

HETEROLEPTIC TRI-*TERT*-BUTOXYSILANETHIOLATE COMPLEXES OF MANGANESE(II)

Thermal studies

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The thermal behavior of Mn(II) silanethiolate series $[\text{Mn}(\text{SR})_2\text{L}(\text{MeOH})_n]$, where $R=\text{SSi}(\text{O}i\text{Bu})_3$, L =heterocyclic nitrogen base and $n=0, 1$ or 2 has been comparatively investigated using differential scanning calorimetry (DSC), thermogravimetry (TG) and TG-infrared spectroscopy (IR) techniques. The TG curves indicate the differences in the thermal decomposition due to presence of distinct N-donor ligands and labile MeOH molecules coordinated to the central atom. The first step on the TG curves (60–110°C) corresponds to the elimination of alcohol from respective complexes. The main step (150–350°C) can be assigned to the decomposition of the complexes yielding Mn_3O_4 and silica as the main final products, identified by X-ray diffraction patterns.

Keywords: manganese(II) complexes, metal thiolates, pyridine, silanethiolate, thermal analysis

Introduction

Thiolate complexes still attract much attention, since they can be widely used in medicine, agriculture, industry or analytical and organic chemistry [1]. Model compounds of several biologically relevant species [2] should be also mentioned. The knowledge of thermal behavior is a very important feature especially in industry since a given substance must be sufficiently stable for an effective action. Therefore, the interest in the stability of thiolates has been recently greatly enhanced because of their utilization as catalysts [3] or precursors of sulfides thin films [4].

TG is the simplest method that can be utilized to determine the compound stability within the given temperature range or the mode of its thermal decomposition. Not only the well-established thermogravimetry but also DSC techniques have been reliably used over last decades in characterization of many organic compounds (particularly solids) as well as studying the thermal behavior and properties of various types of complexes and evaluating the thermal parameters for their degradation processes [5]. Numerous coordination compounds of transition metals with S-donor ligands have been investigated nevertheless the thermal analysis in the case of earlier transition elements comparing to the later 1st row ones seems to be undeveloped. It is associated with a small number of known S-donor ligated complexes formed

by the 'a' class metals which show greater affinity to ligands with hard oxygen than soft sulfur atom. The thermal behavior of complexes (mainly with O-donors) based on Mn(II) is widely discussed in the literature [6–8] what is in sharp contrast to Mn(II) thiolate complexes. Till now, the conditions of thermal decomposition of various complexes of manganese(II) with such rests as thiolate have not been studied. A survey of the available literature also shows that relatively little work on thermal decomposition of other complexes with Mn–S bond [9–14], as well as silanethiolates [15] has been done so far. Recently, we have reported on syntheses of a series of heteroleptic manganese(II) tri-*tert*-butoxy-silanethiolates incorporating solvent molecules (MeCN, MeOH) [16], chelating N-donors (phen, bipy, neo) [17] and monodentate N-donor ligands (Py, MePy, ImH, etc.) [18, 19] as coligands. What more, we have found that the complex with 2-methylimidazole is in fact a N–H⋯S hydrogen bonded assembly of two complexes $[\text{Mn}\{\text{SSi}(\text{O}i\text{Bu})_3\}_2(2\text{-MeIm})]$ and $[\text{Mn}\{\text{SSi}(\text{O}i\text{Bu})_3\}_2(2\text{-MeIm})(\text{MeOH})]$ [18]. The last one has MnNOS₂ core closely related to the ZnNOS₂ kernel of horse liver alcohol dehydrogenase catalytic site. Now, we have focused our attention on thermal properties of these species, since this is one of the most important factors, which have to be considered if we want to think about application of these

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complexes. This work presents the results obtained when a series of 11 manganese(II) silanethiolate complexes (**2–12**) with various additional N-donor ligands have been investigated using TG, DSC and TG coupled with IR.

Experimental

Complete details of the syntheses and characterization of the title complexes as well as their structure are published elsewhere [16–19]. Table 1 presents the formulae of studied compounds.

Thermal analysis (TG and DTG curves) was performed using PerkinElmer Thermogravimetric Analyzer TGA Pyris 1 at a heating rate of $20^{\circ}\text{C min}^{-1}$ under nitrogen flow and heating program 25–600 $^{\circ}\text{C}$.

DSC measurements were made using PerkinElmer DSC 7 for encapsulated (aluminum pans) samples of ca. 3–10 mg at a heating rate of $20^{\circ}\text{C min}^{-1}$ under nitrogen flow. Samples were heated to melting point (pre-determined using automatic Stuart MP3 device) and then cooled. The second melting scan was also performed. The calibration of the temperature and heat flow scales at the same heating rate was performed with In and Zn.

Thermal analysis coupled with IR was performed in a flow of argon using Netzsch thermobalance TG 209 coupled with Bruker IFS66 FTIR spectrometer. Approximately, 10 mg samples were contained in an Al_2O_3 crucible. The volatiles evolving from the heated sample were transported to the spectrometer chamber via thermostated pipe in the stream of argon.

Infrared spectra of solid residues were recorded on a FTIR Mattson Genesis II Gold, externally controlled by WinFirst software. Spectra were registered in solid state (KBr pellet) in the range 4000–400 cm^{-1} .

The final products of thermal decomposition process were obtained in an oven at the same temperature and atmosphere that they appeared in the TG curves. After 15 min they were cooled down and kept in a desiccator under vacuum. The X-ray patterns of the crystalline residues were recorded in the room temperature using X'Pert Philips diffractometer (source radiation: $\text{CuK}_{\alpha 1}$, $\lambda=0.1546$ nm, 40 kV, 30 mA). For characterization and qualitative analysis the results were compared with standard data from the International Centre for Diffraction Data [20].

Results and discussion

Recently we synthesized and described the structure of a series of manganese(II) silanethiolate complexes, among them species with solvent molecules as coligands, e.g., $[\text{Mn}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(\text{MeOH})_4]$ **1**. Unfortunately **1** was extremely unstable and quickly decomposed, what actually can be considered as a typical property of a hitherto sparse Mn(II) thiolates. In the search of a more stable species we decided to synthesize complexes with additional N-donor ligands such as bipyridine, imidazole or pyridine and their derivatives. Here we discuss the thermal stability of complexes **2–12** and describe their thermal decomposition with emphasis on dependence between structure and thermal stability, what is a key factor for applicability of these systems.

Heteroleptic Mn(II) silanethiolates with chelating heterocyclic bases as coligands

The TG-DTG curves, which characterize the thermal decomposition of the heteroleptic Mn(II) silanethiolate complexes **2–5** are given in Fig. 1 (a, b respectively). The results are summarized in Table 2. The differences in the thermal decomposition behav-

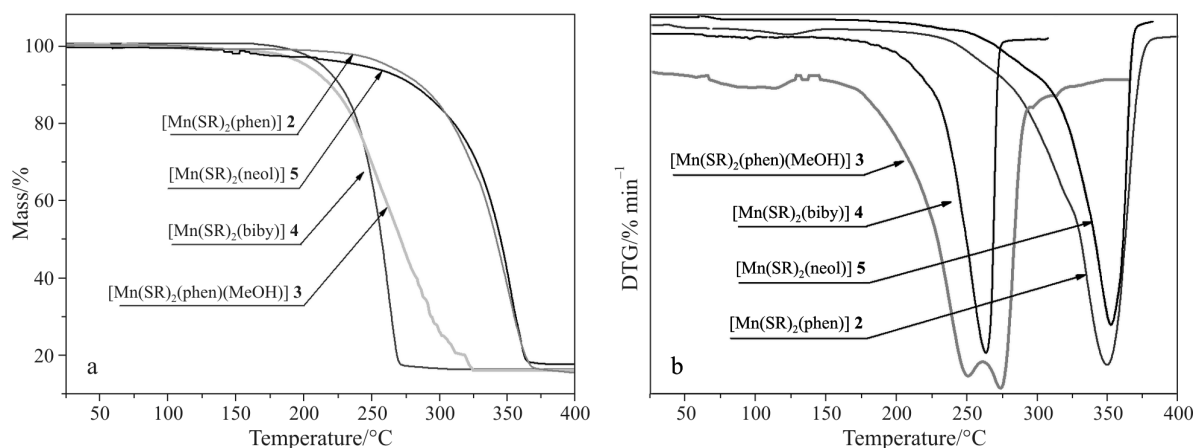


Fig. 1 a – TG and b – DTG curves for **2–5** measured in dynamic nitrogen atmosphere

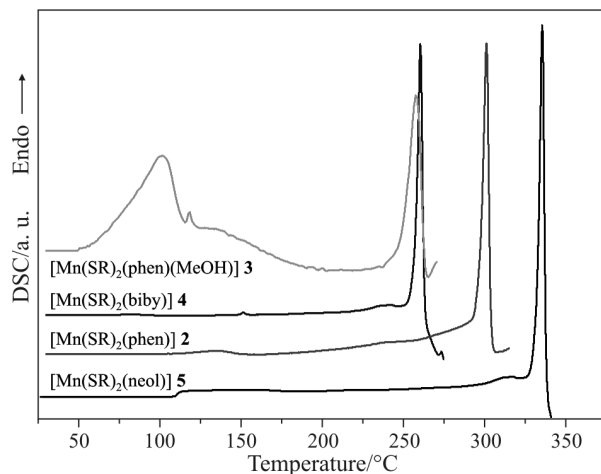
Table 1 Complexes of $[\text{Mn}\{\text{SSi}(\text{O}i\text{Bu})_3\}_2(\text{L})(\text{MeOH})_n]$ type

| | | | |
|-------------------------|-------------------------|-------------------------|---------------------|
| | | | |
| L=phen, n=0 2 | L=phen, n=1 3 | L=biby, n=0 4 | L=neo, n=0 5 |
| | | | |
| L=1-MeIm, n=0 6 | L=Im, n=0 7 | L=2-MeIm, n=1 8* | L=Py, n=2 9 |
| | | | |
| L=2-MePy, n=2 10 | L=3-MePy, n=0 11 | L=4-MePy, n=0 12 | |

Note: H atoms from C-H bonds have been omitted for clarity; hydrogen bonds are presented as dotted lines
 *Compound **8** is an assembly of two distinct complexes [15]

Table 2 Comparison of main thermal parameters of compounds 2–5

| Complex | DSC $T_{\max}/^{\circ}\text{C}$ | DSC T range/ $^{\circ}\text{C}$ | DSC $\Delta H/\text{kJ kg}^{-1}$ | DTG $_{\max}/$ $^{\circ}\text{C}$ | DTG T range/ $^{\circ}\text{C}$ | Total mass loss found/% | Solid decomposition products |
|---------|------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|--------------------------------------|----------------------------|---|
| 2 | 301.1 | 297–303 | 44.91 | 349.6 | 211–386 | 84.4 | SiO ₂ , Mn ₃ O ₄ , MnS, Mn |
| 3 | 101.4 | 56–105 | 36.78 | 89.8 | 64–130 | 84.0 | SiO ₂ , Mn ₃ O ₄ , MnS, SiS ₂ |
| | 258.1 | 242–260 | 27.37 | 250.4 | 273.4 | | |
| 4 | 260.4 | 256–262 | 79.4 | 263.3 | 175–280 | 83.6 | SiO ₂ |
| 5 | 335.7 | 334–337 | 136.8 | 351.7 | 157–376 | 82.4 | SiO ₂ , Mn ₃ O ₄ |

**Fig. 2** DSC curves for 2–5 recorded in dynamic nitrogen atmosphere

ior of these complexes are evident. Close examination of the TG-DTG curves (Fig. 1) reveals that in the case of 2, 4 and 5 a decomposition process proceeds in one-step (at the 211–386°C range for 2, at the 175–280°C range for 4 and at the wide 157–376°C range in the case of 5). In the case of methanol containing compound 3 its decomposition proceeds in two consecutive steps. In the first step elimination of approximately 1 mol of MeOH per 1 mol of 3 (mass loss found 3.6%; calculated 3.88%) is observed using not only TG, but also DSC measurements (Fig. 2). The maximum rate of alcohol detach takes place at about 100°C. Decomposition of the complex continues in the second step, represented by a sharp slope on the TG curve. It should be noted that complex 3 dried at room temperature in a stream of argon simply eliminates methanol and yields complex 2 [17]. It is evident that under applied thermal conditions the elimination of methanol from 3 does not simply lead to the transient formation of 2 since the second decomposition step of 3 is different from that observed for 2.

The TG curve recorded for [Mn{SSi(OBu^t)₃}₂(neo)] 5 is very similar to the one for phenanthroline derivative 2, but the thermal degradation starts at slightly lower temperature.

Changes in the heat flow during process of controlled heating were studied by means of Differential Scanning Calorimetry. The first heating scan, cooling and the second heating run were registered. In Fig. 2 the first heating scan is presented since all examined compounds melt with decomposition and recorded sharp peaks refer to slopes on TG curve.

Thermal stability of [Mn{SSi(OBu^t)₃}₂(N–N)] series (where N–N=phen, bipy, neo) can be thus ordered in relation to the heterocyclic bases (N–N) used as: neo (5) > phen (2) > bipy (4). In the case of compound with MeOH molecule coordinated to manganese (3) the process takes place in lower temperature range and a peak with maximum at about 101°C represents endothermic process of MeOH evolving.

For compounds 2, 4 and 5 also mass spectra were recorded [17]. Although parent ions could not be seen, the spectra give us some insight into the possible fragmentation pattern through elimination of OBU^t and Si–OBU^t fragments from tri-*tert*-butoxysilanethiolate ligand. It is worth mentioning that such fragmentation mode is different from that observed for closely related complexes but with Cd [21] and Zn [22] in the metallic center, where the main fragmentation pattern is characterized by stepwise elimination of butene (*m/z* 56) molecules.

XRD measurement have shown that the final products of thermal decomposition of manganese(II) silanethiolate complexes containing chelating bases as additional ligands consists mainly of manganese oxide and silica. This corresponds well with strong IR absorption ($\nu(\text{Si–O})$ 1080 cm⁻¹) found in spectra of the solid residues. Small quantities of sulfur, silicon disulfide, manganese sulfide and metallic Mn are also present (Fig. 3).

Thermobalance coupled with FTIR spectrometer allowed the recording of IR spectra of volatiles released during decomposition process (Figs 4, 5). One can see, e.g., that during the initial steps of thermogravimetric analysis methanol released in the case of 3 can be found in IR spectra ($\nu(\text{O–H})$ 3650 cm⁻¹, $\nu(\text{C–H})$ 2983 cm⁻¹, 2888 cm⁻¹). At higher temperatures fragments of heterocyclic bases (about 200°C, $\nu(\text{C–H})$ 3022 cm⁻¹) and tri-*tert*-butoxysilyl

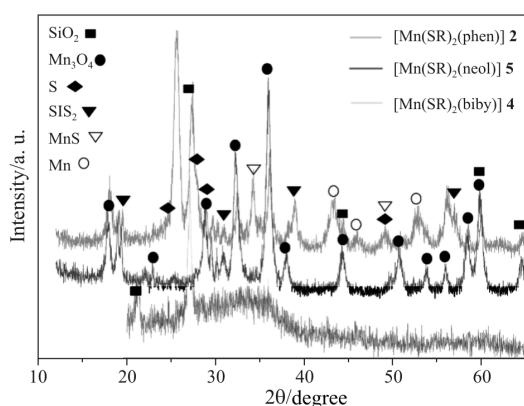


Fig. 3 XRD patterns for products of thermal decomposition of **2**, **4** and **5**

rest ($\nu(\text{C-H})$ 2981 cm^{-1} , $\nu(\text{Si-OC})$ 1078 cm^{-1} , Fig. 5) are evolved from **3** and **5**. IR spectra of volatiles evolving during TG analysis of all three $[\text{Mn}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(\text{N-N})]$ complexes are in fact quite similar (Fig. 4) suggesting an analogous decomposition pathway.

in the first decomposition steps. Table 3 compares characteristic thermal parameters taken from the TG, DTG and DSC curves. Mass losses obtained from the TG curves and those calculated for the corresponding molecules are in relatively good agreement as is the case of all investigated species **2–12**. The XRD measurements confirmed that compounds **6–8** decompose with the formation of silica and manganese oxide as the main end product.

Heteroleptic Mn(II) silanethiolates with pyridine and picolines as coligands

The process of decomposition of manganese(II) silanethiolate complexes incorporating pyridine and its methyl substituted derivatives is presented in Fig. 8. In the case of methanol containing complexes **9** and **10** the first steps of decomposition indicate the loss of alcohol molecules. It is observed in the TG curves of **9** and **10** at 60–80°C range with the maximum rate of mass loss in the DTG curves at temperatures of 70.3 and 65.5°C respectively. In the first step

Fig. 4 3D IR spectra of volatiles evolving during TG analysis in the function of temperature for a – $[\text{Mn}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(\text{phen})]$ **2**, b – $[\text{Mn}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(\text{phen})(\text{MeOH})]$ **3**, c – $[\text{Mn}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(\text{bipy})]$ **4** and d – $[\text{Mn}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(\text{neo})]$ **5**

Heteroleptic Mn(II) silanethiolates with molecules possessing imidazole ring as coligands

Manganese(II) silanethiolate complexes incorporating imidazole and its methyl derivatives (**6–8**) decompose progressively (Fig. 6). First, within the temperature range 45–80°C, methanol molecules are eliminated from **7** and **8**. The corresponding endothermic peaks in the DSC curve are visible at 65–75°C range. Due to the presence of distinct alcohol types – only solvating in **7** but one solvating and one ligating in **8** – both compounds lose methanol differently. The alcohol-free complex **6** begins to decompose at higher temperature range 150–310°C, with slow elimination of N-donor molecules coordinated to metallic center

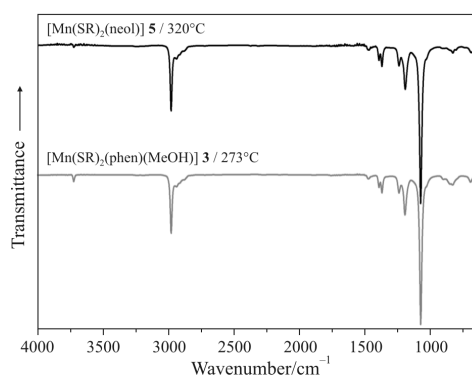


Fig. 5 IR spectra of volatiles evolving during TG analysis of $[\text{Mn}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(\text{phen})(\text{MeOH})]$ **3** and $[\text{Mn}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(\text{neo})]$ **5**

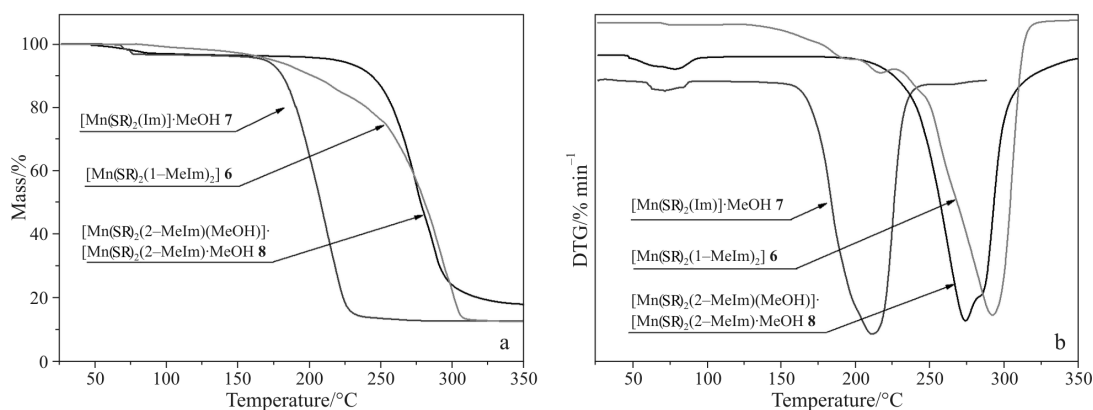


Fig. 6 a – TG and b – DTG curves for 6–8 measured in dynamic nitrogen atmosphere

(up to 75°C) approximately 0.5 mol of MeOH per 1 mole of **10** is eliminated (mass loss found 2.1%; calculated 2.07%). The following mass loss is most probably connected with further alcohol release completed at ca. 150°C. The release of methanol molecule from both compounds is confirmed also in DSC experiments (Fig. 9).

In the case of complexes without coordinated solvent molecule the decomposition takes place at

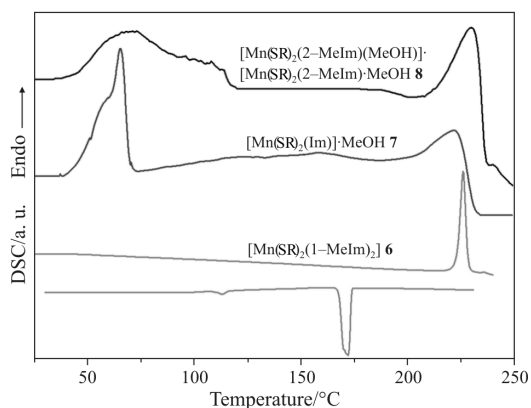


Fig. 7 DSC curves for 6–8 recorded in dynamic nitrogen atmosphere

higher temperature range (146–256°C for **11** and 172–272°C in the case of **12**) what is connected with the simultaneous release of picoline and fragments of tri-*tert*-butoxysilyl group. In fact one can notice a small inflexion on registered DTG curve for **11** and **12** (at 210–215°C range) and then the main step of decomposition with a large and sharp peak. It indicates a rapid and vigorous decomposition feature. The IR analysis of volatiles evolving during decomposition as well as the analysis of solid residues indicated that again similar products as described earlier for other Mn(II) silanethiolates were formed. The main decomposition product in the case of **12** was silica while for **9–11** manganese oxide, however presence of some manganese(II) silicate cannot be excluded. Changes in the heat flow during controlled heating were studied also by means of DSC. In Fig. 9 the first heating scan is presented. Peaks on DCS curve represent melting with decomposition of respective compounds. Performed measurements thus indicate that the thermal stability of $[\text{Mn}\{\text{SSi}(\text{O}i\text{Bu})_3\}_2(\text{N})(\text{MeOH})_n]$ series depends primarily on presence of alcohol molecules and then N-donor ligand used.

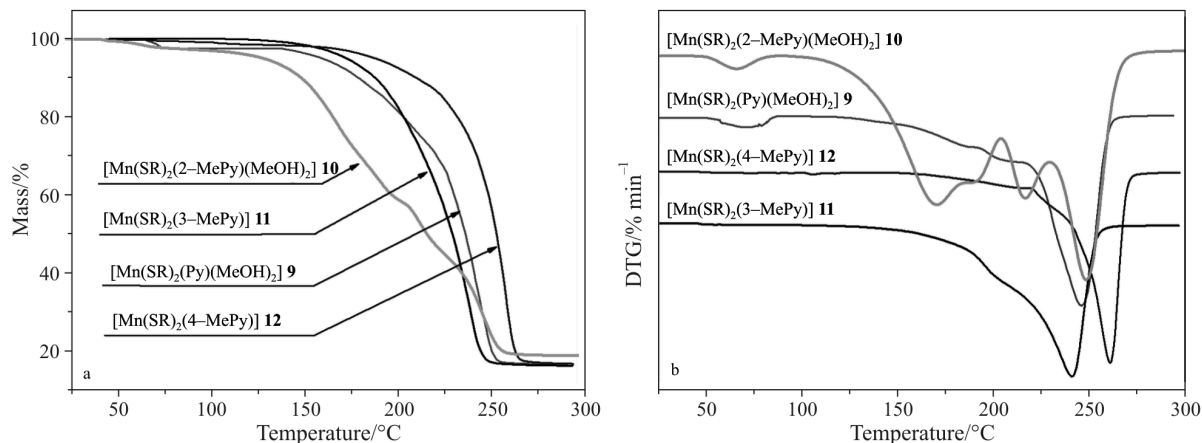


Fig. 8 a – TG and b – DTG curves for 9–12 measured in dynamic nitrogen atmosphere

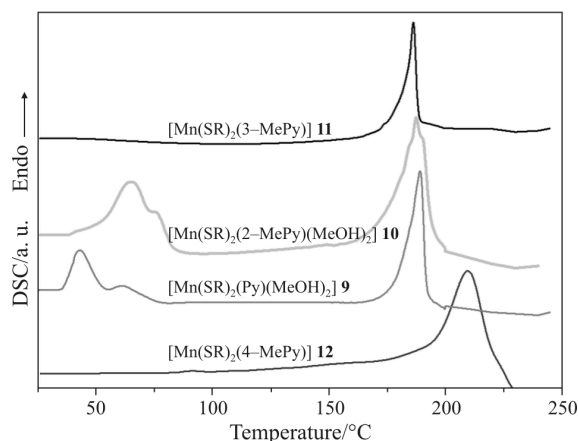
Table 3 Comparison of main thermal parameters of compounds 6–8

| Complex | DSC $T_{\max}/^{\circ}\text{C}$ | DSC T range/ $^{\circ}\text{C}$ | DSC $\Delta H/\text{kJ kg}^{-1}$ | DTG $_{\max}/$ $^{\circ}\text{C}$ | DTG T range/ $^{\circ}\text{C}$ | Total mass loss found/% | Solid decomposition products |
|---------|------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|--------------------------------------|----------------------------|---|
| 6* | 226.0 | 223–228 | 41.0 | 292.6 | 152–311 | 87.2 | SiO ₂ , Mn ₃ O ₄ , MnS |
| 7 | 65.4 | 44–68 | 28.4 | 72.6 | 64–76 | 87.1 | SiO ₂ , Mn ₃ O ₄ |
| | 221.7 | 202–224 | 29.4 | 212.9 | 156–241 | | |
| 8 | 73.2 | 45–76 | 63.1 | 78.8 | 58–72 | 82.0 | SiO ₂ , Mn ₃ O ₄ |
| | 230.5 | 208–235 | 49.3 | 274.1 | 206–338 | | |

*Crystallization parameters for 6: DSC $T_{\max}=171.9^{\circ}\text{C}$; DSC $\Delta H=-13.4 \text{ kJ kg}^{-1}$

Table 4 Comparison of main thermal parameters of compounds 9–12

| Complex | DSC $T_{\max}/^{\circ}\text{C}$ | DSC T range/ $^{\circ}\text{C}$ | DSC $\Delta H/\text{kJ kg}^{-1}$ | DTG $_{\max}/$ $^{\circ}\text{C}$ | DTG T range/ $^{\circ}\text{C}$ | Total mass loss found/% | Solid decomposition products |
|---------|------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|--------------------------------------|----------------------------|---|
| 9 | 62.7 | 37–65 | 22.6 | 70.3 | 67–79 | 83.5 | Mn ₃ O ₄ , SiO ₂ |
| | 189.1 | 177–191 | 57.5 | 245.6 | 134–260 | | |
| 10 | 64.4 | 51–66 | 53.4 | 65.5 | 61–77 | 81.2 | Mn ₃ O ₄ , SiO ₂ |
| | 187.6 | 173–189 | 68.6 | 248.9 | 108–264 | | |
| 11 | 186.1 | 178–192 | 43.1 | 240.5 | 146–256 | 83.5 | Mn ₃ O ₄ , SiO ₂ |
| 12 | 211.1 | 197–213 | 70.2 | 260.5 | 172–272 | 83.5 | SiO ₂ |


Fig. 9 DSC curves for 9–12 recorded in dynamic nitrogen atmosphere

Conclusions

Thermal stability and changes occurring during controlled heating of manganese(II) tri-*tert*-butoxysilanethiolates were investigated by thermogravimetric and calorimetric methods. The measurements revealed that thermal decomposition of manganese(II) silanethiolate complexes containing additional ligands such as N-donor heterocyclic bases and methanol is multistage. Generally the process of methanol elimination occurs in the first step and the decomposition of organic ligands in the next one. The results obtained from the TG and DTG curves confirm therefore the presence of MeOH and the

stoichiometry of the prepared metal complexes. In the investigated case of metal complexes with silanethiolate being S-donor ligand and a group of mutually related N-donor co-ligands, various thermal decomposition behavior and thermal stability are clearly observed. This may be attributed to the differences in N-donors used as well as to the different mode of silanethiolate coordination capable to serve as S-donor, but also as S,O-chelating donor. The shape of endotherms for melting, recorded for manganese(II) silanethiolate species with additional N-donor ligands suggests also, that those compounds can be easily prepared as crystals of good quality and purity. The results obtained using Differential Scanning Calorimetry were compared with those obtained with standard automatic apparatus for melting point determination (again in inert gas atmosphere). Therefore it was possible to confirm finally that changes registered by DSC correspond to the melting of examined species.

Thermal measurements revealed also that manganese(II) silanethiolate complexes with 1,10-phenanthroline, 2,2'-bipyridine and 2,9-dimethyl-1,10-phenanthroline as coligands are especially stable – also in air. These are the first known manganese(II) thiolate complexes exhibiting such high stability in normal conditions. This prompted us to check their applicability in sol-gel related procedures [23] and the vulcanization process of natural rubber systems [24]. Related work is now in progress.

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