

New cobalt trimethylacetate complexes with pyridine

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The reaction of the tetranuclear trimethylacetate complex $\text{Co}_4(\mu_3\text{-OH})_2(\mu\text{-OOCMe}_3)_4(\eta^2\text{-OOCMe}_3)_2(\text{EtOH})_6$ with pyridine in acetonitrile was studied. Two new compounds, viz., the hexanuclear cobalt(II) complex $\text{Co}_6\text{py}_4(\mu_3\text{-OH})_2(\mu\text{-OOCMe}_3)_{10}$ (25% yield) and the unusual ionic compound $[\text{Co}_3\text{py}_3(\mu_3\text{-O})(\mu\text{-OOCMe}_3)_6]^+[\text{Co}_4\text{py}(\mu_4\text{-O})(\mu\text{-OOCMe}_3)_7]^-$ (5% yield), were prepared. The structures of the new compounds were established by X-ray diffraction analysis.

Key words: cobalt complexes, trimethylacetate complexes, pyridine, X-ray diffraction analysis.

Earlier,¹ we have demonstrated that the reaction of pyridine with polymeric cobalt(II) trimethylacetate $[\text{Co}(\text{OH})_n(\text{OOCMe}_3)_{2-n}]_x$ (**1**) in toluene or acetonitrile led to degradation of **1** and formation of the binuclear cobalt(II) complex $\text{Co}_2\text{L}_4(\mu\text{-OH}_2)(\mu\text{-OOCMe}_3)_2(\text{OOCMe}_3)_2$ (**2**) containing the bridging water molecule. Refluxing of complex **2** in toluene afforded the binuclear complex $\text{Co}_2\text{L}_2(\mu\text{-OOCMe}_3)_4$ (**3**) with a Chinese-lantern-like structure. In the case of pyridine derivatives containing various hydrocarbon substituents in the α -position, cobalt and nickel carboxylate complexes were immediately transformed into dimers with a Chinese-lantern-like structure.^{2–4} Earlier, we have prepared analogous complexes⁵ by the reactions of compound **1** with 2-amino-5-methylpyridine and 2,6-diaminopyridine. However, the use of the basic hydroxotrimethylacetate complex $\text{Co}_4(\mu_3\text{-OH})_2(\mu\text{-OOCMe}_3)_4(\eta^2\text{-OOCMe}_3)_2(\text{EtOH})_6$ (**4**) as the starting reagent in the reaction with 2,6-diaminopyridine gave rise to the tetranuclear complex $\text{Co}_4(\mu_4\text{-O})(\mu_2\text{-(NH}_2)_2\text{C}_5\text{H}_3\text{N})_2(\text{OOCMe}_3)_6$. It should be emphasized that by basic carboxylate we mean a complex, which cannot quantitatively be transformed into dicarboxylate compounds through proton transfer from the coordinated acid molecule to the hydroxo group. Apparently, the use of basic carboxylates enables one to prepare new compounds, which are not generated by reactions with divalent transition metal dicarboxylates. Therefore, in the present work, we studied the reaction of pyridine with basic trimethyl-

acetate **4** in the search for unknown types of carboxylate complexes.

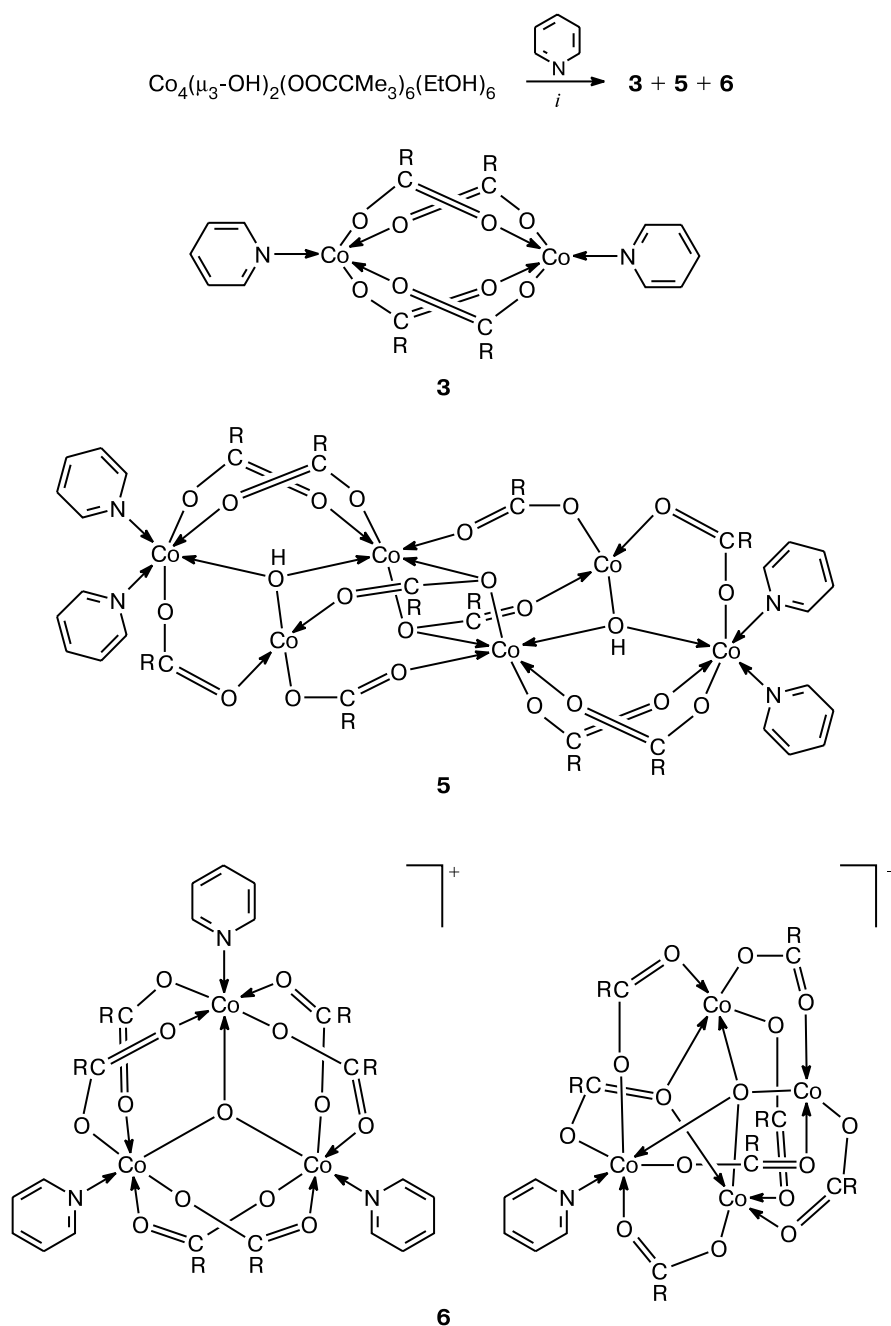
Results and Discussion

The reaction of pyridine with complex **4** under argon in a deficiency of the ligand ($\text{Co} : \text{py} = 4 : 1$) did not afford complex **2**; instead, complex **3** and two new compounds, viz., the hexanuclear cobalt(II) complex $\text{Co}_6\text{py}_4(\mu_3\text{-OH})_2(\mu\text{-OOCMe}_3)_{10}$ (**5**, 25% yield) and the unusual ionic compound $[\text{Co}_3\text{py}_3(\mu_3\text{-O})(\mu\text{-OOCMe}_3)_6]^+[\text{Co}_4\text{py}(\mu_4\text{-O})(\mu\text{-OOCMe}_3)_7]^-$ (**6**, 5% yield), were prepared (Scheme 1).

Compound **5** is structurally similar to the complex prepared by us earlier⁶ in which the coordinated molecule of trimethylacetic acid serves as a neutral ligand. Earlier, amino complexes with this structure of the metal carboxylate core have been unknown.

According to the results of X-ray diffraction analysis, six cobalt atoms in complex **5** are linked in two triangles through the tridentate-bridging hydroxy groups ($\text{Co}-\mu_3\text{-OH}$, 1.989(3)–2.092(3) Å) and three bridging trimethylacetate anions ($\text{Co}-\text{O}$, 1.973(4)–2.122(4) Å) (Fig. 1, Table 1). The Co(3) atom is coordinated by three oxygen atoms of three bridging carboxylate groups. Two of these groups serve as bridges between the Co(3) and Co(1) atoms ($\text{Co}(1)\dots\text{Co}(3)$, 3.485(1) Å), and the third carboxylate group serves as a bridge between the Co(3) and Co(2) atoms ($\text{Co}(3)\dots\text{Co}(2)$, 3.303(1) Å). The envi-

Scheme 1



R = CMe₃

Reagents and conditions: *i.* Ar, MeCN, 80 °C, Co_{at} : L = 4 : 1

ronment about the Co(3) atom is completed to an octahedron due to additional coordination by two pyridine molecules (Co—N, 2.142(5)—2.165(2) Å). The coordination environment about the Co(2) atom is a tetrahedron. Two above-mentioned triangles are linked to each other by the bridging and tridentate-bridging tri-

methylacetate groups. The Co(1) atom is linked to the Co(1A) atom and the Co(2A) atom of another triangle by the tridentate-bridging trimethylacetate anion (Co(1)...Co(1A), 3.476(1) Å; Co(1)...Co(2A), 3.998(1) Å; Co(1)...Co(2), 3.385(1) Å; Co(1)—O(9), 2.196(3) Å; Co(1A)—O(9), 2.179(4) Å; Co(2A)—O(10), 1.985(4) Å).

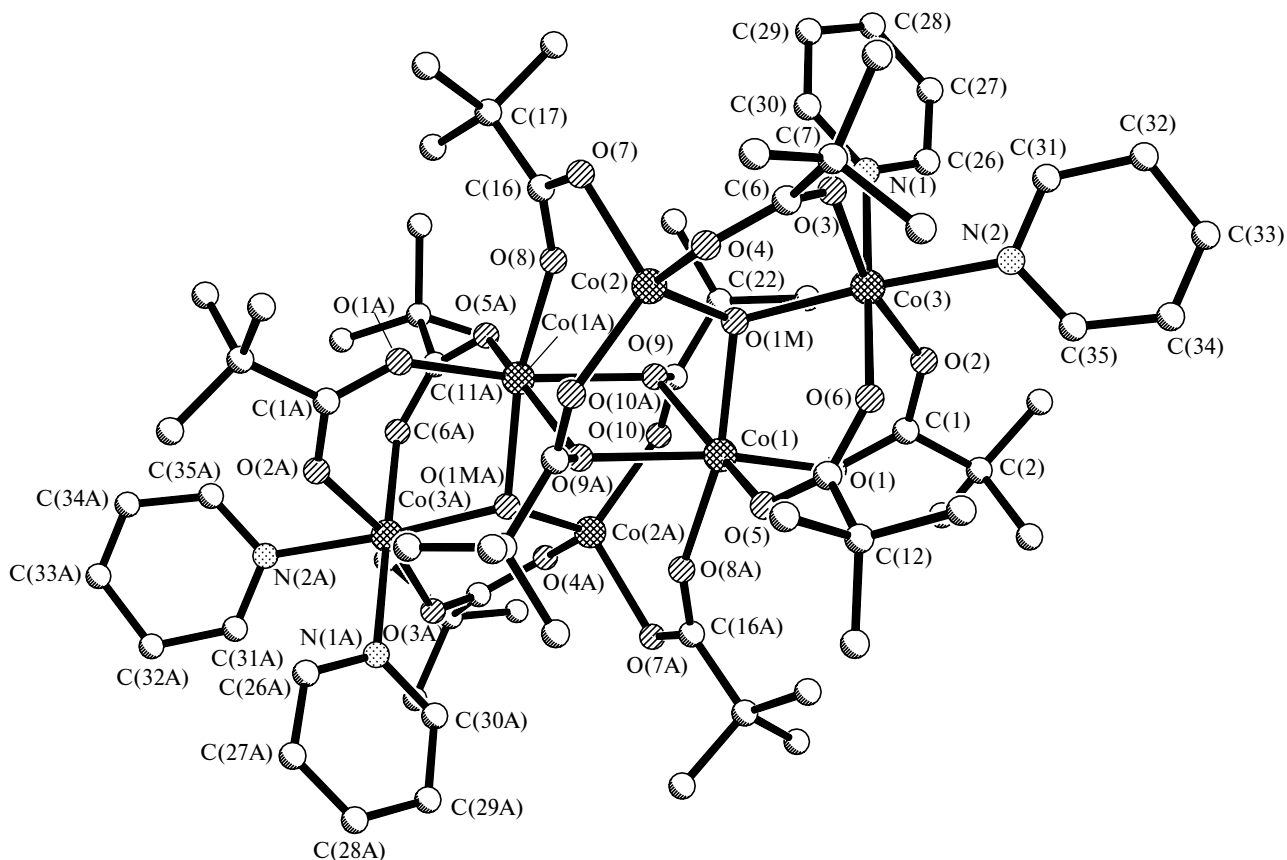


Fig. 1. Structure of complex 5.

Table 1. Selected geometric characteristics of complex 5

Bond	<i>d</i> /Å	Angle	ω /deg	Angle	ω /deg
Co(1)—Co(2)	3.385(1)	O(1M)—Co(1)—O(1)	99.9(1)	O(3)—Co(3)—O(6)	91.1(1)
Co(1)—O(1M)	2.092(3)	O(1M)—Co(1)—O(5)	92.1(1)	O(3)—Co(3)—N(1)	85.7(2)
Co(1)—O(1)	2.020(4)	O(1M)—Co(1)—O(8)	165.4(1)	O(3)—Co(3)—N(2)	86.8(2)
Co(1)—O(5)	2.032(3)	O(1)—Co(1)—O(5)	97.7(1)	O(6)—Co(3)—N(1)	176.8(2)
Co(1)—O(8)	2.077(4)	O(1)—Co(1)—O(8)	85.5(2)	O(6)—Co(3)—N(2)	88.3(2)
Co(1)—O(9)	2.350(3)	O(5)—Co(1)—O(8)	100.6(1)	N(1)—Co(3)—N(2)	90.7(2)
Co(1)—O(9)	2.196(3)	O(1M)—Co(2)—O(4)	117.2(1)	Co(1)—O(1M)—Co(2)	112.1(2)
Co(2)—Co(3)	3.303(1)	O(1M)—Co(2)—O(7)	109.9(1)	Co(1)—O(1M)—Co(3)	113.4(2)
Co(2)—O(1M)	1.989(3)	O(1M)—Co(2)—O(10)	112.5(1)	Co(2)—O(1M)—Co(3)	108.6(2)
Co(2)—O(4)	1.973(4)	O(4)—Co(2)—O(7)	101.5(2)	Co(1)—O(1)—C(1)	132.8(4)
Co(2)—O(7)	1.978(4)	O(4)—Co(2)—O(10)	99.4(2)	Co(3)—O(2)—C(1)	135.9(4)
Co(2)—O(10)	1.985(4)	O(7)—Co(2)—O(10)	115.9(2)	Co(3)—O(3)—C(6)	131.8(4)
Co(3)—O(1M)	2.078(3)	O(1M)—Co(3)—O(2)	95.5(1)	Co(2)—O(4)—C(6)	118.4(4)
Co(3)—O(2)	2.060(4)	O(1M)—Co(3)—O(3)	95.2(1)	Co(1)—O(5)—C(11)	129.3(3)
Co(3)—O(3)	2.122(4)	O(1M)—Co(3)—O(6)	88.3(1)	Co(3)—O(6)—C(11)	138.7(4)
Co(3)—O(6)	2.064(4)	O(1M)—Co(3)—N(1)	92.8(2)	Co(2)—O(7)—C(16)	111.4(3)
Co(3)—N(1)	2.165(4)	O(1M)—Co(3)—N(2)	176.0(2)	Co(1)—O(8)—C(16)	156.0(4)
Co(3)—N(2)	2.142(5)	O(2)—Co(3)—O(3)	168.6(1)	Co(2)—O(10)—C(21)	121.7(4)
		O(2)—Co(3)—O(6)	93.1(2)	Co(3)—N(1)—C(26)	121.7(4)
		O(2)—Co(3)—N(1)	89.8(2)	Co(3)—N(1)—C(30)	120.8(4)
		O(2)—Co(3)—N(2)	82.8(2)		

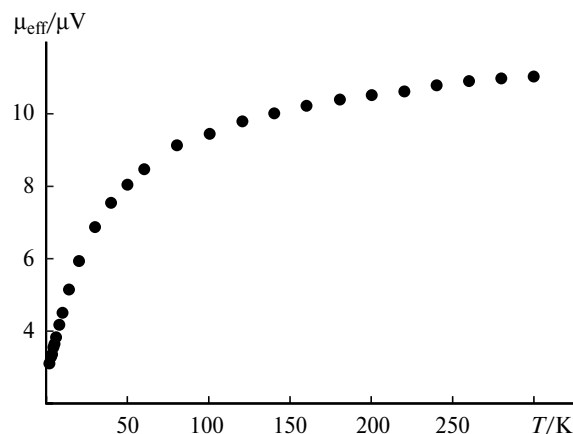


Fig. 2. Effective magnetic moment (μ_{eff}) of complex **5** vs. temperature.

The Co(2) atom is linked to the Co(1A) atom (Co(2)—O(7), 1.978(4) Å; Co(1A)—O(8), 2.077(4) Å) by the bidentate-bridging carboxylate anion.

Complex **5** exhibits the antiferromagnetic type of spin-spin interaction ($\mu_{\text{eff}} = 11.0\text{--}3.2 \mu_{\text{B}}$ (300—2 K) per overall molecule of the complex) (Fig. 2).

Compound **6** contains the trinuclear cobalt(III) carboxylate oxo cluster as the cation. This type of compounds is known for many 3d transition metals.^{7–10} In spite of the absence of an external oxidizing agent, oxidation of cobalt(II) was observed under the thermal reaction conditions. In this case, only the carboxylate anion can act as the oxidizing agent. In complex **6**, the tetranuclear cluster $[\text{Co}_4\text{py}(\mu_4\text{-O})(\mu\text{-OOCMe}_3)_7]^-$ serves as the anion. The latter has not been described earlier.

The structure of compound **6** was established for its solvate (1 : 1) with acetonitrile by X-ray diffraction analysis. The structure consists of two crystallographically independent cations (they have the crystallographic symmetry C_2 and are characterized by similar geometric parameters). These cations are trinuclear complexes in which the equivalent cobalt(III) atoms are linked to each other by the tridentate-bridging oxygen atom (Co...Co, 3.190(1)—3.194(1) Å; Co— $\mu_3\text{-O}$, 1.835(2)—1.859(2) Å) and six trimethylacetate bridges (Co—O, 1.884(4)—1.911(2) Å). The environment about the metal atoms is completed to an octahedron due to coordination by the pyridine molecules (Co—N, 1.991(4)—2.017(7) Å) (Fig. 3, Table 2). The anion is a new tetranuclear cobalt(II) trimethylacetate complex in which the metal atoms are linked to each other by the tetradentate-bridging oxygen atom (Co...Co, 2.895(1)—3.358(1) Å; Co— $\mu_4\text{-O}$, 1.874(4)—2.033(4) Å) and seven bridging trimethylacetate groups (Co—O, 1.958(5)—2.128(4) Å), one of which is tridentate-bridging (Co—O, 2.107(4)—2.286(4) Å) (Fig. 2). The coordination environment about the Co(2) atom is a tetrahedron. Two other cobalt atoms, *viz.*, Co(3) and Co(4), have a trigonal-bipyramidal coordination en-

vironment. The environment about the Co(1) atom is completed to an octahedron through coordination by the pyridine molecule (Co(1)—N, 2.170(6) Å).

As the temperature and reaction time were decreased, the yield of complex **5** increased to 41%, while the yield of complex **3** decreased to 28%, but compound **6** was not generated. Therefore, cobalt(III) compounds were not produced under milder conditions in an inert atmosphere.

2,2'-Dipyridyl is an α -derivative of pyridine. Earlier,¹¹ we have also observed the formation of different compounds in reactions of this ligand with complexes **1** and **4**.

Therefore, the use of basic carboxylates as the starting compounds in the reactions with organic amines makes it possible to synthesize new hydroxo- and oxocarboxylate complexes, which are not produced in reactions with the use of cobalt(II) dicarboxylates. The structure-forming ability of the μ_3 -oxygen atom is used for the formation of polynuclear carboxylate complexes by involving alkoxide bridges. However, the use of basic carboxylates provides the formation of tetrahedral metal fragments centered by the $\mu_4\text{-O}^{2-}$ anion.

Experimental

All operations associated with the synthesis were carried out under an inert atmosphere using anhydrous solvents. The starting cobalt trimethylacetate complex **4** was synthesized according to a known procedure.⁶ The IR spectra 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 Design magnetometer in the International Tomography Center of the Siberian Branch of the Russian Academy of Sciences.

Tetrapyridinocta($\mu_2\text{-O}, \text{O}'\text{-trimethylacetato}$)di($\mu_3\text{-O}, \text{O}'\text{-trimethylacetato}$)di($\mu_3\text{-hydroxo}$)hexacobalt(II), $\text{Co}_6\text{py}_4(\mu_3\text{-OH})_2(\mu\text{-OOCMe}_3)_8(\mu_3\text{-OOCMe}_3)_2$ (5**).** A. Pyridine (0.03 g, 0.38 mmol) was added to a solution of $\text{Co}_4(\mu_3\text{-OH})_2(\mu\text{-OOCMe}_3)_4(\eta^2\text{-OOCMe}_3)_2(\text{EtOH})_6$ (0.44 g, 0.38 mmol) in acetonitrile (30 mL) and the reaction mixture was stirred under argon at 80 °C for 0.5 h. The solution was filtered off from the precipitate that formed, concentrated at 0.1 Torr (20 °C) to 5 mL, and kept at –20 °C for 24 h. The blue-violet crystals of complex **3** (yield was 0.06 g (46%)) were separated from the solution by decantation. The mother liquor was kept at –20 °C for 4 days. The blue crystals that formed were separated from the solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of **5** was 0.04 g (25%). Found (%): C, 49.1; H, 6.7; N, 3.1. $\text{C}_{70}\text{H}_{112}\text{Co}_6\text{N}_4\text{O}_{22}$. Calculated (%): C, 49.01; H, 6.59; N, 3.27. IR (KBr), ν/cm^{-1} : 2960 s, 2928 s, 2864 m, 1608 v.s., 1564 v.s., 1524 w, 1484 v.s., 1448 m, 1420 v.s., 1372 s, 1360 s, 1260 w, 1228 s, 1152 w, 1100 w, 1072 m, 1040 m, 1012 w, 936 w, 892 m, 800 m, 788 m, 756 m, 700 s, 668 w, 624 m, 612 m, 468 s, 428 m.

Crystals of **5** were studied by X-ray diffraction analysis.

B. A solution of pyridine (0.05 g, 0.63 mmol) in acetonitrile (5 mL) was added to a solution of $\text{Co}_4(\mu_3\text{-OH})_2(\mu\text{-OOCMe}_3)_4(\eta^2\text{-OOCMe}_3)_2(\text{EtOH})_6$ (0.73 g, 0.63 mmol) in acetonitrile (30 mL) and the reaction mixture was stirred under

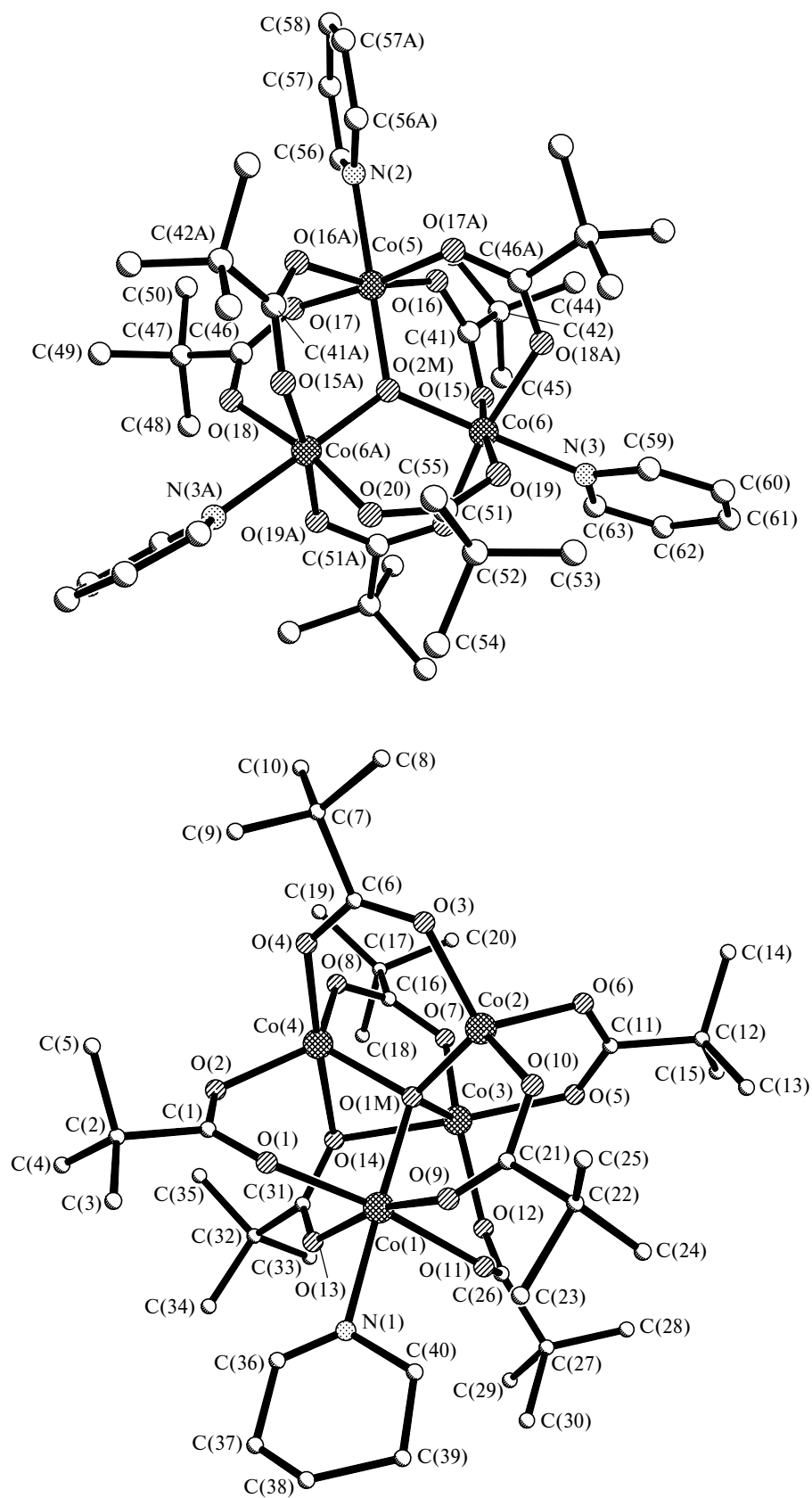


Fig. 3. Structure of compound 6.

Table 2. Selected geometric characteristics of compound **6**

Parameter	Value	Angle	ω/deg	Angle	ω/deg
Bond	<i>d</i> /Å	O(1M)—Co(1)—O(11)	94.44(14)	O(14)—Co(4)—Co(3)	49.75(10)
Co(1)—Co(2)	3.358(1)	O(13)—Co(1)—O(11)	91.36(16)	C(1)—O(1)—Co(1)	129.5(4)
Co(1)—O(1M)	2.033(4)	O(9)—Co(1)—O(11)	85.75(17)	Co(2)—O(1M)—Co(3)	112.43(17)
Co(1)—O(13)	2.107(4)	O(1)—Co(1)—O(11)	172.13(15)	Co(2)—O(1M)—Co(4)	114.41(17)
Co(1)—O(9)	2.108(5)	O(1M)—Co(1)—N(1)	178.3(2)	Co(3)—O(1M)—Co(4)	95.74(15)
Co(1)—O(1)	2.127(4)	O(13)—Co(1)—N(1)	83.5(3)	Co(2)—O(1M)—Co(1)	118.46(17)
Co(1)—O(11)	2.128(4)	O(9)—Co(1)—N(1)	84.1(3)	Co(3)—O(1M)—Co(1)	104.45(16)
Co(1)—N(1)	3.170(6)	O(1)—Co(1)—N(1)	87.7(2)	Co(4)—O(1M)—Co(1)	108.59(16)
Co(2)—Co(3)	3.176(1)	O(11)—Co(1)—N(1)	84.4(2)	C(1)—O(2)—Co(4)	120.0(4)
Co(2)—Co(4)	3.222(1)	O(1M)—Co(2)—O(10)	113.15(19)	C(6)—O(3)—Co(2)	126.6(4)
Co(2)—O(1M)	1.875(4)	O(1M)—Co(2)—O(6)	113.23(16)	C(6)—O(4)—Co(4)	135.7(4)
Co(2)—O(10)	1.958(5)	O(10)—Co(2)—O(6)	97.59(19)	C(11)—O(5)—Co(3)	130.4(4)
Co(2)—O(6)	1.978(4)	O(1M)—Co(2)—O(3)	112.23(16)	C(11)—O(6)—Co(2)	123.9(4)
Co(2)—O(3)	1.988(4)	O(10)—Co(2)—O(3)	110.61(19)	C(16)—O(7)—Co(3)	126.9(4)
Co(1)—Co(3)	3.146(1)	O(6)—Co(2)—O(3)	109.12(18)	C(16)—O(8)—Co(4)	124.7(4)
Co(3)—Co(4)	2.895(1)	O(1M)—Co(3)—O(7)	113.42(18)	C(21)—O(9)—Co(1)	140.6(6)
Co(3)—O(1M)	1.947(3)	O(1M)—Co(3)—O(12)	118.66(16)	C(21)—O(10)—Co(2)	123.3(5)
Co(3)—O(7)	1.969(4)	O(7)—Co(3)—O(12)	125.84(18)	C(26)—O(11)—Co(1)	128.0(4)
Co(3)—O(12)	1.983(4)	O(1M)—Co(3)—O(5)	103.51(15)	C(26)—O(12)—Co(3)	115.8(4)
Co(3)—O(5)	2.067(4)	O(7)—Co(3)—O(5)	91.41(18)	C(31)—O(13)—Co(1)	127.3(4)
Co(3)—O(14)	2.248(4)	O(12)—Co(3)—O(5)	90.28(17)	C(31)—O(14)—Co(3)	119.2(4)
Co(1)—Co(4)	3.240(1)	O(1M)—Co(3)—O(14)	81.93(15)	C(31)—O(14)—Co(4)	114.1(4)
Co(4)—O(1M)	1.957(3)	O(7)—Co(3)—O(14)	82.07(17)	Co(3)—O(14)—Co(4)	79.37(13)
Co(4)—O(2)	1.977(4)	O(12)—Co(3)—O(14)	91.15(15)	C(40)—N(1)—Co(1)	125.5(11)
Co(4)—O(8)	1.988(4)	O(5)—Co(3)—O(14)	172.84(16)	C(36)—N(1)—Co(1)	112.4(7)
Co(4)—O(4)	2.032(4)	O(1M)—Co(3)—Co(4)	42.27(10)	O(2M)—Co(5)—O(16)	96.84(11)
Co(4)—O(14)	2.286(4)	O(7)—Co(3)—Co(4)	79.71(14)	O(17)—Co(5)—O(16)	87.30(16)
Co(5)—Co(6)	3.190(1)	O(12)—Co(3)—Co(4)	133.62(11)	O(2M)—Co(5)—N(2)	180.000(3)
Co(5)—O(2M)	1.859(4)	O(5)—Co(3)—Co(4)	130.95(13)	O(17)—Co(5)—N(2)	87.13(11)
Co(5)—O(17)	1.895(4)	O(14)—Co(3)—Co(4)	50.89(11)	O(16)—Co(5)—N(2)	83.16(11)
Co(5)—O(16)	1.905(4)	O(1M)—Co(4)—O(2)	113.30(16)	O(2M)—Co(6)—O(15)	93.73(14)
Co(5)—N(2)	2.017(7)	O(1M)—Co(4)—O(8)	115.89(17)	O(2M)—Co(6)—O(19)	93.29(13)
Co(6)—O(2M)	1.835(2)	O(2)—Co(4)—O(8)	127.54(18)	O(15)—Co(6)—O(19)	172.96(16)
Co(6)—O(15)	1.887(4)	O(1M)—Co(4)—O(4)	101.96(16)	O(2M)—Co(6)—N(3)	179.06(17)
Co(6)—O(19)	1.893(4)	O(2)—Co(4)—O(4)	93.32(18)	O(15)—Co(6)—N(3)	85.56(17)
Co(6)—N(3)	1.991(4)	O(8)—Co(4)—O(4)	93.47(18)	O(19)—Co(6)—N(3)	87.41(17)
Angle	ω/deg	O(1M)—Co(4)—O(14)	80.74(14)	Co(6)—O(2M)—Co(5)	119.44(12)
O(1M)—Co(1)—O(13)	97.89(15)	O(2)—Co(4)—O(14)	91.34(16)	C(41)—O(15)—Co(6)	124.5(4)
O(1M)—Co(1)—O(9)	94.53(18)	O(8)—Co(4)—O(14)	79.70(16)	C(41)—O(16)—Co(5)	130.7(4)
O(1M)—Co(1)—O(1)	93.40(14)	O(4)—Co(4)—O(14)	173.15(17)	C(46)—O(17)—Co(5)	124.0(4)
O(13)—Co(1)—O(9)	167.44(19)	O(1M)—Co(4)—Co(3)	41.99(10)	C(51)—O(19)—Co(6)	127.3(3)
O(13)—Co(1)—O(1)	88.29(15)	O(2)—Co(4)—Co(3)	129.98(12)	C(56)—N(2)—Co(5)	120.0(4)
O(9)—Co(1)—O(1)	92.91(17)	O(8)—Co(4)—Co(3)	80.87(13)	C(59)—N(3)—Co(6)	121.5(4)
		O(4)—Co(4)—Co(3)	128.96(13)	C(63)—N(3)—Co(6)	120.8(4)

argon at 20 °C for 10 min. The solution was filtered off from the precipitate that formed, concentrated at 0.1 Torr (20 °C) to 10 mL, and kept at ~20 °C for 2 days. The blue crystals that formed were separated from the solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of **5** was 0.11 g (41% with respect to the initial amount of cobalt).

Tripyridinohexa(μ₂-O, O'-trimethylacetato)(μ₃-oxo)tricobalt(III) pyridinohexa(μ₂-O, O'-trimethylacetato)(μ₃-O, O'-trimethylacetato)(μ₄-oxo)tetracobaltate(II), [Co₃py₃(μ₃-O)(μ-OOCCMe₃)₆]⁺[Co₄py(μ₄-O)(μ-OOCCMe₃)₇]⁻ · CH₃CN (6**).**

A solution of pyridine (0.03 g, 0.38 mmol) was added to a solution of Co₄(μ₃-OH)₂(μ-OOCCMe₃)₄(η²-OOCCMe₃)₂(EtOH)₆ (0.44 g, 0.38 mmol) in acetonitrile (30 mL) and the reaction mixture was stirred under argon at 80 °C for 0.5 h. The solution was filtered off from the precipitate that formed, concentrated at 0.1 Torr (20 °C) to 5 mL, and kept at ~20 °C for 24 h. The blue-violet crystals of complex **3** were separated from the solution by decantation. The mother liquor was kept at ~20 °C for 4 days, filtered off from the blue crystals of complex **5** that formed, concentrated at 0.1 Torr (20 °C) to 1 mL, and kept at ~20 °C for 24 h. The dark-red crystals that formed were sepa-

Table 3. Principal crystallographic characteristics

Parameter	Characteristic	
	5	6 • MeCN
Empirical formula	C ₇₀ H ₁₁₂ Co ₆ N ₄ O ₂₂	C ₈₇ H ₁₄₀ Co ₇ N ₅ O ₂₈
<i>M</i>	1715.22	2116.55
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2/ <i>c</i>
Unit cell parameters		
<i>a</i> /Å	13.731(7)	34.570(7)
<i>b</i> /Å	21.251(8)	13.990(3)
<i>c</i> /Å	13.970(8)	23.130(5)
α /deg	90	90
β /deg	98.881(19)	105.55(3)
γ /deg	90	90
<i>V</i> /Å ³	4028(3)	10777(4)
<i>Z</i>	2	4
Number of reflections	16904	49029
Number of reflections with $F^2 > 2\sigma(I)$	8306	21951
ρ_{calc} /g cm ⁻³	1.414	1.304
μ /cm ⁻¹	1.278	1.120
<i>R</i> ₁	0.0612	0.0719
<i>wR</i> ₂	0.1048	0.1591

rated by decantation, washed with cold hexane, and dried under a stream of argon. The yield of **6**•CH₃CN was 0.01 g (5%). Found (%): C, 49.20; H, 6.90; N, 3.40. C₈₇H₁₄₀Co₇N₅O₂₈. Calculated (%): C, 49.37; H, 6.68; N, 3.31. IR (KBr), ν/cm⁻¹: 29656 s, 2924 m, 2872 m, 1664 m, 1600 v.s, 1528 w, 1484 v.s, 1448 s, 1420 v.s, 1372 s, 1360 s, 1224 s, 1152 w, 1072 m, 1044 m, 1016 w, 896 m, 788 s, 756 s, 696 s, 668 w, 636 w, 612 s, 424 m.

The resulting crystals were studied by X-ray diffraction analysis.

X-ray diffraction study. The X-ray diffraction data for complexes **5** and **6** were collected on an automated Bruker AXS SMART diffractometer equipped with a CCD detector (graphite monochromator, 110 K (for **5**) and 120 K (for **6**), ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.¹² The semiempirical absorption correction was applied.¹³ The structures of both complexes were solved by direct methods with the use of the SHELXS97 program package¹⁴ and refined anisotropically by the full-matrix least-squares method using the SHELXL97 program package¹⁵ (the positions of the H atoms were fixed with $U_{\text{H}} = 0.08 \text{ \AA}^2$). The crystallographic parameters are given in Table 3.

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