Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 419 (2004) 67–71
thermochimica acta
www.elsevier.com/locate/tca

Synthesis and thermal characterization of zinc(II) di(*o*-aminobenzoate) complexes of imidazole and its methyl derivatives

M. Olczak-Kobza

Institute of General and Ecological Chemistry, Technical University 90-924 Łódź, Poland

Received 23 July 2003; received in revised form 19 January 2004; accepted 19 January 2004

Abstract

Mixed complexes of the type: $Zn(Han)_2(Him)_3$, $Zn(Han)_2(Him)_5$, $Zn(Han)_2(4\text{-}MeHim)_2$ and $Zn(Han)_2(1,2\text{-}diMeim)_2$ (where Han: $NH_2C_6H_4COO^-$, Him: imidazole, 4-MeHim: 4-methylimidazole, 1,2-diMeim-1,2-dimethylimidazole) have been synthesized. The complexes and the corresponding sinters, obtained at temperatures determined on the basis of the thermogravimetric (TG) curves, have been analyzed by chemical, X-ray, infrared (IR) spectroscopy and thermal methods. The compounds with Him and 4-MeHim decompose in two stages, and those with 1,2-diMeim in three stages. Thermal decomposition pathways have been postulated for these complexes.

Keywords: Zinc(II); *o*-Aminobenzoic acid; Heteroligand complexes; Thermal analysis; Diffractometric analysis

1. Introduction

The investigation of the properties of the heteroligand complexes and possibilities of their formation is very important for many fields of chemistry, e.g. analytical chemistry, materials engineering, biochemistry. These complexes are the most probable compounds in the solution, they can stabilize less stable oxidation forms of the center ions (Co^{3+}, Mn^{3+}), they can inhibit reactions of the hydrolysis or polymerization, and they are transition products in a number of the chemistry processes [1]. The metallic centers of the metalloproteins and metalloenzymes can be considered as the mixed complexes and the conclusions from investigation of the small molecules and metal ions are the starting point for the interpretation of the structures of more complicated molecules. The research of the new medicines able to treat heavy metals poisoning (e.g. Cd) is connected with investigation of heteroligand complexes. The investigations of the complexes in solution provide the important information on properties of biologically active molecules and investigations in solid state are complemented.

In many biological important molecules, zinc(II) is bounded to the pyridine nitrogen of imidazoles and to the carboxylate groups [2]. Therefore, complexes containing such ligands are frequently researched by means of spectroscopic, structural and thermal investigation [3–5]. The mixed zinc(II) complexes with imidazoles and aliphatic as well as amino acids were published [3,4,6,7]. On the other hand, the information—and therefore the knowledge—on mixed complexes zinc(II) with imidazoles and aromatic acids limited is very limited.

Aromatic acids of the H_2L type (such as: *o*-hydroxybenzoic acid, *o*-aminobenzoic acid) and bivalent metals form either di-complexes $M(HL)_2$ or mono-complexes ML (where M: metal ion, HL: OHC_6H_4COO, $NH_2C_6H_4COO$, L: $OC_6H_4COO^{2-}$, $NHC_6H_4COO^{2-}$) [8,9].

The mono-compounds may bind to the other monodentate ligands [10,11] as well as to bidentate [12,13], whereas the di-compounds—only to monodentate ones [14].

Previously, the results of investigations of the zinc(II) [14] and cadmium(II) [10] complexes with *o*-hydroxybenzoic acid and imidazoles were published. Recently, we have prepared new zinc complexes with *o*-aminobenzoic acid and imidazole, 4-methylimidazole or 1,2-dimethylimidazole of general formulae: $Zn(Han)_2(Him)_3$, $Zn(Han)_2(Him)_5$, $Zn(Han)_2(4\text{-}MeHim)_2$, $Zn(Han)_2(1,2\text{-}diMeim)_2$. Structural characteristic and thermal decomposition pathways of these complexes are presented.

E-mail address: wkoba@p.lodz.pl (M. Olczak-Kobza).

0040-6031/$ – see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.tca.2004.01.017

2. Experimental

Analytically pure: $ZnCl_2$, *o*-aminobenzoic acid, ether, toluene (POCh—Gliwice), imidazole (Fluka Chemie AG), 4-methylimidazole, 1,2-dimethylimidazole (Sigma) were used without additional purification.

2.1. Synthesis

Zinc di(*o*-aminobenzoate) was prepared by addition of aqueous solutions of the zinc(II) chloride to a solution of sodium *o*-aminobenzoate. The precipitate was washed with several portions of distilled water and ethanol and afterwards dried at room temperature [15].

2.2. Heteroligand complexes

$Zn(Han)_2(Him)_3$ (a), $Zn(Han)_2(Him)_5$ (b), $Zn(Han)_2(4\text{-}MeHim)_2$ (c) and $Zn(Han)_2(1,2\text{-}diMeim)_2$ (d) synthesis was carried out in two-phase system consisting of solid zinc di(*o*-aminobenzoate) and toluene solution of: imidazole, 4-methylimidazole, 1,2-dimethylimidazole. The mixture was heated to 70 °C and stirred for 12 h. The oil was obtained, when synthesis (a, b or c) was carried out. The oil was treated five-fold with ether and then the precipitate was obtained. Compound (d) was a white precipitate. It was washed with toluene and dried in air. All the reactions (a–d) were performed at different molar ratios of substrates: 1:2, 1:3 and 1:5. No complex was obtained when the molar ratio of the reagents was kept at the level of 1:2 in the synthesis (a) and one complex only was obtained when the different molar ratios of the reagents were kept in the synthesis (c and d).

2.3. Chemical analysis

The zinc(II) was detected by complexometric titration with disodium ethylenediaminotetraacetate (EDTA) [16], while carbon, hydrogen and nitrogen—by elemental analysis using Euro Vector, Euro EA analyzer. The results are presented in Table 1.

2.4. X-ray powder analysis (XRD)

The X-ray analysis was carried out by means of a Siemens D 5000 powder diffractometer, using Cu Kα radiation, 2Θ range 2–80°. The products of synthesis and the sinters, formed as a result of thermal decomposition, were studied using X-ray method. Fig. 1 presents powder diffraction patterns of the complexes. Diffraction patterns of the sinters were compared with PDF ICDD36-1451 in order to identify inorganic zinc compounds.

2.5. Infrared (IR) analysis

IR spectra were recorded using a Zeiss Specord M80 spectrophotometer over a range of 400–4000 cm^{-1}. The samples were prepared in the form of KBr pellets. The valency vibration bands ν_{NH_2} and ν_{COO^-} of *o*-aminobenzoate ion are presented in Table 2.

2.6. Thermal studies

The thermoanalytical measurements were carried out using a Balzers thermogravimetric (TG)/DTA—SETSYS-16/18 thermoanalyzer with a Balzers mass spectrometer. The temperature range 293–1273 K; the heating rate 10 K/min, in air atmosphere; the sample mass—a dozen or so milligrams, the platinum crucible. The sinters were obtained at temperatures determined on the basis of the TG curves. XRD and elemental analyses of the sinters were carried out (Table 1). The gaseous decomposition products of complex were also analyzed. Figs. 2 and 3 present thermogravimetric, differential thermogravimetric (DTG) and differential thermal (DTA) curves of $Zn(Han)_2(4\text{-}MeHim)_2$ and $Zn(Han)_2(1,2\text{-}diMeim)_2$ as an example, and Table 3 presents the temperature range, mass losses, and nature of the peaks in each stage of the decomposition of the complexes.

3. Results and discussion

The heteroligand complexes: $Zn(Han)_2(Him)_3$, $Zn(Han)_2(Him)_5$, $Zn(Han)_2(4\text{-}MeHim)_2$, $Zn(Han)_2(1,2\text{-}diMeim)_2$

Table 1
Results of chemical analysis

Compound	Zn (%)		C (%)		H (%)		N (%)	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Zn(Han)_2(Him)_3$	12.07	12.8	50.95	50.6	4.43	4.5	20.67	20.6
$Zn(Han)_2(Him)_5$	9.65	10.0	51.34	51.0	4.72	4.8	24.79	24.4
$Zn(Han)_2(4\text{-}MeHim)_2$	13.03	12.6	52.36	53.6	4.78	5.1	16.75	17.2
$Zn(Han)_2(1,2\text{-}diMeim)_2$	12.35	12.8	54.37	54.3	5.29	5.4	15.20	15.9
$Zn(im)_2$[a]	32.76	32.0	36.00	39.0	3.00	3.2	28.06	25.8
$Zn(an)$[a]	32.67	32.2	41.90	42.0	2.49	2.5	6.98	7.3

im : $C_3N_2H_3^-$; an: $NHC_6H_4COO^{2-}$.

[a] Sinters.

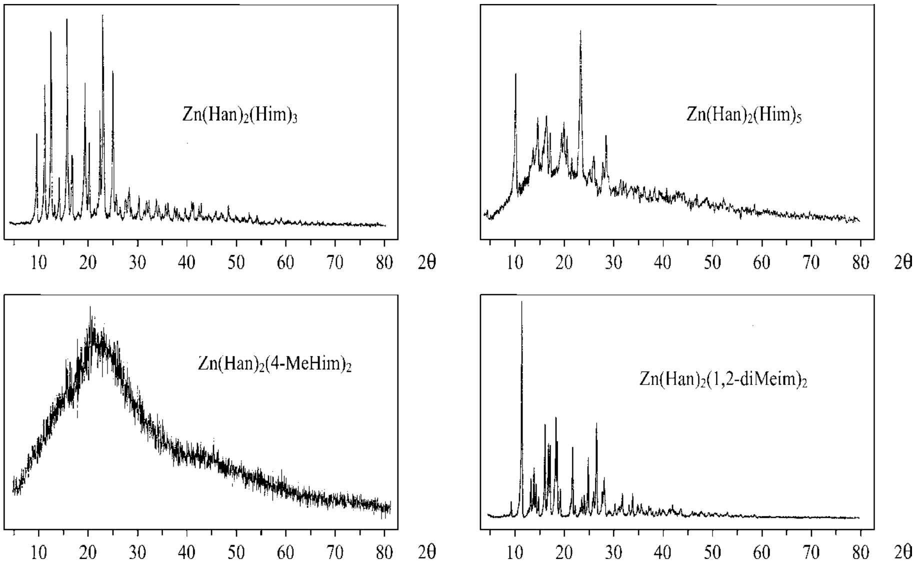

Fig. 1. X-ray diffraction patterns of complexes.

were obtained in the reaction of zinc salts with imidazole or its methyl derivatives. Depending on molar ratio of the reagents, two different mixed complexes were obtained only for imidazole. The XRD analysis showed that three complexes have the crystalline structures, while 4-methylimidazole complex is amorphous (Fig. 1). IR spectroscopic investigation was conducted in order to define the zinc atom surrounding in the complex. The positions of valency vibration bands of COO^-, NH_2 and NH groups were analyzed in the range of 1600–1300 and 3500–3100 cm^{-1}, respectively. The X-ray structure analysis showed that the carboxylate groups in $Zn(Han)_2$ are bidentate bridging groups [17]. In the spectrum of this complex, the splitting $\Delta\nu$ of the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands is smaller than that for the sodium salt in which COO^- group is monodentate (Table 2). The values of the splitting $\Delta\nu$ of the $Zn(Han)_2(4\text{-}MeHim)_2$ and $Zn(Han)_2(1,2\text{-}diMeim)_2$ are higher than for the sodium salt. Due to spectroscopic criterion [18], the monodentate carboxylate groups exist in the prepared complexes. In the mixed compounds of imidazole, COO^- groups are also monodentate and the decrease of the splitting values from $\Delta\nu_{Zn}$ to $\Delta\nu_{Na}$ is connected with participation of these groups in hydrogen bonding. The valency vibration bands of the NH_2 groups are also presented in Table 2. This group forms a bond in $Zn(Han)_2$ and, therefore, two asymmetric $\nu_{as}(NH_2)$ bands at 3300 cm^{-1} and 3260 cm^{-1} and one symmetric $\nu_s(NH_2)$ band at 3140 cm^{-1} appear in the spectrum [17]. The amine group does not form a bond in sodium salt, the $\nu_{as}(NH_2)$ bands appear at 3440 and 3408 cm^{-1} and $\nu_s(NH_2)$ band at 3328 cm^{-1} [15]. The spectra of heteroligand complexes are difficult to interpret in the range of 3500–3100 cm^{-1} because the valency vibration bands for NH_2 group as NH group are also observed here. Additionally, in the case of $Zn(Han)_2(Him)_3$ and $Zn(Han)_2(Him)_5$ there are more imidazole molecules than it would result from preference coordination numbers of zinc complexes—four or six [19]. This suggests that not all molecules of Him are bound to metal.

In the spectrum of the $Zn(Han)_2(1,2\text{-}diMeim)_2$ complex, the bands at 3435 and 3348 cm^{-1} were attributed to $\nu_{as}(NH_2)$ and those at 3308 cm^{-1} to $\nu_s(NH_2)$ vibrations. It indicates that amine group is not bound analogously as for sodium salt (Table 2). In the spectrum of $Zn(Han)_2(Him)_3$, two doublets at 3470, 3440 and 3360, 3330 cm^{-1} are observed. First of them was attributed to the valency vibrations of no bound amine group, and the second one was attributed to zinc bound to imine group of imidazole. The bands of the spectra of $Zn(Han)_2(Him)_5$ and $Zn(Han)_2(4\text{-}MeHim)_2$ are broadening and difficult to interpret. However, the presence of the

Table 2
Valency vibration of COO^- and NH_2 groups (cm^{-1})

Complex	$\nu_{as\,COO^-}$	$\nu_{s\,COO^-}$	$\Delta\nu$	$\nu_{as\,NH_2}$	$\nu_{s\,NH_2}$
Na(Han)	1532	1392	140	3440, 3408	3328
$Zn(Han)_2$	1536, 1546	1408	128, 138	3300, 3260	3140
$Zn(Han)_2(Him)_3$	1525	1382	142	3470	3340
$Zn(Han)_2(Him)_5$	1522	1375	147		
$Zn(Han)_2(4\text{-}MeHim)_2$	1520, 1537	1372	148, 165	Very broad bands	
$Zn(Han)_2(1,2\text{-}diMeim)_2$	1541	1354	187	3435, 3348	3308

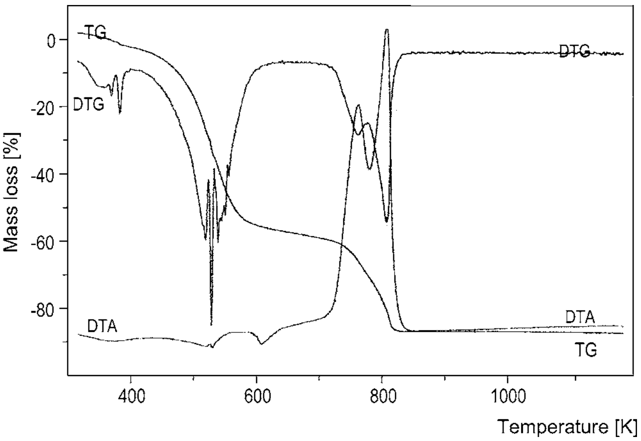

Fig. 2. Thermal curves of $Zn(Han)_2(4MeHim)_2$ complex.

bands at 3450 cm^{-1} suggests that amine group is also not bound.

The thermal analysis indicates that the decomposition of the complexes proceeds in several stages. The $Zn(Han)_2(Him)_3$ decomposes in two stage. The big mass loss and broad peak are observed in the TG and DTG curves, respectively. The course of the DTA curve showed the endothermic peak at 523 K. Mass loss in the beginning of the second stage is slow and becomes rapid as decomposition proceeds. In DTG curve, the intense peak is observed at 833 K, and in DTA two peaks are found: endo—at 733 K and exo—at 823 K. The mass loss, chemical, and diffractometric analysis of sinters obtained at temperature 573 K and 853 K indicate the following decomposition process:

$$Zn(Han)_2(Him)_3 \rightarrow Zn(im)_2 \rightarrow ZnO \qquad (1)$$

The pyrolysis of the $Zn(Han)_2(Him)_5$ begins with the phase transition (endothermic peak at 338 K). The fused sample decomposes similarly to $Zn(Han)_2(Him)_3$ but the mass loss is larger in the first stage. The chemical and diffractometric investigations of sinters obtained at 593 and 834 K indicate the following reaction of pyrolysis:

$$Zn(Han)_2(Him)_5 \rightarrow \xrightarrow[\text{process}]{\text{fusion}} \rightarrow Zn(im)_2 \rightarrow ZnO \qquad (2)$$

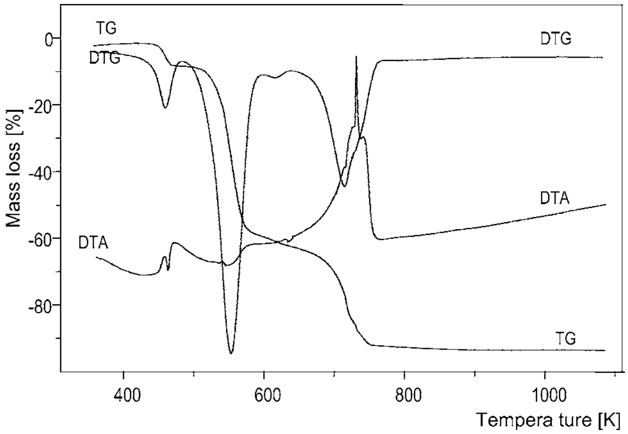

Fig. 3. Thermal curves of $Zn(Han)_2(1,2\text{-}diMeim)_2$ complex.

The reactions (1) and (2) suggest that molecules of imidazole may be bound in different ways: two of them with metal ion, the remaining ones probably joined via intramolecular hydrogen bonds. The molecules of imidazole joined via hydrogen bonds have lost Han$^-$ ions in the first stage as well.

In the case of complexes with 4-methylimidazole and 1,2-dimethylimidazole, both solid and gaseous products of pyrolysis were analyzed. The decomposition of the $Zn(Han)_2(4\text{-}MeHim)_2$, described by TG curve, occurs in two stages (Fig. 2). The mass loss in the first stage proceeds at different rates. The slow beginning is described by two peaks in DTG and one endothermic peak in DTA curve, and analysis of gaseous product shows the emission of fragment ion CH_3 (*m*/*z* 15). The continuation of mass loss to 60% is quick and multicomponent. The chemical and XRD analyses of sinter show that zinc mono(*o*-aminobenzoate) forms. The mass loss of the second stage is described by two peaks in the DTG and two exothermic peaks in DTA curves. Thermal decomposition to zinc oxide proceeds through zinc carbonate [20]. The analysis of gaseous products of decomposition confirms the emission of the following fragment ions: NH_2 (*m*/*z* 16), CO (*m*/*z* 28), NO (*m*/*z* 30), CO_2 (*m*/*z* 44, 46), C_6H_6 (*m*/*z* 50–52, 76–78), $C_6H_5NH_2$ (*m*/*z* 93, 94) and the molecular ion $C_3N_2H_4$ (*m*/*z* 68). Two stages of decomposition are described by reaction (3):

$$Zn(Han)_2(4-MeHim)_2 \rightarrow Zn(an) \rightarrow ZnO \qquad (3)$$

Table 3
Results of thermal analysis

Stage	Temperature (K)	Mass loss (%)		Peak nature	Temperature (K)
		Calc.	Found		
$Zn(Han)_2(Him)_3$					
I	388–593	62.81	61.5	Endo	523
II	698–848	84.97	85.3	Endo	733
				Exo	823
$Zn(Han)_2(Him)_5$	Fusion process			Endo	338
I	393–598	70.55	69.0	Endo	503
II	703–843	87.99	88.0	Endo	708
				Exo	813
$Zn(Han)_2(4\text{-}MeHim)_2$					
I	353–623	60.05	60.7	Endo	538
				Endo	608
II	693–823	83.70	86.6	Exo	753
				Exo	788
$Zn(Han)_2(1,2\text{-}diMeim)_2$					
I	448–483	–	7.2	Endo	463
II	508–633	62.14	62.3	Endo	543
III	633–843	87.65	94.9	Exo	728

The decomposition of $Zn(Han)_2(1,2\text{-}Meim)_2$ complex proceeds in three stages with mass loss of 7.2, 62.3 and 94.9%, respectively. The investigation of the gaseous products of the first stage shows partial decomposition of ligands. The fragment ions of the destruction of benzene (m/z 50, 51, 52,) are found in the mass spectrum. A specified formula has not been found for the product of this stage. The total mass loss of the second stage is described by several overlapping processes (Fig. 3, DTG curve) and the endothermic peak. The mass loss and the analyses of sinter (593 K) show that zinc mono(*o*-aminobenzoate) is formed. The third stage is complicated and described by three peaks in the DTG curve. Zinc is the final product and the big difference between the theoretical mass loss—87.65% and the experimental one—94.9% is explained by evaporation of the metallic zinc. The gaseous products of decomposition include the following fragment ions: CH_3 (m/z 15), NH_2 (m/z 16), H_2O (m/z 18), NO (m/z 30), CO_2 (m/z 44.46), C_6H_6 (m/z 78–76, 50–52), $C_6H_5NH_2$ (m/z 94.93) and the molecular ion $C_3N_2H_4$ (m/z 68). The analysis of sinters and gaseous products indicate the following decomposition reaction (4):

$$Zn(Han)_2(1,2\text{-diMeim})_2 \rightarrow ZnXY \rightarrow Zn(an) \rightarrow Zn \qquad (4)$$

where ZnXY is not a stechiometric compound.

The thermal decomposition indicates that, in the case of imidazole complexes, the metal–ligand bonds are cleaved at first. Zinc imidazolate is the intermediate product of pyrolysis. The decomposition of the complexes with 4-methylimidazole and with 1,2-dimethylimidazole goes through a different path. The bonds of the ligands cleave at the beginning and zinc mono(*o*-aminobenzoate) is the intermediate product.

The strength of the metal–ligand bond is one of the several factors which have an influence on the pathway of pyrolysis. In these compounds, zinc is always bound with the same ion Han^- and imidazole or 4-methylimidazole or 1,2-dimethylimidazole. The strength of metal–neutral ligand bond decreases in the following order: imidazole > 4-methylimidazole > 1,2-dimethylimidazole [21]. This decreasing strength of the metal–N(3) bond of the successive imidazoles explains the formation of $Zn(im)_2$ in the decomposition of $Zn(Han)_2(Him)_x$ ($x = 3, 5$) as well as the production of Zn(an) in the decomposition of $Zn(Han)_2(4\text{-}MeHim)_2$ and $Zn(Han)_2(1,2\text{-}diMeim)_2$ complexes. These conclusions confirm the thermal and structure investigations of the similar zinc complexes of *o*-hydroxybenzoic acid (H_2sal) and imidazoles [14].

4. Conclusion

The composition of complexes of di(*o*-aminobenzoate) zinc(II) with imidazole depends on molar ratio of the reagents, however, that of complexes with derivatives of imidazole does not. Compounds with imidazole and 1,2-dimethylimidazole have a crystalline structure, while compound with 4-methylimidazole is amorphous.

The *o*-aminobenzoate ion ($NH_2C_6H_4COO^-$) is tridentate in homoligand complex $Zn(Han)_2$, however, it is monodentate in heteroligand one. In these complexes, zinc forms bond with monodentate COO^- group of *o*-aminobenzoate ion and with nitrogen N(3) of imidazoles.

Thermal decomposition pathways of the investigated compounds were determined. The metal–ligand bonds are cleaved, at first, when pyrolysis of $Zn(Han)_2(Him)_x$ ($x = 3$, 5) starts to proceed. The $Zn(im)_2$ compound is the intermediate product. The bonds of ligands are cleaved at the beginning of pyrolysis of $Zn(Han)_2(4\text{-}MeHim)_2$ and $Zn(Han)_2(1,2\text{-}diMeim)_2$. The Zn(an) is the intermediate product of decomposition.

The pyrolysis progresses through two stages in the case of the complexes with imidazole and 4-methylimidazole, and through three stages in the case of the complex of 1,2-dimethylimidazole. Thermal stability, described by T_i, is the lowest for $Zn(Han)_2(4\text{-}MeHim)_2$ ($T_i = 353\,K$) and it is the highest for $Zn(Han)_2(1,2\text{-}diMeim)_2$ ($T_i = 448\,K$) (T_i: the temperature at which the rate of the pyrolysis is visible, kinetic characteristic of pyrolysis [22,23]).

References

[1] D. Kroczewska, B. Kurzak, Wiad. Chem. 55 (2001) 267.
[2] R.J. Sundberg, R.B. Martin, Chem. Rev. 74 (1974) 473.
[3] N.M. Sivasankarani, S. Jawaharunnissa, L. Kamakskil, Ind. J. Chem. 29A (1990) 581.
[4] R.N. Patel, R.P. Srivastawa, N. Singh, S. Kumar, K.B. Pandeja, Ind. J. Chem. 40A (2001) 361.
[5] A. Busnot, F. Busnot, J.F. Hemiday, J.F. LeQuerle, Thermochim. Acta 228 (1993) 219.
[6] W.D. Horrocks, J.N. Ishley, R.R. Whittle, Inorg. Chem. 21 (1982) 3265.
[7] R.N. Patel, H.C. Panday, K.B. Panday, G.N. Mukherjee, Ind. J. Chem. 38(A) (1999) 850.
[8] M. Olczak-Kobza, J. Therm. Anal. 29 (1984) 1319.
[9] F.P. Emmenegger, Thermochim. Acta 112 (1987) 63.
[10] M. Olczak-Kobza, Thermochim. Acta 366 (2001) 129.
[11] A. Turek, M. Olczak-Kobza, J. Therm. Anal. Cal. 54 (1998) 133.
[12] M. Olczak-Kobza, Polish J. Chem. 69 (1995) 1396.
[13] M. Olczak-Kobza, J. Therm. Anal. Cal. 55 (1999) 989.
[14] M. Olczak-Kobza, R. Czylkowski, J. Karolak-Wojciechowska, J. Therm. Anal. Cal.74 (2003) 895.
[15] A.G. Hill, C. Curran, J. Phys. Chem. 64 (1960) 1519.
[16] A. Cygański, Chemiczne metody analizy iloœciowej, WNT, Warsaw, 1999, p. 526.
[17] S.M. Boudrean, R.A. Boudrean, J. Solid State Chem. 49 (1983) 379.
[18] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.
[19] J.D. Lee, Zwięzła Chemia Nieorganiczna, PWN, Warsaw 1994, p. 387, 441.
[20] L. Erdey, G. Liptay, Periodica Polytech. 7 (1963) 185.
[21] B. Lenarcik, B. Barszcz, J. Chem. Soc., Dalton Trans. (1984) 24.
[22] E.V. Margulis, G.I. Chufarow, Zh. Fiz. Khim. 45 (1971) 1261.
[23] V. Nikolaev, V.A. Logvinienko, J. Therm. Anal. 13 (1978) 253.