Brief Communications

Synthesis and structure of new polynuclear cobalt(II) complexes with 3,5-di-*tert*-butylbenzoic acid anions*

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Trinuclear complex $Co_3(O_2CR)_6(EtOH)_2$ (**1**) crystals were obtained in good yield (75%) by the exchange reaction between cobalt(II) chloride and potassium 3,5-di-*tert*-butylbenzoate (KO_2CR) in EtOH. Complex **1** undergoes hydrolysis during recrystallization from non-anhydrous benzene to form the hexanuclear hydroxocarboxylate complex $Co_6(OH)_2(O_2CR)_{10}(HO_2CR)_4$ (**2**).

Key words: cobalt(II), 3,5-di-*tert*-butylbenzoic acid, polynuclear complexes, X-ray diffraction analysis.

Polymeric cobalt(II) pivalate $[Co(Piv)_2]_n$, having the structure of coordination 1D-polymer,[1] was shown to be able to quantitatively transform to homo- and heterometal complexes of various structure in the reactions with N-donor ligands.[2—10] Such reactions can proceed in very different solvents, including EtOH. However, upon dissolution of $[Co(Piv)_2]_n$ in ethanol (96%), though the crystallization of the tetranuclear complex $Co_4(OH)_2(Piv)_6(EtOH)_6$ occurs[2], the greater part of the polymer is transformed to the poorly soluble amorphous hydrolysis products.

The cobalt(II) compounds with 3,5-di-*tert*-butylbenzoic acid anions considered below are formed in >50% yields without the loss of the metal as insoluble hydrolysis products. The results obtained are important for understanding of possible reaction pathways in the reaction of polymeric carboxylates of general formula $\{M(O_2CR)_2\}_n$ with molecules of different solvents and O-donor ligands.

As to their chemical properties, such compounds are a convenient source of cobalt-carboxylate fragments, that, depending on the nature of different organic ligands, makes it possible to construct polynuclear cobalt-containing molecules of various structure.[3—11] The bulky *tert*-butyl fragments in substituents at the carboxy group, undoubtedly, play a key role, protecting the metal core from undesirable hydrolysis of the reaction products. At the same time, they considerably increase solubility of new compounds, that allows one to easily handle organic solutions, including processes of growing single crystals of target compounds necessary for the high-quality physicochemical studies. In particular, 3,5-di-*tert*-butylbenzoic acid contains two

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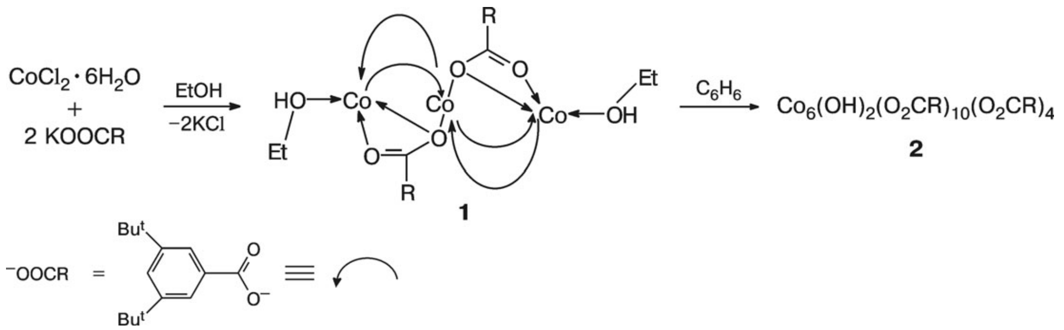
Scheme 1



tert-butyl groups, which are quite remote from the carboxylate fragment. The metal complexes based on such anion should possess good solubility in organic solvents.

In the present work, we consider approaches to the synthesis of polynuclear cobalt-containing molecules through the chemical self-assembling in ethanol and the building-up the complex metal core in nonpolar benzene.

The exchange reaction of $CoCl_2 \cdot 6H_2O$ and potassium 3,5-di-*tert*-butylbenzoate (KO_2CR, obtained by the reaction of 3,5-di-*tert*-butylbenzoic acid with KOH) in EtOH at room temperature was found to form a bluish violet solution, from which the trinuclear complex $Co_3(O_2CR)_6(EtOH)_2$ (**1**, R = 3,5-$(Me_3C)_2C_6H_3$) was isolated as violet crystals in 75% yield (Scheme 1).

Compound **1** has the linear structure, the central Co(1) atom is placed in the inversion center. The cobalt(II) atoms (Co(1)···Co(2) 3.499(1) Å) are bound between each other by four bridged (Co(1)—O 2.0251(17), 2.0890(18) Å, Co(2)—O 1.9309(17), 1.979(2) Å) and two chelate-bridged (Co(1)—O 2.1115(17) Å, Co(2)—O 2.004(2), 2.2713(19) Å) 3,5-di-*tert*-butylbenzoate anions (Fig. 1). The central atom Co(1) is in the distorted octahedral surrounding of six O atoms from six carboxylate anions. The surrounding of the terminal Co(2) atoms (four O atoms from one chelate-bridged, two from bridged carboxylate anions, and one O atom from the EtOH molecule (Co(2)—O 2.0395(18) Å)) corresponds to the distorted trigonal bipyramid, $\tau = 0.23$.[12] The hydrogen atom of the EtOH molecule forms the intermolecular H-bond with the O atom of the bridged carboxylate group of the neighboring complex molecule (O(7)···O(5B) 2.710(3) Å, H···O(5B) 1.84(1) Å, the angle O(7)—H—O(5B) 154.4(1)°), forming a chain parallel to the axis *a*.

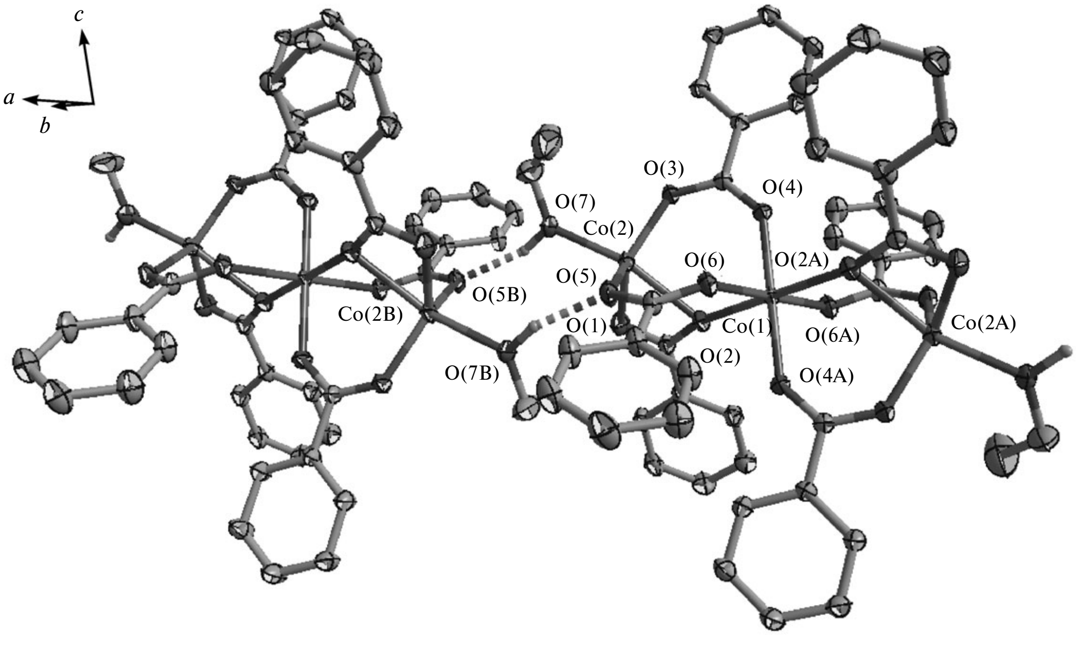


Fig. 1. Fragment of complex **1** crystal packing (*tert*-butyl substituents of 3,5-di-*tert*-butylbenzoic acid anions and hydrogen atoms at carbon atoms are not shown, thermal ellipsoids are given with 30% probability).

Compound **1** is formally a structural analog of the known complexes $Co_3(O_2CR)_6(L)_2$ (R = Ph, L is the quinoline,[13] pyridine[14]), in which the metal chain structure is close to the linear. Nonetheless, the structure **1** considerably differs from the geometry of the heteronuclear complexes with cobalt(II) atoms and 4f-elements of general formulas $Co_2Ln(O_2CR)_7L_2$ and $Co_2Ln(O_2CR)_6(NO_3)L_2$ with a monodentate L, in which the angle Co—Ln—Co of the metal framework is considerably smaller 180° and lie within 133.7—152.4° (see Refs 6 and 15—21). The reason for this is the presence of an additional chelate-coordinated carboxylate or nitrate group bonded with the f-metal to attain coordination number equal to 8.

Linear complex **1** contains an apical labile ligand EtOH capable of easy elimination upon mild heating. This type complexes with the transition element atoms containing a monodentate O-donor neutral ligand are few.[22—24] Supposedly, the formation of compound **1** in ethanol demonstrates one of the possible pathways of fragmentation of the 1D-polymeric cobalt(II) carboxylates in alcoholic solutions.

It was found that mild heating of a solution of **1** in benzene (60 °C) leads to the elimination of the coordinated EtOH molecules. This reaction carried out in air leads to the building-up the metal core and the formation of the hexanuclear hydroxocarboxylate complex $Co_6(OH)_2(O_2CR)_{10}(HO_2CR)_4$ (**2**), which crystallizes as a solvate with nine benzene molecules ($\mathbf{2} \cdot 9C_6H_6$). The same compound can be also obtained by the solid-phase reaction of cobalt(II) chloride and KO_2CR (mechanochemical synthesis) with subsequent crystallization from benzene.

The structure of complex **2** can be pictured as two $\{Co_3(OH)\}$ triangles bound by four carboxylate groups (Fig. 2, Scheme 1). The triangle fragments $\{Co_3(OH)\}$ are combined with each other by two μ_2-bridged and two μ_3-bridged carboxylate groups (Co—O 1.967(2)—2.174(2) Å). In each triangle, the cobalt(II) atoms (Co···Co 3.226(1)—3.458(1) Å) are bound by the OH group (Co—O 1.992(2)—2.132(2), the O atom deviates from the plane of Co_3 atoms by 0.573(2) Å for O(1M) and 0.638(2) Å for O(2M)). The sides of the triangle fragments are fastened by four bridged carboxylate anions (Co—O 1.951(2)—2.137(3) Å). The terminal cobalt atoms (Co(4), Co(6)) additionally coordinate two oxygen atoms of two acid molecules (Co—O 2.129(2)—2.182(2) Å), completing their surrounding to distorted octahedron. Two atoms Co(1) and Co(2) are also in the octahedral surrounding of six O atoms, whereas atoms Co(3) and Co(5) are in the tetrahedral surrounding of four O atoms. The H atoms of the coordinated acid molecules form an intramolecular H-bond with the O atoms of the bridged carboxylate group (HO···O 2.550(4)—2.595(4) Å, H···O 1.72(1)—1.77(1) Å, the angle HO—H—O 165.5(1)—172.3(1)°) (Fig. 2).

Complex **2**, which can be considered as the dimerization and hydrolysis product of compound **1** in the nonpolar solvent, is a structural analog of the known trimethylacetate compounds $Co_6(OH)_2(Piv)_{10}(L)_4$ (L = HPiv,[11] Py (see Ref. 25)) and hexanuclear trimethylacetate complexes, in which two carboxylate anion are substituted by two 2-hydroxy-6-methylpyridine anions.[4]

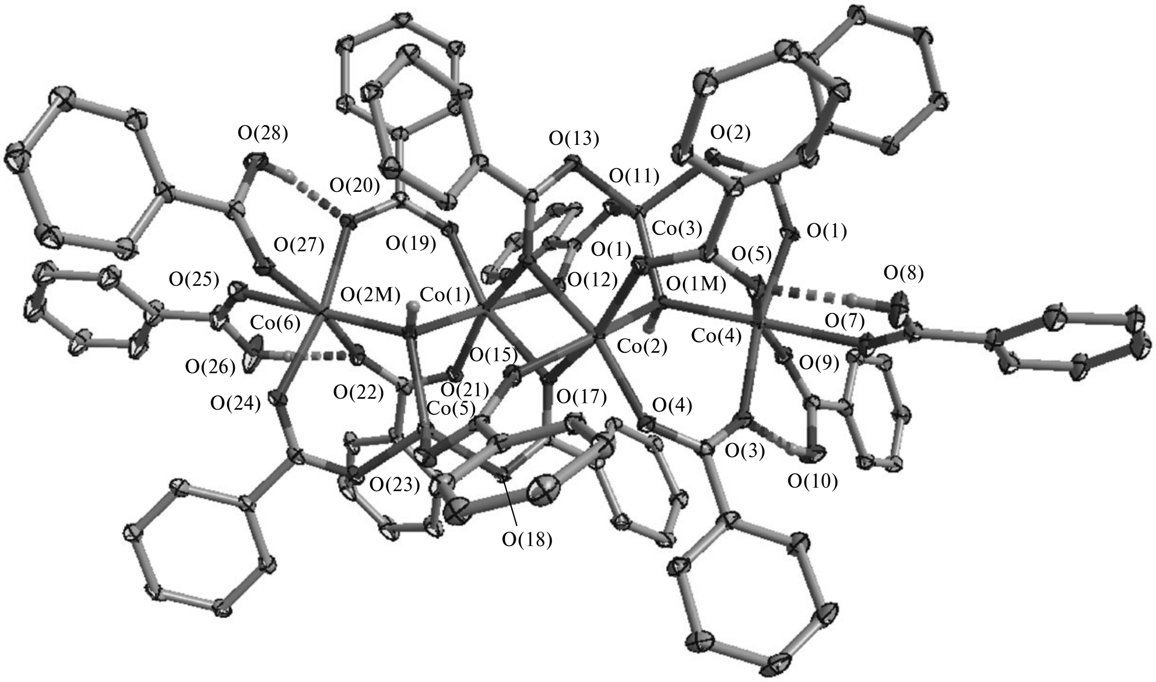


Fig. 2. Molecular structure of **2** (*tert*-butyl substituents of 3,5-di-*tert*-butylbenzoic acid anions and hydrogen atoms at carbon atoms are not shown, thermal ellipsoids are given with 30% probability).

In conclusion, the synthesis of complexes of 3,5-di-*tert*-butylbenzoic acid with cobalt(II) atoms can be carried out under conditions similar to those for the synthesis of pivalate, though, in this case trinuclear molecules with labile apical ligands EtOH are isolated. It can be expected that the synthesized trinuclear complex **1** will be a convenient metal-containing precursor for further building-up the metal framework in the syntheses of both homo- and heteronuclear molecules with cobalt(II) atoms. The cobalt(II) complex with 3,5-di-*tert*-butylbenzoic acid anions demonstrates the higher stability to hydrolysis in ethanol as compared to the trimethylacetate analogs.

It is possible that the stability of **1** to hydrolysis, like in the case of similar complexes with N-donor ligands,**[4,5,26–28]** is determined by both the stabilization of compound by the coordinated ethanol molecules and its insolubility in it. Hydrolysis of **1** in non-anhydrous benzene, in which the complex solubility is relatively high, is probably caused by the presence of water impurities (≤1 wt. %, that is higher by the order of magnitude calculated per 1 mole of cobalt), which reacts with the dissociated forms of the complex.

Experimental

Solvents and reagents were used in syntheses without additional purification: EtOH (96%), C_6H_6 (reagent grade), $CoCl_2 \cdot 6H_2O$ (99%), KOH (98%), 3,5-di-*tert*-butylbenzoic acid (99%). IR spectra of complexes **1** and **2** were recorded on a Perkin Elmer Spectrum 65LS Fourier-transform IR spectrophotometer in KBr pellets. Microanalysis of compounds was performed on a Carlo Erba CHNS-analyzer.

Bis(μ-*O,O,O´*-3,5-di-*tert*-butylbenzoato-κ^2*O,O´*)tetrakis(μ-*O,O´*-3,5-di-*tert*-butylbenzoato)di(ethanol-κ*O*)tricobalt(II), $Co_3(\mu\text{-}O_2CR\text{-}\kappa^2O,O')_2(\mu\text{-}O,O'\text{-}O_2CR)_4(EtOH\text{-}\kappa O)_2$ (1). A solution of potassium 3,5-di-*tert*-butylbenzoate (obtained by the reaction of KOH (0.112 g, 2.0 mmol) and 3,5-di-*tert*-butylbenzoic acid (0.468 g, 2.0 mmol) in EtOH (15 mL)) was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) in EtOH (10 mL). The reaction mixture was stirred at room temperature for 15 min, then a white precipitate of KCl was filtered off. The bluish violet mother liquor obtained was kept at room temperature. The violet crystals formed within 24 h, suitable for X-ray diffraction analysis, were separated from the solution by decantation, washed with cold ethanol (5 °C), and dried in air. The yield of compound **1** was 0.417 g (75 % calculated on the starting amount of $CoCl_2 \cdot 6H_2O$). Found (%): C, 67.81; H, 8.33. $C_{94}H_{138}Co_3O_{14}$. Calculated (%): C, 67.67; H, 8.28. IR, ν/cm^{-1}: 3411 m.br, 2964 v.s, 2905 m, 2869 m, 1612 m, 1571 v.s, 1526 s, 1478 m, 1462 s, 1443 s, 1394 v.s, 1364 s, 1289 m, 1249 m, 1202 w, 1164 w, 1046 w, 924 w, 897 m, 821 w, 790 m, 753 w, 732 m, 704 m, 627 v.w, 550 v.w, 532 v.w, 493 v.w, 437 v.w.

Bis(μ$_3$-hydroxo)bis(μ$_3$-*O,O,O´*-3,5-di-*tert*-butylbenzoato)octakis(μ-*O,O´*-3,5-di-*tert*-butylbenzoato)tetrakis(3,5-di-*tert*-butylbenzoic acid-κ*O*)hexacobalt(II), solvate with nine benzene molecules, $Co_6(\mu_3\text{-}OH)_2(\mu_3\text{-}O,O,O'\text{-}O_2CR)_2(\mu\text{-}O,O'\text{-}O_2CR)_8(HO_2CR\text{-}\kappa O)_4 \cdot 9C_6H_6$ ($2 \cdot 9C_6H_6$). Procedure A. Compound **1**

Table 1. Crystallographic parameters and refinement details for the structure of **1** and $\mathbf{2} \cdot 9C_6H_6$

Parameter	**1**	$\mathbf{2} \cdot 9C_6H_6$
Molecular formula	$C_{94}H_{138}Co_3O_{14}$	$C_{264}H_{354}Co_6O_{30}$
M/g mol^{-1}	1668.83	4361.05
T/K	296(2)	160(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.051(3)	16.9931(7)
b/Å	14.042(4)	22.8217(10)
c/Å	17.074(4)	35.2266(15)
α/deg	73.376(4)	94.8930(10)
β/deg	83.476(4)	90.4370(10)
γ/deg	73.842(4)	108.3680(10)
V/Å^3	2436.8(10)	12909.4(10)
Z	1	2
ρ_{calc}/g cm^{-3}	1.137	1.122
μ/mm^{-1}	0.560	0.438
θ_{max}/deg	27.88	27.48
T_{min}/T_{max}	0.8867/0.9461	0.9175/0.9372
Number of measured/ independent reflections	25093/11609	129358/59056
Number of reflections with $I>2\sigma(I)$	7389	33256
R_{int}	0.0371	0.0611
GOOF	1.071	1.101
R_1 ($I > 2\sigma(I)$)	0.0488	0.0682
wR_2 ($I > 2\sigma(I)$)	0.1265	0.1710
ρ_{min}/ρ_{max}/e Å^{-3}	−0.588/0.583	−0.707/1.319

(0.175 g, 0.105 mmol) was dissolved in C_6H_6 (10 mL) with heating (60 °C) during 20 min. A blue solution obtained was concentrated to 5 mL and kept at room temperature. The violet crystals formed within 24 h, suitable for X-ray diffraction analysis, were separated from the solution by decantation, washed with cold benzene (5 °C), and dried in air. The yield of compound **2** was 0.098 g (51 %). Found (%): C, 68.76; H, 8.32. $C_{210}H_{300}Co_6O_{30}$ (without solvent molecule). Calculated (%): C, 68.97; H, 8.21. IR, ν/cm^{-1}: 3453 m, 3427 m.br, 2964 v.s, 2905 m, 2869 m, 1689 m, 1668 m, 1617 m, 1578 v.s, 1478 m, 1461 s, 1442 s, 1396 v.s, 1364 s, 1334 m, 1288 m, 1271 m, 1249 m, 1202 w, 1163 w, 1130 v.w, 1025 w, 923 w, 898 m, 821 w, 791 m, 735 m, 703 m, 591 v.w, 550 v.w, 531 v.w, 487 v.w, 428 v.w.

Procedure B. The weighed amounts of $CoCl_2 \cdot 6H_2O$ (0.486 g, 2.042 mmol) and sodium 3,5-di-*tert*-butylbenzoate (obtained by mechanical trituration of 3,5-di-*tert*-butylbenzoic acid (0.956 g, 4.084 mmol) and KOH (0.228 g, 4.084 mmol)) were placed into a 25-mL grinding vessel made of stainless steel and steel balls (10 g, 2—8 mm diameter) were added. The mechanochemical synthesis was carried out on a Retsch MM 400 vibrating ball mill for 2 h at the amplitude of 25 Hz, preliminary cooling down the grinding vessels to –60 °C every 30 min. A weighed amount of the mixture obtained (0.152 g) was dissolved in C_6H_6 (10 mL) with heating (60 °C) during 15—20 min. A blue solution was filtered from a white precipitate and kept at room temperature. The violet crystals formed within 24 h, suitable for X-ray diffraction analysis, were separated from the solution by decantation, washed with cold benzene (5 °C), and dried in air. The crystallographic parameters of the crystals (T = 181(2) K, triclinic $P1$, a = 17.064(8), b = 22.889(10), c = 35.320(2) Å, α = 95.090(10)°, β = 90.523(7)°, γ = 108.370(2)°, V = 13030(20) Å^3) were the same as those obtained for a single crystal of the compound synthesized by procedure ***A*** (see Table 1).

X-ray diffraction studies of compounds **1** and $\mathbf{2} \cdot 9C_6H_6$ were performed on a Bruker Apex II diffractometer equipped with a CCD-detector (Mo-Kα, λ = 0.71073 Å, graphite monochromator).[29] A semiempirical correction for the absorption was made for both compounds.[30] The structures of all the complexes were solved by direct method. For compound **1**, the refinement was performed in the full-matrix anisotropic approximation for all the nonhydrogen atoms. In the structure of compound **2**, all the atoms, except the carbon atoms of the benzene solvent molecule, were refined in the full-matrix anisotropic approximation for all the nonhydrogen atoms. Positions of the methyl carbon atoms of the disordered CMe_3 fragments in **1** and $\mathbf{2} \cdot 9C_6H_6$ were localized in differential Fourier synthesis. The occupation of the disordered *tert*-butyl group for **1**: 0.339(15) and 0.661(15) at atom C(12); for $\mathbf{2} \cdot 9C_6H_6$: 0.312(9) and 0.688(9) at atom C(53). The H atoms at carbon and oxygen atoms of organic ligands were generated geometrically and refined using the riding model. The calculations were performed using the SHELXS-97 and SHELXL-97 software.[31] The crystallographic parameters and refinement details of the structures are given in Table 1.

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X-ray diffraction analysis was performed in the Center of Collective Exploitation of N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

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