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Influence of the nature of organic ligands on the character of thermal decomposition products of Co^{II} and Ni^{II} pivalate complexes with amino derivatives of pyridine

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The thermal stability and the solid-state thermal decomposition of the known mononuclear cobalt(II) and nickel(II) complexes $[H_2N(C_5H_3N)N(H)C(Me)=NH]M(OOCBu^t)_2$, $[(NH_2)_2C_6H_2Me_2]_3M(OOCBu^t)_2$ and the new compounds $L_2M(OOCBu^t)_2$ (L = $(2\text{-}NH_2)C_5H_3N$, $(2\text{-}NH_2)(6\text{-}Me)C_5H_3N$), and $[(2,6\text{-}NH_2)_2C_5H_3N]_2Ni(OOCBu^t)_2$ were studied by differential scanning calorimetry and thermogravimetric analysis. Efficient methods were developed for the synthesis of these complexes. The mononuclear complexes are thermally quite stable. The thermal stability of the complexes depends on the nature of the ligand and decreases in the series $(2,6\text{-}NH_2)_2C_5H_3N > H_2N(C_5H_3N)NHC(Me)=NH > (NH_2)_2C_6H_2Me_2 > (2\text{-}NH_2)C_5H_3N > (2\text{-}NH_2)(6\text{-}Me)C_5H_3N$. The nickel(II) complexes are thermally more stable than the related cobalt(II) complexes. The thermolysis (<500 °C) of Co and Ni pivalates is a destructive process. The phase composition of the decomposition products is determined by the nature of metal and coordinated ligands.

Key words: mononuclear cobalt and nickel pivalate complexes, 2-aminopyridine, 2,6-diaminopyridine, 2-amino-6-methylpyridine, *N*-(6-amino-2-pyridyl)acetamidine, 4,5-dimethyl-1,2-phenylenediamine, solid-state thermal decomposition, X-ray diffraction study, magnetic properties.

Nanosized particles of metals[1,2] and oxide materials of different composition,[3—11] which were synthesized with the use of metal complexes as molecular precursors, have unique physical and catalytic properties.[12—18] Evidently, organic components of precursors play an important role in the solid-state thermal decomposition of metal cation-containing complexes performed in the absence of external reducing agents. Thus, it is known that metals can easily be generated in the final step of thermal decomposition with the use of molecules with ligands having strong reducing properties. Recently, this approach has been applied to the thermolysis of 3d metal methylhydrazine complexes; the thermolysis of these complexes at relatively low temperatures (at temperatures below 400 °C) affords metals, and the simultaneous thermolysis of the complexes gives alloys.[19] Presumably, these processes involve the intramolecular reduction of metal atoms with the participation of ligands acting as reducing agents. An increase in the temperature leads to the gradual elimination of organic moieties and the clustering of the metal core up to the formation of metal oxides or metal particles. Evidently, these processes significantly depend on the nature of metal ions in the precursor, as well as on the structural and electronic features of both the ligands with reducing properties and the molecule as a whole.

Previously,[20—22] we have shown that the nature of the α-substituted pyridine ligand (L) in dinuclear d-metal tetracarboxylate complexes with the structure $LM(\mu\text{-}Piv)_4ML$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, or Cu^{II}) has a strong effect on the character of the solid-state thermal (<400 °C) decomposition of the complexes. The phase composition of the final product substantially depends on the nature of both the metal and the substituent in the α position of the apical organic ligand, which is an intramolecular reducing agent and stimulates intramolecular redox reactions during the decomposition.[20—22] Thus, the thermolysis of dinuclear manganese and iron pivalates (M = Mn or Fe) does not afford metals in spite of the presence of strong reducing agents such as aminopyridine ligands L.[20,21] The presence of active CH_3 and NH_2 groups in the apical pyri-

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dine molecules in copper derivatives leads to deeper intramolecular redox processes and the formation of copper metal as the solid decomposition product.[20—22] The thermolysis of tetracarboxylate complexes with nickel atoms affords a metallic phase only in the presence of apical 2,3-dimethylpyridine molecules.[20] It should be noted that the volatile octahedral cluster $Co_8(\mu_4\text{-}O)_2(\mu_2\text{-piv})_6(\mu_3\text{-piv})_6$, which is readily removed from the reaction medium, is formed already in early steps of the thermolysis of related dinuclear and polynuclear cobalt pivalates.[20,21,23,24] However, the thermolysis of cubane-like pivalate complexes with the $[Co^{II}{}_4(\mu^3\text{-OR})_4]$ or $[(Co, Ni)^{II}{}_4(\mu^3\text{-OR})_4]$ core gives oxides as the final solid decomposition products.[25,26]

Mononuclear pivalate complexes with high-spin Group VII and VIII 3d transition metals are known and have attracted considerable attention as models for the study of the magnetic behavior of these systems.[27—32] Since mononuclear pivalate complexes, which are readily soluble in organic solvents, can be synthesized quite easily, these compounds can be considered as promising reagents, for example, for the formation of films or nanosize-particle coatings.

In the present study, we report on the synthesis and investigation of the thermolysis of mononuclear cobalt(II) pivalate complexes and structurally similar nickel(II) complexes containing coordinated pyridine derivatives of different nature (2-aminopyridine, *N*-(6-amino-2-pyridyl)acetamidine, 2,6-diaminopyridine, and 2-amino-6-methylpyridine) or 4,5-dimethyl-1,2-phenylenediamine.

Results and Discussion

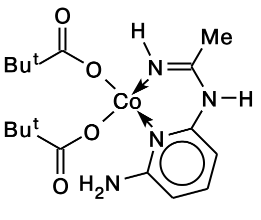
Synthesis of mononuclear cobalt(II) and nickel(II) pivalate complexes. It was of interest to develop an efficient procedure for the synthesis of mononuclear Co^{II} and Ni^{II} pivalate complexes containing pyridine derivatives of different nature as ligands. We used 2-aminopyridine, 2,6-diaminopyridine, and 2-amino-6-methylpyridine for the synthesis of such complexes. The main method for the synthesis of mononuclear complexes was based on the directed degradation of the known pivalates $[M(OOCBu^t)_2]_n$ with the corresponding α-substituted pyridine. It is known[23] that the cobalt pivalate (M = Co, **1**) has a chain structure with two carboxylate bridges between the metal atoms, whereas the nickel derivative (M = Ni, **2**) is a six-membered cyclic structure. It was found that, depending on the reaction conditions, the nature and the number of N-donor ligands L, and the nature of the organic solvent, mononuclear complexes containing pyridine derivatives are formed in high yield.

The reactions of pivalates **1** and **2** with an excess of 2-aminopyridine (L^1= L; Co : L^1 = 1 : 4, CH_3CN; Ni : L^1 = 1 : 2), 2,6-diaminopyridine (L^2 = L; Ni : L^2 = = 1 : 2), or 2-amino-6-methylpyridine (L^3 = L, M : L^3 = = 1 : 2) in benzene under an inert atmosphere at 80 °C afford complexes of the general formula $L_2M^{II}(\eta^2\text{-}OOCBu^t)_2$, where M = Co or Ni.

According to the X-ray diffraction data, the complexes $[(2,6\text{-}NH_2)_2C_5H_3N]_2Ni(\eta^2\text{-}OOCBu^t)_2$ (**3**), $[(2\text{-}NH_2)(6\text{-}Me)C_5H_3N]_2Co(\eta^2\text{-}OOCBu^t)_2$ (**4**), which was isolated with two benzene molecules of solvation ($\mathbf{4}\cdot 2C_6H_6$), $[(2\text{-}NH_2)(6\text{-}Me)C_5H_3N]_2Ni(\eta^2\text{-}OOCBu^t)_2$ (**5**), and $[(2\text{-}NH_2)C_5H_4N]_2Co(\eta^2\text{-}OOCBu^t)_2$ (**6**), which is isostructural with the known cobalt derivative,[28] have similar molecular structures (Fig. 1, Table 1). In mononuclear molecules **3—6**, the metal centers are bound to two molecules of the corresponding substituted pyridine, which are coordinated in a monodentate fashion in the *cis* positions through the nitrogen atom of the pyridine ring. The M—N distances in complexes **3—6** are comparable with those found previously in the related mononuclear cobalt and nickel complexes.[28—30] The spectroscopic characteristics of the nickel-containing complex $[(2\text{-}NH_2)C_5H_4N]_2Ni(\eta^2\text{-}OOCBu^t)_2$ (**7**) are similar to those of cobalt analog **6** characterized by X-ray diffraction.[28]

In the crystal structures of **3—5**, there are intermolecular hydrogen bonding between the hydrogen atoms of the amino groups of the pyridine ligands and the oxygen atoms of the carboxylate groups. In the crystal structures of complexes **3** (N—H...O, 2.187—2.278 Å; N—H...O angles, 153.00—161.71°) and **4** (N—H...O, 2.225 and 2.247 Å; N—H...O angles, 152.19 and 155.02°), the molecules are linked together to form centrosymmetric dimers.

The reaction of stoichiometric amounts of complexes **1** or **2** with 2,6-diaminopyridine (L^2) in acetonitrile (M : L^2 = = 1 : 1, 80 °C, argon) afforded the complexes $[H_2N(C_5H_3N)N(H)C(Me){=}NH]M^{II}(OOCBu^t)_2$, where M = Co (**8**) or Ni (**9**), respectively. Complex **9** was isolated as a solvate with one acetonitrile molecule $\mathbf{9}\cdot MeCN$. According to the X-ray diffraction data, complexes **8** and **9** synthesized according to the method developed in the present study are isostructural with the known pivalates $[H_2N(C_5H_3N)N(H)C(Me){=}NH]M(OOCBu^t)_2$ (M = Co or Ni, respectively), whose structures have been established previously by the complete X-ray diffraction study.[27] The latter compounds contain the chelating *N*-(6-amino-2-pyridyl)acetamidine molecule, $H_2N(C_5H_3N)N(H)$-$C(Me){=}NH$, which is formed as a result of the innersphere interaction between 2,6-diaminopyridine and acetonitrile.



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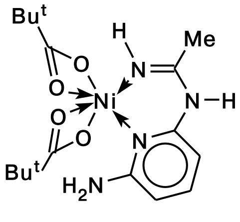

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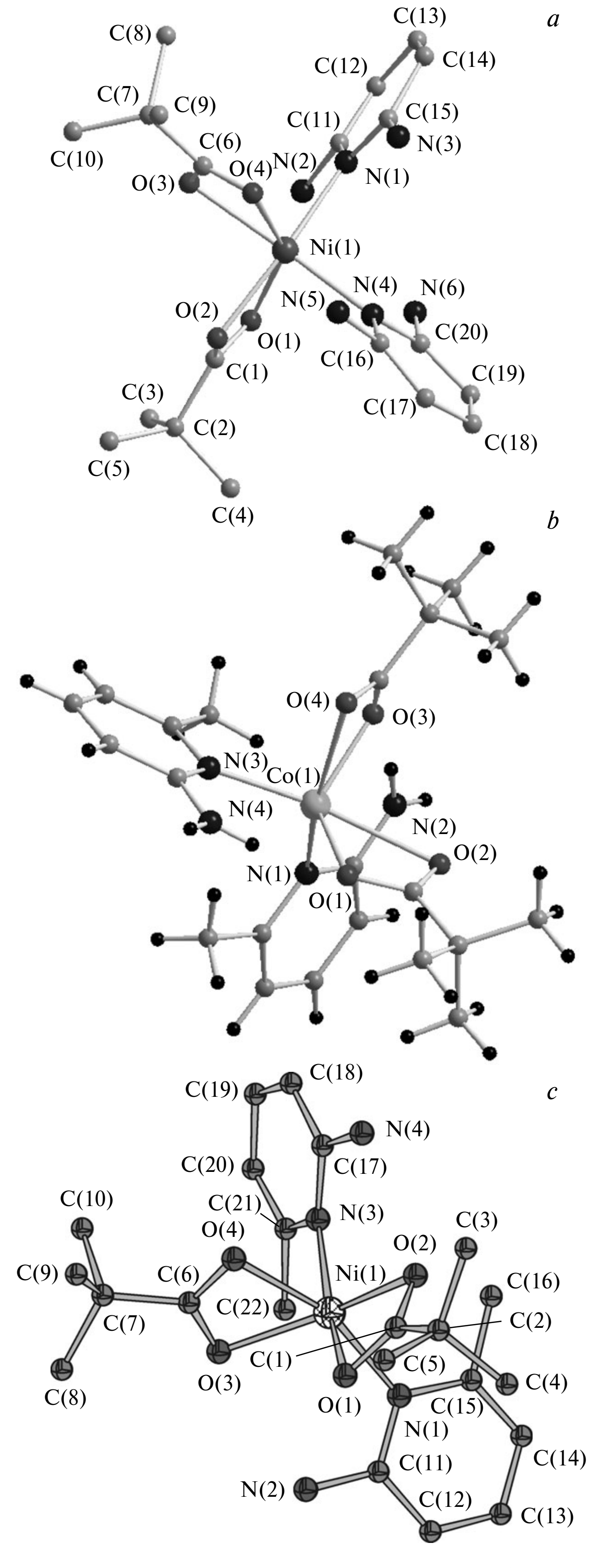

Fig. 1. Structures of the mononuclear molecules $[(2,6\text{-}NH_2)_2\text{-}C_5H_3N]_2Ni(\eta_2\text{-}OOCBu^t)_2$ (**3**) (*a*), $[(2\text{-}NH_2)(6\text{-}Me)C_5H_3N]_2\text{-}Co(\eta_2\text{-}OOCBu^t)_2$ (**4**) (*b*), and $[(2\text{-}NH_2)(6\text{-}Me)C_5H_3N]_2Ni(\eta_2\text{-}OOCBu^t)_2$ (**5**) (*c*). The hydrogen atoms are not shown.

An attempt to synthesize mono- and dinuclear cobalt complexes, in which the metal centers are chelated by the product of the inner-sphere interaction between 2-amino-6-methylpyridine (L^3) and acetonitrile, like in complex **8** and the asymmetric dinuclear complex $[H_2N(C_5H_3N)N(H)C(Me){=}NH]Co_2(OOCBu^t)_4$,**[27]** led to an unexpected result. It appeared that the reaction of polymer **1** with L^3 (Co : L^3 = 1 : 2 or Co : L^3 = 1 : 1) in MeCN under an inert atmosphere at 80 °C afforded the dinuclear complex $[(2\text{-}NH_2)(6\text{-}CH_3)C_5H_3N]_2Co_2(\mu_2\text{-}OOCBu^t)_4 \cdot 4MeCN$ (**10** · 4MeCN) or the asymmetric dinuclear complex $[(2\text{-}NH_2)(6\text{-}CH_3)C_5H_3N]Co_2(\mu_2\text{-}OOCBu^t)_3(\eta^2\text{-}OOCBu^t) \cdot 1.5H_2O$ (**11** · $1.5H_2O$).

The X-ray diffraction study showed that complex **10** has a "Chinese lantern" structure and is isostructural with the known manganese derivative,**[33]** which forms the supramolecular system $[(2\text{-}NH_2)_2C_5H_3N]_2Mn_2(\mu_2\text{-}OOCBu^t)_4 \cdot 4MeCN$, where the amino groups of the diamine ligand are involved in hydrogen bonding with the acetonitrile solvation molecules and the oxygen atoms of the bridging carboxylate groups.

The X-ray diffraction study showed that the cobalt atoms in dinuclear molecule **11** have the coordination numbers 4 and 5; the Co...Co distances are 3.362(1) and 3.352(1) Å in two independent molecules (Fig. 2). The metal centers are linked together by three bidentate bridging carboxylate groups (Co(1)—O, 1.952(7)—1.980(6) Å; Co(2)—O,

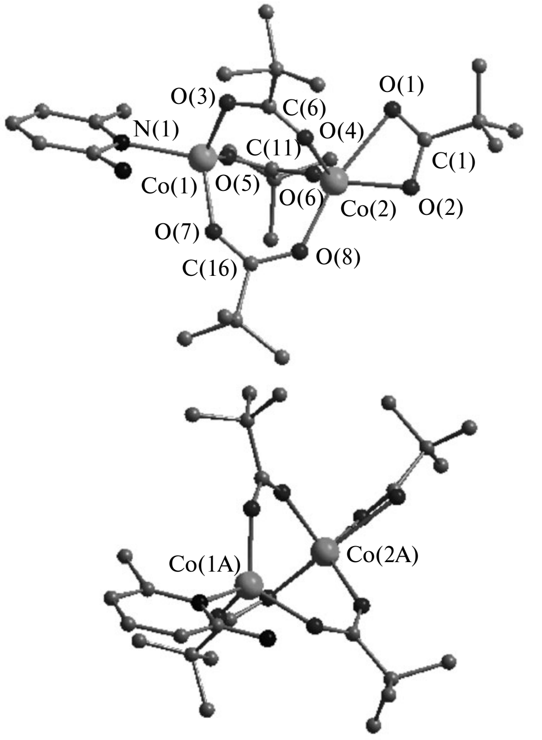

Fig. 2. Structures of two independent dinuclear molecules of the complex $[(2\text{-}NH_2)(6\text{-}CH_3)C_5H_3N]Co_2(\mu_2\text{-}OOCBu^t)_3\text{-}(\eta^2\text{-}OOCBu^t)$ (**11**).

Table 1. Geometric parameters for selected bonds in mononuclear complexes **3**—**6**[a]

Parameter	**3**[b]	**4**	**5**[c]	**6**[d]
Bond		d/Å		
M—O	2.040(11)/2.162(10)	2.0079(16)/2.0118(17)	2.056(6)/2.200(6)	—
M—N	2.083(16)/2.133(14)	2.0899(16)/2.1060(17)	2.085(7)/2.117(7)	2.106/2.085(7)
Angle		ω/deg		
O—M—O	145.2(4)/149.1(5)	123.32	151.7(3)/155.3(3)	—
O—M—O	91.0(5)/93.2(5)	—	95.9(2)/99.1(2)	—
N—M—N	95.6(6)/96.6(5)	106.84(7)	105.9(3)/107.3(3)	95.00

[a] M = Ni (**3**, **5**), M = Co (**4**, **6**).
[b] The crystals contain two independent molecules.
[c] The crystals contain four independent molecules.
[d] See Ref. 28.

1.954(6)—2.014(6) Å; O—C, 1.220(11)—1.274(11) Å; O—C—O angles, 123.1(8)—124.4(8)°; and Co(1A)—O(A) angles, 1.937(6)—1.966(6) Å; Co(2A)—O(A), 1.973(6)—2.002(6) Å; O(A)—C(A), 1.230(12)—1.266(11) Å; O(A)—C(A)—O(A) angles, 123.6(8)—127.1(8)°). The ligand L^3 is bound to the four-coordinate cobalt atom in a monodentate fashion through the nitrogen atom of the pyridine molecule; the Co—N bond lengths are 2.079(6) and 2.061(7) Å in two independent molecules, respectively. The oxygen environment of the five-coordinate metal center additionally involves the chelating carboxylate anion (Co(2)—O, 2.002(6) and 2.351(8) Å; Co(2A)—O(A), 2.014(6) and 2.307(7) Å; O—C, 1.259(12) and 1.288(11) Å; O(A)—C(A), 1.248(12) and 1.261(11) Å; O—C—O angle, 60.0(2)°; O(A)—C(A)—O(A) angle, 59.6(2)°). The crystal structure of **11** is characterized by the hydrogen bonding between the hydrogen atoms of the amino groups of the pyridine ligand and the oxygen atoms of the carboxylate groups (an intramolecular hydrogen bond: N—H...O, 2.073 Å; N—H...O angle, 156.38°; an intermolecular hydrogen bond: N—H...O, 2.102 Å; N—H...O angle, 154.56°).

The IR spectra of compounds **3**—**11** show stretching bands of the free NH_2 group at 3468—3220 cm^{-1}.

Therefore, we synthesized series of mononuclear cobalt and nickel complexes containing various 2-aminopyridine derivatives as ligands. It is known[34,35] that the NH_2 group is easily oxidized and can act as an inner-sphere reducing agent. In further thermal investigations, we used also mononuclear pivalate complexes containing three coordinated diamine molecules, $[(NH_2)_2C_6H_2Me_2]_3M^{II}(\eta^1\text{-}OOCBu^t)_2$, where M = Co (**12**) and Ni (**13**), respectively. In complexes **12** and **13**, one of the three 4,5-dimethyl-1,2-phenylenediamine molecules is chelating, whereas the other two groups are terminal. The synthesis and the structures of complexes **12** and **13** have been reported previously.[25]

Magnetic properties of mononuclear cobalt(II) and nickel(II) complexes. The magnetic measurements showed that the effective magnetic moments (μ_{eff}) decrease with a decrease in the temperature due to the antiferromagnetic spin-spin and spin-orbital coupling from 5.343 μ_B at 300 K to 4.264 μ_B at 2 K for **4** • $2C_6H_6$, from 3.494 μ_B at 300 K to 1.993 μ_B at 2 K for **5**, from 4.851 μ_B at 300 K to 3.753 μ_B at 2 K for **6**, and from 7.277 μ_B at 300 K to 1.029 μ_B at 2 K for **11** • $1.5H_2O$.[36]

As opposed to complexes **4**—**6** and **11**, the magnetic behavior of nickel-containing mononuclear complexes **3** and **13** is more complicated. Thus, the effective magnetic moments (μ_{eff}) of complexes **3** and **13** increase with a decrease in the temperature (**8**: μ_{eff} = 3.668 μ_B (300 K) — 6.646 μ_B (5.03 K); **13**: μ_{eff} = 4.409 μ_B (300 K) — 8.646 μ_B (4.50 K)), which is apparently associated with the intermolecular ferromagnetic spin-spin exchange coupling (Fig. 3, *a* and *b*). In the case of complex **13**, a further decrease in the temperature to 2 K leads to a considerable decrease in the magnetic moment down to 6.636 μ_B due apparently to the intermolecular antiferromagnetic spin-spin exchange coupling (Fig. 3, *b*). The magnetic characteristics of compound **13** differ from those of complex **12**, which has a similar composition but contains cobalt atoms,[25] and the isostructural complex $[(NH_2)_2C_6H_2Me_2]_3Fe(OOCBu^t)_2$.[32] The latter two complexes exhibit antiferromagnetic properties.[31,32]

Thermal decomposition of mononuclear cobalt(II) and nickel(II) pivalate complexes. To study the thermal stability, thermolysis pathways, and the phase composition of the final solid thermolysis product, we used mononuclear compounds **3**—**9** and complexes **12** and **13**, in which not only the metal centers but also the formal ratio between the NH_2 or NH groups and the metal atoms are varied.

The decomposition of nickel-containing complexes **3**, **5**, and **7** is accompanied by the melting (Fig. 4, *b*, Table 2). The temperatures of the onset of the decomposition for **3**, **5**, and **7** are lower than the boiling point of the N-donor ligand. A continuous weight loss is observed during the thermolysis of complexes **3** and **5** in the temperature rang-

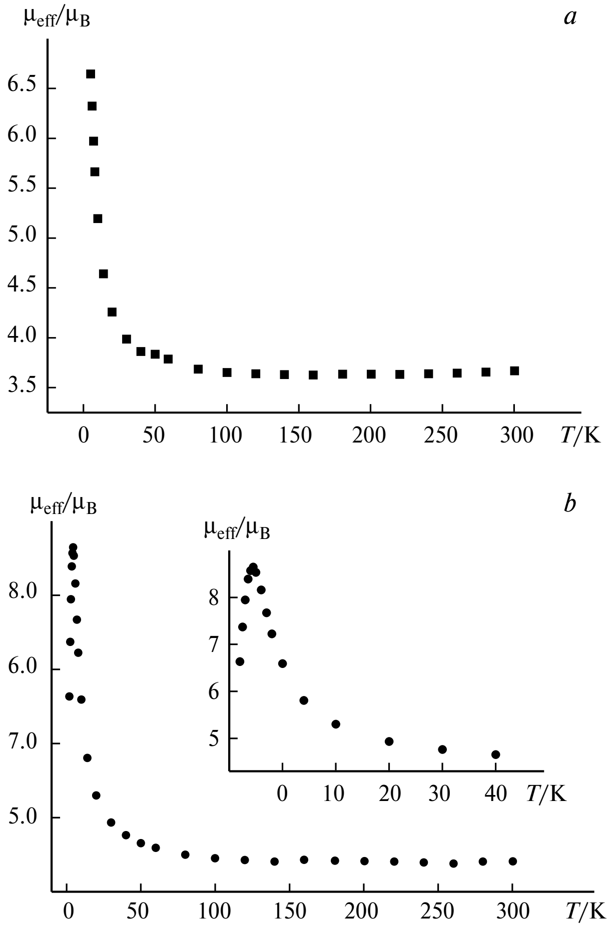

Fig. 3. Temperature dependence of the effective magnetic moment (μ_{eff}) for the complexes $[(2,6\text{-}NH_2)_2C_5H_3N]_2Ni(OOCBu^t)_2$ (**3**) (*a*) and $[(NH_2)_2C_6H_2Me_2]_3Ni(OOCBu^t)_2$ (**13**) (*b*). The inset shows the enlarged low-temperature region of the temperature dependence for complex **13**.

es of 223—415 °C and 160—400 °C, respectively (Fig. 4, *a*). The character of the weight loss and the change in the thermal flux with temperature for complex **7** suggests that the gradual removal of the ligand from the melt at 270 °C is accompanied by intramolecular redox processes to form Ni metal as the solid decomposition product. The initial step of decomposition of all three complexes is endothermic, whereas the final destruction and the formation of the solid decomposition product are accompanied by exothermic effects. The total weight loss in the temperature range under examination is 87.1±1.5%, 88.1±1.5%, and 87.4±1.5% for complexes **3**, **5**, and **7**, respectively.* According to the X-ray powder diffraction data, the decomposition of complexes **3**, **5**, and **7** affords nickel metal as the solid product. The thermogravimetric analysis (TGA) showed that the weigh of the solid product for complexes **3**, **5**, and **7** is 12.9%, 11.9%, and 12.6%, respectively, which is equal, within experimental error, to the theoretical nickel content in complexes **3**, **5**, and **7** (12.15%, 12.21%, and 12.97%, respectively).

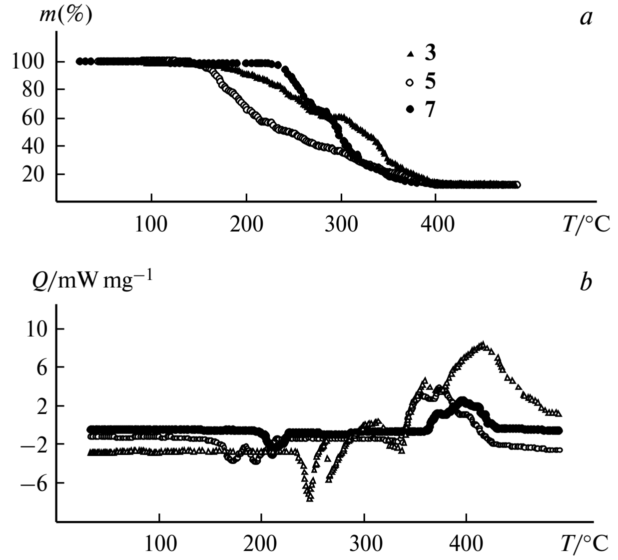

Fig. 4. Temperature dependences of the weight loss (*a*) and the heat flux (*b*) for nickel-containing complexes **3**, **5**, and **7**.

The decomposition of structurally similar cobalt-containing complexes **4** and **6** also occurs with the melting (Fig. 5). In the temperature range of 128—185 °C, the curve of the weight loss *versus* the temperature for complex **4** shows several inflection points, whose temperatures correspond to the extreme points in the curve of the thermal flux of the samples *versus* the temperature (see Fig. 5). The weight loss in this temperature range is 38.5±1.5%. Since the theoretical content of the N-donor ligand in the complex is 45.28%, it can be suggested that the thermolysis of the complex involves intramolecular transformations with the participation of the ligand. In the temperature range of 221—295 °C, the further destructive decomposition of complex **4** occurs without considerable energy changes (see Fig. 6, *b*). Finally, the solid decomposition product is formed in the temperature range of 295—360 °C, which occurs with a considerable exothermic effect but without a weight loss. In the case of complex **6**, the step of the virtually complete removal of the N-donor ligand is quite pronounced (150—260 °C). The weight loss in this temperature range is 40.0±1.5%, whereas the theoretical content of 2-aminopyridine in complex **6** is 42.2%. The gas-phase mass spectrum in the temperature range of 150—250 °C corresponds to the spectrum of 2-aminopyridine (The NIST Chemistry WebBook). On further heating of complex **6** in the temperature range of 265—400 °C, the weight loss is accompanied by the exothermic effect, which apparently corresponds to the complete destructive decomposition and the formation of the solid decomposition product. The total weigh loss for complexes **4** and **6** is

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* The weight losses are given in wt.% based on to the initial weight.

Table 2. Characteristics of the thermolysis of compounds **3—9**, **12**, and **13**

Characteristics	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**12**	**13**
Boiling point of the ligand/°C	285	208	208	207	207	—	—	>257	—
Temperature of the onset of the decomposition/°C	223	128	160	150	180	163	220	162	187
Melting point/°C	221—224	126—130	158—162	148—152	186—190	161—162	243—245	—	—
Final decomposition product	Ni	CoO, Co (~3 : 1)	Ni	CoO	Ni	CoO, Co (~1 : 1)	Ni	CoO	Ni

85.3±1.5% and 82.9±1.5%, respectively. The phase composition analysis of the solid decomposition product of complex **4** showed that a mixture of the oxide CoO and cobalt metal in a ratio of ≈ 3 : 1 is formed as the final products. According to the TGA data, the weight of the solid residue is 14.3±1.5%, which is equal, within experimental error, to the value of 14.88% calculated on the assumption that the decomposition affords 3 CoO + Co. The phase composition analysis of the solid decomposition product of complex **6** showed that oxide CoO is the final product. According to the TGA data, the weight of the solid residue is 17.1±1.5%, which is equal, within experimental error, to the theoretical value of 16.70% (the calculation on the assumption that CoO is the decomposition product).

Complexes **8** and **9** are thermally stable (Table 2). The weight loss of nickel(II) complex **9** containing the chelating *N*-(6-amino-2-pyridyl)acetamidine molecule starts at 220±2.0 °C (Fig. 6, *a*). At temperatures higher than this temperature, the decomposition and the melting are observed. The decomposition of complex **9** occurs in one step (220—350 °C). The decomposition of cobalt-containing analog **8** starts at a considerably lower temperature (163 °C) and is accompanied by the melting. The further decomposition occurs in the temperature range of 163—370 °C (see Fig. 6). The temperature range of the weight loss of complex **8** is substantially larger than that for nickel-containing compound **9**. The processes that occur during heating of complex **8** in the temperature range of 163—268 °C are endothermic. A further weight loss during the heating at 268—370 °C is accompanied by the exothermic effect. The total weight loss for complexes **9** and **8** is 85.4±1.5% and 82.7±1.5%, respectively. The phase composition analysis of the solid decomposition product of complex **9** showed that nickel metal is the final solid product. According to the TGA data, the weight of the solid residue is 14.6±1.5%, which is equal, within experimental error, to the theoretical content of nickel met-

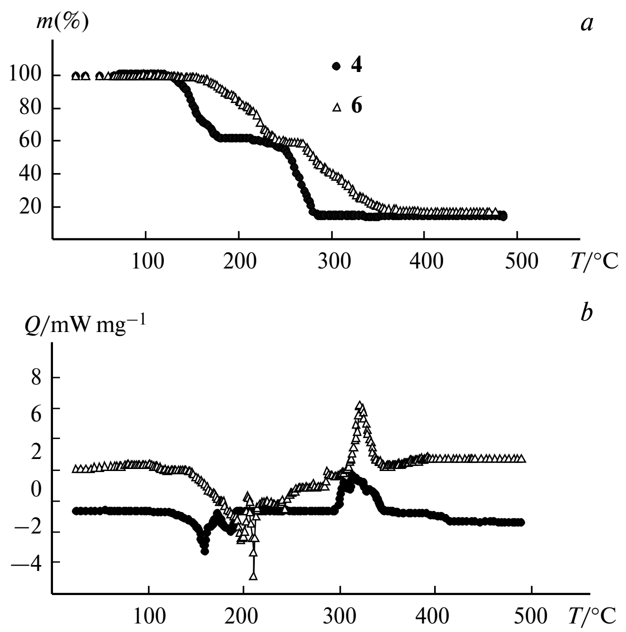

Fig. 5. Temperature dependences of the weight loss (*a*) and the heat flux (*b*) for cobalt-containing complexes **4** and **6**.

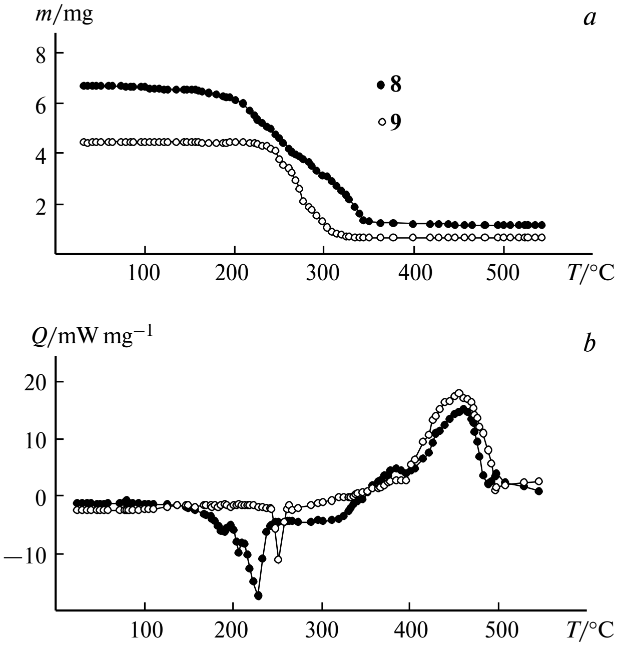

Fig. 6. Temperature dependences of the weight loss (*a*) and the heat flux (*b*) for mononuclear complexes **8** and **9**.

al in complex **9** (13.94%). An equimolar mixture of cobalt metal and oxide CoO is the final solid decomposition product of complex **8**. According to the TGA data, the weight of the solid residue is 17.3±1.5% (the weight of the solid residue, which was calculated from the empirical formula on the assumption that the decomposition affords a mixture of the phases CoO and Co in a ratio of 1 : 1, is 16.30%).

The thermolysis of dinuclear cobalt-containing complexes **10** and **11** leads to the aggregation to form octanuclear complex **14**, which sublimes without decomposition. Previously,[**20,21,23,24**] this has been shown in detail by the quantitative TGA data, differential scanning calorimetry (DSC), and the specific heat capacity measurements in the temperature range of 10—120 °C for the known complex $Co_8(\mu_4\text{-}O)_2(\mu_2\text{-}OOCBu^t)_6(\mu_3\text{-}OOCBu^t)_6$ (**14**) characterized by X-ray diffraction and the intermediates, which are obtained after the decomposition of other di- and polynuclear Co^{II} complexes, as well as synthesized preparatively.

The mononuclear complexes $M(\eta^2\text{-}(NH_2)_2C_6H_2Me_2)(\eta^1\text{-}(NH_2)_2C_6H_2Me_2)_2(OOCBu^t)_2$ (M = Co (**12**) and Ni (**13**)) are thermally quite stable (Fig. 7). Their decomposition starts at 162±2 °C and 187±2 °C, respectively. In the temperature range of 43—107 °C, an endothermic effect was observed that was not accompanied by the weight loss (Fig. 7, *b*), which may be associated with the cleavage of intramolecular hydrogen bonds. The initial decomposition involves two endothermic steps accompanied by the removal of two monodentate diamine ligands in the temperature ranges of 162—194 °C (21.2±1.0%) and 200—248 °C (18.5±1.0%) for cobalt-containing complex **12** and in the ranges of 187—219 °C (20.0±1.0%) and 223—248 °C (20.5±1.0%) for nickel-containing complex **13**. The total weight losses for complexes **12** and **13** are 39.7±1.0% and 40.5±1.0%, respectively (the theoretical content of two diamine ligands is 40.42% and 40.54% for the cobalt- and nickel-containing complexes, respectively). The gas-phase mass spectrum in the temperature range of 150—250 °C corresponds to the spectrum of 4,5-dimethyl-1,2-phenylenediamine (The NIST Chemistry WebBook).

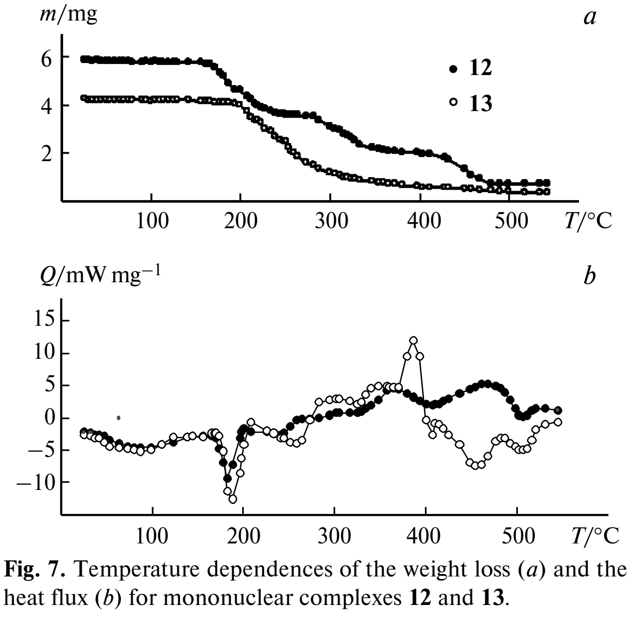

Fig. 7. Temperature dependences of the weight loss (*a*) and the heat flux (*b*) for mononuclear complexes **12** and **13**.

At temperatures higher than 248±2 °C, the thermolysis of complexes **12** and **13** occurs by different mechanisms. Complex **12** loses 48.5±1.0% of the initial weight in two steps in the temperature range of 260—490 °C, which is accompanied by the exothermic effect of a complex shape. In this temperature range, complex **13** gradually loses 50.55±1.0% of the initial eight; the total thermal effect is also negative. Presumably, in the case of cobalt-containing complex **12**, the chelating 4,5-dimethyl-1,2-phenylenediamine ligand is eliminated followed by the complete destructive decomposition. By contrast, the thermal decomposition and intramolecular redox reactions simultaneously occur in the case of nickel-containing complex **13**. The total weight loss for complex **12** in the temperature range under study is 88.2±1.0% (the percentage of the solid decomposition product is 11.8%); the total weigh loss for complex **13** is 91.0±1.0% (the percentage of the solid decomposition product is 9.0%). The phase composition analysis showed that the decomposition of complexes **12** and **13** affords nickel metal and CoO, respectively, as solid products. The theoretical content of Ni in complex **12** is 8.88%; the theoretical content of CoO in complex **13** is 11.29%.

Therefore, mononuclear complexes **3—9**, **12**, and **13** are thermally quite stable. The decomposition of these complexes starts at temperatures lower than the boiling point of the pure ligand. The decomposition of complexes **3—9** containing pyridine derivatives as ligands is accompanied by the melting (see Table 2). The temperatures at which the decomposition of the nickel-containing complexes starts are higher than those of the cobalt-containing derivatives of similar composition. The thermal stability of mononuclear pivalates containing various N-donor ligands decreases in the series $(2,6\text{-}NH_2)_2C_5H_3N$ > > $H_2N(C_5H_3N)NHC(Me){=}NH$ > $(NH_2)_2C_6H_2Me_2$ > >$(2\text{-}NH_2)C_5H_3N$ > $(2\text{-}NH_2)(6\text{-}Me)C_5H_3N$.

The thermolysis of the Co^{II} and Ni^{II} pivalates under study is a destructive process, the phase composition of the decomposition products being determined by the nature of coordinated ligands. The thermolysis of mononuclear cobalt complexes **4**, **6**, **8**, and **12** differs from that observed previously for other cobalt pivalates. Thus, cobalt oxide or a mixture of oxide and cobalt metal rather than volatile octanuclear cluster **14** (see Refs 21, 21, 23, and 24) are obtained as the final decomposition products of monomers **4**, **6**, **8**, and **12** (see Table 2). Unlike other known di- and polynuclear nickel(II) pivalates, which give nickel oxide as the final decomposition product,[**20,21,23,24**] the thermolysis of all mononuclear nickel complexes investigated in the present study afforded only nickel metal (see Table 2).

Experimental

All reactions were carried out under pure argon with the use of deoxygenated solvents and the standard Schlenk technique. Starting pivalates **1** and **2**,[23] the complex $Ni_2(\mu\text{-}H_2O)(OOCBu^t)_4(HOOCBu^t)_4$,[37] and mononuclear complexes **12** and **13** (see Ref. 25) were synthesized according to procedures described previously. Trimethylacetic acid (Acros Organics), 2-aminopyridine (Aldrich), 2,6-diaminopyridine (Acros Organics), and 2-amino-6-methylpyridine (Merck-Schuchardt) were used without additional purification. The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets. Microanalyses were carried out on a Carlo Erba CHN analyzer. The magnetic measurements were performed on a SQUID MPMS-XL Quantum Design magnetometer in the 2—300 K temperature range. The effective magnetic moments were calculated by the equation

$$\mu_{\text{eff}} = (3k/N_A\beta^2 \cdot \chi T)^{0.5} \approx (8\chi T)^{0.5},$$

where N_A is Avogadro's number, β is the Bohr magneton, and k is the Boltzmann constant. The thermal decomposition was studied by differential scanning calorimetry and thermogravimetric analysis. The thermogravimetric measurements were carried out in a flow of dry argon (20 mL min^{-1}) on a NETZSCH TG 209 F1 instrument in alundum crucibles at a heating rate of 10 deg min^{-1}. The composition of the gas phase at temperatures below 250 °C was studied on a QMS 403C Aeolos mass spectrometer under TGA conditions. The ionizing electron energy was 70 eV; the maximum determined mass number (the ratio of the mass of the ion to its charge Z) was 300 amu. The weights of the samples used in thermogravimetric experiments were 0.5—3 mg. The DSC experiments under a dry argon flow (Ar, > 99.998%; O_2, < 0.0002%; N_2, < 0.001%; water vapor, < 0.0003%; CH_4, < 0.0001%) were carried out on a NETZSCH DSC 204 F1 calorimeter in aluminum crucibles at a heating rate of 10 deg min^{-1}. The weights of the samples were 4—10 mg. Each experiment was repeated at least three times. The temperature calibration of the thermobalance and the calorimeter was performed based on the phase transition points of the reference compounds (C_6H_{12}, Hg, KNO_3, In, Sn, Bi, CsCl, 99.99% purity) according to the ISO/CD 11357-1 standard. The samples used for the TGA and DSC experiments were weighed on a SARTORIUS RESEARCH R 160P analytical balance with an accuracy of $1 \cdot 10^{-2}$ mg. The X-ray powder diffraction analysis of the thermolysis products was carried out with a FR-552 monochromator chamber ($CuK_{\alpha1}$ radiation) with the use of germanium as the internal standard (X-ray diffraction patterns were processed with an IZA-2 comparator with an accuracy of ±0.01 mm) and a STOE Powder Diffraction System.

The crystals of complexes **3—11** obtained in the synthesis were used for the X-ray diffraction study.

Di(2,6-diaminopyridino)di(η^2-*O,O´*-trimethylacetato)mononickel(II), $[(2,6\text{-}NH_2)_2C_5H_3N]_2Ni(\eta^2\text{-}OOCBu^t)_2$ (3). A mixture of $Ni_6(\mu_2\text{-}OOCBu^t)_6(\mu_3\text{-}OOCBu^t)_6$ (**2**) (0.3 g, 0.192 mmol) and 2,6-diaminopyridine (0.251 g, 2.30 mmol) in benzene or toluene (50 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 30 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The green crystals that precipitated after 24 h were separated by decantation, washed with cold benzene, and dried under argon. The yield was 0.529 g (96%). Found (%): C, 50.16; H, 6.76; N, 17.55. $C_{20}H_{32}NiN_6O_4$. Calculated (%): C, 50.13; H, 6.73; N, 17.54. IR, ν/cm^{-1}: 3468 s, 3432 s, 3380 s, 3348 s, 3232 s, 2960 s, 2928 m, 2864 m, 1636 s, 1624 s, 1600 s, 1572 s, 1528 s, 1484 s, 1456 m, 1432 s, 1360 m, 1304 m, 1264 m, 1224 s, 1176 m, 1112 m, 1080 m, 1028 m, 1000 m, 960 m, 940 w, 904 s, 892 m, 884 m, 808 m, 784 s, 740 m, 720 m, 684 m, 608 m, 564 w, 536 w, 500 m, 476 w, 424 w, 408 w, 324 w, 312 w.

Di(2-amino-6-methylpyridino)di(η^2-*O,O´*-trimethylacetato)monocobalt(II) benzene disolvate, $[(2\text{-}NH_2)(6\text{-}Me)C_5H_3N]_2Co(\eta^2\text{-}OOCBu^t)_2 \cdot 2C_6H_6$ ($4 \cdot 2C_6H_6$). A mixture of the polymer $[Co(OOCBu^t)_2]_n$ (**1**) (0.4 g, 1.53 mmol; per formula unit $Co(OOCBu^t)_2$) and 2-amino-6-methylpyridine (0.332 g, 3.07 mmol) in benzene (50 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 20 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The crimson crystals that precipitated after 12 h were separated by decantation, washed with cold benzene, and dried under argon. The yield was 0.952 g (98%). Found (%): C, 64.49; H, 7.36; N, 8.89. $C_{34}H_{46}CoN_4O_4$. Calculated (%): C, 64.44; H, 7.32; N, 8.84. IR, ν/cm^{-1}: 3388 s, 3348 s, 3220 s, 2964 s, 2928 m, 2904 m, 2868 m, 1664 s, 1620 s, 1592 s, 1572 s, 1516 m, 1480 s, 1456 m, 1436 m, 1408 s, 1376 m, 1360 m, 1292 m, 1260 m, 1224 s, 1172 m, 1092 m, 1032 m, 1004 m, 940 w, 904 s, 860 w, 800 w, 780 s, 616 m, 548 w, 492 m, 444 w, 424 w, 368 w, 324 w, 312 w.

Di(2-amino-6-methylpyridino)di(η^2-*O,O´*-trimethylacetato)mononickel(II), $[(2\text{-}NH_2)(6\text{-}Me)C_5H_3N]_2Ni(\eta^2\text{-}OOCBu^t)_2$ (5). A mixture of $Ni_6(\mu_2\text{-}OOCBu^t)_6(\mu_3\text{-}OOCBu^t)_6$ (**2**) (0.3 g, 0.192 mmol) and 2-amino-6-methylpyridine (0.249 g, 2.30 mmol) in benzene (50 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 10 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The green crystals that precipitated after 48 h were separated by decantation, washed with cold benzene, and dried under argon. The yield was 0.527 g (96%). Found (%): C, 55.40; H, 7.25; N, 11.77. $C_{22}H_{34}NiN_4O_4$. Calculated (%): C, 55.37; H, 7.18; N, 11.74. IR, ν/cm^{-1}: 3408 s, 3344 s, 3236 s, 2960 s, 2932 m, 2904 m, 2868 m, 1652 s, 1616 s, 1572 s, 1528 s, 1480 s, 1456 m, 1432 s, 1380 m, 1372 m, 1364 s, 1284 m, 1260 m, 1228 s, 1168 m, 1092 m, 1036 m, 1000 m, 960 m, 936 w, 908 s, 856 w, 812 w, 796 s, 792 m, 784 m, 780 m, 740 m, 608 m, 576 w, 536 w, 492 m, 424 w, 408 w, 368 w, 328 w, 312 w.

Complex $[(2\text{-}NH_2)C_5H_4N]_2Co(\eta^2\text{-}OOCBu^t)_2$ (6). A mixture of the polymer $[Co(OOCBu^t)_2]_n$ (**1**) (0.4 g, 1.53 mmol; per formula unit $Co(OOCBu^t)_2$) and 2-aminopyridine (0.577 g, 6.13 mmol) in MeCN (70 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 50 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The crimson crystals that precipitated after 12 h were separated by decantation, washed with cold MeCN, and dried under argon. The yield was 0.661 g (96% based on the initial amount of cobalt). Found (%): C, 53.51; H, 6.78; N, 12.48. $C_{20}H_{30}CoN_4O_4$. Calculated (%): C, 53.45; H, 6.73; N, 12.47. IR, ν/cm^{-1}: 3430 s, 3420 s, 3340 s, 3272 m, 3228 m, 2980 m, 2960 m, 2932 m, 2868 m, 1644 s, 1620 s, 1584 m, 1564 s, 1536 s, 1520 s, 1494 s, 1484 s, 1452 s, 1420 s, 1376 s, 1360 s, 1336 m, 1268 m, 1228 m, 1156 m, 1092 w, 1056 w, 1028 w, 1008 m, 940 w, 900 m, 856 m, 808 m, 792 m, 772 s, 744 m, 660 w, 644 w, 608 m, 520 m, 452 m, 400 w, 364 w, 356 w, 320 w.

The crystallographic data for complex **6** (monoclinic space group $P2_1/c$, $a = 11.2306(5)$ Å, $b = 23.6445(7)$ Å, $c = 8.5436(4)$ Å, $\alpha = 90°$, $\beta = 102.668(4)°$, $\gamma = 90°$; $V = 2213.46(16)$ Å^3, $Z = 4$) correspond to the parameters determined previously[28] by the X-ray diffraction study of the molecular structure of the complex $[(2\text{-}NH_2)C_5H_4N]_2Co(\eta^2\text{-}OOCBu^t)_2$.

Di(2-aminopyridino)di(η²-*O,O´*-trimethylacetato)mononickel(ɪɪ), $[(2\text{-}NH_2)C_5H_4N]_2Ni(\eta^2\text{-}OOCBu^t)_2$ (7). A mixture of $Ni_6(\mu_2\text{-}OOCBu^t)_6(\mu_3\text{-}OOCBu^t)_6$ (**2**) (0.3 g, 0.192 mmol) and 2-aminopyridine (0.216 g, 2.3 mmol) in benzene (70 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 50 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The green fine-crystalline precipitate that formed after 24 h was separated by decantation, washed with cold benzene, and dried under argon. The yield was 0.495 g (96%). Found (%): C, 53.54; H, 6.75; N, 12.48. $C_{20}H_{30}NiN_4O_4$. Calculated (%): C, 53.48; H, 6.73; N, 12.47. IR, ν/cm^{-1}: 3432 s, 3412 s, 3340 s, 3272 m, 3228 m, 2976 m, 2960 m, 2932 m, 2868 m, 2836 w, 1644 s, 1616 s, 1592 m, 1568 s, 1536 s, 1520 s,1492 s, 1484 s, 1452 s, 1432 s, 1380 s, 1360 s, 1336 m, 1264 m, 1228 m, 1156 m, 1096 m, 1056 m, 1028 m, 1008 m, 940 w, 904 m, 856 w, 812 m, 792 m, 772 s, 744 m, 660 w, 648 w, 608 m, 516 m, 452 m, 404 w, 324 w.

Complex $[H_2N(C_5H_3N)N(H)C(Me)=NH]Co(\eta^1\text{-}OOCBu^t)_2$ (8). A mixture of the polymer $[Co(OOCBu^t)_2]_n$ (**1**) (0.4 g, 1.53 mmol; per formula unit $Co(OOCCMe_3)_2$) and 2,6-diaminopyridine (0.167 g, 1.53 mmol) in MeCN (70 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 50 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The pink crystals that precipitated after 12 h were separated by decantation, washed with cold MeCN, and dried under argon. The yield was 0.63 g (98%). Found (%): C, 49.69; H, 6.88; N, 13.68. $C_{17}H_{28}CoN_4O_4$. Calculated (%): C, 49.64; H, 6.86; N, 13.63. IR, ν/cm^{-1}: 3424 m, 3224 m, 2956 s, 2928 m, 2868 m, 1644 s, 1636 s, 1616 s,1600 s, 1572 s, 1552 s, 1536 s, 1464 s, 1400 s, 1356 s, 1256 s, 1220 s, 1172 m, 1124 m, 1092 m, 1048 m, 1024 m, 1008 m, 960 m, 936 m, 892 m, 796 s, 772 s, 732 m, 696 w, 668 w, 612 m, 580 w, 560 m, 492 w, 428 m, 356 w, 328 w, 316 w.

The crystallographic data for complex **8** (monoclinic space group $P2_1/c$, $a = 15.108(13)$ Å, $b = 13.458(10)$ Å, $c = 10.310(8)$ Å, $\alpha = 90°$, $\beta = 103.630(19)°$, $\gamma = 90°$; $V = 2037(3)$ Å^3, $Z = 4$) correspond to the parameters determined previously[27] by the X-ray diffraction study of the molecular structure of the complex $[H_2N(C_5H_3N)N(H)C(Me)=NH]Co(\eta^1\text{-}OOCBu^t)_2$.

Complex $[H_2N(C_5H_3N)N(H)C(Me)=NH]Ni(\eta^2\text{-}OOCBu^t)_2 \cdot MeCN$ (9 · MeCN). ***A.*** A mixture of $Ni_6(\mu_2\text{-}OOCBu^t)_6(\mu_3\text{-}OOCBu^t)_6$ (**2**) (0.3 g, 0.192 mmol) and 2,6-diaminopyridine (0.126 g, 1.16 mmol) in MeCN (70 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 50 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The bright-green crystals that precipitated after 12 h were separated by decantation, washed with cold MeCN, and dried under argon. The yield was 0.499 g (96%). Found (%): C, 50.48; H, 6.94; N, 15.52. $C_{19}H_{31}NiN_5O_4$. Calculated (%): C, 50.47; H, 6.91; N, 15.49. IR, ν/cm^{-1}: 3408 m, 3364 s, 3228 m, 2960 s, 2928 m, 2864 m, 2832 w, 1632 s, 1616 s, 1600 m, 1596 s, 1568 s, 1528 s, 1480 s, 1456 s, 1424 s, 1396 m, 1360 s, 1348 m, 1260 m, 1228 m, 1164 w, 1084 m, 1044 m, 960 m, 904 m, 892 m, 808 m, 800 m, 776 m, 744 w, 684 w, 768 w, 608 m, 560 m, 532 m, 504 w, 488 w, 464 w, 432 m, 412 m, 352 w, 324 w, 312 w.

B. A mixture of $Ni_2(\mu\text{-}H_2O)(OOCBu^t)_4(HOOCBu^t)_4$ (0.3 g, 0.316 mmol) and 2,6-diaminopyridine (0.069 g, 0.632 mmol) in MeCN (40 mL) was heated at 70 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 10 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The bright-green crystals that precipitated after 24 h were separated by decantation, washed with cold MeCN, and dried under argon. The yield was 0.275 g (96%). The spectroscopic characteristics of the product are similar to those of the sample prepared according to the method ***A***.

The crystallographic data for complex **9** (monoclinic space group $P2_1/n$, $a = 12.221(3)$ Å, $b = 12.150(4)$ Å, $c = 16.367(5)$ Å, $\alpha = 90°$, $\beta = 111.017(6)°$, $\gamma = 90°$; $V = 2268.7(12)$ Å^3, $Z = 4$) correspond to the parameters determined previously[27] by the X-ray diffraction study of the molecular structure of the complex $[H_2N(C_5H_3N)N(H)C(Me)=NH]Ni(\eta^2\text{-}OOCBu^t)_2 \cdot MeCN$.

Di(2-amino-6-methylpyridino)tetra(μ₂-*O,O´*-trimethylacetato)dicobalt(ɪɪ) acetonitrile tetrasolvate, $[(2\text{-}NH_2)(6\text{-}CH_3)\text{-}C_5H_3N]_2Co_2(\mu_2\text{-}OOCBu^t)_4 \cdot 4MeCN$ (10 · 4MeCN). A mixture of the polymer $[Co(OOCBu^t)_2]_n$ (**1**) (0.4 g, 1.53 mmol; per formula unit $Co(OOCBu^t)_2$) and 2-amino-6-methylpyridine (0.332 g, 3.06 mmol) in MeCN (50 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 10 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The dark-green crystals that precipitated after 24 h were separated by decantation, washed with cold MeCN, and dried under argon. The yield was 0.378 g (82%). Found (%): C, 53.25; H, 7.19; N, 12.43. $C_{40}H_{64}Co_2N_8O_8$. Calculated (%): C, 53.21; H, 7.15; N, 12.41. IR, ν/cm^{-1}: 3380 s, 3218 m, 2964 s, 2908 m, 2868 m, 1664 m, 1632 m, 1608 m, 1580 s, 1536 s, 1484 m, 1456 m, 1416 s, 1380 m, 1360 m, 1276 w, 1260 m, 1224 s, 1176 w, 1032 w, 938 m, 902 m, 809 m, 792 m, 728 w, 672 m, 612 m, 606 m, 554 w, 532 s, 448 w, 426 m, 408 w, 356 w.

The crystallographic data for **10** · 4MeCN (monoclinic space group $P2_1/n$, $a = 15.43(1)$ Å, $b = 18.58(1)$ Å, $c = 11.17(1)$ Å, $\alpha = 90°$, $\beta = 130.74(1)°$, $\gamma = 90°$; $V = 2426(2)$ Å^3, $Z = 2$) correspond to the parameters determined previously[33] by the X-ray diffraction study of the molecular structure of the complex $(2,6\text{-}NH_2)_2Mn_2(OOCBu^t)_4 \cdot 4MeCN$.

(2-Amino-6-methylpyridino)tri(μ₂-*O,O´*-trimethylacetato)mono(η²-*O,O´*-trimethylacetato)dicobalt(ɪɪ) hydrate, $[(2\text{-}NH_2)\text{-}(6\text{-}CH_3)C_5H_3N]Co_2(\mu_2\text{-}OOCBu^t)_3(\eta^2\text{-}OOCBu^t) \cdot 1.5H_2O$ (11 · 1.5H₂O). A mixture of the polymer $[Co(OOCCMe_3)_2]_n$ (**1**) (0.4 g, 1.53 mmol; per formula unit $Co(OOCBu^t)_2$) and 2-amino-6-methylpyridine (0.166 g, 1.53 mmol) in MeCN (50 mL) was heated at 80 °C until the starting reagents were completely dissolved. The reaction solution was concentrated to 40 mL at 0.1 Torr and 20 °C and the residue was crystallized at 20 °C. The blue crystals that precipitated after 2 h were separated by decantation, washed with cold MeCN, and dried under argon. The yield was 0.443 g (88%). Found (%): C, 47.58; H, 7.29; N, 4.25. $C_{26}H_{47}Co_2N_2O_{9.50}$. Calculated (%): C, 47.50; H, 7.20; N, 4.26. IR, ν/cm^{-1}: 3383 s, 3218 m, 2963 s, 2904 m, 2872 m, 1662 m, 1608 s, 1590 w, 1548 m, 1533 s, 1528 m, 1485 s, 1460 m, 1419 s, 1378 m, 1363 m, 1295 w, 1227 s, 1032 w, 938 s, 902 m, 809 m,

Table 3. Crystallographic parameters and the X-ray data collection and structure refinement statistics for complexes **3**, **4**$\cdot$2C_6H_6, **5**, and **11**$\cdot$1.5H_2O

Parameter	**3**	**4**$\cdot$2C_6H_6	**5**	**11**$\cdot$1.5H_2O
Molecular formula	$C_{20}H_{32}NiN_6O_4$	$C_{34}H_{46}CoN_4O_4$	$C_{22}H_{34}NiN_4O_4$	$C_{26}H_{47}Co_2N_2O_{9.50}$
Molecular weight	479.23	633.68	477.24	657.52
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P1$
a/Å	11.725(4)	12.2172(9)	13.615(5)	9.1804(8)
b/Å	21.077(8)	12.4417(8)	19.941(6)	13.0642(12)
c/Å	19.956(7)	12.7606(9)	21.748(6)	14.7948(13)
α/deg	90	71.3540(10)	64.314(6)	79.5780(10)
β/deg	92.255(9)	75.3870(10)	86.457(9)	81.7580(10)
γ/deg	90	75.3840(10)	72.966(14)	70.9370(10)
V/Å^3	4928(3)	1746.9(2)	5073(3)	1642.6(3)
Z 8	2	8	2	
d_{calc}/g cm^{-3}	1.292	1.205	1.250	1.329
μ/mm^{-1}	0.823	0.531	0.797	1.059
θ-Scan range/deg	1.41—26.02	1.71—30.53	1.04—25.59	2.02—26.37
Number of measured reflections	12726	20386	27293	14409
Number of reflections with $I \geq 2\sigma(I)$	8660	10325	18126	12475
R_1	0.0712	0.0559	0.0671	0.0693
wR_2	0.1536	0.1736	0.0957	0.1993

791 m, 652 m, 612 m, 606 m, 555 m, 536 m, 476 m, 460 m, 448 m, 426 m, 410 w.

X-ray diffraction study. X-ray diffraction data for complexes **3—5** and **11** were measured on an automated Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, Mo-Kα radiation, λ = 0.71073 Å, T = 296(2) K (for **3** and **11**), 200(2) K (for **4**$\cdot$2C_6H_6), and 100(2) K (for **5**), ω-scanning technique with a step of 0.3° and the exposure time of 30 s per frame) according to a standard procedure.[38] Semi-empirical absorption corrections were applied.[39] 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 hydrogen atoms of the *tret*-butyl substituents of the pivalate ligands and the pyridine rings of the coordinated amine molecules were positioned geometrically and refined using a riding model. The calculations were carried out with the use of the SHELX97 program package.[40]

The crystallographic parameters and the structure refinement statistics for **3**, **4**$\cdot$2C_6H_6, **5**, and **11**$\cdot$1.5H_2O are given in Table 3.

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