Mono- and polynuclear Co^{II} complexes with 2-hydroxy-6-methylpyridine*

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The reaction of 2-hydroxy-6-methylpyridine with $Co(NO_3)_2 \cdot 6H_2O$ or $Co(F_3CSO_3)_2 \cdot 6H_2O$ in the absence of a deprotonating agent produces the mononuclear complexes $Co(HL)_4(NO_3)_2$ or $Co(HL)_4(F_3CSO_3)_2$ (HL is 6-methyl-2-pyridone), respectively. In the presence of triethylamine, the reaction affords the trinuclear complex $Co_3(HL)_2(L)_4(NO_3)_2$ or the heptanuclear dicationic complex $[Co_7L_{12}] \cdot (F_3CSO_3)_2 \cdot 4MeCN$ in the case of cobalt nitrate or cobalt trifluoromethanesulfonate, respectively. When HL is deficient, the replacement of the trimethylacetate anions in polymeric cobalt pivalate $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ gives rise to the hexanuclear complex $Co_6(\mu_3\text{-}OH)_2(\eta^2,\mu_3\text{-}L)_2(\mu\text{-}OOCCMe_3)_8(HOOCCMe_3)_4$, whereas the $HLCo_6(\mu_3\text{-}OH)(\eta^2,\mu_3\text{-}L)_3(\eta^2,\mu\text{-}L)(\mu_3\text{-}L)(\mu_3\text{-}OOCCMe_3)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)$ complex is generated when HL is present in excess. The structures of the reaction products were established by X-ray diffraction.

Key words: 2-hydroxy-6-methylpyridine, cobalt complexes, X-ray diffraction study.

Polynuclear complexes with high-spin transition metals generally contain fragments, in which the metal centers are linked to each other by bridging organic groups. The nature of the bridging ligands has a substantial effect on the structure formation and physical properties of the resulting compounds. Three-atom bridging ligands (for example, $RCOO^-$ or $N(R)C(R^1)O^-$) are widespread in such systems as convenient linking groups.[1—12] The presence of different electron-donating atoms in the three-atom bridging system is one of the main parameters responsible for the strength of binding with the metal center or the degree of electron density delocalization in the M—L—M fragment. From this point of view, the carboxylate group —OCO— formally differs from the —NCO— group. Hence, one would expect that the replacement of bridges would lead to a change in the geometric parameters of the resulting molecules or variations of their magnetic properties.

In the present study, we synthesized such compounds containing cobalt atoms by the replacement of acido ligands in the starting inorganic salts or polynuclear carboxylates (pivalates) containing high-spin Co^{II} atoms by 2-hydroxy-6-methylpyridine (**1**). It should be noted that 2-hydroxypyridine exists in the free state predominantly as pyridone[13,14] and, depending on the medium, can be either coordinated as a neutral molecule or deprotonated to generate the 2-pyridonate anion. Transition metal salts with strong acid anions hold promise for the synthesis of complexes with neutral molecules in nonaqueous media, because weak acid anions can act as deprotonating agents.

Results and Discussion

Cobalt(II) nitrate and trifluoromethanesulfonate, $CoX_2 \cdot 6H_2O$ (X = NO_3 (**2**) or CF_3SO_3 (**3**)) were used as the staring reagents. Cobalt trifluoromethanesulfonate was prepared by the reaction of $CoCO_3$ with trifluoromethanesulfonic acid by analogy with the synthesis of the known complex $Ni(CF_3SO_3)_2 \cdot 6H_2O$.[15] The reaction of **1** with **2** in the absence of deprotonating agents in ethanol or acetonitrile produces the mononuclear complex $Co(HL)_4(NO_3)_2$ (**4**, HL is 6-methyl-2-pyridone) (Scheme 1).

X-ray diffraction study demonstrated that the HL ligands in molecule **4** (Fig. 1, Table 1) are present as 6-methyl-2-pyridone and are coordinated to the Co^{II} atom through the oxygen atoms (Co—O(1), 2.115(3) Å; Co—O(2), 2.082(3) Å), and the nitrate groups are terminal (Co—O, 2.094(2) Å; N—O, 1.221(3) Å). The protons

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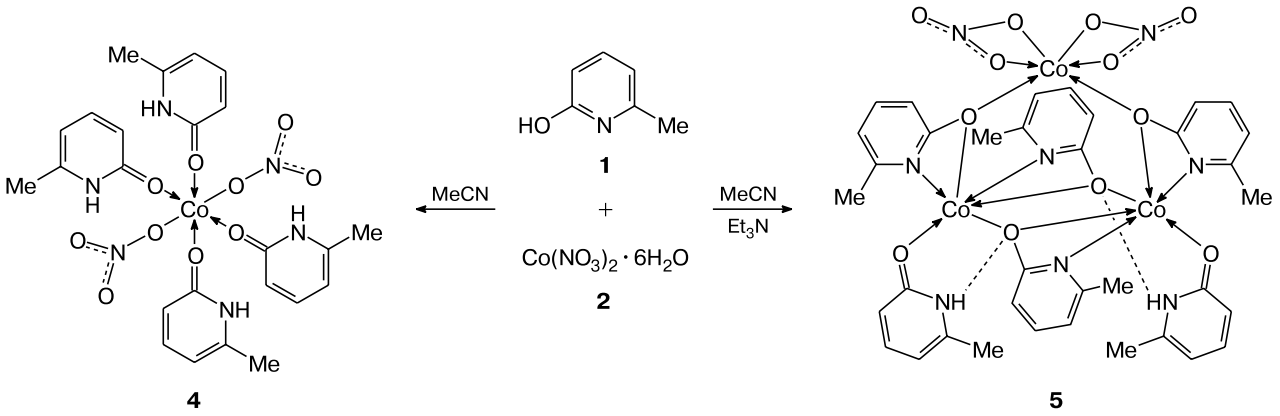
Scheme 1



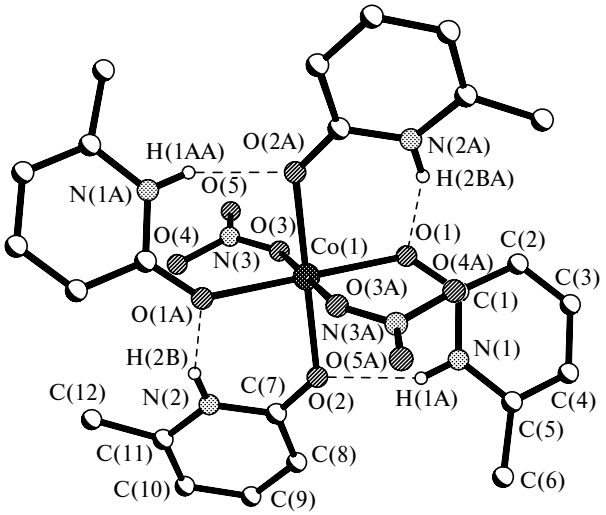


Fig. 1. Structure of mononuclear complex **4**.

of the NH groups are involved in hydrogen bonding with the oxygen atoms of the pyridone ligand (N—H...O, 1.997(3)—2.030(3) Å), resulting in the formation of the pseudocyclic system consisting of four coordinated pyridone molecules.

In the presence of triethylamine having deprotonating ability, the reaction (reagent ratio **2** : HL = 1 : 2) produces a polynuclear structure, *viz.*, the trinuclear complex $Co_3(HL)_2(L)_4(NO_3)_2$ (**5**) (see Scheme 1). X-ray diffraction study demonstrated that the distances between all Co^{II} atoms in the trinuclear molecule are nonbondend (Co(2)...Co(1), 3.875(2) Å; Co(1)...Co(1A), 3.182(2) Å), and the metal atoms are linked to each other by four chelate bridging anions L (Fig. 2, Table 2). The environment of one Co^{II} atom is formed by two chelate NO_3^- anions (Co(2)—O, 2.046(3) Å and 2.333(3) Å) and two bridging oxygen atoms (Co(2)—O(1), 1.973(2) Å) of the anion L. Each bridging oxygen atom is coordinated to one of the two other equivalent Co^{II} atoms (Co(1)—O(1), 2.243(2) Å) and forms a four-membered chelate ring with the metal atom through coordination of the pyridine fragment (Co(1)—N(1), 2.051(3) Å). The coordination environment of these cobalt atoms involves also the additional chelate ring (Co(1)—N(2), 2.081(3) Å; Co(1)—O(2), 2.329(2) Å), in which the oxygen atoms form a bridge between the equivalent metal atoms (Co(1)—O(2A), 2.064(2) Å). The sixth coordination site at each of these two Co^{II} atoms is occupied by the neutral pyridone molecule (Co(1)—O(3), 2.033(2) Å).

The geometric characteristics of the chelate bridging 2-pyridonate anions in the trinuclear complex molecule are different. The chelate bridging metallocycles bound to the $Co(NO_3)_2$ fragment are virtually planar, which are

Table 1. Selected geometric characteristics of complexes **4** and **6**

Parameter	**4**	**6**
Bond	*d*/Å	
Co(1)—O(1)	2.115(3)	2.082(3)
Co(1)—O(2)	2.082(3)	2.094(3)
Co(1)—O(3)	2.094(2)	2.122(4)
O(1)—C(1)	1.269(3)	1.265(5)
O(2)—C(7)	1.276(3)	1.263(5)
O(3)—N(3)	1.221(3)	—
S(1)—O(3)	—	1.458(4)
N(1)—H(1A)...O(2)	2.030(3)	2.032(3)
N(2)—H(2B)...O(1)	1.997(3)	1.983(3)
Angle	ω/deg	
O(1)—Co(1)—O(2)	89.23(7)	91.60(12)
O(1)—Co(1)—O(2A)	90.77(7)	88.40(13)
O(1)—Co(1)—O(3A)	95.86(9)	89.57(16)
O(1)—Co(1)—O(3)	84.14(9)	90.43(16)
O(2)—Co(1)—O(3)	88.01(11)	87.38(16)
O(2)—Co(1)—O(3A)	91.99(11)	92.62(16)
C(1)—O(1)—Co(1)	135.26(17)	128.3(3)
C(7)—O(2)—Co(1)	130.64(16)	135.2(3)
N(3)—O(3)—Co(1)	136.1(2)	—
S(1)—O(3)—Co(1)	—	146.2(3)

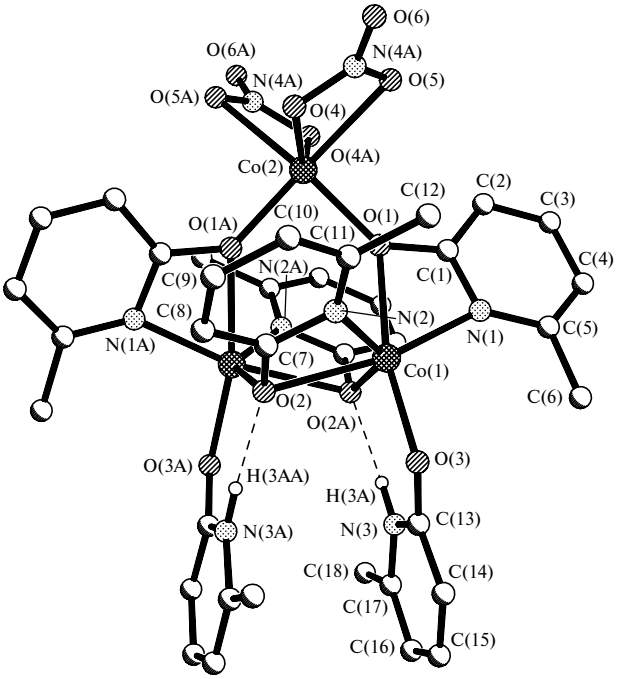


Fig. 2. Structure of complex **5**.

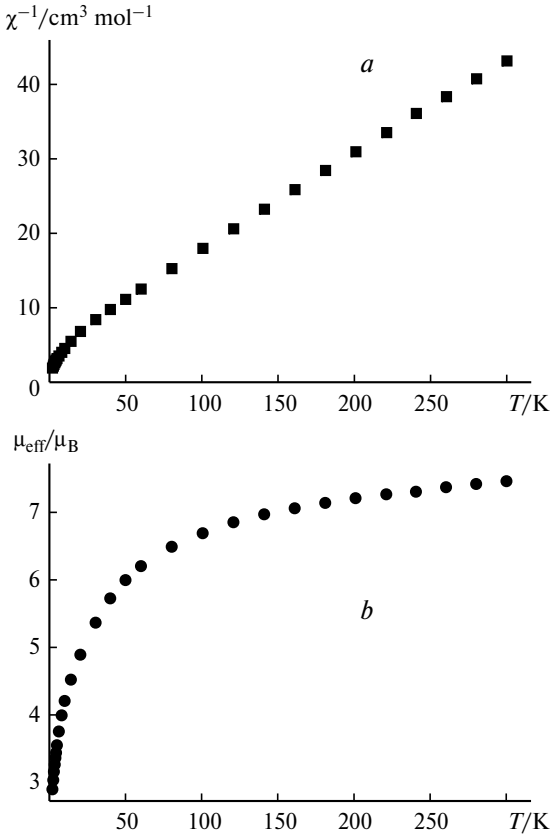


Fig. 3. Magnetic properties of complex **5**. Plots of the magnetic susceptibility (*a*) and the effective magnetic moment (*b*) *vs.* the temperature.

apparently indicative of a high degree of electron density delocalization in such systems. Unlike these systems, analogous rings located between two equivalent Co(1) and Co(1A) atoms coordinated by the pyridone ligands are nonplanar and contain a tetrahedral oxygen atom (see Fig. 2). This is facilitated by hydrogen bonding between the bridging oxygen atoms and the hydrogen atoms of the N—H fragment of the pyridone ligand (O(2)...H—N, 2.665(4) Å).

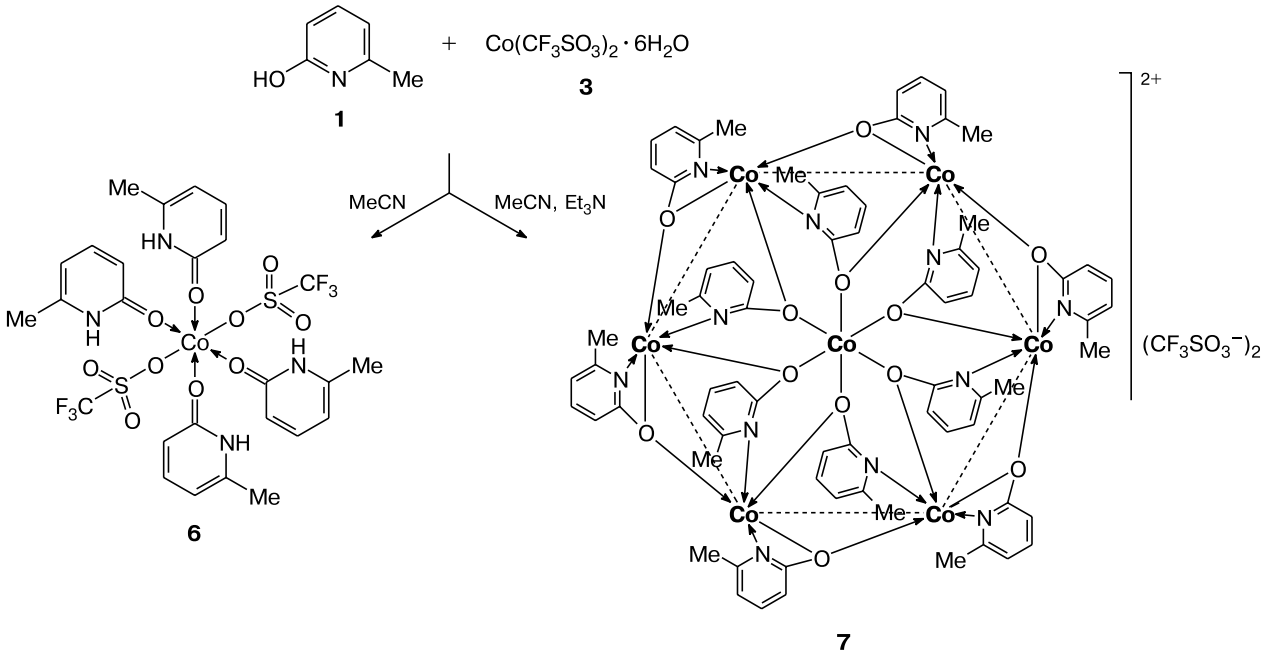
Since molecule **5** contains high-spin Co^{II} atoms, the complex is paramagnetic. The effective magnetic moment of compound **5** monotonically decreases from 7.46 to 2.90 μ_B in the temperature range of 300—2 K (Fig. 3) due to antiferromagnetic spin-orbital and spin-spin interactions.

Since the ligand is only partially deprotonated in the case of cobalt nitrate, we used cobalt(II) trifluoromethanesulfonate as the starting compound. The trifluoromethanesulfonate (triflate) anions belong to labile ligands in coor-

Table 2. Selected geometric characteristics of complex **5**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Co(1)—O(3)	2.033(2)	O(3)—Co(1)—N(1)	105.78(11)	N(2)—Co(1)—O(2)	60.35(10)
Co(1)—N(1)	2.051(3)	O(3)—Co(1)—O(2A)	95.28(10)	O(1)—Co(1)—O(2)	105.57(8)
Co(1)—O(2A)	2.064(2)	O(3)—Co(1)—N(2)	101.69(10)	O(1A)—Co(2)—O(1)	87.78(13)
Co(1)—N(2)	2.081(3)	O(3)—Co(1)—O(2)	86.86(9)	O(1)—Co(2)—O(4)	111.97(11)
Co(1)—O(1)	2.243(2)	O(3)—Co(1)—O(1)	167.56(9)	O(1)—Co(2)—O(5)	89.56(9)
Co(1)—O(2)	2.329(2)	N(1)—Co(1)—O(2)	167.01(10)	O(1)—Co(2)—O(4A)	104.31(10)
Co(2)—O(1)	1.973(3)	N(1)—Co(1)—O(2A)	95.69(11)	O(1)—Co(2)—O(5A)	159.83(10)
Co(2)—O(4)	2.046(3)	N(1)—Co(1)—O(1)	61.78(10)	O(4)—Co(2)—O(5)	58.47(9)
Co(2)—O(5)	2.333(3)	N(1)—Co(1)—N(2)	118.30(11)	O(4)—Co(2)—O(4A)	128.93(15)
Co(1)...Co(2)	3.875(2)	O(2A)—Co(1)—N(2)	135.26(10)	O(4)—Co(2)—O(5A)	88.05(11)
Co(1)...Co(1A)	3.182(2)	O(2A)—Co(1)—O(1)	86.52(9)	O(5)—Co(2)—O(5A)	99.53(14)
N(3)—H(3A)...O(2A)	2.665(4)	O(2A)—Co(1)—O(2)	79.89(9)	Co(1A)—O(2)—Co(1)	92.64(9)
		N(2)—Co(1)—O(1)	85.37(10)	Co(2)—O(1)—Co(1)	133.49(11)

Scheme 2



dination compounds of transition metals and are readily replaced with the N- and O-donor organic molecules thus moving to the outer sphere. However, the reactions of compounds **3** and **1** in the absence of deprotonating agents proceed analogously to the reaction of cobalt nitrate (**2**) (Scheme 2). As a result, regardless of the reagent ratio, the reaction produces the $Co(HL)_4(F_3CSO_3)_2$ complex (**6**), in which both triflate groups are retained in the inner sphere of the metal atom, and the N-donor ligands exist in the pyridone form (see Scheme 2).

X-ray diffraction study demonstrated that mononuclear complex **6** (Fig. 4, see Table 1) is structurally similar to its nitrate analog **4**. The molecule also contains a pseudocyclic system formed by four pyridone ligands (Co—O(1), 2.082(3) Å; Co—O(2), 2.094(3) Å) through N—H...O hydrogen bonds (1.983(3)—2.032(3) Å).

When triethylamine was present as the deprotonating agent in the reaction mixture, the reaction produced an ionic compound, which was isolated from MeCN as the solvate $[Co_7L_{12}] \cdot (F_3CSO_3)_2 \cdot 4MeCN$ (**7**) (see Scheme 2, Fig. 5). In the heptanuclear dication $[Co_7L_{12}]^{2+}$ of compound **7**, intrasphere triflate ligands are absent, and all these ligands are located in the outer sphere.

X-ray diffraction study demonstrated that the metal core of the cluster dication in **7** is virtually planar. Six Co^{II} atoms form a regular hexagon, whose center is occupied by the seventh cobalt atom. A similar structure has been found earlier in the cationic complex $[Na\{CoL_2\}_6]^+(OOCCCH_3)^-$. However, the latter complex contains the main-group metal atom (sodium atom)

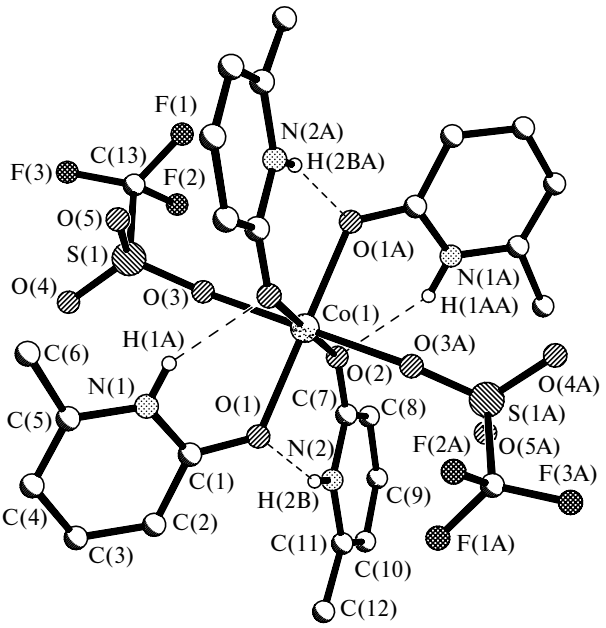


Fig. 4. Structure of complex **6**.

as the central ion in an octahedral environment formed by oxygen atoms.[16]

The metal—metal distances in dication **7** are nonbonded (Co...Co in the hexagon, 3.401(2)—3.419(2) Å; Co_{cent}...Co, 3.389(2)—3.419(2) Å). The central cobalt atom in the dication is linked to the peripheral cobalt atoms through six chelate bridging 2-pyridonate anions (Co—O, 2.030(3)—2.045(2) Å; see Fig. 5, *a*, *b*, Table 3).

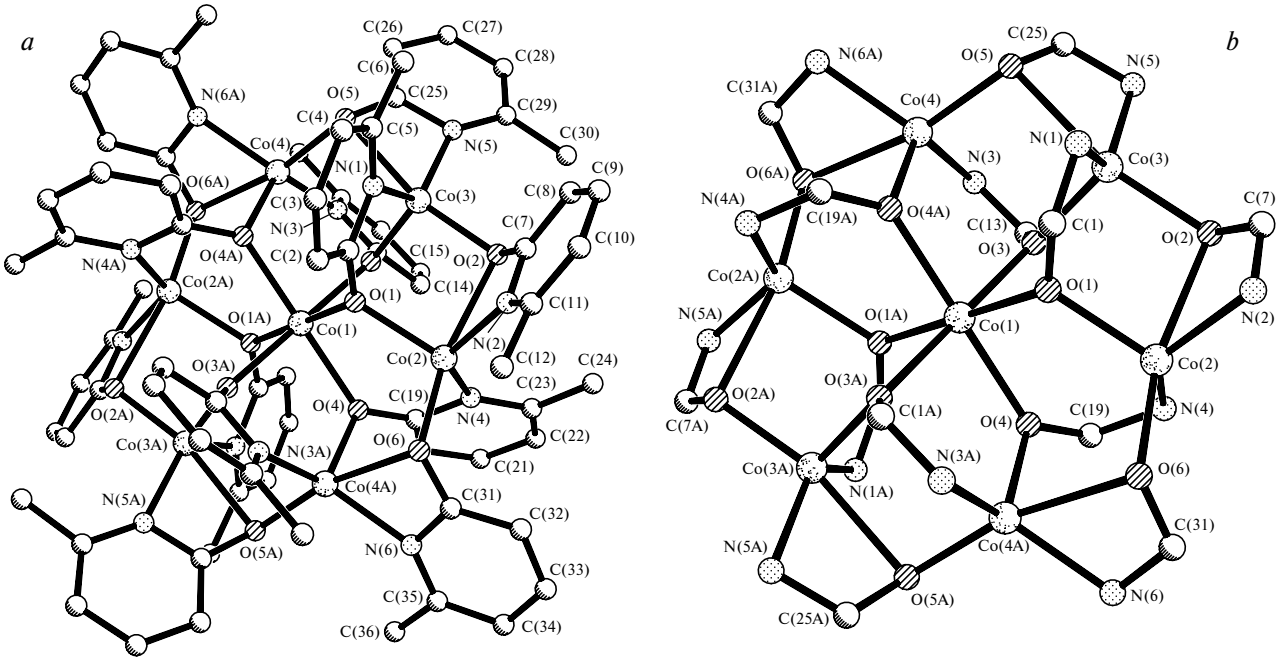


Fig. 5. Structure of the cation in compound **7**: *a*, the molecular structure; *b*, the metal core of the dication.

The environment of the central cobalt atom is formed by six equivalent oxygen atoms (Co(1)—O, 2.096(2)—2.121(2)Å) and can be described as an octahedron slightly distorted due to a decrease in the distance between two opposite faces located parallel to the plane through the metal atoms. These faces (upper and lower) are virtually equilateral triangles (O...O, 3.12—3.14 Å). The O—Co—O angles for the oxygen atoms belonging to the upper and lower faces of the coordination polyhedron and simultaneously belonging to one lateral face are acute

Table 3. Selected geometric characteristics of complex **7**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Co(1)—O(4)	2.096(2)	O(4A)—Co(1)—O(4)	180.0(1)	O(3)—Co(3)—N(1)	116.71(11)
Co(1)—O(1)	2.102(2)	O(4A)—Co(1)—O(1)	95.10(10)	O(3)—Co(3)—O(5)	85.33(9)
Co(1)—O(3)	2.121(2)	O(4)—Co(1)—O(1)	84.90(10)	N(5)—Co(3)—N(1)	128.09(13)
Co(2)—O(6)	1.988(2)	O(4)—Co(1)—O(3A)	83.57(9)	N(5)—Co(3)—O(5)	60.44(10)
Co(2)—N(2)	2.033(3)	O(4)—Co(1)—O(3)	96.43(9)	N(1)—Co(3)—O(5)	87.39(10)
Co(2)—O(1)	2.034(2)	O(1)—Co(1)—O(3A)	95.79(9)	O(5)—Co(4)—N(3)	95.87(11)
Co(2)—N(4)	2.042(3)	O(1)—Co(1)—O(3)	84.21(9)	O(5)—Co(4)—O(4A)	104.31(10)
Co(2)—O(2)	2.394(3)	O(6)—Co(2)—N(2)	108.4 (11)	O(5)—Co(4)—N(6A)	109.38(12)
Co(3)—O(2)	1.981(2)	O(6)—Co(2)—O(1)	104.89(10)	O(5)—Co(4)—O(6A)	167.21(9)
Co(3)—O(3)	2.030(3)	O(6)—Co(2)—O(2)	166.55(9)	N(3)—Co(4)—O(6A)	86.35(10)
Co(3)—N(5)	2.059(3)	O(6)—Co(2)—N(4)	95.53(11)	O(4A)—Co(4)—N(3)	115.98(11)
Co(3)—N(1)	2.071(3)	N(2)—Co(2)—O(1)	101.31(11)	O(4A)—Co(4)—N(6A)	100.83(10)
Co(3)—O(5)	2.361(3)	N(2)—Co(2)—N(4)	127.34(12)	O(4A)—Co(4)—O(6A)	85.88(9)
Co(4)—O(5)	1.987(3)	N(2)—Co(2)—O(2)	60.37(10)	N(6A)—Co(4)—N(3)	128.24(11)
Co(4)—O(4A)	2.045(2)	O(1)—Co(2)—N(4)	117.10(11)	N(6A)—Co(4)—O(6A)	60.31(11)
Co(4)—N(6A)	2.054(3)	O(1)—Co(2)—O(2)	85.52(9)	Co(1)—O(1)—Co(2)	110.04(12)
Co(4)—N(3)	2.058(3)	N(4)—Co(2)—O(2)	86.97(11)	Co(1)—O(3)—Co(3)	110.83(11)
Co(4)—O(6A)	2.355(3)	O(2)—Co(3)—O(3)	104.42(10)	Co(1)—O(4)—Co(4A)	111.31(11)
Co(1)...Co(2)	3.389(2)	O(2)—Co(3)—N(5)	108.22(11)	Co(2)—O(6)—Co(4A)	102.75(10)
Co(1)...Co(3)	3.418(2)	O(2)—Co(3)—N(1)	95.88(11)	Co(3)—O(2)—Co(2)	102.35(10)
Co(1)...Co(4)	3.419(2)	O(2)—Co(3)—O(5)	166.78(10)	Co(4)—O(5)—Co(3)	102.91(11)
Co(2)...Co(4A)	3.401(2)	O(3)—Co(3)—N(5)	101.09(11)		
Co(2)...Co(3)	3.419(2)				
Co(3)...Co(4)	3.408(2)				

(83.57(9)—84.90(9)°); the corresponding angles for the oxygen atoms belonging to the upper and lower faces of the antiprism are obtuse (95.1(1)—96.43(9)°). The polyhedra of the other cobalt atoms are strongly distorted trigonal bipyramids. If the atoms forming the largest X—Co—Y angle (X and Y = O or N, *i.e.*, any atom involved in the donor environment) are considered as the vertices of two triangular pyramids, which form the trigonal bipyramid, these are oxygen atoms through which all six coordination polyhedra of the peripheral cobalt atoms are linked to form a closed ring (O—Co—O, 166.55(9)—167.21(9)°). As a result, seven coordination polyhedra form a symmetrical structure resembling a merry-go-round (see Fig. 5, *b*).

Magnetic measurements showed that the effective magnetic moment of compound **7** monotonically decreases from 11.59 to 9.44 μ_B in the temperature range of 300—8 K due to antiferromagnetic spin-orbital and spin-spin interactions (Fig. 6). Then the magnetic moment increases to 9.54 μ_B due, apparently, to the appearance of an intermolecular ferromagnetic exchange interaction, which generally becomes stronger at helium temperatures due to a unit cell contraction, and, finally, the magnetic moment again decreases to 9.11 μ_B (2 K).

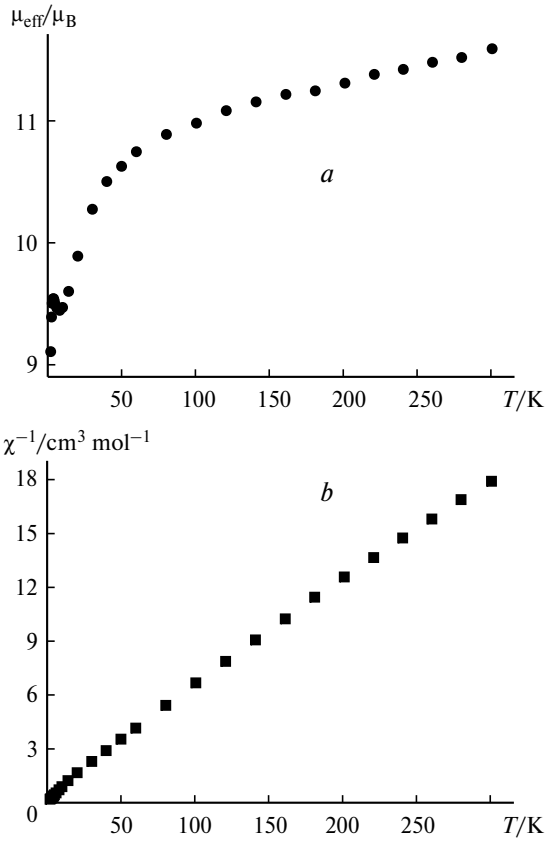
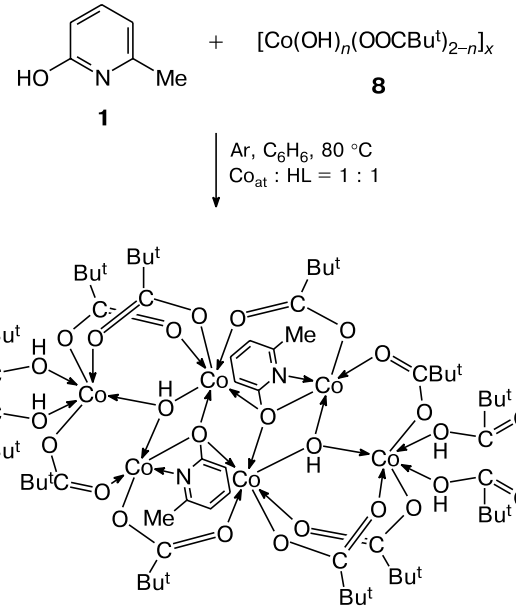


Fig. 6. Plots $\mu_{eff}(T)$ (*a*) and $1/\chi(T)$ (*b*) for compound **7** (C = 14.97(13), θ = –3.8(7), χ_0 = 0.0066(4)).

Unlike strong acid anions, anions of weak alkyl-substituted carboxylic acids in transition metal complexes generally cause deprotonation of hydroxypyridine even in the absence of additional deprotonating agents and generation of the corresponding anion capable of replacing carboxylate ligands. For polynuclear carboxylate systems, this process can be used in the synthesis of mixed-ligand compounds. Actually, the reaction of polymeric cobalt pivalate $[Co(OH)_n(\mu\text{-}OOCCMe_3)_{2-n}]_x$ (**8**) with **1** in acetonitrile (Co : **1** = 2 : 1) led to the partial replacement of pivalate anions to form the antiferromagnetic hexanuclear mixed-ligand complex $Co_6(\mu_3\text{-}OH)_2(\eta^2,\mu_3\text{-}L)_2(\mu\text{-}OOCCMe_3)_8(HOOCCMe_3)_4$ (**9**) (Scheme 3).

Scheme 3



9

According to X-ray diffraction data, the metal carboxylate core of cluster **9** is structurally similar to that of the known hexanuclear complex $Co_6(\mu_3\text{-}OH)_2(\mu_3\text{-}OOCCMe_3)_2(\mu_2\text{-}OOCCMe_3)_8(HOOCCMe_3)_4$ (**10**), which we have synthesized earlier[17] by the reaction of a stoichiometric amount of pivalic acid with polymeric cobalt pivalate.

$$[Co(OH)_n(\mu\text{-}OOCCMe_3)_{2-n}]_x + HOOCCMe_3 \rightarrow Co_6(\mu_3\text{-}OH)_2(\mu_3\text{-}OOCCMe_3)_2(\mu_2\text{-}OOCCMe_3)_8(HOOCCMe_3)_4$$

10

The difference is that compound **9** contains the chelate bridging hydroxypyridinate anions (Fig. 7, Table 4) (Co(3)—N(1), 2.032(6) Å; Co(3)—O(13), 2.390(5) Å;

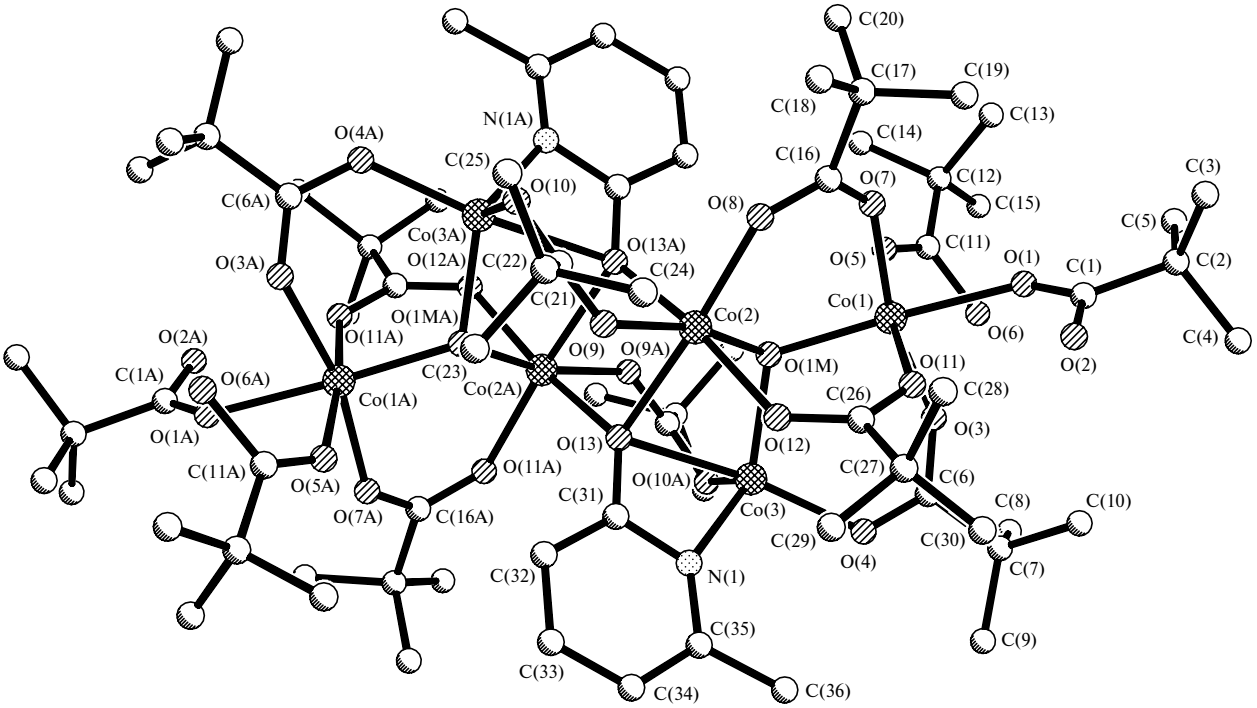


Fig. 7. Structure of complex **9**.

Co(2)—O(13A), 2.081(5) Å) instead of two μ_3-pivalate anions, through which three cobalt atoms are linked in compound **10**. There are two types of metal atoms in molecule **9**: four Co^{II} atoms are in a pseudoequatorial environment and two Co^{II} atoms have a distorted trigonal-pyramidal coordination. Cluster **9** formally consists of two triangles $Co_3(\mu_3\text{-}OH)L(OOCCMe_3)_4(HOOCCMe_3)_2$ (Co...Co,

Table 4. Selected geometric characteristics of complex **9**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Co(1)—O(7)	1.991(5)	O(7)—Co(1)—O(1M)	97.51(19)	O(12)—Co(2)—O(1M)	86.02(18)
Co(1)—O(1M)	2.014(4)	O(7)—Co(1)—O(3)	166.3(2)	O(13)—Co(2)—O(1M)	86.52(18)
Co(1)—O(3)	2.087(5)	O(1M)—Co(1)—O(3)	94.42(19)	O(9)—Co(2)—O(13)	86.90(18)
Co(1)—O(11)	2.117(5)	O(7)—Co(1)—O(11)	93.3(2)	O(8)—Co(2)—O(13)	176.00(19)
Co(1)—O(1)	2.144(5)	O(1M)—Co(1)—O(11)	92.08(18)	O(12)—Co(2)—O(13)	89.88(19)
Co(1)—O(5)	2.155(6)	O(3)—Co(1)—O(11)	92.9(2)	O(13)—Co(2)—O(13A)	80.2(2)
Co(2)—O(9)	2.040(5)	O(7)—Co(1)—O(1)	85.5(2)	O(1M)—Co(2)—O(13)	80.72(17)
Co(2)—O(8)	2.058(5)	O(1M)—Co(1)—O(1)	176.90(19)	O(10)—Co(3)—O(4)	100.9(2)
Co(2)—O(12)	2.077(5)	O(3)—Co(1)—O(1)	82.48(19)	O(10)—Co(3)—O(1M)	100.0(2)
Co(2)—O(13A)	2.081(5)	O(11)—Co(1)—O(1)	88.26(19)	O(4)—Co(3)—O(1M)	107.37(19)
Co(2)—O(1M)	2.094(4)	O(7)—Co(1)—O(5)	85.1(2)	O(10)—Co(3)—N(1)	112.2(2)
Co(2)—O(13)	2.246(5)	O(1M)—Co(1)—O(5)	94.35(19)	O(4)—Co(3)—N(1)	103.8(2)
Co(3)—O(10A)	1.996(5)	O(3)—Co(1)—O(5)	87.3(2)	O(1M)—Co(3)—N(1)	129.2(2)
Co(3)—O(4)	1.996(5)	O(11)—Co(1)—O(5)	173.52(19)	O(10)—Co(3)—O(13)	95.70(18)
Co(3)—O(1M)	1.999(5)	O(1)—Co(1)—O(5)	85.4(2)	O(4)—Co(3)—O(13)	160.60(19)
Co(3)—N(1)	2.032(6)	O(9)—Co(2)—O(8)	91.61(19)	O(1M)—Co(3)—O(13)	79.17(16)
Co(3)—O(13)	2.390(5)	O(9)—Co(2)—O(12)	92.56(19)	N(1)—Co(3)—O(13)	60.1(2)
Co(1)...Co(3)	3.385(1)	O(8)—Co(2)—O(12)	93.89(19)	Co(3)—O(1M)—Co(1)	115.0(2)
Co(2A)...Co(2)	3.311(1)	O(9)—Co(2)—O(13)	92.82(18)	Co(3)—O(1M)—Co(2)	99.88(19)
Co(2)...Co(3)	3.133(1)	O(8)—Co(2)—O(13)	96.18(19)	Co(1)—O(1M)—Co(2)	113.18(19)
		O(12)—Co(2)—O(13)	168.43(19)	Co(2)—O(13)—Co(3)	114.7(2)
		O(9)—Co(2)—O(1M)	167.53(19)	Co(2)—O(13)—Co(3)	84.97(15)
		O(8)—Co(2)—O(1M)	100.84(18)		

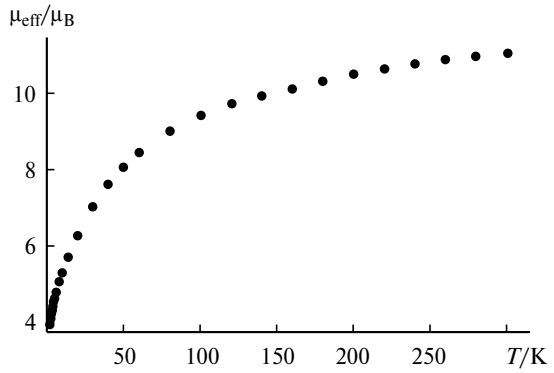


Fig. 8. Magnetic properties of complex **9**.

3.133(1)—3.385(1) Å), which are linked to each other by the bridging oxygen atoms of the deprotonated hydroxypyridine ligands. The planes of the Co_3 triangles are parallel to one another.

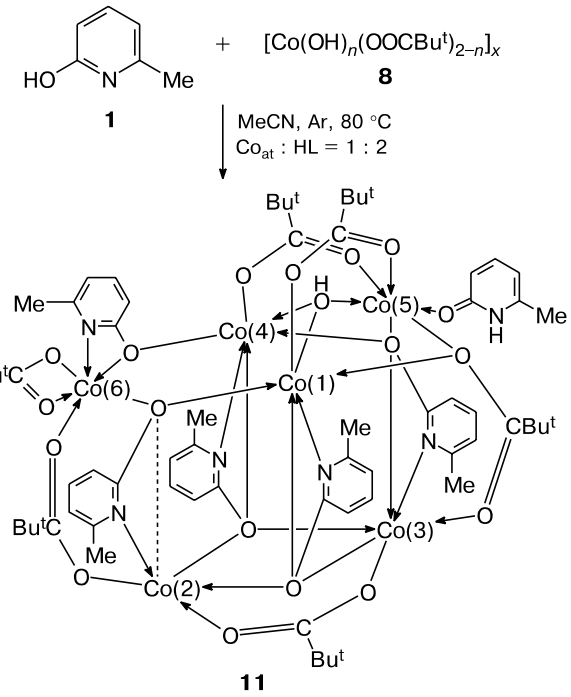
According to the results of magnetic measurements, the behavior of hexanuclear complex **9** (Fig. 8) is similar to that of trinuclear complex **5** (see Fig. 3). The effective magnetic moment of complex **9** monotonically decreases from 11.04 to 3.94 μ_B in the temperature range of 300—2 K due to antiferromagnetic spin-orbital and spin-spin interactions.

At a higher concentration of ligand **1** (ratio Co : HL = 1 : 2), the reaction proceeds further. In MeCN, the pivalate ligands are further replaced to form another antiferromagnetic hexanuclear complex $HLCo_6(\mu_3\text{-}OH)(\eta^2,\mu_3\text{-}L)_3(\eta^2,\mu\text{-}L)(\mu_3\text{-}L)(\mu_3\text{-}OOCCMe_3)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)$ (**11**) (Scheme 4).

In complex **11**, the cobalt atoms are linked to each other by five trimethylacetate bridges (Co—O, 1.986(5)—2.245(5) Å), five tridentate bridging hydroxypyridinate anions (Co—N, 2.082(6)—2.153(8) Å; Co—O, 2.050(5)—2.213(5) Å), and the μ_3-OH group (Co—OH, 2.021(4)—2.042(5) Å), the distances between the metal atoms being nonbonded (Co...Co, 3.033(1)—3.769(1) Å) (Fig. 9, Table 5). In cluster **11**, the Co atoms have an octahedral coordination, although one of these atoms, Co(2), is involved in one very long Co—O distance (O(17)—Co(2), 2.460(4) Å). Compared to cluster **9**, molecule **11** is twisted. As a result, only two metal atoms contain nonbridging ligands. The Co(6) atom is coordinated by the chelate pivalate group (Co—O, 2.090(5)—2.189(5) Å), and the Co(4) atom is coordinated by the pyridone ligand (Co(5)—O(13), 2.077(5) Å) (see Fig. 9). From the viewpoint of the ligand environment, all cobalt atoms in **11** are nonequivalent, resulting in overall asymmetry.

Formally, the metal core of cluster **11** can be described as a bicapped tetrahedron, whose base is the metal tetrahedron Co(1)Co(2)Co(3)Co(4) (Co(1)...Co(2), 3.769(5) Å; Co(2)...Co(3), 3.174(5) Å; Co(3)...Co(4),

Scheme 4



3.638(5) Å; Co(1)...Co(4), 3.680(5) Å). The Co(6) (Co(6)...Co(1), 3.695(5) Å; Co(6)...Co(4), 3.816(5) Å; Co(6)...Co(2), 3.569(5) Å) and Co(5) atoms (Co(5)...Co(1), 3.067(5) Å; Co(5)...Co(3), 3.843(5) Å; Co(5)...Co(4), 3.033(5) Å) are located above the Co(1)Co(2)Co(4) and Co(1)Co(3)Co(4) faces, respectively (Fig. 10).

The differences in the structure of the metal core of cluster **11** and in the number and nature of exchange channels compared to mixed-ligand complex **9** are responsible for the difference in the magnetic characteristics of these compounds. Compound **11** exhibits antiferromagnetic properties in the temperature range of 300—14 K. The effective magnetic moment of compound **11** decreases from 10.88 to 8.06 μ_B (Fig. 11). Then the magnetic moment increases to 8.14 μ_B (6 K) due apparently to the appearance of an intermolecular ferromagnetic exchange interaction. A further decrease in the temperature leads to a decrease in the magnetic moment to 7.25 μ_B (2 K).

The appearance of a peak in the magnetic moment *vs* temperature plot for compound **11** at helium temperatures upon twisting of the metal core of the cluster presumably correlates with the analogous effect observed for heptanuclear dication **7** (see Fig. 6) containing the cyclic metal core with the inner cobalt atom. In spite of the difference in the symmetry of the metal core, both structures (**7** and **11**) contain the largest number of high-spin cobalt atoms (seven in **7** and six in **11**) exchange-coupled

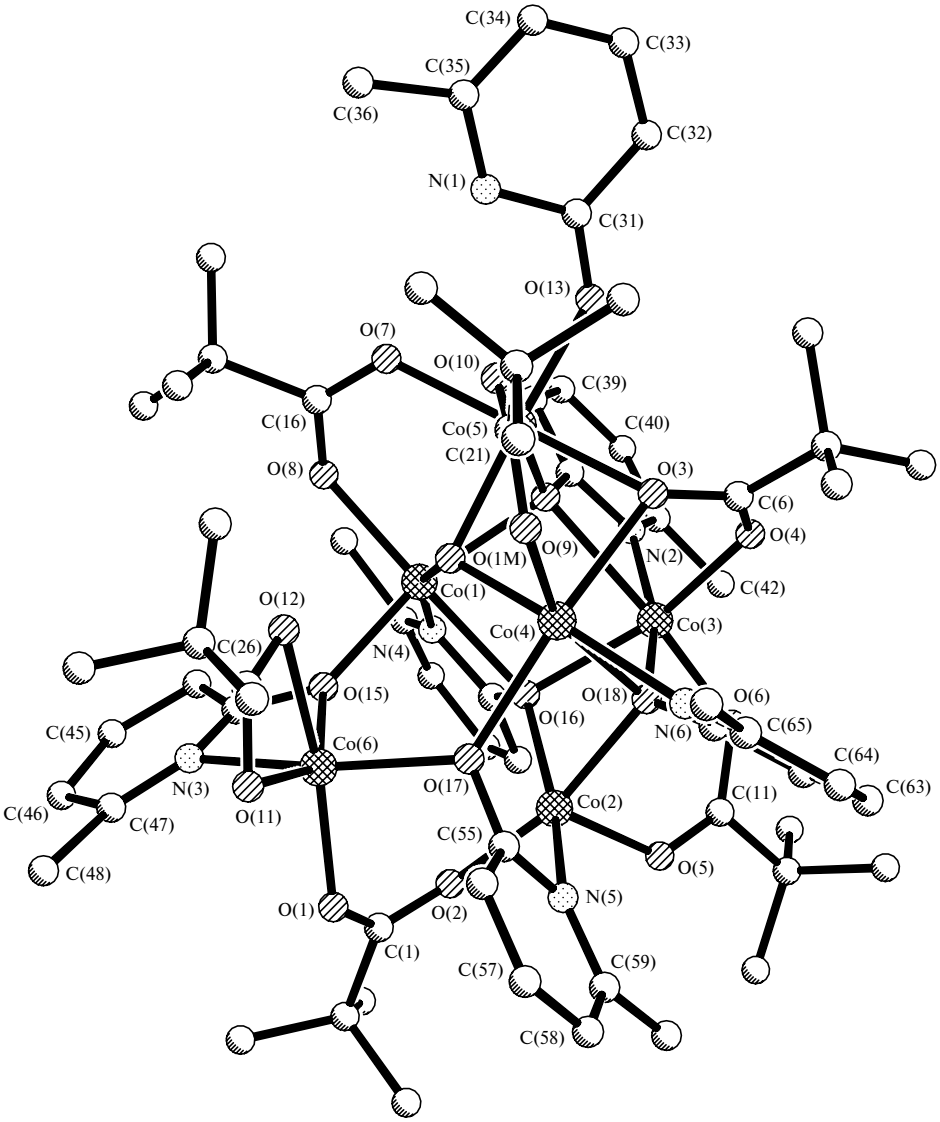


Fig. 9. Molecular structure of cluster **11**.

with more that two adjacent metal atoms (through bridging ligands). An increase in the number of high-spin ions exchange-coupled with each other formally increases the probability of the appearance of orthogonal interacting magnetic orbitals and, as a result, the appearance of a ferromagnetic spin-spin exchange. Therefore, the larger the number of interacting high-spin "magnetic neighbors" in the molecule, the more probable the observation of the ferromagnetic properties. This dependence was observed for at least the polynuclear systems under study containing high-spin Co^{II} atoms coordinated by hydroxypyridinate anions.

Experimental

The complexes were synthesized under argon with the use of commercial anhydrous solvents. New compounds were synthesized starting from cobalt(II) nitrate, cobalt(II) trifluoromethanesulfonate, and 2-hydroxy-6-methylpyridine purchased from Fluka. The starting polymeric pivalate $[Co(OH)_n(\mu\text{-}OOCCMe_3)_{2-n}]_x$ was synthesized according to a known procedure.[2] The IR spectra were recorded on a Specord M-80 instrument in KBr pellets. The static magnetic susceptibility χ was measured on a SQUID MPMS-5S Quantum Desing magnetometer in the temperature range of 300—2 K. The effective magnetic moments were calculated by the equation $\mu_{eff} = (8\chi T)^{1/2}$.[18]

Dinitrato[tetrakis(6-methyl-2-pyridone)]cobalt(II), $[Co(NO_3)_2(HL)_4]$ (4, L = MeC_5H_3NO). A solution of 2-hydroxy-6-methylpyridine (0.2250 g, 2.062 mmol) in acetonitrile (10 mL) was added to a solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.1500 g, 0.516 mmol) in acetonitrile (10 mL). The reaction mixture was stirred at room temperature for 15 min and concentrated to 2 mL (50 °C, 0.1 Torr). Then toluene (1 mL) was added, and the mixture was allowed to crystallize at room temperature for 12 h. The pale-pink crystals that precipitated were washed with tolu-

Table 5. Selected geometric characteristics of complex **11**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Co(1)—O(8)	2.027(5)	Co(5)—O(1M)	2.042(5)	N(4)—Co(1)—O(8)	104.9(2)	O(1M)—Co(4)—O(18)	102.30(18)
Co(1)—O(1M)	2.031(4)	Co(5)—O(10)	2.062(5)	N(4)—Co(1)—O(14)	94.5(2)	O(1M)—Co(4)—O(3)	85.36(18)
Co(1)—O(15)	2.050(5)	Co(5)—O(13)	2.077(5)	N(4)—Co(1)—O(15)	94.0(2)	O(10)—Co(5)—O(13)	94.3(2)
Co(1)—N(4)	2.125(6)	Co(5)—O(7)	2.079(5)	N(4)—Co(1)—O(16)	61.81(19)	O(13)—Co(5)—O(7)	89.2(2)
Co(1)—O(14)	2.146(5)	Co(5)—O(14)	2.097(5)	O(1M)—Co(1)—N(4)	160.5(2)	O(13)—Co(5)—O(14)	94.54(19)
Co(1)—O(16)	2.237(5)	Co(5)—O(3)	2.161(5)	O(1M)—Co(1)—O(8)	93.66(19)	O(13)—Co(5)—O(3)	92.48(19)
Co(2)—O(2)	1.986(5)	Co(6)—O(1)	2.047(5)	O(1M)—Co(1)—O(14)	76.90(18)	O(1M)—Co(5)—O(3)	87.08(18)
Co(2)—O(5)	2.034(5)	Co(6)—O(11)	2.090(5)	O(1M)—Co(1)—O(15)	89.72(19)	O(1M)—Co(5)—O(7)	92.03(19)
Co(2)—N(5)	2.082(6)	Co(6)—O(17)	2.102(5)	O(1M)—Co(1)—O(16)	99.17(17)	O(1M)—Co(5)—O(10)	93.33(19)
Co(2)—O(18)	2.100(5)	Co(6)—O(15)	2.108(5)	O(2)—Co(2)—N(5)	94.7(2)	O(1M)—Co(5)—O(13)	172.3(2)
Co(2)—O(16)	2.107(4)	Co(6)—N(3)	2.153(8)	O(2)—Co(2)—O(5)	96.6(2)	O(1M)—Co(5)—O(14)	77.78(18)
Co(3)—O(4)	2.018(5)	Co(6)—O(12)	2.189(5)	O(2)—Co(2)—O(18)	166.8(2)	O(1)—Co(6)—N(3)	86.0(3)
Co(3)—O(6)	2.024(5)	Co(1)...Co(2)	3.769(5)	O(2)—Co(2)—O(16)	90.46(19)	O(11)—Co(6)—N(3)	99.2(3)
Co(3)—O(16)	2.123(5)	Co(1)...Co(3)	3.376(5)	O(5)—Co(2)—N(5)	105.3(2)	O(11)—Co(6)—O(12)	62.0(2)
Co(3)—N(2)	2.128(6)	Co(1)...Co(4)	3.680(5)	O(5)—Co(2)—O(18)	91.09(19)	O(11)—Co(6)—O(17)	97.8(2)
Co(3)—O(18)	2.148(4)	Co(1)...Co(5)	3.067(5)	O(5)—Co(2)—O(16)	91.60(18)	O(12)—Co(6)—N(3)	94.7(2)
Co(3)—O(14)	2.333(5)	Co(1)...Co(6)	3.695(5)	O(16)—Co(2)—N(5)	161.6(2)	O(15)—Co(6)—N(3)	60.9(2)
Co(4)—O(1M)	2.021(4)	Co(2)...Co(3)	3.174(5)	O(16)—Co(2)—O(18)	78.60(17)	O(17)—Co(6)—N(3)	162.4(2)
Co(4)—O(9)	2.043(5)	Co(2)...Co(4)	3.407(5)	O(18)—Co(2)—N(5)	93.6(2)	O(17)—Co(6)—O(12)	89.30(19)
Co(4)—N(6)	2.092(6)	Co(2)...Co(6)	3.569(5)	O(4)—Co(3)—N(2)	95.5(2)	O(17)—Co(6)—O(15)	101.94(18)
Co(4)—O(17)	2.177(5)	Co(3)...Co(4)	3.638(5)	O(4)—Co(3)—O(14)	86.97(18)	Co(4)—O(1M)—Co(1)	130.5(2)
Co(4)—O(18)	2.213(5)	Co(4)...Co(5)	3.033(5)	O(6)—Co(3)—O(14)	160.16(18)	Co(4)—O(1M)—Co(5)	96.6(2)
Co(4)—O(3)	2.245(5)			O(6)—Co(3)—N(2)	103.3(2)	Co(1)—O(1M)—Co(5)	97.7(3)
				O(14)—Co(3)—N(2)	59.65(19)	Co(5)—O(3)—Co(4)	86.99(18)
				O(16)—Co(3)—N(2)	96.04(19)	Co(5)—O(14)—Co(1)	92.55(18)
				O(16)—Co(3)—O(14)	78.74(17)	Co(5)—O(14)—Co(3)	120.2(2)
				O(18)—Co(3)—O(14)	105.19(17)	Co(1)—O(14)—Co(3)	97.73(18)
				O(18)—Co(3)—N(2)	164.6(2)	Co(1)—O(15)—Co(6)	125.4(2)
				O(3)—Co(4)—N(6)	91.9(2)	Co(2)—O(16)—Co(3)	97.26(19)
				O(9)—Co(4)—N(6)	101.5(2)	Co(2)—O(16)—Co(1)	120.4(2)
				O(17)—Co(4)—N(6)	91.0(2)	Co(3)—O(16)—Co(1)	101.48(19)
				O(18)—Co(4)—N(6)	62.1(2)	Co(6)—O(17)—Co(4)	126.2(2)
				O(1M)—Co(4)—N(6)	164.4(2)	Co(2)—O(18)—Co(3)	96.69(19)
				O(1M)—Co(4)—O(9)	93.58(19)	Co(2)—O(18)—Co(4)	104.4(2)
				O(1M)—Co(4)—O(17)	85.79(18)	Co(3)—O(18)—Co(4)	113.1(2)

ene and dried at 20 °C (0.1 Torr). The yield was 0.25 g (79% based on $Co(NO_3)_2 \cdot 6H_2O$). Found (%): C, 46.60; H, 4.70; N, 13.68. $C_{24}H_{28}CoN_6O_{10}$. Calculated (%): C, 46.54; H, 4.56; N, 13.57. IR (KBr), ν/cm^{-1}: 3544 w, 3416 w, 3372 w, 3156 w, 2964 w, 2856 w, 1640 v.s, 1616 v.s, 1548 s, 1456 s, 1420 s, 1384 s, 1316 s, 1260 m, 1160 s, 1040 m, 1004 m, 876 w, 856 w, 812 m, 800 m, 744 m, 728 m, 608 w, 572 s, 532 m, 428 m.

The crystals were used for X-ray diffraction study.

Bis(nitrato-*O*,*O*′)tetrakis(μ$_2$,η^2-6-methyl-2-pyridonato)bis(η^2-6-methyl-2-pyridone)tricobalt(II), $Co_3(NO_3)_2(HL)_2(L)_4$ (5, L = MeC_5H_3NO). A solution of 2-hydroxy-6-methylpyridine (0.1125 g, 1.031 mmol) in acetonitrile (10 mL) was added to a solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.1500 g, 0.516 mmol) in acetonitrile (10 mL). Triethylamine (0.2 mL) was added to the resulting solution. The reaction mixture was stirred at room temperature for 30 min and concentrated to dryness at 30 °C (0.1 Torr). Then MeCN (5 mL) was added and dissolution was performed at room temperature. The resulting pink-red solution was kept at room temperature for 12 h. The dark-pink crystals that precipitated were washed with cold acetonitrile and dried at 20 °C (0.1 Torr). The yield was 0.21 g (43% based on the starting amount of $Co(NO_3)_2 \cdot 6H_2O$). Found (%): C, 45.53; H, 4.20; N, 11.86. $C_{36}H_{38}Co_3N_8O_{12}$. Calculated (%): C, 45.45; H, 4.03; N, 11.78. IR (KBr), ν/cm^{-1}: 3748 w, 3476 w, 3384 w, 2976 w, 2864 w, 2740 m, 2680 m, 2492 m, 1688 m, 1668 s, 1640 s, 1620 s, 1612 s, 1568 s, 1556 s, 1636 m, 1520 m, 1456 s, 1384 v.s, 1300 s, 1276 s, 1164 s, 1032 s, 1000 s, 796 m, 748 m, 732 m, 640 m, 612 m, 572 m, 532 m, 504 w, 428 w.

The crystals were used for X-ray diffraction study.

Ditrifluoromethanesulfonato[tetrakis(6-methyl-2-pyridone)]cobalt(II), $[Co(CF_3SO_3)_2(HL)_4]$ (6, L = MeC_5H_3NO). A solution of 2-hydroxy-6-methylpyridine (0.1100 g, 1.009 mmol) in acetonitrile (10 mL) was added to a solution of $Co(CF_3SO_3)_2 \cdot 6H_2O$ (0.1173 g, 0.252 mmol) in acetonitrile (10 mL). The resulting solution was stirred at room temperature for 15 min and concentrated to 2 mL (50 °C, 0.1 Torr). Then toluene (1 mL) was added, and the mixture was allowed to crystallize at room temperature for 12 h. The pink crystals that precipitated were washed with toluene and dried at 20 °C (0.1 Torr). The yield was 0.16 g (82% based on $Co(CF_3SO_3)_2 \cdot 6H_2O$). Found (%): C, 39.57; H, 3.70; N, 7.23. $C_{26}H_{28}CoF_6N_4O_{10}S_2$. Calculated (%): C, 39.35; H, 3.56;

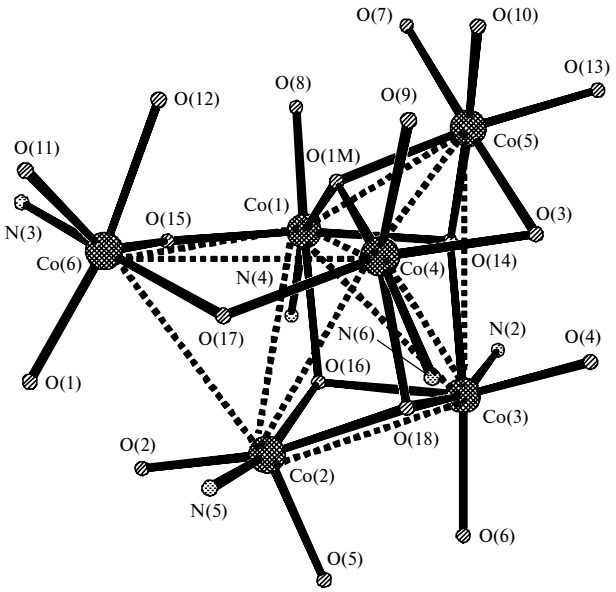


Fig. 10. Structure of the metal core with electron-donating atoms in molecule **11**.

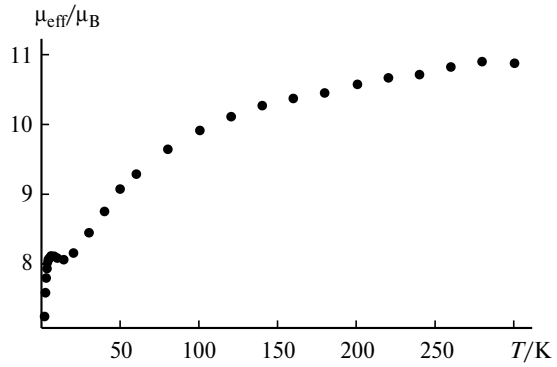


Fig. 11. Plot $\mu_{eff}(T)$ for complex **11**.

N, 7.06. IR (KBr), ν/cm^{-1}: 3288 w, 3044 w, 2956 m, 1644 v.s, 1612 v.s, 1548 s, 1460 s, 1420 s, 1388 s, 1364 s, 1304 s, 1236 s, 1220 s, 1184 w, 1164 s, 1032 s, 1004 s, 944 m, 888 s, 872 s, 808 s, 760 s, 744 s, 732 s, 632 s, 576 s, 532 s, 512 s, 432 m.

The crystals were used for X-ray diffraction study.

[Hexakis(μ_2,η^2-6-methyl-2-pyridonato)hexakis(μ-6-methyl-2-pyridonato)heptacobalt(II)] ditrhifluoromethanesulfonate, solvate with acetonitrile, $[Co_7L_{12}]\cdot(F_3CSO_3)_2\cdot 4MeCN$ (7, L = MeC_5H_3NO). A solution of 2-hydroxy-6-methylpyridine (0.1000 g, 0.942 mmol) in acetonitrile (10 mL) was added to a solution of $Co(CF_3SO_3)_2\cdot 6H_2O$ (0.2132 g, 0.458 mmol) in acetonitrile (10 mL). Triethylamine (0.5 mL) was added to the resulting solution, and the reaction mixture was stirred at 50 °C for 30 min, concentrated to 5 mL (50 °C, 0.1 Torr), and allowed to crystallize at room temperature for 12 h. The blue prismatic crystals that precipitated were washed with cold acetonitrile and dried at 20 °C (0.1 Torr). The yield was 0.20 g (20% based on $Co(CF_3SO_3)_2\cdot 6H_2O$). Found (%): C, 45.40; H, 4.07; N, 10.50. $C_{82}H_{84}Co_7F_6N_{16}O_{18}S_2$. Calculated (%): C, 45.34; H, 3.90; N, 10.32. IR (KBr), ν/cm^{-1}: 3736 w, 3060 w, 3000 w, 2964 w, 2920 w, 1644 m, 1604 v.s, 1560 s, 1468 v.s, 1452 v.s, 1408 s, 1384 s, 1336 s, 1320 v.s, 1272 v.s, 1248 s, 1224 s, 1160 s, 1088 m, 1032 s, 952 s, 876 w, 804 s, 744 s, 636 s, 624 s, 608 s, 572 m, 508 s, 452 w.

The crystals were used for X-ray diffraction study.

Octakis(μ-trimethylacetato-*O*,*O*´)bis(μ_3,η^2-6-methyl-2-pyridonato)bis(μ_3-hydroxo)tetrakis(η^1-trimethylacetic acid)hexacobalt(II), solvate with benzene, $Co_6(\mu_3\text{-}OH)_2(\mu_3,\eta^2\text{-}MeC_5H_3NO)_2(\mu\text{-}OOCCMe_3)_8(HOOCCMe_3)_4\cdot C_6H_6$ ($9\cdot C_6H_6$). *A*. Benzene (30 mL) was added to a mixture of the polymer $[Co(OH)_n(\mu\text{-}OOCCMe_3)_{2-n}]_x$ (x = 0.05—0.1) (0.19 g, 0.73 mmol) (per formula unit $Co(OOCCMe_3)_2$) and 2-hydroxy-6-methylpyridine (0.08 g, 0.73 mmol), and the reaction mixture was stirred under argon at 80 °C for 30 min until the reagents were completely dissolved. The solution was concentrated to 10 mL at 0.1 Torr (20 °C) and cooled to −5 °C. The blue crystals that precipitated after 48 h were separated from the solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of solvate $9\cdot C_6H_6$ was 0.09 g (39% based on the starting amount of cobalt). Found (%): C, 47.90; H, 6.50; N, 1.20. $C_{72}H_{126}N_2Co_6O_{28}$. Calculated (%): C, 47.48; H, 6.99; N, 1.54. IR (KBr), ν/cm^{-1}: 3416 s, 2960 s, 2928 m, 2876 m, 1676 m, 1664 m, 1608 v.s, 1560 s, 1552 s, 1524 w, 1484 v.s, 1464 s, 1416 s, 1372 m, 1360 s, 1340 w, 1264 w, 1228 s, 1208 s, 1108 w, 1032 w, 896 w, 872 w, 800 s, 748 w, 608 m, 540 w, 420 w.

B. Acetonitrile (30 mL) was added to a mixture of the polymer $[Co(OH)_n(\mu\text{-}OOCCMe_3)_{2-n}]_x$ (0.48 g, 1.84 mmol) (per formula unit $Co(OOCCMe_3)_2$) and 2-hydroxy-6-methylpyridine (0.1 g, 0.92 mmol), and the reaction mixture was stirred under argon at 20 °C for 30 min until the reagents were completely dissolved. The solution was concentrated to 10 mL at 0.1 Torr (20 °C) and kept at room temperature for 24 h. The blue crystals that precipitated were separated from the solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of cluster **9** was 0.32 g (60% based on the starting amount of cobalt).

The crystals were used for X-ray diffraction study.

(η^2-Trimethylacetato-*O*,*O*´)(μ_3-hydroxo)tris(μ_3,η^2-6-methyl-2-pyridonato)(μ_2,η^2-6-methyl-2-pyridonato)(μ_3-6-methyl-2-pyridonato)(μ_3-trimethylacetato-*O*,*O*,*O*´)tetrakis(μ-trimethylacetato-*O*,*O*´)(η-6-methyl-2-pyridone)hexacobalt(II), $Co_6(\mu_3\text{-}OH)(\mu_3,\eta^2\text{-}MeC_5H_3NO)_3(\mu_2,\eta^2\text{-}MeC_5H_3NO)(\mu_3\text{-}MeC_5H_3NO)(\eta\text{-}MeC_5H_3NOH)(\mu_3\text{-}OOCCMe_3)(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)$ (11). Acetonitrile (30 mL) was added to a mixture of the polymer $[Co(OH)_n(\mu\text{-}OOCCMe_3)_{2-n}]_x$ (0.6 g, 2.29 mmol) (per formula unit $Co(OOCCMe_3)_2$) and 2-hydroxy-6-methylpyridine (0.50 g, 4.58 mmol), and the mixture was stirred under argon at 80 °C for 30 min until the reagents were completely dissolved. The solution was concentrated to 10 mL at 0.1 Torr (20 °C) and kept at room temperature for 24 h. The pink crystals that precipitated were separated from the solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of compound **11** was 0.51 g (82% based on the starting amount of cobalt). Found (%): C, 48.8; H, 5.4; N, 5.3. $C_{66}H_{92}N_6Co_6O_{19}$. Calculated (%): C, 48.72; H, 5.71; N, 5.17. IR (KBr), ν/cm^{-1}: 2960 s, 2924 s, 2868 m, 1648 s, 1636 v.s, 1624 s, 1592 s, 1560 v.s, 1484 s, 1464 s, 1420 s, 1384 m, 1372 m, 1356 m, 1324 w, 1264 w, 1228 m, 1168 w, 1096 w, 1032 w, 1004 m, 940 w, 900 w, 872 w, 796 s, 744 w, 728 w, 608 m, 584 m, 548 m, 420 w.

The crystals were used for X-ray diffraction study.

Table 6. Crystallographic parameters of complexes **4**—**7**, **9**, and **11**

Parameter	**4**	**5**	**6**	**7**	**9**	**11**
Molecular weight	619.45	951.53	793.57	2172.28	1895.40	1626.03
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$C2/c$	$P\bar{1}$	$P2(1)/c$	$P2(1)/n$	$P2(1)/c$
a/Å	11.198(2)	20.448(2)	8.5070(17)	14.088(5)	13.843(6)	19.724(2)
b/Å	8.8660(18)	13.5960(14)	9.4220(19)	23.734(9)	18.247(8)	15.2677(19)
c/Å	14.319(3)	17.7140(16)	11.001(2)	15.076(5)	19.738(8)	24.727(3)
α/deg	90	90	74.76(3)	90	90	90
β/deg	104.60(3)	123.10(3)	72.70(3)	112.54(3)	108.553(7)	95.962(3)
γ/deg	90	90	89.94(3)	90	90	90
V/Å	1375.7(5)	4125.4(7)	809.4(3)	4656(3)	4726(3)	7405.9(16)
Z	2	4	1	2	2	4
ρ_{calc}/g cm^{-3}	1.495	1.532	1.628	1.550	1.332	1.458
μ/cm^{-3}	0.690	1.262	0.754	1.346	1.100	1.383
Radiation	Mo-Kα (λ = 0.71073 Å)					
Scan range, θ/deg	1.88—29.97	1.91—28.09	2.02—26.97	1.56—29.15	1.56—30.18	1.57—28.02
Number of measured reflections	4219	12575	3238	29773	20430	19851
Number of reflections with $I > 2\sigma(I)$	4009	4389	3210	9879	9437	12140
R_1[a]	0.0437	0.0505	0.0699	0.0559	0.0736	0.0686
wR_2[b]	0.1299	0.1156	0.1731	0.1463	0.1393	0.1600

Note. The molecular formulas: $C_{24}H_{28}CoN_6O_{10}$ (**4**), $C_{36}H_{38}Co_3N_8O_{12}$ (**5**), $C_{26}H_{28}CoF_6N_4O_{10}S_2$ (**6**), $C_{82}H_{84}Co_7F_6N_{16}O_{18}S_2$ (**7**), $C_{78}H_{128}Co_6N_2O_{28}$ (**9**), and $C_{66}H_{91}Co_6N_6O_{19}$ (**11**).

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

X-ray diffraction study. X-ray diffraction data sets were collected using a standard procedure[19] on an automated Bruker AXS SMART 1000 diffractometer (for complexes **5**, **7**, **9**, and **11**) and an automated Enraf-Nonius CAD 4 diffractometer (for **4** and **6**) at 110 (for **11**), 120 (for **5**, **7**, and **9**), and 293 K (for **4** and **6**) (ω-scanning technique, the scan step was 0.3°, the exposure time per frame was 30 s). Semiempirical absorption corrections were applied for all crystals.[20] The crystallographic parameters and the refinement statistics for all structures are given in Table 6. The structures of all complexes were solved by direct methods using the SHELX97 program package[21] and refined by the full-matrix least-squares method with anisotropic displacement parameters (positions of the H atoms were fixed with $U_H = 0.082$) using the SHELXL97 program package.[22] The hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands and the NH groups were calculated geometrically and refined using a riding model. The calculations were performed with the use of the SHELX97 program package.[21] Selected geometric parameters of the complexes are listed in Tables 1—5.

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