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Peculiarities of thermal decomposition of inorganic and organometallic compounds of Ge^{IV} and Ge^{II}. Thermolysis of $(acac)_2GeX_2$ (X = Cl, N_3) and $(CO)_5MGeCl_2(thf)$ (M = Cr, Mo, W)

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Thermal decomposition of the complexes $(acac)_2Ge(N_3)_2$ (**1**), $(acac)_2GeCl_2$ (**2**), and $(CO)_5M{=}GeCl_2(THF)$ (M = Cr (**3**), Mo (**4**), W (**5**)) was studied by differential scanning calorimetry and thermogravimetry. The phase compositions of the products of thermolysis of compounds **1**—**3** and **5** were determined by X-ray phase analysis. Possible schemes of thermal decomposition of these compounds were proposed. The heat capacities of complexes **3**—**5** were studied in the temperature range 113—313 K. The structures of complexes **1** and **5** were established by X-ray diffraction analysis.

Key words: thermal decomposition, heat capacity, complexes of Ge^{II} and Ge^{IV}, synthesis, structure.

Elucidation of peculiar features of thermal decomposition of coordination and organometallic compounds is a topical research avenue in modern inorganic chemistry. This allows one not only to reveal subtle specific thermal effects due to intramolecular rearrangements upon absorption of excess energy but also to obtain, after all, such inorganic compounds that possess unique physicochemical properties but in some cases cannot be synthesized using traditional experimental techniques.[1—3]

In this work we report on the synthesis, structure, thermal decomposition, and determination of the heat capacities of some complexes containing Ge^{II} and Ge^{IV} atoms. Such compounds are of great interest as promising precursors of novel materials with unusual physicochemical (including catalytic) properties.

Results and Discussion

Earlier,[4] we have found that refluxing of $(acac)_2GeCl_2$ with NaN_3 (2 mol) in acetonitrile for 5 h results in bis(acetylacetonato)germanium(IV) diazide, $(acac)_2Ge(N_3)_2$ (**1**), in 82% yield. Complex **1** was isolated as colorless crystals well soluble in organic solvents and readily hydrolyzable in solution. Single crystals of complex **1** were prepared by recrystallization from toluene. X-Ray diffraction study of complex **1** (Fig. 1) revealed that the germanium atom is in a distorted octahedral environment of four oxygen atoms (Ge—O(1) 1.891(9) Å, Ge—O(2) 1.935(9) Å, Ge—O(3) 1.889(9) Å, Ge—O(4) 1.926(9) Å), two acac ligands, and nitrogen atoms of two azide fragments (Ge—N(1) 1.942(12) Å, Ge—N(4) 1.926(11) Å) arranged in *cis*-position relative to each other (in the axial and equatorial positions, respectively).

The presence of diazide groups in complex **1** allowed one to expect generation of carbene analogs upon UV irradiation, which is known for diazide-containing compounds of the Group IVB elements. However, photolysis resulted in a poorly soluble germanium-containing polymer rather than the expected germanium(II) bis(acetylacetonate).

Yet another method for generating carbene analogs is thermal decomposition of the corresponding diorganylsilicon (germanium, tin) diazides.[5] In this work we established that thermal decomposition of complex **1** begins at 80±2 °C and involves two distinct stages. In the first stage, compound **1** melts with decomposition in the temperature range 90—150 °C (Fig. 2). In the second stage, the decomposition continues, being accompanied by a large exothermic effect. At temperatures above 400 °C, no weight loss of the decomposition product was observed.

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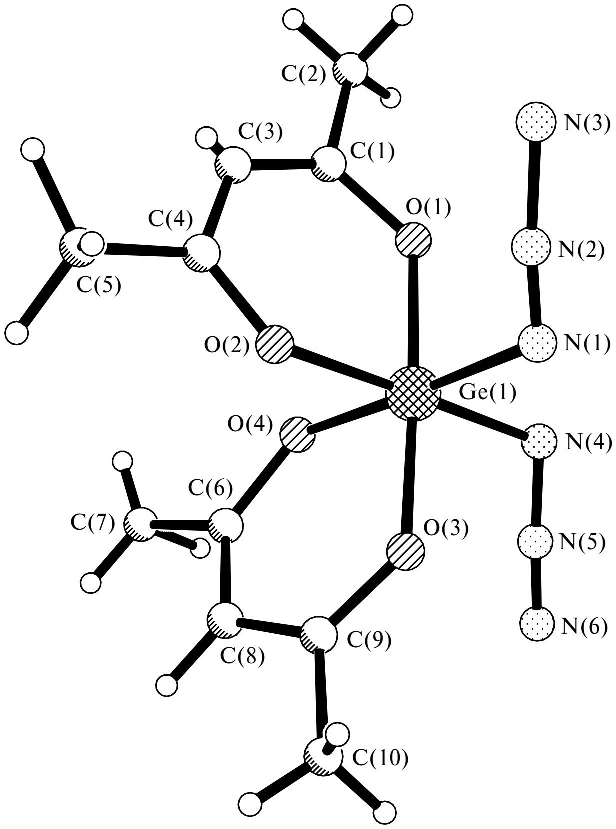

Fig. 1. Molecular structure of complex **1**.

The total relative weight loss due to thermal decomposition is 64.1±2.0%. Thermolysis of compound **1** results in a grey-brown substance containing GeO_2, Ge, and Ge_3N_4 (determined by X-ray phase analysis, see Table 1).

Table 1. Phase analysis of decomposition products of compound **1**

Decomposition product		GeO_2		Ge_3N_4		Ge*	
d/Å	I (%)	d/Å	I (%)	d/Å	I (%)	d/Å	I (%)
4.036	60	4.070	100				
3.432	40			3.477	60		
3.154	25	3.160	40				
2.892	50	2.883	80				
2.820	40			2.815	80		
2.673	15					2.690	100
2.639	40			2.629	100		
2.490	30	2.495	40	2.473	7	2.471	20
2.356	10	2.350	20				
2.320	20	2.228	60				
2.145	10	2.127	40				
2.078	15			2.008	50		
2.000	15	1.957	60				

* Tetragonal modification.

Gaseous products of the decomposition of complex **1** were not analyzed. Nevertheless, based on the relative weight of the solid residue (35.9%), the phase composition of the decomposition product (see Table 1), correspondence between the intensities of the characteristic reflections of the crystalline phases in the X-ray diffraction pattern and their weight content in the decomposition product ($GeO_2 : Ge_3N_4 : Ge = 6 : 4 : 1$), and the results obtained earlier,[6–8] we can propose a possible scheme of thermal decomposition of the compound under study (Eq. (1)).

$$(acac)_2Ge(N_3)_2 \longrightarrow 0.5\ GeO_2 + 0.125\ Ge + 0.125\ Ge_3N_4 + 3\ CO\uparrow + 2.5\ N_2\uparrow + 2\ CH_4\uparrow + C_2H_6\uparrow + 3\ C. \quad (1)$$

A comparison of the data on thermal decomposition of complex **1** containing azide fragments, which can readily generate N_2, with analogous data for the structurally similar complex $(acac)_2GeCl_2$ (**2**) containing rather strongly bound apical chlorine atoms showed that the latter is thermally stable to 200 °C under the experimental conditions. Above this temperature, complex **2** melts with decomposition (see Fig. 2, *b*), the intense weight loss in the temperature range 206—290 °C being accompanied by substantial absorption of energy. Subsequent heating of the sample to 500 °C occurs without pronounced thermal effects and is accompanied by gradual decrease in weight. No weight loss of the decomposition products was observed above 470 °C. The total weight loss of the sample of complex **2** in the temperature range 25—500 °C is 75.6±2.0%. Thermal decomposition of compound **2** results in a dark-grey substance containing metallic germanium (tetragonal and cubic modifications) and germa-

Table 2. Phase analysis of decomposition products of compound **2**

Decomposition product		GeO_2		Ge*		Ge**	
d/Å	I (%)	d/Å	I (%)	d/Å	I (%)	d/Å	I (%)
4.064	80	4.070	100				
3.341	60					3.266	100
3.208	30	3.160	40				
2.907	30	2.883	80				
2.625	30			2.690	100		
2.483	20	2.495	40	2.471	20		
2.357	15	2.350	20				
2.209	30	2.228	60			2.000	50
1.985	30	1.957	60	1.825	60		
1.569	20	1.538	40	1.543	10		
1.446	5	1.442	10	1.456	15		

* Tetragonal modification.

** Cubic modification.

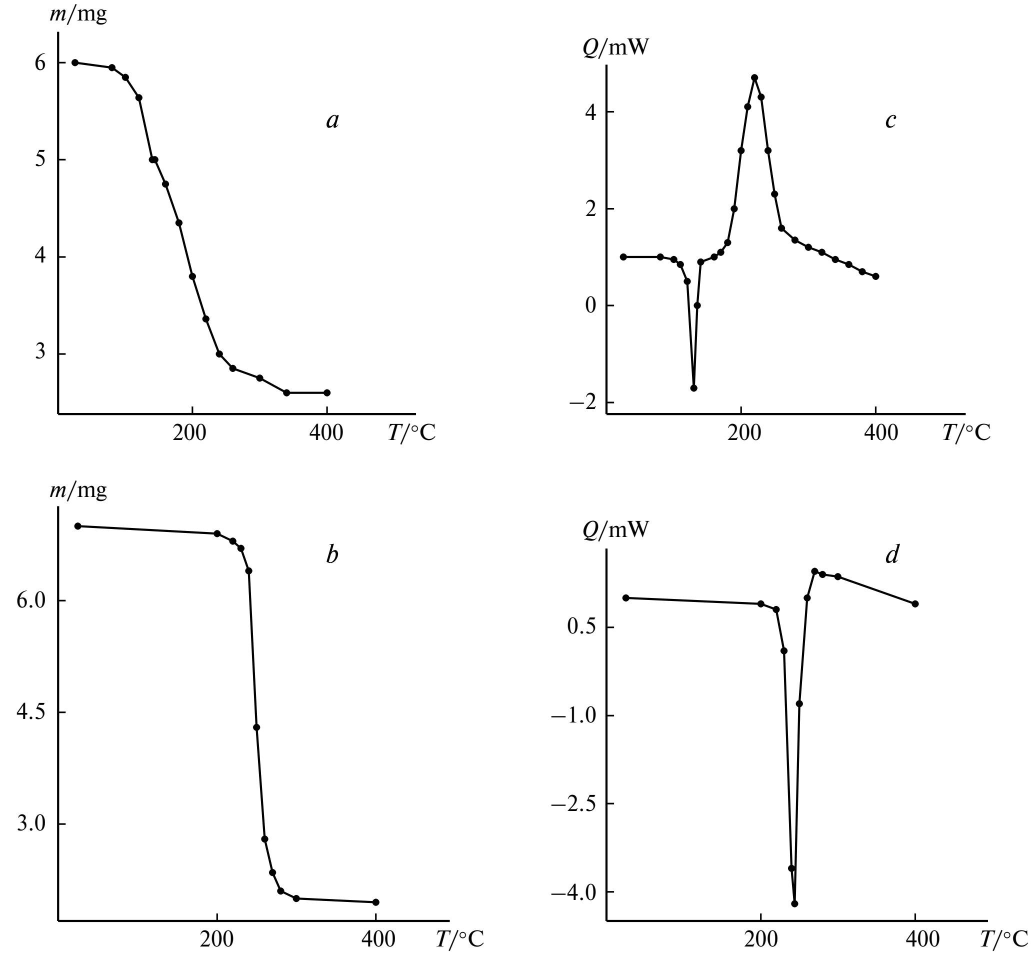

Fig. 2. Weight losses (*a*, *b*) and heat flows (*c*, *d*) of complexes **1** (*a*, *c*) and **2** (*b*, *d*) plotted *vs*. temperature.

nium dioxide (determined by X-ray phase analysis, see Table 2). The GeO_2 : Ge ratio estimated from the correspondence between the intensities of the characteristic reflections of the crystalline phases and their weight content in the decomposition product is 1.5 : 1.

Using the approach employed for compound **1**, we can propose the following scheme of thermal decomposition of complex **2**:

$$(acac)_2GeCl_2 \longrightarrow 0.25\ GeO_2 + 0.25\ Ge + 0.5\ GeCl_4\uparrow + 2\ CH_4\uparrow + C_2H_6\uparrow + 3.5\ CO\uparrow + 2.5\ C. \quad (2)$$

Thus, the results obtained for the two structurally similar complexes studied in this work show that the complex containing azide groups instead of chlorine atoms becomes much less thermally stable. Compounds **1** and **2** melt with decomposition at rather low temperatures, which suggests their use as molecular precursors in preparation of inorganic materials with prescribed stoichiometric compositions.

In this connection it was of interest to study thermolysis of such organometallic complexes that simultaneously

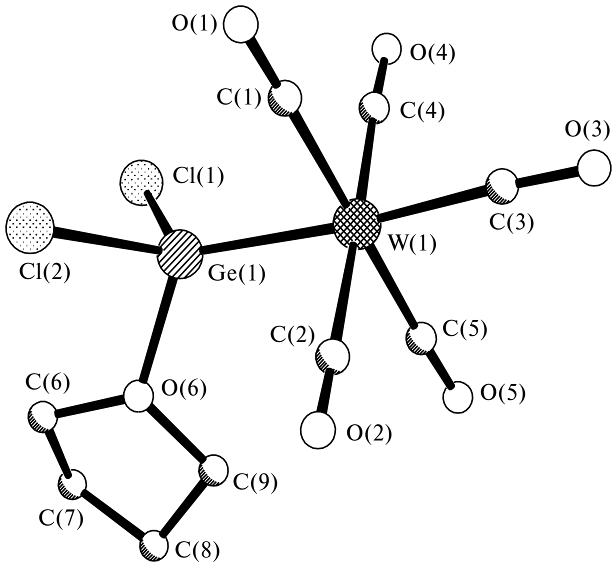

Fig. 3. Molecular structure of complex **5**.

contain (i) Ge atoms and atoms of different transition metals and (ii) ligands capable of leaving the coordination sphere of the metal with ease on heating. The following compounds, $(CO)_5MGeCl_2(thf)$ (M = Cr (**3**), Mo (**4**), W (**5**)), were chosen as containing the rather labile THF molecules and carbonyl groups. Complexes **3**—**5** were synthesized following known procedures.[9,10] The structure of complex **5** was established by X-ray diffraction analysis. In molecule **5** (Fig. 3), the $W(CO)_5$ moiety is directly bound to the germanium atom (2.5335(13) Å) coordinated by two chlorine atoms (Ge(1)—Cl(1) 2.192(3) Å, Ge(1)—Cl(2) 2.192(4) Å) and by the oxygen atom of the THF molecule (Ge(1)—O(6) 1.948(8) Å). As a result, the Ge^{II} atom is in the distorted tetrahedral environment.

Thermogravimetric studies revealed that thermal decomposition of compounds **3**—**5** is a stepwise process. The initial decomposition temperature increases from the chromium-containing complex **3** to the tungsten-containing complex **5** (70±3, 74±3, and 80±3 °C, respectively, see Fig. 4). Melting of the compounds begins nearly simultaneously with decomposition. The weight loss by the time of completion of the corresponding endothermic effect (melting was confirmed by visual observations) was at most 3% for all the three compounds. This allows the energy absorbed to be treated as equal to the heat of

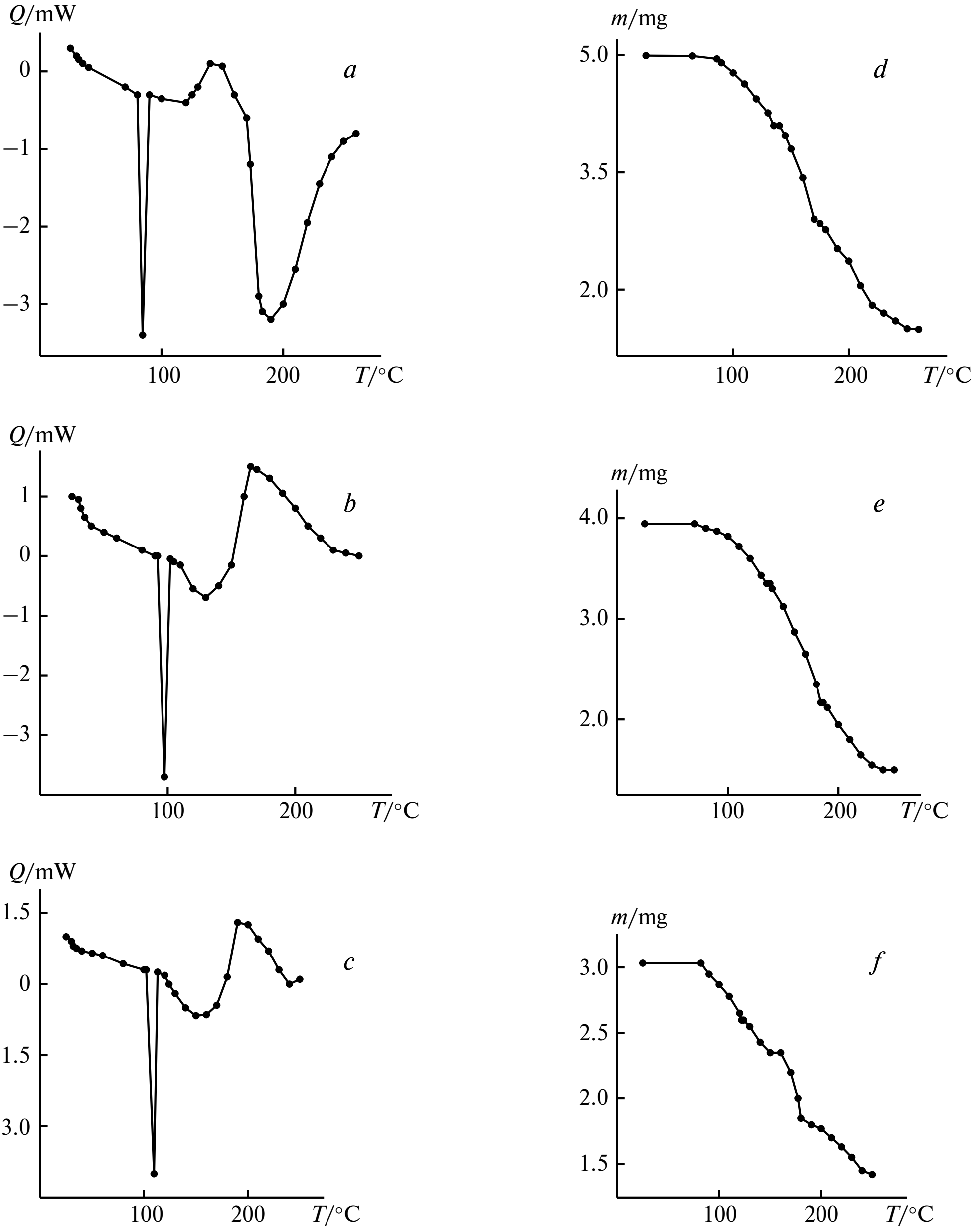

Fig. 4. Heat flows (*a*—*c*) and weight losses (*d*—*f*) of compounds **3** (*a*, *d*), **4** (*b*, *e*), and **5** (*c*, *f*) plotted *vs.* temperature.

melting. Both the temperature and the melting heat of the compounds increase from the Cr-containing to the W-containing compound (t_{melt} = 80.5±1.0 (**3**), 87.5±1.0 (**4**), 109.6±1.0 (**5**); $\Delta_{melt}H$ = 21603±40 (**3**), 25555±60 (**4**), 34036±45 J mol^{-1} (**5**)). Comparison of the calculated content of THF in compounds **3**—**5** (17.6 (**3**), 15.9 (**4**), 13.3% (**5**)) with the weight loss in the first stage of decomposition (17.0±1.0 (**3**), 16.2±1.0 (**4**), 13.3±1.0% (**5**)) suggests that the first stage of thermal decomposition of all the three compounds involves elimination of the THF molecule. Under the experimental conditions, the final THF loss temperature decreases from the Cr-containing to the W-containing compound (t_1 = 140±2 (**3**), 130±2 (**4**), and 120±2 °C (**5**)).

The DSC curves presented in Fig. 4 show that subsequent decomposition of the Cr-containing complex **3** is significantly different from that of the Mo- and W-containing compounds. This is likely due to the fact that thermal destruction at temperatures above the final THF loss temperature corresponding to completion of the first stage is primarily due to elimination of the CO ligands. Under gradual decarbonylation of the complexes, formation of the additional M—Ge and M—M bonds becomes possible, the bonds involving the *3d*-metals being much weaker than those involving the *4d*- and *5d*-metals possessing more extended orbitals. In addition, formation of the multiple bonds, which is typical of molybdenum and tungsten,[11] cannot be ruled out. This seems to be the most probable reason for compensation of the energy expenditure for decarbonylation of complexes **4** and **5** owing to the formation of new bonds. Most likely, these processes are also responsible for the experimentally observed energy release during the decomposition of **4** and **5** in contrast to the decomposition of complex **3** (only endotherm is observed in that case). The temperature corresponding to complete decomposition under the experimental conditions decreases from the Cr-containing compound to the W-containing analog (260±3 (**3**), 250±3 (**4**), and 240±3 °C (**5**)).

The results obtained show that the thermal stabilities of complexes **3**—**5** are insignificantly reduced from the Cr-containing to the W-containing compound. Similarly to compounds **1** and **2**, complexes **3**—**5** have rather low melting points and decomposition temperatures. This also suggests a possibility of using them as molecular precursors of inorganic materials with prescribed stoichiometric compositions.

Indeed, our study of the phase compositions of solid decomposition products of complexes **3** and **5** by X-ray phase analysis (Tables 3 and 4) revealed the presence of the Cr_3Ge (for **3**) and W_5Ge_3 (for **5**) phases. It should be noted that traditional synthetic routes to these compounds involve melt synthesis followed by prolonged annealing to obtain homogeneous samples or long-term solid-phase synthesis at an optimum temperature equal to two thirds of the melting temperature, which is rather high (*e.g.*, for Cr_3Ge intermetallide t_{melt} = 1530±30 °C).[12]

Table 3. Phase analysis of the composition of decomposition products of compound **3**

Decomposition product		Cr_3Ge		Ge	
d/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)
3.256	20	3.263	8	3.266	100
2.312	40	2.307	50		
2.069	100	2.063	100		
1.998	15			2.000	60
1.880	90	1.884	100		
1.695	10			1.706	40
1.405	5			1.414	10
1.292	5			1.298	15
1.226	20	1.233	30		

Table 4. Phase analysis of the composition of decomposition products of compound **5**

Decomposition product		W_5Ge_3		Ge*	
d/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)
3.339	10	3.440	10		
3.235	15			3.266	100
2.486	40	2.460	40		
2.310	80	2.370	100		
2.131	50	2.190	80		
1.980	10			2.000	60
1.711	7			1.706	40

* Cubic modification.

Taking into account the results obtained and the total weight loss during thermolysis of the complexes studied in this work (79.5±1.5% for **3** and 69.5±1.5% for **5**), we can propose the following schemes of thermal decomposition of complexes **3** and **5** (the composition of the gas phase was not studied):

$$(CO)_5CrGeCl_2(thf) \longrightarrow 0.33\ Cr_3Ge + 0.17\ Ge + {} \\ + 0.5\ GeCl_4\uparrow + 5\ CO\uparrow + C_4H_8O\uparrow, \qquad (3)$$

$$(CO)_5WGeCl_2(thf) \longrightarrow 0.14\ W_5Ge_3 + 0.08\ Ge + {} \\ + 0.5\ GeCl_4\uparrow + 3.2\ CO\uparrow + C_4H_8O\uparrow + {} \\ + 0.3\ W(CO)_6\uparrow. \qquad (4)$$

Note that metal carbonyl appears in Eq. (4) in contrast to Eq. (3). This is due to the fact that significant decomposition of $Cr(CO)_6$ occurs at 90 °C, whereas decomposition of $W(CO)_6$ begins at temperatures above 170 °C.[13,14]

The magnetic behavior of the decomposition products of complex **5** (Fig. 5) is indicative of a ferromagnetic

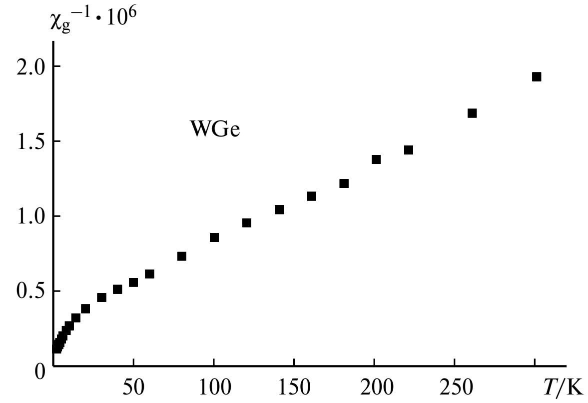

Fig. 5. Inverse magnetic susceptibility of the decomposition product of complex **5** plotted as function of temperature.

character of the interaction between paramagnetic centers. The nature of these centers is still to be clarified.

Obtaining inorganic materials from metal complexes can also be predicted and described based on the thermodynamic analysis of decomposition processes. However, correct thermodynamic calculations require knowledge of the basic thermodynamic characteristics associated with the formation of compounds.

To determine the enthalpy of formation, we studied the decomposition of compound **5** in the dynamic (temperature range 130—250 °C) and isothermic (at 230 °C) regimes. The thermal effects obtained were found to be in reasonable agreement ($\Delta_r H^{\text{dyn}} = -298 \pm 10$ J g^{-1} and $\Delta_r H^{\text{iso}} = -320.0 \pm 4.0$ J g^{-1}, respectively).

The heat capacities of complexes **3**—**5** were determined by differential scanning calorimetry in the temperature range 113—300 K (Table 5). The calculated absolute entropies are 324±7 (**3**), 330±10 (**4**), and 337±8 J K^{-1} mol^{-1} (**5**).

Table 5. Temperature dependences of the heat capacities of compounds **3**—**5**

T/K	C_p/J K^{-1} mol^{-1}		
	3	**4**	**5**
113	170.9	175.5	177.9
118	175.8	182.0	184.2
123	180.6	187.8	190.2
128	186.2	193.5	195.7
133	191.4	199.6	202.5
138	196.2	203.4	207.2
143	201.1	208.3	213.3
148	206.3	214.3	218.4
153	212.0	218.6	223.0
158	216.8	224.1	228.0
163	220.9	228.7	233.1
168	226.5	233.9	238.0
173	230.1	237.2	241.9
183	238.5	245.3	249.7
193	245.2	252.5	256.8
203	252.7	259.1	264.0
213	259.0	266.2	271.1
223	265.7	273.0	277.5
233	271.1	279.1	284.0
243	277.3	284.4	289.4
253	283.6	290.0	294.8
263	289.0	296.2	301.0
273	294.4	300.8	305.9
283	299.7	306.0	315.3
293	305.2	310.5	316.1
298	307.5	312.8	318.2

Thus, our study of thermal decomposition of the complexes $(acac)_2GeX_2$ (X = Cl, N_3) and $(CO)_5MGeCl_2(thf)$ (M = Cr, Mo, W) allowed the determination of their initial and final thermal decomposition temperatures and the phase composition of the solid decomposition products. Possible schemes of thermal decomposition were proposed.

Experimental

Compounds **1**,[4] **2**,[10] and **3**—**5** [8—9] were synthesized following known procedures.

Thermal decomposition of compounds **1**—**5** was studied by differential scanning calorimetry (DSC) and thermogravimetry (TG) on a Mettler TA-3000 thermal analyzer (DSC-20 and TG-50 modules, respectively). Samples were heated in a dry argon atmosphere at a constant rate of 5 deg min^{-1}. Seven DSC and six TG analyses were performed for each compound. The weight loss during thermal decomposition was measured immediately on the TG-50 module with an accuracy of $\pm 2 \cdot 10^{-6}$ g. To carry out a stepwise DSC study of thermal decomposition, the temperature range was divided into several intervals. The number and extension of these temperature intervals were determined after the overall pattern of changes in the weight and energy during decomposition was obtained. This experimental strategy allowed the determination of the weight loss in each temperature interval and comparison of the results of the DSC and TG measurements (reasonable agreement between them served as confirmation of reliability of the results obtained). The accuracy of determination of the features and thermal effects in the thermograms was ±1 deg and ±0.5%, respectively. Heat capacity measurements were carried out using the DSC-25 module (differential calorimeter capable of scanning the jacket temperature and dedicated to quantitative measurements of thermal effects). The base line stability of the calorimeter was ±50 μW and the calibration coefficient was automatically maintained at a constant level over a broad temperature range (−150—600 °C) and was independent of the sample weight (up to a weight of 100 mg), and the noise level was less than 5 μW. The heat capacities were measured in the temperature interval 113—300 K at a sample heating rate of 2 deg min^{-1}. This temperature range was divided into four intervals chosen in such a way that they be overlapped by at least 40 °C. Five to seven series of measurements with different samples were carried out for each sample. The heat capacity at a given temperature was determined as the value averaged over 10 to 12 measurements. This procedure provided a relative error of determination of 2 to 3%. To evaluate a possible systematic error of measurements, the heat capacities of some reference compounds were measured periodically. For instance, the heat capacity of corundum differed from the corresponding values reported by the U.S. National Bureau of Standards by ±1—2%.

The magnetic properties of the decomposition product of complex **5** were studied on a Quantum Design SQUID MPMS-59 magnetometer in the temperature range 20—300 K. The magnetic susceptibility obeys the Curie—Weiss law, $\chi = C/(T - \theta)$, with a Weiss constant, θ, of 55 K. The effective magnetic moment was assessed using the formula $\mu_{\rm eff} = (8\chi_c T)^{0.5}$.

X-Ray diffraction studies were carried out at the X-Ray Structural Center (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) on a Bruker AXS SMART 1000 diffractometer (CCD detector, λMo-Kα, graphite monochromator, 110 K, ω scanning technique with an ω increment of 0.3°, a 30 s exposure per frame, $2\theta_{\rm max} = 60°$) using a standard technique.[15] For compound **5**: $C_9H_8Cl_2Ge_1O_6W_1$, M = 539.49, space group *Pbca*, $a = 6.9214(7)$ Å, $b = 20.791(2)$ Å, $c = 10.4313(10)$ Å, $\beta = 93.135(2)°$, $V = 1498.9(2)$ Å^3 (110 K), $Z = 4$, number of measured reflections is 9046, number of independent reflections with $F^2 > 2\sigma(I)$ is 4004, $\rho_{\rm calc} = 2.391$ g cm^{-3}, $\mu = 10.045$ cm^{-1}, $R_1 = 0.0692$, and $wR_2 = 0.1550$.

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