Formation of bi- and tetranuclear cobalt(II) trimethylacetate complexes with 2-amino-5-methylpyridine and 2,6-diaminopyridine

E. V. Pakhmutova,[a] A. E. Malkov,[a] T. B. Mikhailova,[a] A. A. Sidorov,[a] I. G. Fomina,[a] G. G. Aleksandrov,[a] V. M. Novotortsev,[a] V. N. Ikorskii,[b] and I. L. Eremenko[a]★

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 955 4835. E-mail: ilerem@igic.ras.ru*

[b]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 prosp. Akad. Lavrentieva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 34 4489*

The reactions of the polymeric complex $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (**1**) with 2-amino-5-methylpyridine (L_1) and 2,6-diaminopyridine (L_2) under anaerobic conditions at the ratio M : L = 1 : 1 afforded the binuclear complexes $Co_2(\mu\text{-}OOCCMe_3)_4[\eta\text{-}MeC_5H_3N(NH_2)]_2$ (**2**) and $Co_2(\mu\text{-}OOCCMe_3)_4[\eta\text{-}C_5H_3N(NH_2)_2]_2$ (**3**), respectively, with Chinese-lantern-like structures. The reaction of the tetranuclear cobalt(II) complex $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ (**4**) with 2,6-diaminopyridine under anaerobic conditions at the ratio $M : L_2 = 2 : 1$ gave rise to the antiferromagnetic tetranuclear complex $Co_4(\mu_4\text{-}O)[\mu\text{-}C_5H_3N(NH_2)_2]_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2$ (**5**) with tetradentate-bridging coordination of the oxygen atom. The structures of the compounds synthesized were established by X-ray diffraction analysis.

Key words: 2-amino-5-methylpyridine, 2,6-diaminopyridine, cobalt complexes, X-ray diffraction analysis.

Bulky donor molecules are often used in coordination chemistry for the formation of a specified ligand environment about the metal center. The reactions of nickel and cobalt carboxylate complexes with α-substituted pyridines afforded dimeric complexes with Chinese-lantern-like structures.[1—8] The use of pyridines containing β- or γ-substituents is limited to the formation of monomers[9] or binuclear complexes containing the $\{M_2(\mu\text{-}H_2O)(\mu\text{-}OOCCMe_3)_2\}$ fragment.[10] However, under drastic conditions of thermal reactions, the use of even unsubstituted pyridine gave rise to the four-bridged $Py_2M_2(OOCCMe_3)_4$ ($M = Ni^{II}$, Co^{II}) structures.[5,11]

It is possible to extend a range of polyfunctional N-donor compounds, which can serve as axial ligands in binuclear carboxylate complexes with Chinese-lantern-like structures. It is of particular importance for the preparation of starting complexes, in which apically coordinated organic molecules are can be subjected to further various transformations. In particular, template assembly can be performed. In this respect, pyridine derivatives containing amino groups, *viz.*, 2-amino- or 2,6-diaminopyridines, hold promise. On the one hand, these compounds contain α-substituents facilitating the formation of dimeric complexes with Chinese-lantern-like structures. On the other hand, the presence of additional active amino groups does not exclude the possibility of formation of chelate rings or bridges,[12,13] whose appearance is incompatible with the formation of binuclear structures with four bridging carboxylate ligands. The formal composition of the starting metal carboxylates is yet another important factor that influences the formation of dimers with lantern-like structures. It can be hypothesized that the M : OOCR ratio of nearly 1 : 2 is preferable for the synthesis of dimers in good yields. By contrast, a deficiency of carboxylate groups may be responsible for difficulties in synthesizing binuclear four-bridged structures or even can prevent their formation at all.

In the present study, we compared the reactions of polynuclear cobalt(II) trimethylacetates, which are characterized by various $Co : OOCCMe_3$ ratios in the starting molecules of the $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ polymer ($n \approx 0.05$, $Co : OOCCMe_3 \approx 1 : 2$), and the tetranuclear hydroxotrimethylacetate complex $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(EtOH)_6$ ($Co : OOCCMe_3 = 1 : 1.5$) with 2-amino-5-methylpyridine and 2,6-diaminopyridine. The aim of the present study was to elucidate the influence of the composition and structure of the starting trimethylacetate on the structure of the newly formed

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2006—2012, October, 2003.

1066-5285/03/5210-2117 $25.00

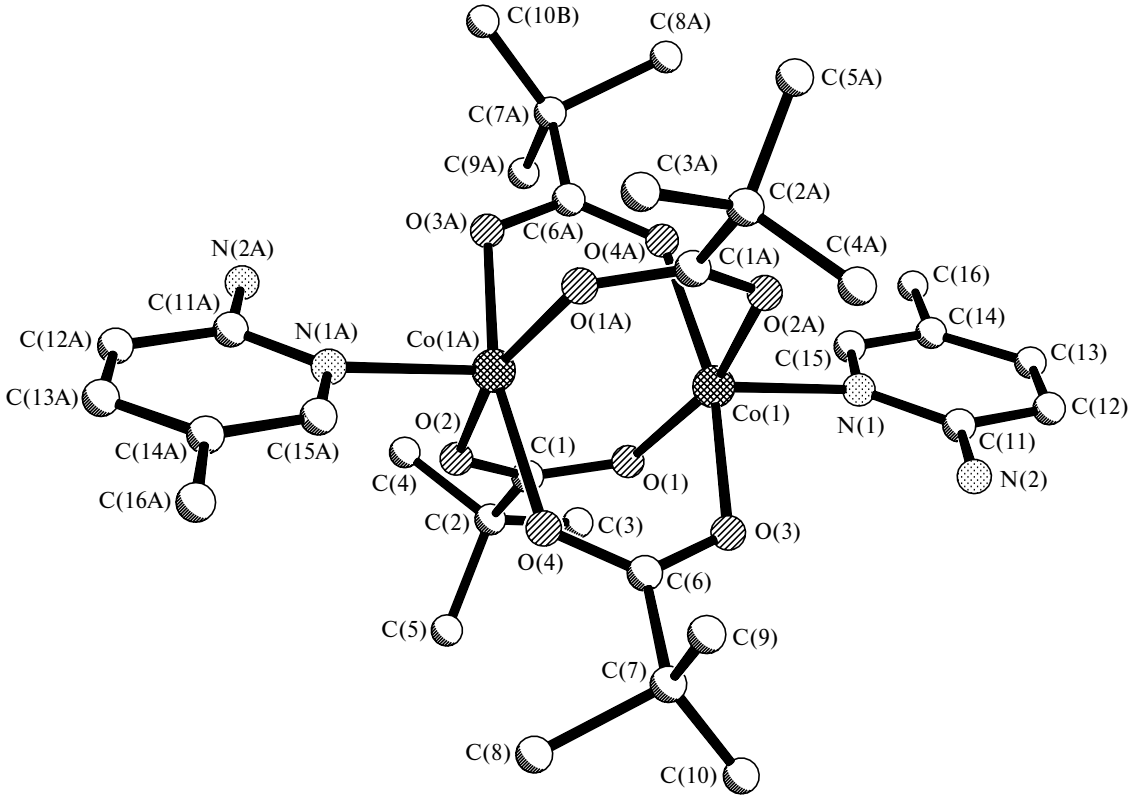


Fig. 1. Structure of complex **2**.

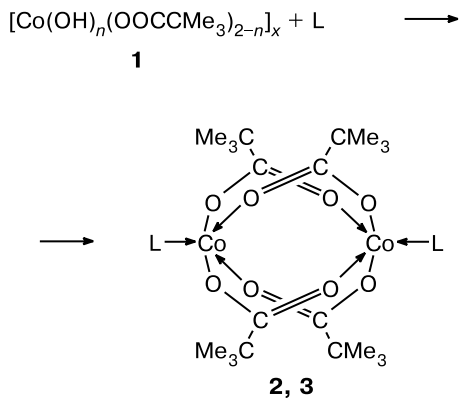
compounds and to found conditions for the preparation of complexes with Chinese-lantern-like structures.

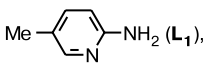
Results and Discussion

The reaction of the $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ polymer (**1**) with 2-amino-5-methylpyridine (L_1) in acetonitrile under an inert atmosphere at 80 °C afforded the binuclear complex $Co_2(\mu\text{-}OOCCMe_3)_4[\eta\text{-}MeC_5H_3N(NH_2)]_2$ (**2**) with a lantern-like structure in 42% yield (Scheme 1, Fig. 1). According to the results of X-ray diffraction analysis, there are two centrosymmetrical crystallographically independent molecules per asymmetric unit (Table 1). The cobalt atoms in these molecules are located at distances of 2.751(1) Å and 2.863(4) Å and are linked to each other by four carboxylate bridges (Co—O, 1.999(4)—2.224(4) Å). The coordination sphere of each metal atom is completed by the monodentate pyridine ligands (Co—N, 2.068(3)—2.072(3) Å). The amino groups of the ligands are linked to the oxygen atoms of the bridging carboxylate groups by intramolecular hydrogen bonds (N(2)—H, 0.86 Å; H—O(3), 2.22 Å; N(2)—H...O(3), 2.98 Å; ∠N(2)—H...O(3), 147.0°; N(4)—H, 0.86 Å; H—O(7), 2.22 Å; N(4)—H...O(7), 3.00 Å; ∠N(4)—H...O(7), 151.5°).

The presence of the second amino group in the α-position with respect to the N atom of the ligand has no effect on the nature of the compound formed. The reaction of polymer **1** with 2,6-diaminopyridine (L_2) under anaerobic conditions (M : L_2=1 : 1, CH_2Cl_2, 40 °C) afforded the binuclear complex $Co_2(\mu\text{-}OOCCMe_3)_4[\eta\text{-}$

Scheme 1



2: L =  ($\mathbf{L_1}$), MeCN, 80 °C, Ar, L : Co_{at} = 1 : 1

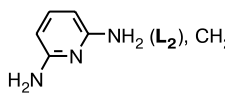
3: L =  ($\mathbf{L_2}$), CH_2Cl_2, 40 °C, Ar, L : Co_{at} = 1 : 1

Table 1. Selected geometric characteristics of complex **2**

Molecule **A**		Molecule **B**	
Parameter	Value	Parameter	Value
Bond:	*d*/Å	Bond:	*d*/Å
Co(1)...Co(1A)	2.751(1)	Co(2)...Co(2A)	2.863(1)
Co(1)—O(1)	2.026(4)	Co(2)—O(5)	2.012(4)
Co(1)—O(2)	2.030(4)	Co(2)—O(6)	1.999(4)
Co(1)—O(3)	2.044(4)	Co(2)—O(7)	2.224(4)
Co(1)—O(4)	2.083(4)	Co(2)—O(8)	2.061(4)
Co(1)—N(1)	2.068(3)	Co(2)—N(3)	2.072(3)
Angle:	ω/deg	Angle:	ω/deg
O(1)—Co(1)—O(2)	164.8(2)	O(5)—Co(2)—O(6)	162.1(2)
O(1)—Co(1)—O(3)	93.9(1)	O(5)—Co(2)—O(7)	82.4(1)
O(1)—Co(1)—O(4)	86.3(1)	O(5)—Co(2)—O(8)	91.2(1)
O(1)—Co(1)—N(1)	94.5(1)	O(5)—Co(2)—N(3)	99.2(2)
O(2)—Co(1)—O(3)	87.5(2)	O(6)—Co(2)—O(7)	87.5(2)
O(2)—Co(1)—O(4)	88.4(2)	O(6)—Co(2)—O(8)	94.0(2)
O(2)—Co(1)—N(1)	100.1(2)	O(6)—Co(2)—N(3)	97.2(2)
O(3)—Co(1)—O(4)	164.6(1)	O(7)—Co(2)—O(8)	162.2(2)
O(3)—Co(1)—N(1)	101.7(2)	O(7)—Co(2)—N(3)	100.0(2)
O(4)—Co(1)—N(1)	93.6(1)	O(8)—Co(2)—N(3)	97.4(2)

$C_5H_3N(NH_2)_2]_2$ with a lantern-like structure (**3**, 86% yield) (see Scheme 1). According to the X-ray diffraction data, the cobalt atoms in complex **3**, like those in complex **2**, are at the nonbonded Co...Co distance (2.926(1) Å), which is the longest distance observed in the known cobalt compounds of this type.[11] The cobalt atoms in **3** are linked to each other by four carboxylate bridges (Co—O, 2.002(2)—2.073(2) Å) (Fig. 2, Table 2). The ligand molecule is monodentately coordinated through the pyridine nitrogen atom (Co—N, 2.1091(19) Å). Two free amino groups L_2 are linked to the oxygen atoms of the carboxylate groups by an intramolecular hydrogen bond (N(2)—H, 0.88 Å; H—O(3), 2.10 Å; N(2)—H...O(3), 2.92 Å; ∠N(2)—H...O(3), 153.7°).

Table 2. Selected geometric characteristics of complex **3**

Bond	*d*/Å	Angle	ω/deg
Co(1)—Co(1A)	2.926(0)	O(1)—Co(1)—O(2)	160.44(7)
Co(1)—O(1)	2.073(2)	O(1)—Co(1)—O(3)	89.67(6)
Co(1)—O(2)	2.028(2)	O(1)—Co(1)—O(4)	86.91(7)
Co(1)—O(3)	2.057(1)	O(1)—Co(1)—N(1)	98.97(6)
Co(1)—O(4)	2.002(2)	O(2)—Co(1)—O(3)	86.03(7)
Co(1)—N(1)	2.109(2)	O(2)—Co(1)—O(4)	90.72(7)
		O(2)—Co(1)—N(1)	100.56(7)
		O(3)—Co(1)—O(4)	160.28(7)
		O(3)—Co(1)—N(1)	99.10(7)
		O(4)—Co(1)—N(1)	100.62(7)

Therefore, in spite of the presence of the additional donor atoms in the α-position of the ligands, the re-

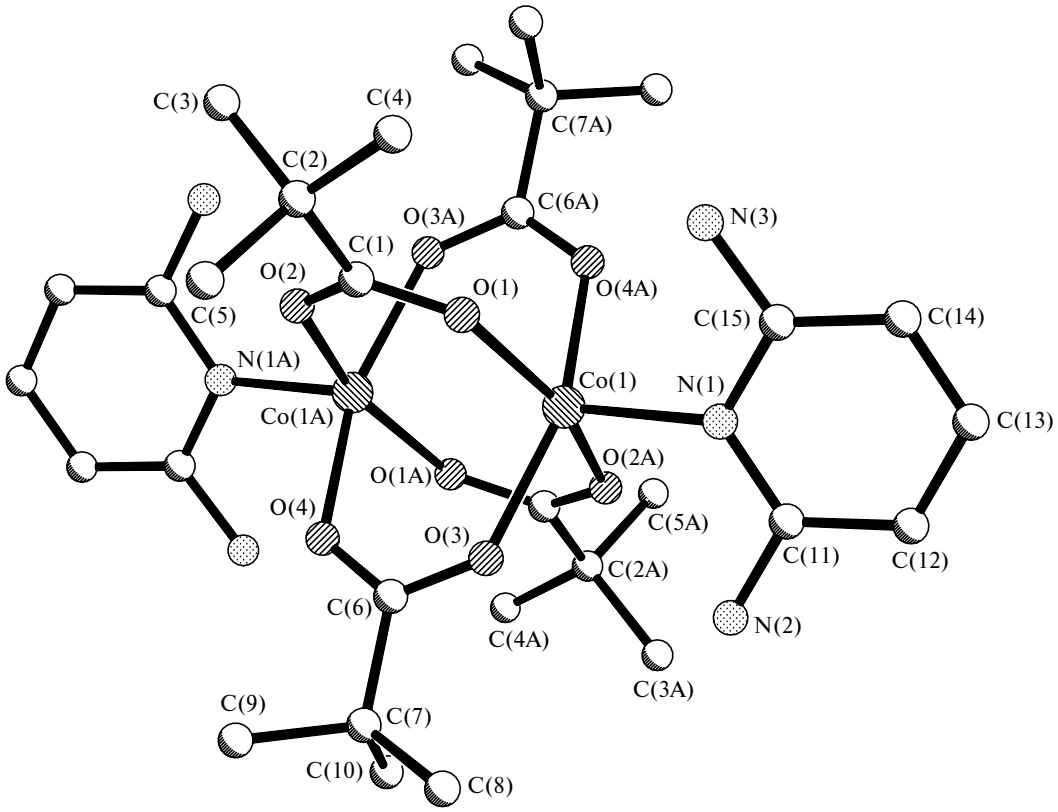


Fig. 2. Structure of complex **3**.

actions of polymeric cobalt(II) trimethylacetate with 2-amino-5-methylpyridine and 2,6-diaminopyridine afforded binuclear complexes with Chinese-lantern-like structures, as has been observed earlier[6—8] for the complexes with quinoline, α-picoline, and other pyridine derivatives containing substituents in the α-position. However, the carboxylate bridges in new compounds **2** and **3** are somewhat nonequivalent due, apparently, to hydrogen bonding between the protons of the uncoordinated amino groups and the oxygen atoms of the trimethylacetate anions.

In the reaction of 2,6-diaminopyridine with the tetranuclear cobalt(II) complex $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ (**4**) as the starting compound, which is characterized by a deficiency of carboxylate anions, the situation reversed. Under anaerobic conditions, the reaction performed with the use of the ratio M : L_2 = 2 : 1 in MeCN at 40 °C afforded the tetranuclear complex $Co_4(\mu_4\text{-}O)[\mu\text{-}C_5H_3N(NH_2)_2]_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2$ (**5**) with the tetradentate-bridging coordination of the oxygen atom in 61% yield (Scheme 2). According to the X-ray data, the 2,6-diaminopyridine ligand in molecule **5** serves as a bridge, only one amino group and the pyridine nitrogen atom being involved in coordination to the metal atoms (Fig. 3, Table 3). The cobalt atoms are linked to each other through the μ_4-oxygen atom (Co—O, 1.928(3)—2.025(3) Å) and six bridging ligands, *viz.*, four trimethylacetate anions (Co—O, 1.964(4)—2.057(4) Å) and two 2,6-diaminopyridine molecules. In complex **5**, two cobalt atoms, *viz.*, Co(1) and Co(4), are in a tetrahedral environment, whereas the Co(2) and Co(3) atoms are in an octahedral environment. The cobalt atoms form a distorted tetrahedron, whose center is occupied by the μ_4-oxo atom O(13). The Co...Co distances in the tetrahedron vary from 3.040(1) Å (for Co(1)...Co(3))

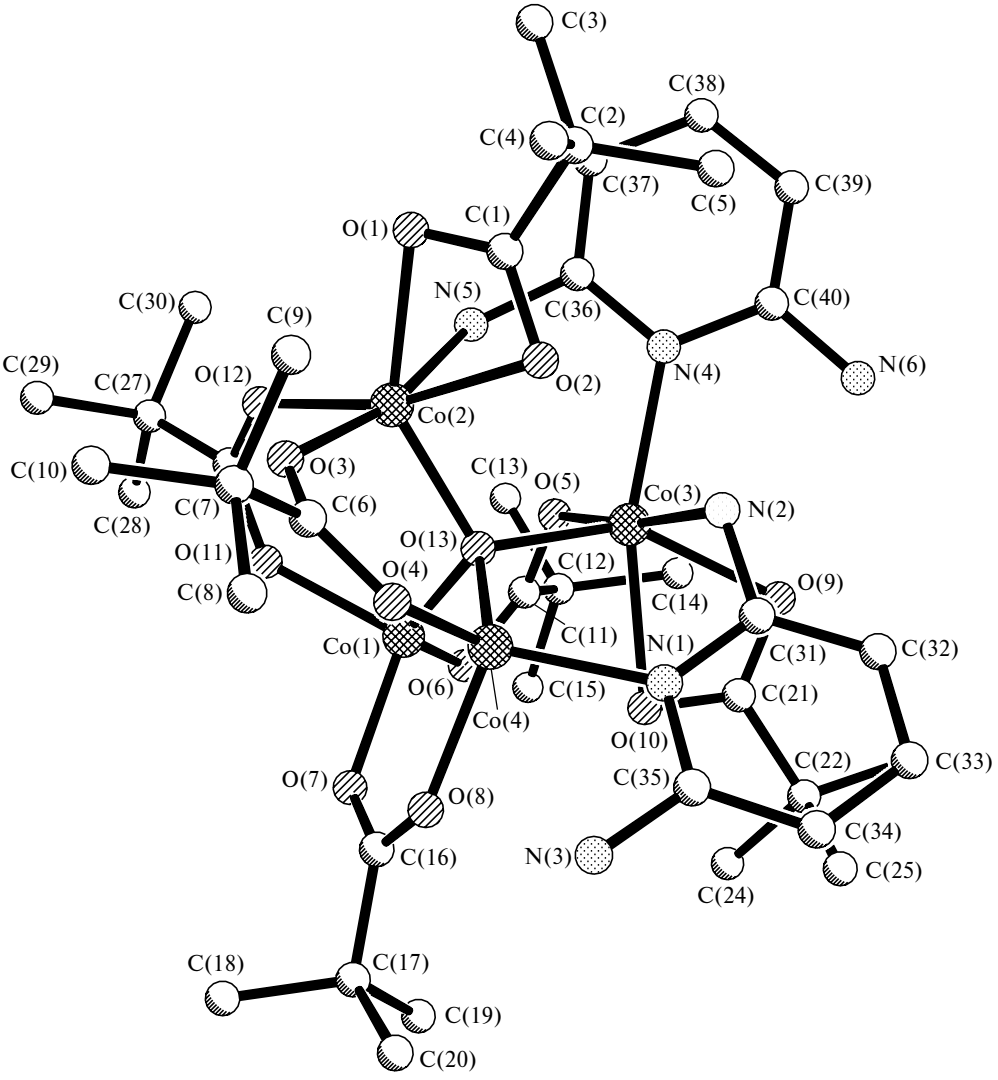


Fig. 3. Structure of complex **5**.

Table 3. Selected geometric characteristics of complex **5**

Parameter	Value	Parameter	Value	Parameter	Value
Bond:	*d*/Å	Angle:	ω/deg	Angle:	ω/deg
Co(1)—Co(3)	3.041(1)	Co(4)—Co(2)—O(2)	71.86(9)	O(9)—Co(3)—O(10)	60.4(1)
Co(1)—Co(4)	3.127(1)	Co(4)—Co(2)—O(3)	70.5(1)	O(9)—Co(3)—O(13)	147.5(1)
Co(1)—O(6)	1.990(4)	Co(4)—Co(2)—O(12)	121.0(1)	O(9)—Co(3)—N(2)	87.2(1)
Co(1)—O(7)	1.965(4)	Co(4)—Co(2)—O(13)	36.15(9)	O(9)—Co(3)—N(4)	101.2(1)
Co(1)—O(11)	1.993(4)	Co(4)—Co(2)—N(5)	120.8(1)	O(10)—Co(3)—O(13)	87.5(1)
Co(1)—O(13)	1.949(3)	O(1)—Co(2)—O(2)	59.3(1)	O(10)—Co(3)—N(2)	93.7(1)
Co(2)—Co(4)	3.138(1)	O(1)—Co(2)—O(3)	93.2(1)	O(10)—Co(3)—N(4)	161.4(2)
Co(2)—O(1)	2.105(3)	O(1)—Co(2)—O(12)	107.5(1)	O(13)—Co(3)—N(2)	89.9(1)
Co(2)—O(2)	2.288(3)	O(1)—Co(2)—O(13)	143.7(1)	O(13)—Co(3)—N(4)	111.1(1)
Co(2)—O(3)	2.044(4)	O(1)—Co(2)—N(5)	82.2(1)	N(2)—Co(3)—N(4)	87.5(2)
Co(2)—O(12)	2.057(4)	O(2)—Co(2)—O(3)	88.0(1)	Co(1)—Co(4)—Co(2)	63.84(2)
Co(2)—O(13)	1.995(3)	O(2)—Co(2)—O(12)	166.8(1)	Co(1)—Co(4)—O(4)	124.8(1)
Co(2)—N(5)	2.326(4)	O(2)—Co(2)—O(13)	88.5(1)	Co(1)—Co(4)—O(8)	74.8(1)
Co(3)—O(5)	2.118(4)	O(2)—Co(2)—N(5)	98.9(1)	Co(1)—Co(4)—O(13)	36.5(1)
Co(3)—O(9)	2.159(4)	O(3)—Co(2)—O(12)	93.4(1)	Co(1)—Co(4)—N(1)	127.8(1)
Co(3)—O(10)	2.184(4)	O(3)—Co(2)—O(13)	102.8(1)	Co(2)—Co(4)—O(4)	80.6(1)
Co(3)—O(13)	2.024(3)	O(3)—Co(2)—N(5)	168.1(2)	Co(2)—Co(4)—O(8)	128.0(1)
Co(3)—N(2)	2.204(4)	O(12)—Co(2)—O(13)	104.0(1)	Co(2)—Co(4)—O(13)	37.6(1)
Co(3)—N(4)	2.183(4)	O(12)—Co(2)—N(5)	77.6(2)	Co(2)—Co(4)—N(1)	126.9(1)
Co(4)—O(4)	1.964(4)	O(13)—Co(2)—N(5)	87.2(1)	O(4)—Co(4)—O(8)	100.2(2)
Co(4)—O(8)	2.006(4)	Co(1)—Co(3)—O(5)	61.9(1)	O(4)—Co(4)—O(13)	117.7(2)
Co(4)—O(13)	1.928(3)	Co(1)—Co(3)—O(9)	121.3(1)	O(4)—Co(4)—N(1)	107.1(2)
Co(4)—N(1)	2.055(4)	Co(1)—Co(3)—O(10)	68.3(1)	O(8)—Co(4)—O(13)	111.2(2)
Angle:	ω/deg	Co(1)—Co(3)—O(13)	39.17(9)	O(8)—Co(4)—N(1)	102.8(2)
O(6)—Co(1)—O(7)	101.5(2)	Co(1)—Co(3)—N(2)	123.7(1)	O(13)—Co(4)—N(1)	115.7(2)
O(6)—Co(1)—O(11)	97.7(1)	Co(1)—Co(3)—N(4)	125.7(1)	Co(1)—O(13)—Co(2)	114.3(2)
O(6)—Co(1)—O(13)	126.0(1)	O(5)—Co(3)—O(9)	93.4(1)	Co(1)—O(13)—Co(3)	99.8(1)
O(7)—Co(1)—O(11)	103.3(1)	O(5)—Co(3)—O(10)	92.9(1)	Co(1)—O(13)—Co(4)	107.5(2)
O(7)—Co(1)—O(13)	114.8(1)	O(5)—Co(3)—O(13)	93.4(1)	Co(2)—O(13)—Co(3)	116.4(2)
O(11)—Co(1)—O(13)	110.3(1)	O(5)—Co(3)—N(2)	172.8(2)	Co(2)—O(13)—Co(4)	106.2(2)
Co(4)—Co(2)—O(1)	129.1(1)	O(5)—Co(3)—N(4)	85.3(2)	Co(3)—O(13)—Co(4)	112.4(2)

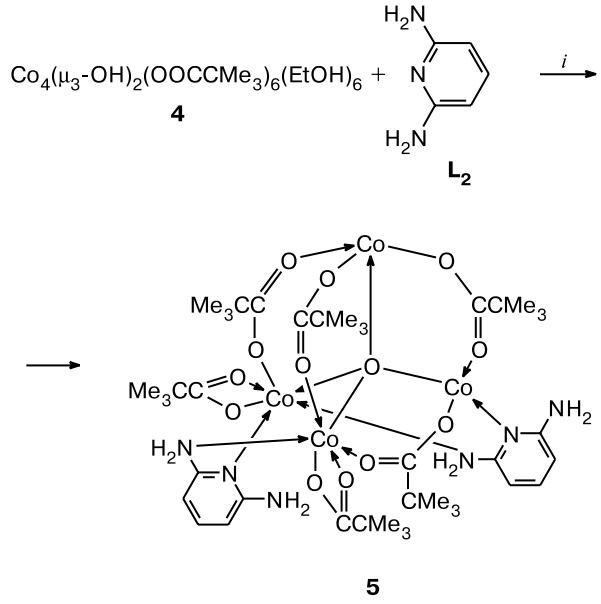
to 3.417(1) Å (for Co(1)...Co(4)). Interestingly, each Co...Co edge in the tetrahedron is "fastened" by one of six bridging ligands (trimethylacetate anions or 2,6-diaminopyridine molecules). The Co(2)...Co(3) and Co(3)...Co(4) edges are "fastened" by the L_2 bridges (Co—N(py), 2.183(4)—2.055(4) Å; Co—$N(NH_2)$, 2.204(4)—2.326(4) Å). The remaining four edges of the tetrahedron are "fastened" by the bridging trimethylacetate groups. The coordination environment about the Co(2) and Co(3) atoms is completed to a distorted octahedron by the chelate trimethylacetate groups (Co—O, 2.105(4)—2.288(4) Å). The coordination environments about the remaining two cobalt atoms in complex **5** are still distorted tetrahedra. As a result, all four metal atoms in molecule **5** are in nonequivalent ligand environment. Molecule **5** has no symmetry elements, and the oxygen atom is chiral with the result that complex **5** crystallizes in the space group $P2_1/c$ as a racemic mixture.

Two amino groups of the ligand, which are not bound to the metal atom, are involved in intramolecular hydrogen bonding with the carboxylate oxygen atoms (N(3)—H, 0.88 Å; H—O(8), 2.37 Å; N(3)—H...O(8), 2.96 Å; ∠N(3)—H...O(8), 124.8°).

Complex **5** exhibits the antiferromagnetic type of spin-spin interaction (μ_{eff} = 3.50—10.50 μB (2—300 K) per overall molecule of the complex).

An increase in the reaction temperature to 80 °C did not lead to the formation of dimer **3**. Attempts to prepare binuclear complex **3** with a lantern-like structure by the reactions of tetranuclear complex **5** with different amounts of 2,6-diaminopyridine, up to its substantial excess, failed. In the latter case, the reaction afforded only amorphous precipitates, which were virtually insoluble in organic solvents. These reaction products are, apparently, clusters or polymers with complex structures containing (judging from the IR spectra) the bridging diamine molecules (δ_{NH_2}, 3420 cm^{-1}) and carboxylate groups ($\nu_{as}(COO^-)$, 1552 cm^{-1}; $\nu_s(COO^-)$, 1456 cm^{-1}). The reaction of complex **4** with aminopyridine L_1 also gave rise to a virtually insoluble amor-

Scheme 2



i. MeCN, 40 °C, Ar, $Co_{at} : L_2 = 2 : 1$.

phous precipitate, while the formation of complex **2** was not observed.

The difference in the chemical behavior of polynuclear cobalt trimethylacetates **1** and **4** with respect to aminopyridines L_1 and L_2 demonstrates the role of the structure of the metal carboxylate core of the starting metal-containing reagents in the formation of the final structures. In the case of polynuclear compound **1**, the polymer undergoes chemical destruction by aminopyridines with the result that the M : OOCR ratio in the final complexes **2** and **3** remains virtually unchanged. Taking into account the optimum metal : ligand ratio, the stable four-bridged binuclear structure of the core forms. In the reaction with the use of tetramer **4** as the starting reagent, the ratio M : OOCR = 1 : 1.5 in final product **5** also remains unchanged. However, in the case of a deficiency of carboxylate ligands, the tetranuclear metal fragment "folds up" and is strengthened, new aminopyridine bridges appear, and the water molecule is eliminated due to disproportionation of two tridentate-bridging hydroxy groups in the starting cluster with generation of the tetradentate-bridging oxygen atom in the final product. In this case, the starting trimethylacetate molecule does not undergo destruction. On the contrary, this molecule is transformed into a more stable species, diaminopyridine serving as an additional tightening agent. As a result, in spite of the steric effects of the α-substituents in L_1 and L_2, these ligands exert different effects on the polynuclear cobalt trimethylacetates depending on the structures of the starting metal-containing reagents.

Experimental

All operations associated with the synthesis were carried out in an inert atmosphere using anhydrous solvents. The starting cobalt trimethylacetate complexes were synthesized according to known procedures.[14] The IR spectra of the complexes were recorded on a Specord M 80 instrument in KBr pellets. The static magnetic susceptibility was measured in the temperature range of 2—300 K on a SQUID MPMS-59 Quantum Desing magnetometer in the International Tomography Center of the Siberian Branch of the Russian Academy of Sciences.

Synthesis of the complexes. Bis(2-amino-5-methylpyridino)tetra(μ$_2$-*O,O′*-trimethylacetato)dicobalt(II), $Co_2[MeC_5H_3N(NH_2)]_2(\mu\text{-}OOCCMe_3)_4 \cdot MeCN$ (2). Acetonitrile (30 mL) was added to a mixture of $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (0.3 g, 1.15 mmol with respect to the formula unit $Co(OOCCMe_3)_2$) and 2-amino-5-methylpyridine (0.12 g, 1.15 mmol). The reaction mixture was stirred under argon at 80 °C for 30 min until the reagents were completely dissolved. The solution was concentrated to 5 mL at 0.1 Torr and 20 °C and allowed to crystallize at ~20 °C. After 24 h, the ruby crystals that formed were separated by decantation, washed with cold hexane, and dried under a stream of argon. The yield of the solvate of compound **2** with MeCN was 0.19 g (42% with respect to the initial amount of cobalt). Found (%): C, 52.75; H, 7.27; N, 8.53. $C_{34}H_{55}Co_2N_5O_8$. Calculated (%): C, 52.33; H, 7.06; N, 8.98. IR (KBr), ν/cm^{-1}: 3432 m, 3348 m, 3232 m, 2960 s, 2928 m, 2868 m, 1652 m, 1600 v.s, 1572 s, 1512 m, 1484 v.s, 1456 m, 1420 v.s, 1376 s, 1360 s, 1328 m, 1228 s, 1148 w, 1040 w, 896 m, 824 m, 788 m, 608 m, 464 w, 432 w.

The crystals synthesized were suitable for X-ray diffraction analysis.

Bis(2,6-diaminopyridino)tetra(μ$_2$-*O,O′*-trimethylacetato)dicobalt(II), $Co_2[C_5H_3N(NH_2)_2]_2(\mu\text{-}OOCCMe_3)_4 \cdot 2CH_2Cl_2$ (3). Dichloromethane (30 mL) was added to a mixture of $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (0.15 g, 0.5 mmol with respect to the formula unit $Co(OOCCMe_3)_2$) and 2,6-diaminopyridine (0.06 g, 0.5 mmol). The reaction mixture was stirred under argon at 40 °C for 15 min until the reagents were completely dissolved. The solution was concentrated to 5 mL at 0.1 Torr and 20 °C and then cooled to −5 °C. After 2 days, the green crystals that formed were separated by decantation, washed with cold hexane, and dried under a stream of argon. The yield of the solvate of compound **3** with two CH_2Cl_2 molecules was 0.18 g (86% with respect to the initial amount of cobalt). Found (%): C, 41.95; H, 5.67; N, 9.53. $C_{32}H_{54}Cl_4Co_2N_6O_8$. Calculated (%): C, 42.18; H, 5.93; N, 9.23. IR (KBr), ν/cm^{-1}: 3496 m, 3364 s, 3232 m, 2960 s, 2814 m, 2868 m, 1644 v.s, 1596 v.s, 1536 m, 1484 v.s, 1456 m, 1420 v.s, 1376 m, 1360 s, 1308 m, 1272 w, 1224 s, 1176 w, 1128 w, 1028 w, 936 w, 896 m, 788 s, 732 m, 696 w, 608 m, 424 w.

The crystals synthesized were suitable for X-ray diffraction analysis.

Bis(μ$_2$-2,6-diaminopyridino)tetra(μ$_2$-*O,O′*-trimethylacetato)di(η^2-trimethylacetato)(μ$_4$-oxo)tetracobalt(II), $Co_4(\mu_4\text{-}O)[\mu\text{-}C_5H_3N(NH_2)_2]_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2 \cdot MeCN$ (5). Acetonitrile (30 mL) was added to a mixture of $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ (0.46 g, 0.4 mmol) and 2,6-diaminopyridine (0.08 g, 0.8 mmol). The reaction mixture was stirred

Table 4. Crystallographic parameters of the complexes

Parameter	**2**·MeCN	**3**·2CH_2Cl_2	**5**·MeCN
Empirical formula	$C_{34}H_{55}Co_2N_5O_8$	$C_{32}H_{54}Co_2N_6O_8$	$C_{42}H_{71}Co_4N_7O_{13}$
Molecular weight	779.69	910.48	1117.78
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	10.902(2)	10.899(3)	13.7362(18)
b/Å	12.395(3)	12.642(3)	18.743(3)
c/Å	15.789(3)	15.374(4)	20.256(3)
α/deg	75.24(3)	90	90
β/deg	89.54(3)	93.518(5)	90.303(4)
γ/deg	84.00(3)	90	90
V/Å^3	2051.5(7)	2114.2(9)	5214.9(13)
Z	2	2	4
ρ_{calc}/g cm^{-3}	1.262	1.430	1.424
μ/cm^{-3}	0.858	1.089	1.314
Radiation		Mo-Kα (λ = 0.71073 Å)	
θ-2θ Scan range/deg	1.33—25.05	2.09—30.10	1.48—31.57
Number of measured reflections	4387	10802	14935
Number of reflections with $I \geq 2\sigma(I)$	4296	4183	6667
R_1	0.0583	0.0434	0.0628
wR_2	0.2081	0.1018	0.1335

under argon at 40 °C for 5 min until the reagents were completely dissolved. The solution was concentrated to 5 mL at 0.1 Torr and 20 °C and then allowed to crystallize at ~20 °C. After 24 h, the blue crystals that formed were separated by decantation, washed with cold hexane, and dried under a stream of argon. The yield of the solvate of compound **5** with MeCN was 0.34 g (61% with respect to the initial amount of cobalt). Found (%): C, 45.25; H, 6.27; N, 8.43. $C_{42}H_{71}Co_4N_7O_{13}$. Calculated (%): C, 45.09; H, 6.35; N, 8.77. IR (KBr), ν/cm^{-1}: 3400 s, 3376 s, 3332 s, 3228 m, 3220 m, 2960 s, 2924 m, 2868 m, 1700 m, 1648 m, 1616 s, 1568 v.s, 1484 v.s, 1456 s, 1416 s, 1372 m, 1360 m, 1320 w, 1228 m, 1140 w, 1124 w, 1088 w, 1016 w, 1004 w, 964 w, 940 w, 922 w, 900 w, 788 m, 756 w, 736 w, 612 m, 504 w, 436 w.

The crystals prepared in the synthesis were suitable for X-ray diffraction analysis.

X-ray diffraction study. The X-ray diffraction data for complex **2** were collected on an automated Syntex $P2_1$ diffractometer (graphite monochromator, 293 K). The X-ray diffraction data for complexes **3** and **5** were collected on an automated Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.[15] The semiempirical absorption corrections were applied.[16] The crystallographic parameters and details of structure refinement for all complexes are given in Table 4.

The structures of all complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms of the *tert*-butyl substituents of the trimethylacetate ligands and pyridine rings in the coordinated amine molecules were generated geometrically and refined using the riding model. All calculations were carried out using the SHELX97 program package.[17,18] The selected geometric parameters are given in Tables 1—3.

We thank the Head and staff of the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) for giving us the possibility to collect the X-ray data sets on a Smart diffractometer (Russian Foundation for Basic Research, Project No. 00-03-32807).

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 02-03-32453, 03-03-06287, and 01-03-32553).

References

1. M. A. Porai-Koshits and A. S. Antsyshkina, *Dokl. Akad. Nauk SSSR,* 1962, **146**, 1102 [*Dokl. Chem.*, 1962 (Engl. Transl.)].
2. A. A. Pasynskii, T. Ch. Idrisov, K. M. Suvorova, V. M. Novotortsev, V. V. Zelentsov, and V. T. Kalinnikov, *Dokl. Akad. Nauk SSSR,* 1975, **220**, 881 [*Dokl. Chem.*, 1975 (Engl. Transl.)].
3. M. Morooka, S. Ohba, M. Nakashima, T. Tokaii, Y. Muto, M. Kato, and O. W. Steward, *Acta Crystallogr., Sect. C*, 1992, **48**, 1888.
4. N. Hirashima, S. Nusebye, M. Kato, K. Maartmann-Moe, Y. Muto, M. Nakashima, and T. Tokaii, *Acta Chem. Scand., Ser. A*, 1990, **44**, 984.
5. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 409 [*Russ. Chem. Bull.*, 1999, **48**, 405 (Engl. Transl.)].

6. G. Smith, E. J. O´Reilly, and C. H. Kennard, *Aust. J. Chem*., 1983, **36**, 2175.
7. J. Catterick, M. B. Hursthouse, P. Thornton, and A. J. Welch, *J. Chem. Soc., Dalton Trans*., 1977, 223.
8. Y. Cui, F. Zheng, and J. Huang, *Acta Crystallogr., Sect. C*, 1999, **55**, 1067.
9. T. Hokelek and H. Necefoglu, *Acta Crystallogr., Sect. C*, 1997, **53**, 187.
10. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, M. A. Golubnichaya, P. V. Danilov, V. N. Ikorskii, Y. G. Shvedenkov, V. M. Novotortsev, and I. I. Moiseev, *Inorg. Chem*., 1999, **38**, 3764.
11. M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, L. T. Eremenko, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Zh. Neorg. Khim.,* 1999, **44**, 1479 [*Russ. J. Inorg. Chem*., 1999, **44**, 1479 (Engl. Transl.)].
12. C.-C. Wang, W.-C. Lo, C.-C. Chou, G.-H. Lee, J.-M. Chen, and S.-M. Peng, *Inorg. Chem*., 1998, **37**, 4059.
13. S.-Y. Lai, T.-W. Lin, Y.-H. Chen, C.-C. Wang, G.-H. Lee, M.-H. Yang, M.-K. Leung, and S.-M. Peng, *J. Am. Chem. Soc*., 1999, **121**, 250.
14. M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, M. O. Ponina, S. M. Deomidov, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim*., 1999, 1773 [*Russ. Chem. Bull*., 1999, **48**, 1751 (Engl. Transl.)].
15. *SMART (Control) and SAINT (Integration) Software, Version 5.0*, Bruker AXS Inc., Madison, WI, 1997.
16. G. M. Sheldrick, *SADABS, Program for Scanning and Correction of Area Detector Data*, University of Göttingen, Göttingen (Germany), 1997.
17. G. M. Sheldrick, *SHELX97, Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.
18. G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.

Received February 17, 2003;
in revised form July 11, 2003