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Some aspects of the formation and structural features of low nuclearity heterometallic carboxylates

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Abstract: Heterometallic carboxylate complexes are of paramount interest in pure and applied coordination chemistry. Despite that plurality of such type compounds have been published to date, synthetic aspects of their chemistry often remain in the shadow of intriguing physical properties manifesting by these species. Present review summarizes reliable data on direct synthesis of low nuclearity molecular compounds as well as coordination polymers on their base with carboxylate-bridged $\{M_2Mg\}$ ($M = Co^{2+}$, Ni^{2+}, Cd^{2+}), $\{M_2Li_2\}$ ($M = Co^{2+}$, Ni^{2+}, Zn^{2+}, VO^{2+}), $\{M_2Ln_2\}$ and $\{M_2Ln\}$ ($M = Cu^{2+}$, Zn^{2+}, Co^{2+}) metal cores. Structural features and stabilization factors are considered and principal outcomes are confirmed by quantum-chemical calculations. Particular attention is paid to consideration of ligand-exchange reactions that allow controllable modification of heterometallic metal core under mild conditions giving diverse molecular complexes with modified ligand environment or Metal-Organic Frameworks with permanent porosity.

Keywords: carboxylate ligands; crystal structure; heterometallic complexes; Mendeleev-21; synthesis; transition metals.

Introduction

Carboxylate compounds attract attention of researchers due to the wide range of their practically important chemical and physical properties. They are manifested in metal complex catalysis or chemical assembly of new organic compounds on the metal core of polynuclear catalyst molecules [1–8], photoluminescence (emission of organic ligands in complexes, emission of 4f-metal ions enhanced by aromatic antenna-ligands [9–18]), molecular magnetism (contrast agents, high-spin labels, spin-spin transitions, molecular magnets, low-temperature cooling agents [19–27]), biological activity (antimicrobial, anti-cancer, etc. [28–31]) or sorption

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properties (gas separation, hydrogen storage, etc. [32–38]). At the same time, the majority of studies in the field of chemistry of coordination polynuclear carboxylates relates to homometallic complexes (compounds of *s*-, *d*-, *f*-metals with variety of carboxylate anions have been published to date), whereas studies on the synthesis and structures of heterometallic molecules containing metal atoms of various nature, including those in stoichiometric ratios, and occupying certain positions in the structure of the polynuclear complex have been studied far less.

Undoubtedly, the study on the chemistry and physics of heterometallic molecules expands the possibilities of preparation of substances with practically important properties, but it also has its own natural limitations. This problem can be exemplified with bimetallic compounds $\{Ln^1Ln^2(O_2CR)_6L_x\}$ (where O_2CR is a carboxylate ligand, Ln is a rare-earth metal atom, L is a donor ligand) [39, 40], in which it is impossible to determine the exact positions of heterometals in crystals by single-crystal X-ray diffraction. Formally, these compounds can easily be obtained, but it is highly probable that they are co-crystallizates of three compounds – the mentioned heterometallic compound $\{Ln^1Ln^2(O_2CR)_6L_x\}$ and two homometallic compounds $\{Ln^1(O_2CR)_6L_x\}$ and $\{Ln^2(O_2CR)_6L_x\}$. The proximity of the properties of lanthanide atoms makes the probability of their localization in the crystal packing approximately the same as for isotopes of one metal. It is therefore no mere coincidence that the criteria for recognition of the truly stoichiometric atomic ratio and localization of the atomic positions of individual metals in a polynuclear metal core have been emphasized. Moreover, when the core contains metals significantly differing in size, atomic mass, electron configuration, unambiguous assignment of respective metal positions becomes possible in heterometal polynuclear complexes. For example, there is a family of mixed-valent trinuclear carboxylate iron complexes $[Fe^{III}{}_2Fe^{II}(O_2CR)_6(L)_3]$ (L is N- or O-donor neutral ligand), and of their heterometallic analogs $[Fe^{III}{}_2M(O_2CR)_6(L)_3]$, where the position of Fe(II) can be occupied by Mn(II), Ni(II), Co(II), Zn(II), Mg(II) [41–45]. Even in a simplified treatment of these structure (leaving out dislocations) scrutiny of details of the molecular and crystalline structure (coordination environment taking into account M–O and M–N bond lengths and relevant bond angles) allows reliable discrimination between the positions occupied by Fe(III) and M(II). Additional information on the magnetic behavior of the complexes allows one to select the desired model of the location of “magnetic” ions in the corresponding architecture, which in the examples presented, as a rule, coincides with the obtained X-ray diffraction data. Note that, in accordance with the Cambridge Crystallographic Data Centre (CCDC), there are significantly fewer examples of similar stoichiometric heterometallic complexes as compared to homometallic compounds.

The methods of formation and determination of the exact structure and properties of stable heterometallic complexes are of undoubted interest both from a scientific point of view and for solving various applied problems. For example, molecular coordination heterometallic compounds with a certain ratio of metal ions are studied as precursors for the preparation of complex oxide materials in the form of bulk samples and various films and coatings, which imposes certain conditions for maintaining the ratio between metal ions in the initial molecular complex and the resulting material, including the requirement of uniformity of the final product [46–49].

Heterometallic carboxylate architectures: formation, structure, and stability

In this review, we consider a family of heterometallic carboxylate complexes in which 3*d*-metal ions (V(IV) in the fragment of VO^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) are combined with Li^+, Mg^{2+} or other alkaline earth element ions and 4*f*-metal ions. Cd^{2+} is capable of forming heterometallic compounds similar in composition and structure, although these compounds have some features related to the large size of the ion and the ability to exhibit coordination numbers greater than six. We limited the review to a low nuclear complexes (up to 4 metal atoms), although there are clusters with higher nuclearity (from 5 or more metal atoms), for example [50–52].

Examples of trinuclear molecular systems with a linear metal core

The simplest case of the formation of a trinuclear heterometallic complex with a linear metal core can be observed with isomorphic substitution of part of the metal atoms in a homonuclear analog. Formally, this process can be attributed to the reactions of transmetallation of the central ion in the starting compound, although the reaction is complicated. Such an example can be demonstrated in the "virtual" conversion of the cobalt(II) homonuclear complex $[Co_3(naph)_6(lut)_2]$ (**1**) into the heterometallic complex $[Co_2Mg(naph)_6(lut)_2]$ (naph is the anion of 2-naphthoic acid; lut is lutidine) (**2**) (Fig. 1).

In homonuclear complex **1**, the central and peripheral Co(II) atoms are nonequivalent and have a different coordination environment. The peripheral cobalt atoms are in a distorted trigonal-bipyramidal environment (CoO_4N), while the environment of the central atom corresponds to a distorted octahedron (CoO_6). As a result, **1** can be considered as the "prototype" of the heterometallic compound in which another divalent metal ion occupies the central position. To replace the ions of a *d*-element, a *s*-metal can be selected, which, according to Pearson's classification, has a large affinity for oxygen atoms in the coordination sphere [53, 54] and coordination numbers close to 3*d*-elements. The indicated requirements are met by the Mg^{2+} ion. This assumption was confirmed by the reaction which afforded magnesium-containing complex **2** in a quantitative yield according to Equation (1) [55]:

$$2[Co_3(O_2CR)_6(lut)_2] + 3Mg(O_2CR)_2 + 2lut \rightarrow 3[Co_2Mg(O_2CR)_6(lut)_2] \quad (1)$$

For energy assessment of pathways of the formation of complex {Co–Mg–Co}, a model reaction between cobalt carboxylate and magnesium trifluoromethanesulfonate was studied by quantum-chemical calculations, which, as shown earlier, is capable of producing the desired trinuclear Co_2Mg compound (**2**). Note that this scheme involves the use of the starting complex $[Mg(MeCN)_4(CF_3SO_3)_2]$ with easily replaceable acetonitrile molecules. The lability of these coordinated solvent molecules is often used in coordination chemistry when generating active fragments with *s*- and *d*-element ions in reaction medium.

$$[Co_3(O_2CR)_6(lut)_2] + [Mg(MeCN)_4(CF_3SO_3)_2] \leftrightarrow [Co_2Mg(O_2CR)_6(lut)_2] + [Co(MeCN)_4(CF_3SO_3)_2] \quad (2)$$

The relative energies of the compounds on the left and right sides of Equation (2) were estimated. The calculations were carried out by the density functional theory method using the B3LYP/Def2-TZVP approximation, as well as its variations, including dispersion interactions (CAM-B3LYP/Def2-TZVP and CAM-B3LYP/Def2-TZVP + D3BJ). As follows from the results of calculations of complexes with naphthoate ligands shown

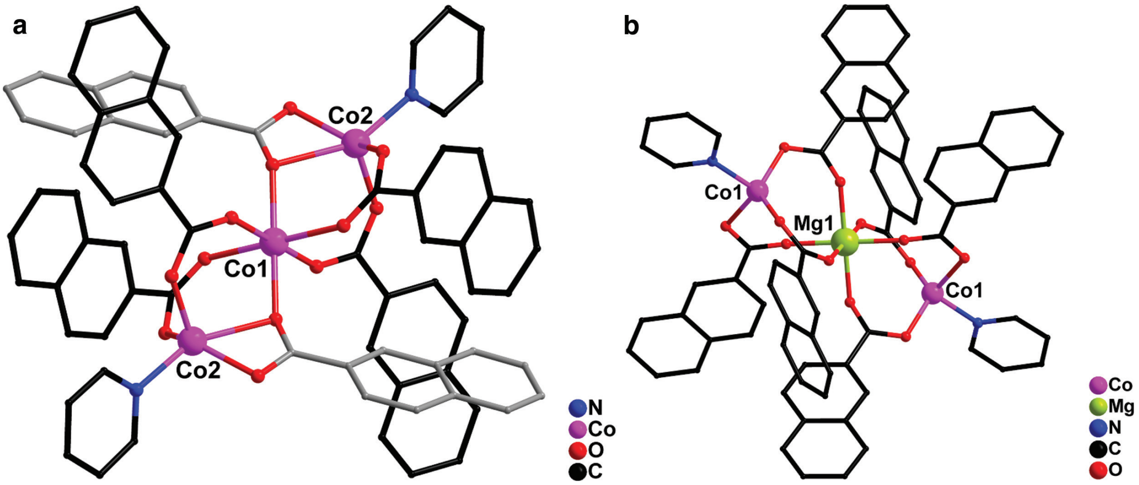
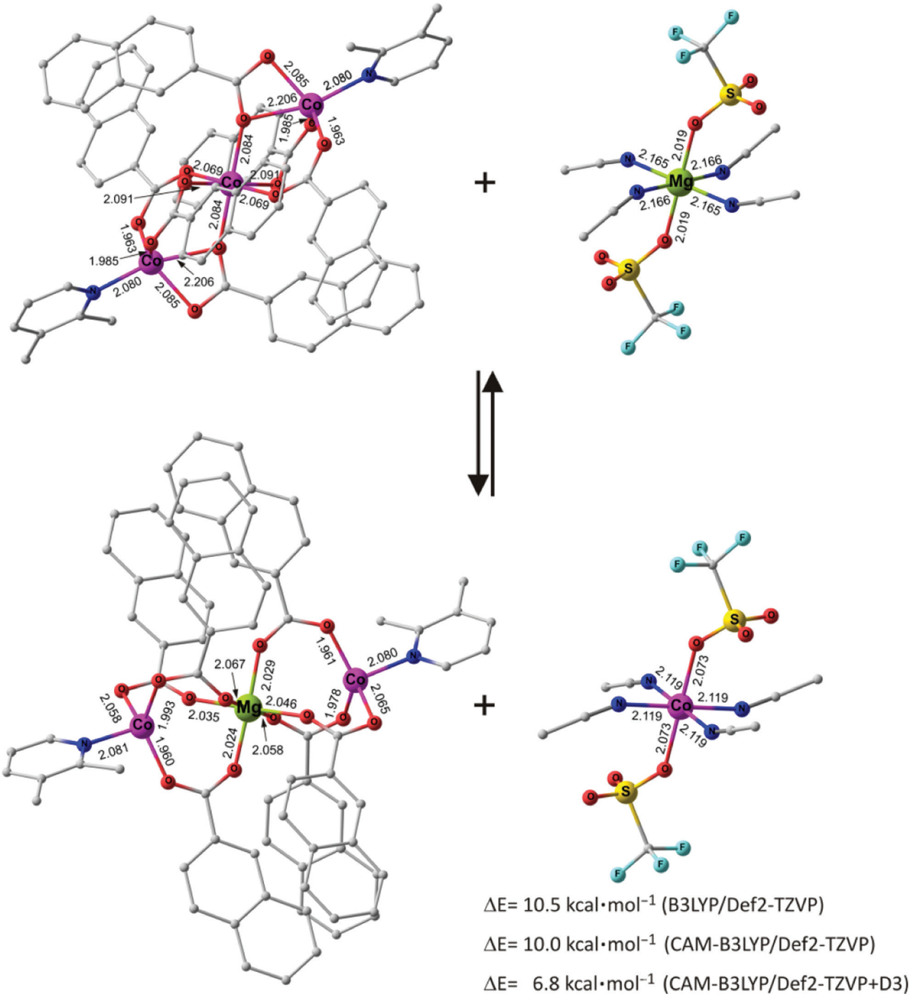


Fig. 1: Molecular structures of compounds **1** (a) and **2** (b) (solvate molecules, CH_3 groups of lutidine molecules and H atoms are omitted).

in Fig. 2, regardless of the approximation used, the substitution of the central cobalt ion by magnesium ion leads to a decrease in the energy of the system under consideration by 6.8–10.5 kcal/mol. Calculations for compounds with bridging pivalate groups led to a similar result; the energy gain was 8.1–9.5 kcal/mol, depending on the approximation used. Therefore, one of the reasons contributing to the formation of this type of heterometallic trinuclear systems is the thermodynamic stability of complexes including Co^{2+} and Mg^{2+} ions.

The process of replacing the central Co(II) atom in **1** with Mg(II) atom can formally be considered as a transmetallation reaction, as a result of which heterometallic molecule **2** is formed, which is similar in structure to **1**, but with completely different magnetic characteristics. However, other starting compounds and reactions can also be used to prepare heterometallic compounds similar to **2**. For example, it is known that the reaction of the binuclear cobalt(II) complex with 2,4-lutidine, $[Co_2(O_2CBu^t)_4(2,4\text{-lut})_2]$, with magnesium pivalate (obtained in situ) leads to the formation of compound $[Co_2Mg(O_2CBu^t)_6(2,4\text{-lut})_2]$ (**3**, Fig. 3a), the structure of which is similar to **2**. It can be assumed that in this case the fragment of magnesium pivalate $\{Mg(O_2CBu^t)_2\}$ is introduced into the binuclear fragment $\{Co(\mu\text{-}O_2CBu^t)_4Co\}$ of the starting cobalt complex [56]. Although the mechanism of this kind of "introduction" has not yet been studied in detail, the fact of the appearance of the magnesium ion in the central position, apparently, involves a rather complex multi-stage transformation of the coordination environment of this ion.



ΔE= 10.5 kcal•mol^{-1} (B3LYP/Def2-TZVP)

ΔE= 10.0 kcal•mol^{-1} (CAM-B3LYP/Def2-TZVP)

ΔE= 6.8 kcal•mol^{-1} (CAM-B3LYP/Def2-TZVP+D3)

Fig. 2: Optimized geometries of complexes **1** and **2** calculated in the CAM-B3LYP/Def2-TZVP approximation with inclusion of dispersion correction D3BJ. Relative energies of homo- and heterometallic systems are given at the bottom right.

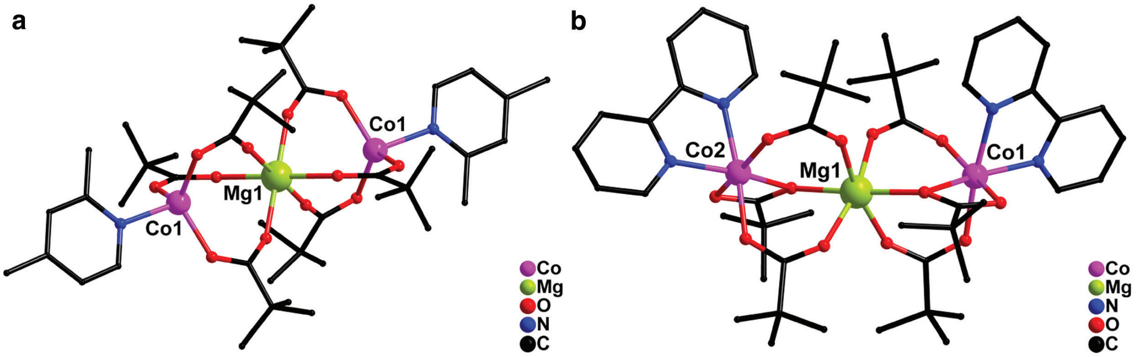


Fig. 3: Molecular structures of compounds **3** (a) and **4** (b) (solvate molecules and H atoms are omitted).

The action of 2,2′-dipyridyl (bpy) on compound **3** leads to the substitution of the monodentate N-donor ligand with the chelating ligand to form $[Co_2Mg(O_2CBu^t)_6(bpy)_2]$ (**4**, Fig. 3b) [57]; although in this case, the peripheral Co(II) atoms change their coordination environment (CN = 4 in **3**, CN = 5 in **4**), which also affects the magnetic characteristics of the molecules. In this case, the trinuclear metal carboxylate core of the heterometallic molecule is quite stable and remains unchanged even with a multiple excess of the chelating ligand bpy. Such resistance to the action of a chelating ligand is very unusual, since in the case of homometallic carboxylate complexes of Co^{2+} and other metal ions M^{2+} ($M^{2+} = Ni^{2+}$, Cu^{2+}, Zn^{2+}, Cd^{2+}) monomers $[M(O_2CBu^t)_2(bpy)_2]$ are observed to form [2, 58–62]. Moreover, the action of magnesium pivalate on $[M(O_2CBu^t)_2(bpy)_2]$ (M = Co(II), Ni(II)) leads to the quantitative formation of the heteronuclear compound $[M_2Mg(O_2CBu^t)_6(bpy)_2]$ (M = Ni(II), Co(II)) [57, 63] and the transition of the excess bpy molecule into the solution in a free state, which, presumably, confirms the thermodynamic stability of the heterometallic structure.

In the structures of the considered trinuclear heterometallic molecules (for example, **2–4**), one can formally distinguish two anionic metal fragments $\{(L)M(O_2CR)_3\}^-$, which are associated with the central metal atom (in this case, Mg(II)) (Fig. 4) and perform the function of a scorpionate anionic metal-containing ligand in a stable heterometallic structure.

Such molecules are stable, because each metal-containing anionic ligand $\{(L)M(O_2CR)_3\}^-$ provides at least three oxygen atoms from its carboxylate groups to coordinate to the central oxophilic metal center. In the case of a divalent central metal ion, for example, the Mg^{2+} ion, this leads to the formation of neutral molecules, but what will happen if monovalent ions of alkali metals are used, for example Li^+?

Heterometallic carboxylate architectures containing 3*d*-metal and lithium ions

To complicate the situation, we consider the replacement of the central position of the type **1** compound with an atom of an oxophilic monovalent metal to form the corresponding heterometallic structures. The formation of these compounds can also be expressed as a substitution of the central divalent Co^{2+} ion

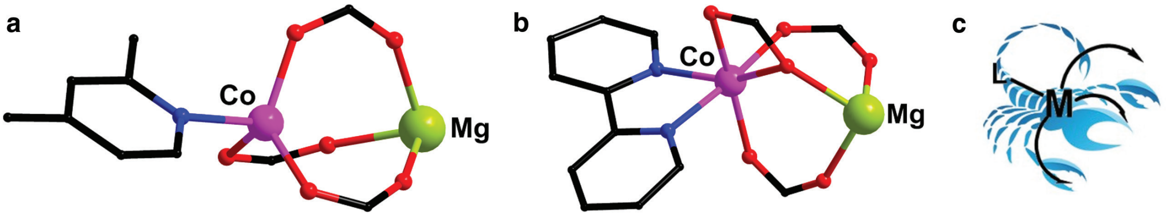


Fig. 4: Structures of $\{(L)M(O_2CR)_3\}$ fragments in compounds **2**, **3** (a) and **4** (b) (Bu^t groups and H atoms are omitted) and their schematic representation (c).

in the type **1** compound or as the introduction of singly charged ions into binuclear homometallic complexes. In the case of the participation of Li^+ ions in the formation of the heterometallic framework and two anionic fragments $\{(L)M(O_2CR)_3\}^-$ (M = Co(II), Ni(II), Cu(II), Zn(II)), the formation of molecular complexes $[M_2Li_2(O_2CR)_6(L)_2]$ (where L is the N-donor ligand) is observed (Fig. 5). This means that one divalent ion is replaced by two monovalent Li^+ ions, although in this situation, the geometric parameters of these ions should be taken into account.

The $\{M_2Li_2\}$ family of molecular compounds can be supplemented with complexes containing bridging L, pyrazine and pyrimidine, which bind the $\{Co_2Li_2(O_2CR)_6\}$ fragments into 1D and 2D coordination polymers (Fig. 6) [64].

The situation becomes complicated if we use the tridentate pincer ligand 2,2′;6′,2″-terpyridine as L. In this case, the geometrical features of terpy, which has all three N donor centers in the same plane, can be a formal obstacle to the formation of $\{M_2Li_2\}$ complexes. Taking into account the limited coordination capabilities of the 3*d*-elements (for example, for Co(II) with CN = 4–6), problems arise with the arrangement of carboxylate bridges in the remaining space between M^{2+} and Li^+ ions using the above anionic fragment $\{M(O_2CR)_3L\}^-$. Taking the complex $[Co_2Li_2(O_2CBu^t)_6(terpy)_2]$ (**7**) as an example, it was shown that in this case an unusual rearrangement of bridging carboxylate groups is observed while maintaining the composition of $[M_2Li_2(O_2CR)_6(L)_2]$. Heterometallic ions in **7** are bound with only two carboxylate bridges, and the other two carboxylic anions participate only in the binding of Li^+ ions to each other (Fig. 7) [65]. As a result, the binding scheme looks like the interaction of two neutral metal-containing ligands $\{(terpy)Co(O_2CR)_2\}$ with the

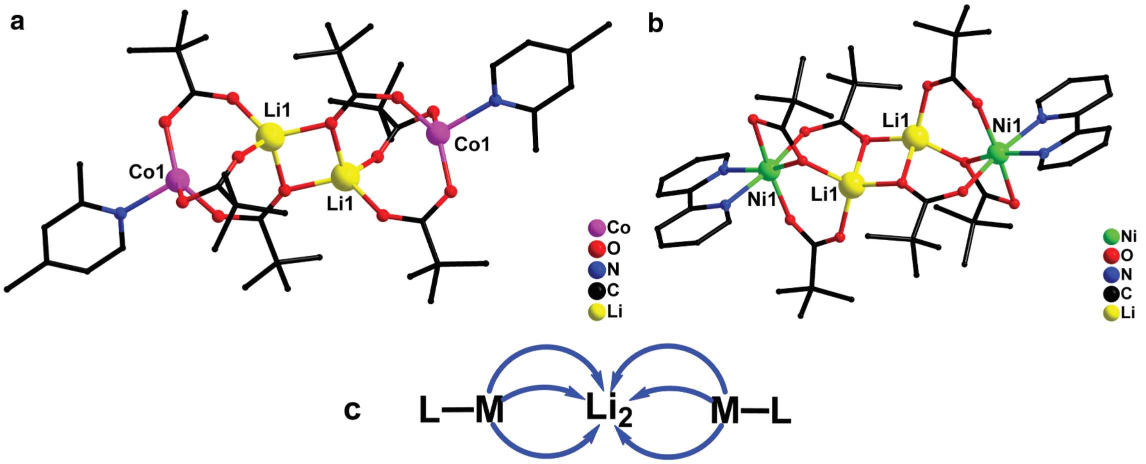


Fig. 5: Molecular structures of compounds **5** (a) и **6** (b) (solvate molecules and H atoms are omitted) and schematic representation of molecules $[Li_2M_2(O_2CR)_6(L)_2]$ (c).

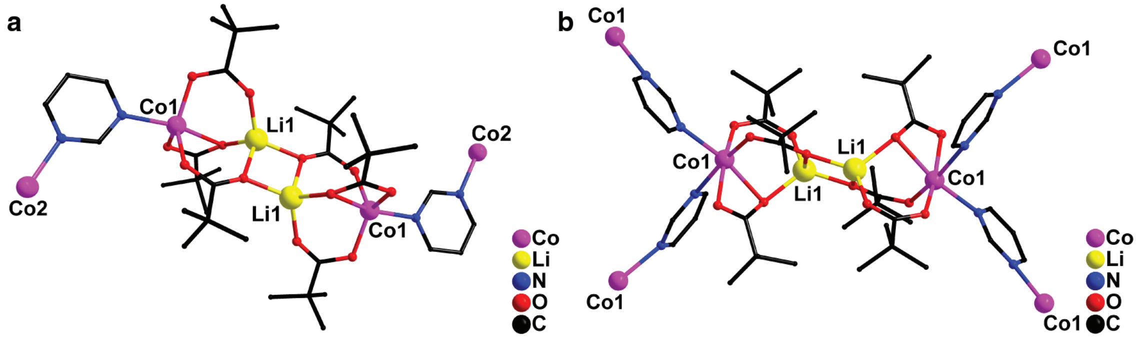


Fig. 6: Binding the $\{Co_2Li_2(O_2CR)_6\}$ fragments by pyrimidine molecules into 1D (a) and 2D (b) coordination polymers (solvate molecules and H atoms are omitted).

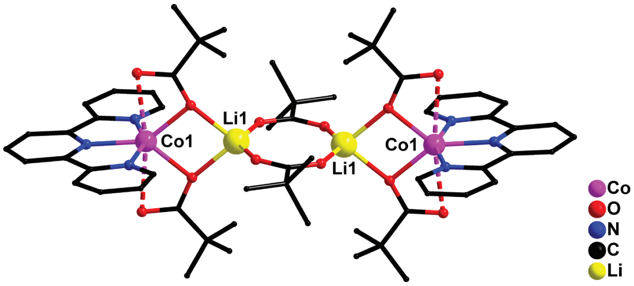


Fig. 7: Molecular structure of compound **7** (solvate molecules and H atoms are omitted).

binuclear fragment {Li(μ-$O_2CR)_2Li$}, which leads to quite ordinary coordination numbers of cobalt(II) (CN = 5) and lithium(I) (CN = 4) atoms.

A similar binding of Li^+ and Cu^{2+} ions is observed in complex $\{[Li(Hcpdc)]_4[Cu(O_2CBu^t)_2(terpy)]_4 \cdot H_2O\}_n$ (**8**) (Hcpdc$^-$ is the anion of cyclopropane-1,1-dicarboxylic acid), in which the coordination environment of copper(II) is also partially hindered by terpy chelate. In this case, the binuclear fragment $\{LiCu(O_2CBu^t)_2(terpy)_2\}$ is part of the composition of the polymeric chain formed by binding of Li^+ ions to Hcpdc$^-$ anions (Fig. 8) [66].

To obtain complexes with lithium(I) and vanadium(IV) atoms, compounds of vanadyl $(V(IV)=O)^{2+}$ (the formal analogue of M^{2+}) and lithium carboxylates were used. Molecular complexes $[Li_2(VO)_2(O_2CR)_6(bpy)_2]$ (**9**: R = Bu^t, **10**: R = CF_3) were synthesized and studied, which, unlike $[M_2Li_2(O_2CR)_6(bpy)_2]$ (M = Co(II), Ni(II), Cu(II)), have a slightly different structure of the $\{(VO)_2Li_2(O_2CR)_6\}$ fragment, taking into account the specific structure of vanadyl. It was found that the vanadyl oxygen atom takes part in the formation of the coordination environment of the Li ion, and the 12-membered macrocycle {-VO-Li-OCO-VO-Li-OCO-} is formed rather than four-membered Li_2O_2 cycle (as it was found in complexes with Co^{2+}, Ni^{2+}, and Cu^{2+} ions) (Fig. 9) [67]. As a result of such binding, both metal atoms, Li(I) and V(IV), are in a coordination environment typical in coordination compounds with CN = 4 and 6, respectively.

Heterometallic architectures containing 3*d*-metal and lanthanide ions

Since lanthanide ions are highly oxophilic and in most cases present in coordination compounds in the form of trivalent metal centers, the formation of triatomic heterometallic molecules similar to 3*d*-Mg and

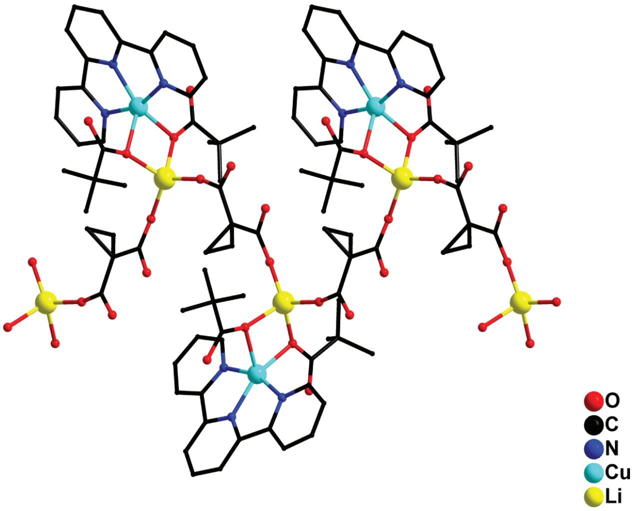


Fig. 8: Fragment of polymeric chain of compound **8** (solvate molecules and H atoms are omitted).

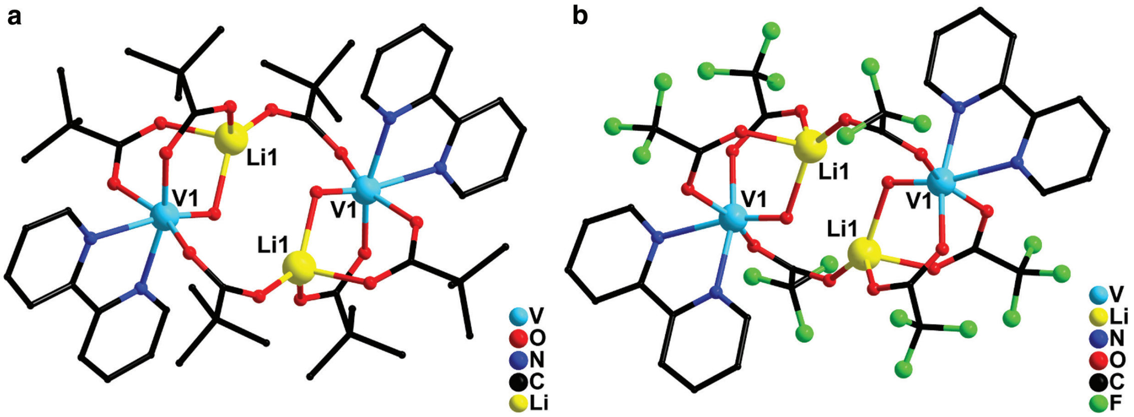


Fig. 9: Molecular structures of compounds **9** (a) and **10** (b) (solvate molecules and H atoms are omitted).

3*d*-Li requires an additional singly charged anion to comply with the principle of electroneutrality. As a result, the formation of molecular complexes $[M_2Ln(O_2CR)_6X(L)_2]$ is observed (Fig. 10), where X is the anion (NO_3^- or RCO_2^-), which compensates for the charge of the Ln^{3+} ion and ensures the electroneutrality of the heteronuclear compound with this composition.

In recent years, a large series of heterometallic complexes with different Ln:M ratios in the metal core were obtained (M = Co(II), Ni(II), Cu(II), Zn(II)) [18, 68–72]. The Zn–Ln complexes were studied in most detail, since they are of great practical interest from the point of view of obtaining luminescent materials [11–13, 73]. For example, for a series of compounds containing Zn^{2+} and Ln^{3+} ions, depending on the substituent on the carboxylate group, the nature of the N-donor ligand and the presence of the NO_3^- anion in the reaction mixture, bi-, tri-, and tetranuclear complexes ZnLn, Zn_2Ln, and Zn_2Ln_2, respectively, were synthesized (Fig. 11) [11–13, 18, 77–80] (Fig. 11). It can be assumed that the reasons for such a variety of complexes are the large coordination numbers of lanthanide ions, the possibility of forming polyhedra with different ligand environments (for example, LnO_8 and LnO_9), and some changes in the ionic radius in the La–Lu series as a result of lanthanide contraction. Using trimethylacetate Zn–Ln complexes with lanthanum(III) and europium(III) as an example, the dependence of the structure of the resulting compound on the radius of the Ln^{3+} ion was shown, and under the same conditions, tetranuclear and binuclear complexes were isolated, respectively (Fig. 11a,b) [74].

It is worth noting that, as in the case of structures having the $\{M_2Mg\}$ or $\{M_2Li_2\}$ core, in the listed lanthanide-containing complexes, the anionic fragment $\{(L)Zn(O_2CR)_3\}^-$ plays the role of a scorpionate

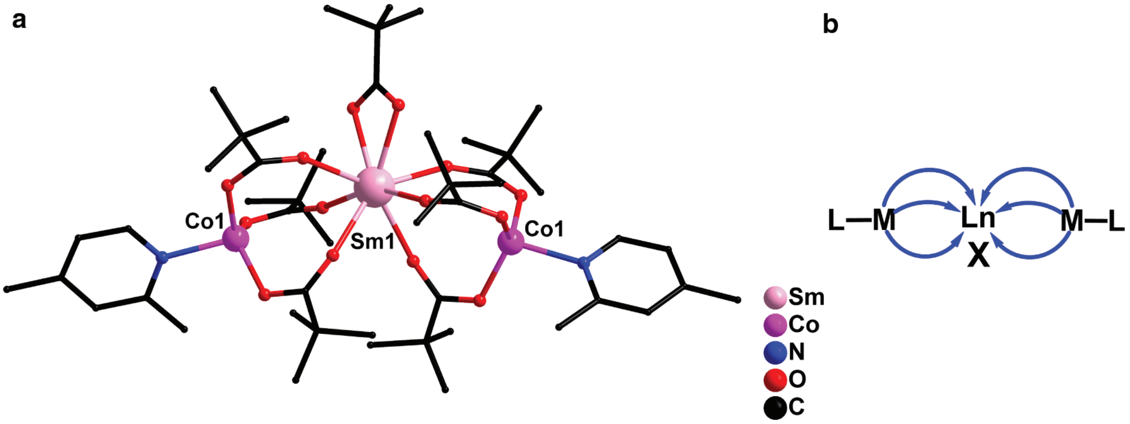


Fig. 10: Molecular structure of compound **11** (a) (solvate molecules and H atoms are omitted) and schematic representation of molecules $[M_2Ln(O_2CR)_6X(L)_2]$ (b).

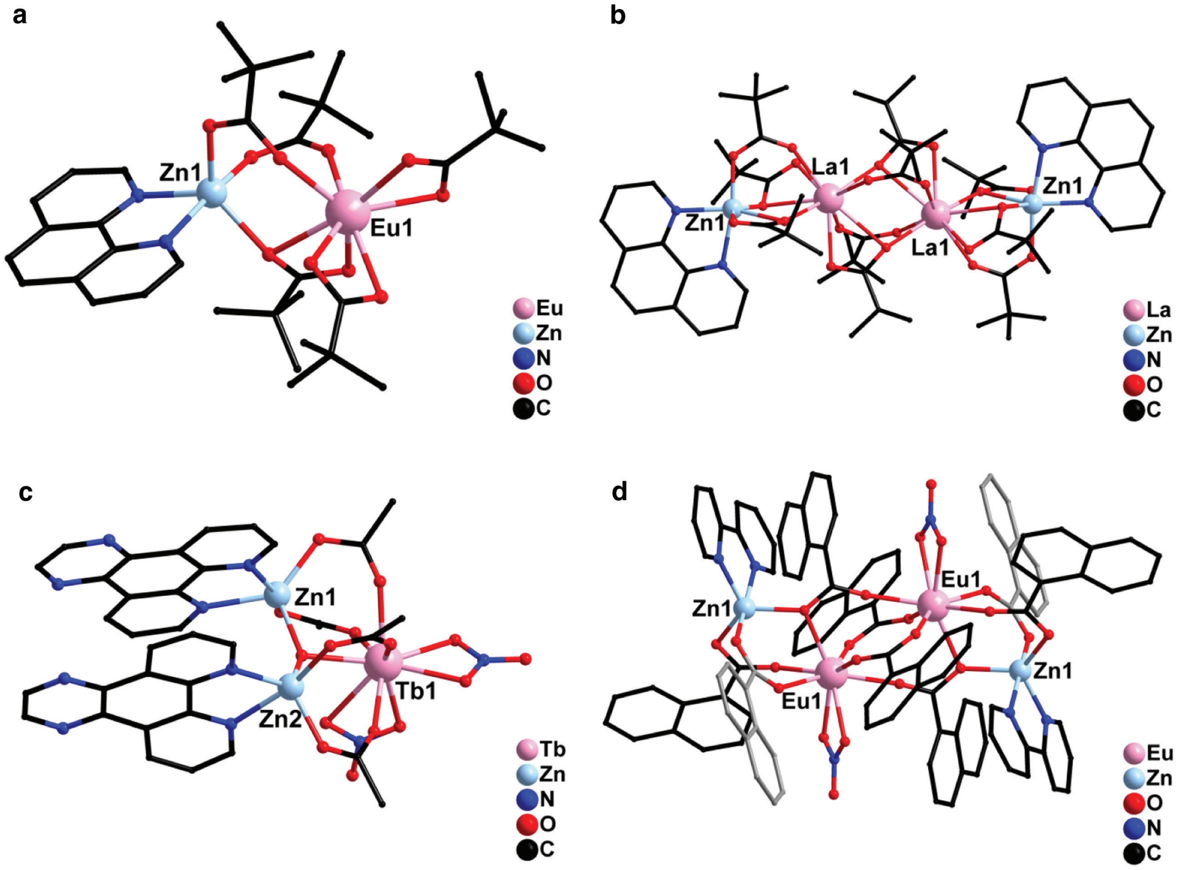


Fig. 11: Molecular structures of compounds **12** (a), **13** (b), **14** (d) and **15** (c) (CH_3 groups in **15**, solvate molecules and H atoms in **12–15** are omitted).

metal-containing ligand. However, here the ratio between this fragment and the lanthanide ion can be different depending on the structure and ligand environment of the lanthanide-containing fragment. Thus, in binuclear complex $[(bpy)ZnEu(\mu\text{-}O_2CBu^t)_3(O_2CBu^t)_2]$ (**12**), the ratio $\{(L)Zn(O_2CR)_3\}^-$: Ln equal to 1 : 1 is observed similar to the situation in tetranuclear molecules $[\{(L)ZnLn(\mu\text{-}O_2CR)_5\}_2]$ (**13**: L = phen, R = Bu^t, Ln = La) (Fig. 11b). However, in the tetranuclear structure, the zinc-containing scorpionate metal ligands $\{(L)Zn(O_2CR)_3\}$ are coordinated to the lanthanide metal centers of the binuclear tetracarboxylate fragment, which is often found in the series of known binuclear lanthanide carboxylates [81–84]. In some cases, when the tetranuclear structure is formed, the nitrate groups present in the initial lanthanide compound are retained and heterometallic molecules of similar structure $[\{(L)ZnLn(\mu\text{-}O_2CR)_4(NO_3)\}_2]$ (**14**: L = bpy, phen, O_2CR = 1-naphtoate, Ln = Eu) are formed (Fig. 11d).

In the formation of trinuclear complexes with Eu^{3+}, Gd^{3+}, and Tb^{3+} ions, two binuclear fragments $\{(L)M(O_2CR)_3\}^-$ (M = Zn(II), L is pyrazino[2,3-f][1, 10]phenanthroline, pyzphen, O_2CR is O_2CBu^t) are transformed into a more complex metal-containing ligand $\{(pyzphen)_2Zn_2(O_2CBu^t)_4OH\}$, which chelates the Ln^{3+} ion in a pentadentate mode (Fig. 11c) [13]. These compounds can be obtained both by self-assembly from the reaction mixture containing $Zn(O_2CBu^t)_2$, pyzphen, and $Ln(NO_3)_3 \cdot xH_2O$ in MeCN and when pyzphen acting on the linear complex $[Zn_2Ln(O_2CBu^t)_6(NO_3)(MeCN)_2]$ [76]. Unlike bpy in the linear complex $[Zn_2Ln(O_2CBu^t)_6(NO_3)(bpy)_2]$ [76], pyridyl moieties in pyzphen cannot rotate around the shared C–C bond, which apparently makes steric hindrances in the environment of Zn^{2+} ions. This is confirmed by the difference in angles in the ZnO_3 fragment: the solid angles O–Zn–O for $[Zn_2Tb(OH)(O_2CBu^t)_4(NO_3)_2(pyzphen)_2]$ (312.2° and 315.8°) are smaller than the corresponding angle in $[Zn_2Eu(O_2CBu^t)_6(NO_3)(bpy)_2]$ (347.4°).

Attempts to introduce the tridentate chelating ligand 2,6-bis(2-pyridyl)-4-(4-pyridyl)pyridine (pyterpy) (terpy derivative) into the coordination sphere of the cobalt atom as L in the trinuclear fragment

$\{Co_2Ln(NO_3)(O_2CBu^t)_6\}$ resulted in the degradation of the $\{(L)M(O_2CR)_3\}$ fragment observed in the above architectures; however, they made it possible to find the conditions for the formation of the heterometallic pentanuclear complex $[\{Co_2Dy(NO_3)(O_2CBu^t)_6\}\{Co(pyterpy)(O_2CBu^t)(H_2O)\}_2](NO_3)_2 \cdot 2MeCN \cdot 3H_2O$ (**16**), in which the mononuclear cations $\{Co(O_2CBu^t)(pyterpy)(H_2O)\}^+$ are coordinated to the cobalt atoms of the central core $\{Co_2Dy(NO_3)(O_2CBu^t)_6\}$ by the free nitrogen atom of the 4-pyridyl moiety (Fig. 12) [71].

The effect of the type of coordination polyhedron on the ability of a particular metal to form heterometallic complexes manifested itself in a very special way in the case of complexes with Cu^{2+} ions. The reaction of the known dimer $[Cu_2(O_2CBu^t)_4(HO_2CBu^t)_2]$ [85] and $Eu(NO_3)_3$ in the presence of NBu_4OH led to the formation of the trinuclear compound $(NBu_4)[Cu_2Eu(O_2CBu^t)_8]$ (**17**, Fig. 13), in which each copper atom is surrounded by a square-planar environment made of four O atoms of four bridging carboxylate groups that bind the peripheral metal ions to the central europium atom [86]. The peculiarity of the electronic structure of copper(II) and the ability to form a square planar environment complements the variety of M–Ln carboxylate complexes with this example.

As noted above, some homometallic polynuclear complexes of transition metals can be considered as unique “prototypes” of heterometallic compounds. Such compounds, the metal atoms in which are in nonequivalent positions, can show the direction of the search for new types of heterometallic compounds. In the synthesis of the copper(II) complex with 1,1-cyclohexanediacetic acid dianions ($chda^{2-}$) and bpy molecules starting from $[Cu_2(O_2CBu^t)_4(HO_2CBu^t)_2]$, the ternary complex $[Cu_3(chda)_2(O_2CBu^t)_2(bpy)_2]$ (**18**) was obtained (Fig. 14a), which combines the anions of two carboxylic acids [87]. The introduction of $[Ln_2(O_2CBu^t)_6$-$(HO_2CBu^t)_6]$ (Ln = Sm, Gd) into the reaction mixture led to the formation of the tetranuclear heterometallic complexes $[Ln_2Cu_2(chda)_2(O_2CBu^t)_6(bpy)_2]$ (Ln = Sm (**19**), Gd) (Fig. 14b). Although the structure of the tetranuclear heterometallic Cu–Ln complex differs markedly from the structure of the trinuclear copper(II) complex, the structural motifs of the homometallic compound are essentially retained. The peripheral metal fragment bonded to the central copper atom in complex **18** is formed by the $Bu^tCO_2^-$ bridging carboxylate group and two oxygen atoms of the carboxylate groups of both $chda^{2-}$ dianions, while for $[Ln_2Cu_2(chda)_2(O_2CBu^t)_6(bpy)_2]$,

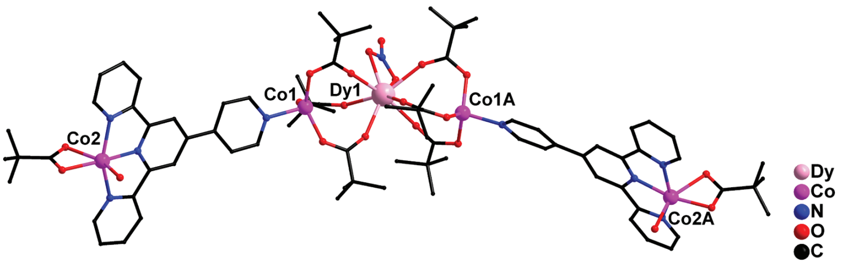


Fig. 12: Structure of the cationic fragment $[\{Co(pyterpy)(O_2CBu^t)(H_2O)\}_2\{Co_2Dy(NO_3)(O_2CBu^t)_6\}]^{2+}$ in compound **16** (H atoms are omitted).

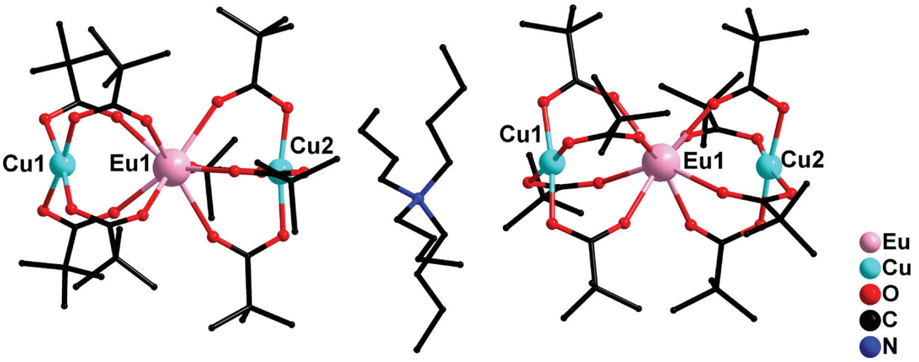


Fig. 13: Fragment of crystal packing of compound **17** (solvate molecules and H atoms are omitted).

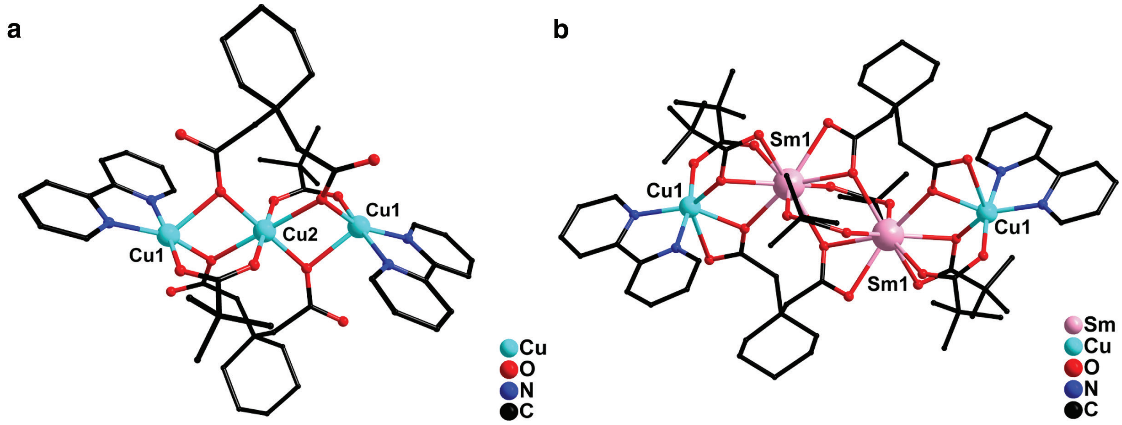


Fig. 14: Molecular structures of compounds **18** (a) and **19** (b) (solvate molecules and H atoms are omitted).

it is formed by the bridging carboxylate group $Bu^tCO_2^-$, the O atom of one of the carboxylate groups of the $chda^{2-}$ anion, and the O atom of the chelate-bridging $Bu^tCO_2^-$ anion. The structures of trinuclear fragments, $\{Cu_3\}$ in **18** and {CuLnLn} in **19**, were found to be similar, which generally allows one to use the proposed scheme for bonding certain metal-containing blocks when forming heteronuclear architectures. In addition, we believe that the modeling of possible transformations of homonuclear molecular systems into heteronuclear ones is promising from the point of searching for a homometallic "prototype" that is similar in structure and electronic properties and its further transformations.

Structural features of cadmium(II) heterometallic complexes

Our analysis of the data on the synthesis and structures of the considered heterometallic complexes makes it possible to use a block combination coupling scheme in such systems in which the anionic scorpionate metal ligand $\{(L)M(O_2CR)_3\}^-$ with anions of 3*d*-elements, namely Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and VO^{2+} (only for Li–V complexes) plays a structure-forming role, binding to Li^+, Mg^{2+} or Ln^{3+} ions. In this case, it can be noted that scorpionate fragments $\{(L)M(O_2CR)_3\}^-$ with a monodentate N-donor as L, for example, NEt_3, pyridine, and its substituted derivatives, were observed only for Co^{2+} and Zn^{2+} ions. Apparently, this is associated with a stable tetrahedral or tetragonal-pyramidal environment of these metals in the divalent state. On the other hand, the Ni^{2+} ion in most heteronuclear carboxylates prefers octahedral environment, whereas Cu^{2+} ions form stable homometallic complexes with monodentate L, such as pyridines [88–92] or NEt_3 [93]. It seems that this explains the fact that heterometallic carboxylate complexes with fragments $\{(L)M(O_2CR)_3\}^-$ (L is a monodentate N-donor ligand) have not been isolated for these metals.

In this situation, it is worth paying attention to a closely related 4*d*-element, cadmium(II), since its increased geometric parameters and, accordingly, a large variety of coordination environments (for example, the existence of carboxylates with CN = 7 and 8 [94]) can change the binding scheme of the $\{(L)Cd(O_2CR)_3\}^-$ fragment in heteronuclear architectures.

An attempt to obtain a heterometallic complex according to the methodology similar to **1**–**3** with the introduction of 1,10-phenanthroline (phen) led to the isolation of the previously known binuclear cadmium homometallic complex $[(phen)_2Cd_2(O_2CBu^t)_4]$ [95]. However, it was found that when $\{Cd(O_2CBu^t)_2\}$ was allowed to react with pivalates of alkaline-earth elements, Mg or Ca and Sr, and 2,4-lutidine (lut) in MeCN, analogues of trinuclear heterometallic 3*d*-metal complexes $[(lut)_2Cd_2M(O_2CBu^t)_6]$ (**20**) (M = Mg(II), Ca(II), Sr(II)) could be easily prepared (Fig. 15a). The centrosymmetric linear metal core is formed by a central atom of an alkaline earth element located in a distorted octahedral environment and connected with two terminal Cd(II) atoms with one bridging and two chelate-bridging anions of pivalic acid (CN(Cd) = 6, CN(Mg) = 6). In this case, the

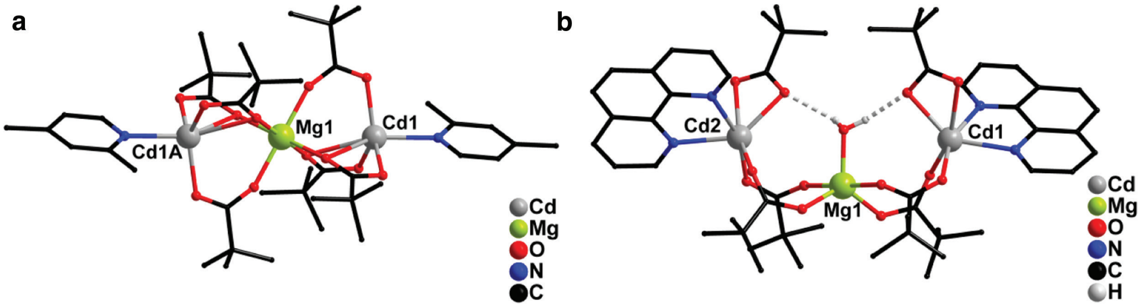


Fig. 15: Molecular structures of compounds **20** (a, solvate molecules and H atoms are omitted) and **21** (b, solvate molecules and H atoms of organic ligands are omitted).

Cd···M and Cd···Cd distances regularly increase with increasing radius of the cation M (Cd···M 3.45 Å (Mg) → 3.63 Å (Ca) → 3.75 Å (Sr)) [94].

Substitution reactions between 2,4-lutidine molecules and 1,10-phenanthroline made it possible to isolate complexes retaining the metal core, namely trinuclear heterometallic complexes $[(H_2O)(phen)_2Cd_2Mg(O_2CBu^t)_6]$ (**21**), $[(phen)_2Cd_2Ca(O_2CBu^t)_6]$ (**22**), and $[(phen)_2Cd_2Sr(O_2CBu^t)_6]\cdot 2MeCN$ (**23**), which cannot be obtained by direct reaction of the starting components. In this case, a new type of heterometallic complex was identified (**21**), in which the central magnesium atom is bonded to each terminal Cd(II) atom only by pairs of carboxylate groups from two fragments $\{(phen)Cd(O_2CBu^t)_3\}^-$ (Fig. 15b), while the third carboxylate anions of these fragments form hydrogen bonds with the protons of the water molecule bound to the Mg(II) atom. As a result, the coordination environment of cadmium atoms is retained, while that of the magnesium atom changes (CN = 5) from an octahedral to a distorted square pyramidal. In the case of Cd–Ca and Cd–Sr compounds **22** and **23**, the metal cores $[(L)_2Cd_2M(O_2CBu^t)_6]$ are similar to those of the starting compounds with 2,4-lutidine (Fig. 16).

Concerning heterometallic molecules with the metal core $\{Cd_2Ln\}$, where Ln^{3+} ions have a large radius, one can notice that they are similar to the mentioned trinuclear heterometallic systems containing the scorpionate fragment $\{(L)M(O_2CR)_3\}$, where M is a *3d*-element. For example, the structures of the synthesized trinuclear complexes $[EuCd_2(O_2CR)_6(NO_3)(bpy)_2]$ ($R = C_6F_5$) (**24**) (Fig. 17) and $[LnCd_2(O_2CR)_6(NO_3)(phen)_2]$ (Ln = Tb(III), Eu(III), O_2CR is the anion of 3,5-di-*tert*-butylbenzoic acid) [96] are similar to those of compounds $[(L)_2M_2Ln(NO_3)(O_2CR)_6]$ [76, 86, 97–104]. However, the electronic characteristics of the central lanthanide ion affect the magnetic properties of the heterometallic molecules of the isolated complexes, and the shape of the metal core can change; in particular, the angle Cd–Ln–Cd in the complex molecule varies from 145° to 175°.

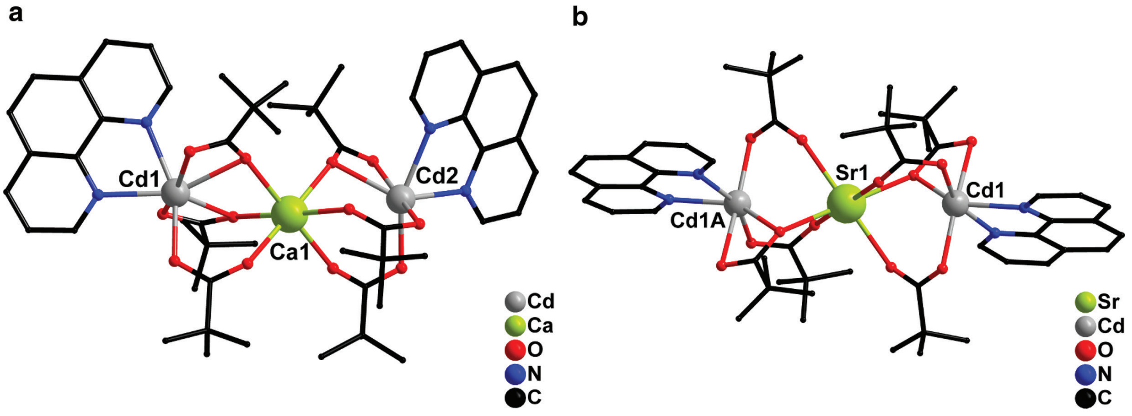


Fig. 16: Molecular structures of compounds **22** (a) and **23** (b) (solvate molecules and H atoms are omitted).

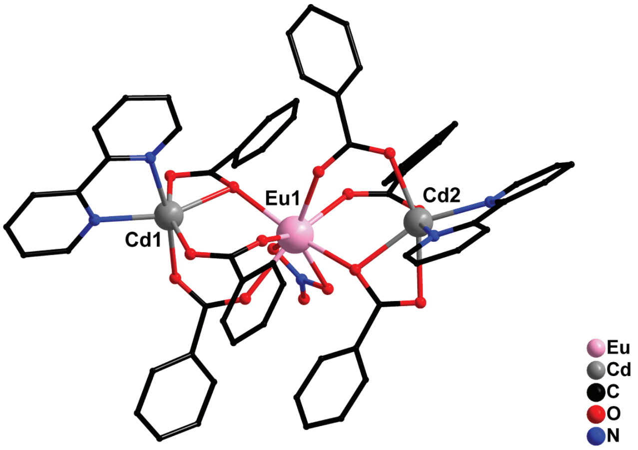


Fig. 17: Molecular structure of compound **24** (solvate molecules, H and F atoms are omitted).

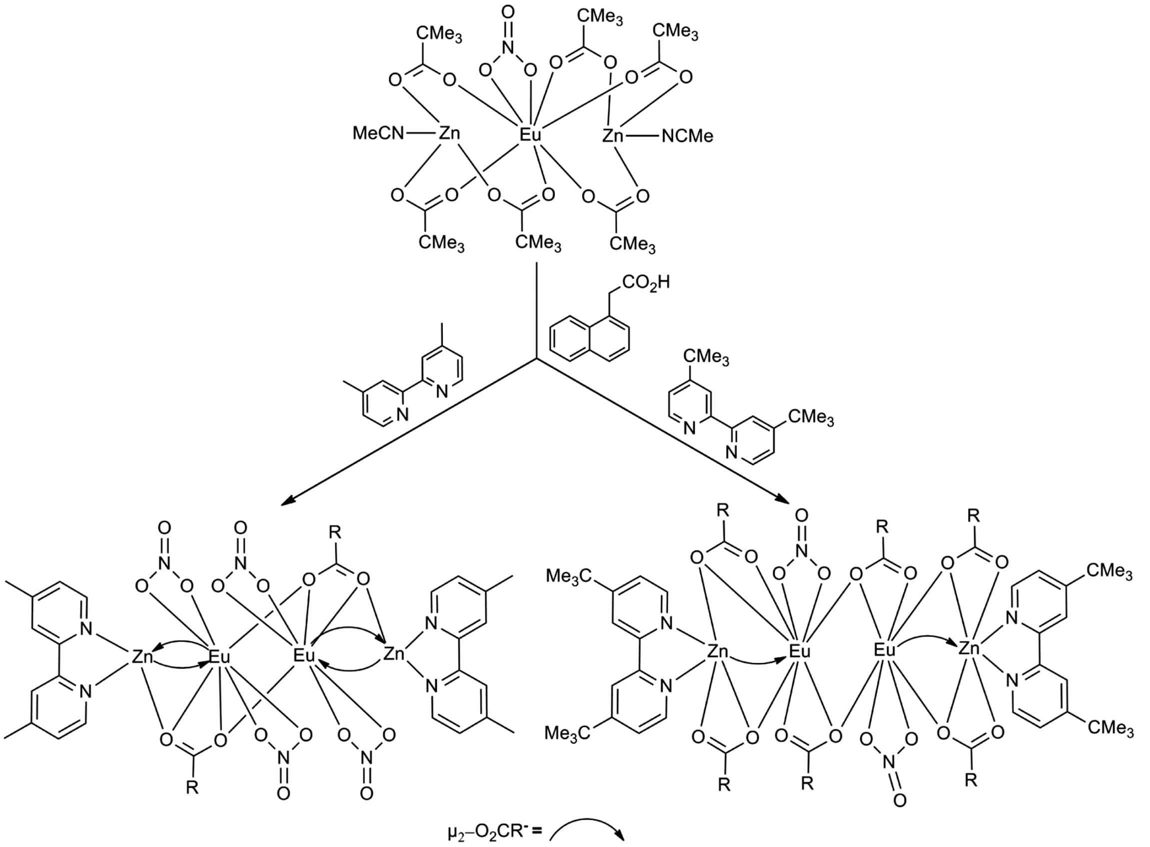
Substitution of carboxylate anions in heterometallic structures

An important property illustrating the high stability of heterometallic complexes is their ability to retain a heterometallic ensemble of metal atoms during the substitution of carboxylate anions. In this way, for example, some poorly soluble 1- and 2-naphthoate complexes were synthesized. In certain cases, when replacing carboxylate anions in heterometallic trinuclear complexes, rearrangement of the metal core can be observed. Thus, when the pivalate complex $[Zn_2Ln(NO_3)(O_2CBu^t)_6(MeCN)_2]$ reacts with 1-naphthylacetic acid (Hnaphac) salts in the presence of a number of N-donor heterocyclic ligands (L), tetranuclear complexes of the composition $[(L)_2Zn_2Ln_2(NO_3)_4(naphac)_6]$ (**25**) and $[(L)_2Zn_2Ln_2(NO_3)_2(naphac)_8]$ (L = 4,4′-dimethyl-2,2′-dipyridyl, 4,4′-di-*tert*-butyl-2,2′-dipyridyl) are formed [12] (see Scheme 1, Fig. 18).

One of the possible ways to synthesize new compounds based on the obtained carboxylate heterometallic complexes is the replacement of the anion of the monocarboxylic acid with the dicarboxylic acid dianion. Since such a reaction is usually accompanied by the replacement of all anions of monocarboxylic acid, this results in the formation of a polymeric structure. Substitution of carboxylate anions can be supplemented by substitution of a monodentate neutral ligand with a bridging one, for example, pyridine with 4,4′-dipyridyl. With such an integrated approach, conditions are created under which coordination polymers, including scaffolds, are formed. The described approach is widely used for the synthesis of metal organic frameworks (MOFs) from acetates or inorganic metal salts in situ. The methodology proposed by us consists in the preliminary assembly of a heterometallic metal core as part of a molecular complex with the subsequent assembly of the framework structure while maintaining or transforming the initial ensemble of metal atoms [104, 106].

Substitution of pivalate anions with terephthalate anions in the molecular complex $[Zn_2Li_2(O_2CBu^t)_6(py)_2]$ (**26**) (Fig. 19a) afforded a series of framework coordination polymers $[Zn_2Li_2(R\text{-}bdc)_3(4,4'\text{-}bpy)] \cdot solv$ ($R\text{-}bdc^{2-}$ is the dianion of substituted terephthalic acid; R = H, Br, NH_2, NO_2), in which the tetranuclear fragment $\{Zn_2Li_2(O_2C)_6N_2\}$ is retained when substituting all ligands [107]. A new type of secondary building block $\{Zn_2Li_2(O_2C)_6\}$ is able to be bound by bridging ligands at eight growth points: six carboxylate residues and two neutral bridging ligands (Fig. 19b). For the resulting range of compounds, the effect of the nature of aromatic guest molecules on luminescence and the excitation wavelength was studied.

In [108] using biphenyldicarboxylic acid (H_2bpdc) as an example, the effect of the N-donor ligand as a stabilizer of the tetranuclear fragment is shown. The reactions between $[Zn_2Li_2(O_2CBu^t)_6(py)_2]$ (**26**) with H_2bpdc in DMA and N-methyl-2-pyrrolidone (NMP) led to the rearrangement of the tetranuclear fragment to form the binuclear fragment $\{ZnLi(OOC\text{-})_3\}$, while the reaction in DMF in the presence of diazabicyclo[2.2.2]octane (dabco) afforded MOF $\{[Zn_2Li_2(bpdc)_3(dabco)] \cdot 9DMF \cdot 4H_2O\}_n$. Thus, the presence of dabco made it possible to stabilize the initial tetranuclear $\{Zn_2Li_2\}$ fragment and form a framework structure, while the absence of an N-donor in the reaction mixture led to the formation of layered honeycomb polymers based on triply-bonded



Scheme 1: Synthesis of compounds $[L_2Zn_2Ln_2(NO_3)_2(naphac)_8]$ (L = 4,4′-dimethyl-2,2′-dipyridyl, 4,4′-di-*tert*-butyl-2,2′-dipyridyl) from initial pivalate complex $[Zn_2Ln(NO_3)(O_2CBu^t)_6(MeCN)_2]$.

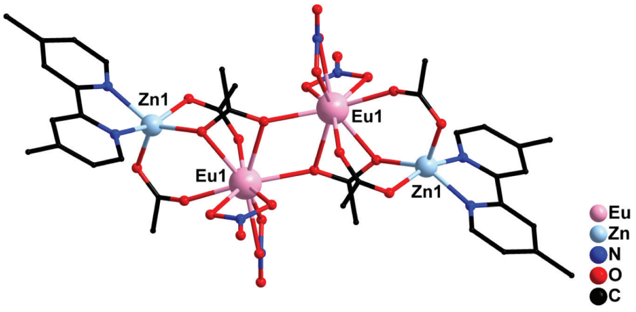


Fig. 18: Molecular structure of compound **25** (solvate molecules and H atoms are omitted).

binuclear {ZnLi} fragments. Studies have shown that $\{[Zn_2Li_2(bpdc)_3(dabco)] \cdot 9DMF \cdot 4H_2O\}_n$ demonstrates reversible crystal transitions to the amorphous phase when the guest molecule is removed or replaced. It was also found that the luminescence and quantum yield of the resulting porous polymers depend on the nature of the guest molecule.

Using reactions with the molecular complexes $[M_2Li_2(O_2CBu^t)_6(py)_2]$ (M = Zn(II), Co(II)) as examples, the possibility of the formation of MOFs with anions of tricarboxylic acids – trimesinic (H_3btc) and 1,3,5-tricarboxylbenzoic (H_3btb) was demonstrated [109]. Two structural types of polymers were distinguished: 3D scaffolds with a chiral topology $SrSi_2$, in which the plane of each carboxylate group lies in the plane of the btc^{3-} benzene ring or 2D honeycomb structures in the case of the btb^{3-} linker, for which the angles between the central

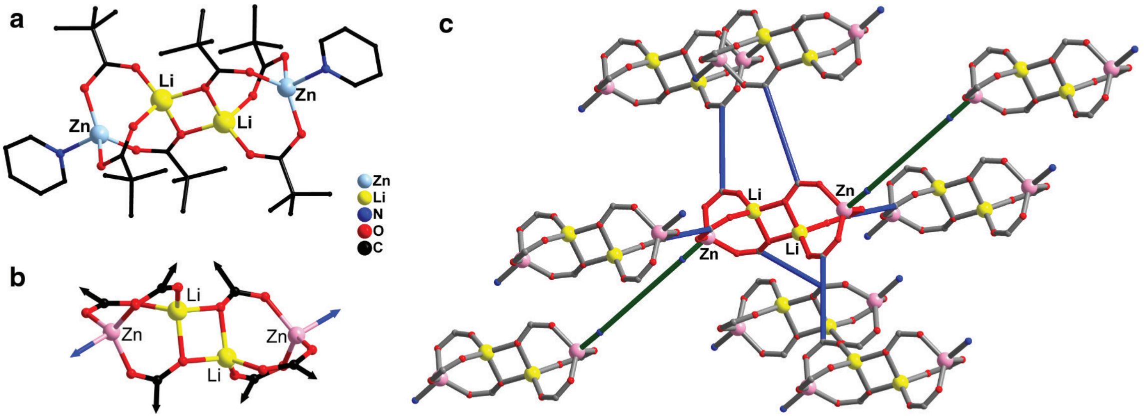


Fig. 19: Molecular structure of compound **26** (a, solvate molecules and H atoms are omitted), view of the secondary building block $\{Li_2Zn_2(O_2CR)_6\}$ with the possible extension of the coordination structure through the bridging ligands (b), and the example of binding $\{Li_2Zn_2(O_2CR)_6\}$ fragments by 4,4′-bipyridine and terephthalate anions (c).

benzene ring and the plane of the CO_2^- group are close to 90°. In both cases, the binuclear triply-bounded fragments $\{MLi(O_2CR)_3\}$ are the building block. Layered Zn-containing coordination polymers are capable of a guest-dependent change in luminescence. A rare example of constant porosity and selectivity of separation of CO_2/N_2 and CO_2/CH_4 mixtures with layered polymers was also demonstrated.

In addition, the reaction between $[Co_2Gd(NO_3)(O_2CBu^t)_6(py)_2]$ and terephthalic acid (H_2bdc) in dimethylacetamide (DMA) is known, which proceeds with partial destruction of the trinuclear heterometallic metal core to the binuclear $\{CoGd(\mu_2\text{-}RCO_2\text{-}\kappa^1,\kappa^1)_3(RCO_2\text{-}\kappa^2)_2\}$, which is the secondary building block for constructing the coordination polymer $[\{CoGd(dma)_2\}_2(bdc)_5]\cdot 4DMA$ (**27**) [110]. The three-dimensional framework **27** is porous and has two types of channels filled with coordinated and guest DMA molecules (Fig. 20).

As the main results of this review of heterometallic carboxylate complexes, it should be noted that due to the high stability of heterometallic fragments, their use in subsequent syntheses allows many reactions to be carried out according to the ligand substitution reaction scheme in mononuclear complexes. Thus, the ability to predict the results of synthesis is significantly increased. The preservation of metal fragments when varying carboxylate anions and neutral N- and O-donor ligands, as well as the allomerism of heterometallic complexes of various 3*d*-metals provide great opportunities for obtaining compounds with a given combination of properties and structural features for further synthesis.

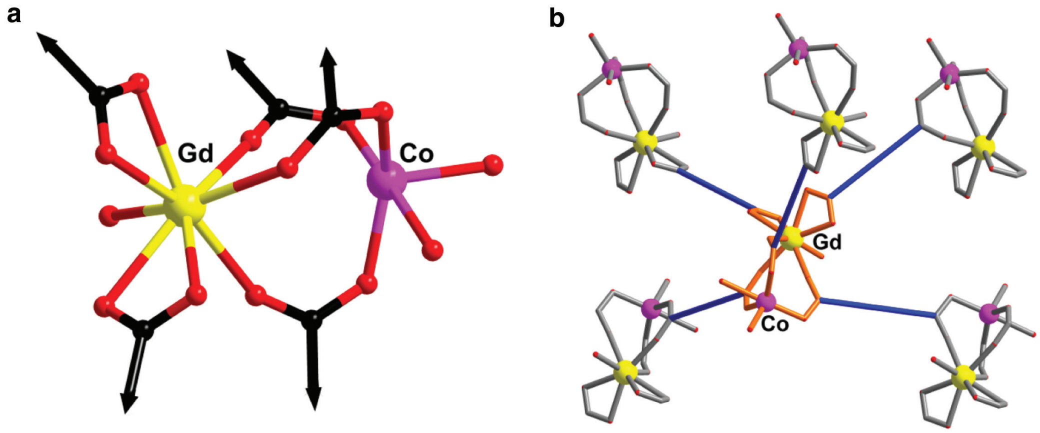


Fig. 20: View of the secondary building block $\{CoGd(\mu_2\text{-}RCO_2\text{-}\kappa^1,\kappa^1)_3(RCO_2\text{-}\kappa^2)_2\}$ with possible extension of the coordination structure through the bridging ligands (a) and the example of binding $\{CoGd(O_2CR)_5\}$ fragments by terephthalate anions (b).

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