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LETTERS TO THE EDITOR

Synthesis of Octanuclear Mixed-Valence Cobalt(II, III) Propionate and Butyrate with the Étagère-like Core

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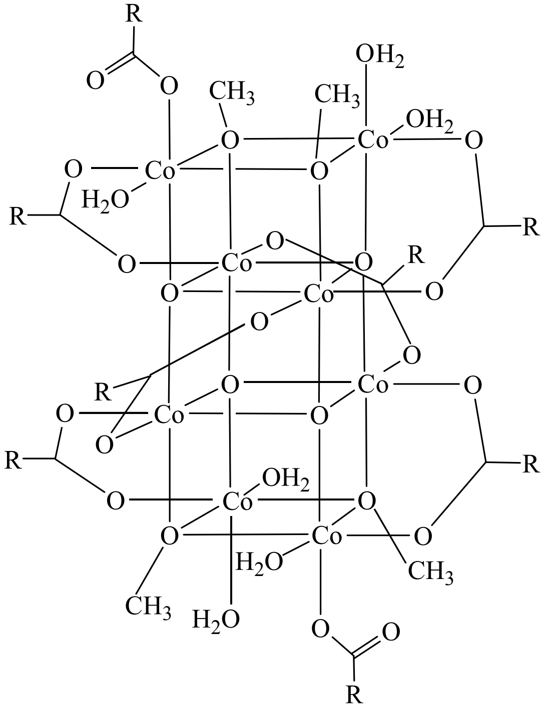
The mixed-valence cobalt carboxylates attract attention due to the role that they play in the catalytic processes of industrial liquid-phase oxidation of hydrocarbons [1–3]. However, only poor information is available about the octanuclear mixed-valence cobalt complexes with a metal containing framework of the étagère-shapedtype [4–6]. We obtained and characterized with the X-ray diffraction two new cobalt carboxylate complexes with such framework: $[Co_4^{II}Co_4^{III}(\mu_4\text{-}O)_4\cdot(\mu_3\text{-}OMe)_4(\mu\text{-}O_2CR)_6(O_2CR)_2(H_2O)_6]\cdot 4H_2O$, where R = Et (**I**) and Pr (**II**).

Compounds **I** and **II** crystallize in the monoclinic system. **I**, space group *Cc*, $a = 17.373(4)$, $b = 15.987(3)$, $c = 20.544(4)$ Å, $\beta = 97.24\ (3)^\circ$, $Z = 4$, $R = 2.90\%$ $[I > 2\sigma(I)]$. **II**, space group $C2/c$, $a = 17.891(4)$, $b = 16.283(3)$, c 20.862(4) Å, $\beta = 94.599(4)^\circ$, $Z = 4$, $R = 4.30\%$ $[I > 2\sigma(I)]$.



Complexes **I** and **II** have the same metal-containing framework of the étagère-shaped type: the framework includes three cubane fragments $\{Co_4O_4\}$ with two common faces. Around the framework there are six bidentate bridging carboxylate ligands forming a double helix motif. In the crystals of complexes **I** and **II** the enantiomeric components (right and left spirals) are in equal amount, that is, these compounds are racemates. The complexes **I** and **II** are valence-trapped: the Co^{III} atoms are located in the central cubane fragment, while the Co^{II} atoms are on the molecule periphery [7].

$[Co_8O_4(MeO)_4(EtCOO)_8(H_2O)_6]\cdot 4H_2O$ (I). A weighed portion of cobalt(II) propionate dihydrate [8] (2.89 g, 12.0 mmol) was dissolved in 45 ml of methanol. After cooling the solution to –10°C to it was added dropwise with stirring 0.44 ml of 40% aqueous hydrogen peroxide (6.0 mmol). The solution color changed from purple to dark green and there was a slight evolution of oxygen. At the stepwise evaporation of the solvent, on the walls of the beaker a light-green precipitate began to form, and then formed dark green crystalline precipitate of compound **I**. Before complete evaporation of the solvent, the solution color changed initially to brown, then to crimson, indicating the predominance of the original cobalt(II) propionate. After evaporation of the solvent, to the residue was added methanol in small portion, each time decanting the formed brown solution until the solution remained dark green at adding next methanol portion. Then to the residue was added a minimum amount of methanol necessary to dissolve the crystals of **I.** The mixture was stirred and filtered from the light green precipitate of unidentified substance (X-ray amorphous, according to X-ray powder diffraction analysis). During evaporation of the solvent, in the filtrate a precipitate of compound **I** separated as thin dark green needles. The precipitate was separated from the mother liquor by decanting the solvent just in the moment when it again began to change color to brown, washed with a small amount of methanol, and dried in air. The mother liquor was mixed with the first brown solution and a few drops of 40% hydrogen peroxide was added to complete the change of color of the mixture to dark green, after which the mixture was treated like the source one to isolate an additional portions of crystals **I**.

The total yield of compound **I** was 93% (based on metal). Complex **I** is readily soluble in methanol, ethanol, butanol, propionic acid, dimethylformamide, tetrahydrofuran, sparingly soluble in water, poorly soluble in acetonitrile and acetone, and insoluble in diethyl ether, hexane, benzene, and dichloromethane. Electron absorption spectrum (methanol), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 345 (6500), 635 (640). IR spectrum, ν, cm^{-1}: 487 v.w, 550, v.w, 586 m, 633 m, 675 v.w, 812 v.w, 833 v.w, 895 v.w, 1030 s, 1042 s, 1076 w, 1088 w, 1244 w, 1303 s, 1371 m, 1419 v.s, 1466 m 1529 v.s, 1558 v.w, 2827 w, 2932 w, 2974 w, 3370 v.s.br. Found, %: Co 32.0; C 23.3; H 4.5. $C_{28}H_{72}Co_8O_{34}$. Calculated, %: Co 33.1; C 23.6; H 5.1.

$[Co_8O_4(MeO)_4(PrCOO)_8(H_2O)_6]\cdot 4H_2O$ (II). The synthesis was performed similarly to compound **I** using 3.17 g (12.0 mmol) of cobalt(II) butyrate 1.7-hydrate [9] instead of cobalt(II) propionate dihydrate. Yield 88% (based on the metal). Complex **II** is readily soluble in methanol, ethanol, butanol, butyric acid, dimethylformamide, tetrahydrofuran, poorly in water, acetonitrile and acetone, insoluble in diethyl ether, hexane, benzene, and dichloromethane. EAS (methanol), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 345 (6400), 635 (630). IR spectrum, ν, cm^{-1}: 484 v.w, 586 m, 634 m, 803 v.w, 833 v.w, 1031 s, 1042 s, 1080 v.w, 1098 w, 1209 w, 1263 w, 1317 m, 1346 m, 1413 v.s, 1458 w, 1528 v.s, 1558 v.w, 2827w, 2876 w, 2932 w, 2964 m, 3375 v.s.br. Found, %: Co 29.8; C 27.7; H 5.4. $C_{36}H_{88}Co_8O_{34}$. Calculated,%: Co 30.7; C 28.1; H 5.8.

The XRD of the complexes was performed on automatic diffractometers Enraf-Nonius CAD-4 (**I**) and Bruker Smart APEX II CCD (**II**) at 293 K [MoK_α radiation, β-filter (**I**), graphite monochromator (**II**)]. The structures were solved by the direct method and refined using the software package SHELXL97 [10]. The X-ray powder diffraction analysis was performed on an automatic diffractometer Rigaku Miniflex II (CuK_α radiation) in the angular range 2θ from 5° to 60° (scanning step 0.05°, exposition 1 s). The EAS were recorded on a SF-56 spectrophotometer in the range of 200–1100 nm (quartz cuvette, l = 1 cm). The IR spectra were registered on a Fourier spectrometer FSM 1202 in the range 4000–400 cm^{-1} (tablets with KBr). Elemental analysis was performed on a LECO CHNS-932 analyzer, the analysis of the cobalt content was performed spectrophotometrically (Specol 11) after mineralization of samples with concentrated nitric acid.

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