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Structural Influence of the Substituent in Carboxylate Anion on Example of α- and β-Naphthoate Complexes of Co(II), Ni(II), Cu(II), and Zn(II)

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Abstract—The results on the synthesis and study of the crystal structures of molecular complexes of transition metals with anions of α- and β-naphthoic acids and monodentate N-donor ligands (MeCN, 2,3-lutidine) are presented. The compositions and structures of the isolated complexes are determined by the following factors: steric hindrances, intermolecular interactions of the aromatic fragments, and the electronic structure of the metal center.

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INTRODUCTION

Carboxylate complexes of 3*d* metals of the end 4 Period (Mn(II), Fe(II), Co(II), Ni(II), and Cu(II)) containing four bridging carboxylate ligands and two apical (usually N-donor) ligands, LM(μ-OOCR)$_4$ML, are convenient models for the description of the magnetic properties of binuclear systems depending on the spin state of the metal centers [1–4]. Similar compounds (including Zn(II) complexes) are also considered as “secondary building blocks” in the formation of 2D and 3D coordination polymers with anions of polycarboxylic acids [5, 6]. There were attempts to explain reasons for which these structures are formed only under certain conditions. As assumed previously [7, 8] for binuclear trimethyl acetates (pivalates) with the mentioned metal atoms, one of the determining factors for the formation of the binuclear tetrabridged structure is the controlling influence of the short contacts $O(\mu\text{-}O_2CMe_3)\cdots(\alpha\text{-RPy})$ initiating the formation of such dimers. However, in the case of cobalt(II) benzoates, a linear trinuclear structure is formed in complex $Co_3(C_9H_7N)_2(O_2CPh)_6$ (C_9H_7N is quinoline). This structure is formed in a deficient of the N donor acting as an apical ligand [9, 10]. On the one hand, it is shown [11] that the binuclear $[Co_2(NEt_3)_2(Piv)_4]$ or trinuclear $[Co_3(NEt_3)_2(Piv)_6]$ complexes can be obtained depending on the synthesis conditions of the reaction of cobalt(II) pivalate with triethylamine. On the other hand, only binuclear complex $[Ni_2(NEt_3)_2(Piv)_4]$ is formed in the reaction of nickel(II) pivalate with triethylamine under any conditions [12]. In similar binuclear compounds, the coordination polyhedron of the metal atom is close to a square pyramid, where four O atoms of the carboxylate groups lie in the base and the fifth donor atom of the ligand occupies the apical vertex. In the trinuclear molecules, the central metal atom (M) exists, as a rule, in a weakly distorted octahedral coordination of six O atoms of the carboxylate groups, whereas the peripheral O atoms are in the distorted formally tetrahedral or trigonal pyramidal environment of three O atoms of the carboxylate groups and the fourth donor atom.

However, numerous examples of the known various binuclear μ_4-bridged copper carboxylates, where acetonitrile, water, and other compact ligands can serve as apical ligands, should be mentioned [13–17]. Similar structures are also formed for cobalt and nickel [18–20]. Probably, the role of steric effects in the formation of binuclear μ_4-bridged molecules with 3*d* metal atoms of the middle and end of 4 Period containing bulky apical ligands of the type of triethylamine or α-substituted pyridines is more important for carboxylate with bulky electron-donating substituents, for example, the *tert*-butyl radical in pivalate anions. At the same time, for other carboxylate anions containing less bulky substituents, the electronic factors begin to play a prevailing role in the formation of molecules. For example, trinuclear nickel(II) carboxylate $(F_3CCO_2H)_6Ni_3(O_2CCF_3)_6$ is known for trifluoroacetates with the CF_3 acceptor group [21]. A similar compound, $(F_3CCO_2H)_6Co_3(O_2CCF_3)_6$, was isolated for cobalt(II) [22]. However, both peripheral metal atoms and the central metal atom are in the octahedral environment in these compounds.

Problems of an interrelation between the ligand nature and the physical properties of the complexes become urgent due to an increasing significance of the carboxylate systems in processes of modeling bioactive molecules, catalysis, and other promising fields of molecular materials science. Aromatic anions of carboxylic acids and neutral N-donor ligands play a special role, since the introduction of them often results in the formation of a complicated supramolecular architecture in the solid phase due to so-called stacking interactions between π systems of aromatic fragments [see, e.g., 23–26]. For example, the use of α- and β-naphthoate anions in which the carboxy group is linked with different carbon atoms of the naphthyl substituent allowed us to find some effects initiating the formation of binuclear or linear trinuclear structures.

The results on the synthesis and study of the crystal structures of the molecular complexes of transition metals with the anions of α- and β-naphthoic acids are presented in this work. These compounds are also interesting, because their crystal structures are substantially determined by intermolecular π–π interactions of the aromatic fragments.

EXPERIMENTAL

All procedures related to the synthesis of new complexes were carried out in air using commercial solvents and reagents ($ZnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, KOH, α-naphthoic acid, β-naphthoic acid, and 2,3-lutidine (2,3-Lut)). The initial copper complexes, $[Cu_2(Piv)_4(HPiv)_2]$ and $[Cu_2(Piv)_4(2,3\text{-Lut})_2]$, were synthesized according to known procedures [27]. Compound $[Co_2(Piv)_4(2,3\text{-Lut})_2]$ was synthesized similarly to $[Cu_2(Piv)_4(2,3\text{-Lut})_2]$ by the reaction of $[Co(Piv)_2]_n$ (obtained by a described procedure [28]) with 2,3-Lut (1 : 1) in MeCN.

IR spectra were recorded in the range 400–4000 cm^{-1} on Specord M-80 and PerkinElmer Spectrum 65 spectrophotometer in KBr pellets. Elemental analyses were carried out on a C,H,N analyzer (Carlo Erba).

Synthesis of $[Cu_2(\beta\text{-Naph})_4(MeCN)_2] \cdot MeCN$ (I). β-Naphthoic acid (0.140 g, 0.814 mmol) was added to a solution of $[Cu_2(Piv)_4(HPiv)_2]$ (0.1 g, 0.136 mmol) in MeCN (30 mL). The obtained reaction mixture was stirred at 50°C for 30 min and then kept at room temperature for 3 days. Precipitated blue-green 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 **I** was 0.10 g (80% based on the initial amount of $[Cu_2(Piv)_4(HPiv)_2]$).

For $C_{48}H_{34}N_2O_8Cu_2$ (ignoring solvate molecules)

anal. calcd., %:	C, 65.15;	H, 3.85;	N, 3.17.
Found, %:	C, 65.08;	H, 3.82;	N, 3.10.

IR (KBr), ν, cm^{-1}: 3700–3250 w, 3058 w, 1688 m, 1632 m, 1606 s, 1570 m, 1504 m, 1466 m, 1436 m, 1403 vs, 1366 m, 1269 vw, 1240 m, 1205 m, 1152 w, 1139 w, 1106 vw, 1019 vw, 956 w, 917 w, 867 w, 836 w, 787 vs, 763 m, 735 m, 643 m, 606 m, 472 m, 410 vw.

Synthesis of $[Cu_2(\beta\text{-Naph})_4(2,3\text{-Lut})_2] \cdot MeCN$ (II). An excess of 2,3-Lut (1 mL) was added to a solution of $[Cu_2(Piv)_4(HPiv)_2]$ (0.1 g, 0.136 mmol) in MeCN (30 mL). The obtained reaction mixture was stirred at 75°C for 30 min, then β-naphthoic acid (0.140 g, 0.816 mmol) was added, and the mixture was stirred for 30 min more. Precipitated blue 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 0.12 g (84% based on the initial amount of $[Cu_2(Piv)_4(HPiv)_2]$).

For $C_{58}H_{46}N_2O_8Cu_2$

anal. calcd., %:	C, 68.50;	H, 4.53;	N, 2.76.
Found, %:	C, 68.31;	H, 4.75;	N, 2.28.

IR (KBr), ν, cm^{-1}: 3059 w, 2946 vw, 2922 vw, 1937 vw, 1825 vw, 1705 vw, 1639 vs, 1620 vs, 1572 s, 1505 m, 1467 s, 1451 m, 1435 s, 1403 vs, 1385 vs, 1368 s, 1355 s, 1281 m, 1269 m, 1240 m, 1204 m, 1187 m, 1145 m, 1136 m, 1105 w, 1078 vw, 1022 w, 999 vw, 970 vw, 956 m, 915 m, 894 vw, 868 m, 831 m, 787 vs, 763 s, 741 m, 724 m, 641 s, 604 s, 517 vw, 491 m, 475 m, 447 s, 405 m.

Synthesis of $[Co_3(\beta\text{-Naph})_6(2,3\text{-Lut})_2] \cdot 3MeCN$ (III). 2,3-Lut (0.04 mL, 0.39 mmol) and a solution of β-naphthoic acid (0.26 g, 1.535 mmol) in acetonitrile (30 mL) were added to a solution of $[Co(Piv)_2]_n$ (0.1 g, 0.39 mmol) in THF (30 mL). The reaction mixture was vigorously stirred at 50°C for 1 h until the initial reactants were dissolved completely. The obtained solution was cooled to room temperature and kept for 2 days. Precipitated violet 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 **III** was 0.14 g (68% based on $Co(Piv)_2$).

For $C_{80}H_{60}N_2O_{12}Co_3$ (ignoring solvate molecules)

anal. calcd., %:	C, 68.47;	H, 4.28;	N, 2.00.
Found, %:	C, 68.09;	H, 4.25;	N, 2.07.

IR (KBr), ν, cm^{-1}: 3602 w, 3436 vw, 3058 w, 2964 vw, 2926 vw, 1688 m, 1633 m, 1603 vs, 1593 vs, 1569 vs, 1505 m, 1469 s, 1435 s, 1395 vs, 1380 vs, 1356 s, 1280 w, 1267 w, 1239 m, 1205 m, 1191 w, 1152 w, 1135 m, 1103 w, 1018 w, 955 w, 918 w, 867 m, 826 w, 789 vs, 764 s, 740 m, 721 m, 638 w, 598 m, 522 vw, 488 m, 474 m, 442 m, 413 w.

Synthesis of $[Zn_2(\alpha\text{-Naph})_4(2,3\text{-Lut})_2]$ (IV). 2,3-Lut (0.025 mL, 0.29 mmol) was added to a suspension of anhydrous $ZnCl_2$ (0.04 g, 0.29 mmol) in MeCN

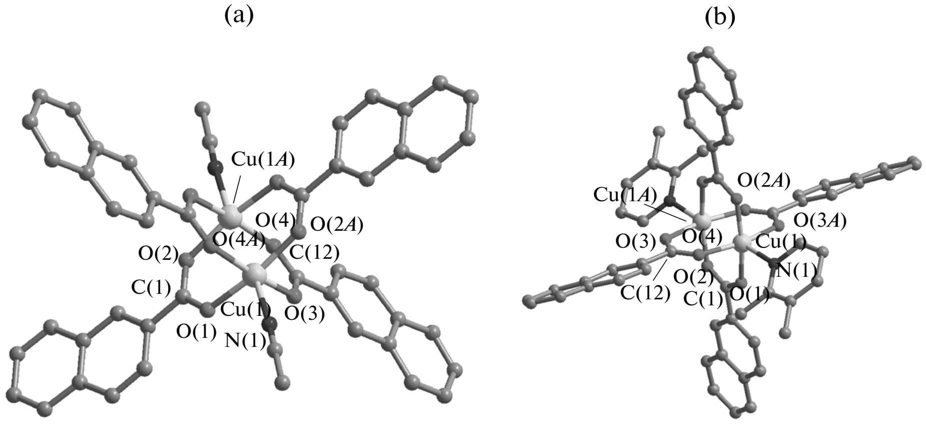

Fig. 1. Molecular structures of complexes (a) **I** and (b) **II**.

(20 mL) and C_6H_6 (10 mL) with stirring. A solution of α-naphthoic acid potassium salt (obtained by the addition of a solution of α-naphthoic acid (0.100 g, 0.58 mmol) to KOH (0.033 g, 0.58 mmol)) in MeCN was poured to the reaction mixture. The obtained reaction mixture was stirred at 75°C for 1 h, a flaky precipitate of potassium chloride was filtered off, and the solution was kept at room temperature for 3 days. Precipitated colorless 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 **IV** was 0.17 g (55% based on $ZnCl_2$).

For $C_{58}H_{46}N_2O_8Zn_2$

anal. calcd., %:	C, 68.24;	H, 4.51;	N, 2.75.
Found, %:	C, 68.13;	H, 4.33;	N, 2.65.

IR (KBr), ν, cm^{-1}: 3530–2890 m, 3088 m, 3048 m, 1948 w, 1716 w, 1700 w, 1668 m, 1624 s, 604 vs, 1580 vs, 1572 vs, 1564 vs, 1532 s, 1508 s, 1460 s, 1456 s, 1404 vs, 1376 vs, 1364 vs, 1340 s, 1256 s, 1216 m, 1196 m, 1164 m, 1136 m, 1072 m, 1028 m, 1008 s, 908 m, 872 s, 820 m, 788 vs, 756 s, 732 m, 720 s, 656 vs, 592 m, 536 m, 508 s, 492 m, 440 s, 396 m, 312 w.

Synthesis of $[Ni_2(2,3\text{-Lut})_2(\alpha\text{-Naph})_4]$ (V). The complex was isolated according to a procedure similar to the synthesis of complex **IV**, and the corresponding amount of $NiCl_2 \cdot 6H_2O$ was used instead of $ZnCl_2$. The yield of compound **V** was 68%.

For $C_{58}H_{46}Ni_2O_8N_2$

anal. calcd., %:	C, 68.54;	H, 4.56;	N, 2.76.
Found, %:	C, 68.20;	H, 4.30;	N, 2.68.

IR (KBr), ν, cm^{-1}: 3435 s, 3047 m, 1629 m, 1611 s, 1585 m, 1574 vw, 1508 vs, 1462 w, 1421 w, 1403 w, 1377 s, 1357 vw, 1344 w, 1268 vw, 1257 m, 1217 m, 1194 w, 1154 w, 1135 m, 1075 w, 1029 m, 1009 w, 873 m, 821 w, 789 vs, 773 m, 753 m, 731 m, 722 m, 658 vs, 604 vw, 538 m, 514 s, 462 vw, 450 vw.

The X-ray diffraction analyses for single crystals of complexes **I–V** were carried out on a Bruker Apex II diffractometer (CCD detector, MoK_α radiation, λ = 0.71073 Å, graphite monochromator) [29]. A semiempirical absorption correction was applied for compounds **II–V** [30]. 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 [31]. The crystallographic parameters and refinement details for structures **I–V** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The coordinates of atoms and other parameters for structures **I–V** were deposited with the Cambridge Crystallographic Data Centre (CCDC 1030529–1030533); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Binuclear copper(II) complexes **I** and **II** were synthesized by the substitution of the Piv^- anions in complexes $[Cu_2(Piv)_4(HPiv)_2]$ and $[Cu_2(Piv)_4(2,3\text{-Lut})_2]$ for anions of β-naphthoic acid (β-NaphH). The use of the pivalate complexes as the initial ones substantially facilitates the synthetic procedures, because no insoluble precipitates of inorganic salts are formed in the course of the crystallization of pure reaction products.

In both compounds **I** and **II**, the double axis passes between two copper atoms symmetrically linked by four carboxylate groups (selected bond lengths and bond angles are given in Table 2). The bridging naphthoate anions in compound **I** are nearly planar (Table 2, Fig. 1). The lutidine fragments in complex **II**

Table 1. Crystallographic data and calculation parameters for crystal structures **I**–**V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
Empirical formula	$C_{50}H_{37}Cu_2N_3O_8$	$C_{58}H_{46}Cu_2N_2O_8$	$C_{86}H_{69}Co_3N_5O_{12}$	$C_{58}H_{46}N_2O_8Zn_2$	$C_{58}H_{46}N_2Ni_2O_8$
FW	934.91	1026.05	1541.25	1029.71	1016.38
T, K	173(2)	173(2)	120(2)	296(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	27.863(2)	32.331(3)	10.745(3)	11.017(2)	10.8303(8)
b, Å	10.1222(9)	8.9721(9)	10.908(3)	11.179(2)	11.0864(8)
c, Å	16.5359(14)	22.126(2)	15.374(5)	11.554(2)	11.4945(9)
α, deg	90	90	89.329(5)	66.735(2)	66.3040(10)
β, deg	106.7670(10)	129.7520(10)	89.411(4)	77.290(2)	77.0690(10)
γ, deg	90	90	83.563(4)	62.883(2)	63.1440(10)
V, $Å^3$	4465.4(7)	4934.4(9)	1790.4(9)	1162.2(4)	1125.96(15)
Z	4	4	1	1	1
ρ(calcd), g/cm^{-3}	1.391	1.381	1.429	1.471	1.499
μ, mm^{-3}	1.010	0.920	0.757	1.094	0.900
Crystal size, mm	0.20 × 0.10 × 0.10	0.17 × 0.12 × 0.06	0.11 × 0.04 × 0.04	0.30 × 0.30 × 0.26	0.10 × 0.05 × 0.05
θ_{min}–θ_{max}, deg	1.53–27.51	1.64–29.64	2.29–26.50	2.08–28.29	2.11–30.35
F(000)	1920	2120	797	532	528
T_{min}/T_{max}		0.859/0.947	0.921/0.970	0.735/0.764	0.915/0.956
R_{int}	0.0516	0.0303	0.0583	0.0212	0.0560
Ranges of reflection indices	$-36 \le h \le 36$, $-13 \le k \le 13$, $-21 \le l \le 21$	$-44 \le h \le 44$, $-12 \le k \le 12$, $-30 \le l \le 30$	$-13 \le h \le 13$, $-13 \le k \le 12$, $-19 \le l \le 19$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-14 \le l \le 15$	$-15 \le h \le 15$, $-15 \le k \le 15$, $-16 \le l \le 16$
Measured reflections	21338	27709	14038	11400	13592
Independent reflections	5131	6974	7220	5642	6672
Reflections with $I > 2\sigma(I)$	3718	5207	4404	4938	4565
Goodness-of-fit	0.999	1.260	0.918	1.001	1.020
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0476$ $wR_2 = 0.1367$	$R_1 = 0.0421$ $wR_2 = 0.1287$	$R_1 = 0.0542$ $wR_2 = 0.1308$	$R_1 = 0.0302$ $wR_2 = 0.0914$	$R_1 = 0.0576$ $wR_2 = 0.1321$
R factors for all reflections	$R_1 = 0.0755$ $wR_2 = 0.1554$	$R_1 = 0.0632$ $wR_2 = 0.1435$	$R_1 = 0.1060$ $wR_2 = 0.1461$	$R_1 = 0.0364$ $wR_2 = 0.0948$	$R_1 = 0.0924$ $wR_2 = 0.1321$
Residual electron density (min/max), *e*/$Å^3$	−0.559/0.735	−0.509/0.775	−0.651/0.906	−0.353/0.467	−0.546/0.494

Table 2. Selected geometric characteristics for complexes **I**–**V**

Parameter	**I**	**II**	**III**	**IV**	**V**
M–O(μ_2-O_2CR), Å	1.957(2)–1.970(2)	1.962(2)–1.969(2)	1.951(3)–2.162(3)	2.0221(13)–2.0761(13)	1.993(2)–2.025(2)
M–O(η, μ_2-O_2CR), Å			2.028(3)–2.333(3)		
M–N, Å	2.195(3)	2.176(2), 2.207(3)	2.076(3)	2.059(2)	2.035(2)
M···M, Å	2.6337(6)	2.7061(15)	3.5735(9)	2.9874(5)	2.6826(7)
C–O, Å	1.254(4)–1.267(4)	2.158(3)–2.254(3)	1.237(4)–1.274(4)	1.255(2)–1.260(2)	1.257(3)–1.270(3)
Angle OCO, deg	125.1(3), 125.9(3)	125.7(2)	118.5(3)–124.9(4)	124.1(2),125.4(2)	123.7(3), 125.0(3)
C(CO_2)–C(C_6) Å and angle between corresponding fragments, deg	1.485(4), 5.2; 1.503(5), 7.5	1.492(3), 3.9; 1.498(3), 18.6	1.468(5), 14.5; 1.478(5), 13.9; 1.507(5), 20.4; 1.522(5), 5.4	1.514(2), 10.6; 1.505(2), 49.5	1.510(4), 11.3; 1.503(4), 50.4

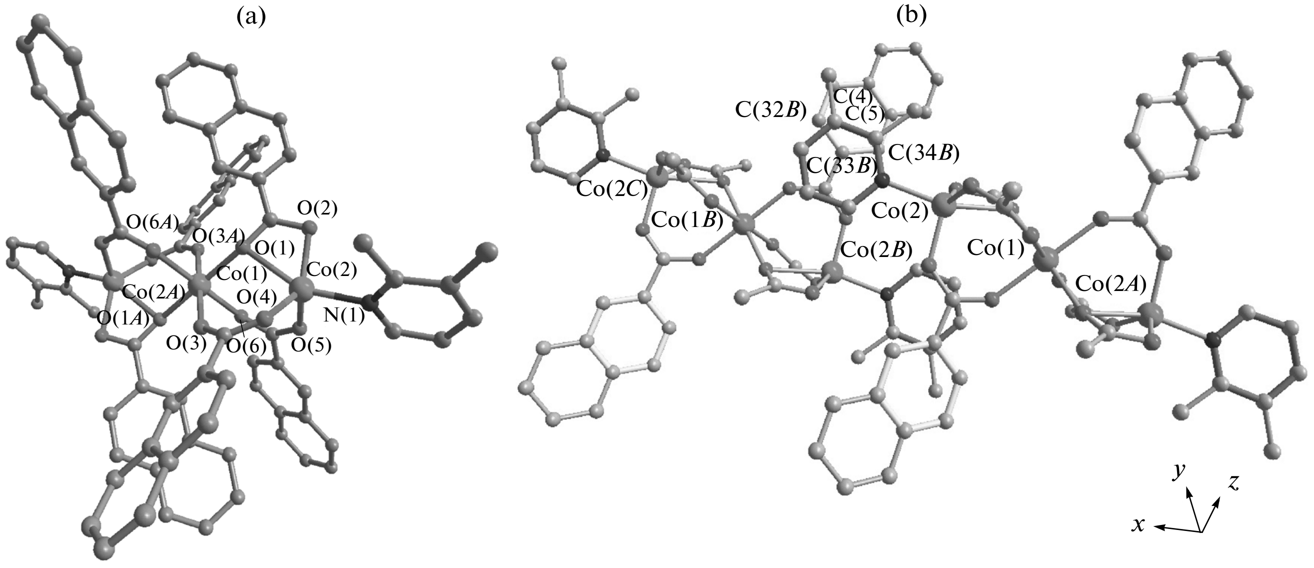

Fig. 2. (a) Structure of molecule **III** and (b) the molecular packing fragment in crystal **III**.

are coplanar. A more substantial deviation of the plane of the COO^- group from the plane of the aromatic system (the value of deviation attains 18.6°) is observed for one of the pairs of the symmetric carboxylate anions (Table 2, Fig. 1). In spite of the "free" aromatic fragments, an analysis of the molecular packing in crystal revealed no formation of intermolecular stacking interactions.

The trinuclear cobalt(II) complex with naphthoate anions (**III**) was isolated using a procedure similar to the synthesis of copper compound **II** from binuclear complex $[Co_2(Piv)_4(2,3\text{-Lut})_2]$. We failed to obtain a binuclear cobalt(II) complex similar to copper compound **II** even under the action of a significant excess of 2,3-Lut on complex **III**. In this case, the ratio of reactants exerts no effect on the composition and structure, as it was observed for the benzoate cobalt(II) complexes with quinoline. Binuclear complex $[Co_2(O_2CPh)_4L_2]$ is formed for a stoichiometric or excessive amount of the N-donor ligand, and the action of dibenzoate polymer $[Co(O_2CPh)_2]_n$ on this complex results in the formation of trinuclear $[Co_3(O_2CPh)_6L_2]$ [9, 10].

In complex **III**, the central Co(1) atom lies at the inversion center and is symmetrically bound to two other metal atoms Co(2) and Co(2)' by two bridging and one chelate-bridging carboxylate groups (Table 2, Fig. 2). The coordination environment of the central Co(1) atom is a distorted octahedron. For the Co(2) atom coordinating four O atoms of the bridging and chelate-bridging CO_2 groups and the N atom of the 2,3-Lut molecule, the coordination polyhedron is close to a square pyramid ($\tau = 0.39$ [32]). The deviation of the planes of the carboxy groups from the planes of the naphthoate substituents ranges from 5.4° to 20.4° in the bridging anions and is equal to 13.9° in the μ_2,η^2-carboxylate anions (Table 2, Fig. 2a). In crystal **III**, the naphthalene fragments are partially overlapped with the coordinated lutidine molecules of the adjacent molecules of the complex (the dihedral angle between the planes of the pyridyl and phenyl fragments is 23.8°, and the shortest C(4)–C(32*A*) distance is 3.44 Å) (Fig. 2b). Polymer 1D chains along the vector *a* are formed due to these stacking interactions.

The complex with zinc atoms of a similar molecular structure, $[Zn_3(\beta\text{-Naph})_6(2,3\text{-Lut})_2]$, was described [23]. The packing in crystal of this compound due to the stacking interactions between the naphthalene fragments of the adjacent molecules was shown to favor the formation of a layered structure, unlike the 1D structure observed for complex **III**. A possible reason for this difference can be the absence of solvate molecules in the composition of the zinc complex.

The influence of the migration of the carboxy group from the β position to the α position in the naphthoic acid anion is the change in the composition and structure of the reaction product. The reaction of $ZnCl_2$, 2,3-Lut, and α-naphthoic acid potassium salt affords binuclear zinc complex **IV**. The inversion center lies between the Zn(1) and Zn(1*A*) atoms symmetrically bound by four bridging carboxylate groups (Table 2, Fig. 3). Unlike the above described metal complexes with β-naphthoic acid, in the α-naphthoate anions the aromatic fragment and carboxy group shift from the coplanar arrangement (the dihedral angle between their planes is 10.6° for one of the symmetric pairs of anions and 49.5° for another pair) because of steric hindrances (the proton at the C(8) atom of the naphthyl group is remote at a distance of ~2.22 Å from the O(1) atom of the carboxy group (C(8)–H 0.93 Å, angle C(8)HO(1) 126°)). This result

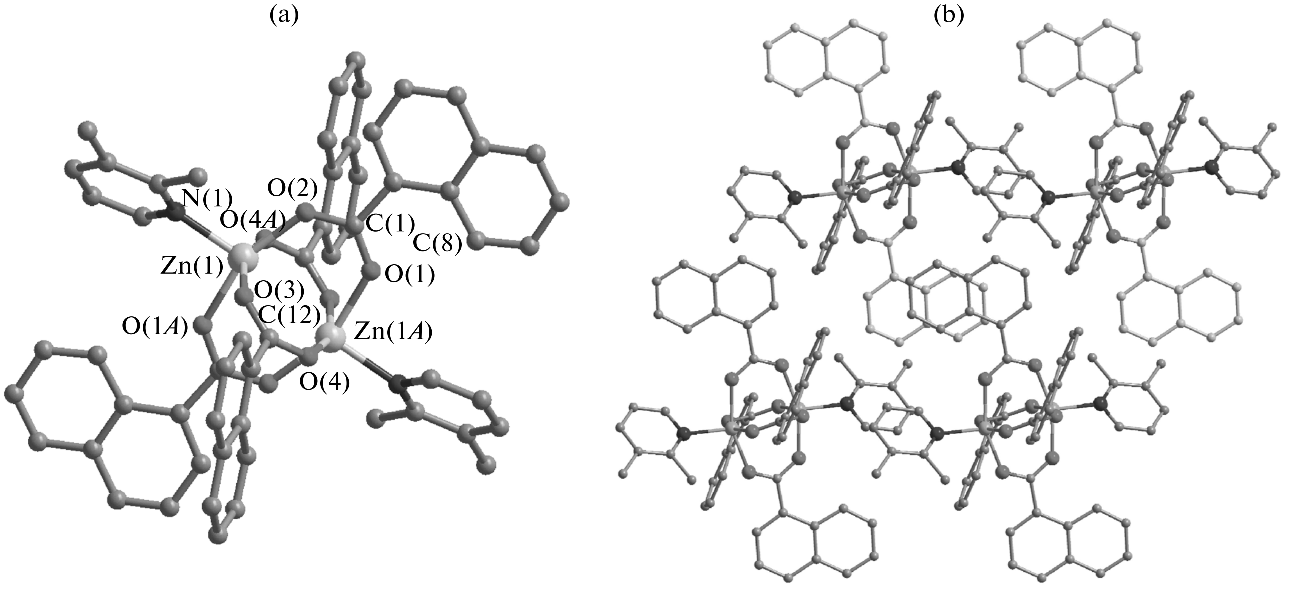

Fig. 3. (a) Structure of molecule **IV** and (b) the molecular packing fragment in crystal **IV**.

is basically important, since it allows one to detect a substantial difference between the structure of the carboxylate ligand in the binuclear complexes with the “paddle-wheel” structure and that in the trinuclear linear complexes. In the case of the α-naphthoate anions, the plane of the aromatic substituent is substantially turned relatively to the plane of the carboxy group, resulting in the substantial weakening of the π–π conjugation compared to that in the β-naphthoate anions in which these fragments are noticeably more coplanar. Interestingly, an insignificant deviation of the naphthoate fragment from the plane of the carboxy group is observed in the similar copper complex with the β-naphthoate anions.

Although the structures of the known [(2,3-Lut)$_2$Zn$_3$(β-Naph)$_6$] complex and complex **IV** with isomeric α- and β-naphthoate anions differ substantially, the type of intermolecular stacking interactions in them remains the same. All the four naphthoate substituents interact to form a layered structure (the distance between the parallel planes is 3.43 Å, and the shortest distances between the atoms of the naphthyl fragments are 3.51 Å (C(19)–C(14)) and 3.47 Å (C(6)–C(8)) (Fig. 3b).

The molecular structure of complex **IV** is similar to those of the known zinc compounds with anions of benzoic, 2-methylbenzoic, and 2-nitrobenzoic acids with pyridine [33–35].

Nickel(II) coordination compound **V** was isolated using the synthesis procedure for complex **IV**. The structure of compound **V** is similar to those of the earlier described nickel(II) dimers with anions of benzoic [36, 37] and 2,6-di(*p*-tolyl)benzoic acids [38] with non-chelating N-donor ligands, 1-methyl-4,5-diphenylimidazole, 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, and pyridine. The crystals of complexes **IV** and **V** are isostructural (Table 1).

The results of this work show that the position of the naphthyl substituent at the carboxylate group substantially affects the molecular and crystal structures of the formed carboxylate complexes of transition metals. Of course, the composition and structure of the isolated complexes are determined by the following factors: steric hindrances, intermolecular interactions of aromatic fragments, and the electronic structure of the metal center. For example, no substantial steric hindrances are observed in the complexes with β-naphthoic acid, which is indicated by small angles between the planes of the naphthyl and carboxylate groups (4°–20°), whereas for the compounds with the α-naphthoic acid the angle between the planes changes from 10° to 50°. To be mentioned for comparison, the known data show that both groups in the β-naphthoic acid lie in one plane [39] and the dihedral angle between the planes of the naphthyl and carboxy groups in α-naphthoic acid is 7.9° [40]. A strong change in a similar angle (up to 50°) in the binuclear zinc and nickel complexes (**IV** and **V**, respectively) is determined by the mutual arrangement of the organic fragments in the molecules of the complexes. It is shown for zinc(II) complex **IV** and [Zn$_3$(β-Naph)$_6$(2,3-Lut)$_2$] [23] that the bi- or trinuclear complex can be formed depending on the position of the naphthyl substituent at the carboxylate group. Unlike the binuclear analogs with α-naphthoic acid (compounds **IV** and **V**), the binuclear copper complexes with β-naphthoic acid (compounds **I** and **II**) exhibit the formation of an isolated arrangement of molecules in crystal, i.e., without intermolecular interactions between the aromatic fragments. It is shown that the binuclear tetracarboxylate-bonded systems for copper(II) are more stable than the trinuclear systems (when comparing the cobalt, copper, and zinc complexes with β-naphthoic acid), which is determined by the electronic structure and more favorable geometry of the coordination environment of the metal ion and is consistent with the crystal field theory [41].

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