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THERMAL BEHAVIOR OF THE COORDINATION COMPOUND $[Co(urea)_6](NO_3)_2$

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Abstract

The coordination compound $[Co(urea)_6](NO_3)_2$ was synthesized and physico-chemically characterized. The thermal decomposition carried out in dynamic air and inert atmosphere under non-isothermal conditions has been investigated by means of combined thermogravimetry/mass spectrometry, X-ray diffraction, IR and UV-VIS spectroscopy as well as magnetic measurements. The course of the thermal decomposition starts with two-phase transitions (melting and a $O_h \rightarrow T_d$ configuration change of the Co^{2+} ion) and continues with seven mass loss steps. According to the thermogravimetric and magnetic investigations a dimeric compound, $[Co(biuret)(NCO)]_2(NO_3)_2$, is assumed to arise. Up ~250°C, an oxohydroxide nitrate intermediate is formed and a gradual oxidation of the Co^{2+} ions is observed. At 550°C, Co_3O_4 with mean crystallite sizes of ~150 Å is identified.

Keywords: Co_3O_4, non-isothermal analysis, urea-cobalt coordination compound

Introduction

Studies concerning transition and non-transition metal ureates have been developed systematically and progressively over the last two decades. The compounds have been studied from the aspects of their preparation, structures and properties, mainly in connection with their ability to form inclusion or coordination compounds [1–7]. There has been some specific interest into their thermal behavior, particularly in the last decade, due to the possibility of their use for the controlled preparation of metal and metal oxide [8–11] powders. For a small number of compounds the thermal decomposition mechanism has been determined with some degree of confidence, due to MS studies [12–14]. Less attention was paid to the type of solid products, which are formed during heating.

The present article, which is part of a systematic study on mono- and polynuclear coordination compounds with urea as ligand [15–17], describes the preparation, the properties and the thermal behavior (in air and inert atmospheres) of the coordination compound $[Co(urea)_6](NO_3)_2$.

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Experimental

Synthesis

The coordination compound containing cobalt and urea was obtained by two synthesis methods, respectively a solid state method and a co-precipitation one. Details about the synthesis method are described elsewhere [15]. Both synthesis methods lead to a pink compound. The elemental analysis of the synthesized coordination compounds agreed with the same molecular formula, respective $[Co(urea)_6](NO_3)_2$. $CoC_6N_{14}H_{24}O_{12}$ Anal. found (solid state/precipitation)/calcd.: Co, 10.63/10.51/10.86; C, 13.33/13.35/13.28; N, 36.04/36.06/36.16; H 4.35/4.42/4.42. Dimeric compound (obtained after fourth reaction) found/calcd.: $Co_2C_6N_8H_{10}O_6$ Anal. found/calcd.: Co, 24.65/21.98; C, 13.43/9.67; N, 20.9/17.02, H, 1.86/1.0. The cobalt content (Co_{total} and Co^{2+}) of some intermediates were determined also.

Characterization

Structural investigation of powder samples have been carried out using a Philips PW 1049 diffractometer at a scanning rate of $1^o(=2\theta)$ min^{-1} using CoK_α radiation. The electron microscopy was performed on a Philips CM120 device. The UV-VIS reflectance spectra were recorded with a Jasco V550 spectrophotometer in the range 11 000–54 000 cm^{-1}. The IR spectra were recorded with a Biorad FTIR 1255 spectrometer type in the range 4000–400 cm^{-1}. The magnetic susceptibilities of the initial coordination compounds and decomposition intermediates were measured on a Faraday balance at room temperature with Ni as standard. The magnetic moments for the paramagnetic compounds were calculated via equation:

$$\mu_{eff}=2.8282\ (T\chi_{mol})^{1/2}$$

where χ_{mol} represents the molar susceptibility and the absolute temperature T. The molar mass of the isolated intermediates was estimated from the thermogravimetric curves.

The thermal decomposition of $[Co(urea)_6](NO_3)_2$ was recorded using a simultaneous thermogravimetry/mass spectrometry unit Netzsch STA 409 coupled by capillary to a Balzers QMS 421 mass spectrometer, under dynamic air and argon atmosphere, with a sample mass of about 20 mg and at heating rates of 2 K min^{-1}. DSC measurements were performed on a DuPont TG 951 type.

Results and discussion

Physico-chemical characterization of the coordination compound

The recorded IR spectrum of the coordination compound compared with urea's one (Figs 1a–b), indicates the coordination of urea to the metal ion through oxygen atoms [17–19]. This coordination mode leads to a decrease of the CO stretching frequencies (1681/1652 cm^{-1} for urea/compound). At 1383 and 823 cm^{-1} bands assigned to the vibration mode of uncoordinated NO_3^- anion were identified too.

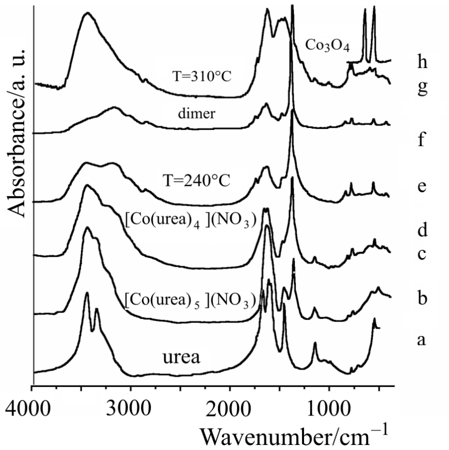


Fig. 1 IR spectra of the [Co(urea)$_6$](NO$_3$)$_2$ coordination compound and its decomposition intermediates

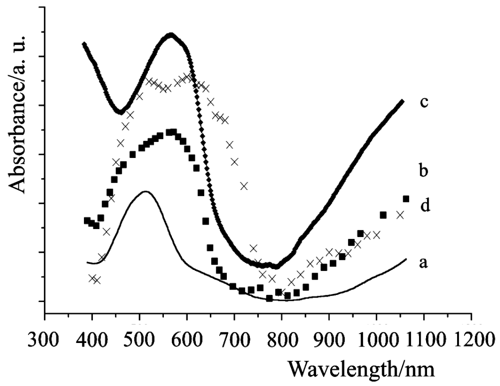


Fig. 2 Electronic spectra of the [Co(urea)$_6$](NO$_3$)$_2$ coordination compound and its decomposition intermediates; a – [Co(urea)$_6$](NO$_3$)$_2$, b – [Co=urea)$_4$](NO$_3$)$_2$·2urea, c – [Co(urea)$_4$](NO$_3$)$_2$ and d – dimer compound

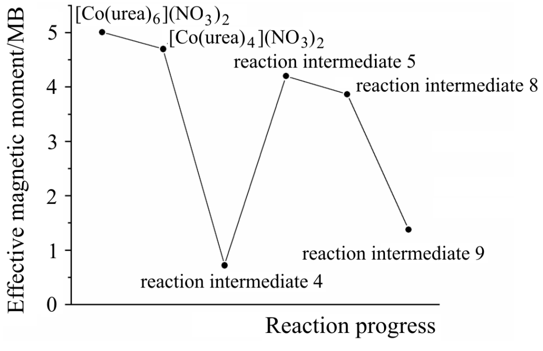


Fig. 3 Changes in the effective magnetic moment of the Co-ion for different reaction steps of the thermal decomposition

In the electronic spectra the bands characteristic to Co(II) ions in an octahedral configuration were evidenced (Fig. 2a). Transitions at 870, 698–622 and 528 nm can be interpreted as $^4T_{1g}\rightarrow{}^3E_g(F)$, $^4T_{1g}\rightarrow{}^4A_{2g}(F)$, and $^4T_{1g}\rightarrow{}^4T_{1g}(P)$, respectively [20].

With respect to the magnetic properties, the cobalt compound proves to be paramagnetic with a magnetic moment of 5.01 B.M. (Fig. 3), lower than the theoretical one of 5.2 B.M. evaluated for a high spin octahedral compound. Taking into account that the deviation from the octahedral symmetry decreases the μ_{eff} value [21], as well as the maxima in the electronic spectra, it can be concluded that $[Co(urea)_6](NO_3)_2$ adopts a distorted octahedral geometry [21].

Thermal behavior and reaction stoichiometries

In the range of 30–650°C two-phase transitions and seven mass loss steps are evidenced. The progress of the thermal decomposition is practically atmosphere independent. Differences between the two experiments arose only in the eighth reaction step, concerning strictly the temperature range of reaction occurrence. The TG, DTG, DTA and DSC curves are depicted in Fig. 4, Table 1 summarized the thermoanalytical and mass spectrometry obtained data.

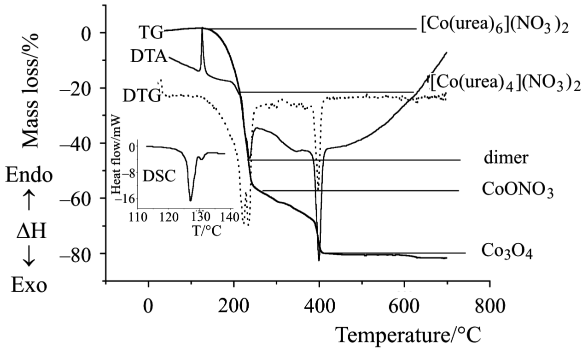


Fig. 4 TG, DTG, DTA and DSC curves (air atmosphere, heating rate 2 K min^{-1}) of the $[Co(urea)_6](NO_3)_2$ coordination compound

The thermal transformation starts with an endothermic peak evidenced on DTA curve ($T_{DTA\ max}$=125.8°C). The DTA peak could be resolved into two maxima on DSC investigation (frame Fig. 3, $T_{DSC\ max}$=125.8 and 130.8°C). The reaction intermediate obtained after the two thermal effects is a blue melt, suggesting the presence of a tetrahedral compound beside an octahedral one, clearly identified (Fig. 2b) by the strong absorption in the region 600–700 nm with asymmetric band at 680 nm ($^4T_1(P)\rightarrow{}^4A_2$) and a weak one at 900 nm ($^4T_1(F)\rightarrow{}^4A_2$) [20]. These two endothermic effects evidenced on DSC curve may be assigned to the compound melting and the migration of two molecules of urea from the coordination sphere to the outer sphere:

$$[Co(urea)_6](NO_3)_{2\ (s)\ (pink)} \rightarrow [Co(urea)_6](NO_3)_{2\ (l)\ (pink)} \qquad (1)$$

$$[Co(urea)_6](NO_3)_{2\ (l)\ (pink)} \rightarrow [Co(urea)_4](NO_3)_2\cdot 2\ urea_{\ (l)\ (blue)} \qquad (2)$$

Table 1 Thermoanalytical and mass spectrometry data obtained for [Co(urea)$_6$](NO$_3$)$_2$ coordination compound

Reaction step	Temp. range/ °C argon/air	Gaseous products evolved	Solid intermediate proposed	Assignation
1	120–132/ 120–129			• melting
2	132–136/ 129–132		[Co(urea)$_4$](NO$_3$)$_2$·2urea	• migration of two urea molecules from the coordination sphere
3–4	136–232/ 134–229	NH$_3$, HNCO	[Co(urea)$_4$](NO$_3$)$_2$	• decomposition of two urea molecules
		N$_2$, HNCO, NO, NO$_2$, *m/z*=44*, H$_2$O	Dimer compound	• evolving of a nitrate anion; • decomposition of urea; • transformation of undecomposed urea in biuret
5	232–270/ 229–259	N$_2$, NO, NO$_2$, *m/z*=44*, H$_2$O	Co$^{2}_{1-x}$Co$^{3}_{x}$O$_y$(OH)$_2$NO$_3$ and organic residues	• dimer decomposition; • Co^{2+} oxidation
6	270–301/ 258–308	NO, H$_2$O, NH$_3$, HNCO		
7	318–345/ 318–362	N$_2$, NO, NO$_2$, *m/z*=44*, H$_2$O (air+HNCO)		• decomposition of the remainder biuret compound • gradual oxidation of Co^{2+}
7	355–386/ 362–385			
8	402–486/ 386–414	NO, NO$_2$, H$_2$O, CO$_2$*, HNCO	Co$_3$O$_4$	• decomposition of the last nitrate ion • oxidation of the organic residues
9	557–629/ 578–647	CO$_2$*, NO, Traces O$_2$	CoO (traces Co$_3$O$_4$)	• oxidation of the organic residues • Co$_3$O$_4$→CoO conversion

* carbon presence in the component of mass *m/z*=44 was clearly identified by MS, due to the comparable shape of the curves corresponding to *m/z*=44 ([CO$_2$]$^+$ or [NH$_2$CO]$^+$) and *m/z*=12 [C]$^+$. In principle, N$_2$O (*m/z*=44 too) can be also formed at the expense of NO. In this case, however oxygen should also be formed, process which was evidenced for reaction steps 3–4, 5, 7, 8.

Two observations have to be pointed out: firstly, the coexistence of octahedral and tetrahedral compounds after reaction (2). This fact may be determined either by the experimental impossibility to isolate the two compounds, or, due to the small stability difference between octahedral and tetrahedral Co(II) complexes, the two types of compounds may be in equilibrium [22]. Secondly, the small enthalpy changes observed for reaction step (2) (respectively 5.1/5.0 kcal mol^{-1} for argon/air) agree with a melt short-range order.

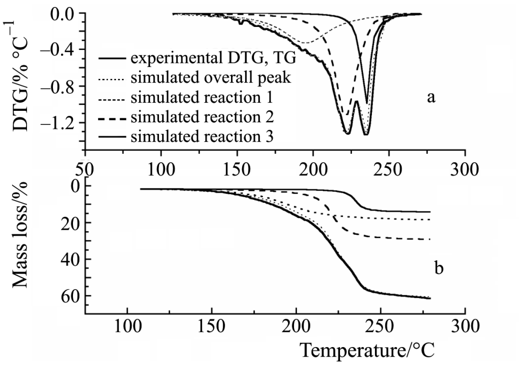


Fig. 5 Experimental and deconvoluted a – DTG and b – TG curves of the reaction steps (3–5)

The first region of mass loss (136–270/134–259°C argon/air) is rather complicated, showing three overlapping decomposition steps. For an accurate estimation of the mass losses corresponding to each process, the DTG curves were deconvoluted (Fig. 5a). To verify the aptness of this mathematical procedure, we compared the experimental TG curve with simulated ones, built up by summarizing the three deconvolutions (Fig. 5b). The first two deep-blue solid intermediates contain only Co^{2+} ions in a tetrahedral coordination (Figs 2c–d). In the third violet-blue intermediate besides Co^{2+}, small amounts of Co^{3+} ions were identified. In this temperature range, the effective magnetic moment (μ) of the intermediates reaches a minimum close to a diamagnetic behavior, corresponding to the fourth reaction step intermediate (Fig. 3). This fact that only Co^{2+} was identified suggests the formation of an intermediate with a dimeric structure. The obtained value of the small magnetic moment is determined by the overlapping of the decomposition steps. The IR spectra (Figs 1d–e) evidenced that the temperature increase leads to the appearance of band characteristics for NCO (~2850 cm^{-1}) and CO groups (~1740 cm^{-1}) [23]. The intensities of the two bands increase with the progress of the fourth reaction step. The broad band from ~3500–3000 cm^{-1} characteristic for the stretching mode of anti- and symmetric OH groups of water (Figs 1d–e) become sharper and is shifted towards higher frequencies (Fig. 1f) for the fifth reaction intermediate, fact that can be assigned to the presence of residual hydroxyl ions.

So, for this temperature range the following reaction sequence can be proposed:

- Decomposition of the two molecules of urea from the outer sphere into ammonia and cyanic acid (mass loss deconvoluted/theoretical curve=21.45/22.10%):

$$[Co(urea)_4](NO_3)_2\cdot 2\ urea_{(blue)} \rightarrow [Co(urea)_4](NO_3)_{2(violet\text{-}blue)}+2(NH_3+HNCO) \quad (3)$$

• The decomposition of $[Co(urea)_4](NO_3)_2$. In this stage besides NO_3^- degradation and reduction during the reaction with NH_3 (existent also in medium) several reactions with the participation of urea are observed, namely, its decomposition (reaction (5)), transformation of undecomposed urea into biuret (reaction (6)) and its hydrolysis in the acidic medium of the thermal decomposition products (reactions (7–8)):

$$xNO_2+yNH_3\xrightarrow{-[O]}(uN_2O+vNO+zN_2)+3y/2H_2O \tag{4}$$

$$(0.5u+v+0.5z=x+y)$$

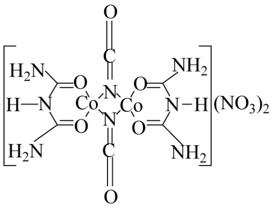
$$H_2NCONH_2\rightarrow NH_3+HNCO \tag{5}$$

$$H_2NCONH_2+HNCO\rightarrow H_2NCONHCONH_2 \tag{6}$$

$$H_2NCONH_2+H_2O\rightarrow [NH_4]_2^+CO_3^{2-} \tag{7}$$

$$[NH_4]_2^+CO_3\rightarrow 2NH_3+CO_2 \tag{8}$$

As solid intermediate, a compound which adopt the most probable molecular formula:



Scheme 1

is isolated. Such a formulation is supported by the close experimental (from the deconvoluted curve) and theoretical values of the mass loss (29.1/28.5%), the presence of the IR bands characteristic for NCO and CO groups and close to diamagnetic magnetic behavior. It has to be mentioned that the chemical analysis of the compound leads to lesser values of the CHN content (experimental part) as resulted from the molecular formula, mainly due to the overlapping processes. Formation of polynuclear compounds during thermal decomposition of some Co(III) amine mononuclear complexes are reported by literature also [24].

• The decomposition of the dimer with formation of an oxohydroxide nitrate intermediate in which part of the Co^{2+} ions are oxidized to Co^{3+} ones:

$$\text{dimer}\rightarrow Co_{1-x}^{2+}Co_x^{3+}O_y(OH)_zNO_3\cdot\text{organic residues absorbed}+\text{gaseous products} \tag{9}$$

$$(2y+z=1+x)$$

In the temperature range 270–386/258–385°C three decomposition stages associated with small exothermic thermal effects and a decrease of the effective magnetic moments are registered. These effects may be assigned to the decomposition of remaining biuret compounds and continuous oxidation of Co^{2+} ions. The temperature ranges of thermal decomposition occurrence are nearly identical to the one of urea degradation (decomposition performed under similar conditions [25]).

The next reaction step characterized by a strong exothermic effect represents the simultaneous decomposition of the last nitrate ion and the oxidation of the remaining organic residue still present on the solid surface. It is worth to mention the different profile of the curves obtained during the two experiments, due to the different magnitude of the temperature range of occurrence, respective 84°C (argon) in comparison to 29°C (air). Generally, the reaction in the eighth decomposition step can be written as:

$$Co^{2+}_{1-x}Co^{3+}_{x}O_y(OH)_zNO_3 \rightarrow Co^{2+}_{1-x}Co^{3+}_{x}O_y + \alpha NO + \beta NO_2 + \varepsilon O_2 + \phi H_2O \qquad (10)$$

$$1+x=2y+z$$

$$\alpha+\beta=1$$

The solid residue obtained after this decomposition step was identified as a spinel (Fig. 6). The infrared spectrum (Fig. 1g) shows two absorption bands, characteristic for cobaltites, at 668 and 575 cm^{-1} corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites [26]. Evaluated by electron microscopy the mean crystallites size of the sample calcined at 550°C is 180 Å (Fig. 7), higher than the one obtained from diffraction data, i.e. 149 Å (applying the Scherrer formula to the reflections with the *hkl*-indices 220, 311, 511). It is important to mention here the broad particle size distribution of 53–340 Å due probably to local combustion occurrences.

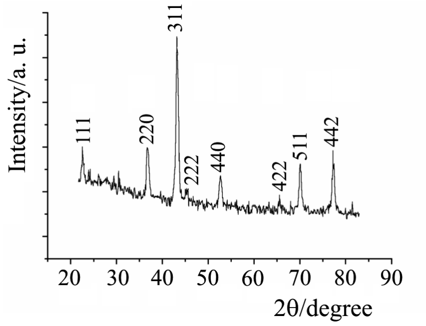


Fig. 6 X-ray diffractogram of the $Co^{2+}_{1-x}Co^{3+}_{x}O_y$ compound obtained at 550°C, *t*=1 h

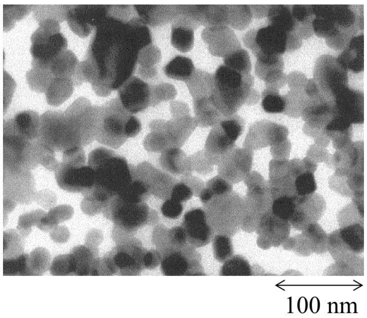


Fig. 7 Transmission electron micrograph of Co_3O_4 calcined at 550°C for 1 h

The final decomposition step is identified in the temperature range 557–629/580–647°C. The traces of O_2 identified in the last process can be explained by the conversion of cobalt oxides, i.e. the reduction of $Co^{2+}_{1-x}Co^{3+}_{x}O_y$ to CoO.

Concluding remarks

The thermal decomposition of the investigated compounds is rather complicated involving a combination of decomposition and redox processes. The dissociation of the coordination compounds is assumed to be the elementary step of the process. Further on the reaction progress is governed by the interaction of the gaseous decomposition products either with each other or with the solid reactive intermediates.

Several interesting features of the thermal decomposition can be pointed out:

- an $O_h \rightarrow T_d$ configuration change of the Co^{2+} ions take place in the initial stages of the thermal decomposition;
- it is assumed that during the thermal decomposition an additional reaction of HNCO evolved previously with the coordinated urea leads to the formation of a biuret ligand;
- a novel dimer compound $[Co(biuret)(NCO)]_2(NO_3)_2$ is presumed to be obtained as one of the reaction intermediates;
- a gradual oxidation of $Co^{2+} \rightarrow Co^{3+}$ starts at ~250°C and progresses till 550°C, when the last nitrate ion undergoes decomposition.

What is the cause of the relatively high thermal stability of the studied compound compared with the pure nitrate $CoNO_3 \cdot 2H_2O$ ivković *et al.* [27] and Małecki *et al.*[28] found that the thermal decomposition of this cobalt nitrate is accomplished at 250–300°C. The formation of decomposition intermediates, i.e. complex ions such as $[Co^{2}_{1-x}Co^{3}_{x}(OH)_z(NO_3)_v]^{2+x-z-v}$, or the existence of hydrogen bonds between the oxohydroxides intermediates are reasonable arguments for the high thermal stability found for the investigated coordination compound.

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References

1 B. F. Hoskins, C. J. Mckenzie, I. A. S. Macdonald and R. Robson, J. Chem. Soc.-Dalton Transitions, 11 (1996) 227.
2 S. Uozumi, N. Furutachi, M. Ohba, H. Okawa, D. E. Fenton, K. Shindo, S. Murata and D. Kitko, Inorg. Chem., 37 (1998) 6281.
3 T. Koga, H. Turatich, T. Nakamura, N. Fukita, M. Ohba, K. Takahashi and H. Okawa, Inorg. Chem., 37 (1998), 989.
4 R.Thaimattam, N. Reddy, F. Xue, T. C. W. Chak, A. Nanjia and C. R. Desiraju, J. Chem. Soc.-Perkin Trans., 2 (1998) 1783.

5 T. Todorov, R. Petrova, K. Kossev, J. Macicek and O. Angelova, Acta Crystall. C-Cryst. Struct. Com., 54 (1998) 456.
6 T. Todorov, R. Petrova, K. Kossev, J. Macicek and O. Angelova, Acta Crystall. C-Cryst. Struct. Com., 54 (1998) 927.
7 M. D. Hollingsworth and K. D. M. Harris, in J. L. Arwood, D. D. MacNicol, J. E. D. Davies, F. Vogtle, J. M. Lehn (Eds), Comprehenaive Supramolecular Chemistry, Vol. 4, Pergamon, Oxford 1966, Chap. 7, p. 177.
8 B. C. Stojceva-Radovanovic and P. I. Premovic, J. Thermal Anal., 38 (1992) 715.
9 A. Yogodin, J. Therm. Anal. Cal., 38 (1998) 537.
10 A. Kozak, K. Wieczorek-Ciurowa and A. Pielichowski, J. Thermal Anal., 45 (1995) 1245.
11 V. T. Orlova, E. A. Konstantinova, V. I. Kosterina, M. A. Sherbamski and I. N. Lepeshkov, J. Thermal Anal., 33 (1988) 929.
12 G. Gyoryova and V. Balek, J. Thermal Anal., 40 (1993) 519.
13 G. Gyoryova and V. Balek, Thermochim. Acta, 269 (1995) 425.
14 M. Amirnasr, R. Houriet and S. Meghdadi, J. Therm. Anal. Cal., 67 (2002) 623.
15 L. Patron, O. Carp, I. Mindru, L. Petre and M. Brezeanu, Rev. Roum. Chim., 43 (1998) 173.
16 O. Carp, L. Patron and M. Brezeanu, J. Therm. Anal. Cal., 56 (1999) 561.
17 O. Carp, L. Patron, L. Diamandescu and A. Reller, Thermochim. Acta, 390 (2002) 169.
18 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Ed. 4, Wiley, London 1978.
19 R. B. Penland, S. Mizushima, C. Curran and J. V. Qugliana, J. Am. Chem. Soc., 79 (1957) 1575.
20 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam 1968, Chap.9.
21 B. N. Figgis and J. Lewis, Prog. Inorg. Chem., 6 (1964) 37.
22 F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley 1966, p. 866.
23 A. R. Chugtai and R. N. Keller, J. Inorg. Nucl. Chem., 32 (1969) 633.
24 J. Szakó, G. Pokol, Cs. Novák, Cs. Várhelyi, A. Dobó and G. Liptay, J. Therm. Anal. Cal., 64 (2001) 843.
25 O. Carp, Rev. Roum.Chim., 46 (2001) 735.
26 B. Lefez, P. Nkeng, J. Lopitaux and G. Poillerat, Mat. Res. Bul., 31 (1996) 1263.
27. . D. ivković, D. T. ivković and D. B.Grujičić, J. Therm. Anal. Cal., 53 (1998) 617.
28 A. Małecki, R. Gajerski, S. Łabuś, B. Prochwska-Klisch and K. T. Wojciechwski, J. Therm. Anal. Cal., 60 (2000) 17.