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Carboxylate clusters with the M_4O_4 cubane-like core: pivalate cocrystal containing Co^{II} and Ni^{II}

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Joint thermolysis of the dinuclear pivalate complexes $M_2(\mu\text{-}H_2O)(\mu\text{-Piv})_2(\text{Piv})_2(\text{HPiv})_4$ (M = Co (**1**) and Ni (**2**), Piv^- is the pivalate anion), in decane at 174 °C at the reactant ratio 1 : 1 followed by treatment of the dry thermolysis product with methanol afforded crystals of a new cocrystallization product of the molecules containing the heterometallic cubane-like core $M_4(\text{Co,Ni})O_4$. According to the X-ray diffraction data and the results of magnetic measurements, inductively coupled plasma atomic emission spectrometry (ICP-AES), and investigations of the solid-state thermal decomposition products, the isolated cocrystallization product has the general formula $[Co_{1.6}Ni_{2.4}(\mu_3\text{-OMe})_4(\mu_2\text{-Piv})_2(\eta^2\text{-Piv})_2(\text{MeOH})_4]\cdot 4\text{MeOH}$ (**3**·4MeOH). Thermolysis of the crystals of the solvate **3**·4MeOH is a destructive process accompanied by the intramolecular redox reaction. A mixture of metallic Ni and cobalt oxide (CoO) are the final solid decomposition products of **3**·4MeOH in an argon atmosphere, whereas a mixture of the phases NiO, Co_3O_4, and $NiCo_2O_4$ is formed in air.

Key words: cubane-like cobalt and nickel pivalate clusters, cocrystallization, solid-state thermal decomposition, X-ray diffraction study, magnetic properties.

Homonuclear 3d-metal carboxylates containing the cubane-like core M_4O_4 with high-spin cobalt(II) and nickel(II) atoms are well known and have attracted attention because of unusual magnetic properties.[1—16] These compounds with alkanoate anions can serve as molecular precursors for a wide range of oxide materials[2,3,9,17—20] where the composition of the final material can be specified in the step of the chemical assembly of the starting precursor molecule. Taking into account the high volatility of many alkanoate clusters and the fact that the metal core M_4O_4 (M is a divalent metal) in cubane-like systems is ready for the formation of an oxide lattice through the elimination of organic components of the complexes, the formation of oxide ultrathin films would be expected upon mild thermolysis (at temperatures below 450—500 °C) of molecular alkanoate cubane-like compounds deposited on a substrate, for example, by the CVD (chemical vapor deposition) method. However, there is no progress in the development of this strategy for the synthesis of oxide materials because of the lack of efficient methods for the synthesis of the corresponding heterometallic molecular precursors. There are only a few publications on the methods for the assembly and physicochemical properties of the latter compounds.[9,18—20]

In the present study, we report on the method for the synthesis of the heterometallic pivalate derivative containing the cubane-like core $M_4(\text{Co,Ni})O_4$ and the results of investigation of the structure, magnetic properties, and mild thermolysis under argon and in air. A new compound was isolated as crystals with the composition $[Co_{1.6}Ni_{2.4}(\mu_3\text{-OMe})_4(\mu_2\text{-Piv})_2(\eta^2\text{-Piv})_2(\text{MeOH})_4]\cdot 4\text{MeOH}$ (Piv^- is the pivalate anion).

Results and Discussion

Previously,[21] we have shown that the mild thermolysis of the isostructural dinuclear complexes $M^{II}_2(\mu\text{-}H_2O)(\mu\text{-Piv})_2(\text{Piv})_2(\text{Piv})_4$ (M = Co (**1**) or Ni (**2**)) in decane at 174 °C afforded polynuclear pivalates having different structures. The thermolysis of cobalt complex **1** resulted in the elimination of the water molecule and the coordinated pivalic acid molecules to form the coordina-

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tion polymer $[Co(Piv)_2]_n$ having a chain structure in the crystals. As opposed to cobalt pivalate **1**, the thermolysis of dinuclear complex **2** under the same conditions afforded crystalline cyclic hexanuclear complex $Ni_6(\mu_2\text{-}Piv)_6(\mu_3\text{-}Piv)_6$.[21]

We found that the joint thermolysis of dinuclear complexes **1** and **2** in a ratio of 1 : 1 in decane at 174 °C gives an extremely air-sensitive fine-crystalline blue product. Recrystallization of this product from methanol resulted in pink crystals of $[M^{II}_4(\mu_3\text{-}OMe)_4(\mu_2\text{-}Piv)_2(\eta^2\text{-}Piv)_2(MeOH)_4]$ (**3**, M = Co, Ni), which are very sensitive to atmospheric moisture. The crystals were isolated as the solvate with four molecules of methanol (**3** • 4MeOH) in 76% yield. According to the inductively coupled plasma atomic emission spectrometry (ICP-AES) data, the Co to Ni ratio in the crystals of the solvate **3** • 4MeOH is 2 : 3.

According to the X-ray diffraction data, the general geometric characteristics of product **3** are virtually identical to those of the known homonuclear complexes containing the cubane-like core $\{M^{II}_4O_4\}$ (M = Co or Ni);[6,12] the M—μ^3-O (M—O, 2.023(7)— 2.062(8) Å), M(1)...M(2) (2.830(3) Å), and M(3)...M(4) (2.896(3) Å) bond lengths (Fig. 1) are equal, within the experimental error, to those found in the homonuclear analogs. Since it is virtually impossible to distinguish between the positions of nickel and cobalt atoms in the metal core and taking into account that the occupancies of the metal positions are different, the structure was refined using the model with four nickel atoms (the refinement using the $\{Co_4\}$ model led to similar results).

It should be noted that there are four methanol solvation molecules in the crystal structure of **3** as opposed to the known homonuclear complexes with cobalt and nickel atoms isolated as solvates with 4.5 methanol molecules.[6,12] In the structure of **3**, the methanol molecules coordinated in a monodentate fashion are linked to methanol solvation molecules by short hydrogen bonds ($O_{MeOH}...O_{solv}$, 2.61—2.65 Å). The methanol solvation molecules also interact with the oxygen atoms of the carboxylate groups of the cluster ($O_{OOCR}...O_{solv}$, 2.60—2.64 Å) (Fig. 2).

Since we failed to unambiguously establish the heterometallic nature of the molecule based on the X-ray diffraction data (product **3** can be a cocrystallization product of two homonuclear cobalt and nickel complexes in the ratio 2 : 3), we studied the magnetic properties of the crystals of the solvate **3** • 4MeOH. According to the results of magnetic measurements, the effective magnetic moment μ_{eff} of the product **3** • 4MeOH per molecule monotonically decreases with decreasing temperature (μ_{eff} = = 8.158—3.729 μ_B (300—2 K)) (Fig. 3). This behavior is typical of antiferromagnetically coupled systems and strongly differs from the properties of the analogous homonuclear nickel-containing complex characterized by ferromagnetic spin-spin exchange interactions.[6] This is evidence for the absence of pure nickel complexes in the crystals, which, according to the above-considered ICP-AES data, suggests the presence of cocrystals containing heterometallic structures. Taking into account the analytical data, the general formula of **3** can be represented as $[Co_{1.6}Ni_{2.4}(\mu_3\text{-}OMe)_4(\mu_2\text{-}Piv)_2(\eta^2\text{-}Piv)_2(MeOH)_4]$.

At the same time, the deficiency in cobalt atoms in the structure of **3** suggests that pure cobalt complexes are absent in the crystals. Hence, the formula of **3** can be represented, for example, as the solvate of two cocrystallized heterometallic pivalate complexes containing the

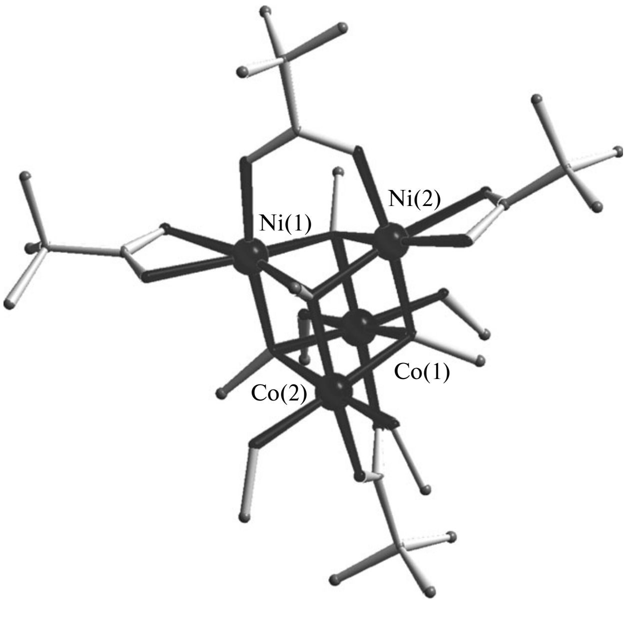

Fig. 1. Structure of product **3** (the molecule with two cobalt atoms and two nickel atoms is shown).

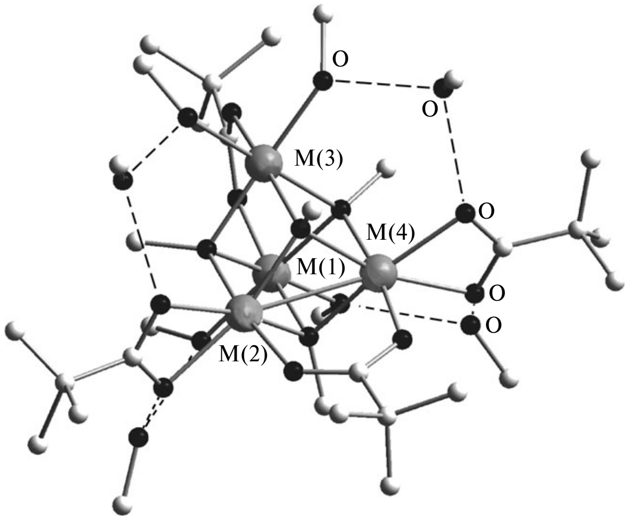

Fig. 2. Fragment of the packing of the complex $[M^{II}_4(\mu_3\text{-}OMe)_4(\mu_2\text{-}Piv)_2(\eta^2\text{-}Piv)_2(MeOH)_4]$ (**3**, M = Co, Ni) with four methanol solvation molecules (**3** • 4MeOH). The hydrogen atoms are not shown.

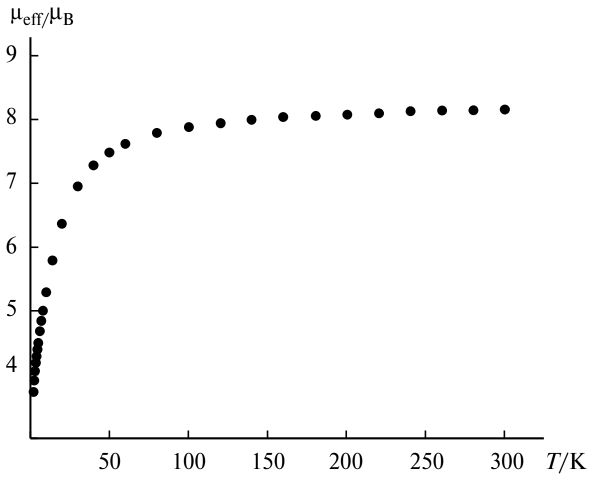

Fig. 3. Temperature dependence of the effective magnetic moment (μ_{eff}) for the product **3**·4MeOH.

cubane-like cores: $3[Co_2Ni_2(\mu_3\text{-}OMe)_4(\mu_2\text{-}Piv)_2(\eta^2\text{-}Piv)_2(MeOH)_4]\cdot 2[CoNi_3(\mu_3\text{-}OMe)_4(\mu_2\text{-}Piv)_2(\eta^2\text{-}Piv)_2(MeOH)_4]\cdot 20MeOH$.

The investigation of the solid-state thermolysis of the crystals of the solvate **3**·4MeOH in an inert atmosphere and in air showed that the character of decomposition at temperatures below 174 °C in air is virtually identical to that under argon (Fig. 4). During heating of the sample, the endothermic processes are observed at 35±2 °C (see Fig. 4, *a*), whereas the weight loss occurs only on heating to temperatures higher than 49±2 °C (see Fig. 4, *b*). The results of the stepwise DSC experiment with the visual control after each step suggest that no melting of the sample occurs at temperatures below 200 °C. The results of structural studies according to which the methanol molecules coordinated in a monodentate fashion are linked to the methanol solvation molecules by short hydrogen bonds and the analysis of the observed thermal effects (the first endothermic effect Q = 18±3 kJ mol^{-1} of the complex is comparable to the hydrogen bond energy[22] and the second endothermic effect Q = 220±10 kJ mol^{-1} (this is the sum of the energies of detachment of the coordinated methanol molecules, the evaporation of the solvation and coordinated molecules, and the formation of new bonds) provide evidence that the hydrogen bond cleavage is the first thermal transformation.

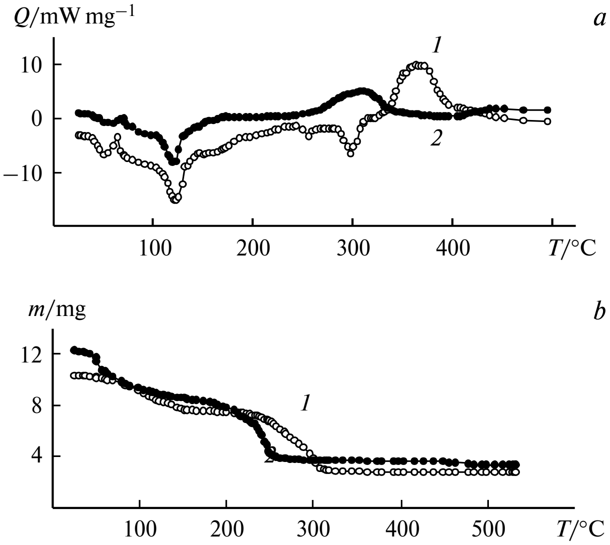

Fig. 4. Temperature dependences of the heat flux (*a*) and the weight loss (*b*) during heating of the product **3**·4MeOH in an inert atmosphere (*1*) and in air (*2*).

In an argon atmosphere, the weight loss during heating started at 49±2 °C and was accompanied by the energy absorption (the endothermic effect of a complex shape). The mass spectrum of the gas phase in the temperature range of 50—170 °C corresponds to the spectrum of methanol (The NIST Chemistry WebBook). Hence, the decomposition step under consideration is apparently accompanied by the removal of volatile methanol solvation molecules and coordinated methanol molecules. However, we failed to separate the steps of the removal of different types of methanol molecules. In the temperature range of 49—170 °C, the weight loss was 25.8±1.0%. The theoretical content of four methanol solvent molecules and four coordinated methanol molecules is 25.17%, which is in good agreement, within the experimental error, with the results of thermogravimetry.

It was noted that the the initial decomposition step of the sample affords intermediates stable in the temperature range of 170—210 °C. At temperatures above 210 °C, final destruction of the sample occurs, the process being accompanied by complex energy changes. In the temperature range of 220—310 °C, the weight loss occurs with an endothermic effect. In the temperature range of 310—470 °C, the process is exothermic and occurs without weight loss, which is characteristic of the formation of a solid decomposition product. According to the X-ray powder diffraction data, the decomposition affords a mixture of metallic nickel and CoO. The total weight loss in the temperature range under study is 73.1±1.5%. According to the TGA data, the weight of the solid product is 26.9±1.5% of the weight of the initial sample.

According to the ICP-AES analysis, the Ni : Co ratio in the product **3**·4MeOH is 3 : 2. These data suggest that the solid decomposition product contains 2.4 moles of Ni and 1.6 moles of CoO, whereas the weight of the solid residue calculated taking into account the molecular formula should be 26.67%, which is equal, within the experimental error, to the value 26.9±1.5% determined by TGA. This result additionally confirms the quantitative metal content in the sample under study.

Apparently, the phase composition of the decomposition products of **3**·4MeOH is determined by the different nature of the metal centers, as well as by the nature of the coordinated ligands and the structural features of the metal core, as has previously been shown for other pivalate complexes of nickel(II)[16,21,23,24] and cobalt(II).[16,21,23—25]

The first decomposition step of the crystals of **3**·4MeOH in air is also accompanied by the elimination of the methanol molecules and their transition to the gas phase. In the temperature range of 49—65 °C, four methanol solvation molecules (12.5±1.5%) are apparently removed; the coordinated methanol molecules (14.6±2.0%) are eliminated in the temperature range of 65—130 °C. According to the TGA data, the total content of methanol is 27.1±2.0%, which is, within experimental error, equal to eight methanol molecules in the solvate **3**·4MeOH (25.17%) calculated from the molecular formula. According to the TGA data, the decomposition of the sample in air affords virtually no stable intermediates. The first decomposition step is followed by the complete oxidative destruction. It should be noted that the weight loss is not accompanied by energy changes in the temperature range of 140—270 °C. In the temperature range of 250—390 °C, exothermic processes occur, but they are not accompanied by the weight loss, which can be associated with the formation of new solid decomposition products. According to the X-ray powder diffraction data, the decomposition affords a mixture of the phases NiO, Co_3O_4, and $NiCo_2O_4$ as solid products (Table 1). The formation of oxides upon thermolysis is associated with the presence, first, of the oxidizing atmosphere and, second, of the bridging pivalate groups, when the CO_2 fragments that are formed as a result of the cleavage of the pivalate ligands serve as the oxidizing agent.

It was demonstrated above that, based on the analysis of the magnetic behavior and the analytical ICP-AES data, the crystals of the solvate **3**·4MeOH is the solvate of the cocrystallized heterometallic complexes containing the cubane-like core M_4O_4. This suggestion is confirmed also by the results of the comparative analysis of the solid-state thermolysis under argon of two homometallic complexes $[M_4(\mu_3\text{-OMe})_4(\mu_2\text{-Piv})_2(\eta^2\text{-Piv})_2(MeOH)_4]\cdot 4MeOH$ ($M = Co^{II}$ (**4**·4MeOH) and Ni^{II} (**5**·4MeOH)) with μ^3-methoxide bridges, which we have synthesized and characterized previously,[16] and the newly synthesized product **3**·4MeOH (Fig. 5).

It can be seen that the onset of the endothermic processes for the crystals of **3**·4MeOH, **4**·4MeOH, and **5**·4MeOH corresponds to 35±2 °C. The first endothermic effect for all samples is observed in the temperature range of 35—65 °C. Apparently, the processes associated with the hydrogen bond scission and the removal of the methanol solvation molecules occur in this temperature range.

For the complexes **4**·4MeOH and **5**·4MeOH, the weight loss in this temperature range is 12.5±1.0 and 13.1±1.0%, respectively (the theoretical percentage of the methanol solvation molecules is 12.55%), and further heating of the complexes in the temperature ranges of 65—145 and 65—180 °C accompanied by the energy absorption (the double endothermic effect) leads to the weight loss of 13.08±1.0 and 12.6±1.0%, respectively The latter process corresponds to the removal of coordinated methanol, whose theoretical percentage is 12.55%. For the product **3**·4MeOH, it is impossible to separate the elimination step of the methanol solvation molecules based on the TGA data because the continuous weigh loss occurs in the

Table 1. Data from the analysis of the phase composition of the solid thermolysis product of the cocrystal **3**·4MeOH in air

Product		NiO[44-1159]*		Co_3O_4[43-1003]*		$NiCo_2O_4$[20-0781]*	
d/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)
—	—	—	—	—	—	4.69	14
4.67 br	10	—	—	4.6670	16	—	—
—	—	—	—	—	—	2.869	25
2.87 br	30	—	—	2.8580	33	—	—
—	—	—	—	—	—	2.447	100
2.44 br	100	—	—	—	—	2.4374	100
2.42	20	2.412	61	—	—	—	—
2.35	5	—	—	—	—	2.342	10
2.085	100	2.089	100	—	—	—	—
—	—	—	—	—	—	2.029	25
2.03 br	30	—	—	2.0210	20	—	—
—	—	—	—	—	—	1.562	30
1.56 br	40	—	—	1.5558	32	—	—
1.48	40	1.4768	35	—	—	—	—
1.44	10	—	—	—	—	1.434	45
1.43	10	—	—	1.4291	38	—	—

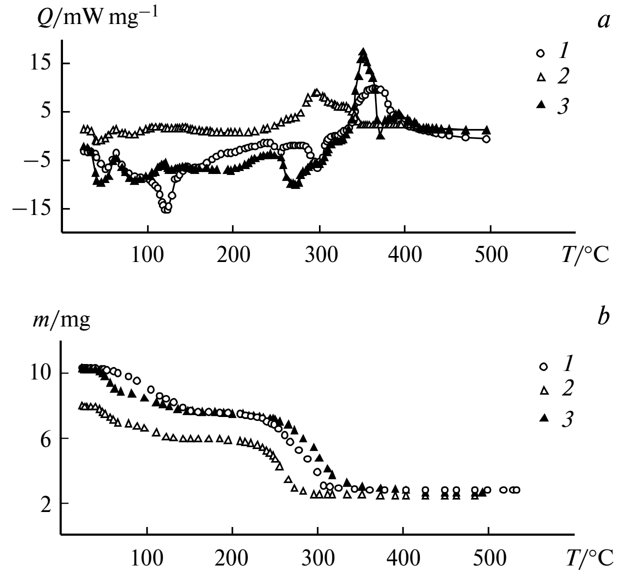

Fig. 5. Temperature dependences of the heat flux (*a*) and the weight loss (*b*) during heating of the product **3**·4MeOH (*1*) and the complexes **4**·4MeOH (*2*) and **5**·4MeOH (*3*) in an inert atmosphere.

range of 49—170 °C, which corresponds to the removal of both types of methanol molecules. This process is accompanied by energy changes, whose character differs from that observed for **4**·4MeOH and **5**·4MeOH. The absence of individual homometallic complexes in the crystals of **3**·4MeOH is confirmed by the character of the further destructive decomposition of the intermediate. For all the samples under consideration, the onset of energy changes in this decomposition step corresponds to 200±5 °C. For the cobalt-containing complex **4**·4MeOH, the exothermic effect is observed in the range of 205—350 °C, and the weight loss (43.6±1.0%) occurs in the range of 210—310 °C. For the nickel-containing compound **5**·4MeOH, the energy changes in the temperature range of 205—430 °C have a complex character (successive alternation of the exo- and endothermic effects), and the weight loss in the range of 230—350 °C is 47.9±1.0%. This character of the energy changes in the last decomposition step for compounds **4**·4MeOH and **5**·4MeOH is apparently attributed to the difference in the redox processes[16] that occur in the thermolysis in an inert atmosphere. Thus the mixed-valence oxide Co_3O_4 is the only solid thermolysis product of **4**·4MeOH, whereas the thermal decomposition of compound **5**·4MeOH affords a virtually equimolar mixture of Ni and NiO. For the product **3**·4MeOH, the weigh loss is also observed in the range of 215—325 °C, and complex energy changes occur in the range of 210—440 °C, but their character differs from that observed for compound **5**·4MeOH.

Therefore, the data from the analysis of the solid-state thermolysis under argon of the crystals of the homometallic complexes **4**·4MeOH and **5**·4MeOH and the product **3**·4MeOH suggest that the product **3**·4MeOH is neither a mechanical mixture nor the cocrystallization product of the homometallic complexes **4**·4MeOH and **5**·4MeOH.

The physicochemical studies (X-ray diffraction, ICP-AES, magnetic measurements, DSC, and TGA) showed that the product **3**·4MeOH is the solvate of the cocrystallized heterometallic pivalate clusters containing the cubane-like core $M_4(Co,Ni)O_4$. The thermolysis of the cocrystal **3**·4MeOH, like the thermolysis of the analogous homometallic cubane-like structures **4**·4MeOH and **5**·4MeOH, is a destructive process and is accompanied by the intramolecular redox process. The phase composition of their decomposition products is determined by the nature of the metal centers and the coordinated ligands, as well as by the structural features of the metal core. A mixture of metallic Ni and cobalt oxide (CoO) are the final solid decomposition products of **3**·4MeOH in an argon atmosphere, whereas the decomposition of compounds **4**·4MeOH and **5**·4MeOH affords oxide Co_3O_4 and an equimolar mixture of Ni and NiO, respectively. The decomposition of **3**·4MeOH in air gives a mixture of the phases NiO, Co_3O_4, and $NiCo_2O_4$. In our opinion, these results provide evidence that the desired oxide materials of different nature can be synthesized with the use of cubane-like divalent cobalt and nickel complexes as molecular precursors.

Experimental

All synthetic operations were carried out under pure argon with the use of the standard Schlenk technique. The starting compounds **1** and **2** were synthesized according to known procedures.[6,26] The synthesis of **3**·4MeOH was carried out with the use of decane (Merck, 95% *for synthesis*) and methanol (Merck, 99.8% *for liquid chromatography*). The elemental analysis for C and H was carried out on an Euro Vector CHN Elemental Analyser (Model EA 3000) at the Center of Collective Use of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences. The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets. The static magnetic susceptibility measurements were carried out on a SQUID MPMS-5S Quantum Design magnetometer in the 2—300 K temperature range. The effective magnetic moments were calculated by the equation $\mu_{eff} = (8\chi T)^{0.5}$. The metal contents were determined by inductively coupled plasma atomic emission spectrometry on an IRIS Advantage instrument. The thermal decomposition was studied by differential scanning calorimetry and thermogravimetric analysis on DSC-20 and TG-50 units of a Mettler TA-3000 thermoanalyzer. For each sample, three DSC experiments and three TGA experiments were performed (the heating rate in all experiments was 10 deg min^{-1}). The weight loss upon thermal degradation was determined directly on the TG-50 unit; the accuracy of weighing was $\pm 2 \cdot 10^{-3}$ mg. The accuracy of the determination of anomalous points in the thermograms and of the thermal effects was ±1° and ±0.5%, respectively. The X-ray powder diffraction analysis of the decomposition products was carried out with a FR-552 monochromator chamber (Cu-Kα_1 radiation) using germanium as the internal standard (X-ray diffraction patterns were processed on an IZA-2 comparator with an accuracy of ±0.01 mm) and on a STOE Powder Diffraction System. In addition, the thermogravimetric measurements were carried out in a flow of artificial air (20 ml min^{-1}) and 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 200 °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 *m/z* ratio) was 300 amu.

Tetra(μ_3-methoxo)di(μ_2-*O,O´*-trimethylacetato)di(η^2-*O,O´*-trimethylacetato)tetra(η^1-methanol)1.6cobalt(II)2.4nickel(II) methanol tetrasolvate [$Co_{1.6}Ni_{2.4}(\mu_3\text{-OMe})_4(\mu_2\text{-Piv})_2(\eta^2\text{-Piv})_2(\eta^1\text{-MeOH})_4$] · 4MeOH (3 · 4MeOH). The complex $Ni_2(\mu\text{-}H_2O)(\mu\text{-Piv})_2(Piv)_2(HPiv)_4$ (0.25 g, 0.264 mmol) and oxygen-free decane (50 mL) were added to $Co_2(\mu\text{-}H_2O)(\mu\text{-Piv})_2(Piv)_2(HPiv)_4$ (0.25 g, 0.264 mmol). The resulting blue-green solution was heated under argon to 174 °C and kept until a dry blue fine-crystalline product formed. The latter was cooled to 20 °C, and then methanol (60 mL) was added. The reaction mixture was stirred under argon at 60 °C until the starting compound completely dissolved. The resulting crimson-gray solution was filtered, concentrated to 40 mL at 0.1 Torr and 20 °C, and kept at 5 °C for 8 h. Pink crystals that formed were separated from the solution by decantation, washed with cold methanol, and dried under a stream of argon. The yield of the solvate of product **3** with four MeOH molecules was 0.41 g (76%). Found (%): C, 37.75; H, 8.18. $C_{32}H_{80}Co_{1.6}Ni_{2.4}O_{20}$. Calculated (%): C, 37.68; H, 7.91. The quantitative ratio Co : Ni = 2 : 3. IR, ν/cm^{-1}: 3384 m, 3268 m, 2956 s, 2928 s, 2908 m, 2872 m, 2836 m, 1684 m, 1668 m, 1584 s, 1572 s, 1552 s, 1536 s, 1484 s, 1456 m, 1416 s, 1372 m, 1360 s, 1260 w, 1224 s, 1104 w, 1032 m, 936 w, 896 m, 796 s, 604 m, 416 m, 324 w.

Table 2. Crystallographic parameters for the product **3** · 4MeOH

Parameter	Characteristics
Molecular formula	$C_{32}H_{80}Ni_4O_{20}$
Molecular weight	1019.80
Space group	*Pbca*
a/Å	15.327(1)
b/Å	41.83(3)
c/Å	15.887(9)
α/deg	90
β/deg	90
γ/deg	90
V/Å^3	10186(1)
Z	8
ρ_{calc}/g cm^{-3}	1.330
μ/mm^{-1}	1.520
Radiation	Mo-Kα (λ = 0.71073 Å)
θ—2θ-Scan range/deg	1.91—30.17
Number of measured reflections	61940
Number of reflections with $I \geq 2\sigma(I)$	14631
R_{int}	0.1106
R_1	0.0811
wR_2	0.1534
T_{min}/T_{max}	0.5611/0.7213

The synthesized crystals were suitable for X-ray diffraction analysis.

X-ray diffraction study. The X-ray diffraction data for the crystals of **3** · 4MeOH were measured on a Bruker AXS SMART 1000 diffractometer equipped with a CCD area detector (graphite monochromator, 120(2) K, ω-scanning technique with a step of 0.3° and exposure time of 30 s per frame) according to a standard procedure.[27] A semiempirical absorption correction was applied.[28] The crystallographic parameters and the refinement statistics for the structure of **3** · 4MeOH are given in Table 2. The structure of the complex was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms (except for the methyl carbon atoms of the disordered *tert*-butyl group at the C(7) atom (C(8)—C(10) and C(8a)—C(10a), which were refined isotropically with the occupancies of 0.6 and 0.4, respectively). The metal centers were refined as the Ni atoms. The refinement of the metal core using the Co_4 model led to similar results. The hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands were positioned geometrically and refined using a riding model. The calculations were carried out with the use of the SHELX97 program package.[29]

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