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The Formation of Heterometallic Molecular Architectures with 3*d*-Metal Atoms Linked by Carboxylate Bridges with Alkali and Alkaline-Earth Metal Ions or with Lanthanides

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Abstract—Data on the synthesis of carboxylate complexes combining transition 3*d* metals and diverse heterometals (Li-, Mg-, and Ln-M(3*d*)) are reviewed. The factors that are essential to the structure of heterometallic complexes were revealed. Stable metal-containing moieties capable of forming both molecular and polymeric structures were identified.

Keywords: heterometallic complexes, transition metals, lithium, magnesium, lanthanides, synthesis, structure

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INTRODUCTION

Many recent publications in chemical literature are concerned with the synthesis and study of polynuclear heterometallic carboxylates combining 3*d*-metal ions and other metal centers (e.g., the atoms of alkali, alkaline-earth, and posttransition metals or lanthanides [1–15]). No wonder that such molecular systems are of interest because their molecules combine metal ions having different electronic and spatial characteristics, which often gives rise to unique molecular entities exhibiting unexpected physical and chemical properties. By developing the chemistry of such compounds, researchers try not only to devise a unified method of controlling the molecular properties via combination of dissimilar metal ions in the same structure (which enables designed variation of the properties of the final molecular structure), but also to control the properties of 3D materials: crystals, films, coatings, etc. In essence, this is a jump from nanochemical to molecular materials science, when the properties of a substance are “embedded” at an appreciably smaller level, depending on the size of its molecules. Formally, it is not surprising that the mechanisms of catalytic reactions are known to have long been associated with the properties of metal-containing catalyst molecules [16, 17], and that the bioactivity of some coordination compounds containing metal ions depends on both the metal centers and the organic component of the complexes [18, 19].

From this standpoint, carboxylate molecules enjoy some advantages because carboxylate anions can function as ligands with very different ways of coordination (from monodentate to μ_4-bridging [20]), which can be expected to enable the formation of a very wide set of molecular architectures with considerably different properties. Certain problems arising in the synthesis of carboxylates are due, first of all, to the fact that the same starting materials yield different products, depending on the reaction conditions. Undoubtedly, this necessitates the development of new synthetic approaches.

Here we discuss some of the promising routes to heterometallic carboxylate complexes that seem to be suitable for the targeted synthesis of systems combining 3*d*-metal ions (Co(II), Ni(II), Cu(II), and Zn) with alkali (Li^+), alkaline-earth (Mg^{2+}), and Ln^{3+} ions (Ln = Nd, Pr, Sm, Eu, and Gd).

MOLECULAR COMPLEXES AND POLYMERS CONTAINING LITHIUM AND TRANSITION METAL IONS (M = Cu, Co, AND Ni). A NEW REACTION FOR INSERTION OF LiPiv INTO THE PIVALATE MATRICES OF 3*d* ELEMENTS

Polymeric carboxylates combining 3*d*-metal and lithium ions have been described in [21]; their dimensionality depends on the basicity of the carboxylic acid and the Li : M ratio. Structurally, they are similar in many respects to homometallic coordina-

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† Deceased.

tion polymers of 3*d* metals. Despite this similarity, no attempts have been made earlier to obtain, as in the case of 3*d*-metal carboxylates, molecular complexes that would combine lithium(I) and 3*d*-metal atoms. Note that the Li(I) ion is characterized by a tetrahedral coordination geometry with only slightly different Li–O bond lengths. In addition, the lithium ion is the "softest" one among all alkali metal ions, which are the hardest Lewis acids (according to Pearson) [22–25]. Since an approach involving stabilization of polynuclear molecular structures by neutral O- and N-donating ligands is well known for homometallic complexes [26–37], it would be reasonable to use the same approach for the synthesis of Li-M(3*d*) molecular complexes. Such molecular systems are of particular interest among heterometallic carboxylate complexes because they can serve as molecular precursors to cathodic materials for lithium cells [1, 6, 38] or to new catalysts suitable for electrochemical synthesis [39–46]. In addition, unusual effects may be revealed in the study of the magnetic properties of such molecules; adsorption promoting the catalytic transformations of substrates is possible as well.

Since reactions of pyridine and its α-derivatives (L) with cobalt pivalate $[Co(Piv)_2]_n$, which has a 1D-polymer architecture (X-ray powder diffraction data [47, 48]), are known to produce stable dinuclear complexes $[Co_2(\mu\text{-}Piv)_4(L)_2]$ (Piv is the trimethylacetate anion), the starting complex $[Co_2(Piv)_4(2,4\text{-}Lut)_2]$ (2,4-Lut is 2,4-lutidine) was obtained in situ and used in a reaction with lithium pivalate to give the heterometallic complex $[Co_2Li_2(Piv)_6(2,4\text{-}Lut)_2]$ (**I**) [38]. The center of symmetry of structure **I** is at an intersection point of the diagonals of the nearly square unit O_2Li_2. The metal core is a CoLiLiCo zigzag chain, with all the atoms being coplanar. Structure **I** consists of two identical moieties $LiCo(O_2CR)_3(2,4\text{-}Lut)$ (Fig. 1a), in which the Co atoms are coordinated through the N atom of 2,4-Lut. The Co and Li atoms are linked by three carboxylate bridges. Not all bridging anions are equivalent: two are bidentate bridges, while the third one is a tridentate ligand bridging two Li atoms by the same O atom. This ensures the linkage of two {Li-Co} units by two Li–O bonds. The tetrahedral geometry of either Co atom is completed with a weak contact with the O atom of one bridging group (Co(1)···O(6), 2.634 Å), which thus can formally be considered both chelating and bridging. The participation of one bridging group in the chelate ring rigidly secures the adjacent Co and Li atoms. The conformational flexibility of one bridging anion is additionally hindered by its coordination to the second Li atom, which also stabilizes the zigzag geometry of the CoLiLiCo chain.

Formally, heterometallic complex **I** may probably be regarded as a product of insertion of the lithium ion (or LiPiv) into the dinuclear structure $\{Co(\mu\text{-}O_2CR)_4Co\}$. This is not surprising because this structure contains many O atoms (hard Lewis bases [21]) eager to bind to the lithium ion (a hard Lewis acid).

Interestingly, heteronuclear complex **I** can easily be prepared in nearly quantitative yield by a reaction of 2,4-Lut with a mixture of the coordination polymers $[Co_2Li_7(Piv)_{11}(HPiv)_2]_n$ and $[Co_2Li_{13}(Piv)_{17}(H_2O)_2] \cdot 2THF$ synthesized in [21]. This fact may be considered evidence for the stability of the tetranuclear structure of heterometallic {Li-Co} complexes containing pyridine derivatives (relatively soft Lewis bases [22]) coordinated to the Co atoms.

Taking into account that such heterometallic {Li-M} tetranuclear structures are stable if N-donating ligands are coordinated to 3*d*-metal ions, we obtained the heterometallic complex $[Co_2Li_2(Piv)_6(NEt_3)_2]$ (**II**) [37] by an immediate reaction of LiPiv, the polymer $[Co(Piv)_2]_n$, and NEt_3 in THF at 60°C. Complex **II** was isolated as violet crystals; its structure (Fig. 1b) is similar to structure **I**, with some distinctions due to the individual geometrical parameters of the N-donating ligand.

Using monodentate N-donating ligands, we failed to obtain copper or nickel analogs of complexes **I** and **II** in a similar way. The destabilization of a heteronuclear complex combining the Li(I) and Cu(II) or Ni(II) atoms is probably due, among other factors, to the coordination geometry of the 3*d*-metal ion. Indeed, the coordination polyhedra of the Co atoms in complexes **I** and **II** are distorted tetrahedra, which are not always favorable in carboxylate complexes for the nickel (normally, its preferential polyhedron is an octahedron) and copper atoms (these are known to adopt an octahedral, tetragonal pyramidal, or square planar coordination geometry [28, 49–54]. To overcome this difficulty, bidentate N- or O-donating apical ligands such as dimethoxyethane (DME) or 2,2'-bipyridyl (2,2'-Bipy) could be employed since they increase the coordination number (C.N.) of the transition metal in the complex. This assumption was confirmed by the synthesis of the heterometallic complexes $[Li_2Ni_2(Piv)_6(DME)_2]$ (**III**) and $[Li_2M_2(Piv)_6(2,2'\text{-}Bipy)_2]$ (M = Ni (**IV**) and Cu (**V**)). Complex **III** was obtained by a reaction of $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ [28] with excess LiPiv in DME. Addition of 2,2'-Bipy to a solution of complex **III** yielded its analog **IV**. Complex **IV** was also synthesized in a new reaction of insertion of LiPiv into the dinuclear nickel complex $[Ni_2(Piv)_4(2,2'\text{-}Bipy)_2(\mu\text{-}H_2O)]$. Here the starting nickel complex has a three-bridge structure, in contrast to the aforementioned four-bridge cobalt complex $[Co_2(Piv)_4(2,4\text{-}Lut)_2]$ used as a starting material for the synthesis of complex **I**. This suggests that the number and even geometry of carboxylate bridges between two 3*d*-metal ions are of minor importance for the insertion of LiPiv, whereas the presence of the donating O atoms (which the lithium ion tends to coordinate with) is crucial. Copper-containing complex **V** is formed by

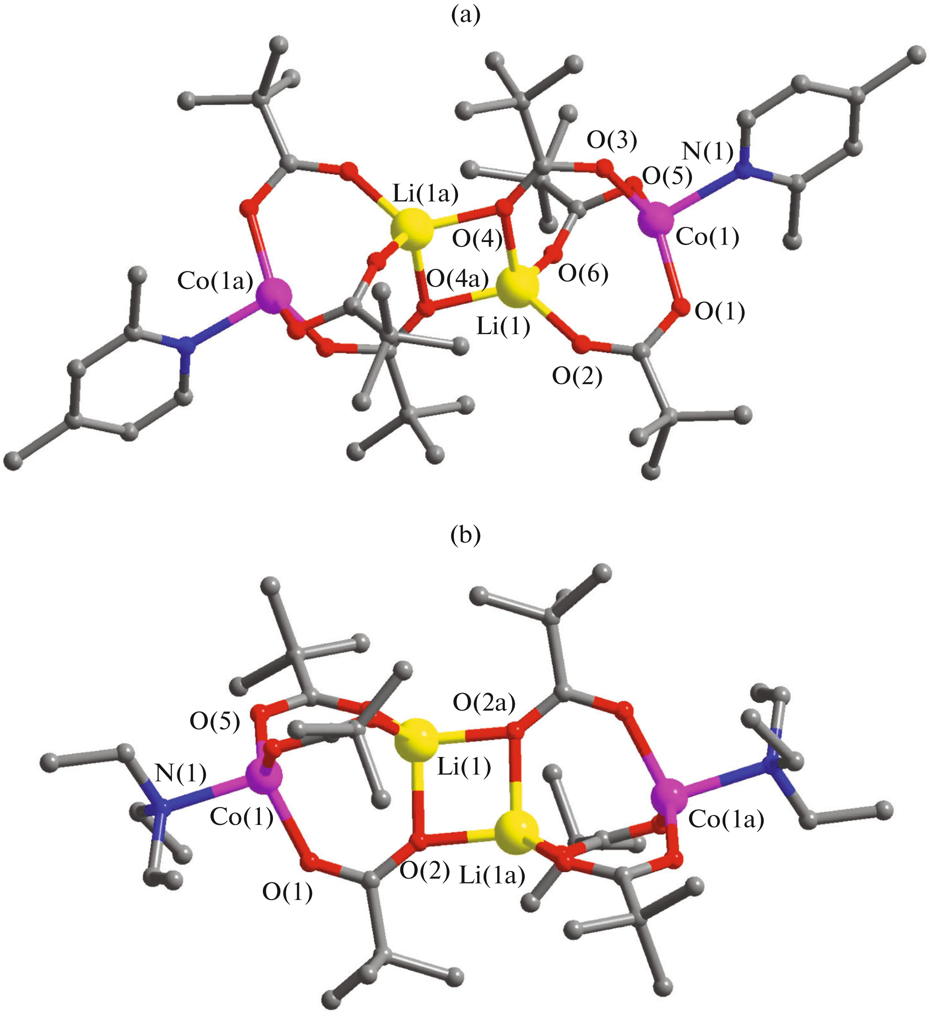


Fig. 1. Molecular structures of complexes **I** (a) and **II** (b) (only one crystallographically independent molecule is shown; the H atoms are omitted from Figs. 1–10).

self-assembly from LiPiv (2 mol), $[Cu_2(Piv)_4(HPiv)_2]$ (1 mol), and 2,2'-Bipy (2 mol) in MeCN [55, 56]. Apparently, the reaction proceeds through the intermediate $\{Li_2Cu_2(Piv)_6(HPiv)_2\}$, from which the coordinated HPiv molecules are then displaced by the bipyridyl ligand.

Both complexes **III** and **IV** have similar structures (X-ray diffraction data). The metal core of the nickel-containing complexes $\{Li_2Ni_2(Piv)_6\}$ is much the same as that in the cobalt-containing units $\{Li_2Co_2(O_2CR)_6\}$ of tetranuclear complexes **I** and **II** (Fig. 2). The chelating-bridging coordination of two carboxylate groups is the only distinction. The chelation produced by the neutral ligands (DME and 2,2'-Bipy) gives rise to a distorted octahedron around the Ni atoms. In the crystal of complex **IV**, the 2,2'-Bipy ligands of the adjacent molecules of the complex show weak π-stacking interactions ($d \approx 3.5$ Å).

Centrosymmetric complex **V** is structurally similar to complex **IV** (Fig. 2c). It is worth noting that the Cu(1) atom is surrounded by two N atoms of 2,2'-Bipy and three O atoms of three bridging carboxylate groups; the resulting coordination geometry corresponds to a distorted trigonal bipyramid ($\tau = 0.05$) [57]. One Piv group uses only one O atom to bridge the Li(1) and Cu(1) atoms, while its other O atom is above the Cu atom and seems to interact very weakly with it (2.668 Å). As in complex **IV**, the 2,2'-Bipy ligands of the adjacent molecules of complex **V** in the crystal are linked by π-stacking ($d \approx 3.44$ Å).

Addition of LiPiv to a homometallic coordination polymer already precipitated from a solution proved to yield the heterometallic unit $\{Li_2Co_2\}$ as well. In this case, we also used a reaction of insertion of LiPiv into a prepared metal carboxylate matrix. A polymeric cobalt complex with pyrimidine (Pym), $[Co_2(Piv)_4(OH_2)(Pym)_2]_n$ (**VI**), obtained by us earlier

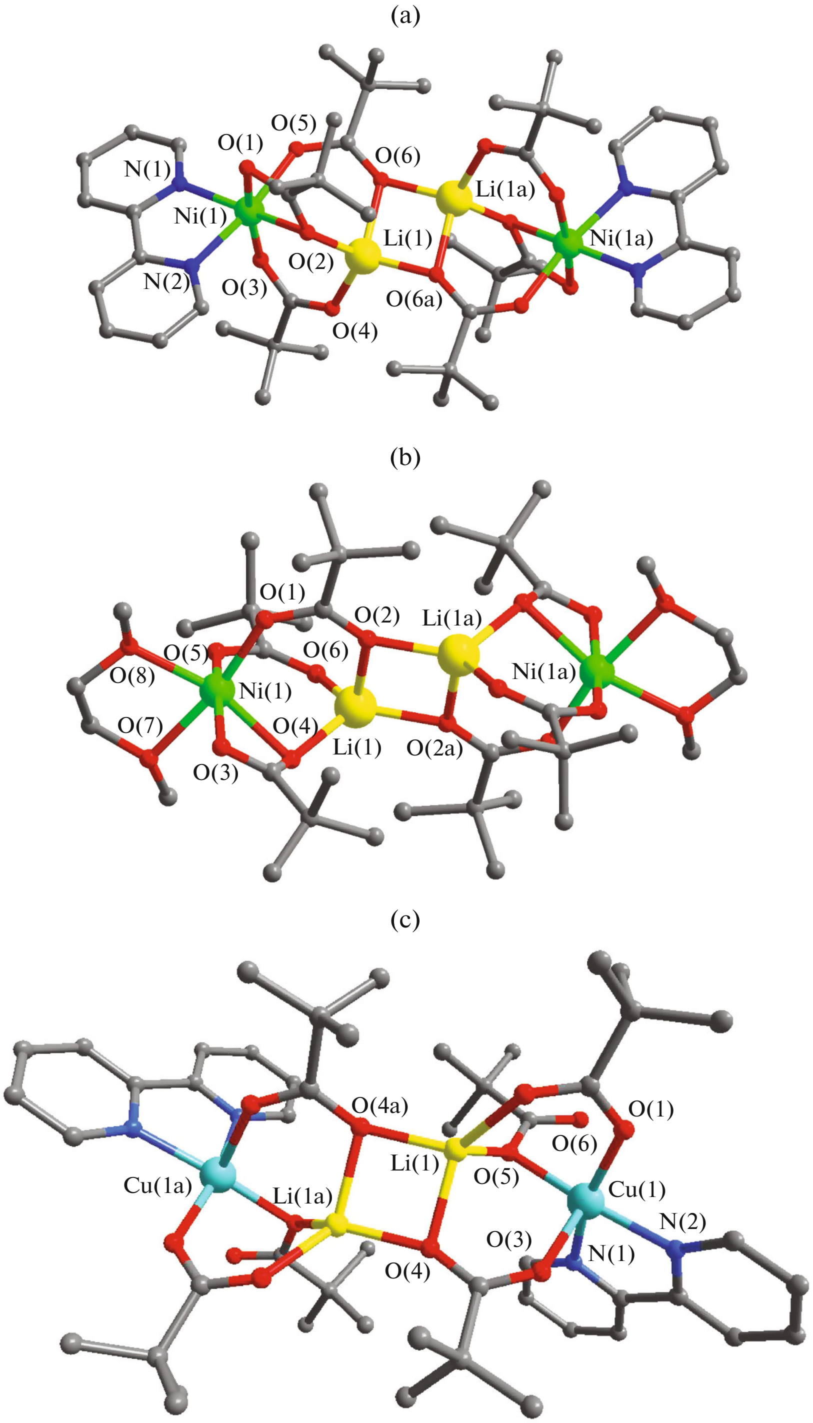


Fig. 2. Molecular structures of complexes **III** (a), **IV** (b), and **V** (c).

was employed as such a matrix. The polymer structure of complex **VI** is built from the dinuclear moieties $\{Co_2(\mu\text{-}OH_2)(\mu\text{-}Piv)_2(Piv)_2\}$, in which the cobalt(II) ions (Co···Co, 3.630 Å) are bridged by a water molecule and two pivalate groups [58], as in the aforementioned starting dinuclear Ni(II) complex successfully used in the reaction with LiPiv. It turned out that cobalt polymer **VI** also reacts with LiPiv (Li : Co = 1 : 1) in MeCN to form the coordination 1D-polymer $[Co_2Li_2(Piv)_6(Pym)]_n$ **(VII)** in high yield [59]. The repeating unit of complex **VII** consists of two symmetrical moieties $\{Li_2Co_2(Piv)_6\}$, which are identical in composition but different in structure and are linked by pyrimidine bridges (Fig. 3). Although the general

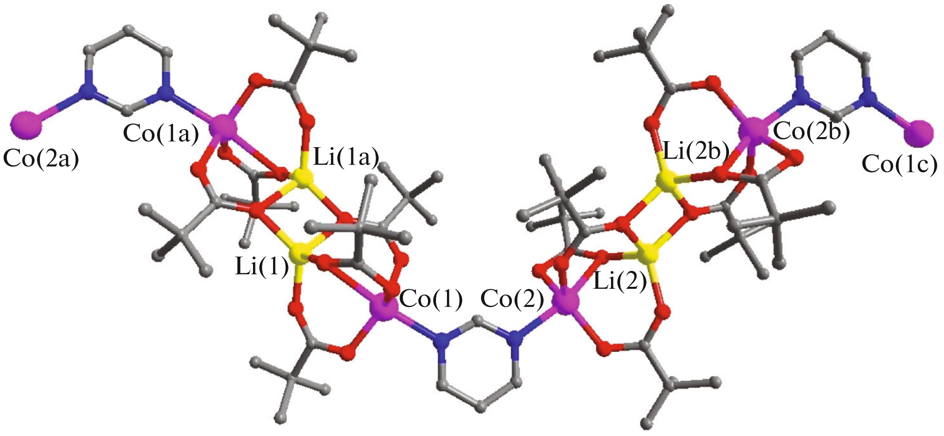


Fig. 3. Fragment of the polymer chain of complex **VII**.

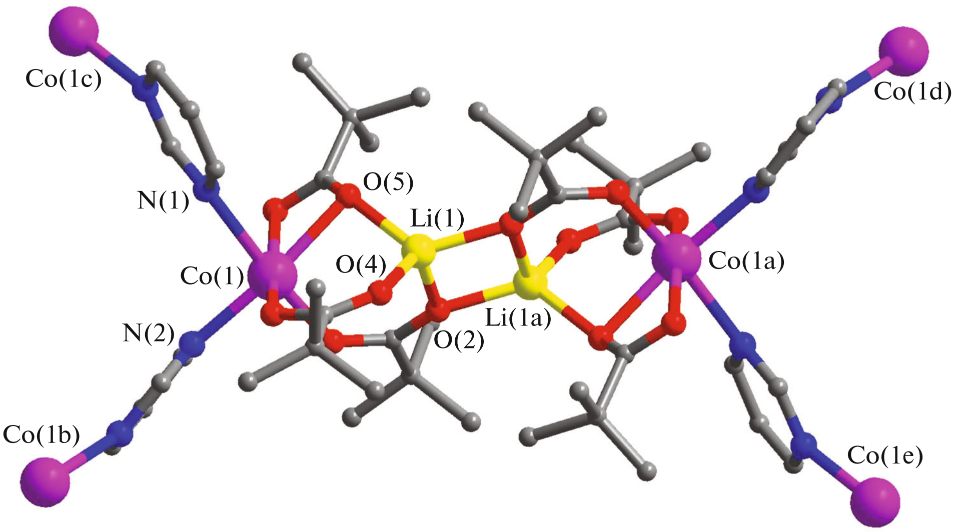


Fig. 4. Fragment of a layer formed by complex **VIII**.

core architecture of the two moieties $\{Li_2Co_2(Piv)_6\}$ is formally similar to that found in complexes **I** and **II**, the Co atoms in these moieties have different coordination geometries. In one $\{Li_2Co_2\}$ unit, the coordination polyhedron of the Co atom is a distorted tetrahedron made up of three O atoms of one η^2,μ_2-bridging and two μ_2-bridging pivalate anions and the N atom of the Pym bridge, while in the other unit, one carboxylate group bridging the cobalt and lithium atoms acts as a chelating-bridging ligand forming a lengthened Co–O bond (2.308 Å) (Fig. 3). As a result, the coordination polyhedron of the Co(2) atom is a trigonal bipyramid ($\tau = 0.08$).

Note, however, that the reaction of complex **VI** with LiPiv produces not only the major product **VII** but also small amounts (~10%) of the polymer $[Co_2Li_2(Piv)_6(Pym)_4]_n$ (**VIII**) with a layered 2D-architecture. Apparently, the formation of complex **VIII** is preferred when the reaction mixture contains excess pyrimidine. The centrosymmetric repeating unit $\{Li_2Co_2(Piv)_6(Pym)_4\}$ in polymer **VIII** is similar to that found in complex **VII**: the Co and Li atoms are linked by the μ_2-, η^2,μ_2-, and μ_3-bridging carboxylate groups (Fig. 4). Either Co atom also coordinates two pyrimidine molecules. The latter link the tetranuclear unit with its four neighbors to form a layered structure.

The use of 2-amino-5-methylpyridine (Ampy) as a "unit-linking" bridging ligand yielded an unexpected outcome. The coordination polymer $[Co_2Li_2(Piv)_6(\mu\text{-}Ampy)_2]_n$ (**IX**) was obtained in a reaction between $[Co(Piv)_2]_n$, LiPiv, and Ampy (Li : Co : Ampy = 2 : 2 : 2) in THF, though this method can rather be called "hybrid" (self-assembly + insertion).

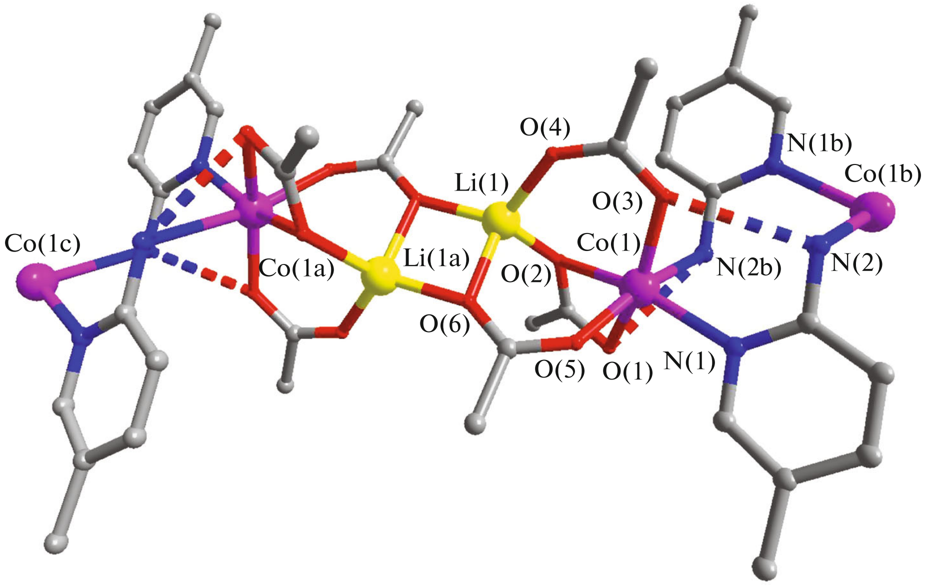


Fig. 5. Fragment of the polymer chain of complex **IX** (in the carboxylate ligands, the methyl substituents of the *tert*-butyl groups are omitted).

Complex **IX** is a chain polymer in which the tetranuclear units $\{Li_2Co_2\}$ are linked by the Ampy molecules. Either Co atom is coordinated by one bridging Ampy ligand through the pyridine N atom and by the bridging Ampy ligand of the adjacent moiety through the N atom of the amino group (Fig. 5). The coordinated amino group is hydrogen-bonded to the O atoms of the bridging and chelating-bridging carboxylate groups (H(N2)···O(1), 2.38 Å; N(2)H(2*A*)O(1), 113.7°; H(N2)···O(3), 1.96 Å; N(2)H(2*B*)O(3), 158.3°) (Fig. 5). The geometrical parameters of the tetranuclear unit $\{Li_2Co_2\}$ are close to those found in such Co complexes that one chelating-bridging and two bridging carboxylate groups form distorted octahedra around the Co atoms.

Analysis of the synthetic routes to the complexes described above shows that the order of addition of the reactants ($\{M(Piv)_2\}_x$ (M = Co, Ni, or Cu), LiPiv, and an N-donating ligand) is of minor (if any) importance for the final reaction product. This suggests that the preliminary formation of a 3*d*-metal complex with a N-donor is formally unnecessary: such a complex can be prepared in situ because the Li(I) ions are inferior to 3*d*-metal ions in coordination to, say, heterocyclic N-donating ligands or triethylamine.

Note that the both molecular and polymeric {Li-M} complexes (M = Co, Ni, and Cu) we obtained are convenient molecular precursors for the targeted synthesis of complex oxides (including thin films of $LiCoO_2$) carried out by Zh.V. Dobrokhotova (Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences) and her colleagues at the Moscow State University [38].

MOLECULAR HETEROMETALLIC PIVALATES CONTAINING MAGNESIUM AND TRANSITION METAL IONS (M = Co OR Ni)

In their chemical properties (including the ability to coordinate carboxylate anions and other organic ligands), magnesium(II) ions can be classified among “hard” Lewis acids (according to Pearson) [22]. Therefore, they are similar in this respect to the lithium(I) ions (though they are differently charged) used as pivalates in the synthesis of heteronuclear structures. Presumably, reactions of Mg(II) pivalates with 3*d*-metal carboxylate matrices could produce heterometallic architectures with Mg : M(3*d*) = 1 : 2 instead of Li : M(3*d*) = 1 : 1, as shown above. Indeed, the nonanuclear Ni(II) complex $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ [28] reacts with $Mg(Piv)_2$ (prepared from $Mg(NO_3)_2$ and KPiv) in the presence of 2,2'-Bipy to give the trinuclear complex $[MgNi_2(Piv)_6(2,2'\text{-}Bipy)_2]$ (**X**) with Mg(II) : Ni(II) = 1 : 2 in high yield [60].

According to the X-ray diffraction data (Fig. 6a), the metal core in complex **X** is a nearly linear Ni···Mg···Ni chain (the angle NiMgNi is 165°; Ni···Mg, 3.442 and 3.491 Å). The metal ions in complex **X** are bridged by carboxylate groups (N–O, 1.987–2.107 Å; Mg–O, 2.071–2.191 Å). All the metal centers have a distorted octahedral geometry made up

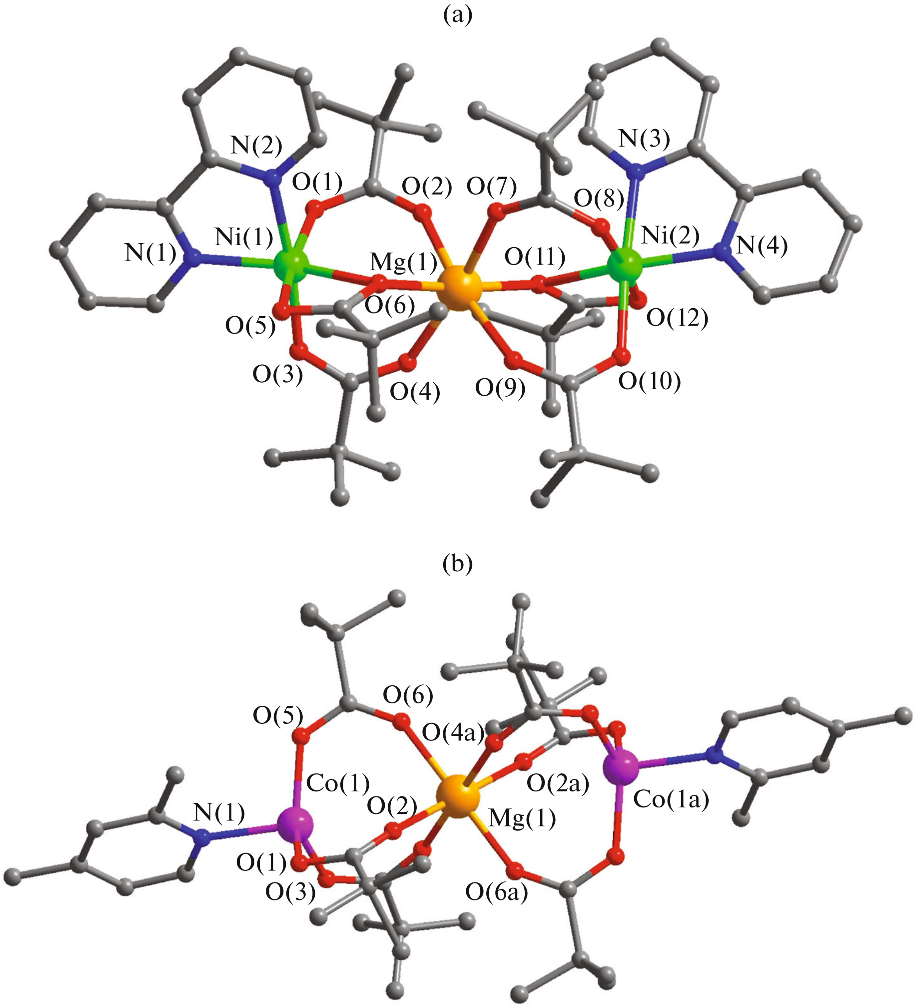


Fig. 6. Molecular structures of complexes **X** (a) and **XI** (b).

of six carboxylate O atoms (for Mg(II)) or four O atoms of the carboxylate bridges and two N atoms of 2,2'-Bipy (for Ni(II)). Geometrically, the formation of such an architecture can formally be represented as the "approach and fusion" of two singly charged ions (e.g., Li(I)) at an intersection point of the diagonals of the rhombic unit M_2O_2 (e.g., Li_2O_2 in complex **IV**) with allowance for the replacement of the two singly charged ions by a Mg(II) ion. This results in the alkaline-earth metal ion occupying a central position, which actually establishes the composition of the heterotrinuclear metal core with a doubly charged "hard" metal center.

While developing this approach, we obtained in a similar way a heterometallic complex combining a Mg atom and two Co atoms. In the resulting complex $[Co_2Mg(Piv)_6(2,4\text{-}Lut)_2]$ (**XI**), the metal atoms are collinear (the angle CoMgCo is 180°) (Fig. 6b) [61, 62]. The Mg atom has an octahedral coordination geometry and is linked with two Co atoms by one chelating-bridging and two bridging pivalate anions. In turn, the coordination polyhedron of either Co atom is a strongly distorted trigonal bipyramid made up of four pivalate O atoms and the N atom of 2,4-Lut.

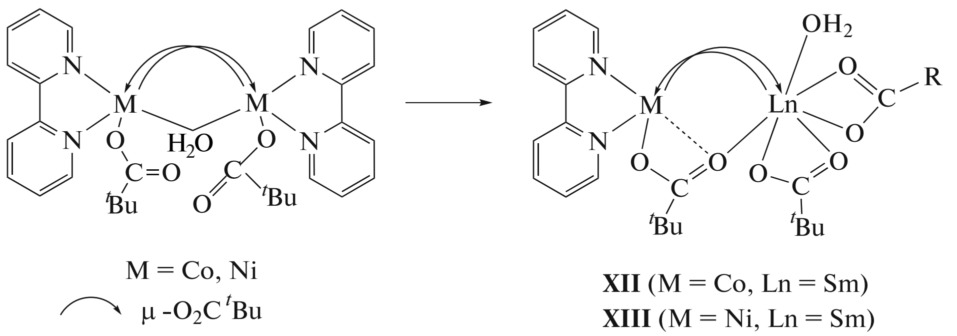
Heteronuclear complexes **X** and **XI** can be used as molecular precursors in the thermal *in situ* formation of an efficient catalytic oxide system containing transition metal and magnesium atoms and suitable as a catalyst for the synthesis of carbon nanotubes [60, 63].

THE FORMATION OF POLYNUCLEAR CARBOXYLATES COMBINING 3*d*-METAL (Co(II), Ni(II), OR Cu(II)) AND LANTHANIDE(III) IONS

Lanthanide(III) ions are known to have large ionic radii (1.06–1.20 Å) and many vacant orbitals, which is largely responsible for their higher coordination numbers (C.N. 8–10) in various mono- and polynuclear complexes [64]. When discussing the synthetic ways to

Ln(III)-containing complexes, one should keep in mind that lanthanide ions may be regarded as hard Lewis acids (like the aforementioned Li(I) and Mg (II) ions), though many lanthanide complexes with N-donating organic ligands are known (e.g., dinuclear carboxylates with pyridine, 2,2'-bipyridyl, 1,10-phenanthroline (Phen) derivatives, etc. [65–67]). With all these specific characteristics of the Ln(III) centers taken into account, it is difficult to imagine a priori what polynuclear molecules will form in reactions of lanthanide carboxylates with 3*d*-metal carboxylates. One can only assume that the moiety $LM(OOCR)_2$ (M is a 3*d*-metal ion, L is an organic or inorganic donating ligand) can potentially act as a sort of metal-containing ligand donating a necessary number of electrons to the vacant orbitals of the lanthanide ion from the carboxylate O atoms coordinated to the 3*d*-metal center. The number of such metal-containing ligands to the lanthanide ion can probably vary with the solvent (e.g., its donating activity) and the reaction temperature; i.e., this formally depends on the competition in reactivity between the metal-containing ligand and other electron donors (molecules or ions) present in the reaction mixture.

A reaction between the dinuclear Co(II) and Sm(III) complexes $[Co_2(Piv)_4(2,2'\text{-Bipy})_2(H_2O)]$ [68] and $[Sm_2(Piv)_6(HPiv)_6]$ [69] yields the heterometallic dinuclear complex $[CoSm(Piv)_5(2,2'\text{-Bipy})(H_2O)]$ (**XII**) containing only two dissimilar metal atoms (Scheme 1) [70]:



XII (M = Co, Ln = Sm)
XIII (M = Ni, Ln = Sm)
XIV (M = Co, Ln = Gd)
XV (M = Ni, Ln Gd)

Scheme.

In complex **XII**, the Sm and Co atoms are linked by three pivalate bridges (Co···Sm, 3.900 Å; Co–O, 2.009–2.048 Å; Sm–O, 2.321–2.350 Å) (Fig. 7a). The Sm atom in structure **XII** has a distorted dodecahedral geometry (monocapped pentagonal bipyramid) because of its additional coordination with two chelating pivalate anions and a water molecule (Sm–O(Piv), 2.418–2.544 Å; Sm–O(H_2O), 2.471 Å). The coordination polyhedron of the Co atom is completed with two N atoms of 2,2'-Bipy (Co–N, 2.088(6) and 2.171(6) Å) to form a distorted trigonal bipyramid. In the crystal, two adjacent molecules of the complex are symmetrically linked by hydrogen bonds between water molecules and pivalate groups (Fig. 7a).

Under similar conditions, a reaction between $[Sm_2(Piv)_6(HPiv)_6]$ and $[Ni_2(Piv)_4(2,2'\text{-Bipy})_2(H_2O)]$ [49] yields the dinuclear complex $[NiSm(Piv)_5(2,2'\text{-Bipy})(H_2O)]$ (**XIII**) (Scheme 1) crystallizing as a solvate with two molecules of pivalic acid (**XIII** · 2HPiv). The Sm and Ni atoms in complex **XIII** are linked by three pivalate bridges, one acting as a chelating ligand (Ni···Sm, 3.753 Å; Ni–O, 2.016–2.342 Å; Sm–O, 2.326–2.383 Å). The Sm atom is additionally coordinated by two chelating pivalate groups and a water molecule (Sm–O(Piv), 2.445–2.501 Å; Sm–O(H_2O), 2.433 Å). The Ni atom is coordinated by a 2,2'-Bipy molecule (Co–N, 2.035 and 2.062 Å) (Fig. 7b). This gives rise to an octahedral geometry of the Ni(II) ion in structure **XIII** (in contrast to **XII**). Hydrogen bonding between dinuclear molecules like that in **XII** is impossible in complex **XIII** because the coordinated water molecule is blocked by the solvate molecules of pivalic acid. In the crystal of complex **XIII**, the pyridyl rings of its adjacent molecules show stacking interactions ($d \approx 3.2$ Å) (Fig. 7b).

The composition of the final product does not vary with lanthanide ion. The complexes $[CoGd(Piv)_5(2,2'\text{-Bipy})(H_2O)]$ (**XIV**) and $[GdNi(Piv)_5(2,2'\text{-Bipy})(H_2O)] \cdot 2HPiv$ (**XV** · 2HPiv) were obtained according to a similar procedure employing Gd(III) pivalate instead of Sm(III) pivalate.

In contrast to the methods used to obtain heterodinuclear Co(II)-Ni(II) complexes **XII–XV**, the synthesis of heterometallic {Cu-Ln} complexes involved the complex $[Cu_2(Piv)_4(HPiv)_2]$ containing no N-donating apical ligands; the dinuclear lanthanide pivalates $[Ln_2(Piv)_6(HPiv)_6]$ (Ln = Sm or Gd) were separately

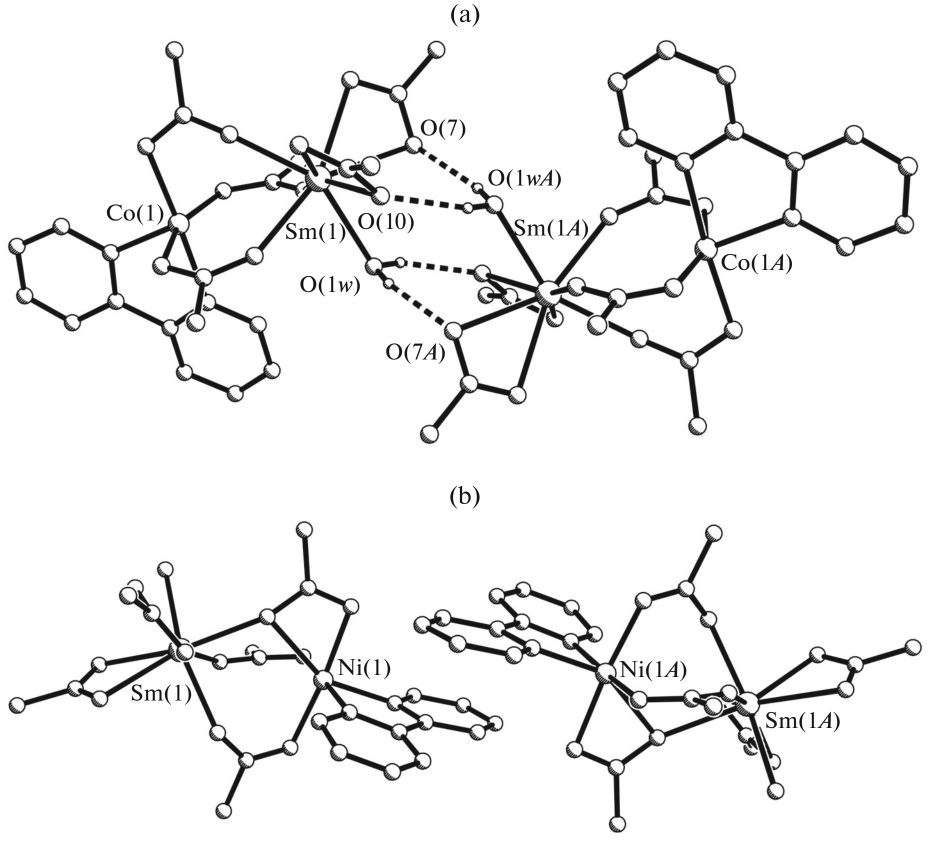


Fig. 7. Fragment of the packing pattern for complexes **XII** (a) and **XIII** (b) (the methyl substituents at the carboxylate groups are omitted).

added to 2,2'-Bipy. The reactions yielded crystalline dinuclear complexes [CuLn(Piv)$_5$(2,2'-Bipy)(HPiv)] (Ln = Sm (**XVI**) and Gd (**XVII**)) [70].

The metal atoms in complex **XVII** (Cu(1)···Gd(1), 3.819 Å) are linked by one chelating-bridging and two bridging pivalate groups. The coordination polyhedron of the Cu atom is a distorted trigonal bipyramid made up of three carboxylate O atoms (Cu–O, 1.915, 1.958, and 2.303 Å) and two N atoms of 2,2'-Bipy (Cu–N, 1.972 and 2.051 Å). The Gd atom is coordinated by four O atoms of one chelating-bridging and two bridging pivalate groups (Gd–O, 2.247–2.479 Å), three O atoms of the chelating and monodentate pivalate anions (Gd–O, 2.303–2.447 Å), and the O atom of HPiv (Gd–O, 2.329 Å); its resulting coordination polyhedron is a distorted dodecahedron (square antiprism). It should be noted that the Gd atom in structure **XVII** is chelated by the chelating-bridging pivalate anion, as distinct from {Co-Gd} complex **XIV** showing only μ-O,O'-bridging. Hydrogen bonds in complex **XVII** are formed between the H atom of the HPiv ligand and the O atom of the Piv$^-$ anion coordinated in a monodentate fashion (O(12)–H, 0.82 Å; O(12)···O(10), 2.43 Å; H···O(10), 1.64 Å; O(12)HO(10), 159.2°).

The synthesis of such heterodinuclear complexes with Phen afforded the complexes [EuM(Piv)$_5$(Phen)] (M = Zn(II) (**XVIII**) and Co(II) (**XIX**)) [71]. In their crystal structures, as in complex **XV**, the aromatic rings of the Phen ligands of adjacent molecules (related by a center of inversion) show π-stacking interactions. The planes of the Phen molecules are parallel; the shortest distances between the planes are 3.34 (M = Zn) and 3.40 Å (M = Co). The coordination number of Eu in complexes **XVIII** and **XIX** is eight, although they do not contain (in contrast to complexes with 2,2'-Bipy) a water molecule coordinated to the lanthanide ion. This C.N. is achieved by coordination of the chelating-bridging pivalate anion through two O atoms to the lanthanide rather than 3*d*-metal ion. The following coordination polyhedra are characteristic of the 3*d* metals in dinuclear complexes: a tetragonal pyramid (Co, L = Bipy), a trigonal bipyramid (Co, L = Phen), an octahedron (Ni), and a trigonal bipyramid (Cu and Zn). Note that similar dinuclear complexes with quinoline, [CoLn(Piv)$_5$(C$_9$H$_7$N)(H$_2$O)] (Ln = Gd or Dy), are known; the coordination numbers of Ln and Co in these complexes are eight and four (tetrahedral geometry), respectively [72].

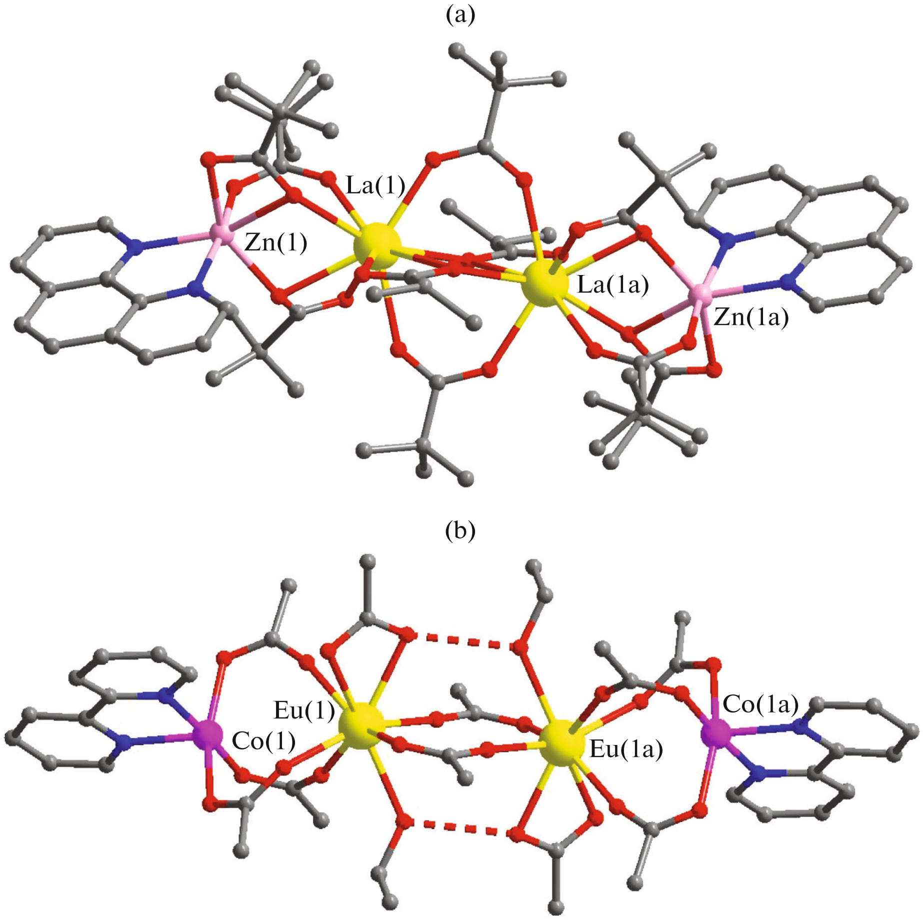


Fig. 8. Molecular structures of complexes **XX** (a) and **XXI** (b) (the naphthyl substituents of the 2-naphthoate anions are omitted).

Thermogravimetric measurements of heterodinuclear {3*d*–4*f*} complexes show that their molecules at 50–95°C sequentially eliminate neutral ligands (water, coordinated acid, and, finally, the N-donating ligand) [70]. Of course, reactions between transition metal and lanthanide carboxylates (e.g., pivalates), which usually involve gentle heating, can be accompanied by dimerization or even polymerization of the initially formed heterodinuclear architectures. It should be taken into consideration that the large ionic radii of lanthanides allow the formation of tetranuclear structures featuring a dilanthanide unit (via dimerization of the dinuclear moieties containing coordinatively unsaturated lanthanide ions). Heterometallic moieties tend to dimerize even during the crystallization from solutions because of an increased ionic radius of lanthanide. For instance, the attempted synthesis of heterodinuclear structures from La(III) pivalate ($r(La^{3+}) = 1.20$ Å) yielded the tetranuclear complex $[La_2Zn_2(Piv)_{10}(Phen)_2]$ (**XX**) composed of two moieties $\{(Phen)ZnLa(Piv)_3\}$ linked by four pivalate bridges (Fig. 8a). Note that a similar reaction with Eu(III) pivalate ($r(Eu^{3+}) = 1.18$ Å $< r(La^{3+})$) produces no tetranuclear structure [73]. This suggests the importance of steric effects in the formation of heterometallic 3*d*–4*f* carboxylate complexes. The metal atoms in complex **XX** are arranged in a nearly linear pattern (the angle ZnLaLa is 165.59°; La···Zn, 3.674 Å; La···La, 4.157 Å). The structure of $[La_2Zn_2(Piv)_{10}(Phen)_2]$ can formally be regarded as a dimerization product of $[LaZn(Piv)_5(Phen)]$, which is similar to the dinuclear {3*d*–4*f*} complexes discussed above.

The architecture of {3*d*–4*f*} complexes appreciably depends on the structure of substituents in the carboxylate anion. When the bulky *tert*-butyl 3D-groups in the pivalate anions are replaced by naphthoate 2D-substituents, the aforementioned heteronuclear assembly results only in tetranuclear structures. For instance, we obtained several types of tetranuclear complexes with the anions of 2-naphthoic acid (2-NaphH). A reaction of cobalt nitrate with a stoichiometric amount of potassium 2-naphthoate followed by addition of $Eu(NO_3)_3 \cdot 6H_2O$

(Co : Eu = 3 : 1) gave the complex $[Co_2Eu_2(2\text{-}Naph)_{10}(2,2'\text{-}Bipy)_2(EtOH)_2]$ (**XXI**) [74]. The above Co : Eu ratio is explained by partial consumption of cobalt(II) in binding nitrate anions to form the target product and $Co(NO_3)_2$, which is more soluble in MeCN and thus remains in solution. In tetranuclear complex **XXI**, the center of inversion is between the central Eu(1) and Eu(1*A*) atoms (Co···Eu, 3.940 Å; Eu···Eu, 4.807 Å) (Fig. 8b). The metal atoms show somewhat worse collinearity than those in tetranuclear complex **XX** (the angle CoEuEu is 158.9°). The coordination number of the Eu atom is eight (monocapped pentagonal bipyramid) because of its additional coordination with two O atoms of the chelating 2-naphthoate group and the O atom of EtOH. The coordination polyhedron of either Co atom is a distorted square pyramid.

Interestingly, reactions between $ZnCl_2$ (or $Zn(NO_3)_2$), $Eu(NO_3)_3$, and 1-naphthoic acid (1-NaphH) derivatives in EtOH–MeCN also yield tetranuclear complexes yet containing no coordinated EtOH molecule. Using appropriate zinc salts, one can obtain naphthoate (from $ZnCl_2$) or nitrate-naphthoate complexes (from $Zn(NO_3)_2$): $[Eu_2Zn_2(1\text{-}Naph)_{10}(2,2'\text{-}Bipy)_2]$ (**XXII**), $[Eu_2Zn_2(1\text{-}Naph)_8(NO_3)_2(2,2'\text{-}Bipy)_2]$ (**XXIII**), and $[Eu_2Zn_2(1\text{-}Naph)_8(NO_3)_2(1,10\text{-}Phen)_2]$ (**XXIV**) [75].

The metal core of the $\{Zn_2Eu_2\}$ complexes has the same local geometry: the central unit ($\{Eu_2(Naph)_6\}$ or $\{Eu_2(Naph)_4(NO_3)_2\}$ consists of two Eu(III) atoms bridged by four naphthoate anions (Fig. 9a). The central unit is linked with the Zn atoms by naphthoate bridges to form the zigzag tetranuclear core {ZnEuEuZn} (Zn···Eu, 3.735–3.890 Å; Eu···Eu, 4.084–4.389 Å; the angles ZnEuEu are 103.6°–115.5°). Either terminal Zn atom is chelated by the N-donating ligand (2,2'-Bipy or Phen). The ligands to either Zn atom make up a distorted trigonal bipyramid (ZnO_3N_2). The coordination polyhedron of either Eu(III) ion can be described as a monocapped pentagonal bipyramid (C.N. 8). The difference in composition between the complexes with the 1- and 2-Naph anions gives rise to some structural (for their metal cores) and functional differences (for their bridging groups). For instance, all three carboxylate groups in the moieties $\{CoEu(2\text{-}Naph)_3\}$ of the $\{Co_2Eu_2\}$ complex act as bridging ligands, while the $\{Zn_2Eu_2\}$ complexes feature a μ_3-bridging carboxylate group, which strengthens the linkage between the metal ions.

Particular attention should be given to the packing pattern for naphthoate complexes in the crystal. For instance, the $\{Co_2Eu_2\}$ complex with 2-naphthoate is composed of discrete molecules showing no intermolecular stacking between the aromatic rings, whereas the $\{Zn_2Eu_2\}$ complexes form supramolecular 2D- and 3D-polymers, depending on the chelating ligand (2,2'-Bipy or 1,10-Phen) and on the number of 1-Naph anions in the complex [75].

Trinuclear {3*d*–4*f*–3*d*} complexes, whose metal core is formally similar to that in magnesium complexes **X** and **XI** (as regards the proportion and arrangement of the metal centers), can be obtained from $[Co(Piv)_2]_n$, $[Sm_2(Piv)_6(HPiv)_6]$, and 2,4-Lut used in stoichiometric amounts. For instance, the complex $[Co_2Sm(Piv)_7(2,4\text{-}Lut)_2]$ (**XXV**) was obtained in nearly quantitative yield (with respect to Sm) [76]. Unlike the Li-M(3*d*) and Mg-M(3*d*) complexes described above, heterometallic complex **XXV** contains a pivalate anion coordinated (via chelation) only by the Sm atom (Fig. 9b). The composition and structure of this complex are due to the necessity of compensating for the charge on the Sm ion as well as to its high coordination number. The metal atoms are not collinear (the angle CoSmCo is 138.14°); their coordination polyhedra are a tetrahedron (for Co) and a square antiprism (for Sm).

The trinuclear nitrate-pivalate complexes $[Co_2Ln(NO_3)(Piv)_6L_2(MeCN)_2]$ (L = MeCN (**XXVI**), L = Me-Nit (Me-Nit = 2,4,4,5,5-pentamethyl-2-imidazoline-3-oxide-1-oxyl) (**XXVII**)), $[LnNi_2(NO_3)(Piv)_6(HPiv)_2(MeCN)_2]$ (**XXVIII**), $[LnNi_2(NO_3)(Piv)_6(2,2'\text{-}Bipy)_2]$ (**XXIX**), $[Cu_2Ln(NO_3)(Piv)_6(2,2'\text{-}Bipy)_2]$ (**XXX**), and $[LnZn_2(NO_3)(Piv)_6L_2]$ (L = MeCN (**XXXI**), 2,4-Lut (**XXXII**), and 2,2'-Bipy (**XXXIII**)) can be obtained from appropriate 3*d*-metal pivalates, N-donating ligands, and lanthanide nitrates [55, 77–79]. For instance, the yields of complexes **XXX** and **XXXI** are nearly quantitative.

The metal core of such complexes is similar to that in complex **XXV**, except that the central lanthanide atom is chelated by the NO_3 rather than Piv anion and that the coordination geometries of the transition metal ions vary from tetrahedral (for Co and Zn) to octahedral (for Ni) [78, 79].

Interestingly, dinuclear Cu(II) and Ni(II) complexes with four pivalate bridges and strongly bound apical N-donating ligands (e.g., pyridine derivatives), which stabilize such an architecture, proved to be ineffective in the synthesis of {3*d*–Ln–3*d*} structures, probably because of their high chemical stability. For the formation of trinuclear structures, 3*d*-metal pivalates containing no coordinated pyridines were always used. Alternatively, trinuclear structures can be obtained, for example, from the highly labile complex $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ or $[Cu_2(Piv)_4(HPiv)_2]$. The use of the former, as already mentioned, affords complex **XXVIII**; the synthesis from $[Cu_2(Piv)_4(HPiv)_2]$ in the presence of NBu_4OH gives the heterometallic trinuclear anionic Cu(II) complexes $(NBu_4)[Cu_2Ln(Piv)_8]$ (Ln = Eu (**XXXIV**) or Gd (**XXXV**)) [78] (Fig. 10). The complex anion $[Cu_2Ln(Piv)_8]^-$ is built from two moieties

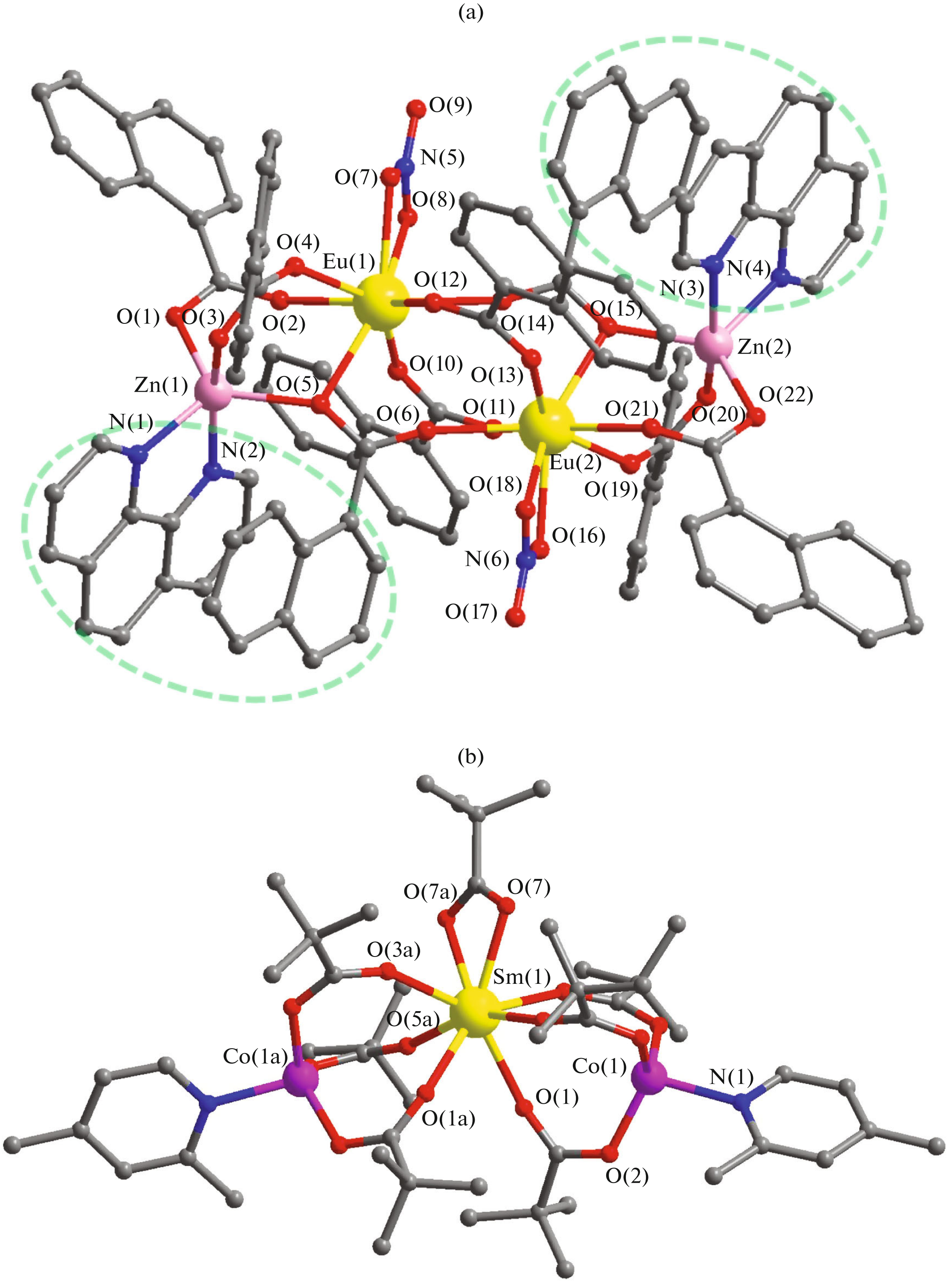


Fig. 9. Molecular structures of complexes **XXIV** (a) (the aromatic rings involved in intramolecular stacking are circumscribed with dashed lines) and **XXV** (b).

$\{Cu(O_2CR)_4Ln\}$, in which the metal atoms are bridged by four pivalate groups. The moieties share the Ln center, so its coordination polyhedron is a distorted tetragonal antiprism. The anion $[Cu_2Ln(Piv)_8]^-$ is nearly linear (the angle CuEuCu is 177.5°); either Cu(II) ion has a distorted square planar geometry

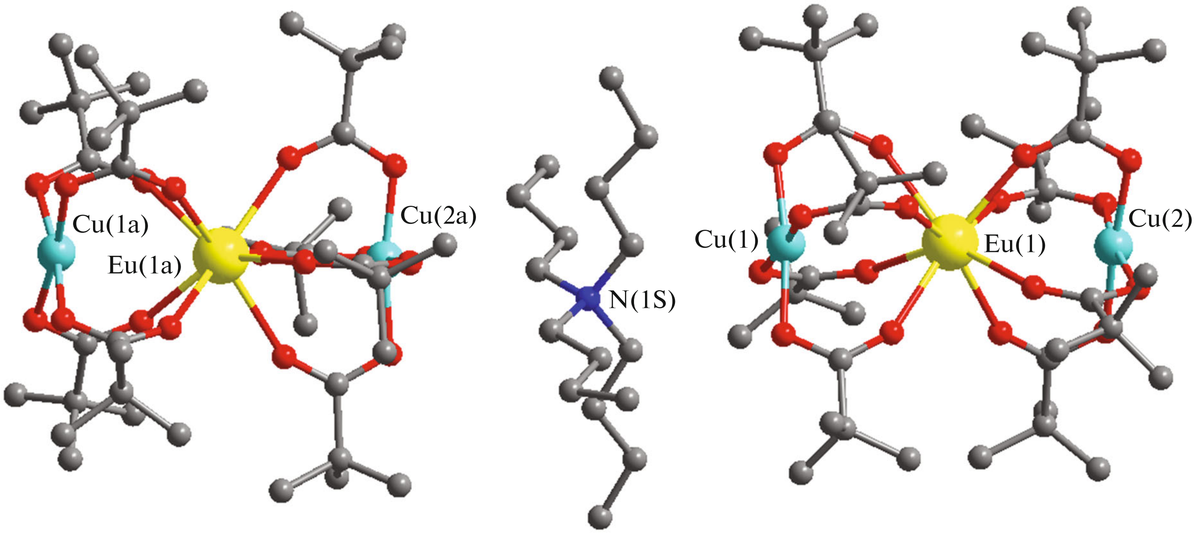


Fig. 10. Fragment of the packing pattern for the complex $(NBu_4)[Cu_2Eu(Piv)_8]$.

made up of four O atoms (the deviation of the Cu(II) ions from the O_4 plane is ~0.11 Å). Because the metal ions are linked in pairs by four carboxylate bridges (as in the dinuclear transition metal complexes $LM(\mu_2\text{-}O_2CR)_4ML$, where R = Me, ^{t}Bu, Ph, etc.), the Cu...Ln distance is considerably shorter (3.35 Å) than that in neutral dinuclear {3*d*–4*f*} complexes. In the crystal, the N atom of the tetrabutylammonium cation comes very close to an imaginary line passing through the nearby copper(II) ions (Cu···Cu, 8.062 Å) of two adjacent anions $[Cu_2Ln(Piv)_8]^-$.

To sum up, the formation of various {3*d*–4*f*} monocarboxylate architectures largely depends, first of all, on the specific characteristics of lanthanide(III) ions such as large ionic radii (including some difference between them), the composition of the starting lanthanide reactant, the tendency toward high coordination numbers, and finally the "hardness" of the ion. In all tri- and tetranuclear structures, the lanthanide ions occupy a central position, as in the complexes containing the hard Li and Mg ions. However, in contrast to the latter, the use of lanthanide ions enables structural diversification of the target architectures (from dinuclear to tetranuclear). Finally, the peripheral substituent in lanthanide-containing systems distinctly affects the resulting heteronuclear structure, and the presence of the nitrate anion bound to the Ln(III) atom (as in the starting lanthanide nitrates) makes it possible to obtain both carboxylate and nitrate-carboxylate complexes.

REFERENCES

1. Tey, S.L., Reddy, M.V., Subba Rao, G.V., et al., *Chem. Mater.*, 2006, vol. 18, no. 6, p. 1587.
2. Bazhina, E.S., Aleksandrov, G.G., Sidorov, A.A., and Eremenko, I.L., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 11, p. 730.
3. Burkovskaya, N.P., Nikiforova, M.E., Kiskin, M.A., et al., *Polyhedron*, 2012, vol. 35, p. 116.
4. Zauzolkova, N.V., Zorina, E.N., Sidorov, A.A., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2012, no. 7, p. 1404.
5. Wei, Z., Han, H., Filatov, A.S., and Dikarev, E.V., *Chem. Sci.*, 2014, vol. 5, no. 2, p. 813.
6. Wei, Z., Filatov, A.S., and Dikarev, E.V., *J. Am. Chem. Soc.*, 2013, vol. 135, p. 12216.
7. Navulla, A., Huynh, L., Wei, Z., et al., *J. Am. Chem. Soc.*, 2012, vol. 134, no. 13, p. 5762.
8. Cheprakova, E.M., Verbitskiy, E.V., Kiskin, M.A., et al., *Polyhedron*, 2015, vol. 100, p. 89.
9. Dobrokhotova, Zh.V., Gogoleva, N.V., Zorina-Tikhonova, E.N., et al., *Eur. J. Inorg. Chem.*, 2015, p. 3116.
10. Ryumin, M.A., Dobrokhotova, Zh.V., Emelina, A.L., et al., *Polyhedron*, 2015, vol. 87, p. 28.
11. Zauzolkova, N., Dobrokhotova, Zh., Lermontov, A., et al., *J. Solid State Chem.*, 2013, vol. 197, p. 379.
12. Gavrikov, A.V., Koroteev, P.S., Dobrokhotova, Z.V., et al., *Polyhedron*, 2015, vol. 102, p. 48.
13. Zheng, Y.-Z., Zhou, G.-J., Zhenga, Z., and Winpenny, R.E.P., *Chem. Soc. Rev.*, 2014, vol. 43, p. 1462.
14. Feltham, H.L.C. and Brooker, S., *Coord. Chem. Rev.*, 2014, vol. 276, p. 1.
15. Liu, K., Shi, W., and Cheng, P., *Coord. Chem. Rev.*, 2015, vols. 289–290, p. 74.
16. Krompiec, S., Penkala, M., Szczubialka, K., and Kowalska, E., *Coord. Chem. Rev.*, 2012, vol. 256, p. 2057.
17. *Homogeneous Catalysis with Metal Complexes: Kinetic Aspects and Mechanisms,* Temkin O.N., Ed., Chichester: Wiley, 2012.
18. Gupta, K.C. and Sutar, A.K., *Coord. Chem. Rev.*, 2008, vol. 252, p. 1420.
19. Seo, J.S., Whang, D., Lee, H., et al., *Nature*, 2000, vol. 404, p. 982.
20. *Coordination Polymers: Design, Analysis and Application*, Batten S.R., Neville S.M., and Turner D.R., Eds., Cambridge: The Royal Society of Chemistry, 2009.
21. Fursova, E.Yu., Kuznetsova, O.V., Romanenko, G.V., and Ovcharenko, V.I., *Izv. Akad. Nauk, Ser. Khim.*, 2006, no. 11, p. 1863.

22. Pearson, R.G., *J. Am. Chem. Soc.*, 1963, vol. 85, p. 3533.
23. Pearson, R.J., *Usp. Khim.*, 1971, vol. 40, no. 7, p. 1259.
24. Garnovskii, A.D., Sadimenko A P., Osipov O.A., and Tsintsadze G.V. *Zhestko-myagkie vzaimodeistviya v koordinatsionnoi khimii* (Hard–Soft Interactions in Coordination Chemistry), Rostov-on-Don, 1986.
25. *Hard and Soft Acids and Bases*, Pearson R.G., Ed., Stroudsburg: Dowden, Hutchinson and Ross, 1973.
26. Sidorov, A.A., Danilov, P.V., Nefedov, S.E., et al., *Russ. J. Inorg. Chem.*, 1998, vol. 43, no. 6, p. 846.
27. Sidorov, A.A., Deomidov, S.A., Nefedov, S.E., et al., Russ. J. Inorg. Chem., 1999, vol. 44, no. 3, p. 345.
28. Eremenko, I.L., Nefedov, S.E., Sidorov, A.A., and Moiseev, I.I., *Izv. Akad. Nauk, Ser. Khim.*, 1999, no. 3, p. 409.
29. Golubnichaya, M.A., Sidorov, A.A., Fomina, I.G., et al., *Izv. Akad. Nauk, Ser. Khim.*, 1999, no. 9, p. 1773.
30. Golubnichaya, M.A., Sidorov, A.A., Fomina, I.G., et al., *Russ. J. Inorg. Chem.*, 1999, vol. 44, no. 9, p. 1401.
31. Sidorov, A.A., Fomina, I.G., Talismanov, S.S., et al., *Russ. J. Coord. Chem.*, 2001, vol. 27, no. 8, p. 548.
32. Sidorov, A.A., Nikiforova, M.E., Pakhmutova, E.V., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2006, no. 11, p. 1851.
33. Pakhmutova, E.V., Malkov, A.E., Mikhailova, T.B., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2003, no. 1, p. 131.
34. Mikhailova, T.B., Malkov, A.E., Sidorov, A.A., et al., *Russ. J. Inorg. Chem.*, 2002, no. 11, p. 1680.
35. Gol'dberg, A.E., Kiskin, M.A., Sidorov, A.A., and Eremenko, I.L., *Izv. Akad. Nauk, Ser. Khim.*, 2011, no. 5, p. 829.
36. Gol'dberg, A.E., Kiskin, M.A., Kozyukhin, S.A., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2011, no. 5, p. 987.
37. Zauzolkova, N.V., Nikiforova, M.E., Sidorov, A.A., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2010, no. 6, p. 1161.
38. Dobrohotova, Z.V., Sidorov, A.A., Kiskin, M.A., et al., *J. Solid State Chem.*, 2010, vol. 183, no. 10, p. 2475.
39. Frycek, R., Vyslouzil, F., Myslik, V., et al., *Sens. Actuators, B*, 2007, vol. 125, p. 189.
40. Thakuria, H., Borah, B.M., and Das, G., *Eur. J. Inorg. Chem.*, 2007, p. 524.
41. Condorelli, G.G., Malandrino, G., and Fragala, I.L., *Coord. Chem. Rev.*, 2007, vol. 51, p. 1931.
42. Stefanescu, M., Stefanescu, O., Stoia, M., and Lazau, C., *J. Therm. Anal. Calorim.*, 2007, vol. 88, p. 27.
43. Revaprasadu, N. and Mlondo, S.N., *Pure Appl. Chem.*, 2006, vol. 78, p. 1691.
44. Sabo, T.J., Grguric-Sipka, S.R., and Trifunovic, S.R., *Synth. React. Inorg. Met. Org. Chem.*, 2002, vol. 32, p. 1661.
45. Deb, N., Baruah, S.D., and Dass, N.N., *J. Therm. Anal. Calorim.*, 2000, vol. 59, p. 791.
46. Wullens, H., Bodart, N., and Devillers, M., *J. Solid State Chem.*, 2002, vol. 167, p. 494.
47. Fomina, I.G., Aleksandrov, G.G., Dobrokhotova, Zh.V., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2006, no. 11, p. 1841.
48. Eremenko, I.L., Kiskin, M.A., Fomina, I.G., et al., *J. Cluster Sci.*, 2005, vol. 16, p. 331.
49. Eremenko, I.L., Nefedov, S.E., Sidorov, A.A., et al., *Inorg. Chem.*, 1999, vol. 38, p. 3764.
50. Fomina, I.G., Sidorov, A.A., Aleksandrov, G.G., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2004, p. 116.
51. Liao, J.-H., Su, C.-T., and Hsu, C.-C., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2001, vol. 57, p. m501.
52. Kurmoo, M., Estournes, C., Oka, Y., et al., *Inorg. Chem.*, 2005, vol. 44, p. 217.
53. Evstifeev, I.S., Kiskin, M.A., Mironov, V.S., et al., *Inorg. Chem. Comm.*, 2010, vol. 13, p. 498.
54. Fomina, I., Dobrokhotova, Z., Aleksandrov, G., et al., *Polyhedron*, 2010, vol. 29, p. 1734.
55. Kiskin, M.A., *Doctoral (Chem.) Dissertation*, Moscow: Kurnakov Institute of General and Inorganic Chemistry, RAS, 2013.
56. Kiskin, M.A. and Eremenko, I.L., *Private Comm.*, 2006, CCDC 1470331.
57. Addison, A.W., Rao, T.N., Reedijk, J., et al., *J. Chem. Soc., Dalton. Trans.*, 1984, no. 7, p. 1349.
58. Kiskin, M.A., Aleksandrov, G.G., Bogomyakov, A.S., et al., *Inorg. Chem. Commun.*, 2008, vol. 11, p. 1015.
59. Evstifeev, I.S., Kiskin, M.A., Bogomyakov, A.S., et al., *Cryst. Rep.*, 2011, vol. 56, no. 5, p. 842.
60. Sidorov, A.A., Nikiforova, M.E., Zauzolkova, N.V., et al., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2010, vol. 53, no. 7, p. 69.
61. Zauzolkova, N.V., *Cand. Sci. (Chem.) Dissertation*, Moscow: Kurnakov Institute of General and Inorganic Chemistry, RAS, 2010.
62. Gogoleva, N.V., Aleksandrov, G.G., Sidorov, A.A., and Eremenko, I.L., *Private Commun.*, 2015, CCDC 1062460.
63. Zharikova, E.F., Zyuzin, V.V., Shishagin, V.V., et al., RF Patent 2431600 (2010).
64. Cotton, S., *Lanthanide and Actinide Chemistry*, Chichester: Wiley, 2006.
65. Singh, U.P. and Kumar, R., *J. Mol. Struct.*, 2007, vol. 214, p. 837.
66. Ma, D.-Y., Guo, H.-F., Qin, L., and Xu, J., *Bull. Korean Chem. Soc.*, 2013, vol. 34 P, p. 2774.
67. Wang, S.P., Xu, L.J., Gao, Z.H., and Wang, R.F., *Russ. J. Coord. Chem.*, 2010, vol. 36, no. 10, p. 794.
68. Talismanova, M.O., Sidorov, A.A., Novotortsev, V.M., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 11, p. 2149.
69. Fomina, I.G., Kiskin, M.A., Martynov, A.G., et al., *Russ. J. Inorg. Chem.*, 2004, vol. 49, no. 9, p. 1463.
70. Orlova, E.V., Gol'dberg, A.E., Kiskin, M.A., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2011, no. 11, p. 2195.
71. Kiskin, M.A., Dobrokhotova, Zh.V., Bogomyakov, A.S., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2016, no. 6, p. 1488.
72. Cui, Y., Chen, G., Ren, J., et al., *Inorg. Chem.*, 2000, vol. 39, p. 4165.
73. Gogoleva, N.V., Sidorov, A.A., Kiskin, M.A., and Eremenko, I.L., *CSD Commun.*, 2016, CCDC 1470301.
74. Gol'berg, A.E., Nikolaevskii, S.A., Kiskin, M.A., et al., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 12, p. 777.
75. Goldberg, A., Kiskin, M., Shalygina, O., et al., *Chem. Asian J.*, 2016, vol. 11, no. 4, p. 604.
76. Bykov, M.A., Emelina, A.L., Orlova, E.V., et al., *Russ. J. Inorg. Chem.*, 2009, vol. 54, no. 4, p. 601.
77. Fursova, E.Yu., Kuznetsova, O.V., Ovcharenko, V.I., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2007, no. 9, p. 1742.
78. Burkovskaya, N.P., Orlova, E.V., Kiskin, M.A., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2011, no. 12, p. 2442.
79. Egorov, E.N., Mikhaleva, E.A., Kiskin, M.A., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2013, no. 10, p. 2141.

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