Asian Journal of Chemistry Vol. 19, No. 6 (2007), 4880-4888

Synthesis and Characterization of *bis*(N,N-Diethylnicotinamide) *p*-Halogenobenzoate Complexes of Co(II)

ELIF F. ÖZTÜRKKAN†, DURSUN ALI KÖSE*, HACALI NECEFOGLU† and IBRAHIM UZUN‡
Department of Chemistry, Hacettepe University, Beytepe Campus, 06532 Ankara, Turkey
E-mail: dkose@hacettepe.edu.tr

Halogenobenzoates are commonly applied in industrial and medical fields. Four novel mixed ligand complexes of Co(II) with *p*-florobenzoate, *p*-chlorobenzoate, *p*-bromobenzoate, *p*-iodobenzoate and N,N-diethylnicotinamide were synthesized and characterized on the basis of elemental analysis, FT-IR spectroscopic study, solid state UV-Vis spectrometric and magnetic susceptibility data. The thermal behaviour of the complexes was studied by simultaneous TG-DTA methods in static air atmosphere and the mass spectra data are recorded. According to the microanlytical results, formulae of complexes are $C_{34}H_{36}N_4O_8FCo$, $C_{34}H_{36}N_4O_8ClCo$, $C_{34}H_{36}N_4O_8BrCo$ and $C_{34}H_{36}N_4O_8ICo$. The complexes contain two mole of coordination waters, two mole of *p*-halogenobenzoate and two mole of N,N-diethylnicotinamide (dena) ligands per formula unit. In these complexes, the *p*-halogenobenzoate and N,N-diethylnicotin-amide behave as monodentate ligand through acidic oxygen and nitrogen of pyridine ring. The decomposition pathways and the stability of the complexes are interpreted in the terms of the structural data. The final decomposition products were found to be the CoO.

Key Words: Co(II) complexes, N,N-diethylnicotinamide, *p*-Halogenobenzoate, Thermal decomposition.

INTRODUCTION

The diversity of inorganic compounds and their applications in medicine encompass cancer chemotheraphy, arthritis, antimicrobial agents, metalloenzyme inhibitors, antimanic agents and many others[1]. Metal complexes of biologically important ligands are sometimes more effective than the free ligands[2]. It is well documented that heterocyclic compounds play a significant role in many biological systems, especially N-donor ligand systems being a component of several vitamins and drugs[3-6]. Benzoic acid

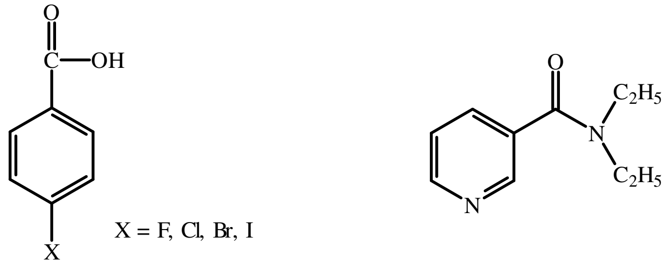
---

†Department of Chemistry, Faculty of Art and Science, Kafkas University, Pasaçayiri, 36100 Kars, Turkey.

‡Department of Mechanical Engineering, Faculty of Engineering, Kirikkale University, 71450, Kirikklale, Turkey.

and derivatives are widely used as antimicrobial agents in foods and drugs[7]. Some carboxylate compounds (*e.g.* benzoates) are also known to have antibacterial activity. Benzoic acid is used in combination with salicylic acid in dermatology as a fungicidal treatment for fungal skin diseases[8]. In the coordination compounds of some transition metals of aryl carboxylic acid and derrivatives of halogeno, the bonding occurs by acidic -OH group of carboxylic acid as monodentate[9]. According to X-ray structures in literature, halogeno group of aryl carboxylic acid has not participated to coordination. The N,N-diethylnicotinamide (dena) ligand has been coordinated by hetero nitrogen atom of pyridine ring. These type of complexes are resemble to the complexes reported in literature[10-14]. Many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of several central atoms. The pyridine ring is present in numerous naturally abundant compounds and hence the adducts of dena are also of scientific interest. Therefore, the structure of dena has been the subject of many studies[15-17]. The thermal decomposition properties of title compounds are compatible with literature[18-22].

In the present paper, we report the synthesis, spectroscopic and thermal properties of some new mixed-ligand complexes of Co(II) containing *p*-halogenobenzoate-N,N-diethylnicotinamide. The structures of the ligands are shown in Fig. 1.



p-halogeno benzoic acid (*p*-hal.ba) N,N-Diethylnicotinamide (dena)

Fig. 1

EXPERIMENTAL

All chemicals used were analytical reagent products. $CoSO_4 \cdot 6H_2O$, *p*-florobenzoic acid, *p*-chlorobenzoic acid, *p*-bromobenzoic acid and *p*-iodobenzoic acid were obtained from Merck (Darmstadt, Germany). Diethylnicotinamide was purchased from Darmitsa Chemicals Union (Kiev, Ukraine). Elemental analyses (C, H, N) were performed by standard methods in TUBITAK Laboratory (Scientific and Technical Research Council of Turkey). Magnetic susceptibility measurements at room temperatures were determined on a Sherwood Scientific MXI model magnetic balance

(Gouy Method) using $Hg[Co(SCN)_4]$. IR spectra were recorded in 4000-400 cm^{-1} region with a Perkin-Elmer 1000 FT-IR spectrophotometer using KBr pellets. Thermal analysis curves (TG-DTA) were recorded simultaneously in a static air atmosphere with a Schimadzu DTG 60 thermal analyzer. The samples weighed *ca.* 10 mg and highly sintered α-Al_2O_3 was used as a reference material. The heating rate was 10°C min^{-1} and the DTG sensitivity was 0.05 mg s^{-1}. Shimadzu UV3600/UV-VIS-NIR model spectrophotometer for solid state ultraviolet-visible range studies is used in present studies. Mass spectrum data was recorded Agilent Technologies 5973 spectrophotometer using DIP-MS method.

Preparation of *p*-hydroxybenzoate complexes: At the first step, *p*-halogenbenzoic acid sodium salts were prepared according to the following equation:

$$2p\text{-hal.ba} + 2NaHCO_3 \rightarrow 2Na(p\text{-hal.ba}) + 2CO_2 + 2H_2O$$

(*p*-hal.ba = *p*-floro-, *p*-chloro-, *p*-bromo- and *p*-iodo-benzoic acid)

At the second step, Co(II)-*p*-hal.ba salts were synthesized from Na(*p*-hal.ba) salt by substitution reaction:

$$2Na(p\text{-hal.ba}) + CoSO_4{\cdot}6H_2O \rightarrow Co(p\text{-hal.ba})_2{\cdot}nH_2O + Na_2SO_4$$

The compounds of $Co(p\text{-hal.ba})_2{\cdot}nH_2O$ were occurred in aqua media.

Synthesis of mixed-ligand complexes: A solution of dena (2 mmol) in distilled water (30 mL) was added dropwise with stirring to a solution of $Co(p\text{-hal.ba})_2(H_2O)_n$ (1 mmol) in hot distilled water (50 mL). The solutions were heated to 50°C in a temperature-controlled bath and stirred for 4 h and then cooled to room temperature and allowed 10-12 d for crystallization. The crystals formed were filtered and washed with cold water and acetone and dried *in vacuo*. The mixed-ligand complexes were prepared according to the following equations:

$$Co(p\text{-hal.ba})_2(H_2O)_n + 2\text{dena} \rightarrow Co(p\text{-hal.ba})_2(\text{dena})_2(H_2O)_n$$

RESULTS AND DISCUSSION

The complexes were synthesized with high purity. The results of the elemental analysis indicated that the complexes contain 2 mol of *p*-halogenobenzoate and 2 mol of N,N-diethylnicotinamide ligands per mole formula units. Each complex has 2 mol of hydrated waters. Analytical results and compositions of the complexes are given in Table-1. In the complexes, octahedral coordination of the Co(II) ion formed by carboxylic acid oxygen atoms from 2 mol *p*-halogenobenzoates as monoanonic bidentate chelating ligand and two donor nitrogen atoms from two N,N-diethylnicotinamides. The suggested coordination of metal was compatible with literature[23]. The elemental analysis data in Table-1 confirm the proposed formula of the complexes.

TABLE-1
ANALYTICAL DATA OF THE Co(II) COMPLEXES

Complex/m.f.	M g mol^{-1} [Yield (%)]	Elemental analysis: Found (Calcd.) % C	H	N	Colour	d.p.* (°C) [μ_{eff} BM]
[Co(*p*-Fba)$_2$(dena)$_2$](H$_2$O)$_2$	729.45	56.05	4.87	8.70	Pink	93
$C_{34}H_{40}N_4O_8F_2Co$	[65]	(55.97)	(5.48)	(7.69)		[2.85]
[Co(*p*-Clba)$_2$(dena)$_2$](H$_2$O)$_2$	762.21	52.71	4.48	7.58	Pink	100
$C_{34}H_{40}N_4O_8ClF_2Co$	[75]	(53.54)	(5.51)	(7.35)		[2.98]
[Co(*p*-Brba)$_2$(dena)$_2$](H$_2$O)$_2$	851.05	48.26	4.22	7.00	Pink	105
$C_{34}H_{40}N_4O_8Br_2Co$	[84]	(47.95)	(4.70)	(6.58)		[3.26]
[Co(*p*-Iba)$_2$(dena)$_2$](H$_2$O)$_2$	945.89	43.44	3.52	6.50	Pink	114
$C_{34}H_{40}N_4O_8I_2Co$	[81]	(43.18)	(4.23)	(5.99)		[3.47]

*Decomposition point.

p-Florobenzoic acid (*p*-Fba), *p*-Chlorobenzic acid (*p*-Clba), *p*-Bromobenzoic acid (*p*-Brba) and *p*-Iodobenzoic acid (*p*-Iba)

Due to the low solubility, solid sample recorded satisfactory UV-Vis spectra for the complexes. The electronic spectrum of the Co(II) complexes shows absorption bands at about 8000 cm^{-1} and overlapped a multiple absorption band at about 20000 cm^{-1}. These peaks belong to the *d-d* transitions in Co(II) complexes which may be assigned to $^4T_{2g} \leftarrow {}^4T_{1g}$ for and $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transitions, respectively. The peaks belonging to the $\pi \rightarrow \pi^*$ transitions are shifted to a longer wavelength as a consequence of coordination when binding with metal, confirming the formation of *p*-hal.ba-dena Co(II) complexes. All the Co(II) complexes are of the high-spin type and paramagnetic complexes. These values suggest octahedral coordination around the metal ions.

FT-IR spectra: Characteristic FT-IR spectrum peaks of the complexes are given in the Table-2. FT-IR spectra of complexes show -OH absorbtion bands of aqua ligands in the range of 3500-3000 cm^{-1} correspond to the asymmetric and symmetric stretching vibration of water molecule. Conjugation between the carbonyl group and the amide nitrogen causes small frequency shifts. The strong bands observed 1620 cm^{-1} region are assigned to this mode. Pyridine ring vibrations of free diethylnicotinamide at 1580 cm^{-1} shifts to lower frequencies in the spectrum of the Co(II) complexes. These shifts are shown in range of *ca.* 1441-1424 cm^{-1}. It may indicate that the pyridine ring is coordinated to the cobalt ion. The main difference in the spectrum of *p*-halogenbenzoic acid is that the (C=O) stretching vibration of the carboxyl group at 1730-1708 cm^{-1} is shifted to lower frequency in all the Co(II) complexes. The absorbsition bands of carboxylate in the Co(II) complexes occur in the range of 1690-1677 cm^{-1}. This may be a consequence of coordination takes place through the

TABLE-2
CHARACTERISTIC FT-IR PEAKS OF METAL COMPLEXES

Gruplar	I	II	III	IV
$\nu(\text{-OH})_{H_2O}$	3530-3100	3550-3060	3500-3050	3500-3000
ν(C-H)	3327,3067	3127	3351,3186	3350,3187
$\nu(C{=}O)_{ester}$	1693	1697	1698	1700
$\nu(COO^-)_{as}$	1544	1541	1538	1533
$\delta(H_2O)$	1579	1593	1595	1580
$\nu(COO^-)_s$	1384	1390	1395	1398
$\Delta\nu$	160	151	143	135
ν(C-O-C)	1150	1138	1136	1133
$\nu(\text{C-H})_{CH_3}$	1390	1391	1384	1399
$\nu(\text{C-N})_{py}$	1424	1440	1441	1436
$\nu(\text{C-N})_{amide}$	1280	1279	1276	1273
$\nu(C{=}O)_{amide}$	1648	1623	1622	1610
ν(C-halogen)	786	776	774	767
ν(Me-N)	703	695	692	690
ν(Me-O)	501	495	475	465

carboxyl group by deprotonation of the *p*-hal.ba molecule during coordination. When the Co(II)-halogenbenzoate-dena mixed ligand complexes are occured, the peak of acidic COOH group at 1688 cm^{-1} disappears[14]. At the same time, in these complexes, the $(COO^-)_{as}$ is located at 1544 cm^{-1} for *p*-Fba, 1541 cm^{-1} for *p*-Clba, 1538 cm^{-1} for *p*-Brba and 1533 cm^{-1} for *p*-Iba complexes. $(COO^-)_s$ peak observed at 1384 cm^{-1} for *p*-Fba, 1390 cm^{-1} for *p*-Clba, 1395 cm^{-1} for *p*-Brba and 1398 cm^{-1} for *p*-IFba complexes. The splitting of the ν_{as} and ν_s bands of COO^- groups for *p*-Fba, *p*-Clba, *p*-Brba and *p*-Iba complexes almost identical (160, 151, 143 and 135 cm^{-1}, respectively) and slightly higher than for the sodium salts of these acid (135, 119, 116 and 110 cm^{-1}, respectively)[24] suggesting that monodentate carboxylate group exist[25]. For monodentate geometry of carboxylate group, the bands of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ in synthesized complex are shifted to higher and lower region or $\nu_{as}(COO^-)_{\text{prepared complex}} > \nu_s(COO^-)_{\text{sodium salt}}$. The bands of ν(C-F) at 786 cm^{-1}, ν(C-Cl) at 776 cm^{-1}, ν(C-Br) at 774 cm^{-1} and ν(C-I) at 767 cm^{-1} are almost in the same position in the FT-IR spectra of prepared complexes as in the spectrum of sodium salt. This result is supported, the halogenbenzoate ligands don't coordinate to metal atom *via* halogen groups[26]. The -OH bending peak for the *m*-hydroxybenzoic acid remained almost same position at around 1259 cm^{-1} in all Co(II) complexes. The low intensity bands in the region of 710-450 cm^{-1} are attributed to (Co-N) for dena ligand and (Co-O) for *p*-hal.ba vibrations[27,28].

Thermal data

[Co(*p*-Fba)$_2$(dena)$_2$(H$_2$O)$_2$]: The complex is stable in room conditions. Its thermal decompositions began at 63°C. The 2 mol of coordinated waters of *p*-Fba complex are dehydrated in the one-step temperature in the range of 93°C endothermic DTA peak (exp. 4.98 %; cal. 4.94 %). The decomposition of the complex associated with the complete pyrolysis of the organic part of the compound starts above this temperature. The organic part of the complex decomposes with the release of CO_2 molecules. The descending continuous TG curve is obtained in the temperature range of 135-735°C (endothermic DTA peaks at 201 and 430°C). The final decomposition product is CoO (exp. 9.50 %; calc. 10.27 %).

[Co(*p*-Clba)$_2$(dena)$_2$(H$_2$O)$_2$]: The thermal dehydration of the *p*-Clba complex occured in one-step by giving endothermic DTA peak at 100°C correspond to the loss of two water molecules that are coordinated to metal ion (exp. 4.23%; calc. 4.72%). The temperature range of this step is 70-115°C. The anhydrous *p*-Clba complex is stable in the range of 115-135°C. In the second stage, all of the organic ligands decompose and remove in the temperature range of 135-740°C by giving exothermic DTA peaks at 155, 212 and 418°C. The final decomposition product, namely CoO was identified (exp. 10.40 %; calc. 9.85 %) by IR spectroscopy with corresponding spectra obtained under the same conditions as the pure oxides.

[Co(*p*-Brba)$_2$(dena)$_2$(H$_2$O)$_2$]: The TG-DTA curves for the *p*-Brba complex contained 2 mol crystal water and they removed in the temperature range of 77-135°C and at 105°C DTA peak (exp. 5.03 %; calc. 4.23 %). The anhydrous complex is stable until to temperature of 152°C. After that *p*-Brba and dena ligands start to decomposing together. The decomposition occurs in the temperature range of 153-697°C at four-steps by giving endothermic DTA peaks at 204, 292, 339 and 400°C. At the result of the removing organic ligands produced CoO (exp. 10.22 %; calc. 8.92 %).

[Co(*p*-Iba)$_2$(dena)$_2$(H$_2$O)$_2$]: The first stage of the thermal decomposition of *p*-Iba complex starts at the 84-160°C temperature range with the release of the 2 mol water ligands (exp. 3.77 %; calc. 3.82 %). The decomposition is occured one-step by giving endothermic DTA peak at 114°C. The anhydrous product, Co(*p*-Iba)$_2$(dena)$_2$ is not stable and begins to decompose with removing the water molecules from structure. At 240, 323, 425 and 614°C. DTA peaks dena and *m*-hba ligands decompose in the temperature range of 168-785°C. At the result of the removing ligands produced CoO (exp. 8.21 %; calc. 7.93 %). Similar decomposition behaviours are shown in literature[19-23,30].

In general, the decomposition steps of aqua ligands show that metal-water bond strength is almost the same for all of the water molecules. The complexes lose water molecules in one-step. After the dehydration process, decomposition stages of the anhydrous complexes are related to release nicotinamide and the partial decomposition of concerned halogenbenzoate involving the release of CO_2. Previous studies show that the benzoate-metal complexes decompose by releasing of CO_2[30-33]. The IR spectra of the intermediate products show similar results. In all the Co(II) complexes, all ligands are coordinated to the metal ion as monodendate and their structures are octahedral that in the each complex, 2 mol water, 2 mol concerned halogen benzoate and 2 mol dena ligands coordinate to Co(II) ion. The stabilities of complexes are limited I > II > III > IV, anhydrous complexes are limited III > II > I > IV. The final decomposition products were metal oxides (CoO) in the 700-900°C temperature intervals. Suggested structure of the complexes are given Fig. 2.

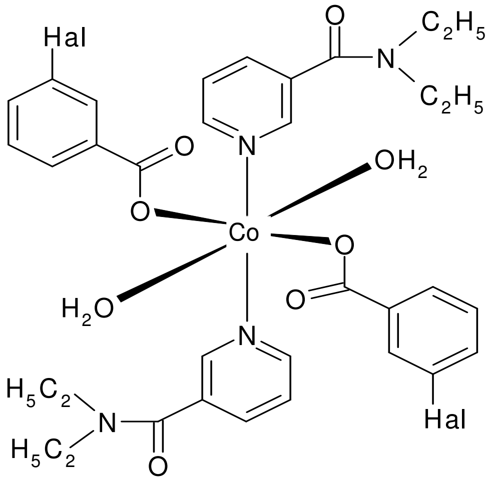


Fig. 2. Suggested structure of the Co(II) complexes

Mass spectra: To conclude the thermal decomposition pathway of the $[Co(p\text{-}Brba)_2(dena)_2(H_2O)_2]$ complex mass spectrum was recorded (Fig. 3) using direct insertion probe pyrolysis mass spectrometry method. The molecular ion peak is not detected in the mass specrum recorded. The obtained mass spectrum is relatively complex and exhibits a large number of peaks that extend to m/z value above 750. These peaks belong to decomposition products of complex and ligands.

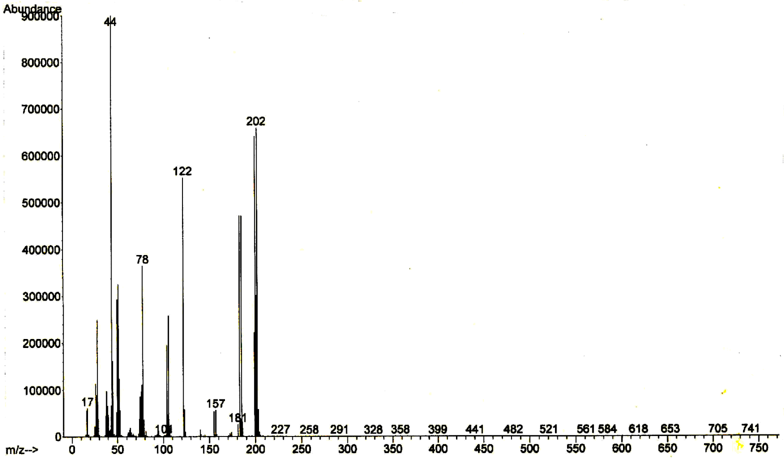


Fig. 3. Mass spectrum of $[Co(p\text{-}Brba)_2(dena)_2(H_2O)_2]$ complex

REFERENCES

1. R. Bakhtiar and E.I. Ochiai, *General Pharmacol.*, **32**, 525 (1999).
2. J.R.J. Sorensen and H. Sigel, Metal Ions in Biological Systems, 14, Marcel Dekker, New York, Vol. 14, p. 77 (1982).
3. M. Kato and Y. Muto, *Coord. Chem. Rev.*, **92**, 45 (1988).
4. R. Nagar, *J. Inorg. Biochem.*, **40**, 349 (1990).
5. G. Cavigiolio, L. Benedetto, E. Boccaleri, D. Colangelo, I. Viano and D. Osella, *Inorg. Chim. Acta*, **305**, 61 (2000).
6. U. Brühlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974).
7. A. Hossaini, J.J. Larsen and J.C. Larsen, *Food Chem. Toxicol.*, **38**, 19 (2000).
8. (a) K.B. Diehl, *Am. Fam. Physician*, **54**, 1687 (1996); (b) D. Russell and A.D. Russell, *J. Infect.*, **24**, 333 (1992).
9. M.R. Sundberg, R. Uggla and R. Kivekas, *Inorg. Chim. Acta*, **232**, 1 (1995).
10. T. Hökelek and H. Necefoglu, *Anal. Sci.*, **15**, 1043 (1999).
11. N.N. Hoang, F. Valanch, M. Melnik, *Zeitschrift Für Kristalographie*, **208**, 27 (1999).
12. T. Hökelek and H. Necefoglu, *Acta Cryst.*, **C53**, 187 (1997).
13. H. Necefoglu, W. Clegg and A.J. Scott, *Acta Cryst.*, **E57**, 462 (2001).
14. W. Woodkiewicz and T. Glowiak, *J. Coord. Chem.*, **56**, 563 (2003).
15. T.S. Khodashova, M.A. Poray-Koshits, B.Ya. Rubinchik, L.A. Butman and G.V. Tsintzade, *Koord. Khim.*, **4**, 1753 (1978).
16. M.A. Poray-Koshits, B.Ya. Rubinchik, L.A. Butman, G.V. Tsintzade and V.S. Segienko, *Koord. Khim.*, **4**, 1760 (1978).
17. V.N. Shurkina, T.S. Khodashova, M.A. Poray-Koshits, G.V. Tsintzade and V.S. Segienko, *Koord. Khim.*, **6**, 1606 (1980).
18. H. Icbudak, H. Olmez, O.Z. Yesilel, F. Arslan, P. Naumov, G. Jovanovski, A.R. Ibrahim, A. Usman, H.K. Fun, S. Chantrapromma and S.W. Ng, *J. Mol. Struct.*, **657**, 255 (2003).
19. H. Icbudak, V.T. Yilmaz and H. Olmez, *J. Therm. Anal.*, **53**, 843 (1998).
20. W. Brzyska and W. Woodkiewicz, *Thermochim. Acta*, **242**, 131 (1994).
21. J. Skorsepa, E. Godocikova and J. Cernak, *J. Therm. Anal. Catal.*, **75**, 773 (2004).

22. W. Woodkiewicz and W. Brzyska, *J. Therm. Anal. Catal.*, **55**, 639 (1999).
23. D.A. Kose, A. Kaya and H. Necefoglu, *Russian J. Coord. Chem.* (2007) in press.
24. E. Regulska, M. Samsonowicz, R. Swislocka and W. Lewandowski, *J. Mol. Struct.*, **744**, 353 (2005).
25. D.A. Kose, B. Zümreoglu-Karan, O. Sahin and O. Büyükgüngör, *J. Mol. Struct.*, **789**, 147 (2006).
26. W. Wolodkiewicz and W. Brzyska, *Polish J. Chem.*, **72**, 2366 (1998).
27. J. Zsakó, G. Pokol, Cs. Novák, Cs. Várhelyi, A. Dobó and G. Liptay, *J. Therm. Anal. Catal.*, **64**, 843 (2001).
28. K. Györyova, E. Szunyogova, J. Kovarova, D. Hudecova, D. Mudronova and E. Juhaszova, *J. Therm. Anal. Catal.*, **72**, 587 (2003).
29. H. Icbudak, Z. Heren, D.A. Kose and H. Necefoglu, *J. Therm. Anal. Catal.*, **76**, 837 (2004).
30. P. Kokkonen, L.H.J. Lajunen, A. Jaakola and H. Ruotsalainen, *Thermochim. Acta*, **79**, 289 (1984).
31. B.R. Srinivasan and S. C. Sawant, *Thermochim. Acta*, **402**, 45 (2003).
32. W. Ferenc and B. Bocian, *J. Therm. Anal. Catal.*, **74**, 521 (2003).
33. M. Olczak-Kobza, R. Czylkowski and J. Karolak-Wojciechowska, *J. Therm. Anal. Catal.*, **74**, 895 (2003).

(*Received*: 4 April 2007; *Accepted*: 4 May 2007) AJC-5637