ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2023, Vol. 49, No. 11, pp. 695–709. © Pleiades Publishing, Ltd., 2023.
Russian Text © The Author(s), 2023, published in Koordinatsionnaya Khimiya, 2023, Vol. 49, No. 11, pp. 669–684.

Heterometallic Carboxylate Complexes with $\{Co_2Ln\}$ and $\{Co_2Li_2\}$ Metal Cores: Synthesis, Structures, and Magnetic Properties

I. K. Rubtsova[a], S. A. Nikolaevskii[a], *, I. L. Eremenko[a], and M. A. Kiskin[a]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*

**e-mail: sanikol@igic.ras.ru*

Received October 4, 2022; revised December 1, 2022; accepted December 9, 2022

Abstract—The results of studying the heterometallic trinuclear $\{Co_2^{II}Ln\}$ and tetranuclear $\{Co_2^{II}Li_2\}$ carboxylate coordination compounds are systematized. The methods of the syntheses are discussed, and the structures and magnetic properties are considered.

Keywords: carboxylate ligands, heterometallic complexes, cobalt(II), synthesis of coordination compounds, magnetic properties

DOI: 10.1134/S1070328423600766

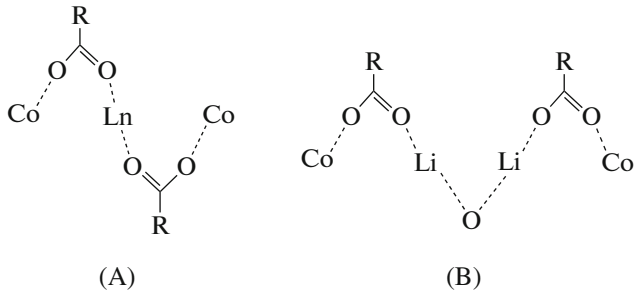
INTRODUCTION

Carboxylate ligands combined with transition metal ions are convenient "building" materials for the target assembling of mono- and polynuclear complexes. Design of these compounds is performed by changes in the synthesis conditions, variation of the solvent nature and substituent at the carboxylate group, and other factors. The extension of possibilities of this system by donor ligands makes it possible to tune their electronic characteristics, optical and magnetic properties, catalytic activity, and many other parameters. The development of the chemistry of heterometallic compounds favored the formation of new unique compounds combining in one molecule metal ions of different nature, whose synergy imparts new functional properties to the compounds [1–4].

A particular field on the synthesis of the 3*d*–4*f* complexes [5–10] combining ions with quite different radii and degrees of shielding of partially filled external *d*/*f* levels provides a rich structural chemistry of new compounds with valuable physicochemical properties [11, 12]. In particular, the complexes based on Co(II) and Ln(III) cations are promising as single-molecule magnets [13], materials with a pronounced magnetocaloric effect [14–16], materials for spintronics [17], catalyst precursors [18], high-precision sensors to aromatic hydrocarbon vapors [19], luminescent thermometers [20], magnetic luminescent materials [21, 22], and efficient agents for phototheranostics [23].

Other promising subjects of the chemistry of heterometallic complexes are the compounds bearing *d*- and *s*-metal ions. In the case of lithium cations, the structure-forming role of lithium in molecular complexes is accomplished and supplemented by other important functions. For instance, in the Co–Li complexes, the lithium cations can stabilize uncommon oxidation states of cobalt ions [24, 25] and modulate their redox potential [26, 27]. Another important feature stimulating interest in studying the Co–Li heterometallic complexes is the possibility of using these compounds as precursors of redox-active materials (particularly, $LiCoO_2$) for batteries [28–30] and as catalytically active nanoparticles [31]. The cobalt and lithium heterometallic compounds are important intermediates in many syntheses of organoelement compounds along with significant practically useful properties [32, 33].

The carboxylate heterometallic complexes $\{Co^{II}Ln^{III}\}$ and $\{Co^{II}Li\}$ form numerous structural types. In the present review, we focused on the consideration of relatively stable trinuclear $\{Co_2Ln\}$ (A) and tetranuclear $\{Co_2Li_2\}$ (B) heterometallic complexes predominantly with anions of monocarboxylic acids (Scheme 1) that can be used as platforms for the modification of the properties due to the substitution of the carboxylate and terminal ligands and formation of new oligomeric and polymer structures similar to the known building blocks $M_2(\mu\text{-}O_2CR)_4$ (M = Cu, Zn), $M_3O(\mu\text{-}O_2CR)_4$ (M_3 = Fe_3, Fe_2Co, Fe_2Ni, Fe_2Zn), $Zn_4O(\mu\text{-}O_2CR)_6$, and others [34–37]. The main attention in the review is given to specific features of the synthesis of these compounds and the existence of properties of single-molecule magnets in them.



(A) (B)

Scheme 1.

CARBOXYLATE HETEROMETALLIC COMPLEXES WITH {Co_2Ln} METAL CORE

Depending on the nature of the ancillary ligand, the presently known carboxylate heterometallic complexes with the {Co_2Ln} metal core can be grouped as follows:

(1) complexes with monodentate N-donor ligands,

(2) complexes with bidentate N-donor ligands,

(3) complexes with C-, O-, and P-donor ligands,

(4) complexes with polydentate ligands.

Monodentate N-donor ligands. An analysis of the published data shows that the compounds bearing monodentate N-donor ligands, such as acetonitrile, pyridine (Py), 2-phenylpyridine (2Ph-Py), 2-ethynylpyridine (Et-Py), quinolone (Quin), and 2,4-lutidine (2,4-Lut), are most abundant among the complexes with the {Co_2Ln} metal core.

Six methods for the synthesis of the complexes with the monodentate N-donor ligands were described and are shown in Scheme 2.

$$Co(NO_3)_2 + Ln(NO_3)_3 + HPiv + Quin \xrightarrow{EtOH} [Co_2Ln(NO_3)(Piv)_6(Quin)_2] \quad (I)$$

Co : Ln : HPiv : Quin = 2 : 1 : 6 : excess

Ln = Nd (**1a**), Gd (**1b**)

$$[Co_2(Piv)_4(2,4\text{-}Lut)_2] + [Sm_2(Piv)_6(HPiv)_6]\cdot HPiv \xrightarrow{MeCN} [Co_2Sm(Piv)_7(2,4\text{-}Lut)_2]\ (\mathbf{2}) \quad (II)$$

Co : Sm = 2 : 1

$$[Co(Piv)_2]_n + Gd(NO_3)_3 + Py \xrightarrow{MeCN} [Co_2Gd(NO_3)(Piv)_6(Py)_2]\ (\mathbf{3}) \quad (III)$$

Co : Gd : Py = 3 : 1 : excess

$$[Co(Piv)_2]_n + Ln(NO_3)_3 \xrightarrow{MeCN} [Co_2Ln(NO_3)(Piv)_6(MeCN)_2] \quad (IV)$$

Co : Ln = 3 : 1

Ln = Dy (**4a**), La (**4b**), Gd (**4c**)

$$[Co_2Dy(NO_3)(Piv)_6(MeCN)_2] + 2Py \xrightarrow{MeCN} [Co_2Dy(NO_3)(Piv)_6(Py)_2]\ (\mathbf{5}) \quad (V)$$

$$[Co(Piv)_2]_n + Ln(NO_3)_3 + L \xrightarrow{MeCN} [Co_2Ln(NO_3)(Piv)_6(L)_2] \quad (VI)$$

Co : Ln : L = 3 : 1 : 2

Ln = Gd; L = 2,4-Lut (**6**), 2Ph-Py (**7**), Et-Py (**8**)

Ln = Eu; L = Et-Py (**9**)

Piv is pivalic acid anion.

Scheme 2.

The heterometallic pivalate complexes were synthesized by the reaction of cobalt nitrate, lanthanide nitrate, pivalic acid, and quinolone in ethanol [38, 39]. The stoichiometric ratio Co : Ln : HPiv = 2 : 1 : 6 (method I, Scheme 2) is demanded for the formation of the trinuclear complexes. The complexes with neodymium and gadolinium were synthesized using this procedure. Note that the reaction involving erbium nitrate conducted in the same ratio of reagents led to the formation of a principally different product: tetranuclear complex $[Co_2Er_2(NO_3)_2(Piv)_8(Quin)_2]$.

The heterometallic compound with the {Co_2Sm} metal core was synthesized [40] by the reaction of complex $[Co_2(Piv)_4(2,4\text{-}Lut)_2]$ and samarium pivalate in a ratio of 2 : 1 (method II, Scheme 2). Complex $[Co_2(Piv)_4(2,4\text{-}Lut)_2]$ was synthesized by analogy to compound $[Co_2(Piv)_4(2\text{-}NH_2\text{-}5\text{-}Me\text{-}Py)_2]$, the synthesis of which was described [41].

The reaction of cobalt pivalate, gadolinium nitrate, and pyridine excess in acetonitrile afforded complex $[Co_2Gd(NO_3)(Piv)_6(Py)_2]$ (**3**) (method III, Scheme 2) [42]. When this complex is heated with terephthalic acid in *N*,*N*-dimethylacetamide (DMA) at 110°C, the coordination polymer $[\{CoGd(DMA)_2\}_2(Bdc)_5]\cdot 4DMA$ with the 3D core is formed having channels of two types filled with the coordinated DMA guest molecules.

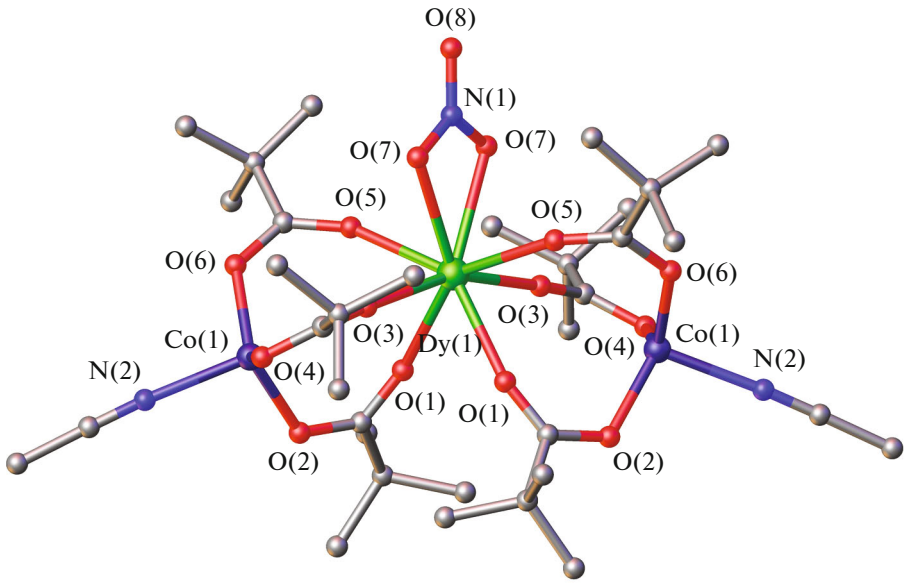


Fig. 1. Structure of complex $[Co_2Dy(NO_3)(Piv)_6(MeCN)_2]$ (**4a**) (hereinafter in the figures hydrogen atoms are omitted for clarity).

A series of heterometallic compounds with the {Co_2Ln} metal core was synthesized [43] by the reactions of cobalt pivalate and lanthanide nitrates in a ratio of 3 : 1 in acetonitrile (method IV, Scheme 2).

The reaction of complex $[Co_2Dy(NO_3)(Piv)_6(MeCN)_2]$ (**4a**) (Fig. 1) with the stoichiometric amount of pyridine in acetonitrile was shown to afford complex $[Co_2Dy(NO_3)(Piv)_6(Py)_2]$ (**5**) (method V, Scheme 2) [43]. Since this reaction contains no pyridine excess, the possibility of this substitution of the ligand can be explained by a higher donor ability of pyridine compared to that of MeCN. Compound **5** can also be synthesized by the reaction of $[Co_2(Piv)_4(Py)_2]$, which is formed in situ in the reaction of cobalt pivalate and pyridine in acetonitrile, with $Dy(NO_3)_3{\cdot}5H_2O$ at the ratio Co : Dy = 3 : 1. The order of mixing of the reagents and/or isolation of intermediates exerts no effect on the composition of the final product.

New complexes $[Co_2Ln(NO_3)(Piv)_6(L)_2]$ (Ln = Gd, L = 2,4-Lut (**6**), 2Ph-Py (**7**), Et-Py (**8**); Ln = Eu, L = Et-Py (**9**)) were synthesized using method VI (Scheme 2) [44]. The key feature of method VI is that the procedure makes it possible to conduct the reactions in acetonitrile using metal pivalates without significant excess of N-donor ligands. Two last factors provide a distinct stoichiometry of the reaction. An acetonitrile medium is preferable over ethanol, since the final trinuclear compounds $[Co_2Ln(NO_3)(Piv)_6(L)_2]$ were found [43] to be products of the thermodynamically controlled self-assembling and complex $[Co_2Ln(NO_3)(Piv)_6(MeCN)_2]$ can be considered as the key intermediate leading to the formation of the target compound bearing terminal N-donor ligands L.

An information about the reagents and products in the synthesis of the heterometallic complexes with the {Co_2Ln} metal core and monodentate N-donor ligands is given in Table 1.

The molecular structures of compounds **1**–**9** are built of the trinuclear metal core with the central lanthanide atom and peripheral cobalt atoms, each of which is linked with the central atom via three carboxylate bridges. In all cases, the lanthanide atoms are in the octacoordination environment built of six oxygen atoms of the monodentate pivalate anions and two oxygen atoms of the chelating nitrate anion. Seven pivalate anions compose the structure only in the case of complex $[Co_2Sm(Piv)_7(2,4\text{-}Lut)_2]$ (**2**), since this compound was synthesized in the absence of nitrate anions. In all cases, the cobalt atoms have a coordination number of 4 due to three oxygen atoms of the pivalate anions and the nitrogen atom of the coordinated ligand molecule.

Complex **2** (Fig. 2) was structurally characterized at 293 and 160 K. At 160 K the space group changes from $C2/c$ to $P2_1/c$, the Co...Sm distances and bond lengths between the metal ions and the nitrogen and oxygen atoms become shorter, and all *tert*-butyl groups are ordered. According to the XRD data and the results of measuring the heat capacity of complex **2**, the complex was found to undergo the phase transition in the 210–260 K temperature range.

A set of the following thermodynamic functions was determined for complex **2**: heat capacity (C_p), enthalpy ($H_T^0 - H_{180}^0$), entropy (S_T), and parameters of

Table 1. Reagents and products in the syntheses of the complexes with the monodentate N-donor ligands

Compound	Source of Co	Source of Ln	Acid	Ligand	Product
1a,**b** [38, 39]	$Co(NO_3)_2·6H_2O$	$Ln(NO_3)_3·6H_2O$ Ln = Nd, Gd	HPiv	Quin	$[Co_2Ln(NO_3)(Piv)_6(Quin)_2]$
2 [40]	$[Co_2(Piv)_4(2,4\text{-Lut})_2]$	$[Sm_2(Piv)_6(HPiv)_6]·HPiv$			$[Co_2Sm(Piv)_7(2,4\text{-Lut})_2]$
3 [42]	$[Co(Piv)_2]_n$	$Gd(NO_3)_3·6H_2O$		Py	$[Co_2Gd(NO_3)(Piv)_6(Py)_2]$
4a–**c** [43]	$[Co(Piv)_2]_n$	$Ln(NO_3)_3·xH_2O$ Ln = Dy, La, Gd		MeCN	$[Co_2Ln(NO_3)(Piv)_6(MeCN)_2]$
5 [43]	$[Co_2Dy(NO_3)(Piv)_6(MeCN)_2]$			Py	$[Co_2Dy(NO_3)(Piv)_6(Py)_2]$
5 [43]	$[Co(Piv)_2]_n$	$Dy(NO_3)_3·5H_2O$		Py	$[Co_2Dy(NO_3)(Piv)_6(Py)_2]$
6 [44]	$[Co(Piv)_2]_n$	$Gd(NO_3)_3·6H_2O$		2,4-Lut	$[Co_2Gd(NO_3)(Piv)_6(2,4\text{-Lut})_2]$
7 [44]	$[Co(Piv)_2]_n$	$Gd(NO_3)_3·6H_2O$		2Ph-Py	$[Co_2Gd(NO_3)(Piv)_6(2Ph\text{-Py})_2]$
8 [44]	$[Co(Piv)_2]_n$	$Gd(NO_3)_3·6H_2O$		Et-Py	$[Co_2Gd(NO_3)(Piv)_6(Et\text{-Py})_2]$
9 [44]	$[Co(Piv)_2]_n$	$Eu(NO_3)_3·6H_2O$		Et-Py	$[Co_2Eu(NO_3)(Piv)_6(Et\text{-Py})_2]$

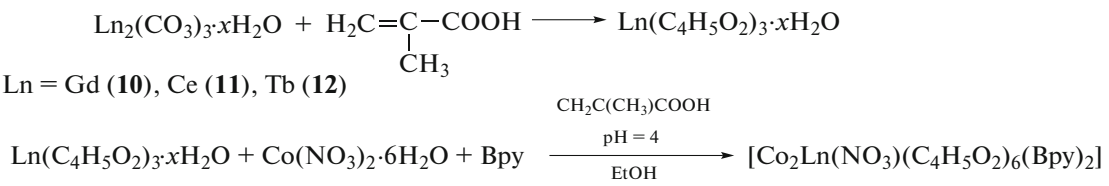
the solid-phase thermolysis that affords samarium cobaltate $SmCoO_3$.

The complexes with the $\{Co_2Ln\}$ metal core are of interest from the viewpoint of their magnetic properties. Such anisotropic ions as cobalt(II) can demonstrate a slow magnetization relaxation, which is a property characteristic of a single-molecule magnet (SMM). Therefore, the magnetic behavior of the synthesized compounds was studied in many works (Table 2).

As can be seen from Table 2, the gadolinium-containing compounds are characterized by ferromagnetic exchange interactions. None of the complexes exhibits SMM properties. A slow magnetization relaxation was observed for compound **9**. The $\tau(1/T)$ dependence of complex $[Co_2Eu(NO_3)(Piv)_6(Et\text{-}Py)_2]$ (**9**) is well described by the Orbach relaxation mechanism in the whole temperature range. An analysis of the experimental data gave the following values of operational parameters: magnetization reversal barrier $\Delta E/k_B = 4$ K and relaxation time $\tau_0 = 4.7 \times 10^{-6}$ s. Thus, this compound is a single-molecule magnet.

Bidentate N-donor ligands. Such bidentate ligands as 2,2'-bipyridine (Bpy) and 1,10-phenanthroline (Phen) are used along with the monodentate N-donor ligands for the synthesis of trinuclear complexes with the $\{Co_2Ln\}$ metal core.

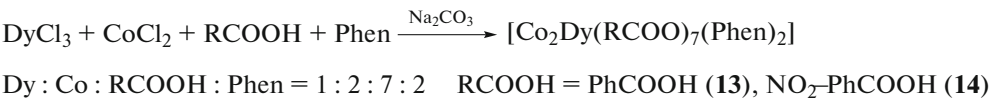
The trinuclear heterometallic complexes $[Co_2Ln(NO_3)(C_4H_5O_2)_6(Bpy)_2]$ with methacrylic acid anions and Bpy as an ancillary N-donor ligand were prepared [45–47] by the two-step syntheses: (Scheme 3).



Scheme 3.

Lanthanide carbonate and methacrylic acid reacted in the first step of the synthesis according to a published procedure [48]. In the second step, the synthesized lanthanide methacrylate and cobalt nitrate were dissolved in water and methacrylic acid was added to attain pH 4. Then a solution of Bpy in ethanol was added.

The trinuclear complexes based on anions of benzoic and 3-nitrobenzoic acids with Phen were synthesized (Scheme 4) [49].



Dy : Co : RCOOH : Phen = 1 : 2 : 7 : 2 RCOOH = PhCOOH (**13**), NO_2–PhCOOH (**14**)

Scheme 4.

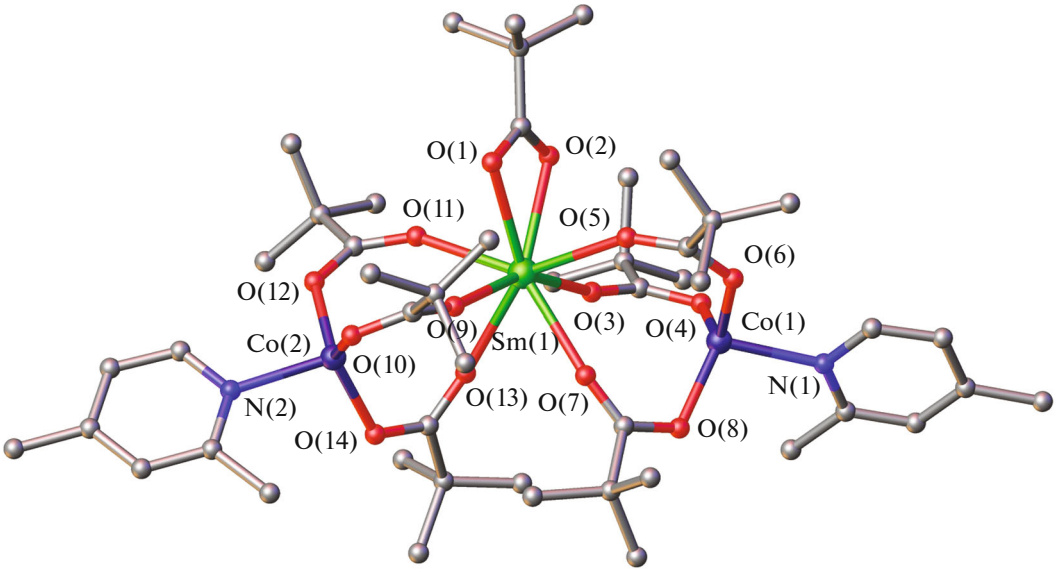


Fig. 2. Structure of complex $[Co_2Sm(Piv)_7(2,4\text{-}Lut)_2]$ (**2**).

Aqueous solutions of $DyCl_3$, $CoCl_2$, benzoic or 3-nitrobenzoic acid, 1,10-phenanthroline, and Na_2CO_3 were mixed when synthesizing complexes $[Co_2Dy(RCOO)_7(Phen)_2]$. The resulting solution in a sealed reactor was heated to 210°C for 5 days and then cooled to room temperature (3°C/h). The following factors are significant for the synthesis of these compounds:

– reaction temperature (the lowest admissible temperature is 180°C, but the pure phase can be obtained only at 210°C);

– necessary presence of such a weak base as Na_2CO_3 or K_2CO_3 (the pure phase is formed only in the presence of Na_2CO_3);

– stoichiometry (the formation of the trinuclear complexes requires the 1 : 2 ratio of dysprosium chloride and cobalt chloride and seven equivalents of the acid).

An information about the reagents and products in the synthesis of the heterometallic complexes with the {Co_2Ln} metal core and bidentate N-donor ligands is summarized in Table 3.

Table 2. Magnetic properties of complexes **1**–**9**

Compound	Complex	Exchange interactions (Co–Ln)	SMM behavior
1a [38]	$[Co_2Nd(NO_3)(Piv)_6(Quin)_2]$	Antiferromagnetic	Was not studied
1b [39]	$[Co_2Gd(NO_3)(Piv)_6(Quin)_2]$	Ferromagnetic	Is not SMM
2 [40]	$[Co_2Sm(Piv)_7(2,4\text{-}Lut)_2]$	Antiferromagnetic	Was not studied
3 [42]	$[Co_2Gd(NO_3)(Piv)_6(Py)_2]$	Ferromagnetic	Is not SMM
4a [43]	$[Co_2Dy(NO_3)(Piv)_6(MeCN)_2]$	Ferromagnetic	Is not SMM
4b [43]	$[Co_2La(NO_3)(Piv)_6(MeCN)_2]$	Absent	Was not studied
4c [43]	$[Co_2Gd(NO_3)(Piv)_6(MeCN)_2]$	Ferromagnetic	Is not SMM
5 [43]	$[Co_2Dy(NO_3)(Piv)_6(Py)_2]$	Ferromagnetic	Was not studied
6 [44]	$[Co_2Gd(NO_3)(Piv)_6(2,4\text{-}Lut)_2]$	Ferromagnetic	Is not SMM
7 [44]	$[Co_2Gd(NO_3)(Piv)_6(2Ph\text{-}Py)_2]$	Ferromagnetic	Is not SMM
8 [44]	$[Co_2Gd(NO_3)(Piv)_6(Et\text{-}Py)_2]$	Ferromagnetic	Is not SMM
9 [44]	$[Co_2Eu(NO_3)(Piv)_6(Et\text{-}Py)_2]$	Absent	SMM

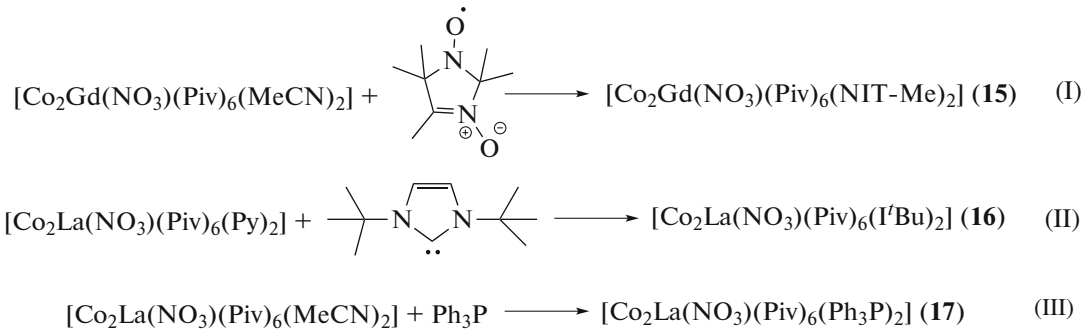
Table 3. Reagents and products in the syntheses of the complexes with the bidentate N-donor ligands

Compound	Source of Co	Source of Ln	Acid	Ligand	Product
10 [45]	$Co(NO_3)_2{\cdot}6H_2O$	$Gd(C_4H_5O_2)_3{\cdot}H_2O$		Bpy	$[Co_2Gd(NO_3)(C_4H_5O_2)_6(Bpy)_2]$
11 [46]	$Co(NO_3)_2{\cdot}6H_2O$	$Ce(C_4H_5O_2)_3{\cdot}2H_2O$		Bpy	$[Co_2Ce(NO_3)(C_4H_5O_2)_6(Bpy)_2]$
12 [47]	$Co(NO_3)_2{\cdot}6H_2O$	$Tb(C_4H_5O_2)_3{\cdot}H_2O$		Bpy	$[Co_2Tb(NO_3)(C_4H_5O_2)_6(Bpy)_2]$
13 [49]	$CoCl_2$	$DyCl_3$	PhCOOH	Phen	$[Co_2Dy(PhCOO)_7(Phen)_2]$
14 [49]	$CoCl_2$	$DyCl_3$	NO_2-PhCOOH	Phen	$[Co_2Dy(NO_2\text{-}PhCOO)_7(Phen)_2]$

The molecular structures of compounds **10**–**14** are based on the trinuclear metal core with the central lanthanide atom and peripheral cobalt atoms each of which is linked with the central atom via three carboxylate bridges. The cobalt atoms are characterized by a coordination number of 5 due to three oxygen atoms of the carboxylate groups and two nitrogen atoms of the chelating ligand molecule. The lanthanide atoms exist in the octacoordination environment LnO_8, which is formed of six oxygen atoms of the monodentate methacrylate anions and two oxygen atoms of the chelating nitrate anion for compounds **10**–**12**, whereas for compounds **13** and **14** the environment is built due to the coordination of seven carboxylic acid anions: six monodentate anions and one chelating anion.

The study of the magnetic properties of the Co_2La complex (**4b**) shows that the paramagnetic cobalt(II) ions in the molecule do not interact with each other and the magnetic behavior of the sample is determined by the orbital moment of the cobalt ions in the tetrahedral environment [43]. The positive value of parameter D_{Co} indicates the planar anisotropy of the ion, and a similar electronic structure is observed for cobalt(II) ions in other complexes with analogous geometry [43, 50]. The replacement of diamagnetic lanthanum by isotropic paramagnetic gadolinium resulted in the ferromagnetic exchange interactions, but the J_{Co-Gd} parameter does not exceed 1 cm^{-1}, which is consistent with the magnetic exchange proceeding via the bridging carboxylate ligands [43, 44]. The complexes with the anisotropic noninteracting cobalt(II) ions supplemented by the ferromagnetically coupled central anisotropic dysprosium(III) ion can manifest a slow magnetization relaxation induced by the magnetic field, which indicates the SMM properties in these complexes.

C-, O-, and P-donor ligands. In addition to the complexes with the N-donor ligands, the trinuclear complexes with the $\{Co_2Ln\}$ metal core containing O-donor [51], C-donor [52], or P-donor ligands [53] are also met. In all cases described, the target compounds were synthesized by the substitution of the ligands in the previously synthesized $[Co_2Ln(NO_3)(Piv)_6(L)_2]$ complexes. The synthesis of the complexes with the O-, C-, and P-donor ligands is shown in Scheme 5.



Scheme 5.

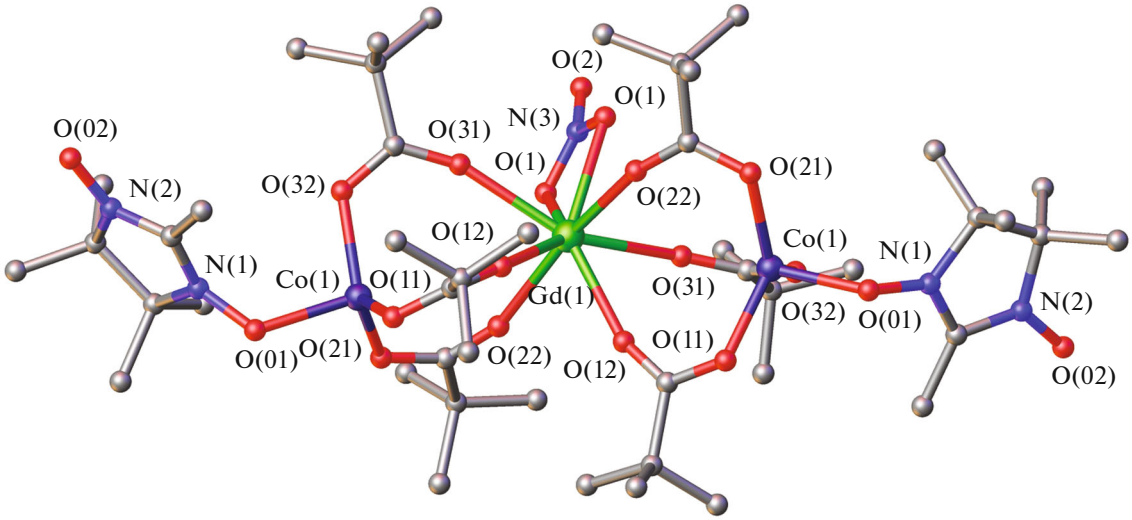


Fig. 3. Structure of complex $[Co_2Gd(NO_3)(Piv)_6(NIT\text{-}Me)_2]$ (**15**).

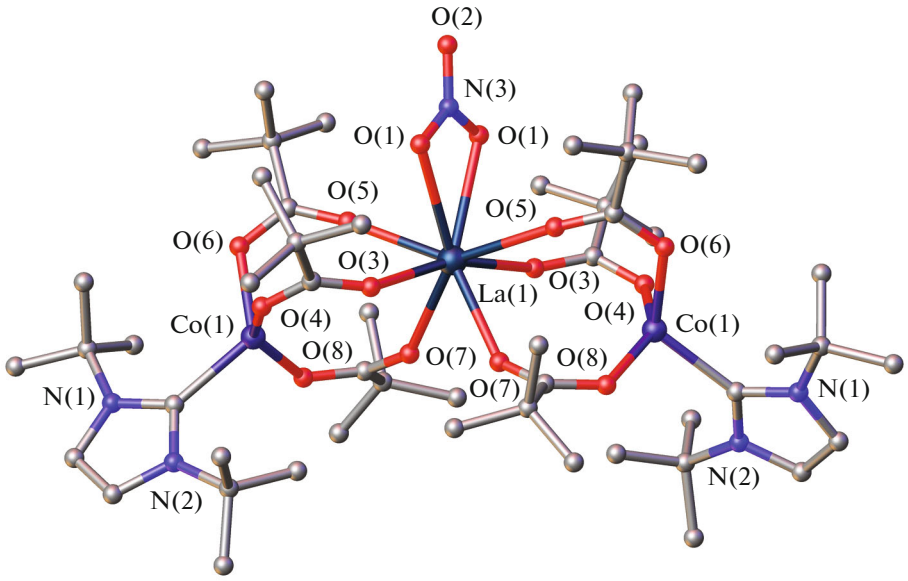


Fig. 4. Structure of complex $[Co_2La(NO_3)(Piv)_6(I^tBu)_2]$ (**16**).

The reactions of complex $[Co_2Gd(NO_3)(Piv)_6(MeCN)_2]$ with nitronyl nitroxide (NIT-Me) in different solvents (Et_2O, PhMe, CH_2Cl_2) (synthesis I, Scheme 5) were conducted [51]. The $[Co_2Gd(NO_3)(Piv)_6(NIT\text{-}Me)_2]$ complex (**15**) was formed in all cases (Fig. 3).

According to the data of magnetic measurements of this compound in the 2–300 K temperature range, strong antiferromagnetic exchange interactions are observed between unpaired electrons of the coordinated NIT-Me molecules and cobalt ions and result in the nearly complete spin coupling of the coordinated nitroxyl groups with one of unpaired electrons of each Co(II) ion already at 200 K.

Simple synthetic protocol to obtain 3*d*–4*f* heterometallic carboxylate complexes with N-heterocyclic carbenes was developed [52]. The approach is based on ligand substitution in the compounds with the stable polynuclear metal core. Complex $[Co_2La(NO_3)(Piv)_6(I^tBu)_2]$ (**16**) was synthesized

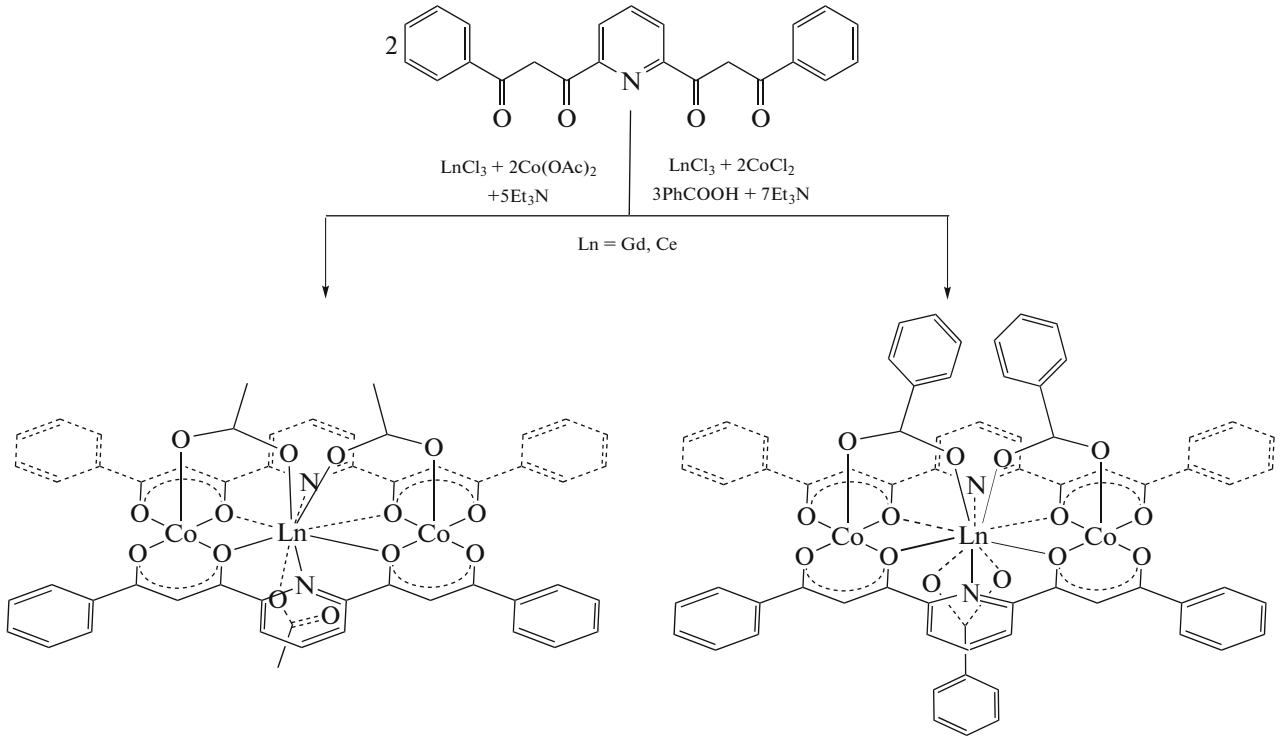
using this procedure by the substitution of pyridine in the previously synthesized $[Co_2La(NO_3)(Piv)_6(Py)_2]$ complex by 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu) (synthesis II, Scheme 5, Fig. 4).

Compound $[Co_2La(NO_3)(Piv)_6(Ph_3P)_2]$ (**17**) was synthesized by the reaction of heterometallic complex $[Co_2La(NO_3)(Piv)_6(MeCN)_2]$ with triphenylphosphine (synthesis III, Scheme 5, Fig. 5) [53]. A similar reaction of pyridine substitution in complex $[Co_2La(NO_3)(Piv)_6(Py)_2]$ by triphenylphosphine gave no target product. This unsuccessful attempt can be explained by the apparently higher stability constants of the complexes with triphenylphosphine over the analogous stability constant of the complex with acetonitrile.

Complex $[Co_2La(NO_3)(Piv)_6(Ph_3P)_2]$ (**17**) is interesting by its SMM properties in the nonzero field (1 kOe) with the low magnetization reversal barrier $\Delta E/k_B = 5$ K and relaxation time $\tau_0 = 2.7 \times 10^{-6}$ s.

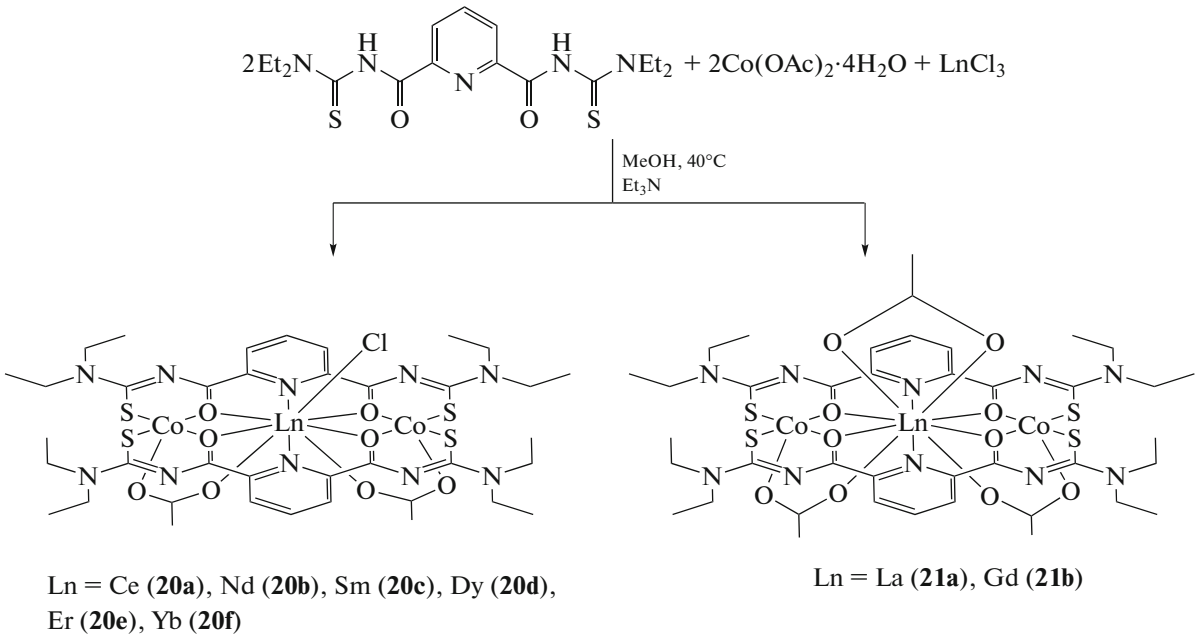
Polydentate ligands. The trinuclear complexes with the $\{Co_2Ln\}$ metal core and polydentate ligands were synthesized in a series of works.

A number of complexes with the $\{Co_2Ln\}$ metal core and 2,6-bis(acetobenzoyl)pyridine (H_2L^1) was synthesized [54]. Lanthanide chloride, H_2L^1, and cobalt acetate reacted in a ratio of 1 : 2 : 2 afforded complexes $[Co_2Ln(L^1)_2(OAc)_3]$ (Ln = Gd (**18a**), Ce (**18b**)). Similar reactions were carried out, where cobalt chloride was used instead of cobalt acetate and three equivalents of benzoic acid were added. All reactions were conducted in the presence of triethylamine. As a result, the $[Co_2Ln(L^1)_2(O_2CPh)_3]$ complexes with 2,6-bis(acetobenzoyl)pyridine (Ln = Gd (**19a**), Ce (**19b**)) were obtained (Scheme 6).



Scheme 6.

A series of the $\{Co_2Ln\}$ complexes (Ln = La, Ce, Nd, Sm, Gd, Dy, Er, and Yb) with 2,6-dipicolinoylbis-*N*,*N*-diethylthiourea (H_2L^2) was synthesized [55]. The reaction of H_2L^2, cobalt acetate, and lanthanide chloride in a ratio of 2 : 2 : 1 in methanol in the presence of triethylamine was carried out. Depending on the lanthanide, the products of two types were obtained: $[Co_2Ln(L^2)_2(OAc)_2Cl]$ in the case of Ln = Ce (**20a**), Nd (**20b**), Sm (**20c**), Dy (**20d**), Er (**20e**), and Yb (**20f**) and $[Co_2Ln(L^2)_2(OAc)_3]$ for Ln = La (**21a**) and Gd (**21b**) (Scheme 7).



Scheme 7.

The summarized information about details of the described syntheses [54, 55] are given in Table 4.

The molecular structures of compounds **18**–**21** are based on the trinuclear metal core with the central lanthanide atom and peripheral cobalt atoms each of which is linked with the central atom via one carboxylate bridge and two oxygen atoms of coordinated ligand L^1 or L^2. In all cases, the cobalt atoms are characterized by the coordination number 5 and their environment is formed by one oxygen atom of the bridging carboxylate group and four oxygen atoms of ligand L^1 (complexes **18**–**19**) or two oxygen atoms and two sulfur atoms of ligand L^2 (complexes **20** and **21**). In complexes **18** and **20**, the lanthanide atoms have a coordination number of 9 due to the tridentate coordination of two molecules of ligand L^1 or L^2 and the monodentate coordination of three acetate anions in the case of complexes **18a**,**b** or the monodentate coordination of two acetate anions and one chlorine atom in the case of complexes **20a**–**f**. In complexes **19** and **21**, the lanthanide atoms have a coordination number of 10 due to the tridentate coordination of two molecules of ligand L^1 or L^2 and one chelating and two monodentate benzoate anions (**19a**,**b**) or acetate anions (**21a**,**b**).

The temperature dependence of the magnetic susceptibility was measured for a series of complexes

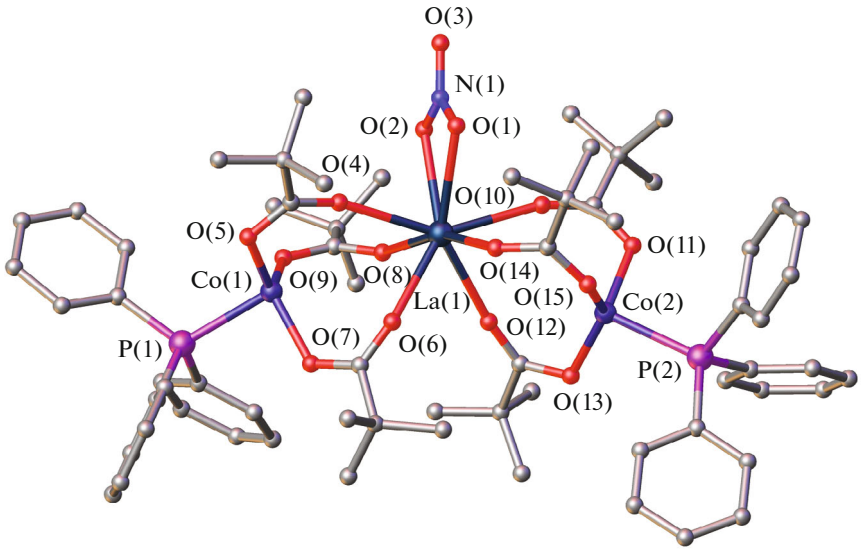


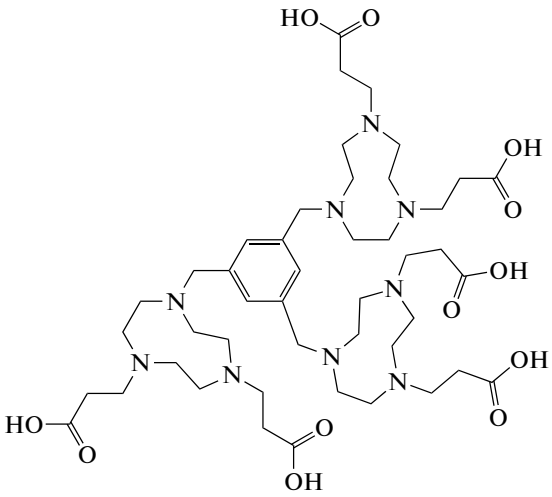
Fig. 5. Structure of complex [$Co_2La(NO_3)(Piv)_6(Ph_3P)_2$] (**17**).

Table 4. Reagents and products in the published syntheses [54, 55]

Compound	Source of Co	Source of Ln	Acid	Ligand	Product
18a,**b** [54]	$Co(OAc)_2·4H_2O$	$LnCl_3·xH_2O$ Ln = Gd, Ce	PhCOOH	H_2L^1	$[Co_2Ln(L^1)_2(OAc)_3]$
19a,**b** [54]	$CoCl_2·6H_2O$	$LnCl_3·xH_2O$ Ln = Gd, Ce		H_2L^1	$[Co_2Ln(L^1)_2(O_2CPh)_3]$
20a–**f** [55]	$Co(OAc)_2·4H_2O$	$LnCl_3$ Ln = Ce, Nd, Sm, Dy, Er, Yb		H_2L^2	$[Co_2Ln(L^2)_2(OAc)_2Cl]$
21a,**b** [55]	$Co(OAc)_2·4H_2O$	$LnCl_3$ Ln = La and Gd		H_2L^2	$[Co_2Ln(L^2)_2(OAc)_3]$

(compounds **20** and **21**). The antiferromagnetic exchange interactions were found to occur between the Co(II) and Ln(III) metal ions in the case of the complex with Dy^{3+}, and the ferromagnetic exchange interactions were observed for the complexes with Ce^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, and Er^{3+}.

Hexanuclear complexes $[Co_4Ln_2(LH_{2.5})_2(H_2O)_4]·(ClO_4)_6·NO_3·nH_2O$ (Ln = Dy, n = 12 (**22**); Ln = Yb, n = 9 (**23**)) were synthesized [56] by the reactions of 1,3,5-tris((4,7-bis(2-carboxyethyl)-1,4,7-triazacyclonon-1-yl)methylbenzene (H_6L, Scheme 8), $Co(ClO_4)_2·6H_2O$, and $Ln(NO_3)_3·6H_2O$ (Ln = Dy, Yb) in a ratio of 1 : 3 : 1. The synthesized compounds are isostructural and differ only by the number of water molecules existing in the crystalline lattice. The structure of these complexes is shown in Fig. 6.

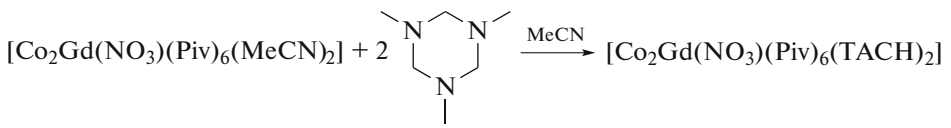


Scheme 8.

In the synthesized complexes, two individual trinuclear fragments with the $\{Co_2Ln\}$ metal core are linked with each other via two tris(triaza)macrocyclic ligands. One tricyclic ligand can act as a potential trinuclear framework, but only two of three its substituted macrocycles coordinate to the cobalt atoms by three nitrogen atoms and two oxygen atoms. Each peripheral cobalt atom is bound to the central lanthanide atom via the bridging carboxylate fragment and the oxygen atom of the carboxylate group of the coordinated macrocycle of the ligand.

These complexes being heterometallic 3*d*–4*f* cores can be used as fluorescent chemosensors for nitroaromatic compounds owing to these luminescence emission properties and framework structures resistant to the action of nitroaromatic compounds, including those of the acidic nature.

Complex $[Co_2Gd(NO_3)(Piv)_6(TACH)_2]$ (**24**) was synthesized (Scheme 9) [57] by the substitution of the acetonitrile molecules in the previously prepared $[Co_2Gd(NO_3)(Piv)_6(MeCN)_2]$ complex by hexahydro-1,3,5-trimethyl-1,3,5-triazine (TACH).



Scheme 9.

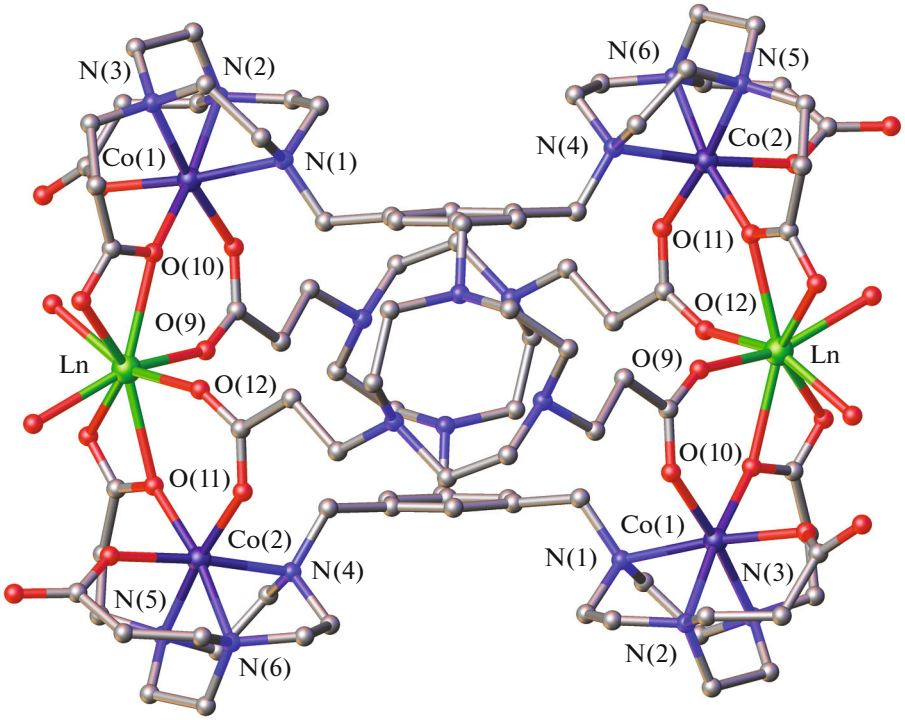


Fig. 6. Structure of complexes $[Co_4Ln_2(LH_{2.5})_2(H_2O)_4]\cdot(ClO_4)_6\cdot NO_3\cdot nH_2O$ (Ln = Dy (**22**), and Yb (**23**)).

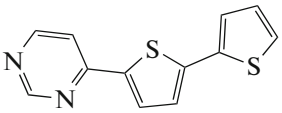
In the synthesized complex, the central gadolinium atom is linked with the terminal cobalt atoms via three bridging pivalate anions. The cobalt atoms coordinate the TACH molecules via the tridentate mode and have a coordination number of 6. The coordination of the TACH molecules to the cobalt(II) ions leads to a significant distortion of the coordination environment and conformational changes in 1,3,5-trimethyl-1,3,5-triazacyclohexane.

COMPLEXES WITH {Co_2Li_2} METAL CORE

Seven methods for the synthesis of the complexes with the {Co_2Li_2} metal core were described and are shown in Scheme 10.

$$[Co(Piv)_2]_n + Li(Piv) + L \longrightarrow [Co_2Li_2(Piv)_6(L)_2] \quad (I)$$

Co : Li : L = 1 : 1 : 1

L = Et_3N (**25**), L^3 =  (**26**), Py (**27**), 2Ph-Py (**28**), Ph_3P (**29**)

$$[Co(Piv)_2]_n + Li(Piv) + HFur + Py \longrightarrow [Co_2Li_2(Fur)_6(Py)_2]\ (\mathbf{30}) \quad (II)$$

Co : Li : HFur : Py = 1 : 1 : 3 : 1

$$[Co_2Li_2(Piv)_6(Py)_2] + 2IMes \longrightarrow [Co_2Li_2(Piv)_6(IMes)_2]\ (\mathbf{31}) \quad (III)$$

$$[Co_2(Piv)_4(2,4\text{-Lut})_2] + 2Li(Piv) \longrightarrow [Co_2Li_2(Piv)_6(2,4\text{-Lut})_2]\ (\mathbf{32}) \quad (IV)$$

$$CoCl_2\cdot 6H_2O + Li(^tBuCH_2COO) + 2,4\text{-Lut} \longrightarrow [Co_2Li_2(^tBuCH_2COO)_6(2,4\text{-Lut})_2]\ (\mathbf{33}) \quad (V)$$

$$Co(NO_3)_2\cdot 6H_2O + Bpy + KNaph + HNaph + LiOH \longrightarrow [Co_2Li_2(Naph)_6(Bpy)_2]\ (\mathbf{34}) \quad (VI)$$

$$[Co_3(Myr)_6(2,4\text{-Lut})_2] + LiOH + HMyr \longrightarrow [Co_2Li_2(Myr)_6(2,4\text{-Lut})_2]\ (\mathbf{35}) \quad (VII)$$

Scheme 10.

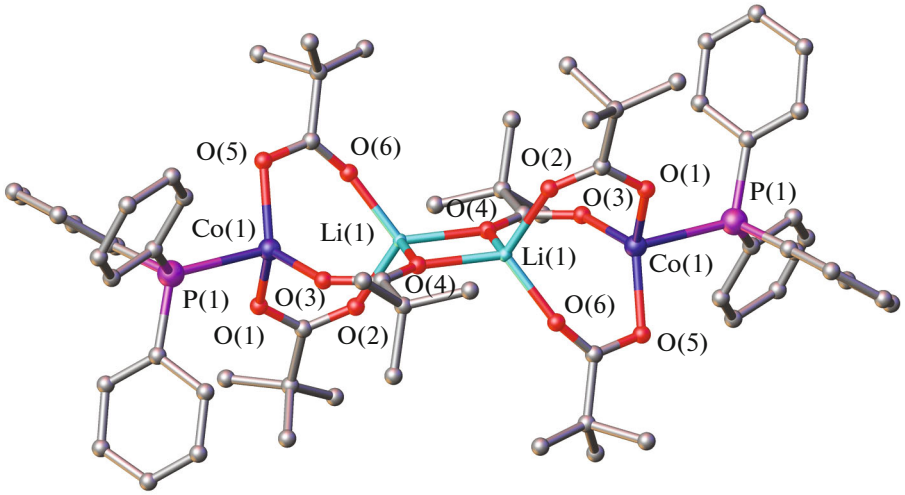


Fig. 7. Structure of complex $[Co_2Li_2(Piv)_6(Ph_3P)_2]$ (**29**).

The target compounds were obtained [50, 58–61] by the reaction of cobalt pivalate, lithium pivalate, and the corresponding ligand (triethylamine, 4-[2,2']-bithiophen-5-yl-pyrimidine (L^3), pyridine, 2-phenylpyridine, or triphenylphosphine) in a ratio of 1 : 1 : 1 (method I, Scheme 10).

In addition to compound $[Co_2Li_2(Piv)_6(Ph_3P)_2]$ (**29**) (Fig. 7), complexes $[Co_2Li_2(Fur)_6(Py)_2]$ (**30**) and $[Co_2Li_2(Piv)_6(IMes)_2]$ (IMes is 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) (**31**) (Figs. 8, 9) were synthesized [50]. The complex based on 2-furancarboxylic acid anions was synthesized by the reaction of cobalt pivalate, lithium pivalate, 2-furancarboxylic acid, and pyridine in a ratio of 1 : 1 : 3 : 1 (method II, Scheme 10). The pivalate complex with IMes was synthesized by pyridine substitution in the previously prepared $[Co_2Li_2(Piv)_6(Py)_2]$ complex (**27**) by IMes molecules (method III, Scheme 10).

Two complexes with the $\{Co_2Li_2\}$ metal core were synthesized [62]. The reaction of the previously synthesized compound $[Co_2(Piv)_4(2,4\text{-Lut})_2]$ and two equivalents of lithium pivalates afforded complex $[Co_2Li_2(Piv)_6(2,4\text{-Lut})_2]$ (**32**) (method IV, Scheme 10). Complex $[Co_2Li_2(^tBuCH_2COO)_6(2,4\text{-Lut})_2]$ (**33**) was synthesized by the reaction of cobalt chloride, *tert*-butylacetic acid lithium salt, and 2,4-lutidine (method V, Scheme 10).

2,2'-Bipyridine and 2-naphthoic acid potassium salt were added to cobalt nitrate [63], and the reaction mixture was stirred for 30 min after which 2-naphthoic acid and lithium hydroxide were added. The reaction mixture was stirred for 1 h to obtain complex $[Co_2Li_2(Naph)_6(Bpy)_2]$ (**34**) (Naph is 2-naphthoate anion) (method VI, Scheme 10).

Complex $[Co_2Li_2(Myr)_6(2,4\text{-Lut})_2]$ (**35**) was prepared [64] by the two-step synthesis. Potassium hydroxide, myrtenic acid, cobalt chloride, and 2,4-lutidine reacted in the first step to form the $[Co_3(Myr)_6(2,4\text{-Lut})_2]$ complex (Myr is myrtenic acid anion). Then lithium hydroxide and myrtenic acid were added to the formed product to afford complex $[Co_2Li_2(Myr)_6(2,4\text{-Lut})_2]$ (**35**) (method VII, Scheme 10).

The generalized information about the synthesis of the complexes with the $\{Co_2Li_2\}$ metal core is given in Table 5.

Complexes **25**–**35** are heterometallic tetranuclear compounds. The cobalt and lithium atoms are linked with each other via three carboxylate bridges, and the lithium atoms are bound to each other via the oxygen atom of the acid anions. Each cobalt atom coordinates one ligand molecule and is characterized by a coordination number of 4 in the cases of complexes **25**–**33** and **35**, and complex **34** is characterized by the coordination number 6.

Only specific structural features were studied for complexes **28**, **34**, and **35**.

The thermal properties of compounds **25**, **32**, and **33** were studied. The solid-state thermolysis experiments showed that these complexes can be considered as potential precursors in the synthesis of lithium cobaltate thin films.

Metal-organic frameworks (MOFs) $[LiCo(Btc)(DMA)_2]\cdot 2DMA$, $[LiCo(Btb)(DMF)_2]\cdot 2DMF$, and $[LiCo(Btb)(DMA)_2]\cdot 2DMA$ [60] were synthesized from complex $[Co_2Li_2(Piv)_6(Py)_2]$ (**27**) and such organic tricarboxylate ligands as trimesate (Btc^{3-}) and 1,3,5-benzenetribenzoate (Btb^{3-}).

Complexes $[Co_2Li_2(Piv)_6(Ph_3P)_2]$ (**29**), $[Co_2Li_2(Fur)_6(Py)_2]$ (**30**), and $[Co_2Li_2(Piv)_6(IMes)_2]$ (**31**) were shown to be single-molecule magnets in an alternating magnetic field. The *ab initio* calculations

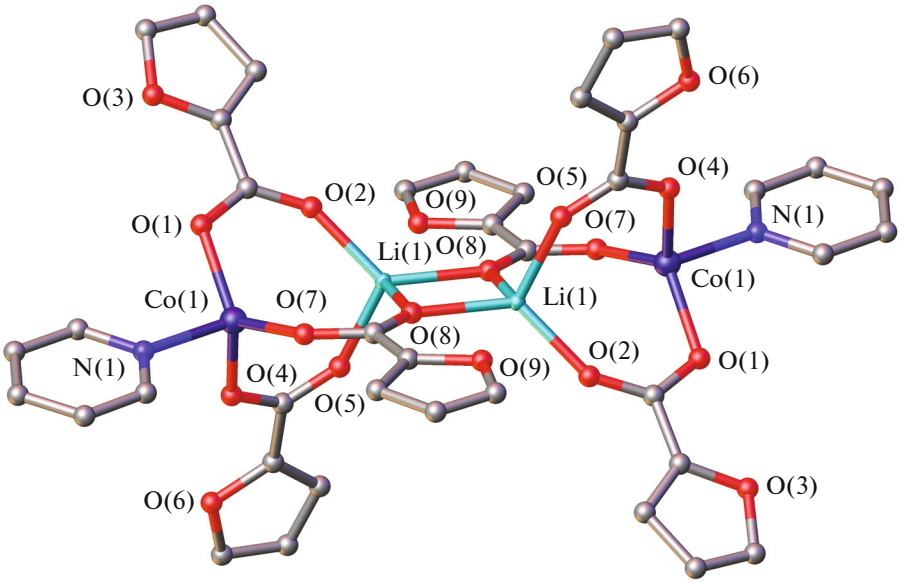


Fig. 8. Structure of complex $[Co_2Li_2(Fur)_6(Py)_2]$ (**30**).

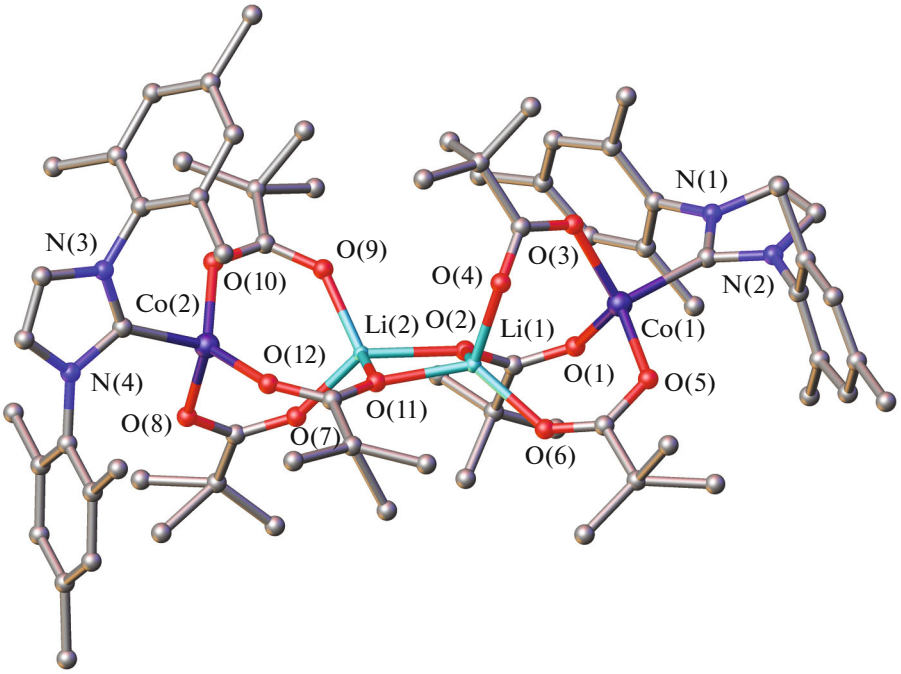


Fig. 9. Structure of complex $[Co_2Li_2(Piv)_6(IMes)_2]$ (**31**).

showed the easy-plane magnetic anisotropy of the cobalt(II) ions in these compounds, which induces relaxation accomplished by the sum of the Raman and direct mechanisms.

CONCLUSIONS

An analysis of the published data shows that the carboxylate complexes with the $\{Co_2Ln\}$ and $\{Co_2Li_2\}$ metal cores are presented by a relatively small number of structurally characterized compounds, and the magnetic properties (including those in alternating magnetic fields) of the majority of these compounds were not studied systematically. At the same time, since the Co^{2+} ion has the intrinsic unquenched orbital momentum and the total spin of the system and the character and strength of spin–spin exchange interactions can be tuned due to the variation of Ln^{3+}

Table 5. Reagents and products in the syntheses of the complexes with the $\{Co_2Li_2\}$ metal core

Compound	Source of Co	Source of Li	Acid	Ligand	Product
25 [58]	$[Co(Piv)_2]_n$	Li(Piv)		Et_3N	$[Co_2Li_2(Piv)_6(Et_3N)_2]$
26 [59]	$[Co(Piv)_2]_n$	Li(Piv)		L^3	$[Co_2Li_2(Piv)_6(L^3)_2]$
27 [60]	$[Co(Piv)_2]_n$	Li(Piv)		Py	$[Co_2Li_2(Piv)_6(Py)_2]$
28 [61]	$[Co(Piv)_2]_n$	Li(Piv)		2Ph-Py	$[Co_2Li_2(Piv)_6(2Ph\text{-}Py)_2]$
29 [50]	$[Co(Piv)_2]_n$	Li(Piv)		Ph_3P	$[Co_2Li_2(Piv)_6(Ph_3P)_2]$
30 [50]	$[Co(Piv)_2]_n$	Li(Piv)	HFur	Py	$[Co_2Li_2(Fur)_6(Py)_2]$
31 [50]	$[Co_2Li_2(Piv)_6(Py)_2]$			IMes	$[Co_2Li_2(Piv)_6(IMes)_2]$
32 [62]	$[Co_2(Piv)_4(2,4\text{-}Lut)_2]$	Li(Piv)			$[Co_2Li_2(Piv)_6(2,4\text{-}Lut)_2]$
33 [62]	$CoCl_2{\cdot}6H_2O$	Li(^{t}BuCH$_2$COO)		2,4-Lut	$[Co_2Li_2(^t BuCH_2COO)_6(2,4\text{-}Lut)_2]$
34 [63]	$Co(NO_3)_2{\cdot}6H_2O$	LiOH	HNaph	Bpy	$[Co_2Li_2(Naph)_6(Bpy)_2]$
35 [64]	$[Co_3(Myr)_6(2,4\text{-}Lut)_2]$	LiOH	HMyr		$[Co_2Li_2(Myr)_6(2,4\text{-}Lut)_2]$

ions, the complexes of the $\{Co_2Ln\}$ type are promising systems for the search for new single-molecule magnets. The tetranuclear $\{Co_2Li_2\}$ systems in which the lithium atoms separating the cobalt(II) atoms in space generate magnetic dilution at the molecular level are also promising in this respect, which should favor the suppression of undesirable intramolecular exchange interactions and relaxation processes decreasing the efficiency of single-molecule magnets. Available starting reagents, a relative simplicity of the synthesis of the compounds with the $\{Co_2Li_2\}$ and $\{Co_2Ln\}$ metal cores, and a high resistance of heterometallic complexes of this type to air oxygen and moisture would provide further prolong interest of researchers in the development of this field of coordination chemistry.

FUNDING

This review was supported by the Russian Science Foundation, project no. 19-13-00436-P.

CONFLICT OF INTEREST

The author of this work declares that they has no conflicts of interest.

ADDITIONAL INFORMATION

Authors congratulate heartily Academician M.P. Egorov on the occasion of his 70th jubilee.

REFERENCES

1. Yang, D., Chen, Y., Su, Z., et al., *Coord. Chem. Rev.*, 2021, vol. 428, p. 213619.
2. Rice, A.M., Leith, G.A., Ejegbavwo, O.A., et al., *ACS Energy Lett.*, 2019, vol. 4, no. 8, p. 1938.
3. Lamiel, C., Hussain, I., Rabiee, H., et al., *Coord. Chem. Rev.*, 2023, vol. 480, p. 215030.
4. Shen, J.-Q., Liao, P.-Q., Zhou, D.-D., et al., *J. Am. Chem. Soc.*, 2017, vol. 139, no. 5, p. 1778.
5. Rosado Piquer, L. and Sañudo, E.C., *Dalton Trans.*, 2015, vol. 44, no. 19, p. 8771.
6. Dey, A., Acharya, J., and Chandrasekhar, V., *Chem. Asian J.*, 2019, vol. 14, no. 24, p. 4433.
7. Wang, J., Feng, M., Akhtar, M.N., and Tong, M.-L., *Coord. Chem. Rev.*, 2019, vol. 387, p. 129.
8. Monteiro, B., Coutinho, J.T., and Pereira, L.C.J., *Lanthanide-Based Multifunctional Materials*, Elsevier, 2018, p. 233.
9. Sidorov, A.A., Kiskin, M.A., Aleksandrov, G.G., et al., *Russ. J. Coord. Chem.*, 2016, vol. 42, no. 10, p. 621.
10. Sidorov, A.A., Gogoleva, N.V., Bazhina, E.S., et al., *Pure Appl. Chem.*, 2020, vol. 92, no. 7, p. 1093.
11. Andruh, M., Costes, J.-P., Diaz, C., and Gao, S., *Inorg. Chem.*, 2009, vol. 48, no. 8, p. 3342.
12. Andruh, M., *Dalton Trans.*, 2015, vol. 44, no. 38, p. 16633.
13. Darago, L.E., Boshart, M.D., Nguyen, B.D., et al., *J. Am. Chem. Soc.*, 2021, vol. 143, no. 22, p. 8465.
14. Zheng, Y.-Z., Evangelisti, M., Tuna, F., and Winpenny, R.E.P., *J. Am. Chem. Soc.*, 2012, vol. 134, no. 2, p. 1057.
15. Zheng, Y.-Z., Evangelisti, M., and Winpenny, R.E.P., *Chem. Sci.*, 2011, vol. 2, no. 1, p. 99.
16. Peng, J.-B., Zhang, Q.-C., Kong, X.-J., et al., *J. Am. Chem. Soc.*, 2012, vol. 134, no. 7, p. 3314.
17. Le Roy, J.J., Cremers, J., Thomlinson, I.A., et al., *Chem. Sci.*, 2018, vol. 9, no. 45, p. 8474.
18. Elias, J.S., Risch, M., Giordano, L., et al., *J. Am. Chem. Soc.*, 2014, vol. 136, no. 49, p. 17193.
19. Zhang, H., Ma, J., Chen, D., et al., *J. Mater. Chem. A*, 2014, vol. 2, no. 48, p. 20450.
20. Kumar, K., Chorazy, S., Nakabayashi, K., et al., *J. Mater. Chem. C*, 2018, vol. 6, no. 31, p. 8372.
21. Wang, J., Chorazy, S., Nakabayashi, K., et al., *J. Mater. Chem. C*, 2018, vol. 6, no. 3, p. 473.

22. Xin, Y., Wang, J., Zychowicz, M., et al., *J. Am. Chem. Soc.*, 2019, vol. 141, no. 45, p. 18211.

23. Zhu, M., Zhang, H., Ran, G., et al., *J. Am. Chem. Soc.*, 2021, vol. 143, no. 19, p. 7541.

24. Hong, S., Pfaff, F.F., Kwon, E., et al., *Angew. Chem., Int. Ed. Engl.*, 2014, vol. 53, no. 39, p. 10403.

25. Hong, S., Pfaff, F.F., Kwon, E., et al., *Angew. Chem., Int. Ed. Engl.*, 2017, vol. 56, no. 36, p. 10630.

26. King, E.R. and Betley, T.A., *J. Am. Chem. Soc.*, 2009, vol. 131, no. 40, p. 14374.

27. Andrez, J., Guidalb, V., Scopelliti, R., et al., *J. Am. Chem. Soc.*, 2017, vol. 139, no. 25, p. 8628.

28. Wei, Z., Han, H., Filatov, A.S., and Dikarev, E.V., *Chem. Sci.*, 2014, vol. 5, no. 2, p. 813.

29. Tey, S.L., Reddy, M.V., Subba Rao, G.V., et al., *Chem. Mater.*, 2006, vol. 18, no. 6, p. 1587.

30. Boyle, T.J., Rodriguez, M.A., Ingersoll, D., et al., *Chem. Mater.*, 2003, vol. 15, no. 20, p. 3903.

31. Chen, C., Hecht, M.B., Kavara, A., et al., *J. Am. Chem. Soc.*, 2015, vol. 137, no. 41, p. 13244.

32. Goetz, M.K., Hill, E.A., Filatov, A.S., and Anderson, J.S., *J. Am. Chem. Soc.*, 2018, vol. 140, no. 41, p. 13176.

33. Nurdin, L., Spasyuk, D.M., Fairburn, L., et al., *J. Am. Chem. Soc.*, 2018, vol. 140, no. 47, p. 16094.

34. Rowsell, J.L.C. and Yaghi, O.M., *Microporous Mesoporous Mater.*, 2004, vol. 73, nos. 1–2, p. 3.

35. Chui, S.S.Y., Lo, S.M.F., Charmant, J.P.H., et al., *Science*, 1999, vol. 283, no. 5405, p. 1148.

36. Serre, C., Mellot-Draznieks, C., Surblé, S., et al., *Science*, 2007, vol. 315, no. 5820, p. 1828.

37. Agafonov, M.A., Alexandrov, E.V., Artyukhova, N.A., et al., *J. Struct. Chem.*, 2022, vol. 63, no. 5, p. 671.

38. Cui, Y., Chen, J.-T., Long, D.-L., et al., *Dalton Trans.*, 1998, no. 18, p. 2955.

39. Cui, Y., Chen, G., Ren, J., et al., *Inorg. Chem.*, 2000, vol. 39, no. 18, p. 4165.

40. Bykov, M.A., Emelina, A.L., Orlova, E.V., et al., *Russ. J. Inorg. Chem.*, 2009, vol. 54, no. 4, p. 548.

41. Pakhmutova, E.V., Malkov, A.E., Mikhailova, T.B., et al., *Russ. Chem. Bull.*, 2003, vol. 52, no. 10, p. 2117.

42. Sapianik, A.A., Lutsenko, I.A., Kiskin, M.A., et al., *Russ. Chem. Bull.*, 2016, vol. 65, no. 11, p. 2601.

43. Kiskin, M., Zorina-Tikhonova, E., Kolotilov, S., et al., *Eur. J. Inorg. Chem.*, 2018, vol. 2018, no. 12, p. 1356.

44. Lutsenko, I.A., Kiskin, M.A., Nikolaevskii, S.A., et al., *ChemistrySelect*, 2019, vol. 4, no. 48, p. 14261.

45. Wu, B., *J. Coord. Chem.*, 2008, vol. 61, no. 16, p. 2558.

46. Wu, B. and Hou, T., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, vol. 66, no. 4, p. m457.

47. Wu, B. and Zhao, C.-X., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, vol. 66, no. 9, p. m1075.

48. Lu, W.M., Wu, J.-B., Dong, N., and Chun, W.-G., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, vol. 51, no. 8, p. 1568.

49. Zhu, Y., Luo, F., Feng, X.-F., et al., *Aust. J. Chem.*, 2013, vol. 66, no. 1, p. 75.

50. Yambulatov, D.S., Nikolaevskii, S.A., Shmelev, M.A., et al., *Mendeleev Commun.*, 2021, vol. 31, no. 5, p. 624.

51. Fursova, E.Yu., Kuznetsova, O.V., Ovcharenko, V.I., et al., *Russ. Chem. Bull.*, 2007, vol. 56, no. 9, p. 1805.

52. Nikolaevskii, S.A., Petrov, P.A., Sukhikh, T.S., et al., *Inorg. Chim. Acta*, 2020, vol. 508, p. 119643.

53. Nikolaevskii, S.A., Yambulatov, D.S., Voronina, J.K., et al., *ChemistrySelect*, 2020, vol. 5, no. 41, p. 12829.

54. Trieu, T.N., Nguyen, M.H., Abram, U., et al., *Z. Anorg. Allg. Chem.*, 2015, vol. 641, no. 5, p. 863.

55. Jesudas, J.J., Pham, C.T., Hagenbach, A., et al., *Inorg. Chem.*, 2020, vol. 59, no. 1, p. 386.

56. Tang, Q., Sun, Y., Li, H.-Y., et al., *Appl. Organomet. Chem.*, 2019, vol. 33, no. 4, p. e4814.

57. Shmelev, M.A., Voronina, Yu.K., Chekurova, S.S., et al., *Russ. J. Coord. Chem.*, 2021, vol. 47, no. 8, p. 551.

58. Dobrohotova, Zn.V., Sidorov, A.A., Kiskin, M.A., et al., *J. Solid State Chem.*, 2010, vol. 183, no. 10, p. 2475.

59. Cheprakova, E.M., Verbitskiy, E.V., Kiskin, M.A., et al., *Polyhedron*, 2015, vol. 100, p. 89.

60. Sapianik, A.A., Kiskin, M.A., Kovalenko, K.A., et al., *Dalton Trans.*, 2019, vol. 48, no. 11, p. 3676.

61. Kuznetsova, G.N., Nikolaevskii, S.A., Yambulatov, D.S., et al., *J. Struct. Chem.*, 2021, vol. 62, no. 2, p. 184.

62. Dobrokhotova, Z., Emelina, A., Sidorov, A., et al., *Polyhedron*, 2011, vol. 30, no. 1, p. 132.

63. Gol'dberg, A.E., Nikolaevskii, S.A., Kiskin, M.A., et al., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 12, p. 777. https://doi.org/10.1134/S1070328415120015

64. Zorina-Tikhonova, E.N., Aleksandrov, G.G., Kiskin, M.A., et al., *Russ. J. Coord. Chem.*, 2019, vol. 45, no. 10, p. 689. https://doi.org/10.1134/S1070328419100099

Translated by E. Yablonskaya