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Syntheses and Structures of Heterometallic Complexes M–Co(II) (M = Li(I), Mg(II), and Eu(III)) with Anions of 2-Naphthoic Acid. An Influence of the Heterometal on the Structure of the Complex

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Abstract—A series of polynuclear heterometallic cobalt(II) 2-naphthoate complexes with lithium(I), magnesium(II), and europium(III) is synthesized: $[(2,2'\text{-Bipy})_2Li_2Co_2(Naph)_6]$, $[(2,4\text{-Lut})_2Co_2Mg(Naph)_6]$, and $[(2,2'\text{-Bipy})_2(EtOH)_2Co_2Eu_2(Naph)_{10}]$ (Naph is 2-naphthoic acid anion, 2,2'-Bipy is 2,2'-bipyridine, and 2,4-Lut is 2,4-lutidine). The single crystals of the synthesized compounds are characterized by X-ray diffraction analysis (CIF files CCDC 1401987 (**I**), 1401988 (**II**), 1401989 (**III**), and 1401990 (**IV**)). The compositions and structures of the molecular heterometallic complexes based on cobalt(II) cations and anions of 2-naphthoic acid are determined by the radius and coordination number of the introduced heterometal: the isomorphic substitution of one of the cobalt(II) ions is observed for the magnesium(II) complex, and tetranuclear complexes are formed in the case of lithium(I) and europium(III).

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INTRODUCTION

Search for methods of the synthesis of heterometallic compounds is one of the urgent problems of the modern inorganic chemistry. This is due to the fact that the presence of two and more metals of different nature in the complex makes it possible to purposefully isolate stoichiometric substances that are promising as precursors for the preparation of heterometallic compounds upon thermal decomposition [1–6] and new functional substances with unique magnetic [7–10], luminescence [11–14], and/or catalytic properties [15, 16]. For example, as previously shown cobalt and nickel trimethyl acetates can react with the lithium salt to form trinuclear complexes $[Li_2M_2(Piv)_6L_2]$ (M = Co, Ni; L is NEt_3, 2,4-Lut (2,4-lutidine), or 2,2'-Bipy (2,2'-bipyridine)), whose decomposition leads to the formation of lithium cobaltate or nickelate at relatively low temperatures (<500°C) [17–20]. In the synthesis of carbon nanotubes from a mixture of CH_4 and H_2, the heterometallic complex $[Ni_2Mg(Piv)_6(2,2'\text{-Bipy})_2]$ can act as a catalyst precursor, replacing a mixture of inorganic nickel(II) and magnesium(II) salts [21]. The introduction of a paramagnetic heterometal, for example, an ion of 4*f*-element, can favor the formation of a magnetically active system consisting of paramagnetic sites of different nature linked to each other by anti- or ferromagnetic interactions [22, 23]. Among these unique compounds there are single-molecule magnets exhibiting an effect of magnetic ordering of spins of individual molecules and retaining spin orientation when the external magnetic field is changed [24–27].

The studies in the field of the synthesis of heterometallic compounds show that the formation of complexes of different nuclearity should be expected, depending on the metal introduced into the reaction mixture. The nuclearity is determined by coordination possibilities of the heterometal, the ratio of metals in the reaction mixture, the nature of bridging ligands, etc. In turn, this enlarges the variety of coordination compounds.

In this work, we studied the possibility of synthesizing heterometallic cobalt(II) complexes with anions of 2-naphthoic acid. Lithium(I), magnesium(II), and europium(III) ions earlier tested in the trimethylacetate systems [17–20, 28, 29] were chosen as heterometals. A comparison of the results obtained for the structures of the M–Co(II) heterometallic complexes with published data makes it possible to establish relationships "nature of heterometal–structure of complex" and to reveal the structure-forming role of the substituent at the carboxylate group.

EXPERIMENTAL

All procedures associated with the synthesis of new complexes were carried out in air using commercial solvents (MeCN, EtOH, THF, and benzene) and reagents (2-naphthoic acid (NaphH), (>99%), 2,2'-bipyridine (>99.8%), 2,4-lutidine (>99%), $Co(NO_3)_2 \cdot 6H_2O$ (>99.8%), $Eu(NO_3)_3 \cdot 6H_2O$ (>99.9%), KOH

(>99%), and LiOH (>99%)). The starting compounds $[Co(Piv)_2]_n$ and $[(2,4\text{-Lut})_2Co_2Mg(Piv)_6]$ were synthesized using known procedures [28, 30].

The IR spectra of the compounds were recorded on a Perkin Elmer Spectrum 65 spectrophotometer in a range of 400–4000 cm^{-1} in KBr pellets. Elemental analyses were conducted on a Euro EA-3000 C,H,N,S analyzer (Euro Vektor).

Synthesis of $[(2,2'\text{-Bipy})_2Co_3(Naph)_6] \cdot 2C_6H_6$ (I). A solution of $[Co(Piv)_2]_n$ (0.1 g, 0.39 mmol) in EtOH (10 mL) and THF (10 mL) was added by 2,2'-Bipy (0.03 g, 0.19 mmol) and a solution of NaphH (0.26 g, 1.535 mmol) in benzene (30 mL). The reaction mixture was vigorously stirred at 75°C for 1 h until the initial reagents were dissolved completely. The obtained solution was cooled to room temperature and kept for 4 days. The precipitated pink crystals suitable for X-ray diffraction analysis were decanted from the mother liquor, washed with cold THF, and dried in air. The yield of compound **I** was 0.24 g (74% based on the initial amount of $Co(Piv)_2$).

For $C_{86}H_{58}N_4O_{12}Co_3$ (ignoring solvate molecules)

anal. calcd., %:	C, 68.13;	H, 3.86;	N, 3.70.
Found, %:	C, 68.41;	H, 3.71;	N, 3.57.

IR (KBr, cm^{-1}): 3720–3200 w, 3054 w, 1633 m, 1606 s, 1569 s, 1537 m, 1503 m, 1470 m, 1439 m, 1400 vs, 1381 s, 1309 w, 1263 w, 1239 w, 1204 w, 1152 w, 1102 w, 1058 w, 1021 w, 956 vw, 915 vw, 867 w, 832 vw, 806 m, 790 s, 763 m, 756 m, 735 m, 679 w, 651 vw, 637 vw, 598 m, 489 w, 474 w, 418 m.

Synthesis of $[(2,2'\text{-Bipy})_2Co_2Li_2(Naph)_6]$ (II). A suspension of $Co(NO_3)_2 \cdot 6H_2O$ (0.08 g, 0.29 mmol) in MeCN (30 mL) was added by 2,2'-Bipy (0.045 g, 0.29 mmol) with stirring. A solution of 2-naphthoic acid potassium salt, prepared by the addition of a solution of NaphH (0.100 g, 0.58 mmol) to KOH (0.033 g, 0.58 mmol), in a MeCN–EtOH (4 : 1) mixture (10 mL) was added to the reaction mixture. The resulting mixture was stirred at 75°C for 30 min, NaphH (0.100 g, 0.58 mmol) and lithium hydroxide (0.014 g, 0.58 mmol) were added, and the reaction mixture was stirred for 1 h. Then the solution was filtered to remove a flaky precipitate and kept at room temperature for 3 days. The precipitated pink crystals suitable for X-ray diffraction analysis were decanted from the mother liquor, washed with cold MeCN, and dried in air. The yield of compound **II** was 0.75 g (53% based on $Co(NO_3)_2$).

For $C_{86}H_{58}N_4O_{12}Li_2Co_2$

anal. calcd., %:	C, 70.21;	H, 3.97;	N, 3.81.
Found, %:	C, 69.98;	H, 3.80;	N, 4.00.

IR (KBr, cm^{-1}): 3631 vw, 3430 w, 3082 w, 3057 w, 1633 s, 1605 vs, 1567 s, 1504 m, 1488 m, 1470 s, 1442 s, 1398 vs, 1381 vs, 1359 s, 1309 m, 1269 m, 1240 m, 1204 m, 1157 m, 1136 w, 1102 w, 1057 w, 1043 w, 1021 m, 976 vw, 966 vw, 955 w, 927 vw, 913 m, 897 w, 867 m, 826 w, 808 m, 791 vs, 757 s, 734 m, 669 vw, 651 w, 637 w, 597 m, 576 w, 537 w, 491 m, 482 m, 469 m, 417 m.

Synthesis of $[(2,4\text{-Lut})_2Co_2Mg(Naph)_6] \cdot 4C_6H_6$ (III). A solution of complex $[(2,4\text{-Lut})_2Co_2Mg(Piv)_6]$ (0.100 g, 0.104 mmol) in THF (30 mL) and benzene (10 mmol) was added by NaphH (0.107 g, 0.623 mmol) with stirring at room temperature. The obtained reaction mixture was stirred for 30 min, and then the solution was kept at 5°C for 2 days. The precipitated violet crystals suitable for X-ray diffraction analysis were decanted from the mother liquor, washed with cold benzene, and dried in air. The yield of compound **III** was 0.11 g (62% based on the initial complex).

For $C_{80}H_{60}N_2O_{12}MgCo_2$ (ignoring solvate molecules)

anal. calcd., %:	C, 69.45;	H, 4.37;	N, 2.02.
Found, %:	C, 67.65;	H, 4.41;	N, 1.98.

IR (KBr, cm^{-1}): 3435 vw, 3053 m, 2966 w, 2924 w, 1633 s, 1614 vs, 1593 s, 1571 s, 1505 m, 1468 s, 1436 s, 1424 s, 1394 vs, 1380 vs, 1364 s, 1302 m, 1269 w, 1239 m, 1204 m, 1180 vw, 1150 w, 1137 w, 1104 w, 1024 w, 955 m, 921 m, 912 w, 868 m, 814 m, 793 vs, 765 s, 738 m, 639 m, 598 m, 545 w, 517 vw, 488 m, 474 m, 444 s.

Synthesis of $[(2,2'\text{-Bipy})_2(EtOH)_2Co_2Eu_2(Naph)_{10}] \cdot 4EtOH$ (IV). A suspension of $Co(NO_3)_2 \cdot 6H_2O$ (0.084 g, 0.29 mmol) in MeCN (30 mL) was added by 2,2'-Bipy (0.045 g, 0.29 mmol) with stirring. A solution of 2-naphthoic acid potassium salt, prepared by the addition of a solution of NaphH (0.100 g, 0.58 mmol) to KOH (0.033 g, 0.58 mmol), in a MeCN–EtOH (4 : 1) mixture (10 mL) was poured to the reaction mixture. The resulting mixture was stirred at 50°C for 15 min, and $Eu(NO_3)_3 \cdot 6H_2O$ (0.043 g, 0.10 mmol) was added. The reaction mixture was heated for 1 h, and a flaky pinkish precipitate was filtered off. The obtained solution was kept at room temperature for 4 days. The precipitated brown-pink crystals suitable for X-ray diffraction analysis were decanted from the solution, washed with cold MeCN, and dried in air. The yield of compound **IV** was 0.10 g (85% based on the initial amount of europium nitrate).

For $C_{126}H_{74}N_4O_{18}Co_2Eu_2$ (ignoring solvate molecules)

anal. calcd., %:	C, 64.30;	H, 3.17;	N, 2.38.
Found, %:	C, 64.60;	H, 3.29;	N, 2.61.

IR (KBr, cm^{-1}): 3680–3100 m (3523 m, 3337 m), 3105 w, 3056 m, 2963 vw, 1633 s, 1616 s, 1601 s, 1586 s, 1551 vs, 1504 s, 1490 s, 1475 s, 1435 s, 1404 vs,

Table 1. Crystallographic data and calculation parameters for the crystals structures of complexes **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
FW	1672.37	1471.10	1695.90	2537.94
Crystal system	Triclinic			
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	11.183(5)	10.760(10)	10.547(2)	15.4274(9)
b, Å	13.088(6)	13.390(12)	13.683(2)	15.5490(9)
c, Å	13.640(7)	13.543(12)	15.950(2)	15.7465(9)
α, deg	78.282(8)	69.688(14)	68.493(2)	72.7560(10)
β, deg	84.889(9)	89.47(2)	88.167(2)	68.4430(10)
γ, deg	86.298(9)	72.68(2)	79.649(2)	62.4580(10)
V, Å^3	1944.8(16)	1737(3)	2105.2(6)	3078.0(3)
Z	1	1	1	1
ρ_{calc}, g/cm^3	1.428	1.406	1.338	1.369
μ, mm^{-3}	0.703	0.548	0.468	1.339
Crystal size, mm	0.09 × 0.03 × 0.03	0.15 × 0.08 × 0.03	0.30 × 0.30 × 0.05	0.30 × 0.30 × 0.10
θ_{min}–θ_{max}, deg	2.29–25.50	2.18–25.50	1.70–25.99	1.41–26.94
F(000)	863	758	884	1286
T_{min}/T_{max}	0.597/0.745	0.572/0.746	0.872/0.977	0.690/ 0.878
R_{int}	0.0863	0.0749	0.0327	0.0310
Ranges of reflection indices	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-16 \leq l \leq 16$	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-19 \leq l \leq 19$	$-19 \leq h \leq 19$, $-19 \leq k \leq 19$, $-20 \leq l \leq 19$
Measured reflections	14705	13028	18664	29075
Independent reflections	7143	6349	8255	13298
Reflections with $I > 2\sigma(I)$	3153	3607	5806	10503
GOOF	0.928	0.967	1.108	1.008
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0815$ $wR_2 = 0.1831$	$R_1 = 0.0715$ $wR_2 = 0.1619$	$R_1 = 0.0681$ $wR_2 = 0.1928$	$R_1 = 0.0401$ $wR_2 = 0.1118$
R factors for all reflections	$R_1 = 0.1853$ $wR_2 = 0.2184$	$R_1 = 0.1361$ $wR_2 = 0.1855$	$R_1 = 0.0975$ $wR_2 = 0.2084$	$R_1 = 0.0534$ $wR_2 = 0.1184$
Residual electron density (min/max), e/Å^3	−0.442/0.662	−0.517/0.857	−0.503/0.786	−1.318/0.922

1384 vs, 1364 s, 1319 m, 1267 m, 1239 m, 1205 m, 1171 w, 1153 m, 1137 m, 1105 w, 1056 w, 1042 vw, 1024 w, 982 vw, 969 vw, 956 m, 949 m, 917 m, 896 m, 866 m, 831 w, 792 vs, 762 s, 735 m, 651 w, 637 m, 595 s, 558 m, 517 w, 487 m, 473 m, 429 m, 418 m.

X-ray diffraction analyses for single crystals of complexes **I–IV** were carried out on a Bruker Apex II diffractometer at 173(2) K (CCD detector, MoK_α, radiation, $\lambda = 0.71073$ Å, graphite monochromator) [31]. A semiempirical absorption correction was applied for compounds **I–IV** [32]. The structures were solved by direct methods and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of the organic ligands were generated geometrically and refined in the riding model. The calculations were performed using the SHELX-97 program package [33]. The crystallographic parameters and refinement details for structures **I–IV** are presented in Table 1. The bond lengths and bond angles are listed in Table 2.

The coordinates of atoms and other parameters for structures **I–IV** were deposited at the Cambridge Crystallographic Data Centre (CIF files CCDC 1401987–1401990; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

We assumed that the homometallic cobalt complexes with anions of 2-naphthoic acid would be con-

Table 2. Selected geometric characteristics of complexes **I–IV**

Distance	d, Å			
	I (M = Co)	**II** (M = Li)	**III** (M = Mg)	**IV** (M = Eu)
Co–O (μ_3-Naph)		2.054(3)		
Co–O (μ_2-Naph)	2.028(4)–2.085(4)	2.031(4)	1.944(2)–1.976(3)	2.011(3)–2.054(3)
Co–O (μ_2,η^2-Naph)	2.151(4)–2.165(5)	2.181(4), 2.219(4)		
M–O (μ_3-Naph)		1.943(9)		
M–O (μ_2-Naph)		1.869(10)	2.043(3)–2.076(3)	2.297(2)–2.395(3)
M–O (μ_2,η^2-Naph)		1.910(9)		
M–O (η^2-Naph)				2.484(3), 2.516(3)
Co–N	2.069(3), 2.130(3)	2.078(4), 2.129(4)	2.048(3)	2.081(3), 2.125(3)
Co···M, M···M	3.474(2)	3.020(9), 2.54(2)	3.6017(7)	3.9397(6), 4.8072(3)
C–O	1.242(7)–1.279(8)	1.247(6)–1.884(10)	1.239(4)–1.274(4)	1.244(4)–1.271(5)
Angle	ω, deg			
OCO	118.3(6), 126.9(7)	119.49(5)–124.9(4)	121.4(4)–125.7(3)	119.9(4)–124.4(4)

venient for the synthesis of heterometallic compounds by analogy to the earlier published procedures for the synthesis of similar complexes from transition metal trimethyl acetates. The known trinuclear complex $[(2,3\text{-Lut})_2Co_3(Naph)_6]$ [34] and the newly obtained complex **I** having the metal fragment $\{Co_3(Naph)_6\}$ of similar structure could be used as the initial compounds. Compound **I** was synthesized by the treatment of the earlier obtained complex $[(2,2'\text{-Bipy})_2Co_2(Piv)_4]$ with an excess of NaphH [35].

Finely crystalline products unsuitable for X-ray diffraction analysis were obtained by attempts to synthesize heterometallic naphthoate complexes using the interaction of the cobalt naphthoate complex with the corresponding N-donor ligand and lithium, magnesium, or lanthanide naphthoate. A low solubility of the formed cobalt(II) naphthoate complexes in polar and nonpolar organic solvents ($<10^{-3}$ mol/L) is a drawback impeding the further quantitative reactions. Therefore, other methods for the synthesis of heterometallic naphthoate complexes were found for the preparation of the target heterometallic compounds with Naph anions and provided the formation of crystals suitable for X-ray diffraction analysis.

The heterometallic lithium–cobalt complex **II** was isolated in the reaction of $Co(NO_3)_2 \cdot 6H_2O$ with 2,2'-Bipy followed by the addition of a solution of 2-naphthoic acid potassium salt (Co : 2,2'-Bipy : Naph = 1 : 1 : 2) and the addition of a twofold excess of 2-naphthoic acid lithium salt (Co : Li = 1 : 2) to the obtained reaction mixture. The reaction was carried out in MeCN on heating. At the stages of the addition of the potassium and lithium salts, the reaction mixture was stirred for 15–30 min on heating to remove potassium nitrate formed and a lithium salt excess. The crystals of complex **II** were obtained by the storage of the mother liquor at room temperature for 3 days. Although the solubility of the obtained crystals is very low like that of the most part of other naphthoate complexes, fairly stable solutions of intermediate compounds are formed by the procedure described above and give the final products in the form of large crystals.

We synthesized the cobalt–magnesium complex **III** from the known compound $[(2,4\text{-Lut})_2Co_2Mg(Piv)_6]$ [28] by the action of NaphH in a THF–benzene (3 : 1) mixture at room temperature. The crystals of complex **III** were obtained by keeping the mother liquor at 5°C for 2 days. As in the previous synthesis, solutions of intermediate compounds or stable oversaturated solutions are formed first. This makes it possible to obtain reaction products as large crystals suitable for X-ray diffraction analysis.

The cobalt–europium complex **IV** was synthesized similarly to complex **II**, but $Eu(NO_3)_3 \cdot 6H_2O$ (Co : Eu = 3 : 1) was added instead of 2-naphthoic acid lithium salt after the addition of the stoichiometric amount of potassium naphthoate to a solution of cobalt nitrate. An insufficient amount of the europium(III) salt is related to the fact that a portion of cobalt is consumed to the binding of nitrate anions. This results in the formation of the target product **IV** and cobalt nitrate, which has a higher solubility in MeCN and remains in the solution. The crystals of complex **IV** were obtained by the storage of the mother liquor at room temperature for 4 days. As in the synthesis of the Li(I)–Co(II) and Mg(II)–Co(II) complexes (**II** and **III**), the use of cobalt nitrate as the initial compound made it possible to obtain solutions of

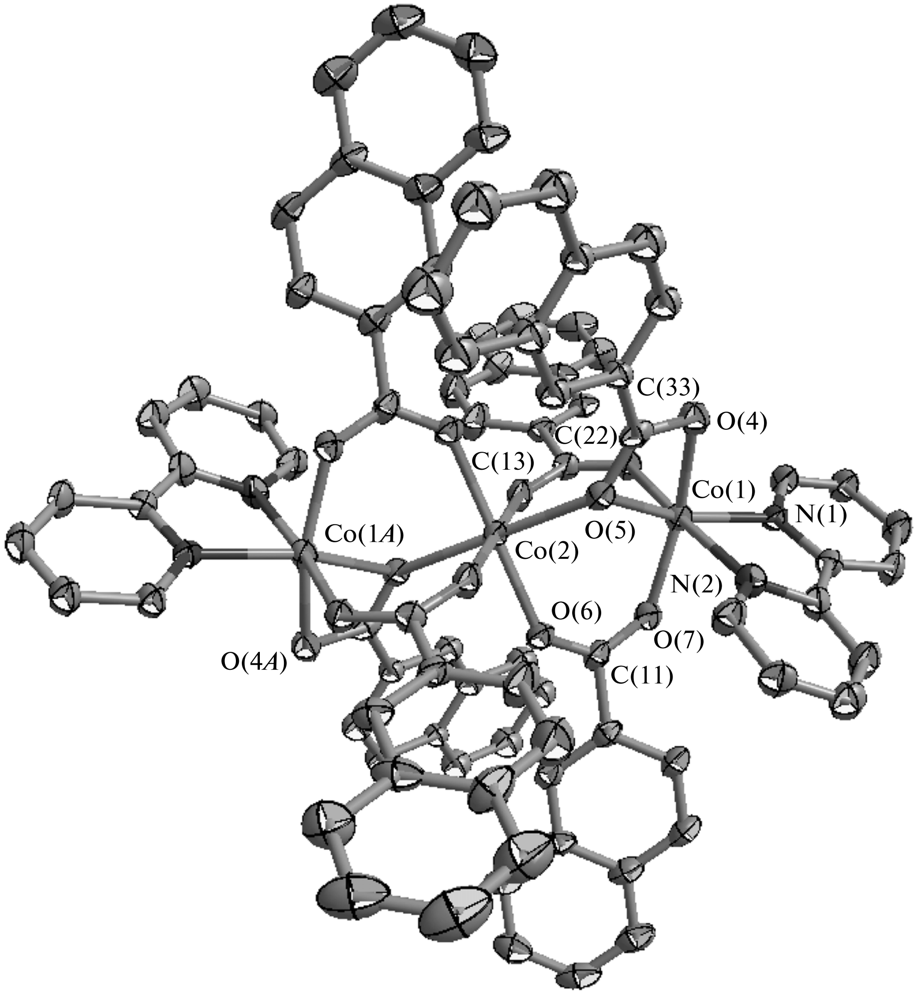

Fig. 1. Molecular structure of complex **I** (hydrogen atoms are omitted, thermal ellipsoids of 30% probability).

intermediate products and prevent the formation of finely crystalline precipitates.

In the trinuclear compound **I**, the central Co(1) atom is localized at the inversion center (Fig. 1). The Co(1) atom is octahedrally coordinated by six oxygen atoms of four bridging and two chelate-bridging anions of the acid (Table 2) by which the Co(1) atom is bound to the Co(2) and Co(2*A*) atoms. The Co(2) atom coordinates four O atoms of the carboxylate groups and builds its environment to the octahedral one by two N atoms of the 2,2'-Bipy chelate molecule. An analysis of the packing shows that the naphthoate fragments of the adjacent molecules are overlapped due to stacking interactions to form 1D supramolecular chains. The dihedral angles between the planes of the naphthoate fragments is 0.74°, and the distance between them is 3.38–3.42 Å.

The molecular structure of complex **I** differs from that of the earlier described trinuclear complex [(2,3-Lut)$_2$Co$_3$(Naph)$_6$] [34] by the fact that the coordination number of the peripheral cobalt atoms increases from 4 to 6 due to the chelate binding of 2,2'-Bipy and the transition of the bridging coordination mode of one of the naphthoate anions to the chelate-bridging mode.

In complex **II**, the inversion center lies between the central Li(1) and Li(1*A*) atoms (Table 2, Fig. 2). The Co(1) and Li(1) atoms are linked by three carboxylate groups: bridging, chelate-bridging, and tridentate-bridging. These two μ_3 groups bind the binuclear fragments {LiCo(Naph)$_3$} into a tetranuclear molecule due to the coordination of the carboxyl O atom by both Li(1) and Li(1*A*) atoms. The coordination environment of Li(1) is close to the tetrahedral one, and the Li–O distances are typical of similar coordination compounds earlier obtained by us [17–20].

The mutual arrangement of the metal atoms and the coordination mode of the bridging carboxylate groups and 2,2'-Bipy molecules are similar to those of the previously described cobalt and nickel complexes

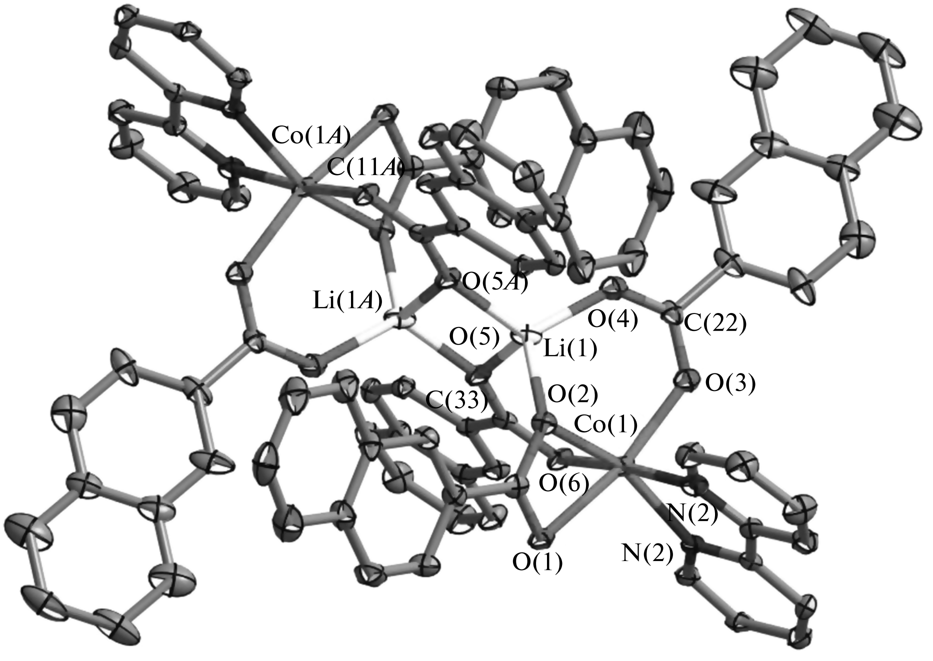

Fig. 2. Molecular structure of complex **II** (hydrogen atoms are omitted, thermal ellipsoids of 30% probability).

with trimethylacetic acid anions and various mono- and bidentate ligands [17, 19]. In the absence of N-donor ligands, Li–3*d* heterometallic coordination polymers can be formed: $[Li_2Zn(Crot)_4]_n$ (Crot is 2-butenoic acid anion) [36], $[Li_2Cu(Piv)_4]_n$, $[(HPiv)_2Li_7Co_2(Piv)_{11}]_n$, and $[Li_{13}Co_2(Piv)_{17}]_n$ [37].

Complex **III** is a structural analog of the homometallic trinuclear complex $[(2,3\text{-Lut})_2Co_3(Naph)_6]$ obtained by us earlier [34]. The central Mg(1) atom (at the inversion center) is symmetrically bound to two cobalt atoms by six carboxylate groups (Fig. 3, Table 2). The Co(1) atom builds the coordination environment to the tetrahedral one by the coordination of the N atom of the 2,4-Lut molecule.

Thus, the metall core of compound **III** remains unchanged due to the substitution of the Piv anions by Naph. The obtained compound is an analog of the known heterometallic complex $(\text{v-Py})_2Co_2Mg(Crot)_6$ (v-Py is 4-vinylpyridine) [38] and similar compounds [39, 40].

In tetrahedral complex **IV**, the inversion center lies between the central Eu(1) and Eu(1*A*) atoms. Two binuclear fragments $\{(2,2'\text{-Bipy})CoEu(Naph)_4(EtOH)\}$ are linked by the μ anions of 2-naphthoic acid (Table 2, Fig. 4). The metal atoms in $\{(2,2'\text{-Bipy})CoEu(Naph)_4(EtOH)\}$ are bound by three μ-bridging carboxylate groups. The Co(1) atom builds its environment to a square pyramid ($\tau = 0.25$ [41]) by the coordination of two N atoms of the chelate 2,2'-Bipy molecule. The environment of the Eu(1) atom is built to a coordination number of 8 (one-capped pentagonal bipyramid) by the coordination of three O atoms of the chelate carboxy group and EtOH molecule. The metall core is strengthened by two hydrogen bonds between the hydrogen atom of the EtOH molecule and the oxygen atom of the chelate carboxylate group (O(11)···O(8*A*) 2.75 Å, H···O(8*A*) 1.81 Å, angle O(11)–H–O(8*A*) 168.5°).

There are analogs of the described $\{M_2Ln_2\}$ compound among the 3*d*–4*f* heterometallic carboxylate complexes. The known binuclear compounds {MLn} should be mentioned as evident precursors of the tetranuclear complexes, since the neutral donor ligands coordinated by the 4*f* metal atoms (for example, water or pyridine molecules) block the coordination environment of the metal atom thus preventing the bridging function of the carboxylate group. The trinuclear carboxylate compounds $\{M_2Ln\}$ are also known. These data show that bi- and trinuclear complexes can be formed with anions of trimethylacetic acid, depending on the radius of the 4*f* metal ion. For example, binuclear compounds $[(Py)_3ZnLn(Piv)_5]$ are observed for heavy atoms of the yttrium subgroup (Tb, Dy, Er, Yb), whereas trinuclear compounds $[(Py)_2Zn_2Ln(Piv)_7]$ are formed for metal atoms of the cerium group (Pr, Nd, Sm), whose ion radius is somewhat longer. The replacement of the bulky *tert*-butyl group by “planar groups” containing unsaturated bonds (methacrylic acid, aromatic benzoic acid and its derivatives) makes it possible to obtain bi-, tri-, and tetranuclear heterometallic complexes in which the lanthanide radius is not determining for the nuclearity of the compound. For example, both tri- and tetranuclear benzoate complexes Dy(III)–Co(II) can be syn-

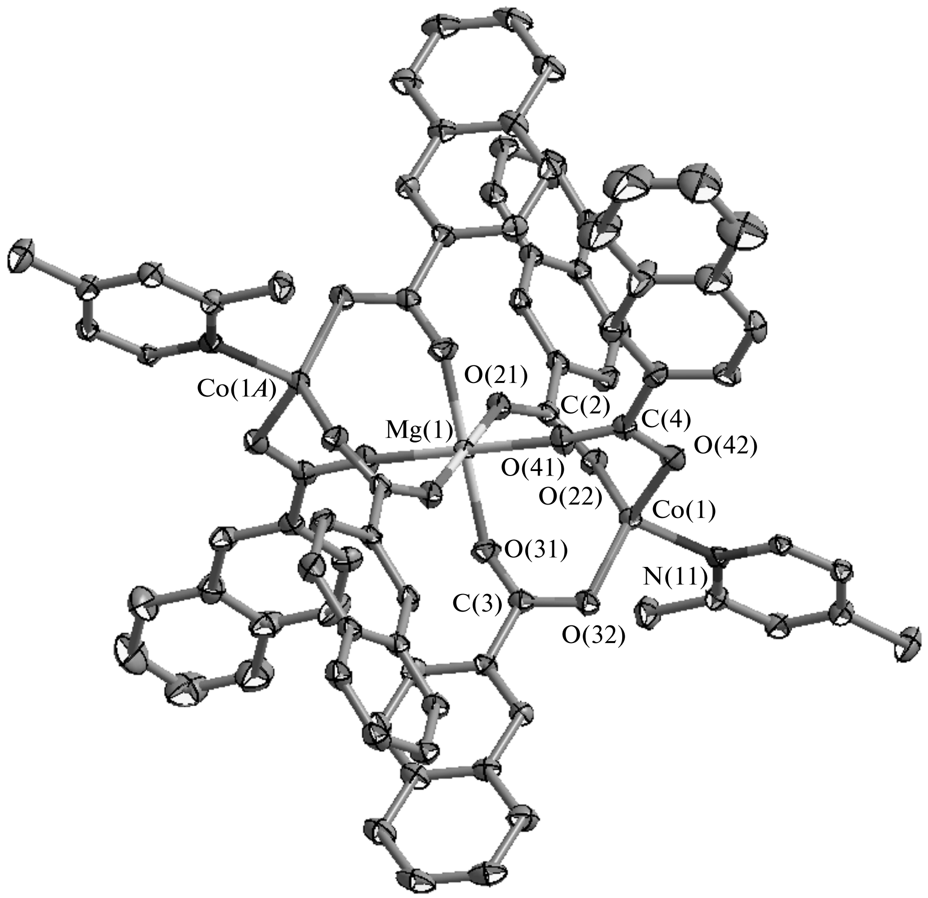

Fig. 3. Molecular structure of complex **III** (hydrogen atoms are omitted, thermal ellipsoids of 30% probability).

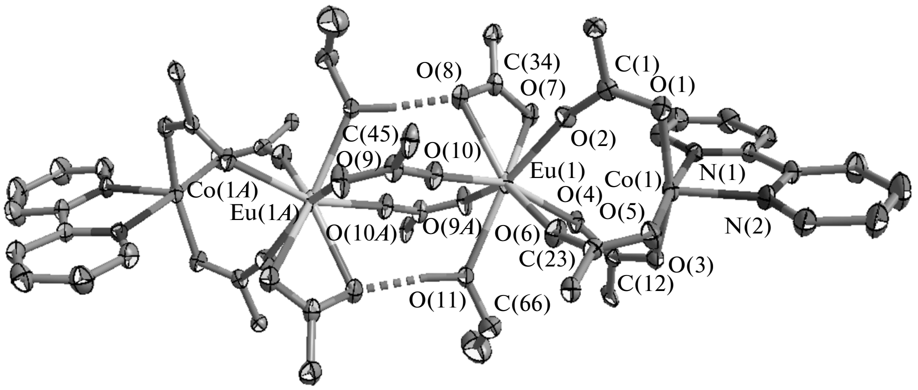

Fig. 4. Molecular structure of complex **IV** (naphthyl substituents of 2-naphthoic acid anions and hydrogen atoms are omitted, thermal ellipsoids of 30% probability).

thesized: [(1,10-Phen)$_2$Co$_2$Dy(O$_2$CPh)$_7$] and [(1,10-Phen)$_2$Co$_2$Dy$_2$(O$_2$CPh)$_{10}$] [42]. A general tendency should also be mentioned: binuclear compounds are formed at the ratio M : Ln = 1 : 1, trinuclear complexes {M$_2$Ln} are formed in a deficient of the lanthanide salt (M : Ln = 2 : 1), and tetranuclear complexes {M$_2$Ln$_2$} are formed either for the ratio M : Ln = 1 : 1, or with a 1.5–2-fold increase in the amount of the lanthanide salt (Table 3). The exception is the case described in this work, which can be explained by a poor solubility of the formed product and crystalline

Table 3. Known bi-, tri-, and tetranuclear M–Ln heterometallic complexes and some conditions of their isolation

Complex	Reaction mixture (hydrate composition of metal salts is omitted)	Ratio of metals M : Ln in reaction	Literature
{MLn}			
[(2,2'-Bipy)MLn(Piv)$_5$(H$_2$O)] (M = Co, Ni, Ln = Sm, Gd)	[(2,2'-Bipy)$_2$M$_2$(Piv)$_4$], [Ln$_2$(Piv)$_6$(HPiv)$_7$] molar ratio = 1 : 1	1 : 1	43
[(2.2'-Bipy)CuLn(Piv)$_5$(HPiv)] (Ln = Sm, Gd)	[Cu$_2$(Piv)$_4$(HPiv)$_2$], [Ln$_2$(Piv)$_6$(HPiv)$_7$], 2,2'-Bipy (1 : 1 : 2)	1 : 1	43
[(Py)$_3$ZnLn(Piv)$_5$] (Ln = Tb, Dy, Er, Y, Yb)	Ln[N(Si(CH$_3$)$_3$)$_2$]$_3$, ZnEt$_2$, HPiv (1 : 1 : 5, Py excess)	1 : 1	44
[(1,10-Phen)(H$_2$O)CoDy(*m*-CH$_3$-PhCO$_2$)$_7$]	DyCl$_3$, CoCl$_2$, *m*-CH$_3$-PhCO$_2$H, 1,10-Phen and Na$_2$CO$_3$ (1 : 1 : 5 : 1 : 2.5)	1 : 1	42
[(2,2'-Bipy)(H$_2$O)CoDy(*m*-CH$_3$-PhCO$_2$)$_5$]	DyCl$_3$, CoCl$_2$, *m*-CH$_3$-PhCO$_2$H, 2,2'-Bipy and Na$_2$CO$_3$ (1 : 1 : 5 : 1 : 2.5)	1 : 1	42
{M$_2$Ln}			
[(2,4-Lut)$_2$Co$_2$Sm(Piv)$_7$]	[(2,4-Lut)$_2$Co$_2$(Piv)$_4$], [Ln$_2$(Piv)$_6$(HPiv)$_7$] (2 : 1)	2 : 1	20
[(Py)$_2$Zn$_2$Ln(Piv)$_7$] (Ln = Pr, Nd, Sm)	Ln[N(Si(CH$_3$)$_3$)$_2$]$_3$, ZnEt$_2$, HPiv (1 : 2 : 7, Py excess)	2 : 1	44
[(1,10-Phen)$_2$Co$_2$Dy(O$_2$CPh)$_7$]	DyCl$_3$, CoCl$_2$, PhCO$_2$H, 1,10-Phen, Na$_2$CO$_3$ (1 : 2 : 7 : 2 : 3.5)	2 : 1	42
[(1,10-Phen)$_2$Co$_2$Dy(*m*-NO$_2$-PhCOO)$_7$]	DyCl$_3$, CoCl$_2$, *m*-NO$_2$-PhCOOH, 1,10-Phen, Na$_2$CO$_3$ (1 : 2 : 7 : 2 : 3.5)	2 : 1	42
{M$_2$Ln$_2$}			
[(1,10-Phen)$_2$(H$_2$O)$_2$Cu$_2$Tb$_2$L$_{10}$]	TbL$_3$ (HL = methacrylic acid), Cu(NO$_3$)$_2$, 1,10-Phen (2 : 1 : 1)	1 : 2	45
[(1,10-Phen)$_2$(EtOH)$_2$Cu$_2$La$_2$L$_{10}$]	LaL$_3$ (HL = methacrylic acid), Cu(NO$_3$)$_2$, 1,10-Phen (2 : 1 : 1)	1 : 2	46
[(1,10-Phen)$_2$(H$_2$O)$_2$Co$_2$Ln$_2$L$_{10}$] (Ln = La, Sm, Nd, Gd)	LnL$_3$ (HL = methacrylic acid), Co(NO$_3$)$_2$, 1,10-Phen (4 : 3 : 3)	3 : 4	47
[(1,10-Phen)$_2$(EtOH)$_2$Co$_2$Ce$_2$L$_{10}$]	CeL$_3$ (HL = methacrylic acid), Co(NO$_3$)$_2$, 1,10-Phen (5 : 3 : 3)	3 : 5	48
[(1,10-Phen)$_2$(EtOH)$_2$Cu$_2$Nd$_2$L$_{10}$]	NdL$_3$ (HL = methacrylic acid), Cu(NO$_3$)$_2$, 1,10-Phen (2 : 1 : 1)	1 : 2	49

Table 3. (Contd.)

Complex	Reaction mixture (hydrate composition of metal salts is omitted)	Ratio of metals M : Ln in reaction	Literature
$[(Py)_2(H_2O)_2Zn_2Ce_2L_{10}]$	CeL_3 (HL = methacrylic acid), $Zn(NO_3)_2$ (2 : 1, Py excess)	1 : 2	50
$[(1,10\text{-Phen})_2Zn_2Tb_2(O_2CPh)_{10}]$	ZnO, $TbCl_3$, $PhCO_2H$, 1,10-Phen (2 : 1 : 7 : 1)	1 : 2	51
$[(1,10\text{-Phen})_2Co_2Dy_2(O_2CPh)_{10}]$	$DyCl_3$, $CoCl_2$, $PhCO_2H$, 1,10-Phen, Na_2CO_3 (1 : 1 : 5 : 1 : 2.5)	1 : 1	42
$[(1,10\text{-Phen})_2Zn_2Tb_2L_{10}]$	ZnO, $TbCl_3$, 2-thiophenecarboxylic acid, 1,10-Phen (2 : 1 : 7 : 1)	1 : 2	51
$[(2,2'\text{-Bipy})_2Co_2Dy_2(3\text{-Nitrobenzoato})_{10}]$	$DyCl_3$, $CoCl_2$, *m*-NO_2-$PhCO_2H$, 2,2'-Bipy, Na_2CO_3 (1 : 1 : 5 : 1 : 2.5)	1 : 1	42
$[(1,10\text{-Phen})_2Co_2Dy_2(3\text{-Nitrobenzoato})_{10}]$	$DyCl_3$, $CoCl_2$, *m*-NO_2-$PhCO_2H$, 1,10-Phen, Na_2CO_3 (1 : 1 : 5 : 1 : 2.5)	1 : 1	42
$[(1,10\text{-Phen})_2Zn_2Ln_2L_{10}]$ (Ln = Nd, Tb, Ho)	$Zn(Ac)_2$, $Ln(NO_3)_3$, {NaOH-HL}, HL = 4-methylbenzoic acid, 1,10-Phen (1 : 1 : 1 : 1) in the presence of Na_2CO_3	1 : 1	14
$[(2,2'\text{-Bipy})_2Co_2Dy_2L_{10}]$	$Co(NO_3)_2$, $Dy(NO_3)_3$, HL = 3,5-dichlorobenzoic acid, 2,2'-Bipy (3 : 2 : 20 : 3) in the presence of Na_2CO_3	2 : 3	52
$[(2,2'\text{-Bipy})_2Ni_2Ln_2L_{10}]$ (Ln = La, Gd, Tb, Dy, Ho)	$Ni(NO_3)_2$, $Ln(NO_3)_3$, HL = 3,5-dichlorobenzoic acid, 2,2'-Bipy (3 : 2 : 20 : 3)	2 : 3	52
$[(2,2'\text{-Bipy})_2M_2Dy_2L_{10}]$ (M = Cu, Mn)	MCl_2, Dy_2O_3, HL = 3,5-*bis*(trifluoromethyl)benzoic acid , 2,2'-Bipy (2 : 1 : 10 : 2)	1 : 2	53
$[(2,2'\text{-Bipy})_2(EtOH)_2Co_2Eu_2(Naph)_{10}]$	$Co(NO_3)_2$, $Eu(NO_3)_3$, KNaph, 2,2'-Bipy (3 : 1 : 6 : 1)	3 : 1	This work

packing effects determining the more energetically favorable structure of the formed complex.

Thus, it is shown that the insertion of the heterometal into the cobalt(II) 2-naphthoate complexes is accompanied by the formation of linear structures based on two peripheral Co atoms and the central atom(s) of another nature. The number of heterometal atoms is determined by the size and coordination number of the ion. The radius of the magnesium(II) ion (0.72 Å) is equal to the ion radius of cobalt(II) (0.72 Å), due to which isomorphic substitution occurs with the retention of the trinuclear metal core of the molecule. A decrease or an increase in the ion radius and a change in the electronic characteristics, including the coordination number, for example of the lithium(I) (0.68 Å, coordination number 4) and europium(III) (0.95 Å, coordination number 8 or 9) ions, result in the rearrangement of the metal core of the initial compounds to form tetranuclear complexes. An analysis of the obtained and known data on the synthesis and structures of the transition metal and lanthanide complexes shows that the nuclearity of the complexes is determined by the coordination number and radius of the lanthanide atom, the presence of neutral ligands blocking the dimerization of the binuclear fragments $\{(L)MLn(O_2CR)_5\}$, and/or the nature of the substituent at the carboxylate group.

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