High-spin carboxylate polymers $[M(OOCCMe_3)_2]_n$ of Group VIII 3d metals*

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A coordination polymer of the general formula $[Co(OOCCMe_3)_2]_n$ (**2**) was prepared by mild thermolysis of the coordination polymer of variable composition $[(HOOCCMe_3)_xCo(OH)_n(OOCCMe_3)_{2-n}]_m$, the dinuclear cobalt complex $Co_2(\mu\text{-}H_2O)(OOCCMe_3)_4(HOOCCMe_3)_4$, the tetranuclear cobalt cluster $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$, and the hexanuclear cluster $[Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(C_4H_8O)_3(H_2O)]\cdot 1.5(C_4H_8O)$ (**7**) in organic solvents. In the crystal, the polymer has a chain structure. Unlike thermolysis of cobalt pivalates, thermolysis of the dinuclear complex $Ni_2(\mu\text{-}H_2O)(OOCCMe_3)_4(HOOCCMe_3)_4$ gave rise to the hexanuclear complex $Ni_6(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (**3**). The magnetic properties of compound **2** are substantially different from those of **3**. Compound **2** undergoes the magnetic phase transition into the ordered state at T_c = 3.4 K (H = 1 Oe), whereas compound **3** exhibits antiferromagnetic properties. Solid-state decomposition of polymeric cobalt carboxylate **2** (below 350 °C) afforded the octanuclear cluster $Co_8(\mu_4\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (**9**) as the major product, which sublimes without decomposition. Decomposition of **3** gave nickel oxide as the final product. Pivalates **2** and **3** reacted with 2,3-lutidine in acetonitrile at 80 °C to form the isostructural dinuclear complexes $(2,3\text{-}Me_2C_5H_3N)_2M_2(\mu\text{-}OOCCMe_3)_4$ (M = Co or Ni). The structures of compounds **3** and **7** were established by X-ray diffraction. The structure of polymer **2** was determined by powder X-ray diffraction analysis.

Key words: polymeric cobalt and nickel complexes, trimethylacetate complexes, X-ray diffraction study, magnetic properties, thermolysis.

The development of efficient methods for the synthesis of convenient starting "spin materials" is of importance for the chemical design of molecular magnets with desired properties and the preparation of precursors for the production of various inorganic materials by thermochemical methods. Polynuclear (or even polymeric) metal complexes of constant composition with particular structures, which are highly reactive toward various organic donors and are readily decomposed at moderate temperatures (60—450 °C), hold promise as spin materials. It is desirable that the starting complexes be able to generate "magnetic molecules" (for example, in reactions with organic donors) or form materials (for example, oxides by mild thermolysis) with desired physical properties. Among such compounds are pivalate coordination polymers of simple composition $[M(OOCCMe_3)_2]_n$ (M is a 3d element). Compounds with M = Fe (S = 2),[1,2] Co (S = 3/2),[3,4] or Ni (S = 1)[5,6] have already found use in the synthesis of carboxylate complexes. However, only the structure of $[Fe(OOCCMe_3)_2]_n$ (**1**) was established by X-ray diffraction.[7] Most of analogous Co^{II} and Ni^{II} compounds, which were prepared from salts of these metals by the exchange reactions with $KOOCCMe_3$ in water or by melting aqua acetates (M = Co) with pivalic acid,[3,5] have variable composition $[(HOOCCMe_3)_xM(OH)_n(OOCCMe_3)_{2-n}]_m$ (M = Co or Ni). The structures of these compounds are unknown,

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and the presence of different amounts of solvent or coordinated pivalic acid molecules and hydroxo, oxo, and aqua ligands is a serious obstacle to their use as the starting reagents.

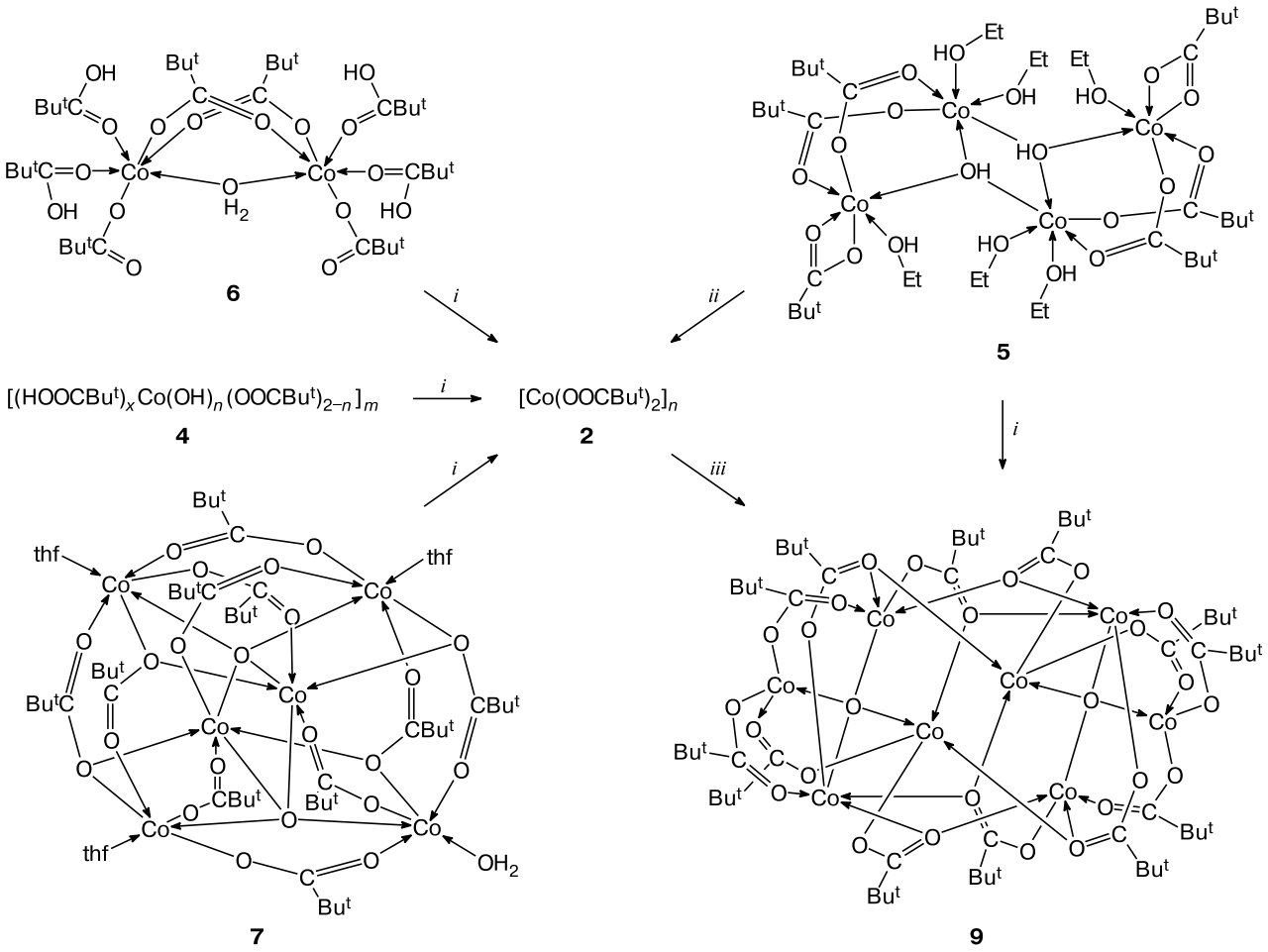
The aim of the present study was to search for conditions of the formation of stable polymers of constant composition $[M(OOCCMe_3)_2]_n$ containing high-spin atoms M = Co^{II} (**2**) or Ni^{II} (**3**), which are analogs of polymeric iron pivalate **1**, from various polynuclear compounds, investigate their structures, the magnetic properties, and solid-state thermolysis, and simulate their chemical behavior toward α-substituted pyridines, which initiate the formation of tetracarboxylate dimers.[8—10]

Results and Discussion

We found that mild thermolysis (below 175 °C) of some polynuclear high-spin cobalt(II) pivalates, such as the polymer of variable composition $[(HOOCCMe_3)_xCo(OH)_n(OOCCMe_3)_{2-n}]_m$ (**4**),[3] the tetranuclear cobalt antiferromagnetic cluster $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ (**5**),[3] or the dinuclear cobalt antiferromagnetic complex $Co_2(\mu\text{-}H_2O)(OOCCMe_3)_4(HOOCCMe_3)_4$ (**6**),[11,12] which differ in the geometry of the metal core as well as in the composition and nature of the bridging groups, in organic solvents affords the stable polymer of the general formula $[Co(OOCCMe_3)_2]_n$ (**2**) as violet thin fiber crystals sensitive to atmospheric moisture (Scheme 1).

Heating of the hexanuclear complex $[Co_6(\mu_4\text{-}O)_2(\mu\text{-}OOCCMe_3)_{10}(C_4H_8O)_3(H_2O)]\cdot 1.5(C_4H_8O)$ (**7**$\cdot 1.5(C_4H_8O)$) containing the Co^{II} and Co^{III} atoms to 174 °C in decane also led to the formation of polymer **2** in good yield (53%). The compound **7**$\cdot 1.5(C_4H_8O)$ was prepared by recrystallization from THF of the hexanuclear pivalate cluster $Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(HOOCCMe_3)_4$ (**8**) (n = 2 and 3), which we have synthesized earlier.[12,13] X-ray diffraction study demonstrated that the oxo metal carboxylate cores of clusters **7** and **8** are identical. The metal core

Scheme 1



Reagents and conditions: *i*. Ar, decane, 174 °C; *ii*. MeCN, 80 °C; *iii*. Ar, 30 min at 20—350 °C and 5 h at 350 °C.

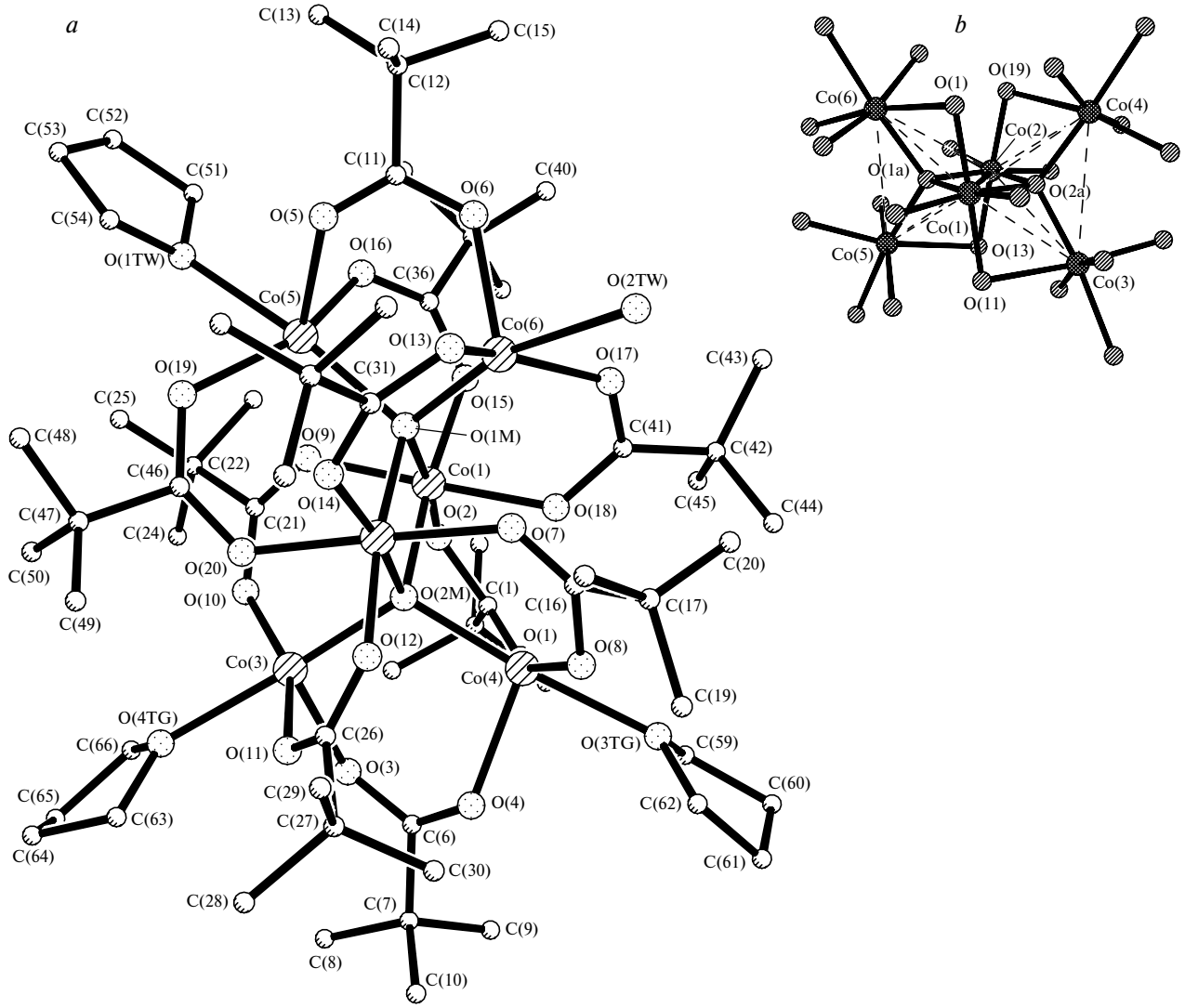


Fig. 1. Structures of the hexanuclear complex $[Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(C_4H_8O)_3(H_2O)]\cdot 1.5(C_4H_8O)$ (**7**) (*a*) and the metal oxygen core of the cluster **7** (*b*).

of cluster **7** is formed by two edge-sharing metal tetrahedra Co_4O (Co—O, 1.878(6)—2.063(6) Å; nonbonded Co...Co distances, 2.848(3)—3.454(3) Å) (Fig. 1).

X-ray diffraction study demonstrated that the crystals of the solvate $\mathbf{7}\cdot 1.5(C_4H_8O)$ consist of the hexanuclear clusters $Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(C_4H_8O)_3(H_2O)$ and the THF solvate molecules, which are held in the crystal by hydrogen bonds and van der Waals interactions. In the crystal structure, hexanuclear molecules **7** are disordered and are present as two isomers, in which two coordinated THF molecules (O(1TW) and O(2TW)) are randomly (with equal occupancies) replaced by two water molecules. Figure 1, *a* shows the isomer, in which the Co(5) atom is coordinated by a tetrahydrofuran molecule, whereas the Co(6) atom is coordinated by a water molecule. Although the composition of the complex $\mathbf{7}\cdot 1.5(C_4H_8O)$ corresponds to the above-given formula, the crystal apparently contains a total set of molecules, *viz.*, $Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(C_4H_8O)_3(H_2O)$, $Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(C_4H_8O)_2(H_2O)_2$, and $Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(C_4H_8O)_4$. The complex $\mathbf{7}\cdot 1.5(C_4H_8O)$ exhibits antiferromagnetic properties (μ_{eff} = 8.006 (300 K)—1.431 μ_B (2 K)) (Fig. 2).

In spite of the fact that we failed to grow single crystals of polymer **2** suitable for complete X-ray diffraction study, crystals of this compound (prepared from different starting samples) were identified by powder X-ray diffraction analysis. It appeared that polymer **2** (crystals are triclinic, a = 6.285(4), b = 10.083(13), c = 11.136(10) Å, α = 103.35(5), β = 102.15(3), γ = 94.40(3)°; V = 665.4(14) Å^3) is an isostructural analog of iron-containing polymer **1**.[7] The IR spectra of coordination polymers **1** and samples of **2** prepared from different starting compounds are also very similar.

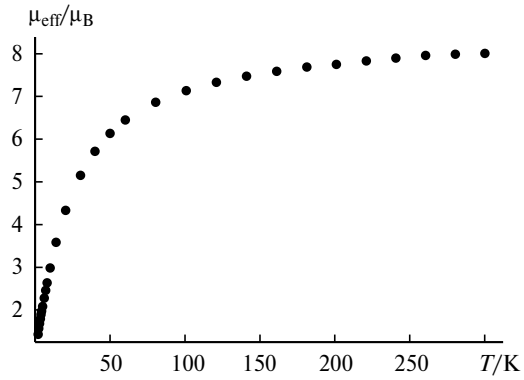


Fig. 2. Magnetic properties of complex **7**.

Presumably, the crystals of **2** consist of chains of cobalt(II) atoms, which are linked to each other by pairs of carboxylate bridges, like the crystals of the iron-containing analog[7] (Fig. 3).

It appeared that polymer **2** is the only thermolysis product of **6**. However, thermolysis of compounds **4** and **7** · 1.5(C_4H_8O) in boiling decane afforded, along with the above-mentioned polymer **2**, the octanuclear antiferromagnetic cluster $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{12}$ (**9**) ($n = 2$ and 3) in high yield (see Scheme 1). The crystallographic characteristics of cluster **9** are consistent with the parameters obtained earlier[6] by single-crystal X-ray diffraction

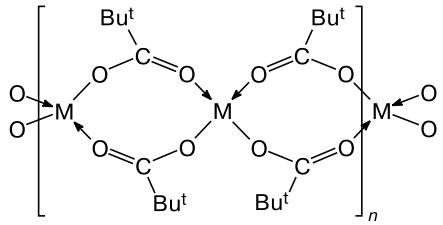


Fig. 3. Fragment of the polymeric chain $[M(OOCCMe_3)_2]_n$ (M = Fe (**1**) or Co (**2**)).

study of the molecular structure of compound **9**. Besides, compound **9** is the only thermolysis product of tetranuclear cluster **5** in boiling decalin or decane.[6,14]

The data on the thermal transformations of the polynuclear pivalate molecules in solution correlate with the results of solid-state thermolysis of these compounds published earlier.[15] For example, elimination of the neutral ligands from complexes **5**—**7** · 1.5(C_4H_8O) is observed in the initial steps of thermolysis of their crystals (below 180 °C). However, the identification of the intermediate structure (earlier, thermolysis of cobalt compounds has been studied up to 450 °C) required additional investigation. For this purpose, we studied thermal decomposition of one of the starting cobalt pivalates, *viz.*, dinuclear complex **6**, at different heating rates (3 and 10 deg min^{-1}; in the study,[15] the heating rate was 5 deg min^{-1}) (Fig. 4).

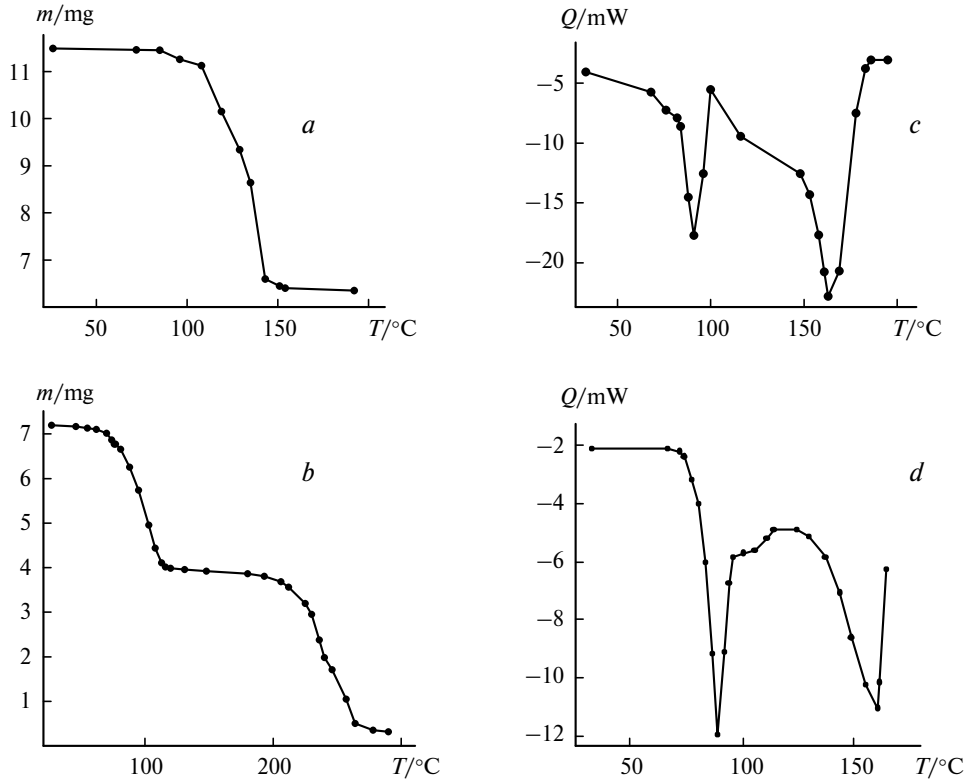


Fig. 4. Temperature dependences of the weight loss (*a*, *b*) and the heat flux (*c*, *d*) for complex **6** at a heating rate of 3 (*a*, *c*) and 5 deg min^{-1} (*b*, *d*).[15]

Heating at a lower rate enabled us to study decomposition steps in more detail and to more precisely separate the thermal effects of the first and second steps. For example, the first step of thermolysis of the dinuclear complex $Co_2(\mu\text{-}H_2O)(OOCCMe_3)_4(HOOCCMe_3)_4$ (**6**) (below 100 °C) is apparently accompanied by the hydrogen bond cleavage and removal of the bridging water molecules (ΔH = 45.6±2.0 kJ mol^{-1}) with a weight loss of 2.0±1.0% (2.3±1.0%).[15] In the second step occurring with energy absorption (ΔH = 249.6±7.0 kJ mol^{-1}), the weight loss was 42.3±1.0%. In the temperature range of 70—140 °C, the weight loss was 44.4±1.0% (44.9±1.0%),[15] which corresponds to the residual composition $Co(OOCCMe_3)_2$. To identify the resulting product, thermal decomposition was terminated at 170 °C. It was impossible to study the product by spectroscopy or X-ray diffraction after withdraw from the apparatus because of its high activity and instability. Hence, calorimetric measurements of the decomposition product of **6** were carried out without withdraw of the sample from the apparatus (Table 1). For comparison, we measured the heat capacity of structurally characterized compound **2** in the temperature range of 10—140 °C (see Table 1). Table 1 lists also the data, which we have obtained earlier[16] for compound **1**. Slight systematic differences in the heat capacities for the decomposition product of **6** and polymer **2** are apparently attributed to the following facts: first, these differences are substantially smaller than the measurement error of this parameter and, second, it is unlikely that thermal decomposition of **6** affords the perfect crystal structure of **2**. Hence, the initial steps of thermolysis presumably give rise to polymer **2** or at least a polynuclear compound of this composition.

Table 1. Temperature dependence of the heat capacity for polymers **1** and **2** and decomposition product of complex **6**

T/°C	*Cp*±2.5%/J mol^{-1} K^{-1}		
	1 [16]	**2**	Decomposition product of complex **6**
10	389.2	392.2	395.5
20	395.4	397.3	400.2
30	405.0	405.1	407.4
40	—	411.7	413.7
50	—	418.4	420.8
60	—	427.5	430.7
70	—	433.9	436.9
80	—	442.1	444.5
90	—	449.8	452.7
100	—	456.2	459.5
110	—	466.0	467.3
120	—	475.3	477.0
130	—	481.6	483.8
140	—	487.4	489.4

Table 2. X-ray diffraction patterns of the evaporation products of polymer **2** and octanuclear complex **9**

9		Volatile product			
		Experiment 1		Experiment 2	
d/Å	I/I_0 (%)	*d*/Å	I/I_0 (%)	*d*/Å	I/I_0 (%)
11.74	100	11.72	93	11.76	100
10.16	53	10.18	100	10.17	54
8.31	5	8.31	3	8.29	6
7.198	5	7.179	2	7.198	5
5.067	9	5.070	3	5.072	18
4.934	23	4.917	7	4.922	19
4.796	19	4.778	6	4.784	22
4.429	4	4.420	2		
4.148	5	4.152	6	4.179	9
3.909	13	3.902	7	3.908	9
3.385	11	3.380	4	3.385	4
3.096	7	3.091	4	3.093	4
2.928	6	2.924	3	2.929	4
2.711	5	2.707	2	2.710	2
2.599	5	2.596	2		
2.577	6	2.573	3	2.576	5
2.460	18	2.457	5	2.459	4
2.227	11	2.224	6	2.225	7

In the study,[15] it was demonstrated that thermal decomposition of various Co^{II} carboxylate complexes in the temperature range of 190—220 °C is accompanied by aggregation to form the octanuclear complex $Co_8(\mu_4\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (**9**). This cluster was obtained as the major product of solid-state decomposition of polymeric cobalt carboxylate **2** (350 °C) under argon. Study of thermolysis of polymer **2** allowed us to isolate the blue-violet finely crystalline volatile compound that formed in the course of the reaction and analyze it by powder X-ray diffraction (Table 2).

The results of our study (see Table 2) show that decomposition (to 350 °C) of polymer **2** affords octanuclear complex **9** as the final product, which sublimes without decomposition.

The magnetic data (Fig. 5) demonstrate that polymer **2**, like iron-containing polymer **1** (T_c = 3.8 K at H = 1 Oe),[16] undergoes the magnetic phase transition to the ordered state at T_c = 3.4 K (H = 1 Oe) (see Fig. 5, *b*) and exhibits the properties of a soft magnet (without a hysteresis loop). The magnetization of the compound in strong field (H = 50 kOe) is as high as σ_{exp} = 200±5 G cm^3 mol^{-1} (see Fig. 5, *c*).

To prepare the expected coordination nickel-containing polymer of formal composition $[Ni(OOCCMe_3)_2]_n$ (**3**), we used the known ferromagnetic dinuclear complex $Ni_2(\mu\text{-}H_2O)(OOCCMe_3)_4(HOOCCMe_3)_4$ (**10**)[10—12,17] isostructural to cobalt complex **6** as the starting nickel(II) pivalate.

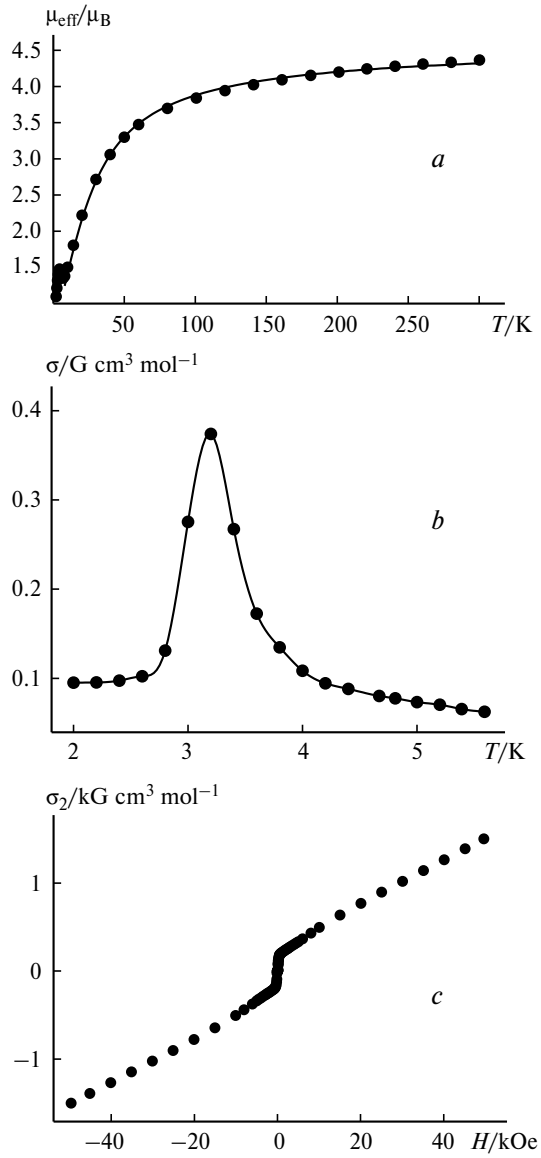


Fig. 5. Temperature dependences of μ_{eff} (*a*) and the magnetization (*b*) and the plot of the magnetization *vs.* the magnetic field strength (*c*) for complex **2** (*a*: $g = 2.4\pm0.1$, $J = -4.5\pm0.1$ cm^{-1}, $\sigma = 0.00094$; *b*: $T_N = 3.4$ K; *c*: $\sigma_s = 200\pm5$ G cm^3 mol^{-1}, $T = 2$ K).

Thermolysis of **10** in a decane solution under argon at 174 °C (Scheme 2) afforded brown-yellow crystals of a complex, which are very sensitive to atmospheric oxygen, whose formal composition agrees with the expected composition.

Scheme 2

$$\underset{\textbf{10}}{Ni_2(\mu\text{-}OH_2)(OOCBu^t)_4(HOOCBu^t)_4} \xrightarrow{i} \underset{\textbf{3}}{[Ni(OOCBu^t)_2]_n}$$

i. Decane, 174 °C.

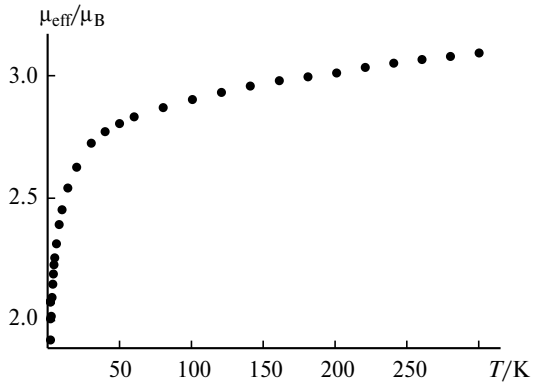


Fig. 6. Magnetic properties of complex **3**.

However, the magnetic properties of this compound are substantially different from those of its iron- and cobalt-containing analogs. Complex **3** exhibits antiferromagnetic properties in the temperature range of 300—2 K ($\mu_{eff} = 3.092$—2.078 μ_B) (Fig. 6).

The results of X-ray diffraction study of crystals of **3** were unexpected. In the crystal structure of the nickel derivative, the cyclic hexanuclear complex is the main structural unit, unlike the crystals of the iron and cobalt derivatives consisting of infinite chains. In molecule **3**, six nickel(II) atoms (Ni...Ni, 3.284(1)—3.325(1) Å; Ni—Ni—Ni, 100.33(3)—103.15(3)°) are linked to each other by twelve carboxylate bridges, only six of these bridges having a usual *O*,*O*′ configuration (Ni—O, 1.935(3)—1.983(3) Å; O—C, 1.240(5)—1.268(5) Å; O—C—O, 125.6(4)—126.3(4)°). Six other bridging carboxylate groups are tridentate (Ni—O, 1.992(3)—2.028(3) Å; C—O, 1.226(5)—1.286(5) Å; O—C—O, 121.6(4)—122.2(4)°). Therefore, there are three bridges, *viz.*, two OCO bridges and one O bridge, between pairs of nickel atoms (Fig. 7, *a*). In the crystal structure, the cyclic molecules of the hexamer form stacks containing a cavity (see Fig. 7, *b*), which is apparently suitable for trapping small molecules. The metal atoms are in a distorted tetragonal-pyramidal environment formed by oxygen atoms.

The magnetic properties of the polymer of constant composition **3** are substantially different from those of the analogous nickel compound of variable composition $[(HOOCCMe_3)_xNi(OH)_n(OOCCMe_3)_{2-n}]_m$ (**11**). For example, polymer **11** exhibits ferromagnetic properties in the temperature range of 4—14 K (Fig. 8).

The earlier study[15] of solid-state thermal decomposition of analogous dinuclear complexes **10**, $Ni_2(\mu\text{-}H_2O)(OOCCMe_3)_4(Py)_4$ (**12**), and $Ni_2(\mu\text{-}H_2O)(OOCCMe_3)_4(bpy)_2$ (**13**) demonstrated that thermolysis to 260—280 °C affords presumably a compound of formal composition $[Ni(OOCCMe_3)_2]_x$, the identity of the resulting products being confirmed by calorimetry.

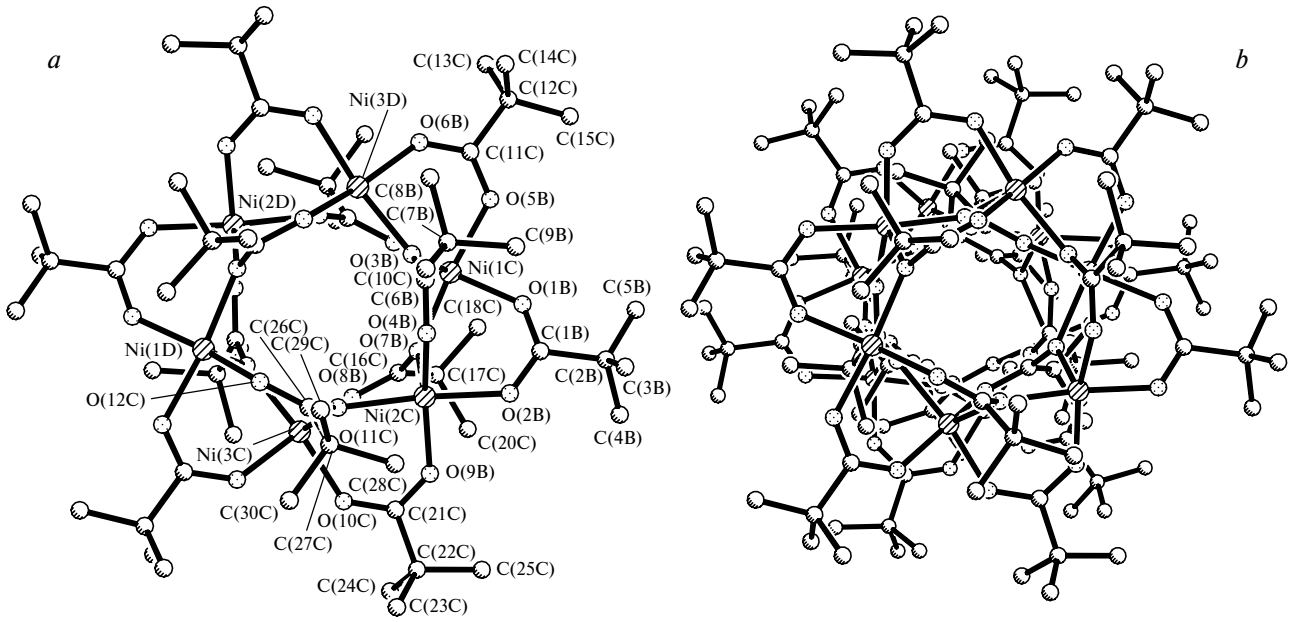


Fig. 7. Molecular structure of the hexanuclear complex $Ni_6(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (**3**) (*a*) and the molecular packing in the stack (*b*).

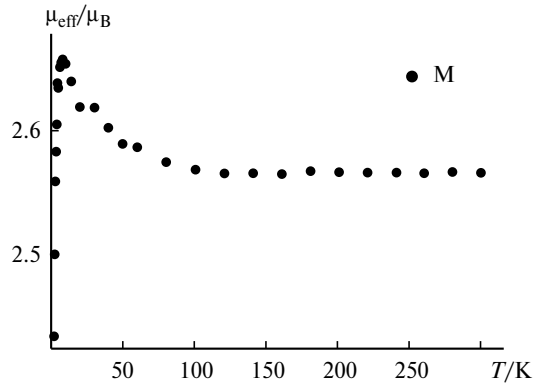


Fig. 8. Magnetic properties of compound **11**.

At the same time, thermal treatment of **10** in solution (decane) produced a cyclic hexanuclear complex. In this case, the question arises about the structural identity of of the products of thermolysis performed in the solid state and solution, in spite of the fact that their compositions are formally identical. Analogous iron- and cobalt-containing compounds consist of polymeric chains. In this connection, we studied solid-state thermal decomposition of cyclic hexanuclear complex **3** and compared these data with the results of study of thermal decomposition of dinuclear complex **10** (Fig. 9), from which the $[Ni(OOCCMe_3)_2]_x$ compound is generated. Complex **3** is thermally stable up to 320±5 °C. Further heating accompanied by energy absorption leads to a sharp weight loss (320—370 °C) (see Fig. 9, *a*, *c*). Nickel oxide was obtained as the final decomposition product. The last step of decomposition of complex **10** (see Fig. 9, *b*, *d*), which apparently gives rise to a compound of formal composition $Ni(OOCCMe_3)_2$, starts at a temperature higher than 322±5 °C and occurs in the temperature range of

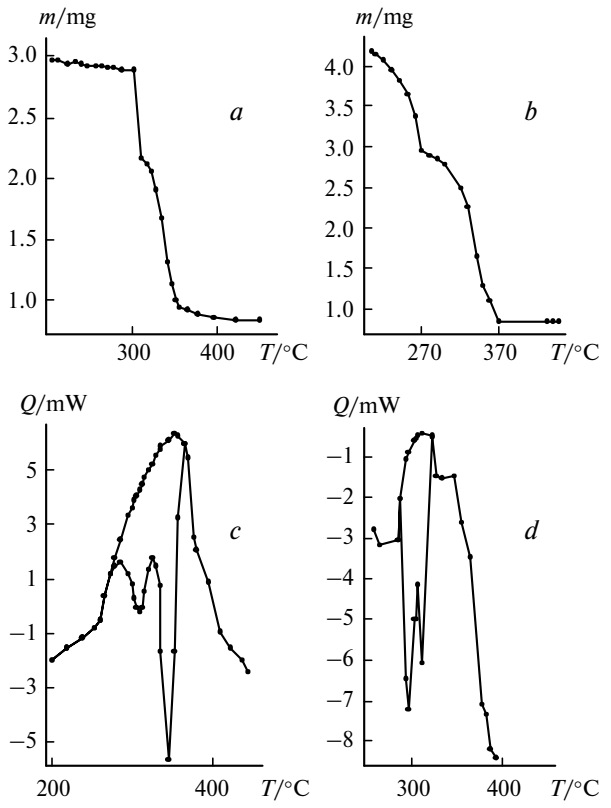
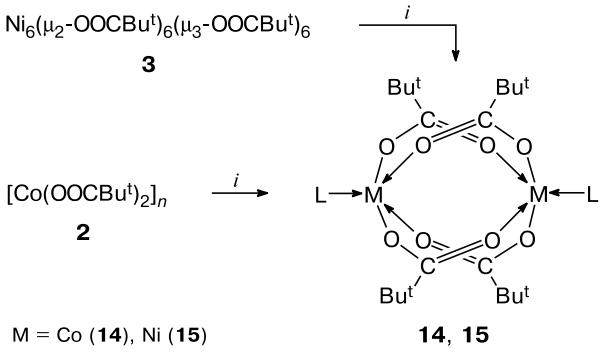


Fig. 9. Temperature dependences of the weight loss (*a*, *b*) and the heat flux (*c*, *d*) for complexes **3** (*a*, *c*) and **10** (*b*, *d*).

322—380 °C. The character of energy changes during decomposition of complex **3** is identical to that for the decomposition product of **10**. The weight losses upon decomposition of **3** and in the last step of decomposition of complex **10** (based on the product of composition $Ni(OOCCMe_3)_2$) are 70.3±1.0% and 71.7±1.5%, respectively. Therefore, the quantitative results of thermogravimetric analysis, the temperature ranges of the decomposition steps, and the qualitative agreement between the thermograms for the compounds under consideration suggest that solid-state thermolysis of dinuclear aqua-bridged nickel complexes **10—13** at temperatures higher than 270±10 °C produces the cyclic compound $[Ni(OOCCMe_3)_2]_6$.

In spite of the different structures and magnetic properties of the pivalates $[M(OOCCMe_3)_2]_n$ containing cobalt **2** and nickel **3**, their reactivities toward pyridine derivatives are virtually identical. For example, complexes **2** and **3** readily react with 2,3-lutidine under an inert atmosphere in acetonitrile at 80 °C. In both cases, the dinuclear complexes with a Chinese-lantern structure $(2,3\text{-}Me_2C_5H_3N)_2M_2(\mu\text{-}OOCCMe_3)_4$ (M = Co (**14**) or Ni (**15**)) (Scheme 3) were prepared in virtually quantitative yields.

Scheme 3



i. 2,3-Lutidine (L), MeCN, 80 °C.

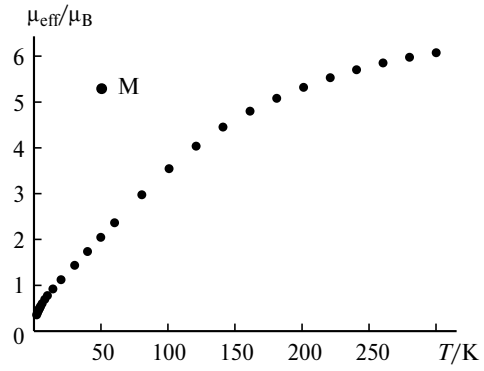


Fig. 10. Magnetic properties of complex **14**.

Earlier, antiferromagnetic complex **15** has been synthesized by the reaction of the nonanuclear cluster $Ni_9(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ with lutidine.[5] Powder X-ray diffraction study demonstrated that dinuclear cobalt complex **14** (space group $P\bar{1}$, a = 9.73(1) Å, b = 10.92(1) Å, c = 11.22(1) Å, α = 118.91(2)°, β = 100.69(2)°, γ = 97.81(2)°; V = 989.4(9) Å^3) is isostructural to compound **12** and also exhibits antiferromagnetic properties (μ_{eff} = 6.076 (300 K)—0.356 μ_B (2 K)) (Fig. 10).

Experimental

All synthetic operations were performed under pure argon with the use of deaerated solvents. The starting polynuclear cobalt[3,11,13] and nickel[6,17] pivalates were prepared according to procedures described earlier. Trimethylacetic acid (Acros Organics) was used in the synthesis. The complexes were synthesized with the use of the standard Schlenk technique.

The IR spectra of compounds **2** and **3** were recorded on a NEXUS Nicolet spectrophotometer; the IR spectra of compounds **7**, **14**, and **15**, on a Specord M-80 spectrophotometer. The static magnetic susceptibility was measured on a SQUID MPMS-59 Quantum Desing magnetometer in the temperature range of 2—300 K. The effective magnetic moments were calculated by the equation $\mu_{eff} = (8\chi_M T)^{1/2}$.

Powder X-ray diffraction analysis of compounds **2**, **9**, and **14** was carried out on a Guinier camera G670(HUBER) using CuKα1 radiation. The X-ray diffraction patterns were indexed using the TREOR90 program.[18]

Thermal decomposition of compounds **2**, **3**, and **6** was studied by the DSC and TG methods on DSC-20 and TG-50 units of a Mettler TA-3000 thermoanalyzer. For each compounds, three DSC experiments and three TG experiments were performed. The weight loss upon thermal destruction was determined directly on a TG-50 thermobalance; the accuracy of weighing was $\pm 2 \cdot 10^{-3}$ mg. A stepwise study of thermal decomposition was performed by differential scanning calorimetry, which involved the division of the total temperature range into intervals. The size and number of these intervals were determined after study of the overall weight and the energy changes upon decomposition. The accuracy of the determination of the anomalous points and the thermal effects in the thermograms was ±1° and ±0.5%, respectively. The heat capacity was measured on a DSC-30 unit, which is a differential scanning calorimeter operating in the sell temperature scanning mode and designed for quantitative thermal measurements. The heat capacity was measured at a heating rate of 2 deg min^{-1} and was determined with a relative error of 2—3%. The systematic measurement error was estimated by determining the heat capacities of well-studied compounds at regular intervals.

Synthesis of complexes

Di(μ_4-oxo)di(μ_3-*O*,*O*,*O*′-trimethylacetato)octakis(μ_2-*O*,*O*′-trimethylacetato)tri(η^1-tetrahydrofuran)monoaquadicobalt(III)tetracobalt(II), solvate with tetrahydrofuran, $[Co_6(\mu_4\text{-}O)_2(\mu\text{-}OOCCMe_3)_{10}(C_4H_8O)_3(H_2O)] \cdot 1.5(C_4H_8O)$ ($7 \cdot 1.5(C_4H_8O)$). The $Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(HOOCCMe_3)_4$ complex (**8**) (0.5 g, 0.28 mmol) was added to

THF (20 mL), and the reaction mixture was stirred in air at 20 °C for 30 min. The resulting dark-brown solution was filtered off and concentrated to 10 mL at 0.1 Torr and 20 °C. Dark-brown crystals that precipitated after 20 h were separated by decantation, washed with cold MeCN, and dried in air. The yield of **7** · 1.5(C_4H_8O) was 0.49 g (98%). Found (%): C, 46.91; H, 7.36. $C_{68}H_{128}Co_6O_{27.5}$. Calculated (%): C, 46.54; H, 7.03. IR (KBr), ν/cm^{-1}: 2960 m, 2928 m, 2872 m, 2820 w, 2800 w, 2372 w, 2326 w, 2320 w, 1696 w, 1664 w, 1592 v.s, 1564 s, 1484 v.s, 1460 m, 1420 v.s, 1376 s, 1356 s, 1316 w, 1276 w, 1224 s, 1068 v.w, 1032 v.w, 940 v.w, 896 w, 872 w, 832 w, 804 w, 784 w, 632 m, 616 m, 592 m, 536 w, 444 w, 400 w, 386 w, 316 w.

The crystals were used for X-ray diffraction study.

Thermolysis of the $[(HOOCCMe_3)_xCo(OH)_n(OOCCMe_3)_{2-n}]_m$ complex (4). Decane (30 mL) was added to the $[(HOOCCMe_3)_xCo(OH)_n(OOCCMe_3)_{2-n}]_m$ complex (**4**) (0.240 g, 0.92 mmol) (per formula unit $Co(OOCCMe_3)_2$), and the reaction mixture was heated under argon at 174 °C for 2 h. Thin violet crystals that precipitated were separated from the blue-violet solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of poly{di(μ_2-*O*,*O*′-trimethylacetato)cobalt(II)} $[Co(OOCCMe_3)_2]_n$ (**2**) was 0.13 g (56% based on the starting amount of cobalt). Found (%): C, 45.78; H, 6.90. $C_{10}H_{18}CoO_4$. Calculated (%): C, 45.98; H, 6.95. IR (KBr), ν/cm^{-1}: 2924 s, 2853 s, 2723 w, 2672 w, 2585 w, 1678 w, 1598 s, 1551 s, 1520 s, 1483 s, 1463 s, 1430 s, 1377 s, 1360 m, 1308 m, 1229 m, 1203 m, 032 w, 971 w, 939 w, 896 m, 872 w, 851 w, 798 m, 723 m, 666 w, 615 m, 583 m, 541 w, 456 m, 436 m, 416 m.

The resulting blue-violet solution was kept at 20 °C. The blue-violet crystals that precipitated after 24 h were separated by decantation, washed with cold hexane, and dried under a stream of argon. The yield of compound **9** was 0.1 g (42% based on the starting amount of cobalt).

The crystals were used for X-ray diffraction study. The crystallographic data for compound **9** (space group *Pa*3, a = 20.1464(2) Å, V = 8177.0(16) Å^3, Z = 4) agree with those obtained earlier[6] in the determination of the molecular structure of $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{12}$ (n = 2 or 3) by X-ray diffraction.

Thermolysis of the $Co_2(\mu\text{-}H_2O)(OOCCMe_3)_4(HOOCCMe_3)_4$ complex (6). Decane (30 mL) was added to the $Co_2(\mu\text{-}H_2O)(OOCCMe_3)_4(HOOCCMe_3)_4$ complex (**6**) (0.3 g, 0.4 mmol), and the reaction mixture was heated under argon at 174 °C for 2 h. The thin violet crystals that precipitated were separated from the colorless solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of compound **2** was 0.392 g (98% based on the starting amount of cobalt). Found (%): C, 45.73; H, 6.65. $C_{10}H_{18}CoO_4$. Calculated (%): C, 45.98; H, 6.90. IR (KBr), ν/cm^{-1}: 2926 s, 2854 s, 2723, w, 2674 w, 2586 w, 1678 w, 1602 s, 1570 s, 1551 s, 1483 s, 1463 s, 1412 s, 1376 s, 1360 m, 1326 m, 1304 m, 1228 m, 1203 m, 1032 w, 971 w, 939 w, 895 m, 872 w, 851 w, 800 m, 723 m, 666 w, 616 m, 578 m, 541 w, 456 m, 436 m, 416 m.

Thermolysis of the $[Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(C_4H_8O)_3(H_2O)] \cdot 1.5(C_4H_8O)$ complex. Decane (30 mL) was added to the $[Co_6(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{10}(C_4H_8O)_3(H_2O)] \cdot 1.5(C_4H_8O)$ complex (**7** · 1.5(C_4H_8O)) (1 g, 0.575 mmol), and the mixture was heated under argon at 174 °C for 2 h. The thin violet crystals that precipitated were separated from the resulting blue-violet solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of compound **2** was 0.53 g (53% basedon the starting amount of cobalt). Found (%): C, 46.24; H, 7.09. $C_{10}H_{18}CoO_4$. Calculated (%): C, 45.98; H, 6.90. IR (KBr), ν/cm^{-1}: 2924 s, 2854 s, 2723 w, 2672 w, 2585 w, 1678 w, 1598 s, 1551 s, 1520 s, 1483 s, 1464 s, 1430 s, 1377 s, 1360 m, 1309 m, 1229 m, 1203 m, 1031 w, 971 w, 939 w, 896 m, 872 w, 851 w, 798 m, 723 m, 666 w, 615 m, 583 m, 541 w, 456 m, 436 m, 416 m.

The remaining blue-violet solution was kept at 20 °C. The blue-violet crystals that precipitated after 24 h were separated by decantation, washed with cold hexane, and dried under a stream of argon. The yield of compound **9** was 0.45 g (45% based on the starting amount of cobalt).

The crystals were used for X-ray diffraction study. The crystallographic data for **9** (space group *Pa*3, a = 20.1464(2) Å, V = 8177.0(16) Å^3, Z = 4) agree with those obtained earlier.[6]

Thermolysis of the $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ complex (5). Acetonitrile (40 mL) was added to the $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ complex (**5**) (0.4 g, 0.35 mmol), and the reaction mixture was heated in air at 80 °C for 15 min. The thin violet crystals that precipitated were separated from the mother liquor by decantation, washed with cold hexane, and dried in air. The yield of compound **2** was 0.343 g (98% based on the starting amount of cobalt). Found (%): C, 45.76; H, 6.65. $C_{10}H_{18}CoO_4$. Calculated (%): C, 45.98; H, 6.90. IR (KBr), ν/cm^{-1}: 2924 s, 2854 s, 2724 w, 2672 w, 2586 w, 1676 w, 1602 s, 1570 s, 1551 s, 1524 s, 1483 s, 1465 s, 1412 s, 1376 s, 1360 m, 1326 m, 1305 m, 1229 m, 1203 m, 1031 w, 970 w, 938 w, 898 m, 872 w, 851 w, 792 m, 723 m, 666 w, 613 m, 584 m, 541 w, 459 m.

Hexa(μ_3-*O*,*O*,*O*′-trimethylacetato)hexa(μ_2-*O*,*O*′-trimethylacetato)hexanickel(II), $Ni_6(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (3). Decane (30 mL) was added to the $Ni_2(\mu\text{-}H_2O)(OOCCMe_3)_4(HOOCCMe_3)_4$ complex (**10**) (0.5 g, 0.67 mmol), and the reaction mixture was heated at 174 °C under argon for 2 h. The yellow-brown crystals that precipitated after 12 h were separated by decantation, washed with cold hexane, and dried under a stream of argon. The yield of compound **3** was 0.49 g (98% based on the starting amount of nickel). Found (%): C, 46.12; H, 7.27. $C_{60}H_{108}Ni_6O_{24}$. Calculated (%): C 45.99; H, 6.90. IR (KBr), ν/cm^{-1}: 2924 s, 2853 s, 2723 m, 2593 m, 1670 s, 1601 s, 1482 s, 1462 s, 1411 s, 1374 s, 1324 m, 1263 w, 1225 s, 1212 s, 1031 m, 937 m, 896 m, 875 m, 788 m, 723 m, 613 m, 541 m, 416 m.

Tetra(μ_2-*O*,*O*′-trimethylacetato)bis(2,3-dimethylpyridine)dicobalt(II), $(2,3\text{-}Me_2C_5H_3N)_2Co_2(\mu\text{-}OOCCMe_3)_4$ (14). A solution containing 2,3-$Me_2C_5H_3N$ (0.164 g, 1.53 mmol) in acetonitrile (20 mL) was added to $[Co(OOCCMe_3)_2]_n$ (0.40 g, 1.53 mmol) (per formula unit $Co(OOCCMe_3)_2$). The reaction solution was stirred at 80 °C for 15 min, the color of the solution being changed from blue-violet to blue-green. Then the solution was concentrated to 10 mL at 0.1 Torr and 20 °C and allowed to crystallize at 20 °C. The green-violet crystals that precipitated after 12 h were separated by decantation, washed with cold benzene, and dried under a stream of argon. The yield of compound **14** was 0.563 g (98% based on the starting amount of the ligand). Found (%): C, 55.97; H, 7.38; N, 3.83. $Co_2C_{34}H_{54}O_8N_2$. Calculated (%): C, 55.45; H, 7.34; N, 3.81. IR (KBr), ν/cm^{-1}: 3736 w, 3688 w, 3648 w, 2956 m, 2924 w, 2860 w, 2364 m, 2336 w, 1732 w, 1612 v.s, 1532 w, 1516 w, 1480 s, 1452 w, 1420 s, 1384 m, 1373 m, 1356 m, 1284 w, 1260 m, 1224 s, 1192 w, 1140 w, 1096 w, 896 w, 808 m, 788 s, 748 w, 724 m, 608 s, 420 m.

The crystals were used for X-ray diffraction study.

Tetra(μ$_2$-*O*,*O*′-trimethylacetato)bis(2,3-dimethylpyridine)dinickel(II), (2,3-Me$_2$C$_5$H$_3$N)$_2$Ni$_2$(μ-OOCCMe$_3$)$_4$ (15). A solution containing 2,3-Me$_2$C$_5$H$_3$N (0.164 g, 1.53 mmol) in benzene (20 mL) was added to Ni$_6$(OOCCMe$_3$)$_{12}$ (0.4 g, 0.255 mmol). The reaction mixture was stirred at 70 °C for 15 min. The resulting pale-green solution was concentrated to 10 mL at 0.1 Torr and 20 °C and allowed to crystallize at 20 °C. The green crystals that precipitated after 12 h were separated by decantation, washed with cold benzene, and dried under a stream of argon. The yield of compound **15** was 0.563 g (98% based on the starting amout of the ligand). Found (%): C, 56.02; H, 7.36; N, 3.82. $Ni_2C_{34}H_{54}O_8N_2$. Calculated (%): C, 55.48; H, 7.34; N, 3.81. IR (KBr), ν/cm^{-1}: 3088 w, 2984 s, 2956 v.s, 2924 m, 2684 m, 2352 w, 2332 w, 2324 w, 1728 w, 1716 w, 1612 v.s, 1480 v.s, 1452 s, 1420 v.s, 1372 s, 1356 s, 1284 m, 1228 v.s, 1192 m, 1136 w, 1084 w, 1028 w, 896 s, 7888 v.s, 752 w, 720 s, 684 w, 612 s, 524 w, 516 w, 432 w, 352 w, 308 s.

The crystals were used for X-ray diffraction study. The crystallographic data for **15** (space group $P\bar{1}$, a = 9.629(2) Å, b = 10.860(2) Å, c = 111.188(2) Å, α = 61.35(3)°, β = 71.90(3)°, γ = 82.65(3)°; V = 975.7(3) Å^3, Z = 1) agree with those obtained earlier[5] in the determination of the molecular structure of (2,3-Me$_2$C$_5$H$_3$N)$_2$Ni$_2$(μ-OOCCMe$_3$)$_4$ by X-ray diffraction.

X-ray diffraction study. X-ray diffraction data sets for complexes **3**, **7**, and **9** were collected using a standard procedure[19] on an automated Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, 120 K, ω-scanning technique, the scan step was 0.3°, the exposure time per frame was 30 s). Semiempirical absorption corrections were applied.[20] The crystallographic parameters and the refinement statistics for the structures of **3** and **7** are given in Table 3.

The structures of all complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The positions of the hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands and the pyridine rings in the coordinated amine molecules were calculated geometrically and refined using a riding model. All calculations were performed with the use of the SHELX97 program package.[21]

Table 3. Crystallographic parameters of complexes **3** and **7**

Parameter	**3**	**7**·1.5(C$_4$H$_8$O)
Molecular formula	$C_{60}H_{108}Ni_6O_{24}$	$C_{68}H_{128}Co_6O_{27.50}$
Molecular weight	1565.72	1739.28
Space group	*C*2/*c*	*C*2/*c*
a/Å	23.652(5)	47.596(9)
b/Å	15.951(3)	18.586(3)
c/Å	21.306(4)	20.044(4)
α/deg	90	90
β/deg	113.20(3)	107.472(9)
γ/deg	90	90
V/Å^3	7388(3)	16913(5)
Z	4	8
ρ_{calc}/g cm^{-3}	1.408	1.366
μ/cm^{-1}	0.1568	0.1221
Radiation	Mo-Kα (λ = 0.71073 Å)	
θ-2θ-Scan range/deg	1.58—27.73	0.90—30.04
Number of measured reflections	29390	20941
Number of reflections with $I \geq 2\sigma(I)$	8499	16489
R_1	0.0569	0.0819
wR_2	0.1145	0.2806

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