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Solid-phase thermal decomposition of polynuclear nickel(II) and cobalt(II) complexes

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Solid-phase thermal decomposition of polynuclear Ni^{II} and Co^{II} pivalate complexes was studied by differential scanning calorimetry and thermogravimetry. The decomposition of the polynuclear (from bi- to hexanuclear) Co^{II} carboxylate complexes is accompanied by aggregation to form a volatile octanuclear complex. Thermolysis of the polynuclear Ni^{II} carboxylates results in their destructure, and the phase composition of the decomposition products is determined by the nature of coordinated ligands.

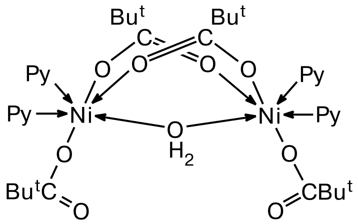
Key words: polynuclear complexes, cobalt and nickel complexes, carboxylate ligands, thermal decomposition.

Metal carboxylates represent a vast class of coordination compounds. Wide abilities of structural functions of acid residues provide diverse structures of the carboxylate complexes. It seems important to study solid-phase thermolysis of transition metal carboxylates for the development of systems for controlling thermal processes of metallic core modification, preparation of thin films and coatings with unusual electrophysical properties, and synthesis of new polymeric organic or inorganic materials.

In the present work, we studied the solid-phase thermal decomposition of a series of structurally characterized polynuclear Ni^{II} and Co^{II} carboxylates (pivalates) by differential scanning calorimetry (DSC) and thermogravimetry.

Results and Discussion

According to the X-ray diffraction data, binuclear nickel and cobalt complexes $Ni_2(\mu\text{-}H_2O)(\mu\text{-}OOCBu^t)_2(OOCBu^t)_2(Py)_4$ (**1**), $Ni_2(\mu\text{-}H_2O)(\mu\text{-}OOCBu^t)_2(OOCBu^t)_2(bipy)_2$ (**2**), $Ni_2(\mu\text{-}H_2O)(\mu\text{-}OOCBu^t)_2(OOCBu^t)_2(HOOCBu^t)_4$ (**3**), $Co_2(\mu\text{-}H_2O)(\mu\text{-}OOCBu^t)_2(OOCBu^t)_2(bipy)_2$ (**4**), and $Co_2(\mu\text{-}H_2O)(\mu\text{-}OOCBu^t)_2(OOCBu^t)_2(HOOCBu^t)_4$ (**5**)[1–4] in the crystalline state are characterized by an important feature: the hydrogen atoms of the bridging water molecule form intramolecular hydrogen bonds with the oxygen atoms of the terminal carboxylate groups.



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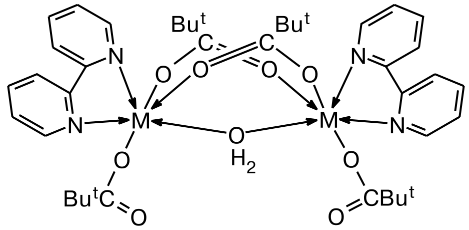
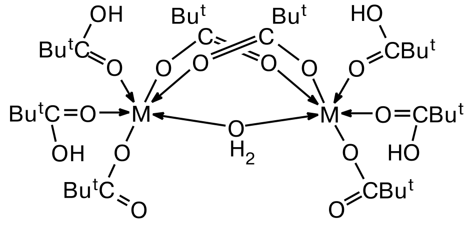


2, **4**



3, **5**

M = Ni (**2**, **3**), Co (**4**, **5**)

Compounds **1—5** decompose in steps (Figs 1 and 2). For compound **1**, this process starts above 70 °C. In the first step (70—130 °C), 19.0±2.0% weight is lost (content of two moles of pyridine in compound **1** is 18.45%). Probably, this process corresponds to the H bond cleavage, the removal of two moles of pyridine, and an increase in the

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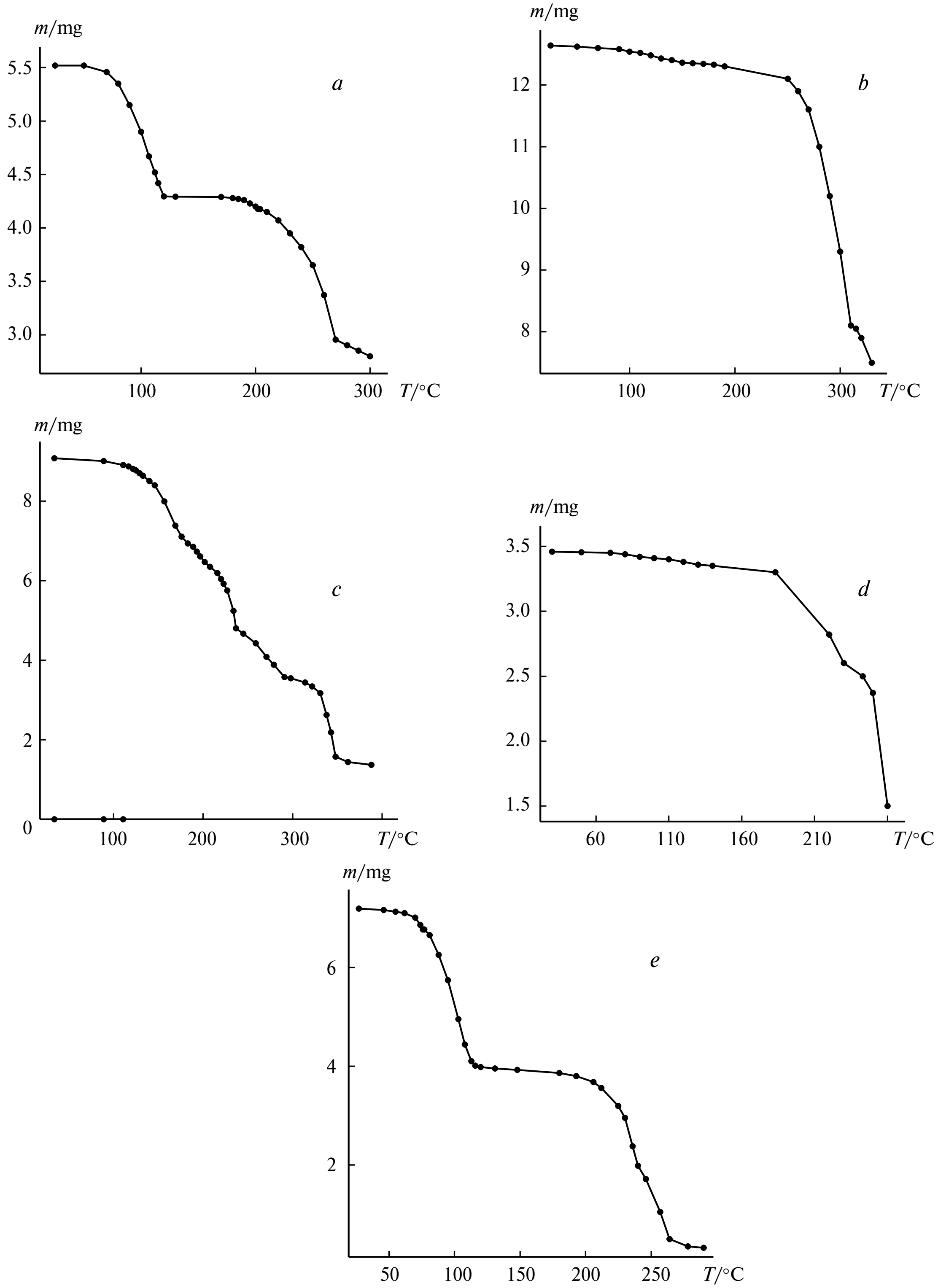


Fig. 1. Temperature dependences of the weight change for complexes **1** (*a*), **2** (*b*), **3** (*c*), **4** (*d*), and **5** (*e*).

dentation of the remaining O-donor ligands (water and carboxylate groups). An intermediate that formed is thermally stable below 170 °C. In the 170—202 °C interval, the energy absorption (ΔH = 20.2±2.0 kJ mol^{-1}) is accompanied by the 2.0±0.7% weight loss. This process (according to the results of studying the thermolysis of compound **1** in solution^{5}) corresponds to the removal of the bridging water and formation of the lantern tetra-

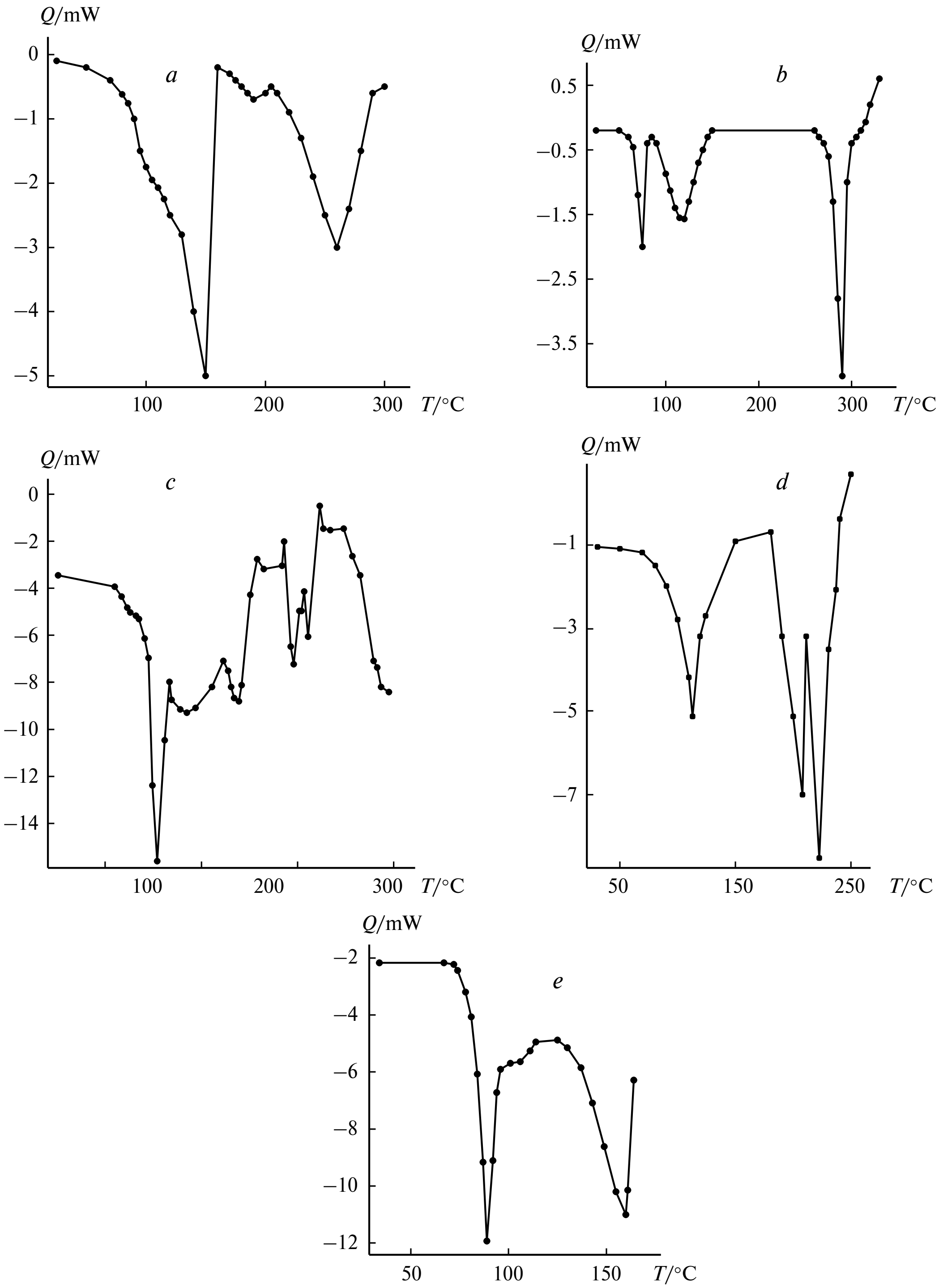


Fig. 2. Temperature dependences of the change in the heat flow for complexes **1** (*a*), **2** (*b*), **3** (*c*), **4** (*d*), and **5** (*e*).

carboxylate complex $Ni_2(\mu\text{-}OOCBu^t)_4(Py)_2$. In the 206—265 °C temperature interval, an additional weight loss is 18.0±2.0% with energy absorption ($\Delta H = 126.2\pm6.8$ kJ mol^{-1}). As a result, the formally possible decomposition product formed on heating of **1** to 260 °C is $Ni(OOCBu^t)_2$.

Dipyridyl complex **2** begins to decompose at a higher temperature than **1** because of a different spatial arrangement of the ligands[3] and a much higher boiling point of the coordinated *N*-donor ligand (b.p. of pyridine is 115.5 °C, while b.p. of 2,2´-dipyridyl is 273.7 °C). This specific feature of compound **2** allowed one the experimental observation of the cleavage of intramolecular H bonds in a temperature interval of 56—86 °C with energy absorption (ΔH = 18.0±2.2 kJ mol^{-1}). This process occurs without changing the sample weight. On heating in the 100—150 °C interval, the weight loss is 2.2±1.0% with energy absorption (ΔH = 74.5±5.5 kJ mol^{-1}). Probably, as for compound **1**, in this temperature range the bridging water is removed along with the formation of the mononuclear bipyNi$(OOCBu^t)_2$ complex containing two chelated pivalate groups in two independent molecules.[5] The resulting product is thermally stable below 260 °C, whereas an additional weight loss of 34.0±2.0% is observed in the 270—300 °C interval along with energy absorption (ΔH = 168.6±3.5 kJ mol^{-1}). The amount of the removed products and the heat effect value (for comparison, ΔH_{vap}(bipy) = 81.9 kJ mol^{-1}) suggest that two moles of dipyridyl are removed. Probably, the product obtained below 310 °C has a composition of $Ni(OOCBu^t)_2$. To identify the assumed intermediate decomposition products (compound **1** below 260 °C and compound **2** below 310 °C), we measured their heat capacities by differential scanning calorimetry. The heat capacity of pivalic acid was measured to confirm reliability of the results (Fig. 3, Table 1).

Our results for pivalic acid agree satisfactorily with published data,[6] and the anomaly found in the temperature plot of the heat capacity corresponds to the melting of pivalic acid.[6]

Compound **3** decomposes similarly to the thermolysis of compound **1**, but decomposition starts at a higher temperature. In the 105—176 °C interval, 21.7±1.0% weight is lost with energy absorption, which corresponds, most likely, to the removal of two moles of pivalic acid. The shape of the first endothermic peak suggests that the decomposition process is preceded by the H bond cleavage.

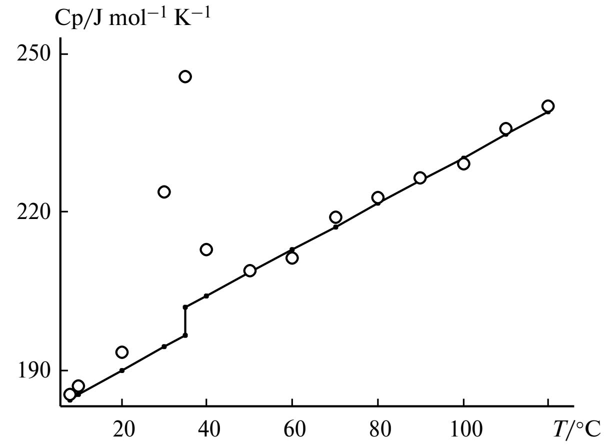


Fig. 3. Temperature dependence of the heat capacity for pivalic acid (our data are given by points, and the data of Ref. 6 are shown by solid line).

Table 1. Temperature dependences of the heat capacity for pivalic acid and intermediate decomposition products of compounds **1** and **2**

T/°C	Cp(±2%)/J mol^{-1} K^{-1}			
	Pivalic acid*		Decomposition products of compounds	
	I	II	**1**	**2**
8	184.37	185.5	—	—
10	185.28	187.0	387.5	388.5
20	189.85	193.2	396.0	394.3
30	194.40	223.7	399.3	401.9
35	196.70	245.8	—	—
40	204.17	213.2	409.2	407.4
50	208.53	209.0	415.8	414.6
60	212.89	211.3	422.9	424.1
70	217.25	219.1	432.6	430.9
80	221.61	222.7	439.5	438.2
90	225.97	226.4	448.2	446.5
100	230.33	229.1	453.0	453.7
110	234.67	235.9	461.5	460.4
120	239.05	240.0	470.9	468.9

* I indicate data in Ref. 6, II are data of the present work.

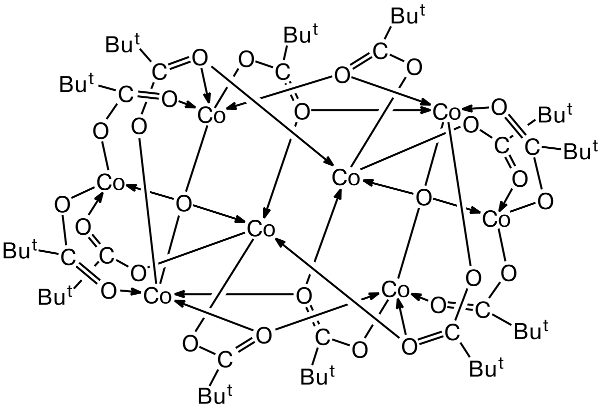
The weight loss in a temperature interval of 176—183 °C is 1.9±0.7%. Probably, this is the removal of the bridging water molecule to form a relatively stable intermediate, which additionally loses 23.6±1.5% weight on further heating. The total weight loss below 237 °C is 47.2±1.5%, which corresponds to the content of the bridging water and coordinated pivalic acid. We failed to terminate the decomposition of compound **3** at the step of formation of the assumed $Ni(OOCBu^t)_2$ compound. On further heating to 360 °C, the product obtained below 237 °C loses additionally 37.8±1.0%. The processes that occur in an interval of 237—360 °C are accompanied by complicated energy changes. The total heat effect is positive, which is probably caused by prevailing of the energy changes associated with the formation of a new structure. The total weight loss in the 25—450 °C interval is 85.0±1.5%. The weight fraction of the solid residue is 15.0±1.5%. According to the X-ray diffraction data for compounds **1—3**, the final decomposition product is nickel(II) oxide.

Compounds **4** and **5** decompose *via* a mechanism that differs from that for the decomposition of complexes **1—3**. For both compounds, decomposition starts above 65 °C. Compound **4** loses 3.0±1.0% weight in the 70—130 °C range with energy absorption (ΔH = 94.0±3.0 kJ mol^{-1}). Probably, in this temperature interval, H bonds are cleaved, the bridging water is removed, and, according to the results of studying the thermolysis of this compound in toluene,[4] a binuclear carboxylate-bridged complex is formed. The obtained product is thermally stable below

180 °C. In the 180—210 °C interval, compound **4** loses 22.3±1.0% weight with energy absorption (ΔH = 134.6±4.5 kJ mol^{-1}). Above 243 °C, the product that formed begins to evaporate intensely, and its complete evaporation is observed below 280 °C.

Compound **5** decomposes in two steps in an interval of 65—130 °C. In the first step (below 74 °C), 2.3±1.0% weight is lost, being, probably, the bridging water. The weight loss in the whole temperature interval is 44.9±1.0%, which is accompanied by a considerable endothermic effect with a complicated shape (345±8 kJ mol^{-1}). It seems unreasonable to integrate separately the heat effect in the 70—135 °C temperature interval, because the result obtained is ambiguous and has a high error. The presented value of the heat effect is comparable with the enthalpy of evaporation of one mole of water and four moles of pivalic acid. No weight loss was observed in the 140—200 °C temperature range but the energy was absorbed, which indicates, possibly, substantial structural changes. The bright violet product formed on heating to 200 °C is sublimed with further heating.

After we studied the solid-phase thermal decomposition of the octanuclear complex $Co_8(\mu_4\text{-}O)_2(\mu_2\text{-}OOCBu^t)_6(\mu_3\text{-}OOCBu^t)_6$ (**6**), whose structure is described in Ref. 7, we could reveal a possible reason for the sublimation of the decomposition products of complexes **4** and **5**.



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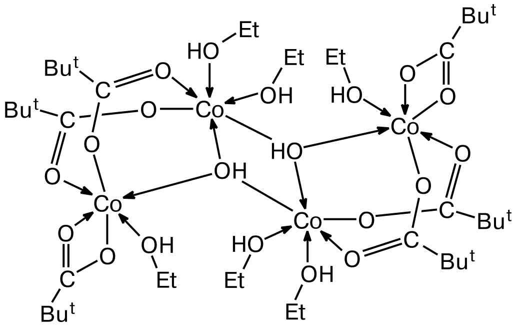
Compound **6** is thermally stable below 130 °C (Fig. 4). Evaporation begins above 130 °C, and 1% weight per 10 °C is lost at a heating rate of 5 deg min^{-1} in the 130—230 °C interval. The evaporation intensity increases above 230 °C, and 240.0±3.0 °C can be assumed to be the equilibrium temperature of evaporation. Thus, cluster **6** has a high vapor pressure and is sublimed without decomposition.

The results obtained suggest that in the last step of decomposition of compounds **4** and **5** the fragments, which appear upon thermal decomposition in the solid phase, undergo aggregation to form octanuclear volatile complexes similar to cluster **6**.

A possibility of aggregation during thermal decomposition in the solid phase can be confirmed by the results of studying the solid-phase thermal decomposition of the tetranuclear complex $Co_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OOCBu^t)_4(\eta^2\text{-}OOCBu^t)_2(HOEt)_6$ (**7**), whose structure has been described earlier.[8]



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This compound also decomposes in steps (see Fig. 4). The first step (50—85 °C) proceeds with the 8.5±0.5% weight loss and an energy absorption of 92.0±2.5 kJ mol^{-1}, which is comparable with the enthalpy of evaporation of two moles of alcohol. The second step (85—115 °C) is accompanied by a weight loss of 15.7±1.0% and energy absorption as well. Finally, 2.0±1.0% weight is additionally lost in an interval of 120—170 °C. The results suggest that the decomposition product is the octanuclear complex $Co_8(\mu_4\text{-}O)_2(\mu_2\text{-}OOCBu^t)_6(\mu_3\text{-}OOCBu^t)_6$ (**6**). In a decalin solution at 170 °C, complex **7** is transformed into octanuclear cluster **6** in high yield.[8]

One more confirmation of aggregation upon the thermal decomposition of the cobalt pivalate complexes in the solid phase can be the results of studies of the thermal decomposition of the hexanuclear complexes (see Fig. 4) $Co_6(\mu_4\text{-}O)_2(OOCBu^t)_{10}(thf)_4$ (**8**) and $Co_6(\mu_4\text{-}O)_2(OOCBu^t)_{10}(HOOCBu^t)_4$ (**9**), whose structure were described in Refs 9 and 10, respectively.

Compound **8** begins to decompose above 70 °C (boiling point of THF is 66 °C). The first step of decomposition (70—145 °C) is accompanied by energy absorption (135±3.0 kJ mol^{-1}) (enthalpy of THF evaporation is 32.0 kJ mol^{-1}), the weight loss being 18.0±1.0% (content of THF is 17.1%). Thus, the coordinated tetrahydrofuran is removed in the first step. The second step of decomposition (175—210 °C) starts above 175 °C with a weight loss of 7.5±1.0% and is accompanied by an energy absorption of 59.2±2.5 kJ mol^{-1}. However, it should be mentioned that a change in the heat flow in the temperature interval is nonmonotonic (combination of endothermic and exothermic peaks in the thermogram). The bright violet product that formed is sublimed above 210 °C.

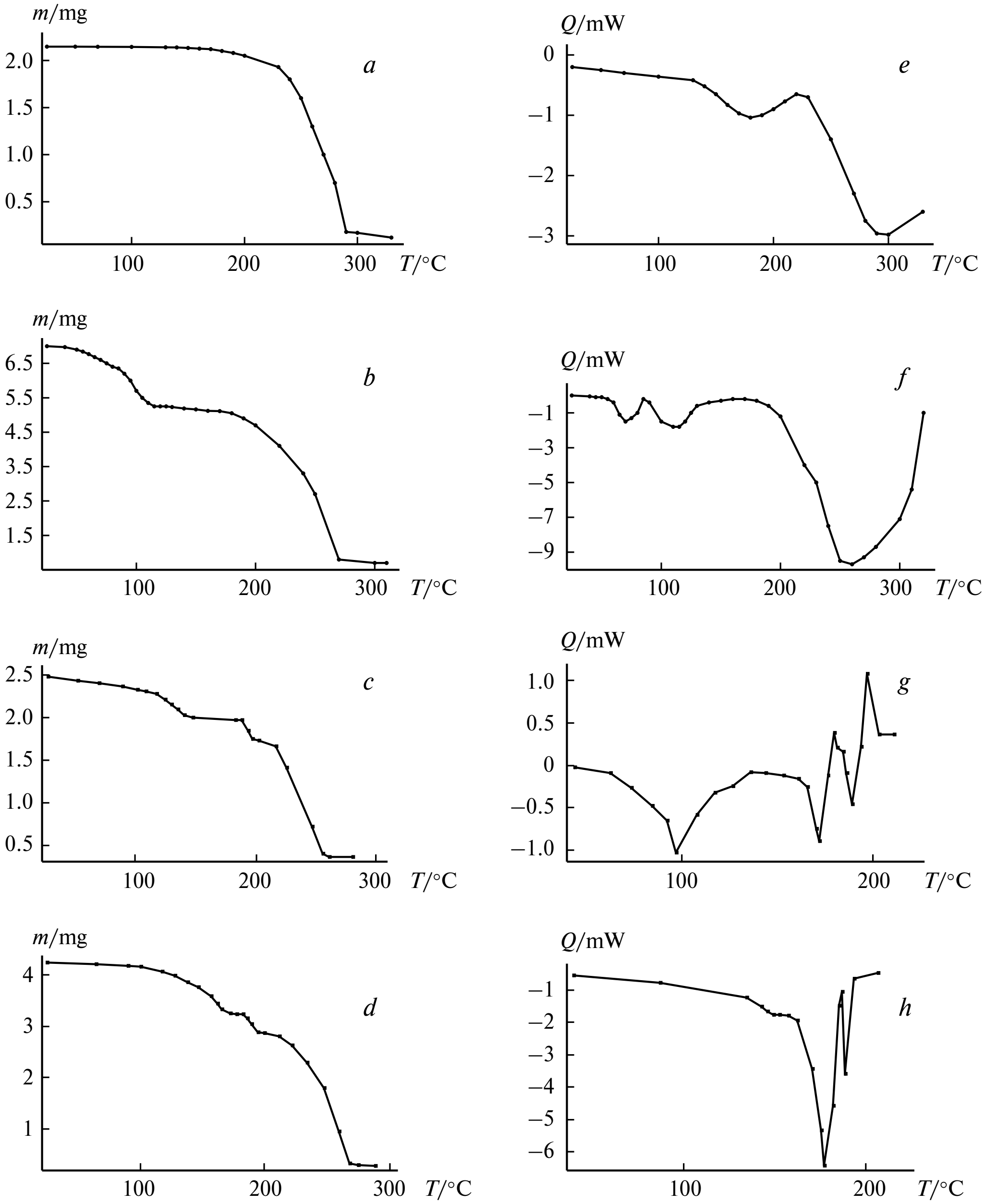
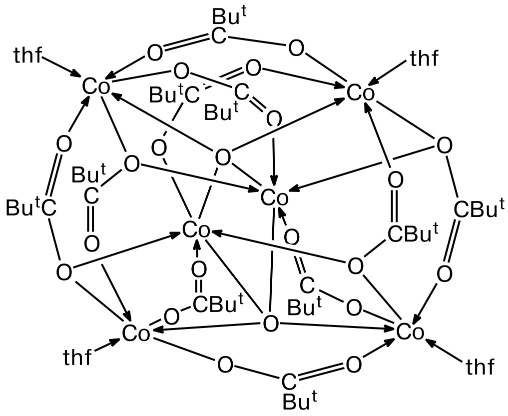


Fig. 4. Temperature dependences of the weight change (*a—d*) and heat flow (*e—h*) for complexes **6** (*a*, *e*), **7** (*b*, *f*), **8** (*c*, *g*), and **9** (*d*, *h*).

Compound **9** begins to decompose above 100 °C. The weight loss in the first step (100—180 °C) is 23.0±1.0% (content of pivalic acid is 22.6%). The weight loss in the second step (185—210 °C) is 6.0±1.0%. Both steps are accompanied by energy absorption but we cannot separate the heat effects. The total heat effect is 352.5±3.5 kJ mol^{-1}. When assuming that pivalic acid, whose evaporation enthalpy is 73.2 kJ mol^{-1}, is removed in the first step and the heat effect of this step almost corresponds to the enthalpy of its evaporation (which can be considered acceptable), then the heat effect of the second step is 59.7±4.0 kJ mol^{-1}. It is seen that the heat effects accompanying the transformations of compounds **8** and **9** in the second step are comparable. The bright violet decomposition product begins to sublime above 210 °C.

To identify aggregation products formed upon the solid-phase thermal decomposition of complexes **7—9**, we measured the specific heat capacity in the 10—120 °C interval for complex **6** and the intermediate thermolysis products of complexes **7—9** (Table 2).

Due to quantitative results of the thermogravimetric study of the thermal decomposition of complexes **7—9** and equal heat capacities of complex **6** and products formed upon thermolysis of complexes **7—9**, we can as-



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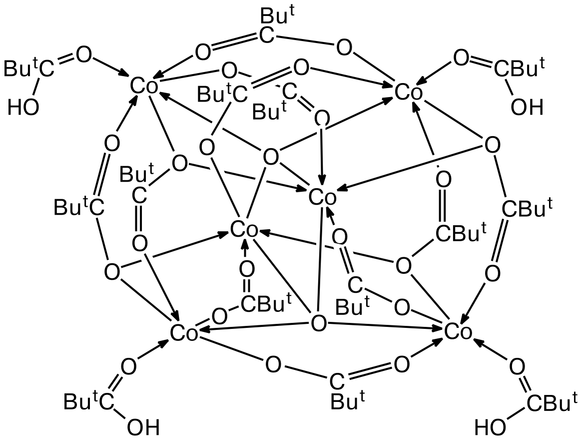

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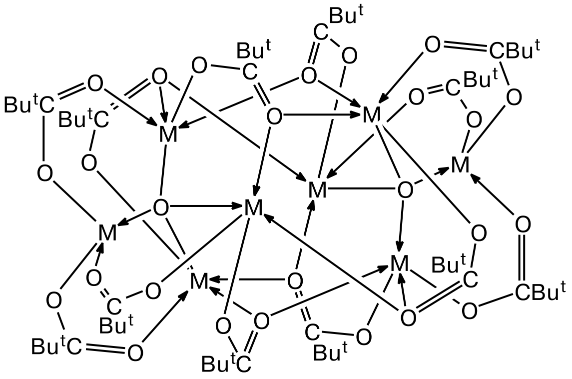
sert the occurrence of aggregation to form an octanuclear metallic cage upon the thermal decomposition of the Co^{II} carboxylate complexes with different number of metal atoms in the 170—210 °C temperature range.

Table 2. Temperature dependences of the specific heat capacity for complex **6** and decomposition products of complexes **7**—**9**

T/°C	Cp(±3%)/J K^{-1} g^{-1}			
	Complex **6**	Decomposition products of complexes		
		7	**8**	**9**
10	1.550	1.523	1.534	1.559
20	1.578	1.575	1.569	1.580
30	1.613	1.625	1.610	1.617
40	1.629	1.631	1.628	1.638
50	1.650	1.664	1.669	1.671
60	1.683	1.690	1.692	1.697
70	1.711	1.705	1.726	1.718
80	1.746	1.738	1.752	1.759
90	1.781	1.796	1.788	1.771
100	1.809	1.800	1.819	1.793
110	1.837	1.845	1.851	1.840
120	1.865	1.870	1.877	1.881

A possibility of formation of a stable heteronuclear pivalate cluster $Co_6Ni_2(\mu_4\text{-}O)_2(\mu_2\text{-}OOCBu^t)_6(\mu_3\text{-}OOCBu^t)_6$ (**10**) with the nickel and cobalt atoms, which is isostructural to cobalt complex **6**, was shown in Ref. 11.



10

M = Co, Ni

It was of interest to compare the mechanism of the solid-phase thermal decomposition of the octanuclear homometallic and heterometallic clusters. Compound **10** is thermally stable up to 165 °C (Fig. 5) (homometallic complex **6**, up to 130 °C). In the 170—350 °C temperature range, the weight decreases stepwise with energy absorption (endothermic peak of a complicated shape). The total weight loss is 65.2±2.0%. A considerable amount of energy is released above 340 °C without a weight change, which is usually caused by energy changes related to the formation of a new structure. The X-ray diffraction analysis of the decomposition product showed the presence of cobalt and nickel oxides (Table 3).

The behavior of **6** and **10** differs, probably, because an unstable nickel-containing octanuclear analog of compound **6** cannot form. Complex **6** contains cobalt atoms with different environments of oxygen atoms (two metal atoms in the tetrahedral environment, and the other six atoms are in a distorted trigonal bipyramidal environment). Unlike the cobalt(II) carboxylate derivatives, the known nickel pivalates contain metal atoms in the octahedral environment only.

Table 3. X-ray diffraction identification of the decomposition products of complex **10**

Decomposition products of **10**		CoO		NiO	
d/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)
2.4721	50	4.4602	65		
2.4254	15			2.412	60
2.1403	100	2.1307	100		
2.0915	40			2.089	100

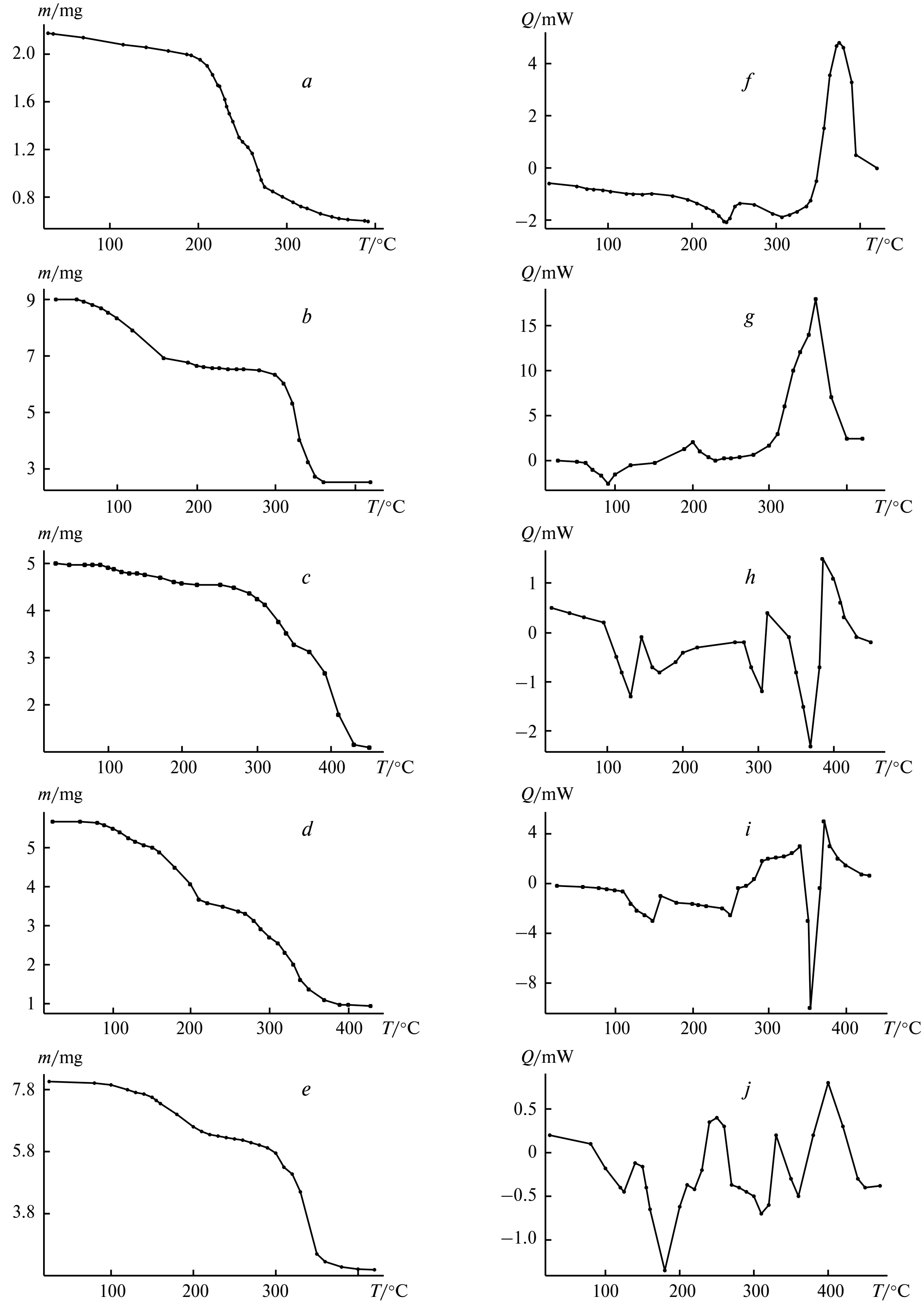
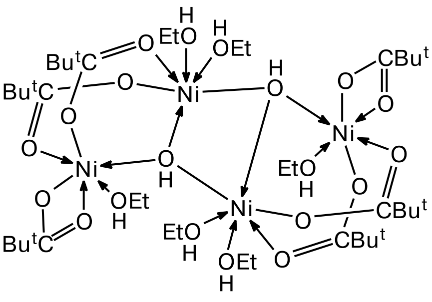


Fig. 5. Temperature dependences of the changes in the weight (*a—e*) and heat flow (*f—l*) for complexes **10** (*a*, *f*), **11** (*b*, *g*), **12** (*c*, *h*), **13** (*d*, *i*), and **15** (*e*, *j*).

As shown above, the solid-phase thermal decomposition of tetranuclear complex **7** is accompanied by aggregation to form octanuclear complex **6**. Therefore, it was of interest to study the thermolysis of the complex $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_4(\eta^2\text{-}OOCBu^t)_2(HOEt)_6$ (**11**), which is isostructural to complex **7**; its structure has been determined earlier.[8]

We studied the thermal decomposition of the $Ni_4[\eta^2\text{-}\{o\text{-}C_6H_4(NH_2)(NHPh)\}]_2(\mu_3\text{-}OH)_2(MeCN)_2(\eta^2\text{-}OOCBu^t)_2(\mu\text{-}OOCBu^t)_4$ complex (**12**) analogous to complex **11** and containing the same structural fragment $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_4(\eta^2\text{-}OOCBu^t)_2$ with similar geometric characteristics and metal charge with compensation of the pivalate and hydroxyl anions.[8] This process was also studied for the $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_6(HOOCBu^t)_4(Ph\text{-}NH_2)_2 \cdot 2HOOCBu^t$ complex (**13**) containing the $Ni_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OOCBu^t)_4$ fragment as complex **11** with ethanol (see Fig. 5).



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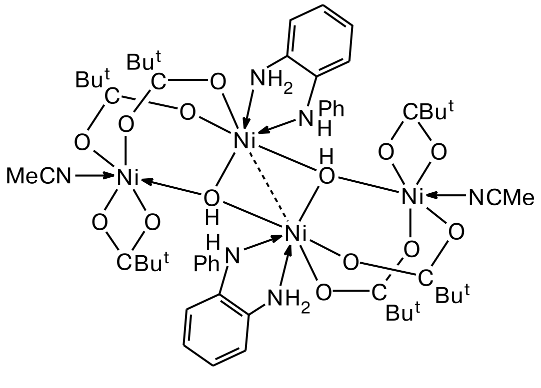

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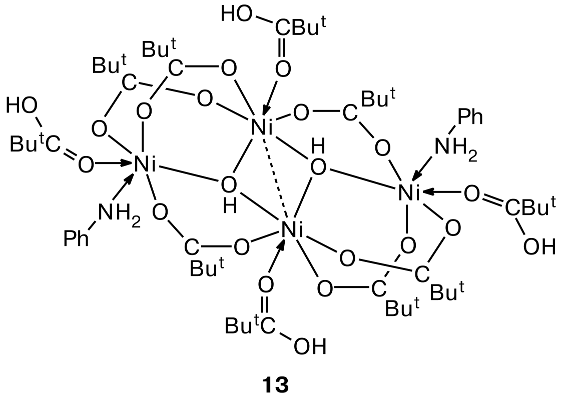

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Complexes **11**, **12**, and **13** begin to decompose at temperatures above 50, 80, and 100 °C, respectively. In the case of compound **11**, 25.0±1.5% weight is lost in the first step of decomposition (55—155 °C) with energy release (ΔH = 262.7±4.8 kJ mol^{-1}). Comparison of the ethanol contents in a molecule of **11** (23.95%) and the enthalpies of ethanol evaporation (ΔH_{vap} = 42.3 kJ mol^{-1}) with the results obtained shows that the coordinated alcohol molecules are removed in this temperature interval. The first step of thermal decomposition of complex **12** also consists of two steps: in an interval of 80—190 °C, coordinated acetonitrile is removed and 7.0±1.0% weight is lost (acetonitrile content is 6.06%) with an energy absorption of 70.7±2.5 kJ mol^{-1} (ΔH_{vap}(MeCN) = 33.4 kJ mol^{-1}). Solvate pivalic acid is removed first during thermolysis of complex **13**. The process occurs in an interval of 100—165 °C (b.p. of $HOOCBu^t$ is 163 °C), the weight loss is 12.5±1.0% (solvate acid content is 12.2%), and the amount of the absorbed energy equals 165.4±3.8 kJ mol^{-1} ($\Delta H_{vap}(HOOCBu^t)$ = 73.2 kJ mol^{-1}). In the 165—230 °C temperature range, 25.6±2.0% weight is additionally lost (content of coordinated acid is 24.35%) with an energy absorption of 337.0±6.0 kJ mol^{-1}. Intermediate products obtained in the first step of decomposition of complexes **11—13** contain, probably, the $Ni_4(\mu_3\text{-}OH)_2(OOCBu^t)_6$ fragment and are stable to 290±5 °C. Above this temperature, the weight decreases intensely: 48.2±2.0% (**11**), 71.7±2.5% (**12**), and 45.4±1.5% (**13**). In the case of compound **11**, the process is accompanied by energy release, while for complexes **12** and **13** energy changes are complicated, although their total heat effect is also negative. The total weight loss in the whole temperature interval under study (25—470 °C) is 73.2±2.0% (**11**), 78.7±2.5% (**12**), and 83.5±2.0% (**13**). The X-ray diffraction analysis of the decomposition products (Table 4) showed the presence of NiO (**11**) and a mixture of NiO and metallic Ni (**12**, **13**).

Probably, the thermolysis of complexes **12** and **13** at high temperatures after removal of coordinated acetonitrile and pivalic acid molecules, under experimental conditions (dry argon atmosphere), results in inner-sphere redox transformations involving the amine-containing ligands and Ni^{II} and in the formation of products with a high nickel content.

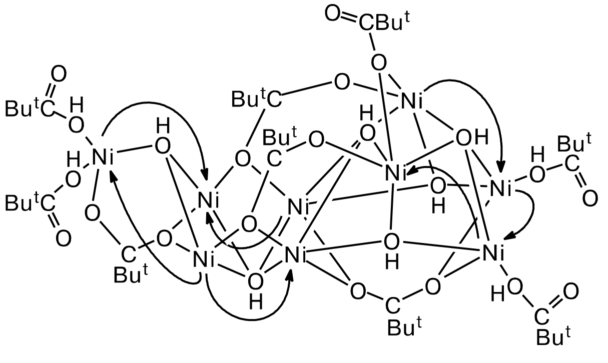
To reveal the effect of the nature of the metal core on the phase composition of the solid decomposition product, we compared the results of thermal decomposition of the tetranuclear isostructural complexes $M_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_4(\eta^2\text{-}OOCBu^t)_2(HOEt)_6$ (M = Co (**7**), Ni (**11**), Fe (**14**)).[12]

Table 4. X-ray diffraction identification of the decomposition products of complexes **11—13** and **15**

Decomposition products of complexes								NiO		Ni	
11		**12**		**13**		**15**					
d/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)
2.4235	60	2.4153	45	2.4185	40	2.4114	50	2.412	60		
2.0921	100	2.0902	65	2.0907	70	2.0846	100	2.089	100		
		2.0354	100	2.0375	100					2.034	100
		1.7598	25	1.7602	20					1.762	40

The decomposition of complexes **7** and **11** is described above. The thermal decomposition of compound **14** starts above 60 °C, coordinated ethanol molecules are removed below 160 °C, and the weight loss is 22.0±1.5% (ethanol content is 22.38%). The process is accompanied by energy absorption. The enthalpy change in the 60—160 °C range is 263.5±6.0 kJ mol^{-1}. This value is comparable with the enthalpy of evaporation of six moles of ethanol (42.3×6 kJ mol^{-1}). An energy release is observed above 160 °C without a noticeable weight change, which is usually related to the formation of a new structure. The intermediate product contains, probably, the $Fe_4(\mu_3\text{-}OH)_2(OOCBu^t)_6$ fragment and is stable up to 270±5 °C. Above this temperature, the weight decreases considerably: 46.6±2.0% in the 270—450 °C temperature interval. The thermal destruction is accompanied by energy release. The total weight loss in the temperature interval under study is 68.6±2.0%. The black-colored decomposition product is pyrophoric. According to the X-ray diffraction data (within an experimental error of ±3%), this is FeO_x (Table 5). Thus, the character of decomposition of the iron-containing and nickel-containing complexes is identical.

We also studied the thermal decomposition of the nonanuclear complex $Ni_9(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_4\text{-}OOCBu^t)(\mu_3\text{-}OOCBu^t)_3(\mu\text{-}OOCBu^t)_8(HOOCBu^t)_4$ (**15**), whose structure has been described earlier[8,13] (see Fig. 5).



15

↷ = μ-O,O′-$OOCBu^t$

Table 5. X-ray diffraction identification of the decomposition products of complex **14**

Decomposition products of **14**		FeO (cubic)		$Fe_{0.98}O$ (hexagonal)	
d/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)
2.5245	20			2.517	80
2.4864	70	2.490	80		
2.3679	10			2.376	80
2.1578	100	2.153	100		
2.0675	30			2.078	100
1.5247	50	1.523	60		
1.5096	10			1.510	50

The decomposition starts above 100 °C. In the first step, probably, coordinated pivalic acid is lost, and the process is stepwise. Below 140 °C, the weight loss is 4.4±1.0%, and the absorbed energy is 80.5±2.5 kJ mol^{-1}. Further, below 220 °C, 14.0±2.0% weight is lost and an energy of 245.7±5.3 kJ mol^{-1} is absorbed. The values of the weight percentage of volatiles and the heat effect values are comparable with the calculated acid content and its evaporation enthalpy. The energy is released below 290±5 °C without a noticeable weight change, which is probably due to the formation of an intermediate identical to the product formed upon thermolysis of complex **11** after removal of coordinated ethanol molecules. Above 300 °C, the character of decomposition of complexes **11** and **15** is the same. The decomposition product is nickel oxide.

Thus, we showed that the decomposition of the polynuclear (from bi- to hexanuclear) Co^{II} carboxylate complexes is accompanied by aggregation to form a volatile octanuclear complex. By contrast, the thermolysis of the polynuclear Ni^{II} carboxylates is destructive, and the phase composition of their decomposition products is determined by the nature of the coordinated ligands.

Experimental

The thermal decomposition of the complexes was studied by differential scanning calorimetry and thermogravimetry analysis on DSC-20 and TG-50 moduli of a Mettler TA-3000 thermal analyzer. Samples were heated under dry argon with a rate of 5 deg $\min^{-1}$, which was the same in all experiments. For each compound, four runs were carried out by differential scanning calorimetry and three thermogravimetric experiments were conducted. The weight loss upon thermal destruction was determined directly on a TG-50 modulus, and the weighing accuracy was $\pm 2 \cdot 10^{-3}$ mg. The step-by-step study of thermal decomposition was carried out by differential scanning calorimetry with partition of the whole temperature area under study into separate intervals. The value and number of these intervals were determined after the total weight and energy changes upon decomposition have been found. This experimental procedure made it possible to measure the weight loss in each temperature interval and compare the DSC results with thermogravimetric data. Satisfactory agreement of the results confirmed confidence and reliability of the data obtained. The accuracy of determination of anomalous points and heat effects in thermograms was ±1° and ±0.5%, respectively.

To measure the heat capacity, we used a DSC-30 modulus of a TA-4000 thermal analyzer. The latter is a differential calorimeter operating in the scan mode of the shell temperature and designed for quantitative thermal measurements. The relative error of heat capacity measurement was 2—3%. Heat capacities of the well studied compounds were periodically determined to estimate a possible systematic measurement error. For instance, the deviation of the obtained values of the heat capacity of corundum from the values presented by the U.S. National Bureau of Standards (NBS) was ±1—2%.

X-ray diffraction analysis of decomposition products was carried out with a STOE Powder Diffraction System and an FR-552 monochromating chamber (Cu-Kα1 radiation) using germanium as the internal standard (X-ray diffraction patterns were processed on an IZA-2 instrument with an accuracy of ±0.01 mm).

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