Destruction of polymeric cobalt(II) trimethylacetate. Synthesis and structures of new complexes $Co_9(\mu_3\text{-}OH)_6(\mu\text{-}OOCCMe_3)_{12}(OCMe_2)_4$ and $Co_6(\mu_4\text{-}O)_2(\mu\text{-}OOCCMe_3)_{10}(\eta\text{-}HOOCCMe_3)_4$

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Recently,[1] we have demonstrated that polymer $[Co(OH)_n(OOCCMe_3)_{2-n}]_m$ (**1**), which was prepared by fusing aqueous cobalt(II) acetate with pivalic acid, is a convenient starting reagent for the preparation of the hexanuclear complex $Co_6(\mu_3\text{-}OH)_2(OOCCMe_3)_{10}(HOOCCMe_3)_4$ and the tetranuclear complex $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$. These complexes were readily obtained by thermal extraction of polymer **1** with nonpolar solvents or ethanol, respectively.

We found that the use of acetone as an extractant (the water content was 2—3%) also led to destruction of the polymer, but cobalt trimethylacetate was extracted in substantially higher yield. The nonanuclear complex $Co_9(\mu_3\text{-}OH)_6(\mu\text{-}OOCCMe_3)_{12}(OCMe_2)_4$, which crystallized with four acetone molecules of solvation, (**2**) was

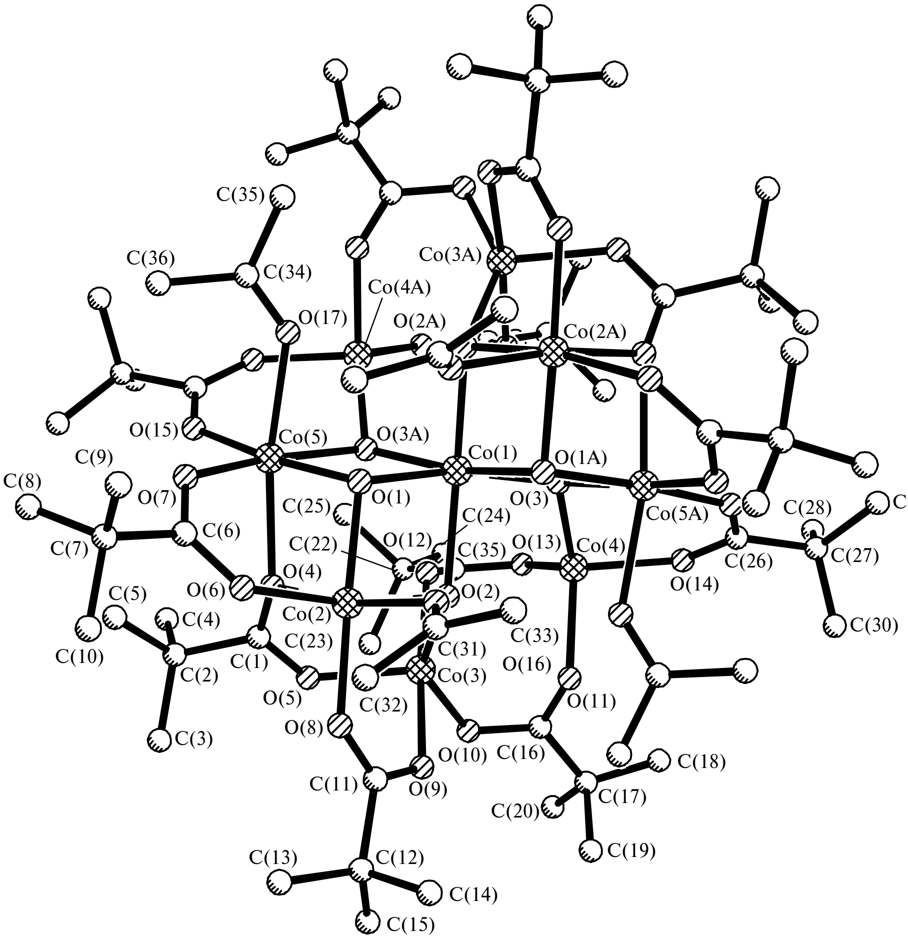

Fig. 1. Crystal structure of cluster **2** (acetate molecules of solvation are omitted).

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isolated in 60% yield. According to the X-ray diffraction data, the central Co(1) atom in cluster **2** (Fig. 1) is in an octahedral environment formed by six OH$^-$ groups (Co—O, 2.060(10)—2.119(8) Å), each group serving as a tridentate-bridging ligand in one of six triangles, *viz.*, Co(1)Co(2)Co(3)(μ_3-O(2)H), Co(1)Co(2A)Co(3A)(μ_3-O(2A)H) (Co—O(H) 2.000(8)—2.119(8) Å), Co(1)Co(2)Co(5)(μ_3-O(1)H), Co(1)Co(2A)Co(5A)(μ_3-O(1A)H) (Co—O(H) 2.01(1)—2.06(1) Å), Co(1)Co(4)Co(5A)(μ_3-O(3)H), Co(1)Co(5)Co(4A)(μ_3-O(3A)H) (Co—O(H) 1.945(6)—2.142(5) Å), linked *via* shared vertices. The Co(2), Co(2A), Co(5), and Co(5A) atoms are also in an octahedral environment, which involves not only the oxygen atoms of the bridging pivalate fragments but also the oxygen atoms of the coordinated acetone molecules (Co—O$_{\text{piv}}$, 1.971(8)—2.206(7) Å; Co—O$_{\text{ac}}$, 2.195(7)—2.205(7) Å). The Co(4) and Co(4A) atoms are in a tetrahedral environment and the Co(3) and Co(3A) atoms are in a trigonal-bipyramidal environment formed by the oxygen atoms of the bridging pivalate anions. It should be noted that all Co—Co distances are nonbonded (Co...Co, 3.069(1)—3.571(1) Å).

The addition of an excess of pivalic acid to polymer **1** (the ratio Co : HOOCCMe$_3$ = 1 : 2) followed by refluxing in THF in air for 15 min resulted in complete dissolution of **1**. After recrystallization of the crude product from toluene, brown crystals of the solvated complex Co$_6$(μ_4-O)$_2$(μ-OOCCMe$_3$)$_{10}$(η-HOOCCMe$_3$)$_4$ · 0.5MeC$_6$H$_5$ (**3**) were isolated in virtually quantitative yield. According to the X-ray diffraction data, two Co$_4$(μ_4-O) tetrahedra (Co—O, 1.878(4)—2.048(4) Å) in cluster **3** (Fig. 2) containing no Co—Co bonds (Co...Co, 2.806(1)—3.408(1) Å) have the shared Co(1)Co(2) edge. The Co(3) and Co(4) atoms and the Co(5) and Co(6) atoms in two tetrahedra are linked to each other *via* the bridging pivalate anions (Co—O, 1.922(3)—2.105(4) Å). The octahedral environment of each cobalt atom in cluster **3** is completed with four tridentate-bridging pivalate fragments through which the cobalt atoms are linked in the Co(1)Co(5)Co(6), Co(1)Co(3)Co(5), Co(2)Co(4)Co(6),

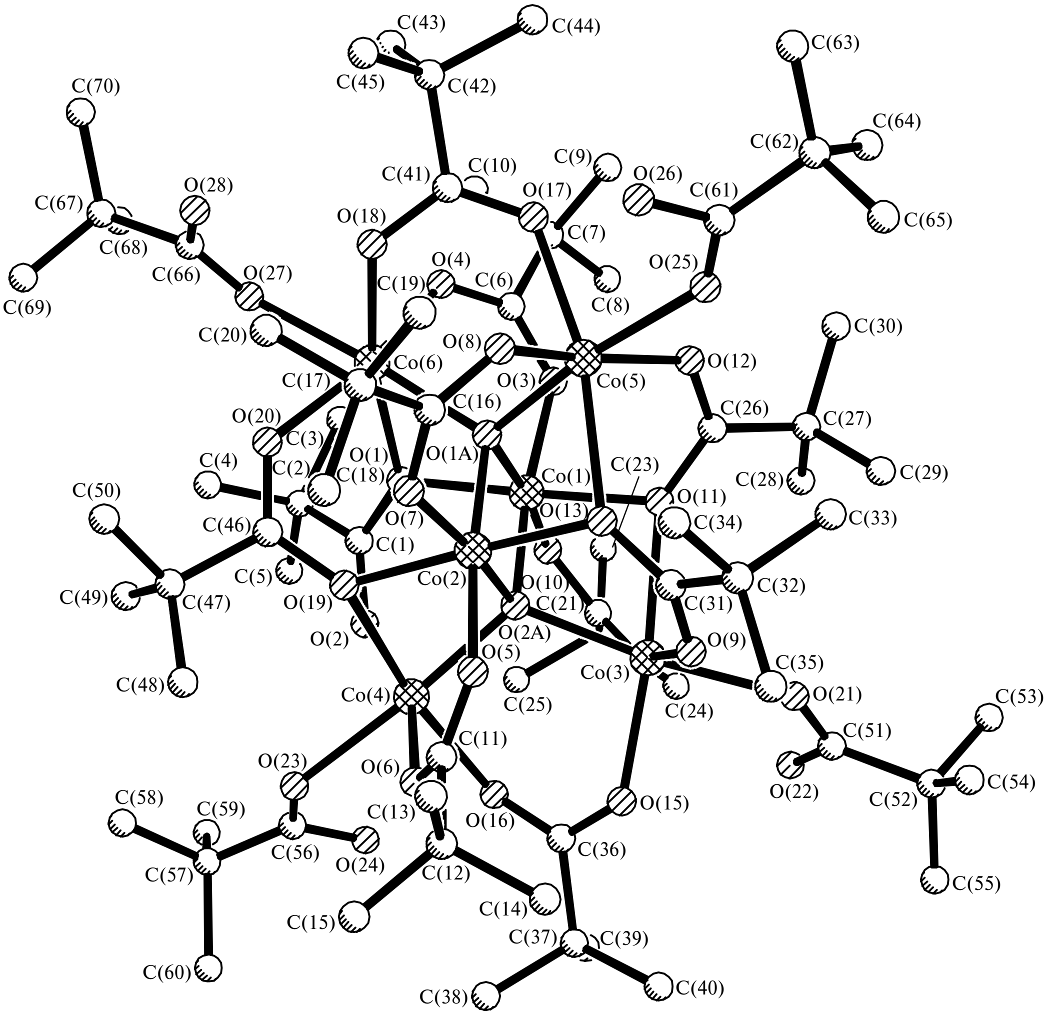

Fig. 2. Crystal structure of cluster **3** (toluene molecules of solvation are omitted).

and Co(2)Co(5)Co(3) triangles (the first pair of the metal atoms is linked to one of the oxygen atoms of the carboxylate group) (Co—O_{μ}, 1.921(4)—2.343(4) Å; Co—O, 2.036(4)—2.076(4) Å). Each peripheral cobalt atom is additionally bound to the oxygen atom of the terminal pivalic acid molecule (Co—O, 2.149(4)—2.236(4) Å).

Hexanuclear cobalt complex **3** is formally a structural analog of the known compound $Mn_6(\mu_4\text{-}O)_2(\mu\text{-}OOCCMe_3)_{10}(\eta\text{-}(H)OOCCMe_3)_4$ (**4**) containing two Mn^{III} atoms and four Mn^{II} atoms.[2,3] Although it is difficult to locate the protons of the hydroxo groups in the neutral coordinated acid molecules in cluster **3**, it can be assumed that the distribution of electrons over the cobalt atoms is analogous to that in **4**. It should be noted that investigations devoted to these problems are being continued and involve the detailed examination of the magnetic behavior of the new compounds.

Synthesis of hexakis(μ_3-hydroxo)bis(μ_3-pivalato-*O,O,O′*)decakis(μ_2-pivalato-*O,O′*)bis(η^1-acetone)nonacobalt tetraacetone solvate, $Co_9(\mu_3\text{-}OH)_6(\mu\text{-}OOCCMe_3)_{12}(OCMe_2)_4 \cdot 4OCMe_2$ (2). Polymer **1** (0.5 g) was dissolved in wet boiling acetone (25 mL) in air. The resulting blue solution was filtered off from the insoluble precipitate, concentrated to 5 mL, and kept at −18 °C for one day. The large blue prismatic crystals thus formed were separated from the solution by decantation, washed with cold hexane, and dried under an argon stream. Complex **2** was obtained in a yield of 0.24 g (60%). Found (%): C, 43.65; H, 7.01. $Co_9C_{84}H_{162}O_{38}$. Calculated (%): C, 43.45; H, 7.14. IR (KBr), ν/cm^{-1}: 3425 w, 2960 m, 2893 w, 2856 w, 1716 w, 1688 w, 1668 w, 1644 w, 1584 m, 1552 s, 1540 w, 1520 w, 1504 m, 1448 s, 1412 s, 1360 s, 1228 m, 892 w, 800 m, 668 m, 620 m, 420 w.

Synthesis of bis(μ_4-oxo)bis(μ_3-pivalato-*O,O,O′*)octakis(μ_2-pivalato-*O,O′*)tetra(η^1-pivalic acid)hexacobalt hemitoluene solvate, $Co_6(\mu_4\text{-}O)_2(\mu\text{-}OOCCMe_3)_{10}(\eta\text{-}HOOCCMe_3)_4 \cdot 0.5MeC_6H_5$ (3). A mixture of polymer **1** (0.69 g) and pivalic acid (0.56 g) was refluxed with THF (25 mL) in air until the polymer was completely dissolved (15 min). The resulting dark-brown solution was concentrated to dryness and the dry residue was dissolved in a 1 : 1 toluene—benzene mixture (10 mL) with heating to 70 °C. The solution thus obtained was concentrated to 5 mL and kept at 5 °C for one day. The dark-brown prismatic crystals that precipitated were separated from the solution by decantation, washed with cold hexane, and dried *in vacuo*. Complex **3** was obtained in a yield of 0.76 g (95%). Found (%): C, 49.02; H, 7.37. $Co_6C_{73.5}H_{134}O_{30}$. Calculated (%): C, 48.91; H, 7.43.

IR (KBr), ν/cm^{-1}: 3426 m, br., 2964 m, 2924 m, 2876 m, 1664 s, 1596 m, 1568 m, 1520 m, 1480 m, 1420 m, 1360 m, 1224 m, 668 w, 592 w.

X-ray diffraction study. X-ray diffraction investigation was carried out in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) according to a standard procedure[6] on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo radiation, graphite monochromator, 110 K, ω scan technique, the scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max} = 60°$). For complex **2**: $C_{84}H_{162}Co_9O_{38}$, $M = 2309$, space group *Pbcn*, $a = 17.068(17)$ Å, $b = 26.71(3)$ Å, $c = 25.177(17)$ Å, $V = 11479(19)$ Å^3, $Z = 4$, a total of 24629 reflections were measured, of which 10203 reflections were with $F^2 > 2\sigma(I)$, $\rho_{calc} = 1.321$ g cm^{-3}, $\mu = 13.37$ cm^{-1}, $R_1 = 0.0688$, $wR_2 = 0.1383$. For complex **3**: $C_{73.5}H_{134}Co_6O_{30}$, $M = 1847.36$, space group $P\bar{1}$, $a = 15.482(3)$ Å, $b = 15.600(3)$ Å, $c = 20.196(4)$ Å, $\alpha = 84.912(4)°$, $\beta = 87.816(5)°$, $\gamma = 88.010(5)°$, $V = 4852.8(16)$ Å^3, $Z = 2$, a total of 17050 reflections were measured, of which 11168 reflections were with $F^2 > 2\sigma(I)$, $\rho_{calc} = 1.264$ g cm^{-3}, $\mu = 10.7$ cm^{-1}, $R_1 = 0.0753$, $wR_2 = 0.1923$.

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