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The Structural Organization of Oligonuclear Cobalt(II, III) and Cobalt(III) Carboxylates

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Abstract—The review deals with the topology of homonuclear carboxylate complexes of cobalt(II, III) and cobalt(III) whose structures are built from the monocarboxylate anions $RCOO^-$ (R is a radical containing no electron-donating substituents), water, and its deprotonated forms.

Keywords: cobalt, polynuclear complexes, carboxylates, X-ray diffraction analysis, topology

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INTRODUCTION

Oligonuclear cobalt carboxylates are of practical interest first of all because a representative of theirs (the so-called "cobalt(III) acetate") is used as a catalyst for commercial homogeneous oxidation of hydrocarbons [1–8]. For instance, in the oxidation of *p*-xylene into terephthalic acid or dimethyl terephthalate, this catalyst (when considering the large-scale production of a polyethylene terephthalate fiber) is among the most demanded ones [3–5].

Extensive investigations into the structural chemistry of cobalt(III) carboxylates did not begin until 1985, when the product obtained in a reaction of pyridine with "cobalt(III) acetate" (Ac-Co) was first identified by X-ray diffraction as $[Co_3^{III}O(O_2CMe)_5(OH)(Py)_3][Co^{II}Br_3(Py)]$ (**I**) [9]. Up to that point, the literature data were contradictory; in particular, although various structures were proposed for Ac-Co, none of them was ever confirmed experimentally. Later, Ac-Co was used to obtain diverse oligonuclear carboxylate (mainly, acetate) complexes usually stabilized by heterocyclic bases [10–23]. However, the structure of Ac-Co itself still remains unclear. Presumably, this substance is a mixture of different forms of acetate complexes [10, 24–31].

Apart from the practical application of Ac-Co, generally cobalt carboxylate complexes, which have unique chemical, thermodynamic, spectral, adsorption, and other properties, are widely used to solve a number of fundamental theoretical and applied problems. The presence of paramagnetic sites arouses interest in their magnetic properties since such compounds are convenient for the study of exchange interactions and revealing of magnetic-structural correlations [32–35].

All structurally characterized Co(III) carboxylates are basic complexes containing deprotonated forms of solvent molecules (O^{2-}, OH^-, OMe^-, etc.) in the inner sphere of the metal complex; this is probably due to solvolysis processes (olation and oxolation) accompanying the oxidation of Co^{2+} to Co^{3+}.

Cobalt carboxylates have been barely reviewed until recently [36]. Only in the last few years, carboxylate complexes have been classified according to the metal core topology (without considering the bridging ligands) [34], the radical R of the carboxylate [35], and the nuclearity (number of metal centers) [7]; note that the reviews [7, 35] are restricted to cobalt(II) carboxylates. The classification parameters listed above seem to be rather formalized, which is why we try here to classify carboxylates according to the topology of the metal-containing framework with the bridging ligands included. This classification is intended to reveal the relationship between such carboxylate complexes that can differ in nuclearity, the radical R of the carboxylate, or the oxidation state of the Co atoms as well as to identify the factors influencing the structure of the resulting carboxylates and predict the conditions for their targeted synthesis and transformation.

For this reason, the carboxylates discussed below should be defined as follows. Apart from the complexing Co^{3+} cation and the ligands $RCOO^-$ (monocarboxylic acid residues containing no electron-donating groups in the radical R), their inner sphere may enclose the Co^{2+} ions, water, its deprotonated forms, and other ligands, the latter being included only if they are believed not to determine the topology of the metal-containing framework of the complexes.

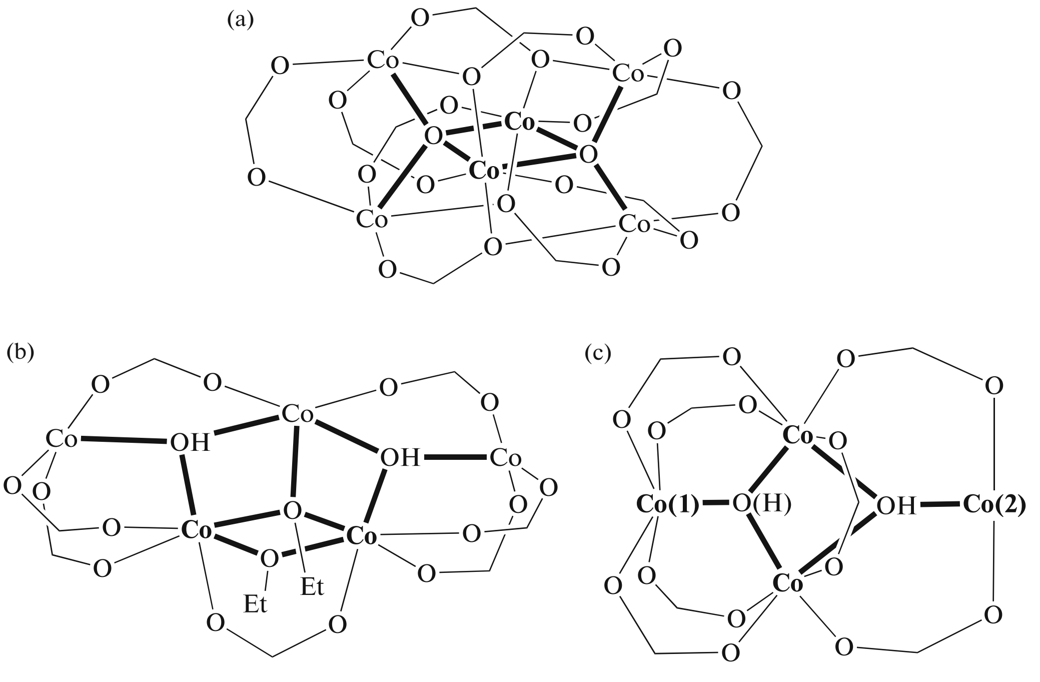

Fig. 1. Frameworks of the complexes with the central cores $Co_4^{II}Co_2^{III}(\mu_4\text{-O})_2$ (a), $Co_3^{II}Co_2^{III}(\mu_3\text{-OEt})(\mu_3\text{-OH})_2(\mu\text{-OEt})$ (b), and $Co_2^{II/III}Co_2^{III}(\mu_3\text{-O/OH})(\mu_3\text{-OH})$ (c) (in these and next figures, the central cores are indicated with thicker bond lines, the Co(III) atoms are set in bold, and the radicals of the carboxylate ligands are omitted).

The nuclearity, topology, and degree of shielding of the metal-containing framework oligonuclear complexes can depend on the steric properties of carboxylate ligands.

MIXED VALENCE CARBOXYLATES

Complexes with the central core $\mathbf{Co_4^{II}Co_2^{III}(\mu_4\text{-O})_2}$. This structural motif occurs in both homo- and heteronuclear carboxylates of 3*d* metals having the oxidation states +2 and +3. This group is mainly constituted by manganese carboxylates. Cobalt forms such complexes with pivalate ligands only. The central core of such complexes is made up of two tetrahedra $Co_2^{II}Co_2^{III}(\mu_4\text{-O})$ sharing the $Co(III)_2$ edge. Either central Co(III) atom is linked with all four peripheral Co(II) atoms by two bridging bidentate and two bridging tridentate pivalate ligands. The peripheral Co(II) atoms are linked in pairs by two bridging bidentate pivalate anions. Therefore, the metal-containing framework of the complexes is $\{Co_6O_2(\mu_3\text{-}O_2C^tBu)_4(\mu\text{-}O_2C^tBu)_6\}$ (Fig. 1a).

In the complex $[Co_6O_2(O_2C^tBu)_{10}(^tBuCO_2H)_4]$ (**II**) [37], each of four peripheral Co atoms additionally coordinates a pivalic acid molecule and hence has a distorted octahedral geometry. Making reference to a well-known manganese analog, Malkov et al. [37] admitted an identical version of valence-trapping. Different coordination geometries of the peripheral Co atoms in the complexes with this topology are worthy of notice. For instance, such atoms in the pivalates $[Co_6O_2(O_2C^tBu)_{10}(^tBuCO_2H)_4]$ [38] and $[Co_6O_2(O_2C^tBu)_{10}(H_2O)(THF)_3]$ (THF is tetrahydrofuran) [39] have a distorted octahedral environment like that in complex **II**. However, in the complexes $[Co_6O_2(O_2C^tBu)_{10}(Me_2CO)_2]$ [18] and $[Co_6O_2(O_2C^tBu)_{10}(MeCO_2Et)_2]$ [38], the solvent molecules are coordinated only to two of four peripheral Co(II) atoms: this coordination involves the Co(II) atoms that are on opposite sides (former complex) and on the same side of the plane $Co_2^{III}(\mu_4\text{-O})_2$, (latter complex). As a result, only these Co(II) atoms have an octahedral geometry, while the coordination polyhedra of the other two Co atoms are distorted tetragonal pyramid (former complex) and distorted tetrahedra (latter complex; only two tridentate pivalate bridges were identified in its structure [38]: $[Co_6O_2(\mu_3\text{-}O_2C^tBu)_2(\mu\text{-}O_2C^tBu)_8(MeCO_2Et)_2]$).

Complexes with the central core $\mathbf{Co_3^{II}Co_2^{III}(\mu_3\text{-OEt})(\mu_3\text{-OH})_2(\mu\text{-OEt})}$. This central core was found only in two pivalate complexes with the metal-containing framework $\{Co_5(\mu\text{-}O_2C^tBu)_7(OEt)_2(OH)_2\}$ [38]. In the molecular structures of both complexes, two Co(III) atoms are linked by two bridging etoxy ligands, one of which also provides a linkage to the central Co(II) atom. The latter is linked by two μ_3-OH groups with either Co(III) atom and either peripheral Co(II) atom (Fig. 1b).

All the Co atoms in the complexes $[Co_5(O_2C^tBu)_8(OEt)_2(OH)_2(^tBuCO_2H)(EtOH)_3]$ (**III**) and $[Co_5(O_2C^tBu)_8(OEt)_2(OH)_2(EtOH)_4]$ have an octahedral environment. In both structures, the central Co(II) atom coordinates an ethanol molecule which comes *trans* to the bridging μ_3-OEt group. The octahedral geometry of the peripheral Co(II) atoms is completed with the pivalate anion, ethanol molecules (in both complexes), and a pivalic acid molecule (in complex **III**) [38].

Complexes with the central core $Co_2^{II/III}Co_2^{III}(\mu_3$-O/OH)($\mu_3$-OH). This structure was found in three cobalt pivalate complexes. The metal-containing framework of such carboxylates can be formulated as $\{Co_4(O/OH)(OH)(\mu\text{-}O_2C^tBu)_7\}$ (Fig. 1c).

One complex [38] consists of two components resulting from the disordered coordination environment of the Co(2) atom. The octahedral geometry of the Co(1) atom is completed with a pivalic acid molecule which is coordinated *trans* to the bridging μ_3-OH group. The proportion of these components is about 3 : 1. In the major component, the Co(2) atom is additionally bound to two pivalate ligands via chelating bidentate and monodentate coordination to form an octahedral environment. In the minor component, a pivalate anion and a pivalic acid molecule are coordinated to the Co(2) atom in a monodentate fashion to make up a distorted tetragonal pyramid. The major and minor components can thus be formulated as $[Co^{II}Co_3^{III}(O_2C^tBu)_9(OH)_2(^tBuCO_2H)]$ and $[Co_2^{II}Co_2^{III}(O_2C^tBu)_8(OH)_2(^tBuCO_2H)_2]$. The sums of the bond valences calculated in [38] correspond to the oxidation state +3 for all the metal centers, and it was pointed out that the oxidation state of the cobalt atoms can be "fitted" by replacing the hydroxide group μ_3-OH by an oxide one μ_3-O [38]. Nonetheless, based on the pyramidal environment of this bridging O atom, those authors concluded that it is protonated.

A second pivalate complex consists of two components as well, also because of the disordered coordination environment of the Co(2) atom [40]. A water molecule is coordinated to the Co(1) atom, coming *trans* to the bridging μ_3-O atom. The proportion of the components is 3 : 1. In the major component, the coordination polyhedron of the Co(2) atom is a distorted tetragonal bipyramid made up of the bridging ligands, a pivalate anion coordinated in a monodentate fashion, and a pivalic acid molecule. In the minor component, the Co(2) atom coordinates the pivalate anion (via bidentate chelation) rather than a pivalic acid molecule to form an octahedral geometry. The major and minor components can be formulated as $[Co^{II}Co_3^{III}O(O_2C^tBu)_8(OH)(^tBuCO_2H)(H_2O)]$ and $[Co_4^{III}O(O_2C^tBu)_9(OH)(H_2O)]$. Therefore, the structure of this complex shows the isomorphism of the hetero- and homovalent forms.

In a third pivalate complex, the Co(1) atom coordinates a pivalic acid molecule coming *trans* to the bridging μ_3-O atom. Two pivalate ligands are bound to the Co(2) atom via bidentate chelation and monodentate coordination [41]. Each metal center has an octahedral geometry; the complex is homovalent: $[Co_4^{III}O(O_2C^tBu)_9(OH)(^tBuCO_2H)]$. Interestingly, although the complex is a hydroxo carboxylate, its aggregate formula (with solvate molecules of pivalic acid) corresponds to the neutral salt $Co(^tBuCO_2)_3 \cdot 0.5H_2O$.

Complexes with the central core $Co_{2/3/4}^{II}Co_4^{III}(\mu_{3/4}$-O)$_4$. The central part of the metal-containing framework of such complexes is a cubane unit, $Co_4^{III}(\mu_{3/4}\text{-}O)_4$, whose O atoms are additionally linked to two, three, or four Co(II) atoms. As a result, the corresponding O atoms function as μ_4 bridges (Fig. 2). The metal-containing frameworks of such carboxylates are topologically similar.

The central cores $Co_2^{II}Co_4^{III}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2$ and $Co_3^{II}Co_4^{III}(\mu_4\text{-}O)_3(\mu_3\text{-}O)$ were found only in complexes with pivalate ligands. The framework of hexanuclear complexes is $\{Co_6O_4(\mu\text{-}O_2C^tBu)_7\}$, while that of a heptanuclear complex is $\{Co_7O_4(\mu\text{-}O_2C^tBu)_9\}$ (Figs. 2a, 2b). The octahedral environment of two Co(III) atoms of the cubane unit in hexanuclear complexes is completed with two water molecules.

In the complex $(Bu_4N)[Co_6O_4(\mu\text{-}O_2C^tBu)_7(O_2C^tBu)_2(H_2O)_2]$ (**IV**) [38], one peripheral Co(II) atom additionally coordinates a pivalate anion in a monodentate fashion, while the other shows bidentate coordination. The charge of the complex anion is compensated by the charge of the tetrabutylammonium cation (Bu_4N^+). In the complex $[Co_7O_4(\mu\text{-}O_2C^tBu)_9(^tBuCO_2H)(H_2O)_3(MeCN)_2][Co_6O_4(\mu\text{-}O_2C^tBu)_7(O_2C^tBu)_2(H_2O)_2]$ (**V**) [38], the charge of the hexanuclear anion is compensated by the charge of the heptanuclear cation. Structurally, the anion differs from that in complex **IV** only in monodentate coordination of the pivalate anions to both peripheral Co(II) atoms. Each of three peripheral Co(II) atoms in the heptanuclear complex cation additionally coordinates two neutral molecules: a water molecule (to each atom), two acetonitrile molecules, and a pivalic acid molecule. The calculated sums of the bond valences for the Co(II) and Co(III) atoms in structures **IV** and **V** fully agree with the suggested valence-trapping [38].

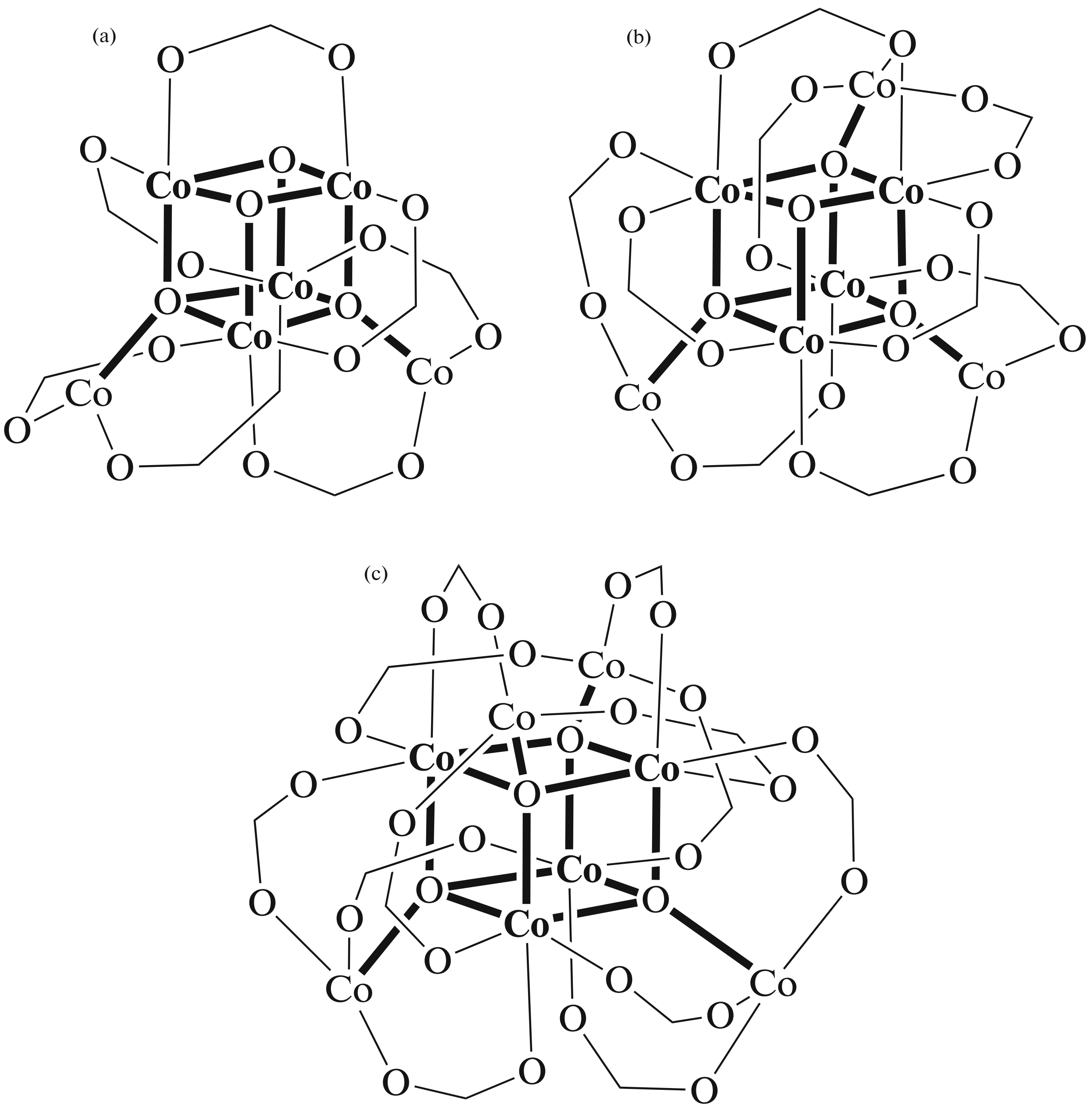

Fig. 2. Frameworks of the complexes with the central cores $Co_2^{II}Co_4^{III}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2$ (a), $Co_3^{II}Co_4^{III}(\mu_4\text{-}O)_3(\mu_3\text{-}O)$ (b), and $Co_4^{II}Co_4^{III}(\mu_4\text{-}O)_4$ (c).

The complex anion in $(Me_5C_3H_2N_2)$ $[Co_6O_4(\mu\text{-}O_2C^tBu)_7(O_2C^tBu)_2(H_2O)_2]$ ($Me_5C_3H_2N_2^+$ is the pentamethyldihydroimidazolium cation) [42] is topologically identical with the anion of complex **V**.

It should be noted that two other structurally characterized hexanuclear complexes with a topologically similar framework are identified as homovalent pivalates: $[Co_6^{III}(\mu_4\text{-}O)_2(\mu\text{-}O_2C^tBu)_9(\mu_3\text{-}OH)_2(OH)_2]$ $(^tBuCO_2)$ (**VI**) [43, 44] and $(Et_3NH)[Co_6^{III}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}O_2C^tBu)_9(OH)_2(^tBuCO_2H)]$ (**VII**) [45].

Crystallographic data have been published for two carboxylates with the central core $Co_4^{II}Co_4^{III}(\mu_4\text{-}O)_4$. In both carboxylates, each Co(III) atom of the cubane unit is linked with the nearest three peripheral Co(II) atoms by three bidentate carboxylate bridges to form a highly symmetric (point group *T*) metal-containing framework $\{Co_8O_4(\mu\text{-}O_2CR)_{12}\}$ (Fig. 2c). Additional coordination of neutral ligands to four peripheral Co(II) atoms gives rise to their distorted trigonal bipyramidal environment. In the benzoate complex $[Co_8O_4(\mu\text{-}O_2CPh)_{12}(H_2O)(MeCN)_3]$ [46, 47], the neutral ligands are water and three acetonitrile molecules; in the isobutyrate complex $[Co_8O_4(\mu\text{-}O_2CPr^i)_{12}(Pr^iCO_2H)_4]$ [22], these are four molecules of isobutyric acid.

Complexes with the central core $Co_4^{II}Co_4^{III}(\mu_4\text{-}O)_4(\mu_3\text{-}OH/OMe)_4$. The molecular structure of these complexes contains the cubane unit $Co_4^{III}(\mu_4\text{-}O)_4$. Its bridging O atoms are bound to four Co(II) atoms, which are linked in pairs with each other and with the Co(III) atoms by four bridging methoxy or hydroxy groups (μ_3-X in Fig. 3). The resulting central core consists of three cubane units sharing two faces (a "étagère-like" central core). Six bridging bidentate carboxylate ligands are arranged around the core in a double helix pattern to form the framework $\{Co_8O_4X_4(\mu\text{-}O_2CR)_6\}$.

The formation of a first structurally characterized octanuclear complex with this central core, $[Co_8O_4(O_2CMe)_6(OH)_4(bis\text{-}Bipy)_2](ClO_4)_2$ (**VIII**) [48], was ensured, as emphasized by those authors, by the use of a chelating tetradentate ligand, viz., 1,2-*bis*-(2,2'-bipyridyl-6-yl)ethane (*bis*-Bipy). In structure **VIII**, the peripheral Co(II) atoms are linked in pairs by two such ligands, so their coordination polyhedron is a distorted octahedron. However, a second acetate complex, $[Co_8Cl_4O_4(O_2CMe)_6(OH_n)_4(OMe)_4]$ ($n = 1$ or 2) [11], was obtained without using any ligands that would form its oligonuclear structure. According to the X-ray diffraction data, the distorted octahedral geometry of the peripheral Co atoms in this complex is completed with such ligands as water, OH^- (*trans* to μ_3-OMe), and Cl^- (*trans* to μ_4-O). Neither the oxidation state of the cobalt atoms nor the Co(II) : Co(III) ratio was reported, although the complex was classified as mixed valent.

The acetate complexes $[Co_8O_4(O_2CMe)_6(OMe)_4(MeCO_2)_2(H_2O)_6]$ and $[Co_8O_4(O_2CMe)_6(OH)_4(MeCO_2)_2(H_2O)_6]$ were obtained from methanolic and ethanolic solutions of Ac-Co, respectively [15, 16]. Two ligands are additionally coordinated in a monodentate fashion to each of four peripheral Co(II) atoms (two water molecules for two Co(II) atoms and a water molecule and an acetate ion for their neighbors). Unlike all the other structurally characterized complexes with the étagère-like central core, which are formally racemates, the hydroxy-bridged complex $[Co_8O_4(O_2CMe)_6(OH)_4(MeCO_2)_2(H_2O)_6]$ is obtained as a racemic conglomerate (it crystallizes in the enantiomorphic space groups $P4_12_12$ and $P4_32_12$; both structures were identified). In the presence of HF, a methanolic solution of Ac-Co yields a more symmetrical complex of the electrolyte type, $[Co_8O_4(O_2CMe)_6(OMe)_4(H_2O)_8]F_2$ [20]. Each of its four peripheral Co(II) atoms coordinates two water molecules.

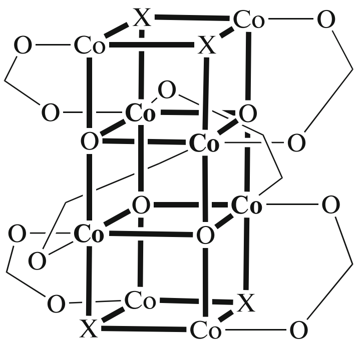

Fig. 3. Framework of the complexes with the central core $Co_4^{II}Co_4^{III}(\mu_4\text{-}O)_4(\mu_3\text{-}X)_4$, where X = OH^- or OMe^-.

Oxidation of Co(II) carboxylates with H_2O_2 in methanol gave the corresponding mixed valence carboxylates $[Co_8O_4(O_2CR)_6(OMe)_4(RCO_2)_2(H_2O)_6]$, where R = Et [49–52], Pr [50–52], Bu [49, 50], n-C_5H_{11} [50], and ^{i}Bu [53]. These complexes are structurally similar to the acetate analog.

The oxidation states proposed for the Co atoms in the complexes with the étagère-like central core were confirmed by the calculated sums of their bond valences.

The following trend is worth noting for the formation of supramolecular structures from complexes with the étagère-like central core. The carboxylates contain four solvate water molecules; each molecule is linked by intermolecular H bonds with one of four water molecules coordinated *trans* relative to the ligands μ_3-X and with one of four bridging ligands μ-O_2CR between the Co(III) and Co(II) atoms to form an eight-membered pseudoring. The only exception is complex **VIII**, in which the *bis*-Bipy molecules preclude such contacts. It is not improbable that the formation of pseudorings stabilizes the octanuclear structures of these complexes [52].

Complexes with the central core $Co_{8/10}^{II}Co_{6/4}^{III}(\mu_{5/4}\text{-}O)_2(\mu_3\text{-}O/OH)_2(\mu_3\text{-}OH)_{12}$. Structures with these central cores were found only in complexes with pivalate ligands. Their centrosymmetric cores consist of four cubane units Co_4O_4 sharing in pairs the Co(III)–O edges and the Co(III) vertices (Fig. 4).

The central core $Co_8^{II}Co_6^{III}(\mu_5\text{-}O)_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_{12}$ (Fig. 4a) was found in three complexes of the general formula $[Co_{14}O_4(\mu\text{-}O_2C^tBu)_8(O_2C^tBu)_6(OH)_{12}(^tBuCO_2H)_2(L)_8]$, where $(L)_8$ is

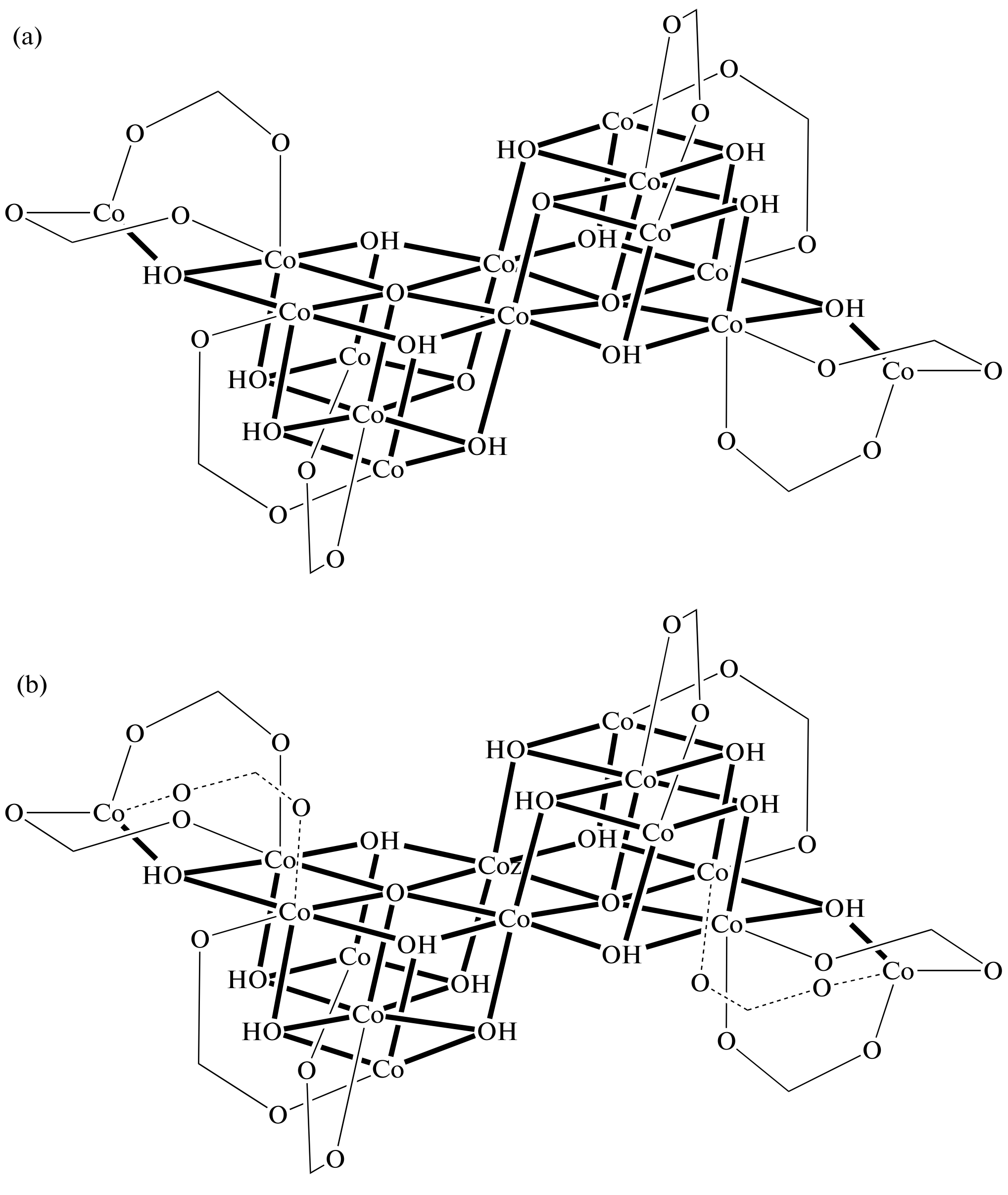

Fig. 4. Frameworks of the complexes with the central cores $Co_8^{II}Co_6^{III}(\mu_5\text{-}O)_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_{12}$ (a) and $Co_{10}^{II}Co_4^{III}(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_{14}$ (b).

$(H_2O)_6(MeCN)_2$ [38], $(H_2O)_8$, and $(H_2O)_4(EtOH)_4$ [19].

As with hexanuclear pivalates **VI** and **VII**, the 14-nuclear complex with a central core topologically similar to those under discussion was identified as a homovalent Co(III) complex, $[Co_{14}^{III}O_4(\mu\text{-}O_2C^tBu)_8(O_2C^tBu)_{10}(OH)_{12}(OH)_4]$ [43, 44].

The central core $Co_{10}^{II}Co_4^{III}(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_{14}$ (Fig. 4b) was found in the complex $[Co_{14}(Hfac)_4O_2(\mu\text{-}O_2C^tBu)_{10}(OH)_{14}(^tBuCO_2H)_4]$ (Hfac is hexafluoroacetylacetonate, **IX**) and in a series of products obtained in reactions of **IX** with various nitroxides: $[Co_{14}(Hfac)_4O_2(\mu\text{-}O_2C^tBu)_8(O_2C^tBu)_2(OH)_{14}(H_2O)_4(NIT)_2]$ (NIT is 4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl, **X**), $[Co_{14}(Hfac)_4O_2(\mu\text{-}O_2C^tBu)_{10}(OH)_{14}(^tBuCO_2H)_2(H_2O)_2]$, and $[Co_{14}(Hfac)_4O_2(\mu\text{-}O_2C^tBu)_{10}(OH)_{14}(^tBuCO_2H)_4]$ (four complexes with the same composition of the inner sphere; these are topologically identical with parent complex **IX**) [54]. Structure **X** has two less pivalate bridges (shown dashed in Fig. 4b) compared to the other complexes.

The final group of the mixed valence carboxylates reviewed here is constituted by reaction products obtained from 14-nuclear pivalate complex **IX** in the

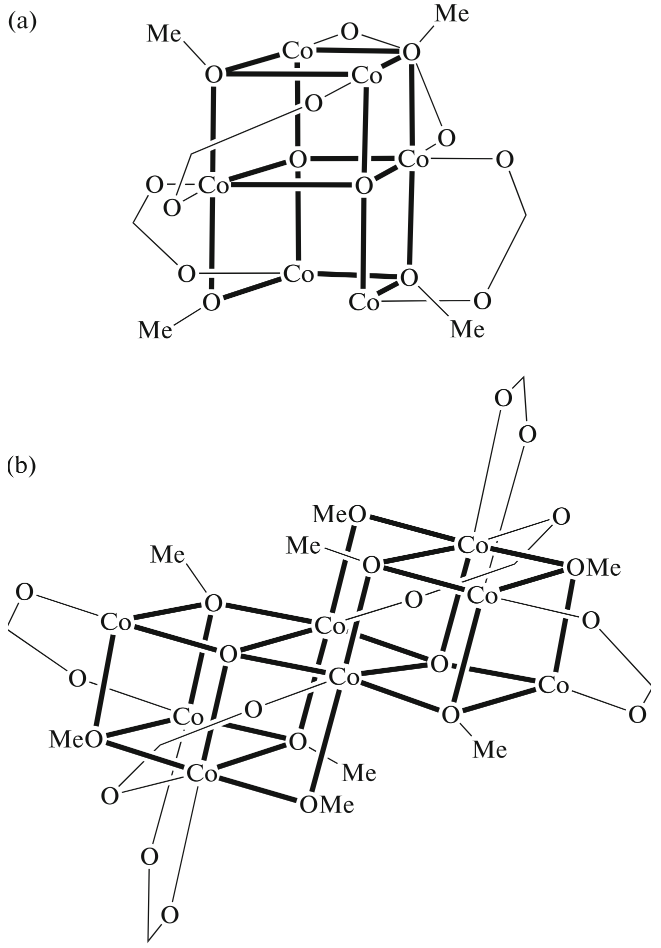

Fig. 5. Frameworks of complexes **XI** (a) and **XII** (b) [54].

presence of methanol: $[Co_3^{II}Co_3^{III}(Hfac)(\mu_4\text{-}O)_2(\mu\text{-}O_2C^tBu)_4(O_2C^tBu)_2(\mu_3\text{-}OMe)_4(H_2O)(MeOH)_2]$ (**XI**) and $[Co_4^{II}Co_4^{III}(Hfac)_2(\mu_4\text{-}O)_2(\mu\text{-}O_2C^tBu)_6(\mu_3\text{-}OMe)_8(MeOH)_2]$ (**XII**) [54]. The metal-containing frameworks of these complexes are shown in Fig. 5. It is easy to see that the framework of centrosymmetric complex **XII** is topologically identical with a part of the central core in parent complex **IX** (Fig. 4b) and that the framework of complex **XI**, in turn, is topologically identical with a part of the framework in octanuclear complexes with the central core $Co_4^{II}Co_4^{III}(\mu_4\text{-}O)_4(\mu_3\text{-}X)_4$ (Fig. 3).

HOMOVALENT CARBOXYLATES

Complexes with the central core $Co_2^{III}(\mu\text{-}OH)_2$. For Co(III) carboxylates, two versions of the binuclear core are known: $\{Co_2(OH)_2(\mu\text{-}O_2CR)\}$ and $\{Co_2(OH)_2(\mu\text{-}O_2CR)_2\}$ (Fig. 6).

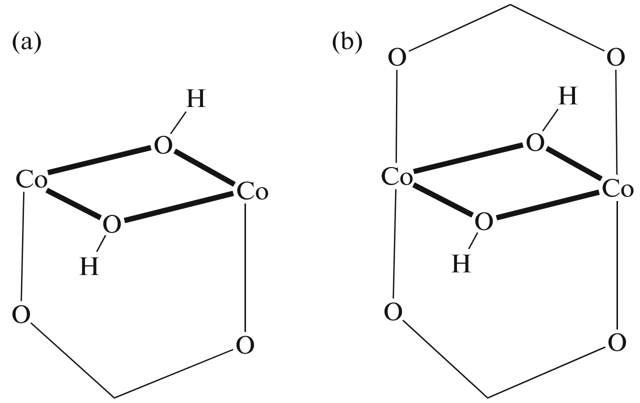

Fig. 6. Frameworks of the complexes with the central core $Co_2^{III}(\mu\text{-}OH)_2$: $\{Co_2(OH)_2(\mu\text{-}O_2CR)\}$ (a) and $\{Co_2(OH)_2(\mu\text{-}O_2CR)_2\}$ (b).

The former version was found in the cations of the complexes $[Co_2(\mu\text{-}O_2CMe)(OH)_2(NH_3)_6]Br_3$ [55], $[Co_2(\mu\text{-}O_2CC_4N_2H_4)(OH)_2(NH_3)_6](ClO_4)_4$ ($O_2CC_4N_2H_4$ is pyrimidine-5-carboxylic acid) [56], $[Co_2(\mu\text{-}O_2CMe)(O_2CMe)_2(OH)_2(Py)_4]PF_6$ [57], and $[Co_2(\mu\text{-}O_2CMe)(O_2CMe)_2(OH)_2(Bipy)_2]ClO_4$ (Bipy is 2,2'-bipyridyl) [58]. The latter version was found in the cations of two complexes $[Co_2(\mu\text{-}O_2C^tBu)_2(OH)_2(HDmpz)_4](CF_3SO_3)_2$ (HDmpz is 3,5-dimethylpyrazole) containing different solvate molecules [59, 60]. The octahedral environment of the Co(III) atoms is completed with acetate ions (coordinated in a monodentate fashion), ammonia molecules, and *N*-heterocyclic aromatic molecules (Py, Bipy, or HDmpz).

Complexes with the central core $Co_3^{III}(\mu_3\text{-}O)(\mu\text{-}OH/OMe)_2$. Only two acetate complexes containing the framework $\{Co_3O(OH/OMe)_2(\mu\text{-}O_2CMe)_3\}$ have been structurally characterized: $[Co_3O(\mu\text{-}O_2CMe)_3(OH)_2(Py)_5](PF_6)_2$ (**XIII**, Fig. 7a) [57] and $[Co_3O(\mu\text{-}O_2CMe)_3(OH)(OMe)(Py)_5](ClO_4)_2$ (**XIV**, Fig. 7b) [14]. The octahedral geometry of the Co(III) atoms is completed with pyridine molecules.

Complexes with the central core $Co_3^{III}(\mu_3\text{-}O)$. The trinuclear framework $\{M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6\}$ is widespread in metal(III) carboxylates [61, 62] (Fig. 8a). Homonuclear Co(III) complexes of this type are relatively few.

First crystallographic data (space group, unit cell parameters, and selected average bond lengths) for a Co(III) complex with this core, $[Co_3O(O_2C^tBu)_6(4\text{-}MePy)_3](^tBuCO_2)$ (4-MePy is 4-methylpyridine), were published in [63]. However, the coordinates of its basic atoms were missing. For cobalt carboxylates with the complex cations $[Co_3O(O_2CMe)_6(Py)_3]^+$ [64] and

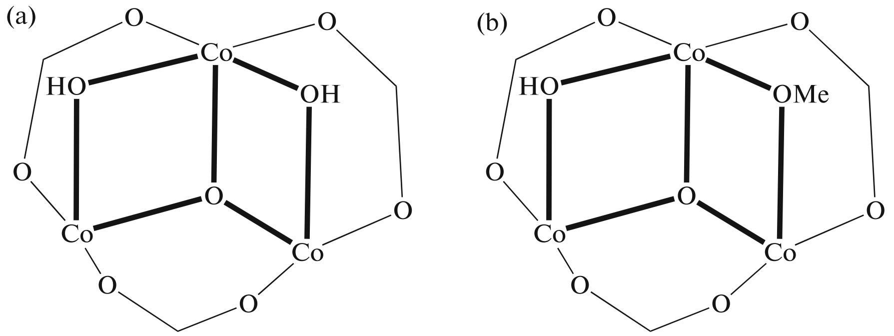

Fig. 7. Frameworks of the complexes with the central core $Co_3^{III}(\mu_3\text{-}O)(\mu\text{-}OH/OMe)_2$: **XIII** (a) and **XIV** (b).

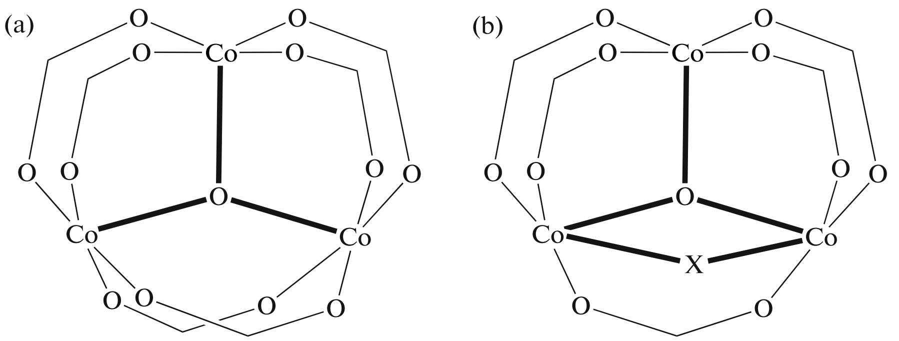

Fig. 8. Frameworks of the complexes with the central cores $Co_3^{III}(\mu_3\text{-}O)$ (a) and $Co_3^{III}(\mu_3\text{-}O)(\mu\text{-}X)$, where $X = OH^-$ or OR'^- (b).

$[Co_3O(O_2C^tBu)_6(Py)_3]^+$ (three complexes) [38, 65, 66], more detailed information is available. In these complexes, the molecules of *N*-heterocyclic bases are coordinated to the Co(III) atoms, coming *trans* to the bridging μ_3-O atom (in the apical positions), to form distorted octahedra around the metal centers.

From the standpoint of reactivity, the complexes $[Co_3O(O_2CMe)_6(H_2O)_3]NO_3$ [21] and $[Co_3O(O_2CCF_3)_6(H_2O)_3]NO_3$ [23] both containing water molecules in the apical positions are of interest. The acetate complex is obtained when Ac-Co is treated with HNO_3. Apparently, the anion NO_3^-, stabilizes the cation $[Co_3O(O_2CMe)_6(H_2O)_3]^+$ in the solid state, which is evident from the different colors of the solution of Ac-Co (green) and the resulting crystalline product (brown) as well as from the high yield of the latter. The green mother liquor seems to predominantly contain the precursors of the trinuclear complex $[Co_3O(O_2CMe)_6(H_2O)_3]^+$ rather than the trinuclear cation itself.

The complex cations $[Co_3O(O_2CR)_6(L)_3]^+$ feature distorted molecular structures because of the arrangement of their carboxylate ligands: in each carboxylate anion, one O atom is close to, while the other O atom is distant from, the plane $Co_3(\mu_3\text{-}O)$. These distortions reduce the idealized symmetry of the complex cations from D_{3h} to D_3. We analyzed the causes of these distortions using quantum chemical DFT calculations (B3LYP/631G**) of the electronic structure of the model cation $[Co_3O(O_2CMe)_6(H_2O)_3]^+$ [21]. This model cation has much the same structure of the cation characterized by X-ray diffraction. In particular, the model structure retains a distorted conformation with symmetry D_3. The results of the calculations suggest that the distortions of the molecular structures of the complex cations $[Co_3O(O_2CR)_6(L)_3]^+$ can be due to partial elimination of the strains associated with the distorted octahedral environment of the Co(III) atoms. These strains can be responsible for the increased lability of the bridging carboxylate ligands in $[Co_3O(O_2CR)_6(L)_3]^+$. Later, we calculated the cation $[Co_3O(O_2CMe)_6(H_2O)_3]^+$ using a more recent DFT procedure (M06/def2-TZVP). According to our calculations, the optimized geometry of this complex cation nearly completely agrees with the X-ray diffraction data.

A distinctive feature of cobalt carboxylates with the framework $\{Co_3O(O_2CR)_6\}$ is that almost all of them (except for **XVI**, see below) are homovalent Co(III) complexes, whereas most other *d* metals can form mixed valence carboxylates $[M^{II}M_2^{III}O(O_2CR)_6(L)_3]$ as well. In connection with this, it is interesting to compare oxidation products of two related carboxyl-

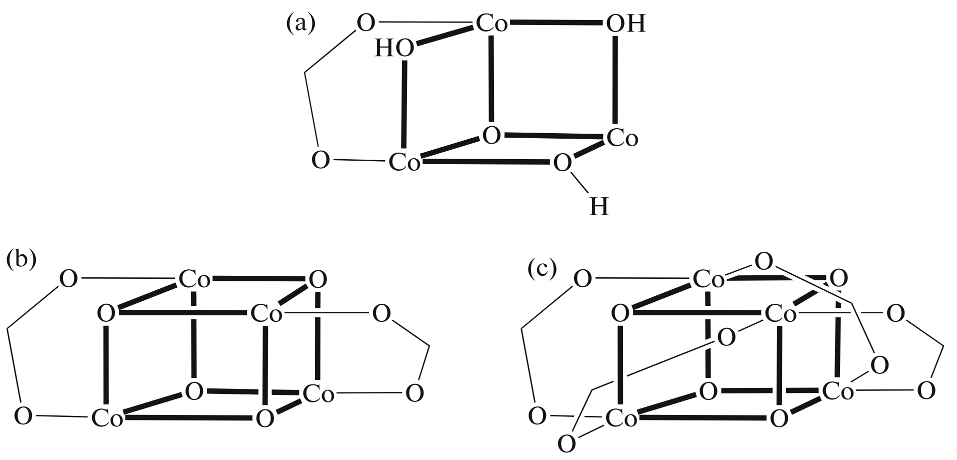

Fig. 9. Frameworks of the complexes with the central cores $Co^{III}_3(\mu_3\text{-}O)(\mu\text{-}OH)_3$ (a) and $Co^{III}_4(\mu_3\text{-}O)_4$ (b, c).

ates $[Co^{II}_2(O_2C^tBu)_4(^tBuCO_2H)_2(OH_2)(Py)_2]$ and $[Co^{II}_2(O_2C^tBu)_4(^tBuCO_2H)_4(OH_2)]$: only oxidation of the former, pyridine-containing complex with atmospheric oxygen yields the homovalent complex $[Co^{III}_3O(O_2C^tBu)_6(Py)_3](^tBuCO_2)$, while oxidation of the latter complex with stronger oxidants (H_2O_2, $KMnO_4$, *tert*-butyl peroxide, or $K_2Cr_2O_7$) gives mixed valence carboxylates [38].

The structures of the trinuclear complexes $[Co_3O(O_2C^tBu)_6(MeOH)_3]Cl$ (**XV**) [67] and $[Co_3O(O_2CMe)_6(H_2O)_3]$ (**XVI**) [68] are worth noting: the Co–O bond lengths are appreciably longer than those typical of all the other complexes $[Co_3O(O_2CR)_6(L)_3]^+$ and rather correspond to the Co(II)–O bonds (according to the calculated sums of the bond valences) even with allowance for the mixed valence composition of complex **XVI**. The color of the complexes (red and dark pink) as well as the absence of an oxidant but atmospheric oxygen in the synthesis of **XV** is also indicative of the oxidation state of Co(II).

Complexes with the central core $Co^{III}_3(\mu_3\text{-}O)(\mu\text{-}OH/OR')$. The trinuclear Co(III) carboxylates $[Co_3O(O_2CR)_6(L)_3]^+$ tend to replace one of their six bridging carboxylate ligands by a bridging hydroxy or alkoxy group [10, 57]. The framework $\{Co^{III}_3(\mu_3\text{-}O)(\mu\text{-}OH/OR')(\mu\text{-}O_2CR)_5\}$ of the resulting products is shown in Fig. 8b. Complexes **I** and $[Co_3O(OCH_2CH_2CH_2Ph)(O_2CMe)_5(Py)_3]PF_6$ were structurally characterized in [10]. Note that the framework of these complexes is topologically identical with a part of the framework of pivalate complexes with the central core $Co^{II/III}_2Co^{III}_2(\mu_3\text{-}O/OH)(\mu_3\text{-}OH)$ (Fig. 1c).

Complexes with the central core $Co^{III}_4(\mu_3\text{-}O)_4$. The so-called cubane (also referred to as “heterocubane” or “pseudocubane”) unit $Co^{III}_4(\mu_3\text{-}O)_4$ (Figs. 9b, 9c) is the most prevalent core in the structurally characterized Co(III) carboxylates. The same core is part of the central cores in mixed valence carboxylates (Figs. 2, 3).

The central core $Co^{III}_3(\mu_3\text{-}O)(\mu\text{-}OH)_3$ (Fig. 9a), which is related to the cubane unit $Co^{III}_4(\mu_3\text{-}O)_4$, was found in the complexes $[Co_3O(\mu\text{-}O_2CMe)(O_2CMe)(OH)_3(Bipy)_3](ClO_4)_2$ [58] and $[Co_3O(\mu\text{-}O_2CMe)(O_2CMe)(OH)_3(Py)_6](PF_6)_2$ [13]. The octahedral environment of the Co(III) atoms is completed with the acetate ions and the 2,2'-bipyridyl or pyridine molecules.

The cubane unit is present in two framework versions found in Co(III) carboxylates: $\{Co_4O_4(\mu\text{-}O_2CR)_2\}$ (Fig. 9b) and $\{Co_4O_4(\mu\text{-}O_2CR)_4\}$ (Fig. 9c), in which two or four bridging carboxylates are opposite each other in pairs. The cobalt complexes with two carboxylate ligands include $[Co_4O_4(O_2CC_6H_4(p\text{-}Me))_2(Bipy)_4](ClO_4)_2$ [58], $[Co_4O_4(O_2CCF_3)_2(Py)_8](ClO_4)_2$ [17], and $[Co_4O_4(O_2CMe)_2(DpaH)_4]_2(V_4O_{12})$ (DpaH is 2,2'-dipyridylamine) [69]. Those containing four carboxylate ligands include $[Co_4O_4(O_2CMe)_4(Py)_4]$ (three complexes) [13, 70, 71], $[Co_4O_4(O_2CMe)_4(4\text{-}MePy)_4]$ [71], $[Co_4O_4(O_2CPh)_4(Py)_4]$ (two complexes) [72, 73], and $[Co_4O_4(O_2CPh)_4(4\text{-}MePy)_4]$ [73]. The octahedral environment of the Co(III) atoms is completed with the molecules of *N*-heterocyclic bases.

The bridging μ_3-O atoms of the cubane units in Co(III) carboxylates can be protonated. Interestingly, this was proved by X-ray diffraction studies of some protonation products: $[Co_4O_3(O_2CC_6H_4(p\text{-}Me))_2(OH)(Bipy)_4][Ce^{III}(NO_3)_6]$ [46, 74], $[Co_4O_2(O_2CC_6H_4(p\text{-}OMe))_2(OH)_2(Bipy)_4](ClO_4)_4$ [74], and $[Co_4O_3(O_2CMe)_4(OH)(Py)_4]^+$ (two complexes) [75].

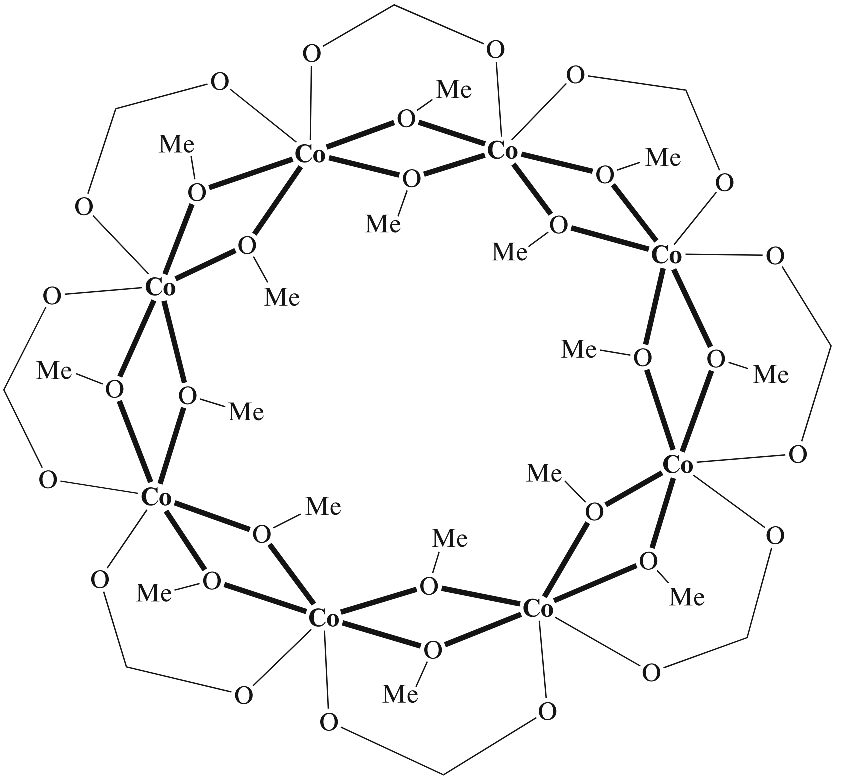

Fig. 10. Framework of complex **XVII** [12].

Another remarkable feature of Co(III) carboxylates containing the cubane unit is a tendency toward one-electron oxidation, with their molecular structures remaining unchanged. The formation of mixed valence products was confirmed by X-ray diffraction data for the complexes $[Co_3^{III}Co^{IV}O_4(O_2CC_6H_4(p\text{-}NO_2))_2(Bipy)_4](ClO_4)_3$ [76], $[Co_3^{III}Co^{IV}O_4(O_2CMe)_4(Py)_4]PF_6$ [75], and $[Co_3^{III}Co^{IV}O_4(O_2CMe)_4(Py)_4]ClO_4$ [77].

Complex with the central core Co_8^{III} $(\mu\text{-}OMe)_{16}$. A toroidal core (Fig. 10) was found only in the cobalt(III) acetate complex $[NH_4][Co_8(\mu\text{-}O_2CMe)_8(OMe)_{16}]PF_6$ (**XVII**) obtained by a reaction between Ac-Co and NH_4PF_6 in methanol [12]. This complex is a rare example of homovalent Co(III) carboxylates containing no coordinated N-donating ligands. The NH_4^+ cation is centrally housed in the host molecule of $[Co_8(\mu\text{-}O_2CMe)_8(OMe)_{16}]$ and is coplanar with eight Co(III) atoms.

When analyzing the current state of the art in the investigations of oligonuclear carboxylate complexes of Co(II, III) and Co(III), one can conclude that mixed valence complexes show an appreciably wider structural diversity compared to homovalent Co(III) complexes. The core topology of mixed valence carboxylates depends on the steric properties of carboxylate ligands. However, this factor still remains poorly studied since the attention of researchers has been mainly focused on pivalate complexes.

To sum up, we can draw some special conclusions: (1) the oxidation of Co(II) carboxylates depends on the presence of N-donating ligands in the system: when these are absent, the oxidation predominantly yields mixed valence products, even with excess oxidant; otherwise, homovalent Co(III) complexes are formed; (2) all mixed valence carboxylates show valence-trapping: the Co(III) atoms are central in the metal-containing framework of their molecular structures, while the Co(II) atoms are peripheral; (3) pyridine and related N-heterocyclic bases favor the fragmentation of mixed valence complexes into homovalent products; (4) homovalent Co(III) carboxylates are mostly complexes stabilized by N-donating ligands.

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