New polynuclear cobalt trimethylacetate complexes: synthesis and structure

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Extraction of polymer (1), formed in the reaction of $CoCl_2$ with $KOOCBu^t$, with boiling hexane gives crystals of hexamer $Co_6(\mu_3\text{-}OH)_2(OOCBu^t)_{10}(HOOCBu^t)_4$ (2). According to data of X-ray study, four Co^{II} atoms in the hexanuclear molecule 2 have an octahedral ligand environment and two Co^{II} atoms have a tetrahedral one. Dissolution of polymer 1 in EtOH results in its splitting into $Co_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(HOEt)_6$ tetramers (3). In molecule 3, two asymmetric dimeric $(\eta^2\text{-}OOCBu^t)(EtOH)Co(\mu\text{-}OOCBu^t)Co(HOEt)_2$ fragments are bound by two tridentate bridging OH groups.

Key words: cobalt trimethylacetates, polynuclear complexes, carboxylate ligands, synthesis, X-ray analysis.

Polynuclear transition-metal complexes with carboxylate bridging ligands often have unusual structures and possess unique chemical and physical (first of all, magnetic) properties.[1,2] In particular, trimethylacetate derivatives, which are highly volatile and readily soluble in organic solvents, can be of interest as initial compounds for preparing thin films (*e.g.*, oxide films) and immobilized catalysts. Particular attention is paid to these compounds because of structural analogies between some of their metal fragments and those of the active sites of natural enzymes.[3—13]

Recently, we have shown that the action of various amines on the nonanuclear hydroxocarboxylate $Ni_9(HOOCBu^t)_4(\mu_4\text{-}O)_3(\mu_3\text{-}OH)_3(\mu\text{-}OOCBu^t)_{12}$, which is readily obtained in 70—90% yields in the reaction of $NiCl_2 \cdot 6H_2O$ with potassium pivalate, results in various nickel(II) trimethylacetates whose structure and magnetic properties can be deliberately modified.[14]

In this context, the availability of the starting oligomeric cobalt complex and relatively easy "control" over reactions also were prerequisites to extending the approaches found to transformations of cobalt trimethylacetates. In this work, we report the results of our studies on the synthesis of the first hexa- and tetranuclear cobalt(II) trimethylacetates.

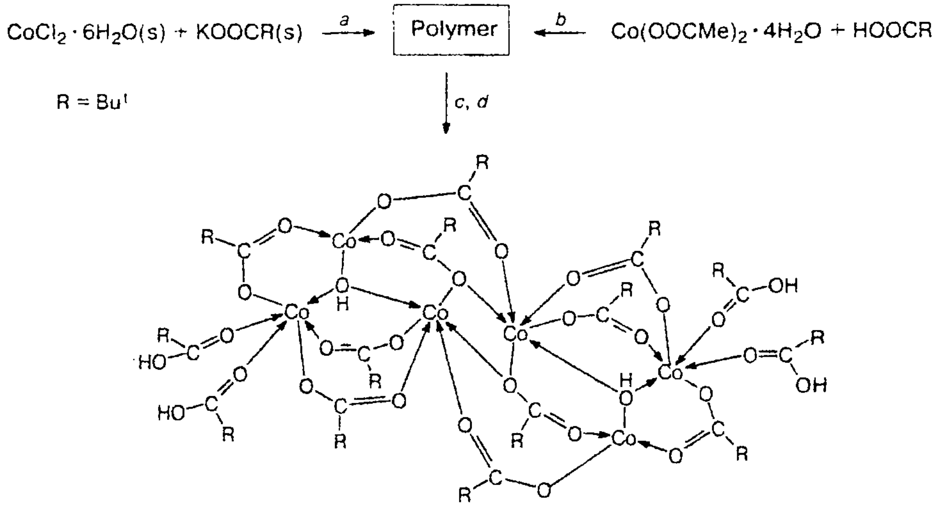
Results and Discussion

As we have found, grinding $CoCl_2 \cdot 6H_2O$ with 2 moles of potassium pivalate in an agate mortar, followed by addition of several drops of water in air and extraction with polar organic solvents, results in the formation of a red-violet polymeric mass of composition $[Co(OOCBu^t)_{2-x}(OH)_x]_n$ (1). The IR spectrum of polymer 1 contains several bands of symmetric (ν_s) and asymmetric (ν_{as}) vibrations of OCO groups in the region 1360—1670 cm^{-1}, which indicate the presence of bridging carboxylate fragments. Weak bands at 1710 cm^{-1} characteristic of terminal carboxylate groups and a weak sharp peak at 3540 cm^{-1}, which can be assigned to vibrations of OH groups, are also observed. Dissolution of this polymer in boiling hexane and subsequent slow evaporation of the red-violet solution obtained result in the crystalline complex $Co_6(\mu_3\text{-}OH)_2(OOCBu^t)_{10}(HOOCBu^t)_4$ (2, Scheme 1).

According to the data of X-ray study, six Co^{II} atoms in complex 2 (Fig. 1) are bound by tridentate bridging hydroxyl groups (Co(1)—O(1) 2.081(7) Å, Co(2)—O(1) 2.029(5) Å, Co(3)—O(1) 1.986(6) Å) to form two triangles. The Co(2) atom is coordinated by three oxygen atoms of three bridging carboxylate groups, two of which link it to the Co(1) atom (Co(1)....Co(2) 3.398(1) Å, Co(1)—O 2.064(6) and 2.048(7) Å, and Co(2)—O 2.025(8) and 2.109(9) Å). The third carboxylate group links the Co(2) atom to the Co(3) atom (Co(2)...Co(3) 3.357(1) Å, Co(2)—O 2.035(9) Å, and Co(3)—O 1.963(7) Å). In this case the octahedral environment of the Co(2) atom is completed with additional bonding to the oxygen atoms of two terminal molecules of pivalic acid (Co(2)—O 2.18(1) and 2.145(7) Å) and a bridging hydroxyl group. The third metal atom in the triangle, Co(3), has a tetrahedral environment. Besides the two mentioned oxygen atoms belonging to hydroxyl and $OOCBu^t$ bridges, two remaining coordination sites of the Co(3) atom are occupied by the bridging car-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1773—1778, September, 1999.

Scheme 1



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Reagents and conditions: *a.* Grinding in a mortar, 2—3 drops of H_2O, extraction with CH_2Cl_2. *b.* Alloying at 165 °C. *c.* For *a*, extraction with boiling hexane (in 82% yield). *d.* For *b*, extraction with THF, recrystallization from hexane (in 5% yield).

boxylate group, which links it to the Co(1A) atom of another triangle (Co(3)....Co(1A) 3.895 (1) Å, Co(3)—O 1.964(11) Å), and by the oxygen atom of one more pivalate ligand, which is a tridentate bridging ligand in the Co(1)Co(3)Co(1A) triangle (Co(1)...Co(3) 3.433(2) Å, Co(3)—O(9) 1.969(7) Å) owing to the bridging position of the O(8) atom between the Co(1) and Co(1A) atoms (Co(1)....Co(1A) 3.375(2) Å, Co(1)—O(8) 2.190(6) Å, and Co(1A)—O(8) 2.247(8) Å). It is these two pivalate ligands that, in fact, "assemble" two triangular Co_3 fragments into a hexamer.

It should also be noted that in complex **2** the Co—O distances for the Co(3) atom in the tetrahedral environment appear to be about 0.2 Å shorter than analogous

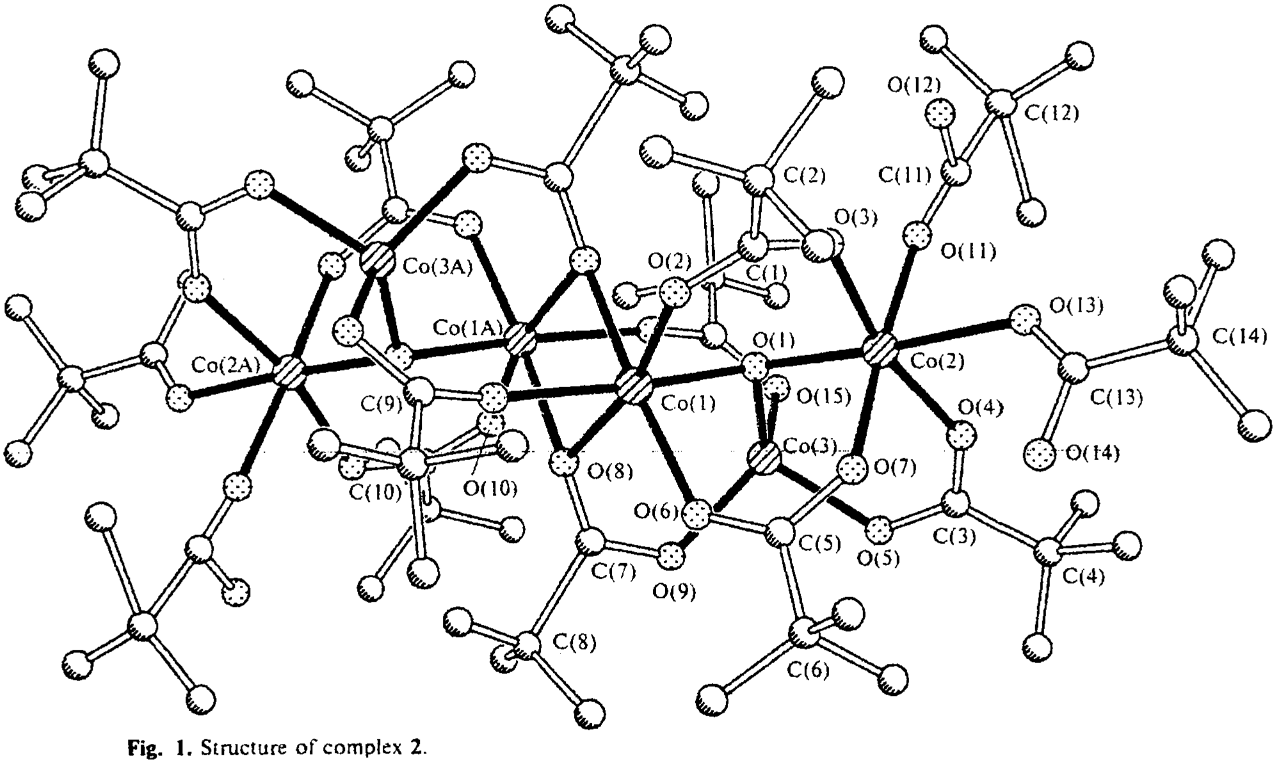


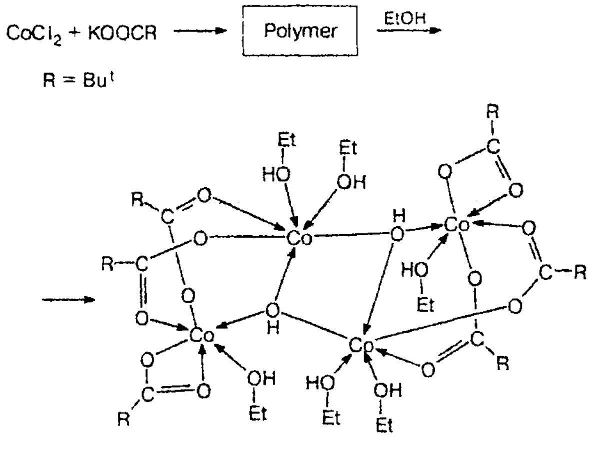
Fig. 1. Structure of complex 2.

distances for Co(1) and Co(2) atoms, which have the octahedral environment.

The reaction of cobalt acetate, $Co(OOCMe)_2 \cdot 4H_2O$, with pivalic acid (at 165 °C, see Scheme 1, route *b*) also results in the formation of a polymer. However, the substance synthesized following this known procedure[15] is virtually insoluble in hydrocarbons, poorly soluble in CH_2Cl_2, and can be dissolved only in THF. The IR spectrum of this compound also contains bands of stretching vibrations of bridging OCO groups (at 1422—1600 cm^{-1}), terminal trimethylacetate fragments (at 1670 cm^{-1}), and an OH group (at 3570 cm^{-1}). Despite the fact that the spectrum of this polymer differs in positions and intensities of the characteristic bands of functional groups, which indicates a difference in the polymer structures, complex **2** is also obtained (though in 5% yield) after removal of polar solvents and recrystallization of the solid residue from hexane. It is believed that in both cases the polymers formed consist mainly of differently bound triangular $Co_3(\mu_3\text{-}OH)$ fragments. Transformation of the polymers into a soluble form is likely determined by the amount of free trimethylacetic acid coordinated to terminal cobalt atoms in a leaving oligomer (four coordinated molecules of pivalic acid are available in the hexamer). The above-mentioned structural motifs and elements were also observed in nickel trimethylacetates; however, a nonanuclear complex, in which three $Ni_3(\mu_3\text{-}OH)$ triangles can be distinguished and terminal nickel atoms also are bonded to four $HOOCBu^t$ molecules, appeared to be the most stable in this case.[16]

If ethanol is used for polymer destruction, most of the polymer goes into solution, which can be slowly concentrated to give red crystals of complex $Co_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(HOEt)_6$ (**3**, Scheme 2) in 15% yield.

Scheme 2



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According to the data of X-ray study, two dimeric fragments, $(\eta^2\text{-}OOCBu^t)(EtOH)Co(\mu\text{-}OOCBu^t)_2Co(EtOH)_2$ (Co...Co 3.325(1) Å) in complex **3** (Fig. 2) are bound by two tridentate bridging hydroxyl groups (Co...Co 3.752(2) Å, Co(1)—O(7) 2.035(3) Å, Co(2)—O(7) 2.068(3) Å, and Co(2A)—O(7) 2.109(3) Å). In each of the dimeric fragments, one Co atom is bound to one EtOH molecule (Co—O 2.145(3) Å) and the η^2-carboxylate group (Co—O 2.157(3) and 2.234(3) Å), while the other Co atom is bound to two ethanol molecules (Co—O 2.105(3)—2.163(3) Å). Eventually, taking into account two bridging carboxylate ligands, each cobalt atom in the dimeric fragment appears to have an octahedral environment (Co—O 2.028(3)—2.099(3) Å). It should be noted that this structure is also formed by two $Co_3(\mu_3\text{-}OH)$ triangles sharing an edge. The coordinated alcohol molecules in complex **3** are weakly bound to metal centers and are readily removed in the absence of solvent traces, which results in the destruction of crystals, formation of a new polymeric form, and, as a result, in the loss of solubility in organic solvents.

Thus, our studies showed that polynuclear cobalt(II) trimethylacetates have a common stable fragment, the $Co_3(\mu_3\text{-}OH)(\mu\text{-}OOCBu^t)_n$ triangle, which is analogous to the case found in similar nickel(II) trimethylacetates.[14] This makes it possible to use new cobalt(II) compounds for targeted assembly of dinuclear trimethylacetates containing $Co_2(\mu\text{-}OOCR)_2(\mu\text{-}OH_2)$ and $Co_2(\mu\text{-}OOCR)_4$ fragments by applying principles and procedures developed for Ni-containing complexes.

Experimental

All operations associated with the synthesis of new complexes were performed both in air and (if necessary) in an inert atmosphere using dehydrated solvents. The IR spectra of the compounds were recorded on a Specord M-82 instrument.

Complex $[Co(OOCBu^t)_{2-x}(OH)_x]_n$ (1). *A* (see Scheme 1, route *a*). $CoCl_2 \cdot 6H_2O$ (2.5 g, 10.5 mmol), moistened with 2 drops of H_2O, and $KOOCBu^t$ (2.79 g, 19.9 mmol) were ground in an agate mortar. The violet mass thus obtained was extracted with CH_2Cl_2 and dried *in vacuo* on heating to give a red-violet powder. IR (KBr), ν/cm^{-1}: 425 m, 546 s, 612 s, 720 w, 796 s, 870 s, 1030 w, 1225 s, 1220 s, 1365 s, 1360 s, 1404 s, 1448 s, 1478 s, 1600 m, 1670 m, 1710 w, 3560 w, br.

B (see Scheme 1, route *b*).[15] The reaction mixture consisting of $Co(OOCMe)_2 \cdot 4H_2O$ (3 g, 5.18 mmol) and a large excess pivalic acid (15 mL) was heated for 2 h at 160—165 °C until a homogeneous red-violet mass was formed. The excess acid was washed off with hexane and the red-violet crystalline product obtained was dried *in vacuo* for 1 h at ~20 °C. Found (%): C, 45.1; H, 6.9. Calculated at $x = 0.1$ (%): C, 45.13; H, 6.81. IR (Nujol), ν/cm^{-1}: 460 m, 580 m, 610 m, 720 w, 792 m, 892 w, 1030 w, 1108 w, 1225 s, 1362 s, 1376 s, 1422 vs, 1460 vs, 1480 vs, 1520 vs, 1550 m, 1600 vs, 1670 w, 3560 w.

Bis(μ_3-hydroxo)bis(μ_3-pivalato-*O,O,O'*)octakis(μ_2-pivalato-*O,O'*)tetrakis(η^1-pivalic acid) hexacobalt(II), $Co_6(\mu_3\text{-}OH)_2(OOCBu^t)_{10}(HOOCBu^t)_4$ (2). *A* (see Scheme 1, route *c*). Polymer **1** (1 g) obtained following route *a* (see Scheme 1)

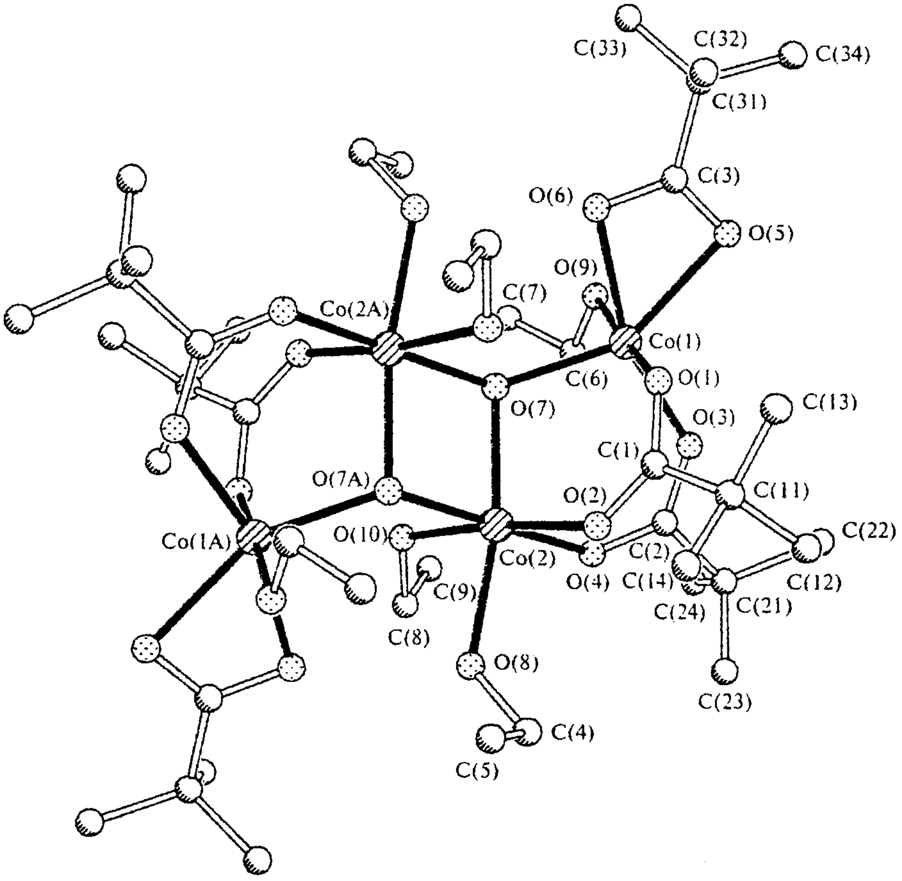

Fig. 2. Structure of complex 3.

was extracted with 50 mL of boiling hexane. A red-violet solution that formed was filtered to remove a blue precipitate and kept at room temperature in air for 2 days. Large red-violet crystals of complex **2** precipitated in the course of solvent

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **2**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Co(1)—O(1)	2.081(7)	O(2)—C(1)	1.23(1)	Co(1)—O(2)	2.064(6)	O(3)—C(1)	1.27(2)
Co(1)—O(6)	2.048(7)	O(4)—C(3)	1.23(1)	Co(1)—O(8)	2.190(6)	O(5)—C(3)	1.25(1)
Co(1)—O(10)	2.05(1)	O(6)—C(5)	1.24(1)	Co(1)—O(8A)	2.247(8)	O(7)—C(5)	1.28(1)
Co(2)—O(1)	2.029(5)	O(8)—C(7)	1.27(1)	Co(2)—O(3)	2.025(8)	O(8)—Co(1A)	2.247(8)
Co(2)—O(4)	2.035(9)	O(9)—C(7)	1.26(2)	Co(2)—O(7)	2.109(9)	O(10)—C(9)	1.21(2)
Co(2)—O(11)	2.12(1)	O(11)—C(11)	1.04(2)	Co(2)—O(13)	2.145(7)	O(12)—C(11)	1.60(3)
Co(3)—O(1)	1.986(6)	O(13)—C(13)	1.19(2)	Co(3)—O(5)	1.963(7)	O(14)—C(13)	1.30(2)
Co(3)—O(9)	1.969(7)	O(15)—C(9A)	1.27(1)	Co(3)—O(15)	1.96(1)		
Angle	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**
O(1)—Co(1)—O(2)	99.4(3)	O(4)—Co(2)—O(7)	91.6(4)	O(1)—Co(1)—O(6)	90.0(3)	O(1)—Co(2)—O(11)	90.2(3)
O(2)—Co(1)—O(6)	96.6(3)	O(3)—Co(2)—O(11)	86.5(4)	O(1)—Co(1)—O(8)	88.9(3)	O(4)—Co(2)—O(11)	87.8(5)
O(2)—Co(1)—O(8)	167.9(2)	O(7)—Co(2)—O(11)	175.9(3)	O(6)—Co(1)—O(8)	92.3(3)	O(1)—Co(2)—O(13)	175.9(3)
O(1)—Co(1)—O(10)	169.2(3)	O(3)—Co(2)—O(13)	83.4(3)	O(2)—Co(1)—O(10)	87.1(3)	O(4)—Co(2)—O(13)	83.8(3)
O(6)—Co(1)—O(10)	98.0(3)	O(7)—Co(2)—O(13)	89.9(3)	O(8)—Co(1)—O(10)	83.5(3)	O(11)—Co(2)—O(13)	86.0(3)
O(1)—Co(1)—O(8A)	79.7(3)	O(1)—Co(3)—O(5)	111.1(3)	O(2)—Co(1)—O(8A)	91.7(3)	O(1)—Co(3)—O(9)	112.9(3)
O(6)—Co(1)—O(8A)	167.7(3)	O(5)—Co(3)—O(9)	101.3(3)	O(8)—Co(1)—O(8A)	81.0(3)	O(1)—Co(3)—O(15)	108.1(3)
O(10)—Co(1)—O(8A)	91.5(3)	O(5)—Co(3)—O(15)	104.4(4)	O(1)—Co(2)—O(3)	94.8(3)	O(9)—Co(3)—O(15)	118.4(3)
O(1)—Co(2)—O(4)	97.7(3)	Co(1)—O(1)—Co(2)	111.5(3)	O(3)—Co(2)—O(4)	166.2(3)	Co(1)—O(1)—Co(3)	115.2(3)
O(1)—Co(2)—O(7)	93.9(3)	Co(2)—O(1)—Co(3)	113.5(3)	O(3)—Co(2)—O(7)	93.3(4)		

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Co(1)—O(1)	2.086(3)	O(1)—C(1)	1.267(5)	Co(1)—O(6)	2.157(3)	O(4)—C(2)	1.255(6)
Co(1)—O(5)	2.234(3)	O(3)—C(2)	1.259(5)	Co(1)—O(9)	2.145(4)	O(6)—C(3)	1.280(5)
Co(1)—O(7)	2.035(3)	O(5)—C(3)	1.259(6)	Co(2)—O(4)	2.028(3)	O(8)—C(4)	1.436(7)
Co(2)—O(2)	2.099(3)	O(7)—Co(2A)	2.109(3)	Co(2)--O(8)	2.105(3)	O(10)—C(8)	1.447(6)
Co(2)—O(7)	2.068(3)	O(9)—C(6)	1.435(7)	Co(2)—O(7A)	2.109(3)		
Co(2)—O(10)	2.163(3)	Co(1)—O(3)	2.033(4)	O(2)—C(1)	1.253(5)		
Angle	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**
O(1)—Co(1)—O(3)	92.1(1)	O(2)—Co(2)—O(7)	97.7(1)	O(1)—Co(1)—O(6)	86.6(1)	O(4)—Co(2)—O(8)	90.1(1)
O(3)—Co(1)—O(5)	101.5(1)	O(2)—Co(2)—O(8)	89.9(1)	O(5)—Co(1)—O(6)	59.9(1)	O(2)—Co(2)—O(10)	174.2(1)
O(3)—Co(1)—O(6)	161.2(1)	O(7)—Co(2)—O(8)	169.5(1)	O(3)—Co(1)—O(7)	105.4(1)	O(7)—Co(2)—O(10)	88.0(1)
O(1)—Co(1)—O(7)	92.7(1)	O(4)—Co(2)—O(10)	87.4(1)	O(6)—Co(1)—O(7)	93.3(1)	O(2)—Co(2)—O(7A)	91.1(1)
O(5)—Co(1)—O(7)	152.6(1)	O(8)—Co(2)—O(10)	84.5(1)	O(3)—Co(1)—O(9)	91.0(1)	O(7)—Co(2)—O(7A)	82.0(1)
O(1)—Co(1)—O(9)	176.1(1)	O(4)—Co(2)—O(7A)	177.7(1)	O(6)—Co(1)—O(9)	89.7(1)	O(10)—Co(2)—O(7A)	90.5(1)
O(5)—Co(1)—O(9)	85.7(1)	O(8)—Co(2)—O(7A)	90.7(1)	O(2)—Co(2)—O(4)	91.1(1)		
O(7)—Co(1)—O(9)	88.8(1)	O(1)—Co(1)—O(5)	91.3(1)	O(4)—Co(2)—O(7)	96.9(1)		

evaporation. The yield was 0.88 g (82%). Found (%): C, 46.9; H, 7.5. $C_{50}H_{131}Co_6O_{29}$. Calculated (%): C, 46.51; H, 7.3. IR (KBr), ν/cm^{-1}: 538 m, 608 m, 782 m, 794 m, 860 m, 890 w, 930 w, 1022 w, 1210 m, 1320 m, 1416 m, 1480 m, 1544 s, 1564 m, 1594 m, 1670 s, 2840 w, 2890 w, 2906 w, 2940 w.

B (see Scheme 1, route *d*). Polymer **1** (2 g) obtained following route *b* (see Scheme 1) was extracted with 50 mL of THF. A red-violet solution that formed was evaporated to dryness *in vacuo* and dissolved in 50 mL of hot hexane. The red-violet solution thus obtained was filtered to remove a blue precipitate and kept at room temperature in air. Large violet crystals of complex **2** precipitated in the course of solvent evaporation. The yield was 0.1 g (5%). Found (%): C, 46.8; H, 7.7. $C_{50}H_{131}Co_6O_{29}$. Calculated (%): C, 46.58; H, 7.21. IR (KBr), ν/cm^{-1}: 538 m, 608 m, 782 m, 794 m, 860 m, 890 w, 930 w, 1022 w, 1210 m, 1320 m, 1416 m, 1480 m, 1544 s, 1564 m, 1594 m, 1670 s, 2840 w, 2890 w, 2906 w, 2940 w.

Bis(μ_3-hydroxo)tetrakis(μ_2-pivalato-*O*,*O'*)bis(η^2-pivalato)hexakis(η^1-ethanol)dicobalt(II), $Co_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(HOEt)_6$ (3). Polymer **1** (1.5 g) obtained following route *a* (see Scheme 1) was extracted with 50 mL of EtOH. The red solution that formed was filtered to remove a rose-colored precipitate and kept at room temperature in air for 7 days. Large red crystals of complex **3** · 2EtOH precipitated in the course of solvent evaporation. The yield was 0.23 g (15%). Found (%): C, 44.3; H, 8.2. $C_{46}H_{104}Co_4O_{22}$. Calculated (%): C, 43.77; H, 7.99. IR (fluorinated Nujol), ν/cm^{-1}: 1406 s, 1456 w, 1480 s, 1546 s, 1565 s, 1600 vs, 1674 s, 2884 w, 2900 m, 2932 s, 3200 w, br.

X-ray study of complexes 2 and 3. Experimental sets of reflections for complexes under investigation were obtained on a four-circle automatic Siemens R3v/m diffractometer (λ(Mo-Kα), λ = 0.71074 Å, at $T = 22$ °C for **2** and at $T = -120$ °C for **3**). The unit cell parameters were determined and refined using 24 equivalent reflections with $2\theta < 24$—28°. Three strong reflections with $0° < \chi < 65°$ were measured as references for each 100 reflections. No changes in the intensities of these reflections were observed for complexes **2** and **3**; therefore no special corrections were introduced in these cases.

The structures of complexes **2** and **3** · 2EtOH were solved by direct methods and refined anisotropically in the full-matrix approximation for all non-hydrogen atoms. Hydrogen atoms of *tert*-butyl substituents and EtOH (for **3**) were found geometrically and refined using the "riding" model. Protons of bridging hydroxyl groups in complexes **2** and **3** were localized from a difference Fourier synthesis and refined isotropically. A disorder of *tert*-butyl substituents in pivalate fragments of complex **3** is observed; in this case the population factors of alternative positions of atoms are close to 0.5. Calculations were performed using the SHELXTL PLUS program package (PC version).[17] The main geometric parameters of the complexes are listed in Tables 1 and 2; selected crystallographic param-

Table 3. Crystallographic parameters and conditions of X-ray study for complexes **2** and **3**

Parameter	**2**	**3** · 2EtOH
Molecular formula	$C_{70}H_{132}Co_6O_{30}$	$C_{46}H_{104}Co_4O_{22}$
Space group	$P\bar{1}$	$P2_1/n$
a/Å	13.524(2)	12.578(3)
b/Å	13.849(3)	13.913(2)
c/Å	14.427(4)	18.562(4)
α/deg	67.87(2)	90
β/deg	82.62(2)	93.73(2)
γ/deg	75.70(2)	90
V/Å^3	2423.5(1)	3241.5(2)
Z	1	2
d_{calc}/g cm^{-3}	1.120	1.702
μ/cm^{-3}	10.59	10.99
θ-2θ scanning range/deg	2—56	2—54
Number of measured reflections	8540	7179
Number of reflections with $I > 4.0\sigma$	4883	5461
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.155866F^2$	$w^{-1} = \sigma^2(F) + 0.002529F^2$
R	0.090	0.067
R_w	0.098	0.080

eters and details of the refinement of the structures are listed in Table 3.

The X-ray study was carried out in the X-ray Structural Center (at the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-15-97577, 96-15-96994, and 99-03-32805).

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Received March 25, 1999