

# Thermal treatment on tin(II/IV) oxalate, EDTA and sodium inositol-hexaphosphate

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**Abstract** The thermal behavior of tin containing oxalate, EDTA, and inositol-hexaphosphate were investigated. The end products of synthesis were identified by Mössbauer-, XRD analyses, and FTIR studies. The thermal decompose of the samples was studied by DTA-TG analysis. The simultaneously obtained DTA and TG data makes it possible to follow the thermal decomposition of the investigated samples. The tin oxalate decomposed in the temperature range of 520–625 K through tin carbonate formation and finally yielded CO<sub>2</sub> and SnO. The tin EDTA complex first lost its hydrate bound water till 520 K. The followed thermal events related to the pyrolysis of anhydrous salt. The intense exothermic process that exists in the temperature range of 820–915 K is due to the formation of SnO<sub>2</sub>. The tin sodium inositol-hexaphosphate lost its hydrate bound water (~10%), up to 460 K. The following sharp exothermic process, in the temperature range of 680–750 K is due to the decomposition and parallel oxidation of organic part of the molecule. At the end of this process, a mixture of phosphorous pentaoxide, sodium carbonate, and tin dioxide is obtained.

**Keywords** Sn(II/IV) · Thermal analysis

## Introduction

Oxalate based compounds have attracted much attention in many areas of chemistry. For example, due to the low thermal stability they can be successfully used as precursors of nano-crystalline oxides or due to the zeolitic properties they can play a role in the synthesis of open-framework materials.

Chelates on the basis of amino-carboxylic acids are for a wide branch of practical fields. Of these, the most common commercially used chelating agents are ethylene diamine tetraacetic acid (EDTA), N-hydroxyethylene diamine tetraacetic acid (HEDTA), diethylene triamine tetraacetic acid (DTPA), and nitrile triacetic acid (NTA).

Phytic acid is the six phosphate ester of inositol. It is known in nine isomers, and they are: cis-, epi-, allo-, neo-, myo-, muco-, scyllo-, L-(–)-chiro-, and D-(+)-chiro-. The myo-isomer was used for these experiments. In nature, it can be found in the form of insoluble Ca and/or Mg-salts in the grains as a fiber of plants. These materials called phytins, are considered as the storage of organic phosphorus in the plants.

Against the wide use of above materials in various practical fields, relatively few words can be found in connection with their thermal behavior [1–10], especially, with regard to the tin containing form of the written materials. Consequently, for syntheses, tin(II) chloride, oxalic acid, disodium EDTA and dodeca-sodium inositol-hexaphosphate (phytate) were used, respectively. The planned investigations are a continuation of the previous study on tin containing phosphates [11].

The results of these investigations are collected in this article.

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## Experimental

### Synthesis

The typical methods of synthesis were:

For *tin oxalate* (Sample No. 1), 6.5 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (Sigma) was dissolved in  $20 \text{ cm}^3$  of 0.001 M HCl and heated in argon atmosphere, at 310 K. On this temperature and under vigorous stirring was slowly added 2.52 g of  $\text{H}_2\text{C}_2\text{O}_4$  (Aldrich), and then the mixture was stirred for another two and a half hours. The resulted tin oxalate was washed with oxygen-free water (to eliminate the chloride ions and the redundant oxalic acid) and finally with dry acetone, and was then dried at room temperature in a vacuum desiccator.

For *tin sodium EDTA* (Sample No. 2), 2.71 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in  $50 \text{ cm}^3$  of oxygen-free water, and the mixture heated at 330 K. At this temperature, the solution ( $20 \text{ cm}^3$ ) of 3.72 g of  $\text{Na}_2$ ethylene-diamine-tetra acetic acid [ $\text{Na}_2$ -edta] (Reanal) was added very slowly with vigorous stirring. The mixture was standing at 330 K for a further 30 min under magnetic stirring. After that the mixture was cooled slowly to room temperature (298 K). The end product was washed with  $20 \text{ cm}^3$  of ethanol (in two parts) and then stored in desiccators above  $\text{CaCl}_2$ .

For *tin sodium inositol-hexaphosphate* (Sample No. 3), 5.0 g of  $\text{C}_6\text{H}_6\text{Na}_{12}\text{O}_{24}\text{P}_6$  [sodium phytate] (Chemos) was mixed with 1.8 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in  $20 \text{ cm}^3$  of 0.001 M HCl solution. The mixture was held for 2 h at 298 K under continuous stirring. The precipitate was thoroughly washed with deionised water to eliminate chloride ions and dried in vacuum desiccators above  $\text{P}_2\text{O}_5$ .

### Chemical composition

The chemical analysis of the synthesis end products was carried out using an inductively coupled plasma mass spectrometer (ICP-MS, ELEMENT 2).

### Identification

#### Mössbauer studies

The  $^{119}\text{Sn}$  Mössbauer spectra of the investigated samples were obtained in transmission geometry, using a  $\sim 600 \text{ MBq}$  activity  $\text{Ba}^{119}\text{SnO}_3$  (room temperature) source. The patterns were recorded at 298 K. The spectra were fitted using “Mosswinn” computer program [12].

#### X-ray powder diffraction analysis (XRD)

The XRD study was performed with a Bragg–Brentano geometry, using powder samples (pressed before into the

sample holder) with DRON-2 computer controlled diffractometer (at 45 kV and 35 mA) with the  $\beta$  filtered  $\text{Co}_{K\alpha}$  radiation ( $\lambda = 1.7890 \text{ \AA}$ ) at 28 K. The goniometer speed chosen was  $1/4^\circ \text{ min}^{-1}$  in the range of  $2\theta = 3\text{--}110$ . The diffraction patterns were evaluated using “EXRAY” peak searching program (Z. Klencsár, personal communication). During the estimation, an effect of texture on line intensity was taken into consideration.

#### Fourier transformed infrared spectrometry (FTIR)

The FTIR spectra of the investigated samples were performed in a KBr pellet in MIDAC M-2010-H type spectrometer at  $2 \text{ cm}^{-1}$  resolution and they are shown on Fig. 2.

### Thermal analysis

The measurements were carried out using Mettler-TA1-HT type computer controlled thermo-balance, which simultaneously provided DTA and TG data. The heating rate chosen was  $5 \text{ K min}^{-1}$ , in the temperature range of 298–980 K. The reference material was using dehydrated  $\alpha\text{-Al}_2\text{O}_3$ , the ambience was air, and in the experiments Pt crucible was used. The found data were evaluated by adequate computer program.

## Results

### Chemical analysis

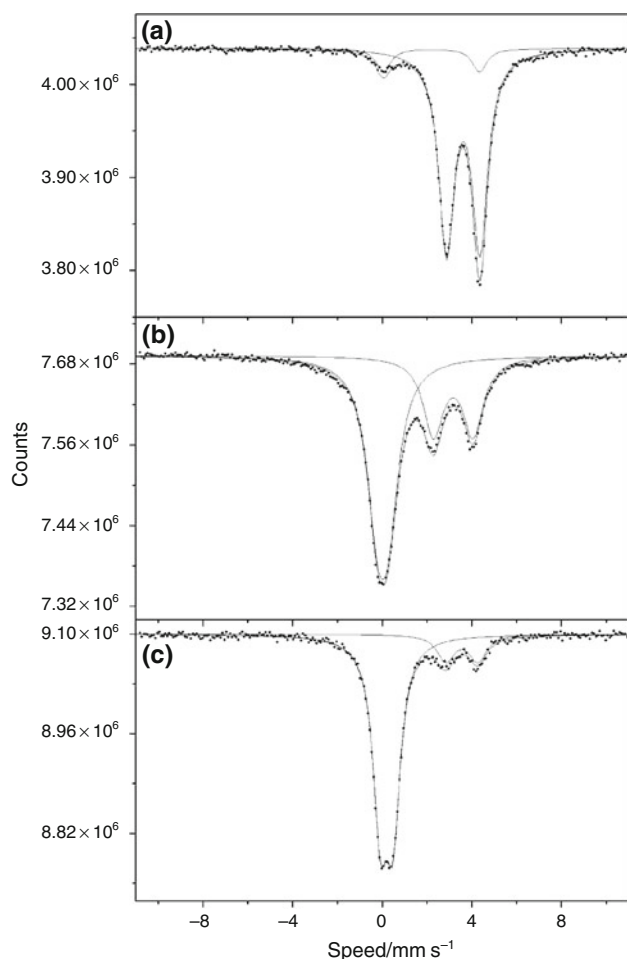
The analytical data (in wt%) were as follows: for tin oxalate Sn = 57%, C = 12% and O = 31%; for tin sodium EDTA Sn = 34%, Na = 6%, N = 2%, C = 17%, H = 4%, and O = 32% (without water oxygen ( $\sim 5\%$ ) at least for tin sodium inositol-hexaphosphate Sn = 12.6%, Na = 16.7%, C = 7.6%, O = 42%, P = 19.7%, and H = 0.6%).

### Mössbauer study

The Mössbauer spectra of the samples, recorded at 298 K, are shown on Fig. 1.

It can be seen, that the spectrum of tin oxalate (Sample No. 1) exhibits a quadrupole split doublet, with parameters of isomer shift and quadrupole splitting equal to  $\delta = 3.61 \text{ mm/s}$  and  $\Delta = 2.19 \text{ mm/s}$ , respectively, characteristic of Sn(II).

The spectrum of tin sodium EDTA complex (Sample No. 2) shows an envelope consisting of three overlapping lines which can be decomposed into the singlet (isomer shift is equal to  $\delta = 0.199 \text{ mm/s}$ ) of Sn(IV) and the



**Fig. 1** Mössbauer spectra of tin oxalate (*upper*), tin sodium EDTA (*middle*), and tin sodium inositol-hexaphosphate (*bottom*).

doublet belonging to Sn(II). The relative amount of Sn(II) to Sn(IV) is 5%:95%.

The spectrum of tin sodium inositol-hexaphosphates (Sample No. 3) shows similar pattern to that found for the previous sample, with exception that the peaks belonging to the doublet characteristic of Sn(II) is smaller since the Sn(II) fraction is less than that in the case of tin sodium EDTA.

#### XRD analysis

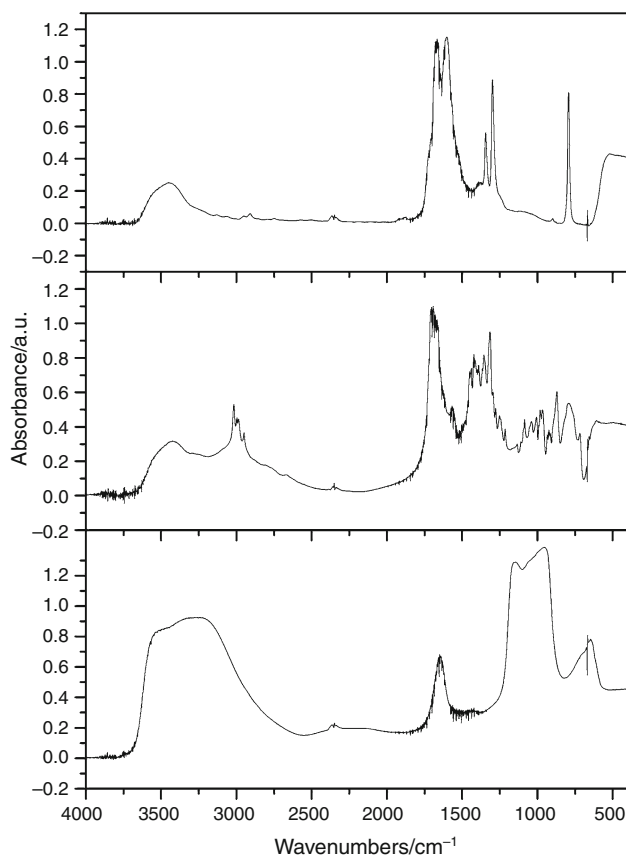
The XRD patterns of the investigated materials indicate a crystalline nature for Samples No. 1 and 2 and an amorphous character for Sample No. 3. Fitting of the patterns were taken using the Powder Cell (PCW 2.3) software [13]. The crystallographic data found are collected in Table 1.

#### FTIR study

The FTIR spectra are shown in Fig. 2.

**Table 1** Crystallographic data

	Sn oxalate	Sn Naedta	SnNa <sub>8</sub> phytate
X-ray tube	Co <sub>Kα</sub>	Co <sub>Kα</sub>	Co <sub>Kα</sub>
Crystal system	Orthorhombic	Monoclinic	Amorphous
Space group no.	62	14	
Space group	<i>Pnma</i>	<i>P2<sub>1</sub>/c1</i>	
<i>a</i> /Å	9.2066/3/	10.7544/3/	
<i>b</i> /Å	9.7590/1/	10.1455/3/	
<i>c</i> /Å	13.1848/5/	16.5130/6/	
Angle/ $\beta^\circ$	–	98.59/2/	
Atoms in assym. units	11	22	
Atoms in unit cell	88	88	
Volume of cell/Å <sup>3</sup>	1184.62/3/	1781.50/4/	
Rel. mass of unit cell	2165.66	1671.20	
X-ray density/g cm <sup>-3</sup>	3.0357	1.5577	
Mass abs. coeff./cm g <sup>-1</sup>	172.54	116.76	



**Fig. 2** FTIR spectra of the tin oxalate (*upper*), tin sodium EDTA (*middle*), and tin sodium inositol-hexaphosphate (*bottom*).

The FTIR spectrum of tin oxalate, showed overlapping bands at 3568, 3449, 3294, 2918, and 2366 cm<sup>-1</sup>, with medium intensity due to the O–H stretching in the water

molecules and oxalate group, respectively. The shoulder at about  $1734\text{ cm}^{-1}$ , the very strong bands at  $1670$  and  $1600\text{ cm}^{-1}$  and the bands at  $1391$ ,  $1346$ , and  $1296\text{ cm}^{-1}$  can be attributed to the CO stretching vibrations. The band at  $901\text{ cm}^{-1}$  is due to the oxalate C–C stretching, while the other band at  $790\text{ cm}^{-1}$  is assigned to the combination of  $\delta(\text{O–C–O}) + \nu(\text{C–C})$  vibrations, respectively. The medium band around  $521\text{ cm}^{-1}$  is attributed to the Sn=O stretching.

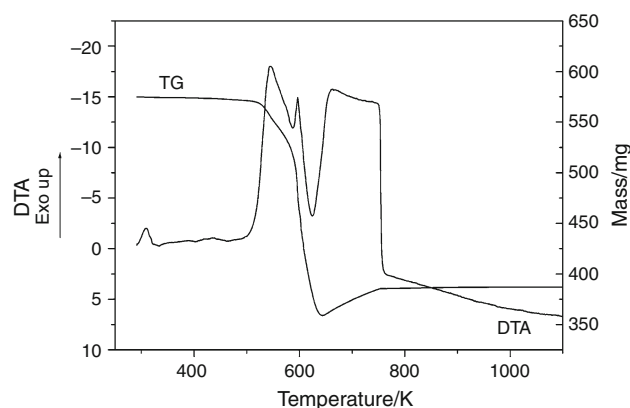
In the spectrum of tin sodium EDTA complex, overlapping bands with different intensity were found at  $3535$ ,  $3421$ , and  $3281\text{ cm}^{-1}$ , due to O–H stretching in the coordinated water molecules. The bands in the region between  $3020$  and  $2940\text{ cm}^{-1}$  are related to the stretching vibrations of  $-\text{CH}_2$  groups. The bands found at about  $1690$ ,  $1620$ , and  $1575\text{ cm}^{-1}$  are assigned to  $\nu_{\text{as}}(\text{COO})$ , while the bands at  $1422$  and  $1391\text{ cm}^{-1}$  belonged to  $\nu_{\text{s}}(\text{COO})$  vibrations. The strong band at  $1312\text{ cm}^{-1}$  is due to the combination vibration of  $\delta(\text{CH}_2) + \nu(\text{CN})$ , respectively. The bands at  $1211$  and  $1085\text{ cm}^{-1}$  are related to  $\nu(\text{CNC})$  and  $\nu(\text{CN})$  vibrations, while the  $\nu(\text{CC})$  vibrations appear at  $922$  and  $674\text{ cm}^{-1}$  with weak and medium intensity, respectively.

In the spectrum of tin sodium inositol-hexaphosphate, very broad strong bands were found in the region of  $3500\text{--}2800\text{ cm}^{-1}$  (with peaks at  $3486$ ,  $3370$ , and  $3266\text{ cm}^{-1}$ ) due to O–H stretching of OH groups of water molecules. The strong bands at  $1143$  and  $974\text{ cm}^{-1}$  with a shoulder at  $1022\text{ cm}^{-1}$  can be assigned to asymmetric and symmetric stretching of P–O vibration in  $\text{PO}_3^{2-}$ , respectively.

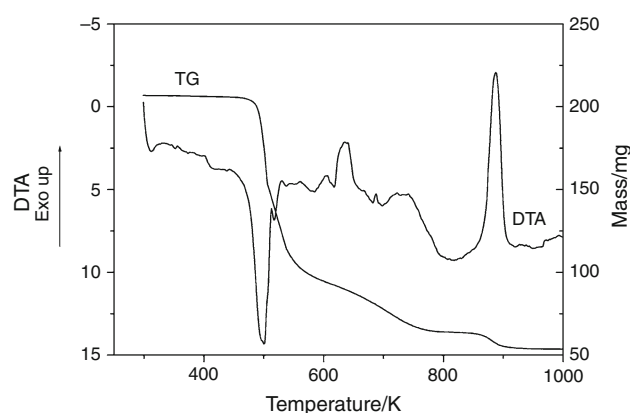
### Thermal analysis

The results of DTA-TG patterns are collected in Table 2.

The observed DTA-TG patterns are shown on Figs. 3, 4 and 5.



**Fig. 3** The DTA–TG curves of tin oxalate.



**Fig. 4** The DTA–TG curves of tin sodium EDTA.

### Discussion

It was determined in the Mössbauer study that most of the tin atoms in tin oxalate have oxidation state of two. The quantity of tin atoms having oxidation state of four was found insignificantly low.

**Table 2** Thermal processes

Material	Process	Temp. range/K	Peak temp./K	Mass loss/%
Sn-oxalate	Exothermic	525–630	598	~50
	Exothermic	630–710		~2.5
SnNa-EDTA	Endothermic	460–525	500	~50
			630	
	Exothermic	525–830	640	~0.5
			680	
SnNa <sub>8</sub> -inositol-hexaphosphate	Exothermic	830–915	885	~3
	Endothermic	330–490	400	10.54
	Exothermic	680–750	700	~0.4

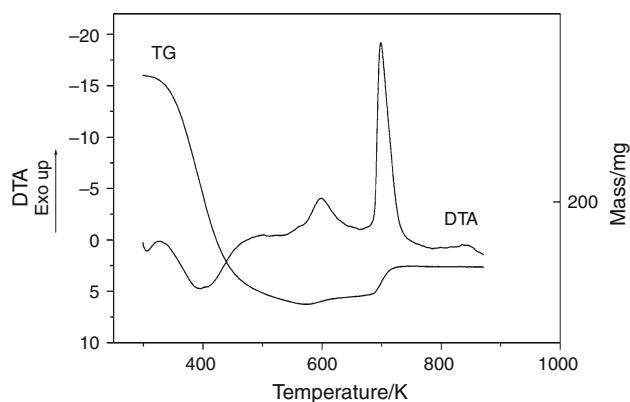


Fig. 5 The DTA–TG curves of  $\text{SnNa}_8$  inositol-hexaphosphate.

In the other two materials, both prepared in open air, the tin atoms mainly have an oxidation state of four. Beside them, in tin sodium EDTA it was found that  $\sim 5\%$  of tin atoms have oxidation state of two, and this fraction was markedly less in the tin sodium inositol-hexaphosphate. Consequently, based on the Mössbauer data, for description of tin sodium EDTA complex two formulas can be proposed, namely:  $\text{NaSn}(\text{HEDTA})(\text{H}_2\text{O})$  for tin (II) and  $\text{NaSn}(\text{OH})(\text{EDTA})(\text{H}_2\text{O})_2$  for tin(IV), respectively. It means that theoretically two oxidation states exist on the basis of the tin environment, but during the investigations we practically detected only the form in which the tin existed in oxidation state of four.

The X-ray diffraction pattern of tin oxalate showed well defined crystalline state of the prepared end products. These evaluated data showed that the tin oxalate had an orthorhombic sheet type structure. The mean distance between two sheets was found to be about  $a/2$ . These sheets are built from a network of oxalate groups, surrounding the tin atoms displaying ellipsoidal apertures from six-member rings. In other words, each tin atom is surrounded by six oxygen atoms from the bi-chelated oxalate groups. Such  $\text{SnO}_6$  polyhedra can be described as a pseudo pentagonal bi-pyramide. The resulting framework, creates holes in which water molecules can be located.

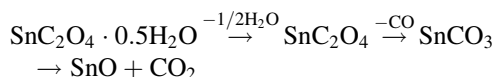
In case of EDTA complex the X-ray diffraction pattern also showed a well determined crystalline end product. Evaluation of these data found that the sodium-tin EDTA had monoclinic structure. Based on the found data it was proposed that a polyhedron was around the tin atom, which can be described as a monocapped octahedron in which the equatorial plane is designed by the carboxylate oxygen atoms. At the same time, the axial plane is defined by the nitrogen atoms on one side of the equatorial plane and by the hydroxyl group on the other side. Taking into consideration the above written, the proposed polyhedron can be shortly described as a square pyramid.

The X-ray diffraction pattern of tin sodium inositol-hexaphosphate showed amorphous character.

The FTIR studies with their results gave support to the identification of the samples based on the evaluation of chemical analysis, Mössbauer, and XRD data.

The DTA-TG curves of tin oxalate showed the first exothermic process in temperature up to about 630 K with mass loss. This process went in two steps with loss of about 49.8% of the original mass. The observed further part of the process went without mass loss. The calculated mass loss corresponds to the decomposition of  $\text{SnC}_2\text{O}_4$ . The character of the DTA curve showed that the decomposition went through tin carbonate by evolution of  $\text{CO}_2$  and formation of  $\text{SnO}$  (because in case of the presence of oxygen the decomposition products undergo oxidation) at the end of the thermal decomposition process.

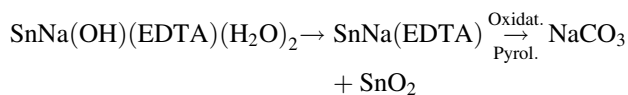
Based on these data the following path of thermal decomposition is proposed:



The thermal decomposition character of tin oxalate is similar to that known for calcium oxalate.

The DTA-TG curves of tin sodium EDTA showed an endothermic process with mass loss of about 40% up to the temperature of 525 K with a peak at 490 K. This process is due to the evolution of hydrate bound water and OH groups, respectively. The fact that up to 480 K the TG curve showed no mass loss indicated the rapid character of this dehydration process. Immediately following the dehydration reaction a series of further thermal events exists in the temperature range of 490–790 K with mass loss, and they are related to the stepwise pyrolysis of the anhydrous complex. The latter process proceeds stepwise as it is evident by the number of observed peaks belonging to the decomposition/oxidation of the ligands. The process which exists in the temperature range of 820–915 K, with intense exothermic peak at 870 K, is due to the formation of the  $\text{SnO}_2$  at the end of the thermal decomposition of the material. In general, these results show a quite comparable picture with data observed by Wendlandt and Horton [14] for some transition metal containing EDTA complexes.

In agreement with the above data, the following path of thermal decomposition may be proposed:



On the DTA-TG curves of tin sodium inositol-hexaphosphate was found an endothermic process between room temperature and 490 K, due to the loss of hydrate bound water and decompose of the material. This

process accompanied with about 10% mass loss. The sharp exothermic process, going practically without mass loss, in the temperature range of 680–750 K with peak at 700 K belongs to the decomposition and parallel oxidation of the organic part of the molecule. At the end of this process, there exists a mixture of phosphorous pentaoxide, sodium carbonate, and tin dioxide.

## Summary

In the synthesis of the end products of the investigated materials, the tin existed primarily in oxidation states of two (oxalate) and in four due to the circumstances of the preparation. The XRD analysis showed that the tin oxalate and tin sodium EDTA complex are crystalline, while the tin sodium inositol-hexaphosphates is amorphous. The tin oxalate had orthorhombic, and the tin sodium EDTA complex had monoclinic sheet type structure. The FTIR results gave support to the above identification of the samples.

Based on the identification, analytical and thermal analysis data for the description of end products of the synthesis, the following formulas could be proposed:  $\text{SnC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$  for oxalate,  $\text{SnNa}(\text{OH})(\text{EDTA})(\text{H}_2\text{O})_2$  for tin sodium EDTA complex, and  $\text{C}_6\text{H}_6\text{SnNa}_8\text{O}_{24}\text{P}_6$  for tin sodium inositol-hexaphosphates.

The tin oxalate decomposed into steps through carbonate by evolution of  $\text{CO}_2$  and formation of  $\text{SnO}$  at the end of process. The EDTA complex lost its hydrate bound water up to 525 K. It followed the pyrolysis of the anhydrous salt. This process goes stepwise due to the decomposition/oxidation of the ligand. The strong exothermic process that existed in the temperature range of 840–915 K was due to the formation of  $\text{SnO}_2$ . These results are quite comparable with that found earlier [14] for some transition metal containing EDTA complexes. The tin containing sodium inositol-hexaphosphate in first stage lost its hydrate bound water till 460 K. During this process, the material loss was about 10% of its original mass. The mentioned process followed with a sharp exothermic one going practically without mass loss. The latter process finished at 750 K, belonging to the decomposition and parallel oxidation of

the organic part of the molecule. At the end of this process, existed a mixture of phosphorous pentaoxide, sodium carbonate, and tin di-oxide.

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