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# New type of compounds based on s- and d-block metal trimethylacetates*

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Heterometallic compounds based on alkali (Li, Na, K, Rb, or Cs) trimethylacetates and transition metal (Cu or Co) trimethylacetates were synthesized. These compounds are characterized by a larger number of s-block atoms compared to d-block atoms. An excess alkali metal trimethylacetate in the reaction system leads to the formation of unusual polymeric systems containing alternating s- and d-block atoms.

**Key words:** alkali metals, transition metals, trimethylacetate, polymers, X-ray diffraction analysis.

Trimethylacetate (pivalate) anions (Piv) are of considerable interest as ligands providing high solubility of their complexes with transition metals in organic solvents. These complexes have attracted attention as components of homogeneous catalytic systems and as starting matrices for metal transport to the surface of substrates.[1—5] The reactions of polynuclear metal trimethylacetates with paramagnetic organic compounds can initiate self-assembly of magnetoactive heterospin high-dimensional structures.[6—11] The trimethylacetate anion is widely used as a ligand for the synthesis of polynuclear transition metal compounds.[12,13] The Cambridge Structural Database contains hundreds of structures of such compounds, including heterometallic complexes.[14] However, data on complexes containing simultaneously s- and d- or f-block elements in polynuclear structures are scarce, and data on structures of polynuclear compounds containing predominantly an s-block element are lacking. Recently, we have described[15] the synthesis and structures of two first compounds of this type, $[K_6Cu_2Piv_{10}(HPiv)(H_2O)_2(THF)]\cdot 2THF$ and $[K_3Co_2Piv_7(THF)_3]$. Further studies demonstrated that potassium is not the only alkali metal capable of forming such phases, and the already-known compounds belong in fact to a specific family of heterometallic complexes, which have formula units with a larger number of alkali metal atoms compared to transition metal atoms. In the present study, we synthesized and structurally characterized a large group of new heterometallic compounds based on alkali metal (Li, Na, K, Rb, or Cs) and transition metal (Cu or Co) trimethylacetates belonging to this family (Table 1).

**Table 1.** Compositions of the resulting compounds and the polymeric structural motifs

| Compound | Motif |
|---|---|
| $[Li_2CuPiv_4]$ (**1**) | Chain |
| $[Na_5Cu_2Piv_9(HPiv)(H_2O)_2EtOAc]\cdot EtOAc$ (**2**) | Chain |
| $[K_6Cu_2Piv_{10}(HPiv)_3(EtOH)]$ (**3**) | Chain |
| $[Rb_4Cu_3\ Piv_8(OH)_2(EtOH)_6]$ (**4**) | Chain |
| $[Cs_2CuPiv_4(H_2O)]$ (**5**) | Framework |
| $[Li_7Co_2Piv_{11}(HPiv)_2]$ (**6**) | Chain |
| $[Li_{13}Co_2Piv_{17}(H_2O)_2]\cdot 2THF$ (**7**) | Chain |
| $[Na_{21}Co_{14}Piv_{49}(THF)_{17}(H_2O)_6]$ (**8**) | Chain |
| $[K_3Co_2Piv_7(H_2O)_2]$ (**9**) | Layer |
| $[Rb_3Co_2Piv_7(THF)(H_2O)]$ (**10**) | Layer |
| $[CsCoPiv_3(H_2O)]$ (**11**) | Layer |

The formulas and the structural motifs of the resulting compounds are listed in the order of increasing atomic number of alkali metal (see Table 1). There are the following main statements, which are confirmed below by experimental evidence.

1. In most of the compounds, the number of s-block atoms is larger than the number of d-block atoms.

2. Structures of the polymers contain neither lantern-type fragments typical of dimeric $Cu^{II}$ monocarboxylates nor fragments of classical polynuclear $Co^{II}$ trimethylacetates, for which the general topology was developed.[5]

3. Increase in the ionic radius leads to an increase in the dimensionality of the polymeric structures of compounds containing simultaneously alkali and transition

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metals (chain (**1—8**), layer (**9—11**), or framework (**5**)). This tendency is indirectly associated with the fact that an increase in the ionic radius leads to an increase in the number of donor atoms, which can surround the metal ion and, consequently, to an increase in the number of the adjacent ions, to which the metal ion can be linked through bridging coordination of ligands.

It is worthwhile to compare Table 1 with Table 2, which gives data from the Cambridge Structural Database[14] on the ratios of s- to d- or f-block elements and the structural motifs in the known heterometallic carboxylates of s- and d- or f-block elements. We do not consider complexes with organic ligands containing additional functional groups with the donor N, P, O, S, *etc.* atoms along with the carboxy group.

An analysis of the published data[16—29] shows that, from time to time, different research groups published data on carboxylates containing simultaneously alkali and transition metals. As can be seen from the first and second columns in Table 2, these are primarily acetates or trimethylacetates (11 entries of 16) containing transition metals along with K or Na atoms (13 entries of 16). It can be concluded that no systematic studies have been carried out in this field, although such studies are of importance not only from the fundamental but also from the practical point of view. In many cases, it is important to know the compositions of phases crystallizing from viscous saturated solutions of transition metal carboxylates and understand why an increase in the concentration of alkali metal carboxylate can lead to an increase in the solubility of transition metal carboxylate, which is simultaneously present in the system.[20] The second column in Table 2 shows that examples of compounds, in which the number s-block atoms is larger than the number of d-block atoms ($Na_4Zn_2$, $Na_2Cu$, $Li_2Cd$, $Na_2Zn$, or $Li_2Zn$), are rather rare. Data on trimethylacetates, which are at the focus of the present study, are lacking.

**Table 2.** Stoichiometric ratios of the s- and d- or f-block elements and the structural motifs in known heterometallic carboxylates

| Carboxylate | Ratio $s^1$/d or f* | Motif | Reference |
|---|---|---|---|
| AcO | $NaRh_2$ | Chain | 16 |
| | $\mathbf{Na_4Zn_2}$ | Layer | 17 |
| | $\mathbf{Na_2Cu}$ | Layer | 18 |
| | $NaCu_2$ | Layer | 19 |
| | $K_2Co_3$ | Layer | 20 |
| | RbLa | Framework | 21 |
| $Bu^tCOO$ | $KFe_3$ | Molecular | 22 |
| | $K_2Fe_4$ | Molecular | 23 |
| | $K_2Mn_9$ | Molecular | 24 |
| | $Na_2Fe_4$ | Molecular | 1 |
| | $KFe_2$ | Chain | 23 |
| PhCOO | $Na_2Mn_9$ | Molecular | 25 |
| EtCOO | $\mathbf{Li_2Cd}$ | Layer | 26 |
| HCOO | $NaRh_2$ | Layer | 27 |
| $C_5H_{11}COO$ | $\mathbf{Na_2Zn}$ | Chain | 28 |
| $C_3H_5COO$ | $\mathbf{Li_2Zn}$ | Chain | 29 |

* Compounds in which the number of s-block atoms is larger than the number of d-block atoms are printed in bold.

The present study fills the gap concerning trimethylacetates as well as calls attention to the fact that such compounds can contain s- and d-block elements not only in a stoichiometric ratio of 2 : 1 (all compounds printed in bold in the second column of Table 2 belong to this group) but also in other ratios. This is confirmed by the fact that, along with the stoichiometric ratios of 1 : 1 and 2 : 1, we also found the ratios of 1.5 : 1, 2.5 : 1, 3 : 1, 3.5 : 1, and 6.5 : 1 for trimethylacetates (see Table 1). In addition, as can be seen from Table 2, although compounds containing a larger number of alkali metal atoms compared to transition metal atoms are known for different carboxylates, no variations in the nature of alkali metal were found in a series of derivatives with the same monocarboxylate. For this reason, in the present study we used solely $OOCCMe_3$ (Piv) as the carboxylate ligand and varied the nature of alkali metal (Li, Na, K, Rb, or Cs). We used $Cu^{II}$ or $Co^{II}$ as transition metals. We found that the above-mentioned statements 1—3 are true for compounds containing both $Cu^{II}$ and $Co^{II}$. Presumably, these statements have a general character and are independent of the nature of transition metal used for the synthesis of compounds belonging to the family of interest.

Alkali metal trimethylacetates (MPiv), which are necessary for the synthesis of heterometallic complexes, were prepared by the reactions of equivalent amounts of trimethylacetic acid and the corresponding metal hydroxide. Then the reactions of copper or cobalt chloride with MPiv were carried out by varying the $CuCl_2$ : MPiv or $CoCl_2$ : MPiv molar ratio from 1 : 2 to 1 : 10 under optimal conditions chosen for each alkali metal. These optimal conditions implied that, after separation of MCl precipitates from the reaction mixture, heterometallic compounds were reproducibly isolated from the mother liquors predominantly as high-quality single crystals suitable for X-ray diffraction study, while crystallization of excess metal trimethylacetate did not start. The presence of crystallization solvent molecules, coordinated solvent molecules, or coordinated $HOOCCMe_3$ molecules in the solid phase of many compounds under study decreased kinetic stability of crystals and complicated X-ray diffraction study. Some of these crystals, for example, the crystals of compounds **6**, **7**, or **8**, began to decompose within a few seconds after separation from the mother liquor. To prevent the loss of quality of single crystals, crystals (before X-ray diffraction study) were taken with a drop of the mother liquor and immersed in a drop of a perfluorinated oil. Then the single crystals were rapidly transferred with the use of a needle to the oil, where they retained the quality suitable for X-ray diffraction.

## Structures of compounds

**Compound [$Li_2CuPiv_4$] (1).** This compound was prepared by the reaction of LiPiv with $CuCl_2 \cdot 2H_2O$ using different initial $CuCl_2$ : LiPiv molar ratios (1 : 5—1 : 10) followed by crystallization from different solvents (THF or EtOH). The solid phase [$Li_2CuPiv_4$] consists of polymeric chains, in which each Cu atom alternates with two lithium atoms (Fig. 1, *a*). The O atoms of the $\mu_3$-trimethylacetate anions form a square environment about the Cu atoms and a distorted tetrahedral environment about the Li atoms. As a result, the coordination units {$CuO_4$} in the solid phase are separated by the double tetrahedra {$Li_2O_6$} (Fig. 1, *b*). The Cu—O and Li—O distances are in the ranges of 1.995(5)—2.008(5) and 1.95(1)—2.04(1) Å, respectively (Table 3).

**Compound [$Na_5Cu_2Piv_9(HPiv)(H_2O)_2EtOAc$] · EtOAc (2).** Compound **2** was prepared by the reaction of NaPiv with $CuCl_2 \cdot 2H_2O$ in ethanol using the initial molar ratio of 1 : 5 followed by crystallization from EtOAc. The reaction with the use of THF instead of EtOAc afforded [$Na_5Cu_2Piv_9(HPiv)(H_2O)_2THF$] · THF as the solid phase. However, the yield of the product prepared by the reaction in THF is lower and the quality of the crystals is much poorer than that required for X-ray diffraction. Since the motif of the polymeric chain in the structure of this compound is exactly identical to that of compound **2**, we described only the structure of the latter compound.

The coordination environment of each Cu atom in the structure of compound **2** can be described as a distorted square (Fig. 2) formed by the O atoms of the bridging trimethylacetate anions; the Cu—O distances are in the range of 1.938(5)—2.039(6) Å. The coordination environment of the Na atoms is formed by four—six O atoms of the trimethylacetate anions and the $H_2O$, $HOOCCMe_3$, and EtOAc molecules. In the heterometallic polymeric

**Table 3.** Principal crystallographic characteristics, the X-ray data collection and refinement statistics, and selected bond lengths for copper-containing compounds **1**—**5**

| Parameter | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| *T*/K | 240 | 200 | 298 | 298 | 240 |
| Molecular weight | 481.91 | 1466.50 | 1725.36 | 1651.90 | 751.86 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | *C*2/*c* | *Ia*-3*d* |
| *a*/Å | 5.755(7) | 13.177(2) | 14.9606(9) | 19.211(4) | 34.795(4) |
| *b*/Å | 11.163(13) | 13.767(2) | 24.912(2) | 21.221(4) | |
| *c*/Å | 11.420(14) | 22.834(3) | 28.323(2) | 19.790(4) | |
| α/deg | 111.09(2) | 87.494(3) | 70.822(1) | | |
| β/deg | 90.55(2) | 78.530(2) | 80.308(1) | 100.62(3) | |
| γ/deg | 90.10(2) | 83.528(2) | 81.912(1) | | |
| $V$/Å$^3$ | 684.5(14) | 4032.8(9) | 9787(1) | 7930(3) | 42125(8) |
| *Z* | 1 | 2 | 4 | 4 | 48 |
| $D_c$/g cm$^{-3}$ | 1.169 | 1.208 | 1.171 | 1.384 | 1.423 |
| μ(Mo-Kα)/mm$^{-1}$ | 0.832 | 0.621 | 0.751 | 3.298 | 2.699 |
| θ/deg | 1.96—23.60 | 0.91—23.32 | 0.77—23.69 | 1.44—23.65 | 2.19—23.37 |
| Number of reflections, $I_{hkl}$ measured/independent | 5214/2011 | 31195/11589 | 77073/28680 | 30124/5827 | 153824/2563 |
| $R_{int}$ | 0.1717 | 0.1197 | 0.2256 | 0.0918 | 0.1687 |
| *N* | 161 | 922 | 2078 | 427 | 165 |
| *GOOF* | 0.943 | 0.988 | 0.690 | 0.912 | 0.821 |
| $R_1$ | 0.0758 | 0.0828 | 0.0738 | 0.0428 | 0.0381 |
| $wR_2$ ($I > 2\sigma_I$) | 0.1788 | 0.2039 | 0.1847 | 0.1067 | 0.1066 |
| $R_1$ | 0.0874 | 0.1386 | 0.1886 | 0.1006 | 0.0616 |
| $wR_2$ [a] | 0.1900 | 0.2270 | 0.2506 | 0.1360 | 0.1228 |
| s-O [b] | 1.95(1)—2.04(1) | 2.241(6)—2.874(8) | 2.601(6)—2.995(4) | 2.832(5)—3.253(4) | 3.021(4)—3.415(3) |
| *n* [c] | 3—4 | 4—6 | 6 | 7 | 8 |
| d-O [b] | 1.995(5)—2.008(5) | 1.938(5)—2.039(6) | 1.923(4)—1.972(4) | 1.896(4)—1.961(4)<br>Cu...Cu 2.892(2) | 1.975(4)—1.976(4) |
| s—d [b] | 3.12(1)—3.28(1) | 3.093(4)—3.421(2) | 3.424(2)—3.564(2) | 3.465(1)—3.692(1) | 3.9387(7)—4.1167(7) |
| s—s [b] | 2.80(2) | 3.202(5)—3.363(3) | 3.723(2)—3.994(2) | 4.114(1) | 4.2573(8) |

[a] Based on all reflections.

[b] s and d are s- and d-block atoms, respectively.

[c] The number of O atoms in the environment of the s-block element.

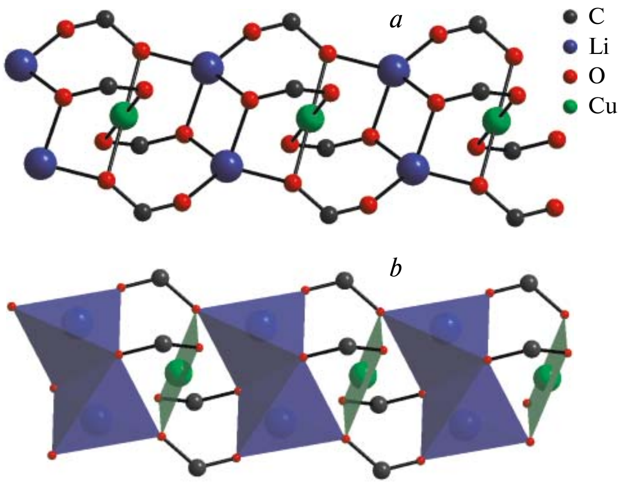

**Fig. 1.** Fragment of the structure of **1** (*a*) and the alternation of $\{CuO_4\}$ squares and $\{Li_2O_6\}$ double tetrahedra (*b*). Hereinafter, the $CMe_3$ groups of the trimethylacetate anions are omitted.

*Note*. Figures 1—10 are available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

chain, the Cu atoms successively alternate with two or three Na atoms. Since the ionic radius of Na is larger than that of Li, the coordination environment of Na involves the larger number of O atoms (six for Na and four for Li; see Table 3).

**Compound $[K_6Cu_2Piv_{10}(HPiv)_3(EtOH)]$ (3).** Earlier,[12] we have reported the synthesis and the structure of the $[K_6Cu_2Piv_{10}(HPiv)(THF)(H_2O)_2]\cdot 2THF$ complex. The reaction with the use of EtOH instead of THF afforded structurally very similar compound **3** in high yield. The crystals of this compound consist of zigzag chains (Fig. 3). In the chains, each Cu atom alternates with three K atoms.

**Compound $[Rb_4Cu_3Piv_8(OH)_2(EtOH)_6]$ (4).** In the RbPiv—$CuCl_2\cdot 2H_2O$ system, the reaction with the use of the $CuCl_2$ : RbPiv ratio of 1 : 5 in EtOH produced high-quality single crystals of a heterometallic compound of the above-mentioned composition. The solid phase is formed by zigzag chains, in which two Rb atoms successively alternate with one or two Cu atoms (Fig. 4, *a*). Unlike the above-mentioned compounds, compound **4** is characterized (for unclear reasons) by the presence of two $\mu_3$-OH groups, which link two Cu atoms and one Rb atom. The nearly square-planar environment of each Cu atom is formed by the O atoms of the trimethylacetate anions and the hydroxy groups; the Cu—O distances are in the range of 1.896(4)—1.961(4) Å (see Table 3). Each Rb atom is surrounded by seven O atoms of the trimethylacetate anions, the hydroxy groups, and EtOH ($d_{Rb-O}$ = 2.832(5)—3.253(4) Å). The distances to four O atoms of the EtOH molecules are 2.855(9) and

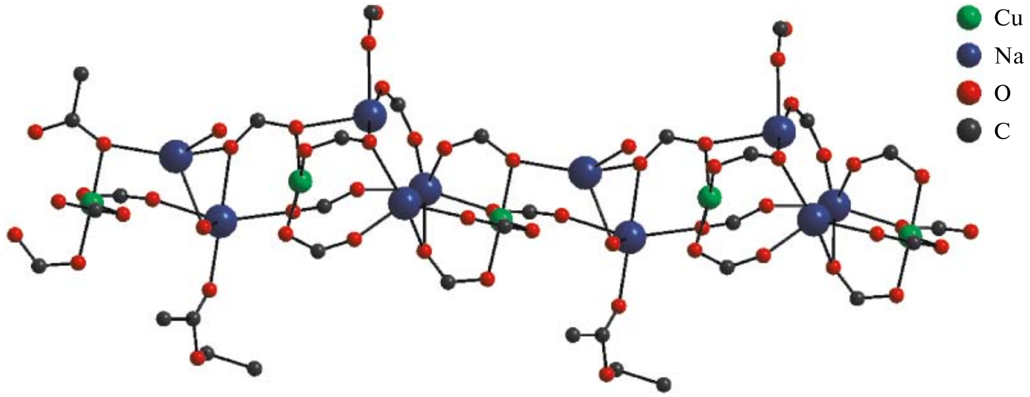

**Fig. 2.** Structure of the chain in compound **2** (see Note to Fig. 1).

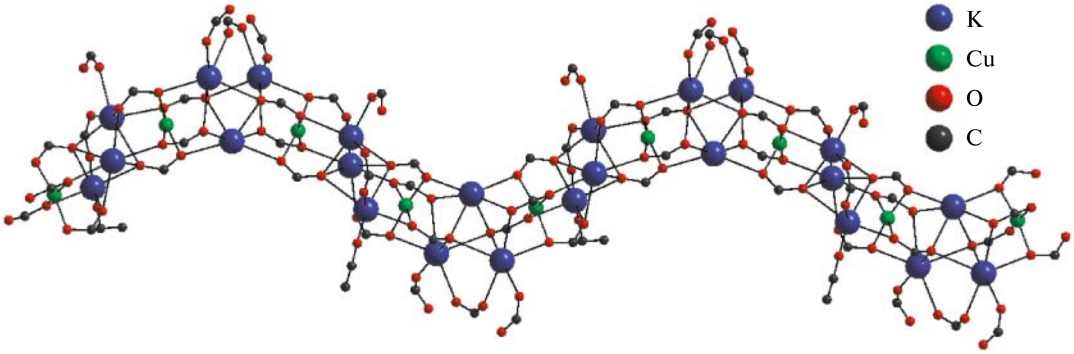

**Fig. 3.** Structure of the chain in compound **3** (see Note to Fig. 1).

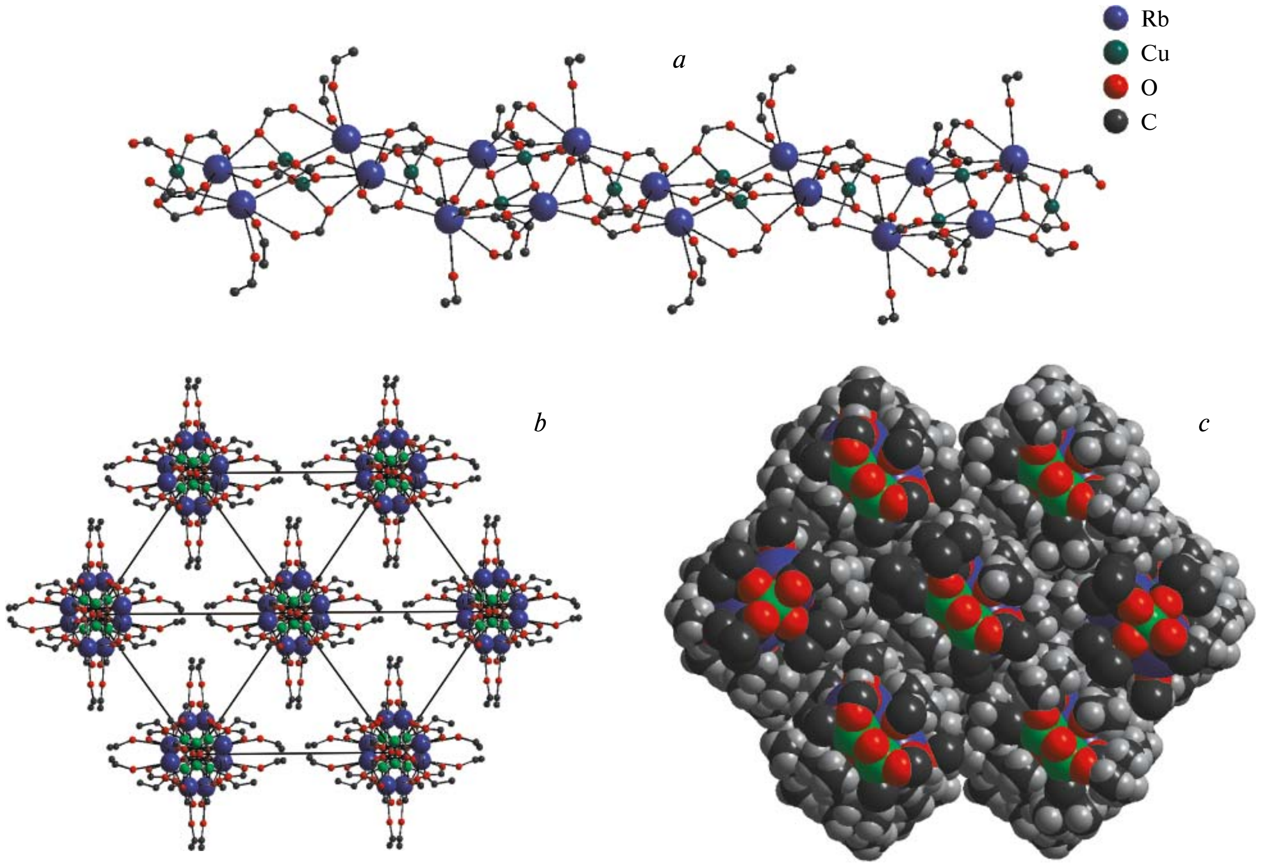

**Fig. 4.** Structure (*a*), the packing of the layers (*b*), and the filling of the space in the solid phase of compound **4** (*c*) (see Note to Fig. 1).

2.912(8) Å, whereas the distances to the O atoms of the two other EtOH molecules are substantially longer (3.45(2) and 3.53(3) Å). It is not improbable that it is these EtOH molecules that are most weakly held in the solid state of compound **4**, and this is responsible for rapid degradation of crystals after their separation from the mother liquor. Figure 4, *b* shows the structure of **4** along the chains. The packing of the chains is typical of the compounds under consideration. The distances between the chains are large. For compound **4**, the shortest distances between the axes of the chains are ~12.5 Å. The representation of this packing of the chains taking into account the van der Walls radii of atoms (Fig. 4, *c*) shows that there are no cavities in the structure, and the metal oxygen fragments of different chains are separated by a hydrocarbon double layer.

**Compound [$Cs_2CuPiv_4(H_2O)$] (5).** The reaction of $CuCl_2 \cdot 2H_2O$ with CsPiv in MeOH using the $CuCl_2$ : CsPiv molar ratio of 1 : 5 followed by crystallization of the reaction product from THF produced kinetically stable compound **5**. This compound has a framework structure, in which each Piv anion serves as a $\mu_4$-bridge between three Cs atoms and one Cu atom. The tetranuclear fragment $\{Cs_4(H_2O)_2\}$ is surrounded by four $\{Cu(Piv)_4\}$ fragments (Fig. 5, *a*), which occupy the vertices of an imaginary tetrahedron (Fig. 5, *b*). The representation of the structure as vertex-sharing tetrahedra substantially simplifies the description of the complex framework structure of compound **5** (Fig. 5, *c*). If the structure of **5** is represented as consisting of tetrahedra (Fig. 5, *d*), this framework is seen to be composed of helices, one of which is shown in Fig. 5, *e*. Since each helix is surrounded by the opposite-handed helices, the crystals of compound **5** are optically inactive.

To conclude the discussion of the structures of the compounds formed in the MPiv—$CuCl_2$ systems, it should be noted that $Cu^{II}$ behaves as transition metal in each structure, because it always tends to exist in a square coordination to form $\{CuO_4\}$ units. All structures contain the common $\{CuPiv_4\}$ fragment, in which two (Fig. 6, *a*, *b*) or one (Fig. 6, *c*) bridging carboxylate groups are tilted in the same direction from the plane of the coordination square, whereas two (Fig. 6, *a*, *b*) or three (Fig. 6, *c*) carboxylate groups are tilted in the opposite direction. Two carboxy groups tilted in the same direction can occupy the vertices of the square diagonal (Fig. 6, *a*) or the vertices of one side of the square (Fig. 6, *b*).

**Compounds [$Li_7Co_2Piv_{11}(HPiv)_2$] (6) and [$Li_{13}Co_2Piv_{17}(H_2O)_2$] $\cdot$ 2THF (7).** Compound **6** was prepared with the use of the initial molar ratio $CoCl_2$ : LiPiv = 1 : 2 in MeOH followed by recrystallization from THF,

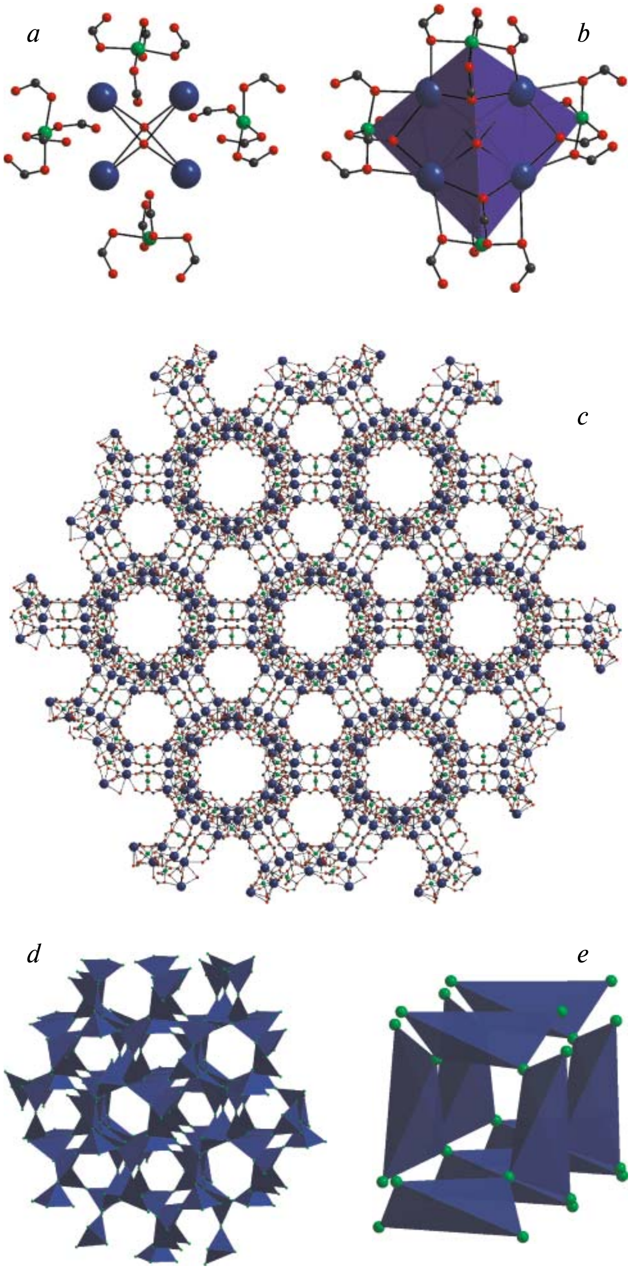

**Fig. 5.** Environment of the $\{Cs_4(H_2O)_2\}$ group formed by the $\{CuPiv_4\}$ fragments (*a*) and the representation of this environment as a tetrahedron (*b*). The fragment of the framework structure (*c*), its representation as tetrahedra (*d*), and the helix of tetrahedra (*e*) (see Note to Fig. 1).

*i.e.*, under conditions of a stoichiometric deficiency of lithium trimethylacetate. An increase in the molar fraction of LiPiv in the reaction system has virtually no effect on the composition of the reaction product up to the ratio $CoCl_2$ : LiPiv ≈ 1 : 5, when crystals of compound **7** begin to precipitate along with the major product **6**.

The structure of the zigzag chain in the solid phase of compound **6** is shown in Fig. 7, *a*. The Co atoms are alternatively separated by four or three Li atoms. The coordination environment of the Co atoms can be described as a distorted tetrahedron (Co—O, 1.960(4), 1.997(4), 2.067(5), and 2.082(5) Å; Table 4), only the O atoms of the bridging Piv groups being involved in the coordination environment. The Li atoms are surrounded by the O atoms of both the bridging anions and the monodentate coordinated trimethylacetic acid ligands. The Li atoms are located either inside triangles or inside tetrahedra formed by O atoms.

The structure of the zigzag chain in the crystals of compound **7** (Fig. 7, *b*) is similar to that in the crystals of **6**. Both chains contain the identical pentanuclear fragments $\{Li_3Co_2Piv_9\}$ (Fig. 7, *c*). In the structure of **6**, these fragments alternate with polynuclear groups consisting of four Li atoms, whereas these fragments in the structure of **7** alternate with groups containing ten Li atoms.

**Compounds $[Na_{21}Co_{14}Piv_{49}(THF)_{17}(H_2O)_6]$ (8), $[K_3Co_2Piv_7(H_2O)_2]$ (9), and $[Rb_3Co_2Piv_7(THF)(H_2O)]$ (10).** Recently,[15] we have described the structure of the $[K_3Co_2Piv_7(THF)_3]$ compound, whose solid phase is formed by double helices twisted about each other (Fig. 8, *a*). The structure of compound **8** can be easily described with the use of the helical fragment shown in Fig. 8, *b*. The structure consists of the same hetero-tetradecanuclear fragments (which are only slightly straightened; these fragments can be easily obtained by stretching the helices to form linear chains), which are indicated by a long bracket in Fig. 8, *c*, and the subsequent two hetero-nonanuclear fragments, which are linked to each other by the $\{Na(H_2O)_2THF\}$ groups to form a chain (see Fig. 8, *d*). The fragment shown in Fig. 8, *c* is also the key structure-forming motif in compound **9**, in which the chains are cross-linked by the bridging $H_2O$ molecules to form layers (see Fig. 8, *e*). The sites of cross-linking by the bridging $H_2O$ molecules alternate with the monodentate coordinated water molecules. Only O atoms (small red spheres) are placed in these sites. This allows us to avoid the repetition of figures and demonstrate that these sites in the very similar structure of **10** are occupied by the O atoms of the monodentate coordinated THF molecules. It should also be noted that compound **10** crystallizes as the only product not only when the initial reagent ratio $CoCl_2$ : RbPiv = 1 : 5 but already when $CoCl_2$ : RbPiv = 1 : 2. In all Co-containing compounds, like in Cu-containing compounds (see Fig. 4, *c*), the metal oxygen fragments from different chains or layers (see Fig. 8, *f*) are far apart (≥8 Å) because they are separated by a hydrocarbon double layer.

**Compound $[CsCoPiv_3(H_2O)]$ (11).** This compound crystallizes in high yield from an ethanolic solution containing a mixture of $CoCl_2$ and CsPiv in a molar ratio of 1 : 5. In the solid phase, the Co atom, like those in all the above-considered compounds, tends to have a tetrahedral coordination environment formed by four O atoms of the $\mu_3$-Piv anions and the coordinated $H_2O$ molecule.

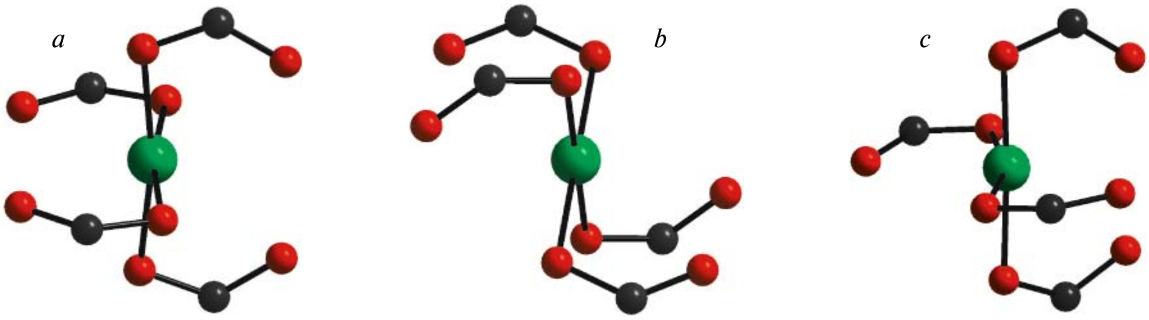

**Fig. 6.** Tilts of the carboxy groups with respect to the plane of the coordination unit (see Note to Fig. 1).

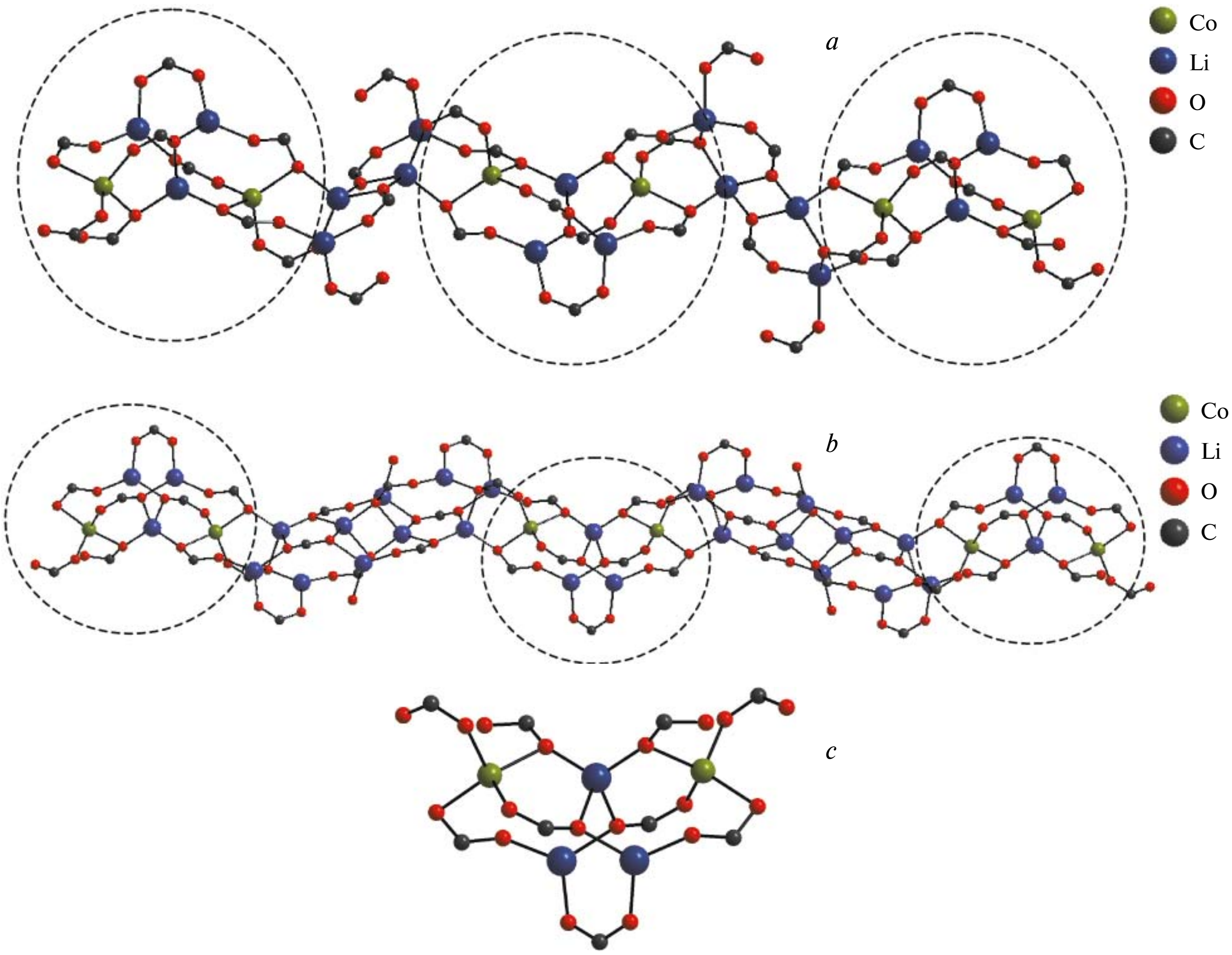

**Fig. 7.** Structures of the chains in compounds **6** (*a*) and **7** (*b*), and the pentanuclear fragment $\{Li_3Co_2Piv_9\}$ common to both chains (*c*) (see Note to Fig. 1).

The tendency of the Cs atom, which has a large radius, to be surrounded by a larger number of donor atoms is favorable for the formation of a high-dimensional structure consisting of polymeric layers (Fig. 9).

The coordination environment of the transition metal in the Co-containing compounds under consideration is characterized by less structural diversity (Fig. 10) compared to Cu-containing compounds (see Fig. 6), because cobalt tends to have a tetrahedral coordination. Formally, its tetrahedral units in the compounds under consideration can be divided into two types according to the nature of metal, to which these units are bound. In compounds **6**, **7**, and **11**, the coordination tetrahedra (see Fig. 10, *a, b*) are linked to alkali metal ions by the bridging ligands, whereas the corresponding tetrahedra in compounds **8**, **9**, and **10** are bound not only to alkali metals

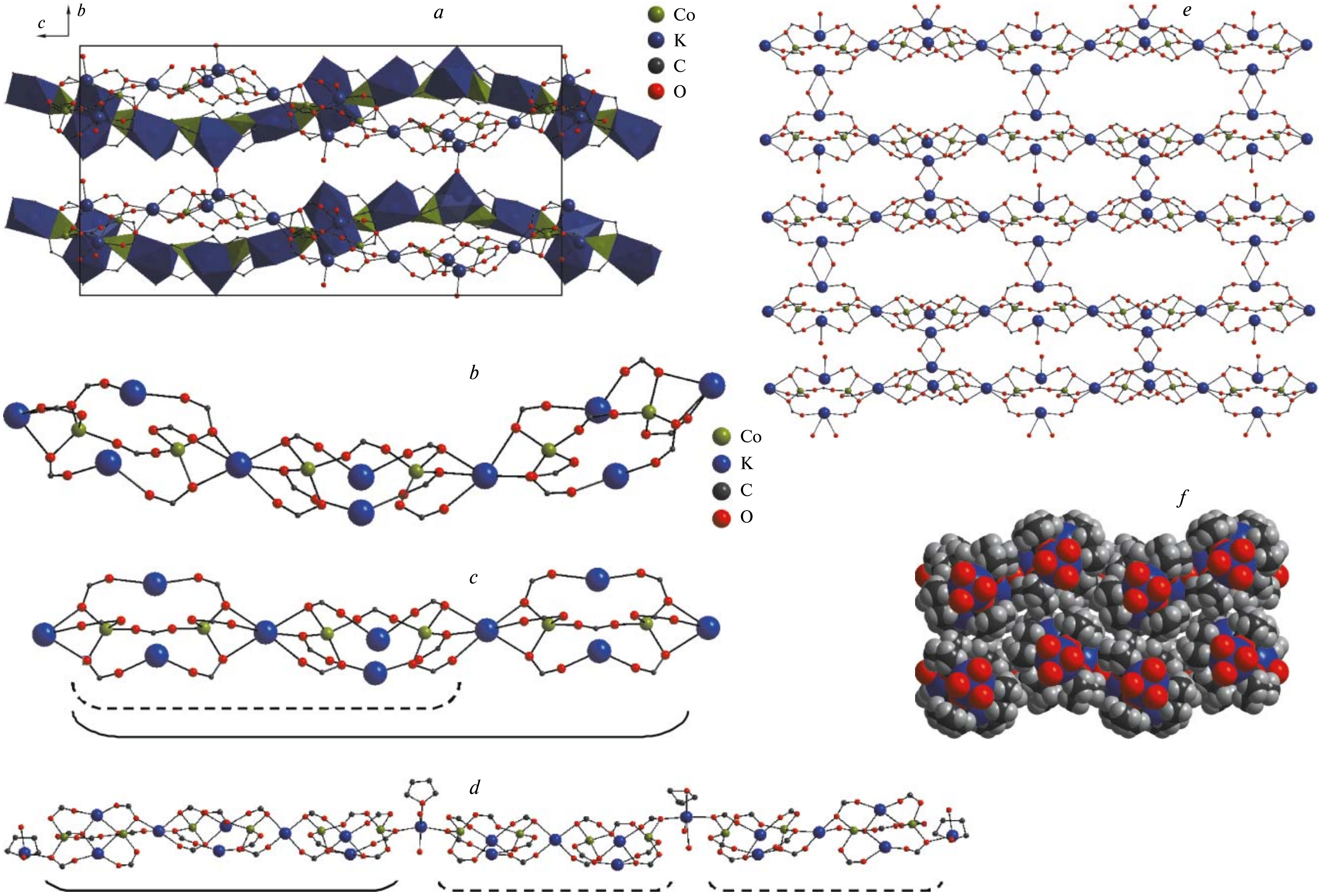

**Fig. 8.** Projection of the structure of [$K_3Co_2Piv_7(THF)_3$] onto the (100) plane, which demonstrates the opposite twist of the alternating helices (*a*). The fragment of the [$K_3Co_2Piv_7(THF)_3$] helix (*b*) and the identical group in the chain of compound **8** (*c*). The structure of the chain in compound **8** (division of the hetero-35-nuclear fragment {$Na_{21}Co_{14}$} into hetero-tetradecanuclear and two hetero-nonanuclear fragments is shown by solid and dashed brackets, respectively) (*d*). The layers in the structures of compounds **9** and **10** (*e*). The filling of the space in the solid phase of compound **9** (*f*) (see Note to Fig. 1).

**Table 4.** Principal crystallographic characteristics, the X-ray data collection and refinement statistics, and selected bond lengths for cobalt-containing compounds **6—11**

| Parameter | **6** | **7** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|---|
| $T$/K | 298 | 298 | 200 | 240 | 298 | 298 |
| Molecular weight | 1483.04 | 2107.39 | 7596.65 | 979.05 | 1172.24 | 513.22 |
| Space group | $C2/c$ | $C2/c$ | $P2_1/c$ | $Cmca$ | $Cmca$ | $P\bar{1}$ |
| $a$/Å | 27.297(4) | 26.98(5) | 26.948(3) | 23.980(2) | 24.942(2) | 11.599(4) |
| $b$/Å | 14.736(2) | 14.55(3) | 41.903(4) | 22.201(2) | 22.0016(19) | 12.279(4) |
| $c$/Å | 22.873(3) | 31.15(6) | 38.016(4) | 20.282(2) | 20.4758(18) | 17.416(6) |
| $\alpha$/deg | | | | | | 110.131(7) |
| $\beta$/deg | 104.111(3) | 97.49(4) | 105.128(3) | | | 90.207(7) |
| $\gamma$/deg | | | | | | 100.404(7) |
| $V$/Å$^3$ | 8923(2) | 12122(39) | 41440(8) | 10798(2) | 11236.6(17) | 2284.8(14) |
| $Z$ | 4 | 4 | 4 | 8 | 8 | 4 |
| $D_c$/g cm$^{-3}$ | 1.104 | 1.155 | 1.218 | 1.205 | 1.386 | 1.492 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 0.435 | 0.345 | 0.642 | 0.899 | 3.228 | 2.347 |
| $\theta$/deg | 1.54—23.29 | 1.32—24.16 | 1.12—23.32 | 1.83—23.34 | 1.59—23.31 | 1.25—23.20 |
| Number of reflections, $I_{hkl}$ | | | | | | |
| measured/ | 34012 | 44087 | 181187 | 40548 | 42603 | 11976 |
| independent | 6415 | 8771 | 59687 | 4016 | 4164 | 6445 |
| $R_{\text{int}}$ | 0.1104 | 0.1338 | 0.1449 | 0.1686 | 0.1861 | 0.1693 |
| $N$ | 521 | 758 | 4801 | 306 | 325 | 488 |
| $GOOF$ | 1.001 | 1.155 | 0.699 | 0.815 | 1.330 | 0.910 |
| $R_1$ | 0.0698 | 0.0900 | 0.0885 | 0.0720 | 0.0639 | 0.0717 |
| $wR_2$ ($I > 2\sigma_I$) | 0.1565 | 0.2018 | 0.1856 | 0.1943 | 0.1088 | 0.1749 |
| $R_1$ | 0.1033 | 0.1367 | 0.2485 | 0.1419 | 0.1269 | 0.1207 |
| $wR_2$ [a] | 0.1740 | 0.2239 | 0.3324 | 0.2381 | 0.1144 | 0.2024 |
| s-O [b] | 1.845(9)—2.033(8) | 1.80(1)—2.15(1) | 2.194(9)—2.921(12) | 2.477(7)—3.243(12) | 2.535(8)—3.566(10) | 2.982(9)—3.868(2) |
| $n$ [c] | 3—4 | 3—4 | 5—6 | 5—6 | 6—8 | 6—2 |
| d-O [b] | 1.969(3)—2.088(3) | 1.960(4)—2.082(5) | 1.955(10)—2.133(13) | 1.939(6)—2.089(5) | 1.970(6)—2.096(6) | 1.990(8)—2.075(9) |
| s—d [b] | 3.1833(8) | 3.135(5)—3.276(11) | 2.988(6)—3.587(6) | 3.3485(9)—3.616(2) | 3.530(1)—3.823(1) | 3.694(2)—3.814(10) |
| s—s [b] | 2.66(2)—2.90(1) | 2.64(2)—3.15(1) | 3.272(8)—3.646(9) | 3.986(4) | 4.322(2) | 6.736(2)—6.793(2) |

[a] Based on all reflections.

[b] s and d are s- and d-block atoms, respectively.

[c] The number of O atoms in the environment of the s-block element.

but also to each other through the bridging trimethylacetate groups to form pairs (see Fig. 10, *c*). These dinuclear fragments are clearly seen at the ends of the structural fragments (see Fig. 8, *b—e*).

The results of the present study reveal a family of heterometallic compounds based on alkali and transition metal trimethylacetates with a larger stoichiometric content of an s-block element. High molar ratios $M^IPiv : M^{II} \approx$ (5 : 1)—(10 : 1) in the reaction mixture are favorable for the formation of such compounds. However, when developing the procedure for the synthesis of compounds **6** and **10**, we found that such compounds can be produced at smaller LiPiv : $CoCl_2$ and RbPiv : $CoCl_2$ ratios (2 : 1), *i.e.*, under the conditions favorable for the formation of $CoPiv_2$. Presumably, analogous heterometallic compounds based on s- and d-block metal trimethylacetates can be prepared not only with $Cu^{II}$ and $Co^{II}$ but also with other transition metals. However, in our opinion, the above discussion of the structures of 11 compounds suffices to illustrate the characteristic features of this type of compounds and to confirm the fact that they are potentially widely distributed. First, it is evident that the presence of a considerable amount of alkali metal ions along with $Cu^{II}$ or $Co^{II}$ ions in the reaction mixture hinders the formation of classical mononuclear transition metal trimethylacetates. Second, the structures of such compounds cannot be identical because an increase in the radius of alkali metal requires the presence of a larger number of atoms involved in its coordination environment. Hence, the introduction of lower-row alkali metals into the reaction mixture promotes the formation of higher-dimensional polymeric structures (see Table 1).

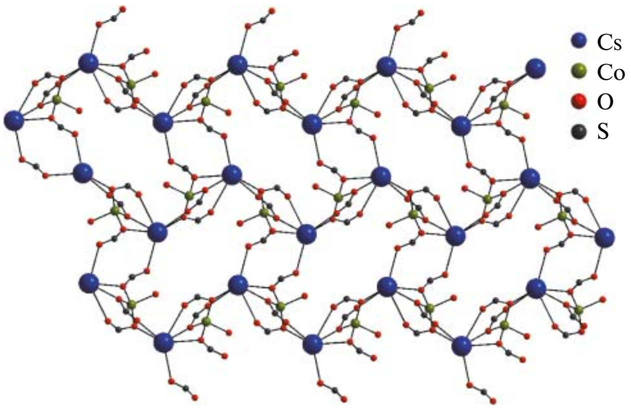

**Fig. 9.** Structure of the layer in the crystal of compound **11** (see Note to Fig. 1).

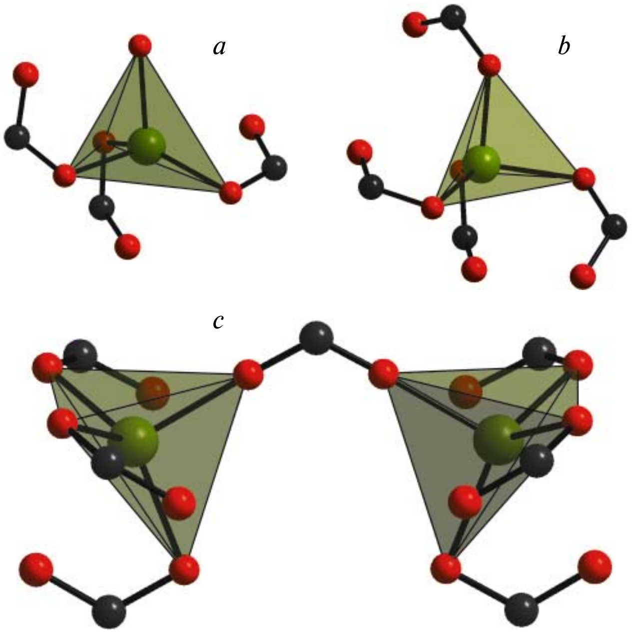

**Fig. 10.** Structure of the Co-containing units (see Note to Fig. 1).

The use of various solvents, which can be involved in the coordination environment of the metal atoms resulting in its expansion, leads to additional structural modifications. In this case, the transition metal ions tend to have a coordination mode typical of their mononuclear compounds. In the above-considered compounds, the $Cu^{II}$ and $Co^{II}$ atoms also have a square and tetrahedral coordination, respectively, regardless of the nature of alkali metal involved in the solid phase. It is easy to distinguish the square coordination of $Cu^{II}$ (see Table 3) or the tetrahedral coordination of $Co^{II}$ (see Table 4) because other $M^{II}$—O contacts are outside the acceptable range of the bond lengths for these metals. The interchain or interlayer $M^I$...O or $M^{II}$...O distances are longer than 6—8 Å (see Fig. 4, *c* and 8, *f*). The cut-off limits for the $M^I$—O bond lengths ($M^I$ is alkali metal) in the chains, layers, or frameworks were chosen based on the known statistical set of structural data on the $M^I$—O bond lengths[30,31] and their upper limiting values, because alkali metals, unlike transition metals, are not stabilized by the crystal field and they do not tend to have a particular spatial orientation of the donor atoms. The possible ambiguity in the cut-off limit for the $M^I$—O bonds had no effect on the observed rather evident tendency; that is, the larger the ionic radius of alkali metal the larger the number of donor atoms involved in its coordination environment (see Tables 3 and 4). In this case, the ion can be linked to a larger number of the adjacent ions through bridging coordination of the ligands. It should be noted that the heterometallic compounds under consideration with a stoichiometric content of alkali metal larger than that of transition metal, like all other monocarboxylate compounds described earlier (see Table 2), are polymers having different motifs. The motif depends on the nature of the solvent used in the synthesis, its polarity, the presence of donor groups, and their steric accessibility. Nevertheless, the fact that this specific family of polynuclear compounds exists is of most importance nowadays. Since all the compounds under consideration were synthesized in organic solvents, the results of the present study are useful to take into account when developing procedures for the synthesis of various polynuclear transition metal monocarboxylates, which are very often prepared in organic media. These compounds containing a larger stoichiometric amount of alkali metal compared to transition metal are of interest in themselves, because they can be used already as the starting components in further transformations.

## Experimental

The following reagents were used: $CoCl_2$ (reagent grade), $CuCl_2 \cdot 2H_2O$ (chemically pure), $Me_3CCOOH$ (99%) Aldrich, ethanol (95.6%), and THF (99%) Merck. Methanol was purified by distillation before use. Alkali metal trimethylacetates were synthesized by the reactions of equivalent amounts of trimethylacetic acid and the corresponding metal hydroxide in MeOH followed by evaporation of the solution to dryness. All syntheses of heterospin complexes were carried out under usual conditions without special precautions.

***Catena*-{tetrakis[$\mu_3$-(2,2-dimethylpropionato-*O*,*O*,*O*´)]dilithiumcopper(II)}, [$Li_2CuPiv_4$] (1).** A solution of $CuCl_2 \cdot 2H_2O$ (1 g, 5.86 mmol) in MeOH (5 mL) was added with stirring to a solution of LiPiv (3.16 g, 29.3 mmol) in MeOH (20 mL). After removal of the solvent with a stream of air, the dry residue was treated with a mixture of THF (15—20 mL) and MeOH (2 mL). The LiCl precipitate was filtered off, and the filtrate was kept for 2—3 days. The needle-like crystals that formed were filtered off, washed with THF, and dried in air. The yield was 1 g (35%). Found (%): C, 49.9; H, 7.5. $Li_2CuC_{20}H_{36}O_8$. Calculated (%): C, 49.9; H, 7.5.

***Catena*-{bis[$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]tris[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)](2,2-dimethylpropionic acid-*O*)trisodium[$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]tris[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]copper(II)aqua($\mu_2$-aqua)ethylacetatedisodiumcopper(II)} ethylacetate solvate, $[Na_5Cu_2Piv_9(HPiv)(H_2O)_2(EtOAc)]\cdot EtOAc$ (2).** A solution of $CuCl_2\cdot 2H_2O$ (0.5 g, 2.93 mmol) in MeOH (5 mL) was added with stirring to a solution of NaPiv (1.82 g, 14.65 mmol) in MeOH (15—20 mL). After removal of the solvent with a stream of air, the dry residue was treated with EtOAc (20 mL). The NaCl precipitate was filtered off, and the filtrate was kept for 5—7 days in an untightly closed flask, during which EtOAc was mainly evaporated and thin needle-like light-blue crystals were obtained. The crystals were filtered off, washed with cold EtOAc, and dried under a stream of air. The yield was 0.62 g (30%). Found (%): C, 46.5; H, 7.4. $Na_5Cu_2C_{50}H_{95}O_{22}$. Calculated (%): C, 46.6; H, 7.4. When THF was used instead of EtOAc, $[Na_5Cu_2(Piv)_9(HPiv)(H_2O)_2(THF)]\cdot THF$ was obtained as very thin needle-like light-blue crystals, but the yield of the product was lower.

***Catena*-{tetrakis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O´,O´*)]ethanol(2,2-dimethylpropionic acid-O)tripotassium[$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]tris[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]copper(II)bis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O´,O´*)]bis(2,2-dimethylpropionic acid-*O*)tripotassiumcopper(II)}, $[K_6Cu_2Piv_{10}(HPiv)_3(EtOH)]$ (3).** A solution of $CuCl_2\cdot 2H_2O$ (0.25 g, 1.47 mmol) in EtOH (5 mL) was added with stirring to a solution of KPiv (2.06 g, 14.7 mmol) in EtOH (8—10 mL). After 5 min, the KCl precipitate that formed was filtered off, and the filtrate was kept for 7—8 days in an open flask. The prismatic blue crystals that formed were filtered off, washed with cold EtOH, and dried under a stream of air. The yield was 0.9 g (70%). Found (%): C, 45.8; H, 7.3. $K_6Cu_2C_{60}H_{110}O_{24}$. Calculated (%): C, 45.7; H, 7.0.

***Catena*-{tetrakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]di($\mu_3$-hydroxo)triethanoldirubidiumdicopper(II)tetrakis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O´,O´*)]triethanoldirubidiumcopper(II)}, $[Rb_4Cu_3Piv_8(OH)_2(EtOH)_6]$ (4).** A solution of $CuCl_2\cdot 2H_2O$ (0.16 g, 0.94 mmol) in EtOH (5 mL) was added with stirring to a solution of RbPiv (0.87 g, 4.70 mmol) in EtOH (10 mL). The RbCl precipitate was filtered off, and the filtrate was kept for 8—9 days in an open flask. The prismatic blue crystals that formed were filtered off, washed with cold EtOH, and dried in air. The yield was 0.084 g (20%). Found (%): C, 36.1; H, 6.3. $Rb_4Cu_3C_{44}H_{86}O_{20}$. Calculated (%): C, 36.0; H, 5.9.

***Catena*-{tetrakis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O´,O´*)]($\mu_4$-aqua)dicesiumcopper(II)}, $[Cs_2CuPiv_4(H_2O)]$ (5).** A solution of $CuCl_2\cdot 2H_2O$ (0.5 g, 2.93 mmol) in MeOH (5 mL) was added with stirring to a solution of CsPiv (3.43 g, 14.65 mmol) in MeOH (10—15 mL). After removal of the solvent with a stream of air, the dry residue was treated with a mixture of THF (15—20 mL) and MeOH (1—2 mL). The CsCl precipitate was filtered off. After 2—3 days, the prismatic blue crystals that precipitated from the filtrate were filtered off, washed with cold THF, and dried under a stream of air. The yield was 0.3 g (15%). Found (%): C, 31.9; H, 5.2. $Cs_2CuC_{20}H_{38}O_9$. Calculated (%): C, 31.9; H, 5.1.

***Catena*-{pentakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]di(2,2-dimethylpropionic acid-*O*)tetralithiumtetrakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]cobalt(II)[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)][$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]trilithiumcobalt(II)}, $[Li_7Co_2Piv_{11}(HPiv)_2]$ (6), and *catena*-{bis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O´,O´*)]bis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O,O´*)]pentakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]bis[$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]diaquadecalithiumtetrakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]cobalt(II)[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)][$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]trilithiumcobalt(II)} bis-tetrahydrofuran solvate, $[Li_{13}Co_2Piv_{17}(H_2O)_2]\cdot 2THF$ (7).** A solution of $CoCl_2$ (0.78 g, 6.01 mmol) in MeOH (10 mL) was added with stirring to a solution of LiPiv (1.29 g, 12.02 mmol) in MeOH (20 mL). After removal of the solvent with a stream of air, the dry residue was treated with THF (10 mL). After 3 days, the LiCl precipitate was filtered off, and the filtrate was kept for 1—2 days. The resulting prismatic pink crystals were filtered off, rapidly washed with a small amount (at most 5—10 mL) of cold THF, and dried under a stream of air. The yield was 0.4 g (30%). Found (%): C, 52.3; H, 7.5. $Li_7Co_2C_{60}H_{109}O_{24}$. Calculated (%): C, 52.2; H, 7.9. Under analogous conditions and with the use of the starting ratio $CoCl_2$ : LiPiv = 1 : 5, a mixture of crystals of compounds **6** and **7** (rhombohedral violet crystals) was reproducibly obtained as the solid phase, with crystals of compound **6** predominating. However, after washing of the crystals on a filter with cold THF, the crystals of compound **6** were dissolved much more rapidly, and only the crystals of compound **7** suitable for X-ray diffraction study remained on a filter.

***Catena*{tris[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]sodiumpentakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)][$\mu_4$-(2,2-dimethylpropionato-*O,O,O,O´*)][$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]diaquatetrakis(tetrahydrofuran)trisodiumdicobalt(II)tetrakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)][$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]bis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O,O´*)]bis(tetrahydrofuran)trisodiumdicobalt(II)tris[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]bis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O,O´*)]bis[$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]tris(tetrahydrofuran)diaquatrisodiumdicobalt(II)tetrakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]bis[$\mu_2$-(2,2-dimethylpropionato-*O,O´*)][$\mu_4$-(2,2-dimethylpropionato-*O,O,O,O´*)]bis(tetrahydrofuran)trisodiumdicobalt(II)tetrakis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)][$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]bis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O,O´*)]bis(tetrahydrofuran)trisodiumdicobalt(II)tetra[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)][$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]bis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O,O´*)]diaquabis(tetrahydrofuran)trisodiumdicobalt(II)bis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]bis[$\mu_4$-(2,2-dimethylpropionato-*O,O,O,O´*)]bis(tetrahydrofuran)disodiumdicobalt(II)}, $[Na_{21}Co_{14}Piv_{49}(THF)_{17}(H_2O)_6]$ (8).** A solution of NaPiv (4.77 g, 38.5 mmol) in MeOH (20 mL) was added with stirring to a solution of $CoCl_2$ (1 g, 7.7 mmol) in MeOH (10 mL). After removal of the solvent with a stream of air, the dry residue was treated with THF (20 mL). The NaCl precipitate was filtered off and the filtrate was kept for 2—3 days in an untightly closed flask. The needle-like violet crystals that formed were filtered off, washed with cold THF, and dried under a stream of air. The yield was 1.05 g (25%). Found (%): C, 45.9; H, 7.2. $Na_{21}Co_{14}C_{245}H_{453}O_{104}$. Calculated (%): C, 46.2; H, 7.2.

***Catena*-{bis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)][$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]potassiumbis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]bis[$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]aqua($\mu_2$-aqua)dipotassiumdicobalt(II)}, $[K_3Co_2Piv_7(H_2O)_2]$ (9).** A solution of $CoCl_2$ (1 g, 7.7 mmol) in EtOH (10 mL) was added with stirring to a solution of KPiv (5.39 g, 38.5 mmol) in EtOH

(20 mL). After 5 min, the KCl precipitate was filtered off. After 5—7 days, the crystals (elongated prismatic violet crystals) that precipitated were filtered off, washed with cold EtOH, and dried under a stream of air. The yield was 1.5 g (40%). Found (%): C, 42.8; H, 6.8. $K_3Co_2C_{35}H_{67}O_{16}$. Calculated (%): C, 42.9; H, 6.9.

***Catena*-{bis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)][$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]rubidiumbis[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]bis[$\mu_2$-(2,2-dimethylpropionato-*O,O´*)]-($\mu_2$-aqua)tetrahydrofurandicobalt(II)dirubidium}, [$Rb_3Co_2Piv_7(THF)(H_2O)$] (10).** A solution of $CoCl_2$ (0.7 g, 5.43 mmol) in MeOH (5 mL) was added with stirring to a solution of RbPiv (2 g, 10.86 mmol) in MeOH (20 mL). After removal of the solvent with a stream of air, the dry residue was treated with THF (20 mL). The RbCl precipitate was filtered off, and the filtrate was kept for 3—4 days in an untightly closed flask, during which THF was mainly evaporated, and prismatic violet crystals were obtained. The crystals were filtered off, washed with cold THF, and dried under a stream of air. The yield was 0.43 g (25%). Found (%): C, 38.4; H, 5.9. $Rb_3Co_2C_{35}H_{65}O_{15}$. Calculated (%): C, 38.2; H, 5.9.

***Catena*-{tris[$\mu_3$-(2,2-dimethylpropionato-*O,O,O´*)]aquacesiumcobalt(II)}, [$CsCoPiv_3(H_2O)$] (11).** A solution of $CoCl_2$ (0.185 g, 1.42 mmol) in EtOH (5 mL) was added with stirring to a solution of CsPiv (1.66 g, 7.1 mmol) in EtOH (20 mL). After 3 days, the CsCl precipitate that formed was filtered off, and the filtrate was kept in an open flask for 7 days. The rhombic plate pink crystals that formed were filtered off, washed with cold EtOH, and dried under a stream of air. The yield was 0.5 g (70%). Found (%): C, 34.6; H, 5.5. $CsCoC_{15}H_{29}O_7$. Calculated (%): C, 35.1; H, 5.7.

**X-ray diffraction study.** X-ray diffraction data sets for all compounds were collected on a Smart Apex diffractometer equipped with a CCD detector ($\lambda$ (Mo-K$\alpha$), graphite monochromator). Absorption corrections were applied using the Bruker SADABS software (version 2.03). The structures were solved by direct methods and refined by the full-matrix least-squares method. The positions of the H atoms were partially located in difference electron density maps. The positions of the other H atoms were calculated geometrically and refined using a riding model. All calculations were carried out using the Bruker SHELXTL Version 6.12 program package. The principal crystallographic characteristics, the X-ray data collection and refinement statistics, and selected bond lengths are given in Tables 3 and 4. Before the X-ray data collection, the crystals were coated with the cryoprotectant Paratone-N. Coating with the oil did not completely protect single crystals from atmospheric effects and did not completely prevent their gradual decomposition. In many cases, crystals were taken from the rather viscous mother liquor and, consequently, the possibility of the formation of single crystals on the surface of the sample under investigation cannot be excluded. These facts could be responsible for diffuseness of reflections and a high background and, as a consequence, high $R_{int}$ (see Tables 3 and 4). Besides, it is known that loose crystal packings of multinuclear trimethylacetates are responsible for strong disorder of the periphery of the molecule (Piv groups of the trimethylacetate ligands and the solvent molecules) and a low reflecting ability of the crystals. This leads to a low accuracy of the X-ray diffraction study resulting in high $R_{int}$ and $R_1$ factors,[32] although the alkali metal—transition metal distances for low-row $s^1$-block elements were determined with high accuracy. It should also be noted that for each compound, X-ray data were collected from crystals prepared in different syntheses (in some cases, up to four structure solutions) and gave reproducible results.

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