., BERCEAN, V., DOCA, N., J. Therm. Anal. Calorim., **114**, no. 3, 2013, p. 1295

33. FULIAŞ, A., LEDEŢI, I., VLASE, G., VLASE, T., J. Pharm. Biomed. Anal., **81–82**, 2013, p. 44

34. TIŢA, B., FULIAŞ, A., BANDUR, G., LEDEŢI, I., TIŢA, D., Rev. Chim (Bucharest), **62**, no. 4, 2011, p. 443

35. FULIAŞ, A., VLASE, T., VLASE, G., SZABADAI, Z., TIŢA, D., DOCA, N., Rev. Chim (Bucharest), **61**, no. 12, 2010, p. 1202

36. LEDETI, I., SIMU, G., VLASE, G., SAVOIU, G., VLASE, T., SUTA, L.-M., POPOIU, C., FULIAS, A., Rev. Chim. (Bucharest), **64**, no. 10, 2013, p.1127

37. FULIAŞ, A., VLASE, G., VLASE, T., TITA, B., TIŢA, D., DOCA, N. Rev. Roum. Chim. **55**, no. 8, 2010, p. 481.

38. VENTER, M.M. CÎNTĂ PÎNZARU, S., HAIDUC, I., BERCEAN, V. Studia Univ. Babes-Bolyai, Physica, **XLYX**, no. 3, 2004, p. 285

39. VENTER, M.M., BERCEAN, V.N., ILICI, M., CÎNTĂ PÎNZARU, S., CHIŞ, V., HAIDUC, I., Studia Univ. Babes-Bolyai, Chem., **LI**, no. 2, 2006, p. 65

40. VENTER, M.M., BERCEAN, V.N., ILICI, M., CÎNTĂ PÎNZARU, S., Rev. Roum. Chim. **52**, 2007, p. 75

41. VENTER, M.M., BERCEAN, V. N., VARGA, R., SASCA, V., PETRIŞOR, T., CIONTEA, L., Studia Univ. Babes-Bolyai, Chem., **XLV**, no. 2, 2010, p. 217

42. GABER, M., AL-SHIHRY, S.S., Sci. J. King Faisal Univ., **5**, 2004, p.181

43. OZAWA, T., Bull. Chem. Soc. Jpn. **38**, 1965, p. 1881.

44. KISSINGER, H.E., Anal. Chem., **29**, 1957, p. 1702.

45. SUNOSE, T., AKAHIRA T., Res. Report, Chiba Inst. Technol (Sci. Technol.), **16**, 1971, p. 22

46. FRIEDMAN, H.L., J. Polym. Sci., **6C**, 1965, p. 183

47. SEMPERE, J., NOMEN, R. SERRA R., SORAVILLA, J., Thermochim. Acta, **388**, 2002, p. 407.

48. SERRA, R., SEMPERE J., NOMEN, R., Thermochim. Acta, **316**, 1998, p. 37.

49. VLASE, T., VLASE, G., DOCA, M., DOCA, N., J. Therm. Anal. Calorim., **72**, 2003, p. 597.

50. VLASE, G., VLASE T., DOCA, N., J. Therm. Anal. Calorim., **99**, 2008, p. 259