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Homo- and heterometallic trinuclear nickel(II) and cobalt(II) pivalate complexes *

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The reaction of the dinuclear complex $Co_2(bpy)_2(OOCBu^t)_4$ with the tetranuclear complex $Ni_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(EtOH)_6$ afforded the trinuclear heterometallic complex $M_3(bpy)_2(\mu_3\text{-}OH)(\mu\text{-}OOCBu^t)_4(OOCBu^t)$ (**6**) (M = Ni, Co; Ni : Co = 1.2 : 1) in which two metal atoms are in an octahedral environment and one metal atom is in a tetrahedral environment. The reaction of 2,2´-bipyridine with $Co_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(HOEt)_6$ (reagent ratio was 2 : 1) or the reaction of bpy with $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCBu^t)_{12}$ (reagent ratio was 4 : 1) produced a homometallic analog of **6**, *viz.*, the trinuclear cluster $Co_3(bpy)_2(\mu_3\text{-}OH)(\mu\text{-}OOCBu^t)_4(OOCBu^t)$ (**8**). The reaction of 1,10-phenanthroline (phen) with the $[Co(OH)_n(OOCBu^t)_{2-n}]_x$ polymer gave the analogous trinuclear cluster $(phen)_2Co_3(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(\eta^1\text{-}OOCBu^t)$. Compounds **6** and **8** exhibit antiferromagnetic spin-spin exchange interactions.

Key words: cobalt(II), nickel(II), heterometallic complexes, 2,2´-bipyridine, 1,10-phenanthroline, synthesis, X-ray diffraction analysis, magnetic properties.

Recently, we have demonstrated[1] that heterodinuclear pivalate complexes with cobalt(II) and nickel(II) atoms in different ligand environments can conveniently be synthesized according to a scheme, in which the dimeric doubly bridged pivalate complex $Co_2(bpy)_2(\mu\text{-}OOCBu^t)_2(\eta^2\text{-}OOCBu^t)_2$ (**1**) serves as an active reagent generating the $Co(bpy)(OOCR)_2$ fragments (R = Bu^t), whereas the tetranuclear complex $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_4(OOCBu^t)_2(MeCN)_2[\eta^2\text{-}o\text{-}C_6H_4(NH_2)(NHPh)]_2$ (**2**) can serve as a source of nickel atoms. Two reaction products, $Ni(bpy)(\mu_2,\eta^2\text{-}OOCBu^t)(\mu_2\text{-}OOCBu^t)_2Co(\eta^2\text{-}OOCBu^t)$ (**3**) and $(Bu^tCOO)Ni(bpy)(\mu\text{-}OH_2)(\mu_2\text{-}OOCBu^t)_2M(OOCBu^t)(HOOCBu^t)(1,2\text{-}(NH_2)(NPhH)(C_6H_4))$ (**4**, M = $Ni_{0.85}Co_{0.15}$), were isolated in approximately equal yields (~45%). In these complexes, the metal atoms are in different ligand environments (Scheme 1). The ratio of metals was determined by elemental analysis for Ni and Co because it is impossible to distinguish between the Ni and Co atoms by X-ray diffraction analysis. The presence of the N-donor ligands in both starting reagents led to stabilization of the final dinuclear structures, although the formation of complexes **3** and **4** was accompanied by the transfer of the bpy ligand from cobalt to nickel. The use of nickel-containing complexes with ligands, which can readily be eliminated (for example, with coordinated ethanol molecules), as the starting reagents increases the probability of assembly of heterometallic compounds containing a large number of metal atoms. To investigate this approach to the formation of heteronuclear pivalate systems, in the present study we examined the reaction of complex **1** with the tetranuclear complex $Ni_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(HOEt)_6$ (**5**).[2]

Results and Discussion

The reaction of complex **1** with $Ni_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(EtOH)_6$ (**5**) in *o*-xylene at 80 °C gave one product, *viz.*, the trinuclear complex $M_3(bpy)_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(\eta^1\text{-}OOCBu^t)$ (**6**), as the solvate with one acetonitrile molecule (acetonitrile is present as solvate molecules in the starting complex **1**) in 85% yield (Scheme 2).

According to the data from inductively coupled plasma atomic emission spectrometry (ICP-AES), complex **6** contains nickel and cobalt atoms in a ratio of 1.2 : 1. X-ray diffraction study of blue prismatic crystals of solvate **6**·MeCN (Fig. 1, Table 1) demonstrated that the molecule contains a triangular metal core centered by the hydroxy group (M(1)—O, 2.085(7) Å; M(2)—O,

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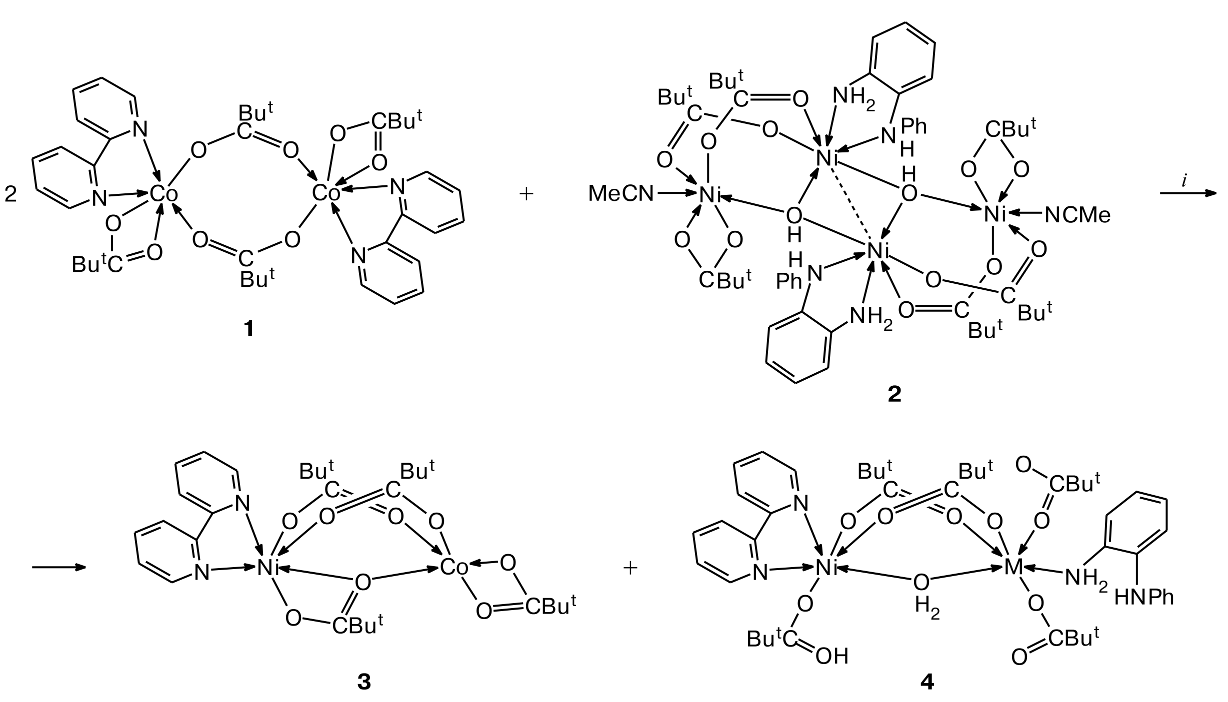
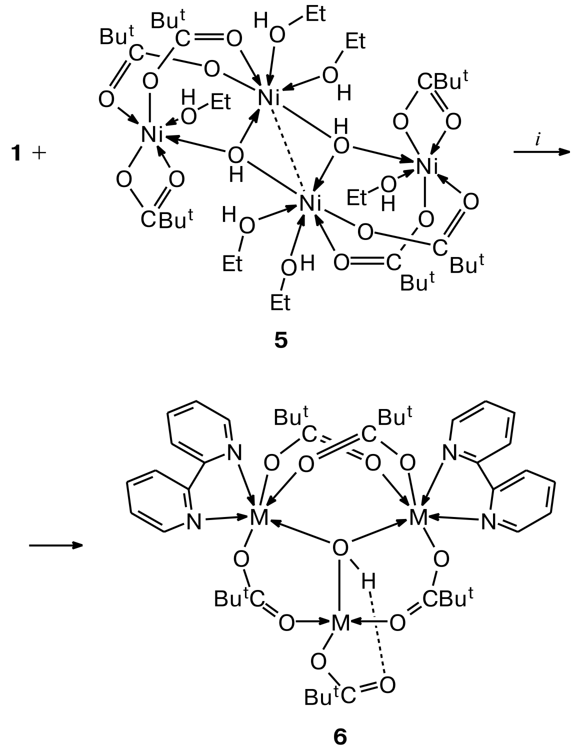
Scheme 1



i. *o*-Xylene, 80 °C.

Scheme 2



i. *o*-Xylene, 80 °C.

2.081(7) Å; M(3)—O, 1.957(6) Å) with nonequivalent nonbonded distances between the metal atoms (M(1)...M(2), 3.504(1) Å; M(2)...M(3), 3.318(1) Å; M(1)...M(3), 3.304(1) Å). Only the M(1) and M(2) atoms are coordinated by the bipyridine ligands (M—N, 2.12(1)—2.15(1) Å). Both metal atoms are in an octahedral ligand environment and are linked two each other through two carboxylate groups (M—O, 2.02(1)—2.08(1) Å). The third metal atom is in a tetrahedral ligand environment and is linked to each of two other metal centers only through one carboxylate bridge (M(3)—O, 1.972(9)—1.98(1) Å). In addition, the latter metal atom is coordinated by the terminal carboxylate group (M(3)—O, 2.036(7) Å), which forms a strong hydrogen bond with the tridentate hydroxy bridge (O—H...O, 1.78(5) Å).

As a result of this ligand environment, all three metal centers have the formal charge +2. Although it is practically impossible to unambiguously distinguish between the positions of the nickel and cobalt atoms in the structure of **6**, a model in which the cobalt atom occupies the tetrahedral Co(3) position (see Fig. 1) seems to be the most probable. Nickel carboxylate complexes with metal atoms in a tetrahedral environment formed by the oxygen atoms of the carboxylate and hydroxy groups are unknown. However, recently we have prepared[3] the triangular cluster $Co_3L_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(\eta^1\text{-}OOCBu^t)$ (**7**, L is

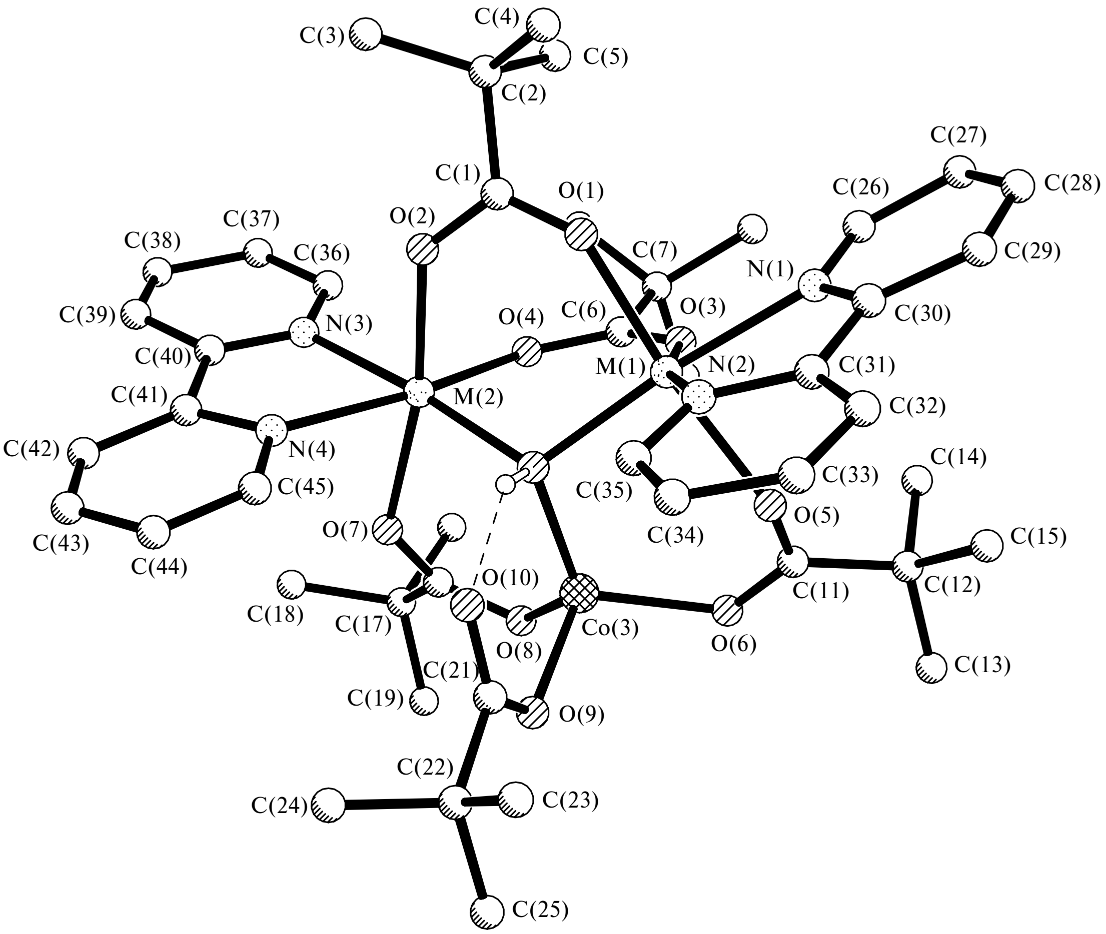


Fig. 1. Structure of the trinuclear complexes $M_2Co(bpy)_2(\mu_3\text{-}OH)(\mu\text{-}OOCBu^t)_4(OOCBu^t)$ (**6**, $M_2 = Ni_2$; **8**, $M_2 = Co_2$).

8-amino-2,4-dimethylquinoline) with the structurally similar metal carboxylate core containing the tetrahedrally coordinated cobalt atom. This complex was synthesized by the reaction of 8-amino-2,4-dimethylquinoline with the $[Co(OH)_n(OOCBu^t)_{2-n}]_x$ polymer or the tetranuclear cluster $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_4(\eta^2\text{-}OOCBu^t)_2(EtOH)_6$. The cobalt atoms in a tetrahedral environment formed by the oxygen atoms of the carboxylate and hydroxy groups are present, for example, in the hexanuclear pivalate cluster $Co_6(\mu_3\text{-}OH)_2(\mu_3\text{-}OOCBu^t)_2(\mu_2\text{-}OOCBu^t)_8(HOOCBu^t)_4$.[4] The M(bpy) positions in cluster **6** are, apparently, occupied primarily by nickel atoms and are only partially occupied by cobalt atoms. In this case, the formula of **6** can be represented as $m[Ni_2Co(bpy)_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(OOCBu^t)] \cdot$ $\cdot n[Co_3(bpy)_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(OOCBu^t)]$, where m and n are 9 and 2, respectively, according to the ratio of metals determined experimentally. Meanwhile, the structures with the $NiCo_2$ core also cannot be excluded. We failed to separate a set of trinuclear clusters by fractional crystallization of a solution of **6** in various solvents (benzene, acetonitrile, CH_2Cl_2), crystals of the compound with the above-mentioned composition being isolated in all cases. Magnetic measurements demonstrated that compound **6** exhibits antiferromagnetic properties. The magnetic moment (per molecular weight of the overall cluster) monotonically decreases with decreasing temperature (Fig. 2).

The magnetic measurements gave the somewhat overestimated upper limit of the effective magnetic moment of compound **6** (6.47 μ_B (300 K) per molecule) compared to the purely spin value corresponding to the trinuclear Ni_2Co system ($S_1 = 1$; $S_2 = 1$, $S_3 = 3/2$; $\mu_{eff} = 5.57$ μ_B), which was calculated by a known equation.[5,6] Apparently, this is attributable to the contribution of structures with the Co_3 or $NiCo_2$ core possessing the larger total spin as well as to spin-orbital coupling typical of the Co^{II} atoms. These data confirm the assumption that molecules containing metals in different ratios coexist in the crystal of **6**.

To correctly estimate a possibility of existence of the compositionally similar homonuclear triangular cluster with the Co_3 core and to reliably compare the magnetic characteristics of compound **6** and the homonuclear

Table 1. Selected geometric characteristics of the trinuclear clusters $M_2Co(bpy)_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(\eta^1\text{-}OOCBu^t)$ (**6**, $M_2 = Ni_2$; **8**, $M_2 = Co_2$)*

Parameter	**6**·MeCN	**8**·MeCN	**8**
Bond length		*d*/Å	
M(1)—O(1M)	2.085(7)	2.084(6)	2.08(1)
M(1)—O(1)	2.02(1)	2.03(1)	2.01(1)
M(1)—O(3)	2.07(1)	2.09(1)	2.02(1)
M(1)—O(5)	2.106(8)	2.135(7)	2.09(1)
M(1)—N(1)	2.128(9)	2.141(8)	2.10(1)
M(1)—N(2)	2.19(1)	2.207(9)	2.10(2)
Co(3)—O(1M)	1.957(6)	1.978(6)	1.96(1)
Co(3)—O(6)	1.98(1)	1.987(8)	1.94(1)
Co(3)—O(8)	1.972(9)	1.988(8)	1.98(1)
Co(3)—O(9)	2.036(7)	2.051(8)	2.00(1)
Bond angle		ω/deg	
O(1M)—M(1)—O(1)	95.6(4)	95.3(3)	97.8(5)
O(1M)—M(1)—O(3)	90.5(3)	90.4(3)	88.6(4)
O(1M)—M(1)—O(5)	91.6(3)	91.6(3)	94.9(4)
O(1M)—M(1)—N(1)	174.7(3)	175.1(3)	177.4(5)
O(1M)—M(1)—N(2)	103.4(3)	103.8(3)	99.9(5)
O(1)—M(1)—O(3)	94.6(4)	93.9(4)	91.7(5)
O(1)—M(1)—O(5)	170.0(4)	170.6(4)	167.2(5)
O(1)—M(1)—N(1)	89.6(4)	89.5(4)	80.5(5)
O(1)—M(1)—N(2)	90.6(4)	91.2(4)	90.5(5)
O(3)—M(1)—O(5)	92.2(3)	92.3(3)	86.6(4)
O(3)—M(1)—N(1)	89.8(4)	89.8(4)	93.4(5)
O(3)—M(1)—N(2)	164.6(4)	164.4(4)	170.9(5)
O(5)—M(1)—N(1)	83.1(3)	83.5(3)	86.9(5)
O(5)—M(1)—N(2)	81.1(3)	80.9(3)	89.3(5)
N(1)—M(1)—N(2)	75.8(4)	75.5(3)	78.3(5)
O(1M)—Co(3)—O(6)	119.6(4)	119.1(3)	119.4(5)
O(1M)—Co(3)—O(8)	119.5(4)	119.1(3)	118.4(4)
O(1M)—Co(3)—O(9)	100.5(3)	100.7(3)	103.7(4)
O(6)—Co(3)—O(8)	99.0(4)	99.1(4)	101.8(5)
O(6)—Co(3)—O(9)	109.7(4)	109.7(4)	108.0(5)
O(8)—Co(3)—O(9)	108.2(4)	108.9(4)	104.5(5)
M(1)—O(1M)—M(2)	114.5(3)	114.9(3)	113.7(5)
M(1)—O(1M)—Co(3)	109.6(3)	109.5(3)	107.8(5)
M(2)—O(1M)—Co(3)	110.5(3)	110.3(3)	109.2(5)

* Since the M(1) and M(2) atoms in the structures of **6** and **8** are chemically equivalent, only the bond lengths and bond angles involving M(1) are given.

system consisting of three cobalt atoms, we synthesized the homometallic cluster $Co_3(bpy)_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(\eta^1\text{-}OOCBu^t)$ (**8**) with the triangular metal core. Compound **8** was prepared in two ways: by the reaction of bipyridine with $Co_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(HOEt)_6$ (MeCN, 50 °C, the reagent ratio was 2 : 1) and by the reaction of bpy with $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCBu^t)_{12}$ (MeCN or benzene, 60—80 °C, the reagent ratio was 4 : 1) (Scheme 3). In both cases, complex **8** was isolated in approximately equal yields (~70%).

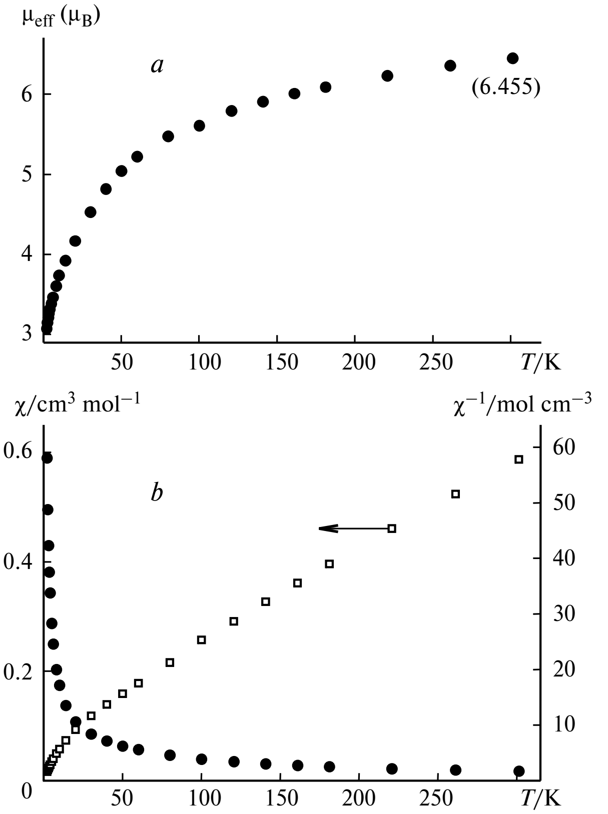
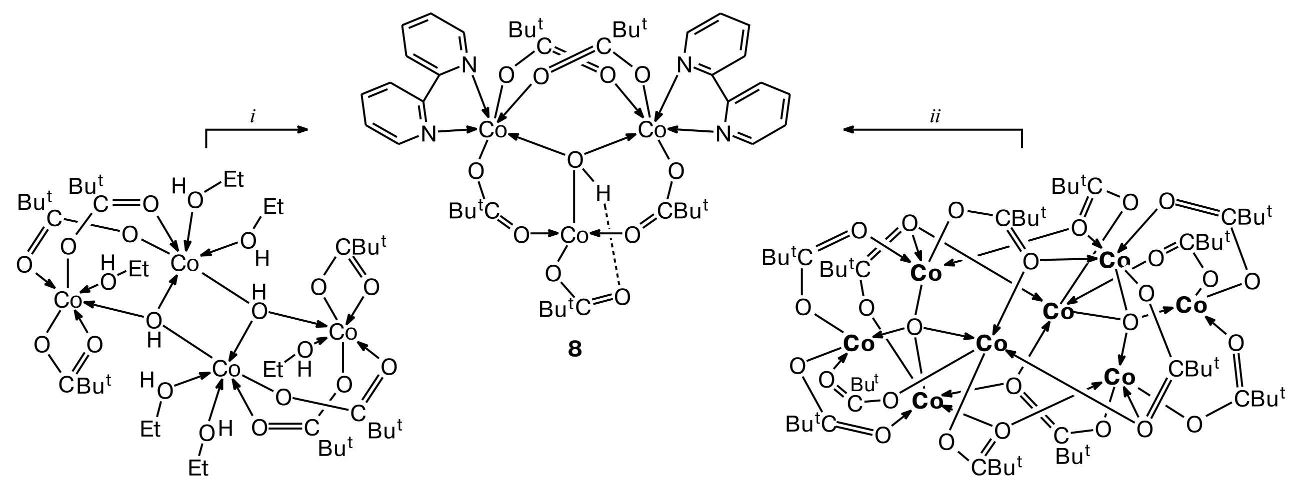


Fig. 2. Magnetic properties of heteronuclear compound **6**: the plots of the effective magnetic moment (*a*) and the magnetic susceptibility (*b*) *vs.* the temperature.

X-ray diffraction study of the crystals of solvate **8**·MeCN and unsolvated complex **8** demonstrated that the molecular structure of cluster **6** is identical to that of **8** (see Fig. 1, Table 1). The clusters of both compounds contain the $Co_3(\mu\text{-}OH)$ core with the nonbonded metal atoms (for example, Co(1)...Co(2), Co(1)...Co(3), and Co(2)...Co(3) in the solvate are 3.521(1), 3.317(1), and 3.342(1) Å, respectively, and these distances in the unsolvated complex are 3.456(1), 3.267(1), and 3.261(1) Å, respectively). In cluster **8**, two Co(bpy) fragments are additionally linked by two carboxylate bridges (Co—O are 2.03(1)—2.09(1) Å and 2.01(1)—2.04(1) Å in the solvate and the unsolvated complex, respectively), and the third tetrahedrally coordinated cobalt atom is linked to the first two atoms by the carboxylate bridges (in molecule **8**·MeCN, Co(3)—O, Co(1)—O, and Co(2)—O are 1.987(8)—1.988(1), 2.135(7), and 2.196(8) Å, respectively; in molecule **8**, these distances are 1.94(1)—1.98(1), 2.09(1), and 2.09(1) Å, respectively) and the bridging oxygen atom of the hydroxy group (Co—O is 2.197(6) and 1.96(1) Å in molecules **8**·MeCN and **8**, respectively). As in complex **6**, the terminal carboxylate group coordinated to the Co(3) atom is linked to the hydroxy group through a hydrogen bond (O—H...O is 1.80(5) Å and 2.09(5) Å in the solvate and the unsolvated complex, respectively). The magnetic properties of the crystals of the solvate are virtually identical to those of the crystals of unsolvated complex **8** but differ from those of **6**·MeCN

Scheme 3



Reagents and conditions: *i*. MeCN, 50 °C, {Co_4} : bpy = 1 : 2; *ii*. MeCN or C_6H_6, {Co_8} : bpy = 1 : 4.

in the values of μ_{eff}. Besides, the solvate and unsolvated complex **8** are characterized by the less flat temperature dependence of the effective magnetic moment compared to that observed for **6** · MeCN (Fig. 3).

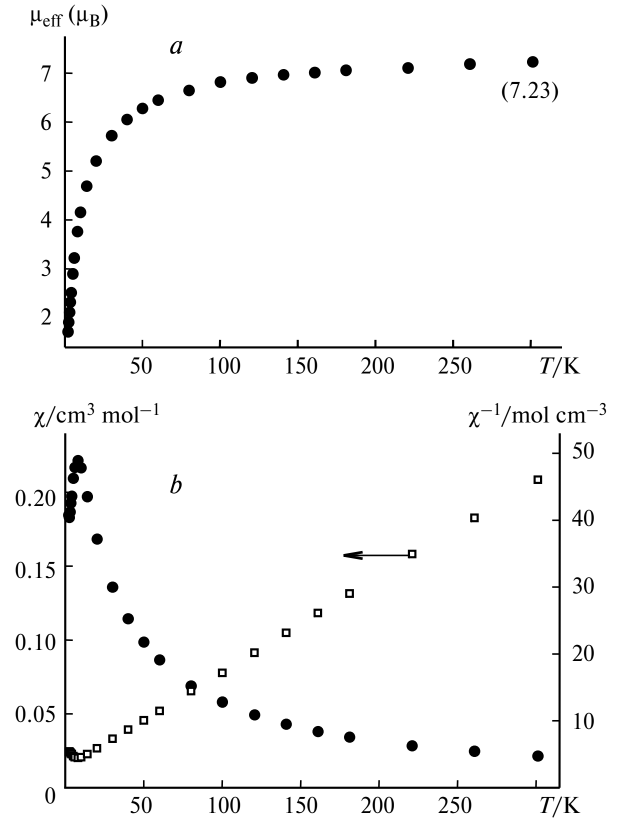
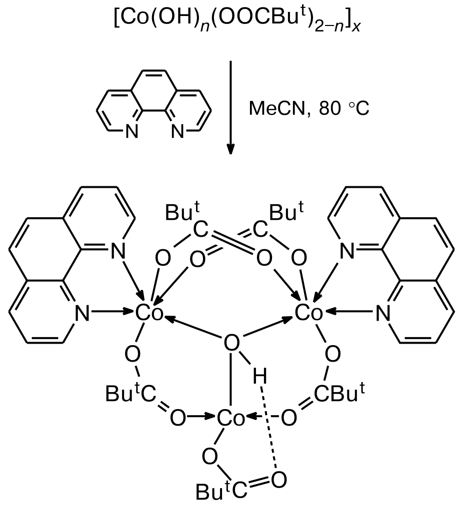


Fig. 3. Magnetic properties of complex **8**: the plots of the effective magnetic moment (*a*) and the magnetic susceptibility (*b*) *vs*. the temperature.

The upper limit of the effective magnetic moment of complex **8** per total molecular weight (7.23 μ_B at 300 K) is substantially higher than the analogous value found for compound **6**. This is consistent with an increase in the total spin of molecule **8** containing only cobalt(II) atoms ($S_1 = S_2 = S_3 = 3/2$; $\mu_{eff} = 6.71$ μ_B is the purely spin value without considering the spin-orbital contribution).

The trinuclear $Co_3L_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(\eta^1\text{-}OOCBu^t)$ structure of clusters **7** and **8** is, apparently, rather stable. The set of the LCo fragments can be expanded by using other chelate ligands, for example, 1,10-phenanthroline. The reaction of 1,10-phenanthroline as L with the $[Co(OH)_n(OOCBu^t)_{2-n}]_x$ polymer in acetonitrile at 80 °C afforded the trinuclear cluster

Scheme 4



9

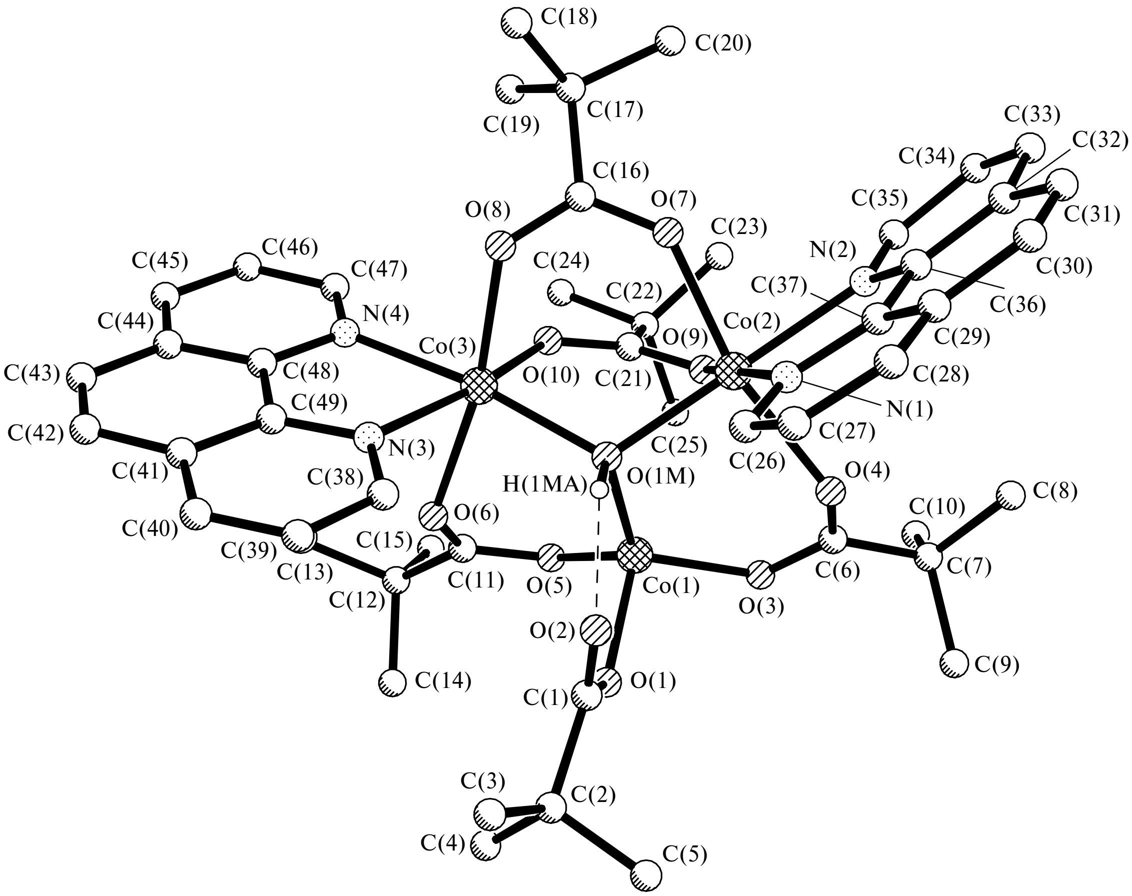


Fig. 4. Structure of the trinuclear complex $(phen)_2Co_3(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(OOCBu^t)$ (**9**).

$(phen)_2Co_3(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(OOCBu^t)$ (**9**), which is an analog of compounds **6**, **7**, and **8** (Scheme 4).

According to the results of X-ray diffraction analysis (Fig. 4, Table 2), complex **9** is structurally similar to other trinuclear cobalt-containing clusters of this type (**7** and **8**). In compound **9**, the distances between the metal atoms are nonbonded (Co(1)...Co(2), 3.457(1) Å; Co(1)...Co(3), 3.267(1) Å; Co(2)...Co(3) 3.261(1) Å). The *o*-phenanthroline molecules are bound in a chelate fashion to only two metal atoms, *viz.*, Co(1) and Co(2) (Co—N, 2.128(6)—2.185(6) Å). Both metal atoms are in an octahedral ligand environment and are linked to each other by two carboxylate groups (M—O, 2.061(5)—2.105(5) Å). The third metal atom is in a tetrahedral ligand environment and is linked to each of two other metal centers only through one carboxylate bridge (Co(1)—O, 1.976(5)—1.992(5) Å). In addition, the latter metal atom is coordinated by the terminal carboxylate group (Co(1)—O, 1.999(5) Å), which forms a strong hydrogen bond with the tridentate hydroxy bridge (O—H...O, 1.95(5) Å).

In conclusion, it should be noted that, unlike the reactions of polynuclear cobalt pivalates, the reactions of polynuclear nickel pivalates, the polymeric $[Ni(OH)_n(OOCBu^t)_{2-n}]_x$ complex, the nonanuclear complex $Ni_9(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_4\text{-}OOCBu^t)(\mu_3\text{-}OOCBu^t)_3(\mu\text{-}OOCBu^t)_8(HOOCBu^t)_4$, and the tetranuclear complex $Ni_4(EtOH)_6(\mu_3\text{-}OH)_2(\mu_2\text{-}OOCBu^t)_4(\eta^2\text{-}OOCBu^t)_2$ with 2,2´-bipyridine afford either the dinuclear complex $Ni_2(bpy)_2(OOCBu^t)_2(\mu\text{-}OOCBu^t)_2(\mu\text{-}OH_2)$[7], or the mononuclear complex $Ni(bpy)(OOCBu^t)_2$ [7,8] depending on the reagent ratio and reaction conditions. In none of the cases, was the trinuclear nickel complex, which is an analog of **7**, **8**, and **9**, formed.

Experimental

The complexes were synthesized in an inert atmosphere using anhydrous solvents. The starting $Co_2(bpy)_2(OOCBu^t)_4$ (**1**),[9] $Ni_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(EtOH)_6$ (**5**),[2] $Co_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(HOEt)_6$,[2,3] $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCBu^t)_{12}$,[2,3] and $[Co(OH)_n(OOCBu^t)_{2-n}]_x$ [8] complexes were prepared according to known procedures. The new compounds were synthesized using commercial 2,2´-bipyridine and 1,10-phenanthroline (Fluka). The IR spectra were recorded on a Specord M-80 instrument in KBr pellets. The static magnetic susceptibilities χ'_m were measured on a SQUID MPMS-5S Quantuim Design mag-

Table 2. Selected geometric characteristics of the trinuclear cluster $Co_3(phen)_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(\eta^1\text{-}OOCBu^t)$ (**9**)*

Bond	*d*/Å	Bond angle	ω/deg
Co(1)—O(1M)	2.013(4)	O(3)—Co(1)—O(1)	104.62(19)
Co(1)—O(1)	1.999(5)	O(5)—Co(1)—O(1)	103.7(2)
Co(1)—O(3)	1.992(5)	O(5)—Co(1)—O(3)	101.8(2)
Co(1)—O(5)	1.976(5)	O(1)—Co(1)—O(1M)	100.41(19)
Co(2)—O(4)	2.143(5)	O(3)—Co(1)—O(1M)	124.91(18)
Co(2)—O(7)	2.061(5)	O(5)—Co(1)—O(1M)	118.72(19)
Co(2)—O(9)	2.099(4)	O(7)—Co(2)—O(9)	90.69(18)
Co(2)—O(1M)	2.061(4)	O(7)—Co(2)—O(1M)	97.98(18)
Co(2)—N(1)	2.158(6)	O(1M)—Co(2)—O(4)	95.85(17)
Co(2)—N(2)	2.128(6)	O(1M)—Co(2)—O(9)	86.90(17)
		O(1M)—Co(2)—N(2)	175.87(19)
		O(7)—Co(2)—O(4)	165.60(18)
		O(9)—Co(2)—O(4)	86.06(18)
		O(7)—Co(2)—N(1)	93.34(19)
		O(7)—Co(2)—N(2)	81.3(2)
		O(9)—Co(2)—N(1)	173.5(2)
		O(9)—Co(2)—N(2)	97.2(2)
		O(4)—Co(2)—N(1)	88.79(19)
		N(2)—Co(2)—O(4)	85.18(19)
		N(2)—Co(2)—N(1)	78.4(2)
		O(1M)—Co(2)—N(1)	97.59(19)
		Co(1)—O(1M)—Co(2)	100.28(18)
		Co(2)—O(1M)—Co(3)	114.49(19)

* Since the Co(2) and Co(3) atoms in the structure of **9** are chemically equivalent, only the bond lengths and bond angles involving Co(2) are given.

netometer in the temperature range of 300—2 K. The effective magnetic moments were calculated by the equation[5,6]

$$\mu_{\text{eff}} = (8\chi'_{\text{m}}T)^{1/2}.$$

The elemental analyses for metal contents in the complexes were performed by inductively coupled plasma atomic emission spectrometry on an IRIS Advantage instrument.

Synthesis of the monosolvate of bis-bipyridine(μ_3-hydroxo)tetra-(μ_2-*O,O*′-trimethylacetato)-η^1-trimethylacetatonickel(II)cobalt(II) with acetonitrile, $Ni_{1.64}Co_{1.36}(bpy)_2(\mu_3\text{-}OH)(\mu_2\text{-}OOCBu^t)_4(OOCBu^t)\cdot MeCN$ (6 · MeCN). A pale-green solution of $Ni_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(EtOH)_6$ (0.5 g, 0.46 mmol) and $Co_2(bpy)_2(OOCBu^t)_4\cdot n$MeCN (*n* = 1—1.8) (0.39 g, 0.46 mmol) in *o*-xylene (20 mL) was kept at 80 °C until elimination of ethanol vapor ceased. Then the reaction solution was concentrated to 5 mL and cooled to ~20 °C, after which large blue crystals suitable for X-ray diffraction analysis precipitated. The crystals were isolated by decantation, washed with cold acetonitrile, and dried under a stream of argon. The yield of solvate **6** · MeCN was 0.42 g (85% with respect to the initial amount of $Co_2(bpy)_2(OOCBu^t)_4\cdot n$MeCN). Found (%): C, 53.80; H, 6.32; N, 6.43. $C_{47}H_{65}N_5M_3O_{11}$ (the atomic weight M was taken to be 58.81, which is the average of the atomic weights of Co (58.93) and Ni (58.69)). Calculated (%): C, 53.61; H, 6.18; N, 6.65. IR (KBr), ν/cm^{-1}: 3475 m, 3413 m, 2956 m, 2926 m, 2858 w, 1678 w, 1629 s, 1610 v.s, 1586 s, 1565 s, 1505 m, 1468 s, 1437 m, 1413 s, 1368 m, 1351 m, 1221 m, 1147 w, 1017 w, 937 w, 894 m, 789 w, 758 m, 628 m, 604 m, 511 w, 468 m.

Synthesis of bis-bipyridine(μ_3-hydroxo)tetra-(μ_2-*O,O*′-trimethylacetato)-η^1-trimethylacetatotricobalt(II), $Co_3(bpy)_2(\mu_3\text{-}OH)(\mu_2\text{-}O,O'\text{-}OOCBu^t)_4(OOCBu^t)$ (8). ***A.*** A solution of $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCBu^t)_{12}$ (0.5 g, 0.29 mmol) and 2,2′-bipyridine (0.18 g, 1.2 mmol) in benzene or acetonitrile (20 mL) was heated to 80 °C for 0.5 h, concentrated to 5 mL, and kept at +5 °C (in the case of benzene) or at –5 °C (in the case of acetonitrile). After 2—3 days, large violet crystals of complex **8** (solvate **8** · MeCN in the case of acetonitrile) suitable for X-ray diffraction analysis were obtained in both cases. The yield was 0.6 g (nearly 70% with respect to the initial amount of $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCBu^t)_{12}$). Found (%): C, 54.05; H, 6.78; N, 5.69. $C_{45}H_{62}N_4Co_3O_{11}$. Calculated (%): C, 53.41; H, 6.13; N, 5.54. IR (KBr), ν/cm^{-1}: 3448 m, 3416 m, 2960 s, 2920 m, 2864 m, 2360 m, 2336 m, 1680 w, 1592 v.s, 1565 s, 1480 s, 1440 m, 1416 s, 1376 m, 1360 m, 1264 w, 1224 m, 1152 w, 1096 m, 1079 m, 1032 m, 1016 m, 896 w, 800 m, 768 m, 736 w, 680 m, 608 s, 568 w, 552 m, 424 w.

***B.* Synthesis of the monosolvate of bis-bipyridine(μ_3-hydroxo)tetra(μ_2-*O,O*′-trimethylacetato)-η^1-trimethylacetatotricobalt(II) with acetonitrile, 8 · MeCN.** A mixture of $Co_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(HOEt)_6$ (1 g, 0.93 mmol) and 2,2′-bipyridine (0.29 g, 1.9 mmol) was dissolved in acetonitrile (15 mL). The red-brown solution was kept at 50 °C until elimination of ethanol vapor ceased, concentrated to 5 mL, and kept at +5 °C. After 48 h, large dark-red crystals of solvate **8** · MeCN suitable for X-ray diffraction analysis were obtained. The yield was 0.77 g (70% with respect to the initial amount of $Co_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(EtOH)_6$). Found (%): C, 53.63; H, 6.94; N, 6.66. $C_{47}H_{65}N_5Co_3O_{11}$. Calculated (%): C, 53.61; H, 6.18; N, 6.65. IR (KBr), ν/cm^{-1}: 3440 m, 3416 m, 2952 s, 2920 m, 2856 m, 1720 w, 1606 s, 1592 v.s, 1559 s, 1480 s, 1440 m, 1416 s, 1364 m, 1352 m, 1312 w, 1224 m, 1152 w, 1086 m, 1056 m, 1040 m, 1024 m, 896 w, 880 m, 792 m, 760 m, 736 w, 648 m, 608 s, 576 m, 456 w, 416 w.

Synthesis of bis(1,10-phenanthroline)(μ_3-hydroxo)tetra(μ_2-*O,O*′-trimethylacetato)-η^1-trimethylacetatotricobalt(II), $Co_3(phen)_2(\mu_3\text{-}OH)(\mu_2\text{-}O,O'\text{-}OOCBu^t)_4(OOCBu^t)$ (9). A mixture of the polymeric cobalt complex $[Co(OH)_n(OOCBu^t)_{2-n}]_x$ (0.70 g, 2.7 mmol with respect to the monomeric $[Co(OH)_{0.1}(OOCBu^t)_{1.9}]$ fragment) and 1,10-phenanthroline (0.54 g, 2.7 mmol) in acetonitrile (15 mL) was kept at 80 °C for 30 min. The violet solution was filtered, concentrated to 10 mL, and cooled to ~20 °C. The violet crystalline product that formed was recrystallized from benzene. The yield of solvate $\mathbf{9}\cdot 0.5C_6H_6$ was 0.35 g (27%). Found (%): C, 55.99; H 6.31; N, 5.01. $C_{52}H_{65}Co_3N_4O_{11}$. Calculated (%): C, 56.79; H, 5.92; N, 5.10. IR (KBr), ν/cm^{-1}: 3435 s, 3074 w, 3054 w, 2951 s, 2923 s, 2836 m, 1589 s, 1515 s, 1481 s, 1455 w, 1415 s, 1372 s, 1356 s, 1224 s, 1143 w, 1104 w, 1026 w, 935 w, 892 w, 881 w, 844 m, 790 m, 730 m, 639 m, 608 m, 570 w, 479 w, 420 w, 403 w.

X-ray diffraction study. The experimental data sets for complexes **6** · MeCN, **8**, **8** · MeCN, and $\mathbf{9}\cdot 0.5C_6H_6$ were collected on an automated Bruker AXS SMART diffractometer equipped with a CCD detector (graphite monochromator, 110 °C, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.[10] The semiempirical absorption correction was applied.[11] The crystallographic parameters and details of refinement of all structures are given in Table 3.

Table 3. Crystallographic parameters of complexes **6** · MeCN, **8**, **8** · MeCN, and **9** · 0.5C_6H_6

Parameter	**6** · MeCN	**8** · MeCN	**8**	**9** · 0.5C_6H_6
Molecular formula	$C_{47}H_{65}N_5M_3O_{11}$	$C_{47}H_{65}N_5Co_3O_{11}$	$C_{45}H_{62}N_4Co_3O_{11}$	$C_{52}H_{65}Co_3N_4O_{11}$
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/c$
a/Å	14.231(4)	14.329(3)	45.26(2)	11.584(8)
b/Å	19.517(6)	19.603(4)	10.767(5)	19.361(13)
c/Å	18.473(6)	18.571(4)	21.907(11)	25.177(18)
β/deg	90.040(13)	90.18(3)	110.65(1)	95.519(1)
V/Å^3	5131(3)	5217(2)	9990(8)	5621(7)
Z	4	4	8	4
ρ_{calc}/g cm^{-3}	1.362	1.340	1.345	1.299
μ/mm^{-1}	1.106	1.002	1.043	0.933
Radiation	Mo-Kα (λ = 0.71073 Å)			
Number of measured reflections	24663	24052	7937	8339
Number of reflections with $I > 2\sigma$	13936	11720	6170	4223
R_1	0.1233	0.1275	0.0761	0.0658
wR_2	0.2585	0.3045	0.1864	0.1193

The structures of all complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The hydrogen atoms in the molecules were located from difference electron density syntheses and refined isotropically with the common thermal parameter. The metal atoms in heteronuclear complex **6** were refined using both homo- (all positions are occupied by nickel atoms or all positions are occupied by cobalt atoms) and heteronuclear models. The best results were obtained for the heteronuclear Ni_2Co model. Calculations were carried out using the SHELX97 program package.[12] The selected geometric parameters of the complexes are given in Tables 1 and 2.

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References

1. I. G. Fomina, A. A. Sidorov, G. G. Aleksandrov, V. I. Zhilov, V. N. Ikorskii, V. M. Novotortsev, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 116 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 118].
2. A. A. Sidorov, I. G. Fomina, S. S. Talismanov, G. G. Aleksandrov, V. M. Novotortsev, S. E. Nefedov, and I. L. Eremenko, *Koord. Khim.,* 2001, **27**, 584 [*Russ. J. Coord. Chem.*, 2001, **27** (Engl. Transl.)].
3. A. A. Sidorov, I. G. Fomina, G. G. Aleksandrov, M. O. Ponina, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 960 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 958].
4. M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, M. O. Ponina, S. M. Deomidov, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1773 [*Russ. Chem. Bull.*, 1999, **48**, 1751 (Engl. Transl.)].
5. J. H. Van Vleck, *The Theory of Electronic and Magnetic Susceptibilities*, Oxford Univ. Press, London, 1932.
6. Yu. V. Rakitin and V. T. Kalinnikov, *Sovremennaya magnetokhimiya* [*Modern Magnetochemistry*], Nauka, St.-Petersburg, 1994 (in Russian).
7. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, M. A. Golubnichaya, P. V. Danilov, V. N. Ikorskii, Yu. G. Shvedenkov, V. M. Novotortsev, and I. I. Moiseev, *Inorg. Chem.*, 1999, **38**, 3764.
8. A. A. Sidorov, Dr. Sc. (Chem.) Thesis, N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, 2002 (in Russian).
9. M. O. Talismanova, A. A. Sidorov, V. M. Novotortsev, G. G. Aleksandrov, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2149 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2251].
10. *SMART (Control) and SAINT (Integration) Software, Version 5.0*, Bruker AXS Inc., Madison (WI), 1997.
11. G. M. Sheldrick, *SADABS, Program for Scanning and Correction of Area Detector Data*, Göttingen University, Götinngen (Germany), 1997.
12. G. M. Sheldrick, *SHELX97, Program for the Solution of Crystal Structures*, Göttingen University, Götinngen (Germany), 1997.

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