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PHYSICAL METHODS OF INVESTIGATION

Thermolysis Specifics of Tin(IV) and Tin(II) Complex Derivatives: Thermolysis of (Acac)$_2$SnX$_2$ (X = Cl, N$_3$), (CO)$_5$MSnCl$_2$(thf) (M = Cr, Mo, W), (CO)$_5$MSn(Acac)$_2$, (CO)$_5$MSn(SCN)$_2$, (CH$_3$)$_4$N(CO)$_5$MoSnCl$_3$ (M = Cr, W), and (CO)$_2$MnCpSnCl$_2$(thf)

Zh. B. Dobrokhotova[a], P. S. Koroteev[a], V. M. Novotortsev[a], M. P. Egorov[b], and O. M. Nefedov[b]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
Leninskii pr. 31, Moscow, 119991 Russia
e-mail: zhdobro@yandex.ru
[b] *Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
Leninskii pr. 47, Moscow, 119991 Russia

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Abstract—Differential scanning calorimetry and thermogravimetry are used to study the thermolysis of following complexes: (Acac)$_2$Sn(N$_3$)Cl (**1**); (Acac)$_2$SnCl$_2$ (**2**); (CO)$_5$MSn(Acac)$_2$ with M = Cr (**3**) or W ((**4**)), (CO)$_5$MSnCl$_2$(thf) with M = Cr (**5**), Mo (**6**), or W (**7**)), (CH$_3$)$_4$N(CO)$_5$MSnCl$_3$ with M = Mo (**8**) or W ((**9**)), (CO)$_2$MnCpSnCl$_2$(thf) (**10**)); and (CO)$_5$MSn(SCN)$_2$ with M = Cr (**11**) or W (**12**). The phase composition of the solid thermolysis products of compounds **1**–**5** and **7**–**12** is determined by X-ray powder diffraction. Thermolysis schemes are suggested.

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Studies of solid-phase thermal transformations in organometal and molecular coordination compounds during the last three decades became an autonomous field of coordination chemistry. The comprehensive analysis of the synthesis of materials via organometal compounds (molecular precursors) is underway. These processes are considered in relation to the structure, reactivity, and stability of organometal derivatives [1–3].

Previously [4], we studied the thermolysis of several germanium(II) complexes with transition-metal carbonyls and acetylacetonatogermanium(IV) derivatives. We showed that the aforementioned compounds can serve as potential precursors for functional materials, in particular, for some intermetallic compounds and germanium nitride. Here, we consider the thermolysis of several tin(II) and tin(IV) complexes.

EXPERIMENTAL

Compound (Acac)$_2$Sn(N$_3$)Cl (**1**) was synthesized for the first time as follows. To 300 mg (1.3 mmol) of (Acac)$_2$SnCl$_2$ and 507 mg (7.8 mmol) of NaN$_3$, 25 mL of absolute thf was added. The reaction mixture was stirred for 5 days at room temperature; then, the solution was filtered and the solvent removed in vacuum. The product was obtained as a colorless substance. Yield: 220 mg (43%). The structure of compound **1** was verified by IR and mass spectra. The IR spectrum was recorded on a Bruker IFS-13V instrument. The mass spectrum was recorded on a Finnigan MAT INCOS instrument (electron impact, 70 eV).

IR spectrum, cm^{-1}: 2089 s (N$_3$), 1590 m (C=O), 1390 m (C=C), 1060 m (C–C), 920 m (C–H).

Mass spectrum, *m*/*z*: 360 [M–Cl]$^+$, 353 [M–N$_3$]$^+$, 318 [M–Cl–N$_3$]$^+$, 254 [M–N$_3$–Acac]$^+$, 219 [M–N$_3$–Acac]$^+$.

Compounds **2**–**12** were synthesized by known procedures: compound **2** [5], compounds **3** and **4** [6], compounds **5**–**7** [7], compounds **8** and **9** [8], compound **10** [9], and compounds **11** and **12** [10]. The thermolysis of compounds **1**–**12** was studied by DSC and TG on a Mettler TA-3000 thermoanalyzer equipped with DSC-20 and TG-50 units. The experiments were carried out at a fixed heating rate (5 K/min) under a dry argon atmosphere. In the DSC experiments, samples were heated in aluminum containers; in the TG experiments, in alundum crucibles. Sample sizes did not exceed 16 mg. The weight change upon heating was controlled directly in the TG-50 unit; the weighing accuracy was $\pm 2 \times 10^{-3}$ mg. For each compound, five replicate experiments were performed. The final results were obtained by statistical data processing. The proportions of tin and SnCl$_2$ in the thermolysis products

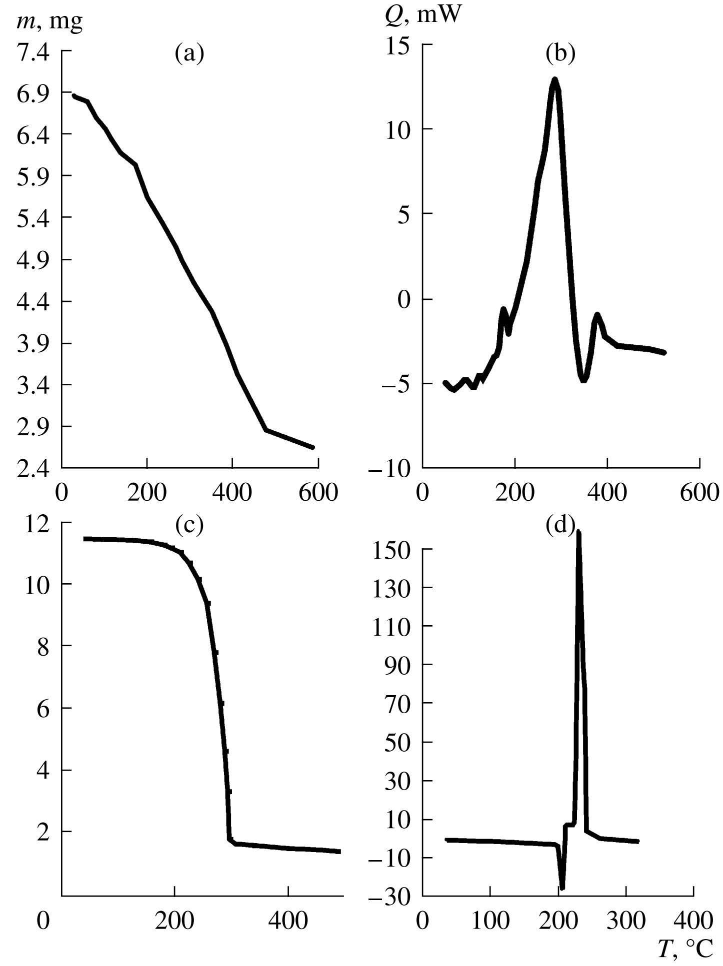

Fig. 1. Sample weight and heat flux vs. temperature for the thermolysis of (a, b) complex **1** and (c, d) complex **2**.

were derived from the heats of melting in the DSC experiments.

RESULTS AND DISCUSSION

Previously [11], we isolated and structurally characterized the complex $(Acac)_2Ge(N_3)_2$, the first β-diketonate of a Group IV element containing azide ligands. We used the exchange reaction between $(Acac)_2SnCl_2$ and NaN_3 in thf to synthesize the complex $(Acac)_2SnCl(N_3)$ (**1**), a new representative of this type of compound. Attempts to obtain complex $(Acac)_2Sn(N_3)_2$, the product of the substitution for the second chlorine atom in complex **1**, by the reaction in acetonitrile (a more polar solvent) were unsuccessful.

The thermal study of complex **1** showed that it is thermally stable only until 55°C (Figs. 1a, 1b). At higher temperature, decomposition starts; in the range 55–150°C, the weight loss with attendant energy absorption is 10.0 ± 1.0%, which corresponds to the nitrogen content of the complex. The ease of nitrogen elimination implies that tin azides can serve as precursors for stannylenes and other unstable species in mild thermolysis.

The thermolysis of complex **1** progresses over a wide temperature range (150–520°C) and is accompanied by energy evolution. The weight loss over the whole range of the temperatures studied is 60.0 ± 2.0%. X-ray powder diffraction showed that the solid product of the decomposition of complex **1** is a mixture of tin and $SnCl_2$. Their proportions were quantified by DSC in the range 170–270°C (Fig. 2). The melting of both components of the mixture was observed. The separate integration of the DSC peak for the thermolysis product gave the following result: (1) $T = 231.7°C$ and $\Delta_m H° = 41.40 \pm 0.62$ J/g for tin, and (2) $T = 247.0°C$ and $\Delta_m H° = 29.80 \pm 0.45$ J/g for $SnCl_2$. Therefore, we can claim that the thermolysis product contains tin and $SnCl_2$ in the ratio 2.5 : 1 mol/mol. Although the gaseous thermolysis products of complex **1** were not analyzed, from the thermogravimetric study and the composition of the solid residue and from the results reported in works [12–14], we can suggest the following likely scenario for the thermolysis of complex **1**:

$$\begin{aligned}(\mathrm{Acac})_2\mathrm{SnCl(N_3)} &\longrightarrow 0.625\mathrm{Sn} + 0.250\mathrm{SnCl_2}\\ &+ 0.125\mathrm{SnCl_4}\uparrow + 1.5\mathrm{N_2}\uparrow + 2\mathrm{CH_2CO}\uparrow\\ &+ \mathrm{CH_3COCH_3}\uparrow + \mathrm{C_2H_4}\uparrow + \mathrm{CO}\uparrow.\end{aligned}$$

We were interested in the comparison of thermolysis data for complex **1**, with its azide fragment which readily generates N_2, and the structurally similar $(Acac)_2SnCl_2$ (complex **2**) which however contains strongly bound apical chlorine atoms.

Compound **2** is stable to 180°C (Figs. 1c, 1d). Above, the decomposition starts, initially accompanied by energy absorption. Qualitatively, the energy pattern of the thermolysis after nitrogen elimination (Fig. 1) is similar to the pattern observed in the thermolysis of $(Acac)_2SnCl(N_3)$ after nitrogen elimination, but all processes occur at lower temperatures and within a narrower temperature range. At 205°C , complex **2** melts with decomposition. Above 225°C, vigorous energy evolution starts in the background of continuing weight loss, which is usually observed upon the formation of a new structure. The process is complete at 300°C. The weight loss is 85.2 ± 1.0%. The X-ray powder diffraction analysis of the solid thermolysis product showed metallic tin. The DSC study of the thermolysis product showed $T_m = 231.4 \pm 0.5$°C with $\Delta H_m = 58.55 \pm 0.75$ J/g, which agrees with the parameters of metallic tin and verifies the product composition. The results enable us to suggest the following likely scenario of thermolysis for complex **2**:

$$\begin{aligned}(\mathrm{Acac})_2\mathrm{SnCl_2} &\longrightarrow 0.5\mathrm{Sn} + 0.5\mathrm{SnCl_4}\uparrow\\ &+ 2\mathrm{CH_2CO}\uparrow + \mathrm{CH_3COCH_3}\uparrow + \mathrm{C_2H_4}\uparrow + \mathrm{CO}\uparrow.\end{aligned}$$

Thus, the thermolysis of two acetylacetonatotin(IV) complexes was studied. These compounds have relatively low decomposition and melting temperatures. Therefore, similar compounds can serve as molecular precursors for phases of a certain composition, whose nature is determined by the substituents at the tin atom.

To compare the thermolysis routes and the compositions of the final solid products for tin(II) and tin(IV) complexes, we studied the thermolysis of CO)$_5$CrSn(Acac)$_2$ (complex **3**) and (CO)$_5$WSn(Acac)$_2$ (complex **4**).

Both compounds melt upon heating (at 91.0 ± 0.5°C for complex **3** and 85.2 ± 0.5°C for complex **4**) with simultaneous decomposition (Fig. 3). Compound **4** loses 2.3 ± 1.0% of its weight upon melting; for compound **3**, the weight loss is 4.1 ± 1.0%. The decomposition is staged. The first stage for both compounds is accompanied by energy absorption and ends by 180.0 ± 2.0°C. The weight loss for compound **3** constitutes 35.3 ± 1.0%, likely corresponding to the removal of 5/6Cr(CO)$_6$ (the calculated amount of Cr(CO)$_6$ that can form upon (CO)$_5$CrSn(Acac)$_2$ decomposition is 35.60% of the starting weight). For complex **4**, the weight loss is 40.5 ± 1.0%; likely, this loss corresponds to the removal of 0.7W(CO)$_6$ and 0.8CO (the calculated content of these products in complex **4** is 41.60 wt %). Above 180°C the weight loss progresses and ends at 330.0 ± 5.0°C for complex **3** and 360.0 ± 5.0°C for complex **4**. At the second stage, for both compounds the process is accompanied by the evolution of a significant amount of energy, which usually signifies the formation of new structures. The weight loss in the range of the temperatures studied is 72.0 ± 2.0 and 70.0 ± 2.0% for complex **3** and **4**, respectively.

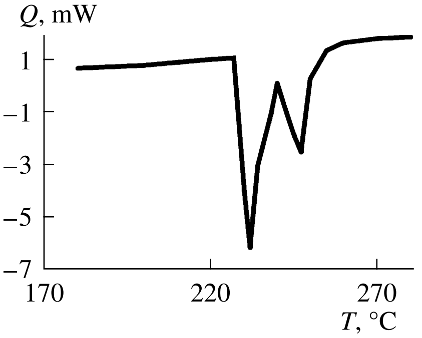

Fig. 2. Thermoanalytical curve for the thermolysis product of complex **1** in the range170–270°C.

The phase analysis of the thermolysis products showed SnO and Cr_2Sn_3 for complex **3**, and SnO and tungsten for complex **4** (Table 1).

We can propose the following thermolysis scenario for the compounds in question. At the first thermolysis stage, whole carbonyl molecules are eliminated (i.e., M=Sn bonds dissociate to an appreciable degree), and carbonyl decomposition occurs. Thermogravimetric data prove an argument in favor of this scenario. At the second stage, the coordination bonds are broken and new structures are formed.

Likely, the significant exotherm associated with tin(IV) reduction to tin(II) is a means for overcoming the energy barrier to tin(II) reduction to the metal via acetylacetonato ligands during the thermolysis of acetylacetonatotin(IV) derivatives. It is for this reason that the thermolysis of complexes **1** and **2** produces metallic tin, which is absent in the thermolysis of complexes **3** and **4**.

The intermetallic compound Cr_2Sn_3 is one thermolysis product of complex **3**. Many similar compounds have useful physicochemical properties, in particular, magnetic properties; synthesis from constituent elements, the conventional method for preparing intermetallic compounds, requires high temperatures and pressures.

In this context, we were interested in studying the thermolysis of other complexes in which tin atoms are

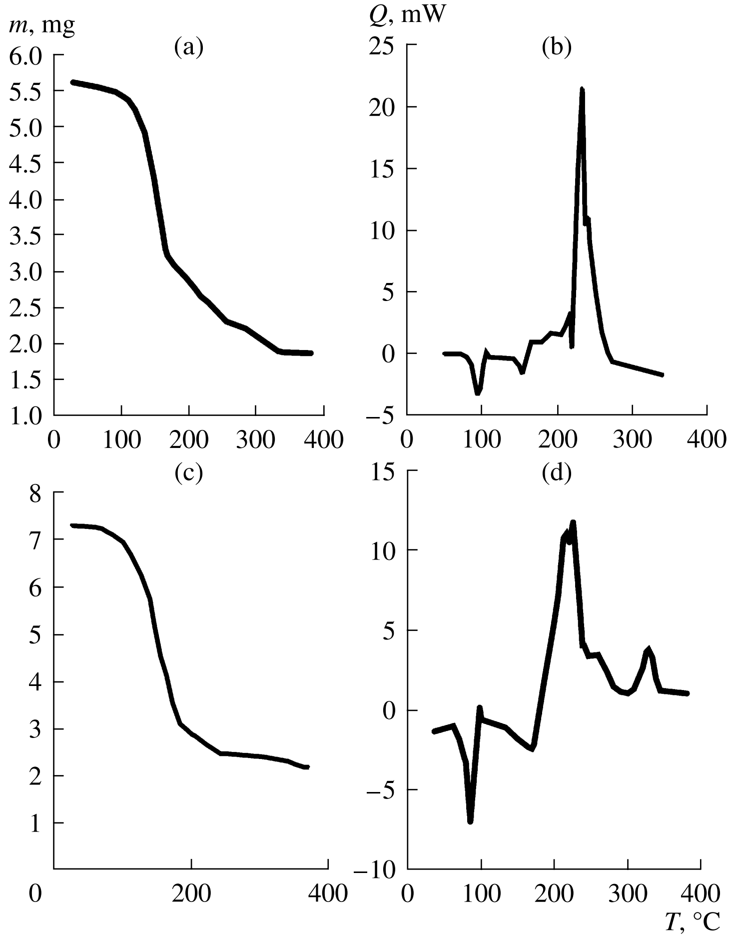

Fig. 3. Sample weight and heat flux vs. temperature for the thermolysis of (a, b) complex **3** and (c, d) complex **4**.

covalently bonded to various transition-metal atoms and in which ligands can readily leave their coordination sphere. We studied previously the thermolysis of dichlorogermylene complexes with group **VI** carbonyls $(CO)_5MGeCl_2(thf)$ (M = Cr, Mo, W) [4]. The thermal study of analogous dichlorostannylene complexes $(CO)_5MSnCl_2(thf)$ with M = Cr (complex **5**), Mo (complex **6**), and W (complex **7**) showed that compounds **5** and **7** are thermally more stable than their dischlorogermylene analogues: these compounds decompose starting at higher temperatures (87.0 ± 1.5°C for complex **5** and 95.5 ± 1.5°C for complex **7**; Fig. 4), while the thermal stability of the $SnCl_2$ complex with molybdenum carbonyl (complex **6**) is virtually comparable with the thermal stability of the germanium analogue. Compounds **5**–**7** melt while decomposing; therefore, the adequate determination of their temperatures and heats of melting is impossible. The first decomposition stage for compounds **5**–**7** is the elimination of the thf molecule. The theoretical thf content in complex **5** is 15.9%; in complex **6**, 14.4%; and in complex **7**, 12.3%. It is impossible to clearly determine the finish temperature of the first stage from integral TG curves. Therefore, we used differential TG curves, which were obtained using the Mettler program package (Figs. 4c, 4f, 4i). The end temperature of thf removal is 108 ± 1°C for complex **5**, 81 ± 1°C for complex **6**, and 110 ± 2°C for complex **7**. The relevant weight loss is 15.4 ± 0.5% for complex **5**, 13.8 ± 1.0% for complex **6**, and 12.9 ± 1.0% for complex **7**; within the experimental error, these values correspond to the theoretical thf percentage. When samples of complexes **5** and **7** are heated above 110°C, they actively lose their weight; for complex **7**, this is accompanied by energy evolution. For compound **5**, the decomposition progresses with energy evolution; above 125°C, the destruction occurs with energy absorption (it is noteworthy that the temperature derivative of the weight curve changes its run at this temperature; Fig. 4c). The destruction of compound **5** ends with energy evolution. Probably, these distinctions in the energy patterns of the thermolysis are due to the fact that the weight loss at temperatures above the end of the first stage is mainly due to the loss of CO ligands. Extra M–M bonds can appear during the staged decarbonylation of complexes; for 3*d* metals, these bonds are far weaker than for 4*d* or 5*d* metals. In addition, the possi-

Table 1. Phase composition of the thermolysis products of compounds **3** and **4**

Thermolysis product of **3**		Thermolysis product of **4**		SnO [24-1342]*		Cr_2Sn_3 [19-0333]*		W [47-1319]*	
d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
2.9000	100	2.9384	80	2.900	80	2.903	80		
2.8040	60	2.8055	60	2.780	80				
2.6460	80	2.6580	30	2.630	100	2.688	80		
2.5910	30					2.599	80		
		2.5500	10					2.525	26
2.2320	5	2.2350	30	2.24	10			2.258	100
2.1285	5			2.12	10				
2.0815	40					2.097	100		
		2.0600	40					2.062	96
1.9755	10	1.9655	10	1.950	30				
1.7745	10			1.750	20				
		1.4485	10					1.458	14

* Here and in Tables 2 and 4–6, taken from the JCPDS PDF database, International Center for Diffraction Data, PCPDFWIN.

bility of formation of multiple bonds, which are characteristic of tungsten, cannot be ruled out [15]. Most likely, it is for this reason that the energy consumed in the decarbonylation of complex **7** is compensated by the energy of formation of new bonds. When samples of compound **6** are heated to temperatures higher than required for removing thf (81°C), subsequent destruction occurs with energy absorption.

The phase analysis showed $SnCl_2$, Cr_2Sn_3, and Cr in the solid thermolysis product of compound **5** and $SnCl_2$ and W in the product of compound **7** (Table 2). The phase analysis of the thermolysis product of complex **6** was not carried out. The $SnCl_2$ percentage in the thermolysis product was derived from the DSC heat of melting of the final thermolysis products (Table 3). For compound **5**, the thermolysis product contains three phases; only $SnCl_2$ was quantified, while the Cr and Cr_2Sn_3 percentages can be derived from the intensity ratio of the main reflections in the X-ray diffraction pattern: the intensity ratio is 1 : 1, and we can claim that Cr and Cr_2Sn_3 in the product are in the ratio 1 : 1 (wt/wt). The following thermolysis scheme can be proposed for complex **5**:

$$12(CO)_5CrSnCl_2(C_4H_8O) \longrightarrow 12C_4H_8O\uparrow$$
$$+ 3SnCl_4\uparrow + 60CO\uparrow + 10Cr + 6SnCl_2 + Cr_2Sn_3.$$

The thermolysis product of compound **7** contains only two phases; the $SnCl_2$ proportion is known exactly, and the intensity ratio of the main X-ray diffraction reflections for $SnCl_2$ and W is 3 : 1, corresponding to their weight ratio. The resulting thermolysis scheme can be

$$3(CO)_5WSnCl_2(C_4H_8O) \longrightarrow 3C_4H_8O\uparrow$$
$$+ 2W(CO)_6\uparrow + 3SnCl_2 + W + 3CO\uparrow.$$

Because of the high lability of $(CO)_5MoSnCl_2(thf)$ (complex **6**), we failed to obtain its thermolysis product in an amount sufficient for X-ray powder diffraction analysis. However, we studied the thermolysis and determined the phase composition of the thermolysis products of $(CH_3)_4N(CO)_5MoSnCl_3$ (**8**) and $(CH_3)_4N(CO)_5WSnCl_3$ (**9**). The thermal study of compound **9** intended to demonstrate the identity of the phase composition of its solid thermolysis product to the phase composition of the thermolysis product of complex **7**. The weight and heat flux during the heating of samples of compound **9** are plotted as functions of temperature in Figs. 5c and 5d. The overall weight loss in the range of the temperatures studied is 48.7 ± 1.0%. The phase analysis of the solid thermolysis product showed $SnCl_2$ and tungsten. The $SnCl_2$ proportion in the thermolysis product of compound **6** was also derived from by the DSC heat of melting of the final product (T_m = 247.7°C, $\Delta_m H°$ = 45.4 J/g); it equals 59.4 wt %. With account for the thermogravimetric data, the phase composition of the thermolysis product, and the $SnCl_2$ proportion in the product, the resulting thermolysis scheme for compound **9** can be written as

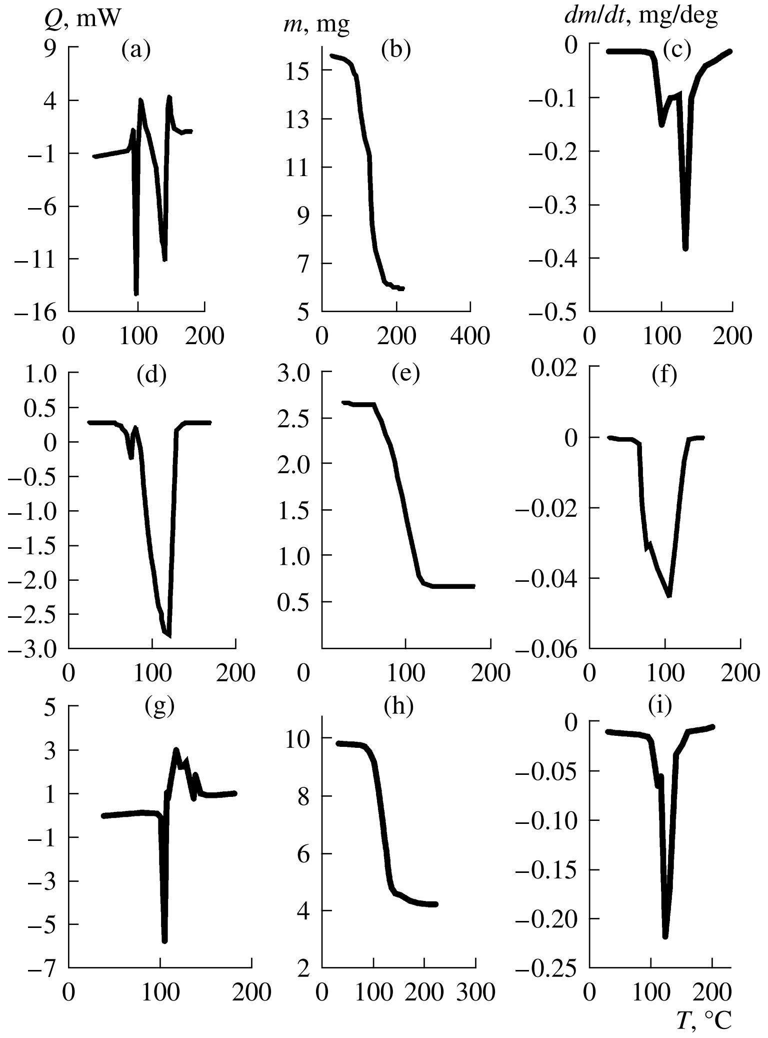

Fig. 4. Heat flux vs. temperature for the thermolysis of complexes (a) **5**, (d) **6**, and (g) **7**; sample weight vs. temperature for complexes (b) (**5**), (e) **6**, and (h) **7**; and derivative weight loss vs. temperature for complexes (c) **5**, (f) **6**), and (i) **7**.

$$10(CH_3)_4N(CO)_5WSnCl_3 \longrightarrow 10(CH_3)_4NCl\uparrow$$
$$+ 3W(CO)_6\uparrow + 10SnCl_2 + 7W + 32CO\uparrow.$$

The verified identity of the phase composition of the thermolysis products of compounds **7** and **9** implies that the results obtained from the thermolysis of compound **8** can be used to determine the phase composition of the thermolysis product of complex **6**. The weight loss and heat flux for samples of compound **8** are plotted in Figs. 5c and 5d as a function of temperature in the heating mode. The overall weight loss between 60 and 380°C is 76.5 ± 1.5%. The results of the phase analysis of the thermolysis product of compound **8** are displayed in Table 4. The $SnCl_2$ proportion in this sample determined calorimetrically is 53.4%. Proceeding from our results, the thermolysis scheme for compound **8** can be represented as

$$6(CH_3)_4N(CO)_5MoSnCl_3 \longrightarrow 6(CH_3)_4NCl\uparrow$$
$$+ 5Mo(CO)_6\uparrow + 2SnCl_4\uparrow + 2SnCl_2 + MoSn_2.$$

In view of the weight loss upon thermolysis for complex **6** and the identity of the phase compositions of the thermolysis products of complexes **6** and **8**, the following thermolysis scheme is suggested for complex **6**:

$$6(CO)_5MoSnCl_2(C_4H_8O) \longrightarrow 6C_4H_8O\uparrow$$
$$+ 2SnCl_4\uparrow + 5Mo(CO)_6\uparrow + 2SnCl_2 + MoSn_2.$$

In order to determine the general thermolysis laws for transition-metal complexes of $SnCl_2$, we studied the thermolysis of $(CO)_2MnCpSnCl_2$(thf) (complex **10**), where dichlorostannylene is the ligand for cyclopentadienyldicarbonylmanganese. Complex **10** is thermolyzed over a wide temperature range (95–535°C;

Table 2. Phase composition of the thermolysis products of compounds **5** and **7**

Thermolysis product of **5**		Thermolysis product of **7**		$SnCl_2$ [72-0137]*		Cr [19-0323]*		Cr_2Sn_3 [19-0333]*		W [47-1319]*	
d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
4.6053	40	4.5988	60	4.603	60						
3.9768	10	3.9804	20	3.992	20						
3.9605	50	3.9547	60	3.963	50						
3.8889	30	3.8978	50	3.897	40						
3.5516	100	3.5512	100	3.553	100						
2.9775	30	2.978	50	2.974	40						
		2.9445	20	2.954	20						
2.9159	20	2.9222	20	2.926	25						
2.9059	60							2.903	80		
2.7878	50	2.7853	60	2.788	50						
2.6788	30							2.688	80		
2.5843	30							2.599	80		
2.5206	60	2.5227	70	2.523	60						
		2.4558	20	2.469	10						
		2.3928	20	2.411	10						
		2.3644	20	2.354	20						
2.3473	20							2.348	50		
2.2960	70	2.3135	10	2.262	30	2.300	60	2.298	80		
		2.2582	20							2.258	100
2.1736	30	2.1758	40	2.177	40			2.190	10		
2.0767	20							2.097	100		
		2.1176	40	2.118	40						
		2.0575	20							2.062	90
2.0475	25					2.049	100				
		1.9259	20	1.934	10						
1.8519	20					1.873	80				
		1.7737	20	1.776	15						
		1.6639	10	1.661	10						
		1.5799	10	1.583	15					1.582	15
		1.4533	10							1.458	15
1.4498	20					1.441	50				

Fig. 6). For complex **10**, as for complexes **5**–**7**, the removal of the stabilizing thf molecule is the first thermolysis stage; the weight loss in the range 95–140°C is 16.0 ± 1.0% against the calculated thf content of 16.4%. The second stage is the removal of labile CO ligands; the weight loss in the range 150–200°C is 13.0 ± 1.0% against the calculated CO content of 12.7%. In the range 250–535°C, the destruction progresses with the evolution of a significant amount of energy, leading to the formation of the intermetallic compound Mn_2Sn

Table 3. Temperatures and heats of melting for individual $SnCl_2$ and that contained in the thermolysis products of compounds **5** and **7**

Melting parameter and concentration	$SnCl_2$	Thermolysis product of **5**	Thermolysis product of **7**
T_m, °C	247.2 [16]	247.5 ± 0.5	247.9 ± 0.5
$\Delta_m H°$, J/g	76.5 [16]	57.8 ± 0.5	41.8 ± 1.0
$SnCl_2$, wt %	100	75.6 ± 1.0	54.6 ± 1.0

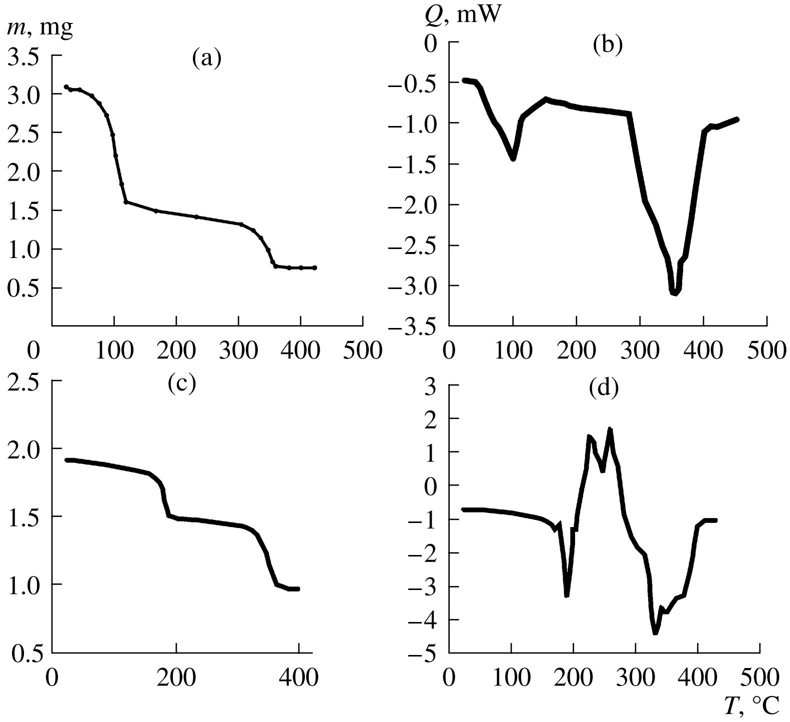

Fig. 5. Sample weight and heat flux vs. temperature for the thermolysis of (a, b) complex **8** and (c, d) complex **9**.

(Table 5). We should note that the results of the previous study of the thermolysis of carbonylchalcogenomanganese complexes [17] are qualitatively similar to our data obtained for complex **10**. The resulting thermal destruction scheme for complex **10** with reference to work [18] is

Table 4. Phase composition of the solid thermolysis product of compound **8**

Thermolysis product of **8**		$SnCl_2$ [72-0137]		$MoSn_2$ [47-1559]	
d, Å	I, %	d, Å	I, %	d, Å	I, %
4.6008	70	4.603	60		
3.5483	100	3.553	100		
2.9685	30	2.974	40		
2.7875	40	2.788	50		
2.6753	40			2.696	60
2.5325	70	2.523	60	2.559	70
2.4252	40			2.434	80
2.1582	50			2.122	100
1.7685	10	1.776	15		
1.5180	15			1.517	40
1.4783	10			1.488	20

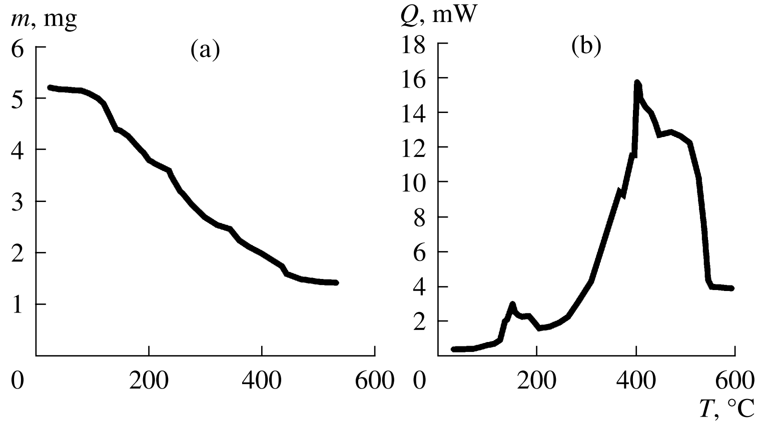

Fig. 6. (a) Sample weight and (b) heat flux vs. temperature for the thermolysis of complex **10**.

$$2(CO)_2C_5H_5MnSnCl_2(C_4H_8O) \longrightarrow 2C_4H_8O\uparrow + SnCl_4\uparrow + 4CO\uparrow + (C_5H_5)_2\uparrow + Mn_2Sn.$$

Thus, from the above results, we can suggest the following scenario for the thermolysis of dichlorostannylene complexes. The first stage is the elimination of the stabilizing coordinated organic molecule (thf or $(Cp)_2$); then, labile CO ligands are lost; and lastly, a quite strong $M{=}SnCl_2$ bond is broken and a metallic or intermetallic phase is formed.

The thermolysis of dithiocyanatostannylene complexes with metal carbonyls $(CO)_5CrSn(SCN)_2$ (**11**) and $(CO)_5WSn(SCN)_2$ (**12**) was of interest as a route to the preparation and study of tin–transition metal–sulfur ternary systems.

The thermolysis character for both compounds is identical (Fig. 7). The thermolysis of compound **11** starts above 120°C; that of compound **12**, above 90°C. Before weight loss starts, processes associated with energy absorption occur in both compounds. The first

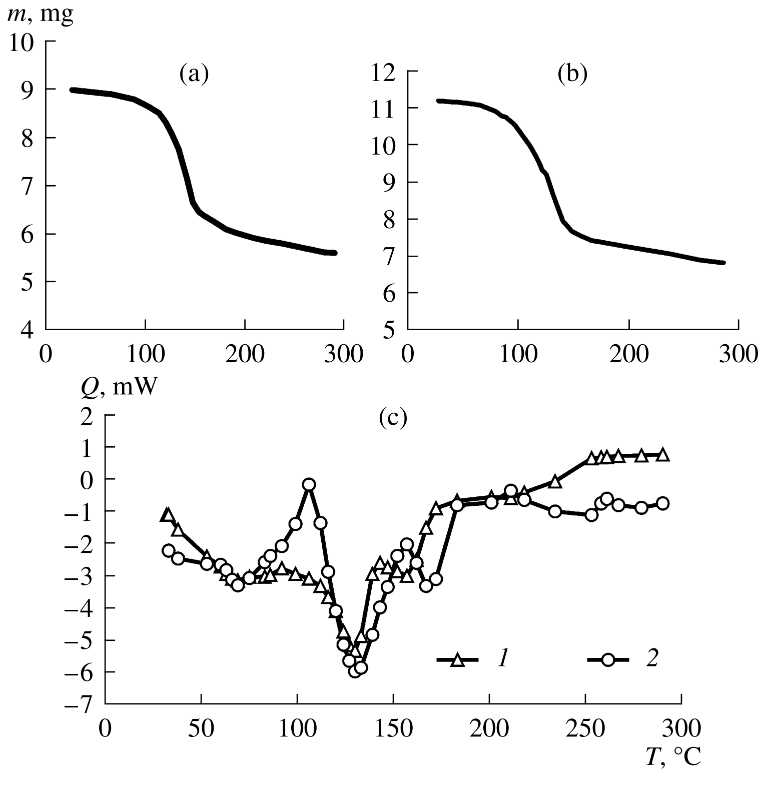

Fig. 7. Panels (a, b): sample weight vs. temperature for the thermolysis of (a) complex **11** and (b) complex **12**. Panel (c): the heat flux vs. temperature for (*1*) complex **11** and (*2*) complex **12**.

Table 5. Phase composition of the solid thermolysis product of compound **10**

Thermolysis product of **10**		Mn_2Sn [18-0816]	
d, Å	*I*, %	*d*, Å	*I*, %
3.1274	50	3.100	60
2.7949	80	2.761	30
2.6836	80	2.680	20
2.5877	80	2.527	20
2.4201	60	2.479	20
2.1840	60	2.179	100
2.1583	40	2.159	60
2.1218	40	2.111	20

thermolysis stage for compound **11** ends at 148°C; for compound **12**, at 157°C. The weight loss is 41.2 ± 1.0% and 26.2 ± 1.0% for compounds **11** and **12**, respectively. Likely, M=Sn bonds dissociate during the first stage, which is accompanied by energy absorption. Thermogravimetric data imply that at the first stage for compound **11**, $5/6Cr(CO)_6$ is removed (the theoretical chromium carbonyl proportion in compound **11** is 42.94%); for compound **12**, tungsten carbonyl decomposes and CO is removed (the theoretical CO percentage in compound **12** is 25.04%). Above 150°C, a progressive decrease in weight is observed for both compounds, accompanied by energy evolution. The weight loss over the temperature range of the investigation (25–350°C) is 61.1 ± 1.5 and 37.2 ± 1.5% for compounds **11** and **12**, respectively. X-ray powder diffraction showed that the thermolysis products are mixtures of Cr_2Sn_3 and SnS phases for compound **11** and tungsten and SnS phases for compound **12** (Table 6).

In summary, as a result of our study of the thermolysis of $(Acac)_2SnX_2$ (X = Cl, N_3), $(CO)_5MSnCl_2(thf)$ (M = Cr, Mo, W), $(CO)_5CrSn(SCN)_2$, $(CO)_5MSn(acac)_2$ (M = Cr, W), and $(CO)_2MnCpSnCl_2(thf)$, we determined the temperature stability limits, the terminal temperatures of thermal destruction, and the phase compositions of solid thermolysis products. For several compounds, possible thermolysis scenarios have been suggested. The stannylene complexes of transition metals can serve as precursors of intermetallic compounds.

Table 6. Phase composition of the thermolysis products of compounds **11** and **12**

Thermolysis product of **11**		Thermolysis product of **12**		SnS [39-0354]		Cr_2Sn_3 [19-0333]		W [47-1319]	
d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
3.2004	50	3.1852	50	3.244	65				
2.9347	50	2.9725	50	2.931	70	2.903	80		
2.8571	70	2.8540	80	2.835	100				
		2.8007	40	2.797	50				
2.7025	30					2.688	80		
2.6010	20					2.599	80		
		2.5480	20					2.525	26
		2.2563	60					2.258	100
2.1421	40	2.1326	40	2.125	25				
2.0905	20					2.097	100		
		2.0648	50					2.062	96
1.8375	40	1.9100	40	1.875	50				
		1.7417	20	1.722	40				

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