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The authors congratulate Academician I.L. Eremenko on his 70th jubilee

Transformations of Cobalt(II) Trifluoroacetates in 1,4-Dioxane: Solvent Effect on the Composition, Structure, and Crystal Packing of the Molecules

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Abstract—The reaction of aqueous cobalt(II) acetate with trifluoroacetic acid in methanol affords complex $[Co(OOCF_3)_2(OH_2)_4]$ (**I**). The same reaction in a methanol–benzene–dioxane mixture of solvents gives mononuclear complex $[Co(OOCF_3)_2(OH_2)_6] \cdot O(CH_2CH_2)_2O$ (**II**) in which the solvate dioxane molecule forms a single crystal by the formation of hydrogen bonds with coordinated water molecules. A similar reaction in pure dioxane affords trinuclear complex $\{Co_3(OOCCF_3)_4(OH_2)_2(OOCCF_3)_2[O(CH_2CH_2)_2O]_2\} \cdot 2HOOCCF_3 \cdot 2O(CH_2CH_2)_2O$ (**III**) containing both solvate and coordinated dioxane molecules. The crystallization of complex **III** from an isopropanol–dioxane mixture leads to complex $[Co(OOCCF_3)_2(OH_2)_4] \cdot 2O(CH_2CH_2)_2O$ (**IV**). The reaction of complex **III** with pyrazole (HPz) affords mononuclear complex $[Co(OOCCF_3)_2(HPz)_4] \cdot 2O(CH_2CH_2)_2O$ (**V**). The reaction of complex **I** with HPz in methylene dichloride leads to mononuclear complex $[Co(OOCCF_3)_2(HPz)_4]$ (**VI**). The structures of coordination compounds **I**–**VI** are determined by X-ray diffraction analysis (CIF files CCDC nos. 1985667 (**I**), 1985666 (**II**), 1985671 (**III**), 1985670 (**IV**), 1985665 (**V**), and 1985669 (**VI**) at $T = 296(2)$ K and 1985668 (**VI**) at $T = 150(2)$ K).

Keywords: cobalt(II) trifluoroacetates, 1,4-dioxane, isopropyl alcohol, structural phase transition, pyrazole, synthesis, X-ray diffraction analysis

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INTRODUCTION

The knowledge of specific features of coordination modes and transformations of anions of the initial compounds and the solvent used for the reaction makes it possible to predict the compositions and structures of the formed coordination compounds [1, 2].

It is known that anions of strong acids (for example, trifluoromethanesulfonic or trifluoroacetic acid) can easily be displaced from the coordination sphere of the metal by solvents containing nucleophilic atoms such as acetonitrile, tetrahydrofuran, and dioxane liberating orbitals for the fixation of various donor molecules. 1,4-Dioxane used as a solvent has two oppositely lying nucleophilic centers and thus can act as a bridging ligand similarly to γ,γ'-bipyridine or pyrazine, which results in the formation of polynuclear complexes or coordination polymers [3–7].

It has recently been shown that coordination polymers [8–10] and difluorides of the corresponding metals during the thermal decomposition of $Fe(OOCCF_3)_2(HOOCCF_3)_2$, $Mn_2(OOCCF_3)_4(HOOCCF_3)_4$, and $Co(OOCCF_3)_2(H_2O)_4$ [11] can be synthesized from 3*d*-transition metal trifluoroacetates.

Note that the heterocyclic pyrazole molecule bearing the pyridinic nitrogen atom and pyrrole fragment capable of deprotonating is considered as a convenient ligand for studying proton transfer reactions and for the synthesis of structural analogs of the active moiety of natural metalloenzymes [12–15].

In this work, we report the syntheses and structures of cobalt(II) trifluoroacetates synthesized in solvents of various nature (methanol, methanol–benzene–dioxane, methanol–dioxane, and dioxane) and products of their reactions with pyrazole (HPz).

EXPERIMENTAL

Synthesis of $[Co(OOCCF_3)_2(OH_2)_4]$ (I). Trifluoroacetic acid (0.6 mL, 8 mmol) was added to a solution of $Co(OOCMe)_2 \cdot 4H_2O$ (1 g, 4 mmol) in methanol (5 mL). An open two-necked flask was left under drawing out. Red single crystals formed during slow evaporation were decanted from the mother liquor, washed consequently with cooled benzene (5 mL) and hexane (5 mL), and dried in argon. The yield of complex **I** was 1.2 g (87%).

For $C_4H_8CoF_6O_8$

Anal. calcd., %	C, 13.46	H, 2.26
Found, %	C, 13.98	H, 2.38

IR (ν, cm^{-1}): 3427 br.s, 1713 s, 1683 s, 1629 m, 1462 w, 1207 s, 1157 s, 849 w, 799 m, 728 m, 610 w, 520 w, 437 w.

Synthesis of $[Co(OOCCF_3)_2(OH_2)_6] \cdot O(CH_2CH_2)_2O$ (II). Trifluoroacetic acid (0.6 mL, 8 mmol), benzene (0.5 mL, 2–3% H_2O), and dioxane (0.3 mL, 3.4 mmol) were added to a solution of $Co(OOMe)_2 \cdot 4H_2O$ (1 g, 4 mmol) in methanol (5 mL). An open two-necked flask was left under drawing out. Red single crystals formed during slow evaporation were decanted from the mother liquor, washed consequently with cooled benzene (10 mL) and hexane (10 mL), and dried in argon. The yield of complex **II** as a powder was 1 g (55%).

For $C_8H_{20}F_6O_{12}Co$

Anal. calcd., %	C, 19.97	H, 4.19
Found, %	C, 20.01	H, 4.27

IR (ν, cm^{-1}): 3434 br.s, 1710 s, 1682 s, 1447 w, 1382 w, 1205 s, 1148 s, 1080 w, 900 w, 870 w, 797 m, 726 m, 601 w, 418 w.

Synthesis of $\{Co_3(\mu\text{-}OOCCF_3)_4(\mu\text{-}OH_2)_2\text{-}(OOCCF_3)_2\text{-}[O(CH_2CH_2)_2O]_2\} \cdot 2HOOCCF_3 \cdot 2O(CH_2CH_2)_2O$ (III). Trifluoroacetic acid (0.6 mL, 8 mmol) and dioxane (5 mL) were added to the crystals of $Co(OOMe)_2 \cdot 4H_2O$ (1 g, 4 mmol). The obtained suspension was refluxed for 30 min, the solvent was removed in an argon flow to a volume of ~2 mL, and the mixture was left to get cold in an oil bath. The precipitated large red crystals were decanted from the solution, washed consequently with cold benzene (10 mL) and hexane (10 mL), and dried under argon. The yield of compound **III** was 1.3 g (69%).

For $C_{28}H_{34}F_{24}O_{26}$

Anal. calcd., %	C, 23.69	H, 2.41
Found, %	C, 23.79	H, 2.34

IR (ν, cm^{-1}): 3445 br.s, 3247 s, 2934 w, 2875 w, 1712 s, 1460 m, 1446 m, 1381 w, 1260 m, 1195 s, 1144 s, 1112 s, 1080 m, 1045 w, 900 w, 870 s, 853 m, 796 s, 726 m, 617 m, 518 w.

Synthesis of $[Co(OOCCF_3)_2(OH_2)_4] \cdot 2O(CH_2CH_2)_2O$ (IV). Single crystals of complex **III** (0.3 g, 0.21 mmol) were dissolved in isopropanol (5 mL), dioxane (0.5 mL) was added, and the mixture was heated to 60°C for 0.5 h. The resulting red solution was left in an open two-necked flask under drawing out. Red single crystals formed after 3 days during slow evaporation in air upon the complete removal of the solvent were consequently washed with cold benzene and hexane and dried under argon. The yield of compound **IV** was 0.27 g (95%).

For $C_8H_{16}F_6O_{10}Co$

Anal. calcd., %	C, 21.57	H, 3.62
Found, %	C, 21.63	H, 4.65

IR (ν, cm^{-1}): 3123 br.m, 1663 s, 1524 w, 1446 m, 1292 w, 1188 s, 1140 s, 988 w, 857 m, 794 s, 724 s, 606 m, 517 m, 500 w, 468 w.

Synthesis of $[Co(OOCCF_3)_2(HPz)_4] \cdot 2O(CH_2CH_2)_2O$ (V). Single crystals of complex **III** (0.3 g, 0.21 mmol) were dissolved in methylene dichloride (5 mL), HPz (0.18 g, 2.62 mmol) was added, and the mixture was refluxed for 0.5 h. Hexane (5 mL) was added to the resulting solution, and the mixture was concentrated to 5 mL and kept in a refrigerator at 5°C for 3 days. The precipitated orange crystals were decanted from the solution, washed consequently with cold benzene and hexane, and dried under argon. The yield of compound **V** was 0.36 g (89%).

For $C_{20}H_{24}F_6N_8O_6Co$

Anal. calcd., %	C, 37.22	H, 3.75	N, 17.66
Found, %	C, 37.11	H, 3.82	N, 17.41

IR (ν, cm^{-1}): 3070 br.w, 1560 s, 1518 s, 1492 w, 1428 s, 1382 s, 1331 m, 1253 w, 1223 w, 1107 w, 1143 w, 1020 w, 872 w, 846 s, 778 w, 738 w, 721 s, 674 m, 659 m, 622 m, 515 w, 429 w.

Synthesis of $[Co(OOCCF_3)_2(HPz)_4]$ (VI). Single crystals of complex **I** (0.5 g, 1.4 mmol) were dissolved in methylene dichloride (5 mL), HPz (0.38 g, 5.6 mmol), and the mixture was refluxed for 0.5 h. Hexane (5 mL) was added to the resulting solution, which was concentrated to 5 mL and kept in a refrigerator at 5°C for 3 days. The precipitated orange crystals were decanted from the solution, washed consequently with cold benzene and hexane, and dried under argon. The yield of complex **VI** was 0.72 g (92%).

For $C_{16}H_{16}F_6N_8O_4Co$

Anal. calcd., %	C, 34.45	H, 2.87	N, 20.09
Found, %	C, 34.62	H, 2.99	N, 20.18

IR (ν, cm^{-1}): 3362 br.s, 3147 m, 2998 w, 2642 w, 2883 w, 2821 w, 1674 s, 1550 w, 1524 m, 1467 m, 1435 m, 1355 m, 1253 m, 1203 s, 1130 s, 1061 s, 1046 s, 941 m, 912 w, 890 w, 865 w, 833 m, 796 m, 766 s, 721 s, 656 w, 604 s, 519 w, 423 w.

The IR spectra of the compounds were recorded on a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer using the attenuated internal reflection (ATR) method in a frequency range of 400–4000 cm^{-1}.

X-ray diffraction analysis (XRD) of the crystals of compounds **I**–**VI** was carried out using a standard procedure on a Bruker SMART Apex II automated diffractometer equipped with a CCD detector (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω scan mode) at room temperature. Structure refinement was performed using the SHELXTL PLUS (PC version) program package [16–19]. Hydrogen atoms in the structures of complexes **I**–**IV** were revealed from the difference Fourier synthesis and refined isotropically. The fluorine atoms of the CF_3 substituents in the complexes were disordered over positions with the multiplicities 0.7 : 0.3 in complex **I**, 0.5 : 0.5 in complex **IV**, and 0.6 : 0.4 in complex **VI**. The crystals of complex **IV** slowly decomposed during the XRD experiment. The crystallographic data and structure refinement details for complexes **I**–**VI** are presented in Table 1. Selected bond lengths and bond lengths are given in Tables 2 and 3.

The full tables of coordinates of atoms, bond lengths, and bond angles for complexes **I**–**VI** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1985667 (**I**), 1985666 (**II**), 1985671 (**III**), 1985670 (**IV**), 1985665 (**V**), and 1985669 (**VI**) at $T = 296(2)$ K and 1985668 (**VI**) at $T = 150(2)$ K; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reaction of aqueous cobalt acetate with trifluoroacetic acid (1 : 2) in methanol at room temperature leads to the exchange of the anions to form mononuclear complex **I** (87% yield). According to the XRD data (298 K), in complex **I** (Tables 1, 2; Fig. 1) the metal atom occupying the partial position (0, 0.5, 0.5) has a octahedral environment of six oxygen atoms, two of which belong to the trifluoroacetate anions (Co–O(1) 2.116(3) Å) and others belong to four coordinated water molecules (Co–O(3) 2.046(3), Co–O(4) 2.128(3) Å). The substantial difference in the M–O distances is probably determined by a complicated systems of hydrogen bonds in the complex. The oxygen atoms of the anions occupying the axial positions are arranged in the anti positions and form hydrogen bonds: not only intramolecular bonds with the coordinated water molecule (O(3)...O(2) 2.686(3) Å) but also intermolecular hydrogen bonds with the O(4) oxygen atoms (O(3)...O(4) 2.898 Å). At the same time, the hydrogen atoms of coordinated water (O(4)) additionally form intermolecular bonds with the O(2) oxygen atom of the molecule of the adjacent layer (O(4)...O(2) 2.860 Å) and with the O(1) oxygen atom of the near-lying molecule of the complex arranged in the crystal (O(4)...O(1) 2.849 Å) including the O(3) oxygen atom (Fig. 2). The fluorine atoms of the CF_3 anion in the complex are disordered over two positions with the multiplicity 0.7 : 0.3.

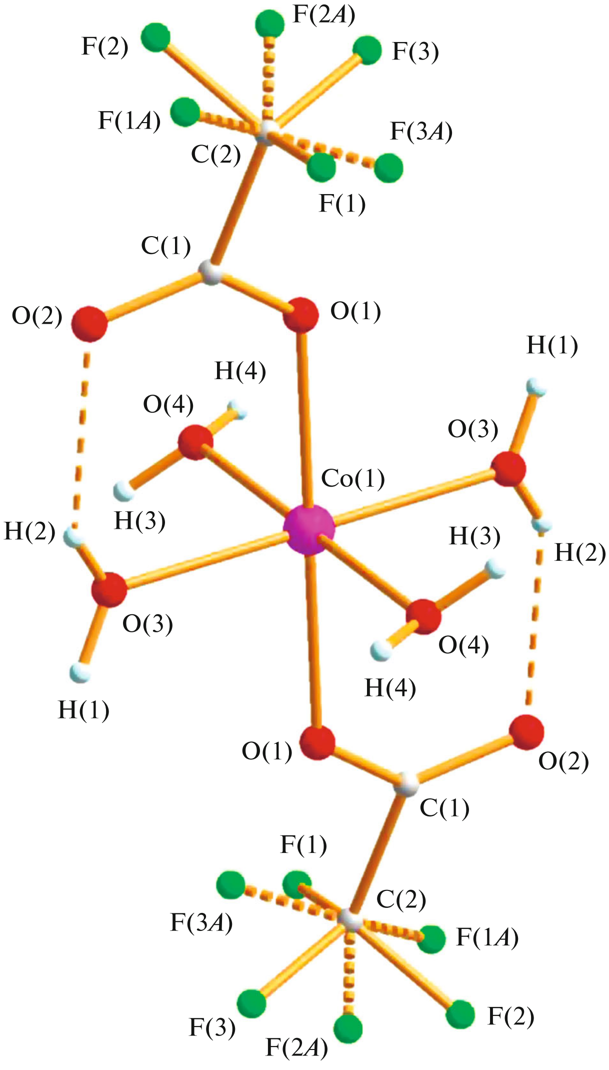

Fig. 1. Structure of complex **I** at 293 K.

The structural experiments at low temperatures ($T = 103$ K [11] and 150 K [20]) unexpectedly showed that the crystals transited from the monoclinic ($P2_1/n$) to triclinic crystal system ($P\bar{1}$: $a = 8.136(0)$, $b = 9.033(0)$, $c = 9.270(0)$ Å, $\alpha = 75.14(0)°$, $\beta = 64.57(0)°$, $\gamma = 71.43(0)°$ (103 K), $R = 3.08\%$; $a = 8.193(1)$, $b = 9.105(2)$, $c = 9.383(2)$ Å, $\alpha = 75.014(1)°$, $\beta = 64.14(1)°$, $\gamma = 71.27(1)°$ (150 K), $R = 13.73\%$). The transition is accompanied by a substantial change in the structure of the molecule. For example, the fluorine atoms of carboxylates $OOCF_3$ are disordered, and the oxygen atoms of the equatorial anions occupy the

Table 1. Crystallographic parameters structure refinement details for complexes **I–VI**

Parameter	**I**	**II**	**III**	**IV**	**V**	**VI**	**VI**
Empirical formula	$C_4H_8O_8F_6Co$	$C_8H_{20}O_{12}F_6Co$	$C_{28}H_{34}O_{26}F_{24}Co_3$	$C_{20}H_{24}N_8O_6F_6Co$	$C_8H_{16}O_{10}F_6Co$	$C_{16}H_{16}N_8O_4F_6Co$	$C_{16}H_{16}N_8O_4F_6Co$
FW	357.03	481.17	1419.34	645.40	445.14	557.30	557.30
Color	Red	Red	Red	Orange	Red	Orange	Orange
T, K	296(2)	150(2)	150(2)	150(2)	296(2)	296(2)	150(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	4.900(3)	5.1477(5)	10.4165(8)	8.2179(8)	5.059(9)	7.1945(16)	8.2457(16)
b, Å	11.990(6)	8.4413(8)	13.5030(10)	8.8075(8)	7.920(9)	10.856(2)	8.3960(16)
c, Å	9.816(5)	10.7821(11)	18.6150(14)	10.3827(10)	11.054(13)	14.580(3)	8.4255(17)
α, deg	90	88.1580(10)	90	111.4930(10)	79.81(2)	90	88.197(3)
β, deg	100.252(8)	80.3310(10)	103.2380(10)	100.8440(10)	89.51(2)	95.775(4)	89.552(3)
γ, deg	90	81.3910(10)	90	91.0770(10)	79.026(14)	90	68.140(3)
V, $Å^3$	567.6(5)	456.65(8)	2548.7(3)	683.58(11)	427.8(10)	1133.0(4)	541.09(18)
Z	2	1	2	1	1	2	1
ρ_{calc}, mg/m^3	2.089	1.750	1.849	1.568	1.728	1.634	1.710
μ, mm^{-1}	1.632	1.054	1.134	0.719	1.109	0.847	0.887
F(000)	354	245	1414	329	225	562	281
Crystal sizes, mm	0.24 × 0.22 × 0.20	0.26 × 0.24 × 0.22	0.26 × 0.24 × 0.22	0.22 × 0.20 × 0.18	0.24 × 0.22 × 0.20	0.24 × 0.22 × 0.20	0.24 × 0.22 × 0.20
θ Scan range, deg	2.71–30.00	2.44–30.57	2.51–30.54	2.50–30.00	2.66–24.99	2.34–29.99	2.42–30.00
Ranges of reflection indices	$-6 \le h \le 6$, $-16 \le k \le 13$, $-13 \le l \le 13$	$-7 \le h \le 7$, $-11 \le k \le 12$, $-15 \le l \le 15$	$-14 \le h \le 14$, $-16 \le k \le 19$, $-26 \le l \le 26$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-14 \le l \le 14$	$-5 \le h \le 6$, $-9 \le k \le 6$, $-13 \le l \le 8$	$-10 \le h \le 10$, $-15 \le k \le 13$, $-20 \le l \le 20$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-11 \le l \le 11$
Number of reflections	4277	5509	21 226	8118	1402	9480	6273
Number of independent reflections (R_{int})	1643 (0.1029)	2747 (0.0117)	7481 (0.0250)	3964 (0.0159)	1327 (0.0801)	3252 (0.0285)	3103 (0.0272)
GOOF	1.112	1.045	1.046	1.037	1.063	0.965	1.052
R_1, wR_2 ($I > 2\sigma(I)$)	0.0840, 0.2424	0.0296, 0.0851	0.0385, 0.0913	0.0392, 0.1053	0.0933, 0.2659	0.0809, 0.2043	0.0390, 0.1163
R_1, wR_2 (for all reflections)	0.0984, 0.2558	0.0306, 0.0859	0.0572, 0.1003	0.0422, 0.1083	0.1383, 0.2990	0.0862, 0.2070	0.0459, 0.1218
$\Delta\rho_{max}/\Delta\rho_{min}$, e $Å^{-3}$	1.586/–1.343	0.900/–0.570	0.517/–0.447	0.701/–0.526	1.131/–1.314	1.970/–0.663	1.069/–0.626

Table 2. Selected bond lengths (Å) and bond angles (deg) in complexes **I–III***

Bond	*d*, Å	Bond	*d*, Å
		I	
Co(1)–O(3)$^{\#1}$	2.046(3)	Co(1)–O(3)	2.046(3)
Co(1)–O(1)$^{\#1}$	2.116(3)	Co(1)–O(1)	2.116(3)
Co(1)–O(4)	2.128(3)	Co(1)–O(4)$^{\#1}$	2.128(3)
		II	
Co(1)–O(3)	2.0674(10)	Co(1)–O(3)$^{\#1}$	2.0674(10)
Co(1)–O(2)$^{\#1}$	2.1001(10)	Co(1)–O(2)	2.1001(10)
Co(1)–O(1)	2.1000(9)	Co(1)–O(1)$^{\#1}$	2.1000(9)
		III	
Co(1)–O(2)	2.0399(14)	Co(1)–O(8)	2.0414(17)
Co(1)–O(6)	2.0517(16)	Co(1)–O(4)	2.0686(14)
Co(1)–O(9)	2.0968(15)	Co(1)–O(1)	2.1760(13)
Co(1)–Co(2)	3.6374(3)	Co(2)–O(7)$^{\#1}$	2.0646(15)
Co(2)–O(7)	2.0647(15)	Co(2)–O(3)	2.0677(14)
Co(2)–O(3)$^{\#1}$	2.0678(14)	Co(2)–O(1)$^{\#1}$	2.1676(12)
Co(2)–O(1)	2.1676(12)		
Angle	ω, deg	Angle	ω, deg
		I	
O(3)$^{\#1}$Co(1)O(3)	180.00(16)	O(3)$^{\#1}$Co(1)O(1)$^{\#1}$	88.79(13)
O(3)Co(1)O(1)$^{\#1}$	91.21(13)	O(3)$^{\#1}$Co(1)O(1)	91.21(13)
O(3)Co(1)O(1)	88.79(13)	O(1)$^{\#1}$Co(1)O(1)	179.999(1)
O(3)$^{\#1}$Co(1)O(4)	90.70(15)	O(3)Co(1)O(4)	89.30(15)
O(1)$^{\#1}$Co(1)O(4)	89.31(13)	O(1)Co(1)O(4)	90.69(13)
O(3)$^{\#1}$Co(1)O(4)$^{\#1}$	89.30(15)	O(3)Co(1)O(4)$^{\#1}$	90.70(15)
O(1)$^{\#1}$Co(1)O(4)$^{\#1}$	90.69(13)	O(1)Co(1)O(4)$^{\#1}$	89.31(13)
O(4)Co(1)O(4)$^{\#1}$	180.000(1)		
		II	
O(3)Co(1)O(3)$^{\#1}$	180.0	O(3)Co(1)O(2)$^{\#1}$	86.50(4)
O(3)$^{\#1}$Co(1)O(2)$^{\#1}$	93.50(4)	O(3)Co(1)O(2)	93.50(4)
O(3)$^{\#1}$Co(1)O(2)	86.50(4)	O(2)$^{\#1}$Co(1)O(2)	180.0
O(3)Co(1)O(1)	88.12(4)	O(3)$^{\#1}$Co(1)O(1)	91.88(4)
O(2)$^{\#1}$Co(1)O(1)	88.78(4)	O(2)Co(1)O(1)	91.22(4)
O(3)Co(1)O(1)$^{\#1}$	91.88(4)	O(3)$^{\#1}$Co(1)O(1)$^{\#1}$	88.12(4)
O(2)$^{\#1}$Co(1)O(1)$^{\#1}$	91.22(4)	O(2)Co(1)O(1)$^{\#1}$	88.78(4)
O(1)Co(1)O(1)$^{\#1}$	180.0		
		III	
O(2)Co(1)O(8)	86.88(7)	O(2)Co(1)O(6)	94.88(7)
O(8)Co(1)O(6)	177.00(6)	O(2) Co(1)O(4)	174.89(6)
O(8)Co(1)O(4)	91.46(7)	O(6)Co(1)O(4)	86.99(7)
O(2)Co(1-O(9)	88.63(6)	O(8)Co(1)O(9)	94.93(7)
O(6)Co(1)O(9)	87.56(6)	O(4)Co(1)O(9)	86.69(6)
O(2)Co(1)O(1)	93.74(6)	O(8)Co(1)O(1)	89.48(6)

Table 2. (Contd.)

Angle	ω, deg	Angle	ω, deg
O(6)Co(1)O(1)	87.98(6)	O(4)Co(1)O(1)	91.08(5)
O(9)Co(1)O(1)	175.11(6)	O(2)Co(1)Co(2)	70.01(4)
O(8)Co(1)Co(2)	110.10(5)	O(6)Co(1)Co(2)	68.36(4)
O(4)Co(1)Co(2)	115.09(4)	O(9)Co(1)Co(2)	145.44(5)
O(1)Co(1)Co(2)	33.06(3)	O(7)$^{\#1}$Co(2)O(7)	180.0
O(7)$^{\#1}$Co(2)O(3)	89.97(7)	O(7)Co(2)O(3)	90.03(7)
O(7)$^{\#1}$Co(2)O(3)$^{\#1}$	90.03(7)	O(7)Co(2)O(3)$^{\#1}$	89.97(7)
O(3)Co(2)O(3)$^{\#1}$	179.999(17)	O(7)$^{\#1}$Co(2)O(1)$^{\#1}$	88.81(5)
O(7)Co(2)(1)$^{\#1}$	91.19(5)	O(3)Co(2)O(1)$^{\#1}$	83.76(5)
O(3)$^{\#1}$Co(2)O(1)$^{\#1}$	96.24(5)	O(7)$^{\#1}$Co(2)O(1)	91.19(5)
O(7)Co(2)O(1)	88.81(5)	O(3)Co(2)O(1)	96.23(5)
O(3)$^{\#1}$Co(2)O(1)	83.77(5)	O(1)$^{\#1}$Co(2)O(1)	180.0
O(7)$^{\#1}$Co(2)Co(1)	72.14(4)	O(7)Co(2)Co(1)	107.87(4)
O(3)Co(2)Co(1)	69.68(4)	O(3)$^{\#1}$Co(2)Co(1)	110.32(4)
O(1)$^{\#1}$Co(2)Co(1)	146.80(3)	O(1)Co(2)Co(1)	33.20(3)
Co(2)O(1)Co(1)	113.74(5)	C(1)O(2)Co(1)	133.91(13)
C(1)O(3)Co(2)	133.89(13)	C(3)O(4)Co(1)	127.88(14)
C(5)$^{\#1}$O(6)Co(1)	137.93(14)	C(5)O(7)Co(2)	131.00(14)

* Symmetry transforms used for the generation of equivalent atoms: $^{\#1}$ $-x, -y+1, -z+1$ (**I**); $^{\#1}$ $-x, -y, -z$ (**II**); $^{\#1}$ $-x+1, -y+1, -z$ (**III**).

syn positions, unlike those in complex **I**, and are bound to the hydrogen atoms by only one coordinated water molecule (O(5)...O(2) 2.748, O(5)...O(4) 2.712 Å) (Fig. 3).

A similar reaction of $Co(OOCMe)_2 \cdot 4H_2O$ with trifluoroacetic acid in a methanol–benzene (2–3% H_2O)–dioxane mixture of solvents on reflux results in the formation of red single crystals of mononuclear

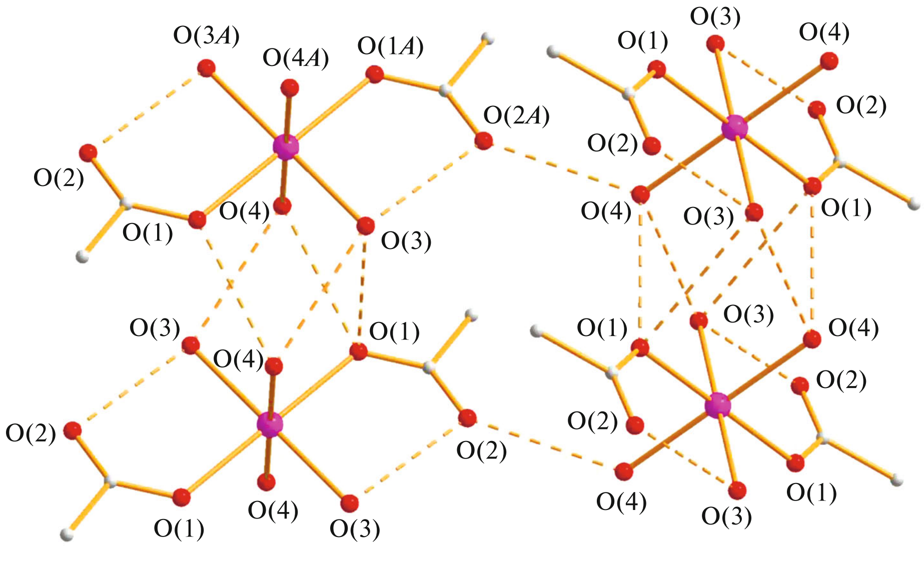

Fig. 2. Distribution of hydrogen bonds in the crystal cell of complex **I**.

Table 3. Selected bond lengths (Å) and bond angles (deg) in complexes **IV**, **V**, and **VI** at T = 296(2) and 150(2) K*

Bond	d, Å	Bond	d, Å
IV			
Co(1)–O(3)	2.108(8)	Co(1)–O(3)$^{\#1}$	2.108(8)
Co(1)–O(4)	2.151(9)	Co(1)–O(4)$^{\#1}$	2.151(9)
Co(1)–O(1)	2.172(7)	Co(1)–O(1)$^{\#1}$	2.172(7)
V			
Co(1)–N(1)$^{\#1}$	2.0800(13)	Co(1)–N(1)	2.0800(13)
Co(1)–N(3)	2.0893(14)	Co(1)–N(3)$^{\#1}$	2.0893(14)
Co(1)–O(1)$^{\#1}$	2.2327(13)	Co(1)–O(1)	2.2327(13)
VI (T = 296(2) K)			
Co(1)–N(1)$^{\#1}$	2.108(4)	Co(1)–N(1)	2.108(4)
Co(1)–O(1)	2.142(3)	Co(1)–O(1)$^{\#1}$	2.142(3)
Co(1)–N(3)	2.155(4)	Co(1)–N(3)$^{\#1}$	2.155(4)
VI (T = 150(2) K)			
Co(1)–N(3)	2.1043(16)	Co(1)–N(3)$^{\#1}$	2.1043(16)
Co(1)–N(1)$^{\#1}$	2.1185(16)	Co(1)–N(1)	2.1185(16)
Co(1)–O(1)$^{\#1}$	2.1979(14)	Co(1)–O(1)	2.1979(14)
Angle	ω, deg	Angle	ω, deg
IV			
O(3)Co(1)O(3)$^{\#1}$	180.0	O(3)Co(1)O(4)	91.0(4)
O(3)$^{\#1}$Co(1)O(4)	89.0(4)	O(3)Co(1)O(4)$^{\#1}$	89.0(4)
O(3)$^{\#1}$Co(1)O(4)$^{\#1}$	91.0(4)	O(4)Co(1)O(4)$^{\#1}$	180.000(1)
O(3)Co(1)O(1)	85.4(3)	O(3)$^{\#1}$Co(1)O(1)	94.6(3)
O(4)Co(1)O(1)	89.2(3)	O(4)$^{\#1}$Co(1)O(1)	90.8(3)
O(3)Co(1)O(1)$^{\#1}$	94.6(3)	O(3)$^{\#1}$Co(1)O(1)$^{\#1}$	85.4(3)
O(4)Co(1)O(1)$^{\#1}$	90.8(3)	O(4)$^{\#1}$Co(1)O(1)$^{\#1}$	89.2(3)
O(1)Co(1)O(1)$^{\#1}$	180.0	C(1)O(1) Co(1)	124.6(6)
V			
N(1)$^{\#1}$Co(1)N(1)	179.999(2)	N(1)$^{\#1}$Co(1)N(3)	89.92(5)
N(1)Co(1)N(3)	90.08(5)	N(1)$^{\#1}$Co(1)N(3)$^{\#1}$	90.08(5)
N(1)Co(1)N(3)$^{\#1}$	89.92(5)	N(3)Co(1)N(3)$^{\#1}$	180.0
N(1)$^{\#1}$Co(1)O(1)$^{\#1}$	88.17(5)	N(1)Co(1)O(1)$^{\#1}$	91.83(5)
N(3)Co(1)O(1)$^{\#1}$	92.54(5)	N(3)$^{\#1}$Co(1)O(1)$^{\#1}$	87.46(5)
N(1)$^{\#1}$Co(1)O(1)	91.83(5)	N(1)Co(1)O(1)	88.17(5)
N(3)Co(1)O(1)	87.46(5)	N(3)$^{\#1}$Co(1)O(1)	92.54(5)
O(1)$^{\#1}$Co(1)O(1)	180.0	C(7)O(1)Co(1)	141.21(13)
C(1)N(1)Co(1)	134.42(12)	N(2)N(1)Co(1)	120.69(10)
C(5)N(3)Co(1)	129.86(12)	N(4)N(3)Co(1)	125.03(12)
VI (T = 296(2) K)			
N(1)$^{\#1}$Co(1)N(1)	180.0	N(1)$^{\#1}$Co(1)O(1)	88.50(15)
N(1)Co(1)O(1)	91.50(15)	N(1)$^{\#1}$Co(1)O(1)$^{\#1}$	91.50(15)
N(1)Co(1)O(1)$^{\#1}$	88.50(15)	O(1)Co(1)O(1)$^{\#1}$	180.0

Table 3. (Contd.)

Angle	ω, deg	Angle	ω, deg
N(1)$^{\#1}$Co(1)N(3)	88.69(14)	N(1)Co(1)N(3)	91.31(14)
O(1)Co(1)N(3)	96.35(14)	O(1)$^{\#1}$Co(1)N(3)	83.65(14)
N(1)$^{\#1}$Co(1)N(3)$^{\#1}$	91.31(14)	N(1)Co(1)N(3)$^{\#1}$	88.69(14)
O(1)Co(1)N(3)$^{\#1}$	83.65(14)	O(1)$^{\#1}$Co(1)N(3)$^{\#1}$	96.35(14)
N(3)Co(1)N(3)$^{\#1}$	180.0	C(1)O(1)Co(1)	143.6(3)
C(3)N(1)N(2)	104.5(4)	C(3)N(1)Co(1)	132.0(3)
N(2)N(1)Co(1)	123.5(3)	C(9)N(3)Co(1)	130.3(3)
N(4)N(3)Co(1)	123.4(3)		
VI (T = 150(2) K)			
N(3)Co(1)N(3)$^{\#1}$	180.0	N(3)Co(1)N(1)$^{\#1}$	89.18(6)
N(3)$^{\#1}$Co(1)N(1)$^{\#1}$	90.82(6)	N(3)Co(1)N(1)	90.82(6)
N(3)$^{\#1}$Co(1)N(1)	89.18(6)	N(1)$^{\#1}$Co(1)N(1)	180.0
N(3)Co(1)O(1)$^{\#1}$	88.93(6)	N(3)$^{\#1}$Co(1)O(1)$^{\#1}$	91.07(6)
N(1)$^{\#1}$Co(1)O(1)$^{\#1}$	94.29(6)	N(1)Co(1)O(1)$^{\#1}$	85.71(6)
N(3)Co(1)O(1)	91.07(6)	N(3)$^{\#1}$Co(1)O(1)	88.93(6)
N(1)$^{\#1}$Co(1)O(1)	85.71(6)	N(1)Co(1)O(1)	94.29(6)
O(1)$^{\#1}$Co(1)O(1)	180.0	C(7)O(1)Co(1)	140.35(13)
C(3)N(1)Co(1)	128.81(13)	N(2)N(1)Co(1)	123.49(12)
C(4)N(3)Co(1)	129.69(14)	N(4)N(3)Co(1)	124.89(13)

* Symmetry transforms for the generation of equivalent atoms: $^{\#1}$ $-x, -y, -z$ (**IV**); $^{\#1}$ $-x + 1, -y, -z + 2$ (**V**); $^{\#1}$ $-x, -y, -z$ (**VI**) at T = 296(2) K and $^{\#1}$ $-x + 1, -y, -z$ (**VI**) at T = 150(2) K.

complex **II** (56% yield). According to the XRD data (Tables 1, 2; Figs. 4, 5), in the centrosymmetric molecule of complex **II** the metal atom has an octahedral environment of six coordinated water molecules (Co–O(1) 2.1000(9), Co–O(2) 2.1001(10), Co–O(3) 2.0674(10) Å). The differences in the M–OH_2 bond lengths are related to the formation of intermolecular hydrogen bonds of the oxygen atoms of the outer-sphere trifluoroacetate anions and solvate dioxane molecules, which form the crystal (O(1)...O(5) 2.670, O(1)...O(7) 2.733, O(2)...O(1) 2.847, O(2)...O(6) 2.706, O(3)...O(5) 2.674, O(3)...O(6) 2.721 Å).

When the solvent is replaced by dioxane, the reaction of $Co(OOCMe)_2 \cdot 4H_2O$ with $HOOCF_3$ (1 : 2, reflux for 30 min) affords red trinuclear complex **III** (69% yield). According to the XRD data (Tables 1, 2; Fig. 6), in the centrosymmetric molecule of complex **III** three cobalt atoms are remote at nonbonding metal–metal distances (3.6374(3) Å) and connected in pairs by two μ-$OOCF_3$ bridges (Co(1)–O(2) 2.040(1), Co(1)–O(6) 2.052(1) Å, Co(2)–O(3) 2.068(1), Co(2)–O(7) 2.065(1) Å) and the bridging water molecule (Co(1)–O(1) 2.176(1), Co(2)–O(1) 2.167(1) Å). Each peripheral cobalt atom has the terminal anion (Co(2)–O(4) 2.069(1) Å) and is coordinated by the dioxane molecule (Co(2)–O(9) 2.097(1) Å) and water molecule (Co(1)–O(8) 2.041(2) Å). Two solvate acid molecules form hydrogen bonds with the O(5) oxygen atom (O(13)...O(5) 2.590 Å) of the terminal anion, which, in turn, is linked with the hydrogen atom of the bridging water molecule (O(5)...O(1) 2.694 Å). The second hydrogen atom of this molecule is bound to the oxygen atom of solvate dioxane (O(1)...O(14) 2.681 Å). The coordinated water molecule form hydrogen bonds with the oxygen atom of the solvate acid molecule (O(8)...O(12) 2.743 Å) and oxygen atom of dioxane belonging to the near-lying molecule of the complex (O(8)...O(10*A*) 2.688 Å), which is arranged at an angle of 94.6°. As a result, wavy 2D polymers are formed in the crystal cell of the complexes, and the crystal is formed via the hydrogen bonds of the solvate dioxane molecules with the bridging water molecule. Note that the paramagnetic trinuclear complex of similar structure $[Co_3(\mu\text{-}OOCCF_3)_4(\mu\text{-}H_2O)_2(OOCCF_3)_2(H_2O)_2(C_4H_8O_2)] \cdot 2C_4H_8O_2$ was synthesized by reflux of $Co(OOCCF_3)_2(H_2O)_4$ (synthesized by the dissolution of CoO in hot $HOOCF_3$) with trifluoroacetic acid and its anhydride (10 : 1) in dioxane and was characterized by the XRD data at room temperature (Co...Co 3.632(3), Co-μ-O_w 2.143(3), 2.160(3), Co-μ-O($OOCF_3$) 2.053(3)–2.072(3) Å) [21].

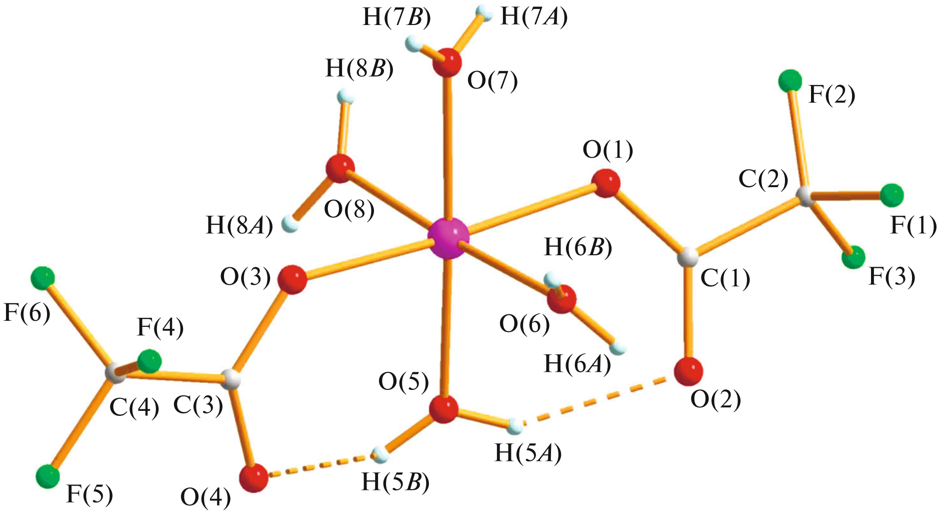

Fig. 3. Structure of complex **I** at 100 K (based on the results obtained by us and coinciding with published data [11, 20]). Selected bond lengths and bond angles: Co(1)–O(5) 2.069(7), Co(1)–O(7) 2.073(7), Co(1)–O(8) 2.087(7), Co(1)–O(6) 2.108(7), Co(1)–O(3) 2.115(7), and Co(1)–O(1) 2.123(7) Å; O(5)Co(1)O(7) 176.8(3)°, O(5)Co(1)O(8) 88.5(3)°, O(5)Co(1)O(6) 94.0(3)°, O(5)Co(1)O(3) 92.4(3)°, and O(5)Co(1)O(1) 92.2(3)°.

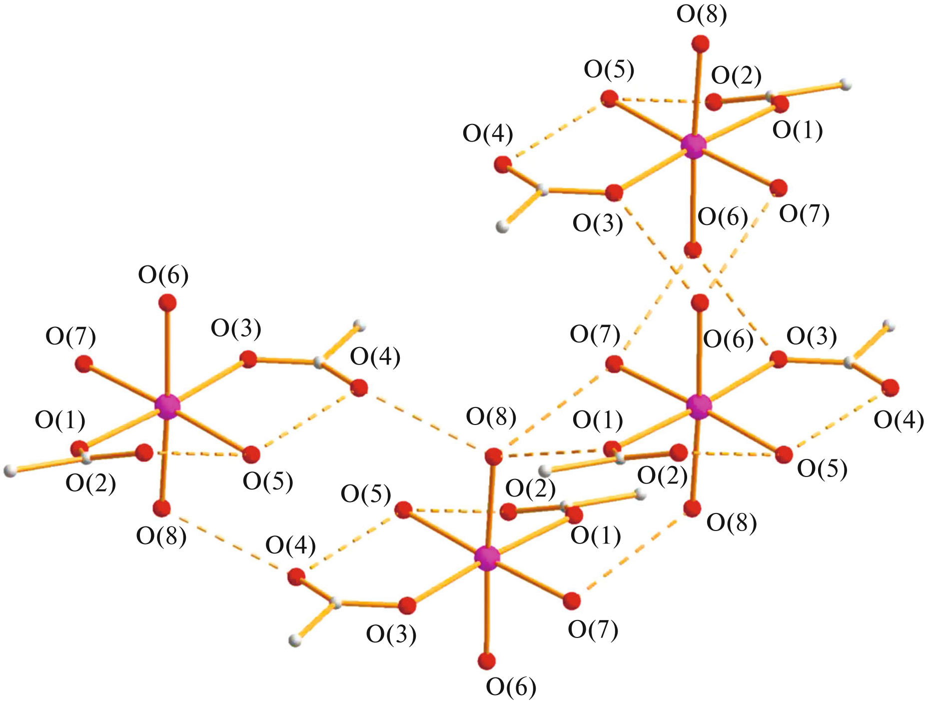

Fig. 4. Hydrogen bonds in the crystal of complex **I** at 100 K (O(1)...O(8) 2.776, O(4)...O(8) 2.678, O(3)...O(6) 2.735, O(6)...O(7) 2.783, and O(7)...O(8) 2.760 Å).

The dissolution of complex **III** in an isopropanol–dioxane mixture followed by heating to 60°C for 15 min gives red single crystals of complex **IV** (96% yield). According to the XRD data (Tables 1, 3; Fig. 7), in complex **IV** at room temperature the cobalt(II) atom is situated at the symmetry center (position (0, 0, 0)) and has an octahedral environment of four oxygen atoms of water (Co–O(3) 2.108(8), Co–O(4) 2.151(9) Å) and two oxygen atoms of the anions (Co–O(1) 2.172(7) Å) arranged in the anti conformation. All metal–oxygen distances in the complex are appreciably increased compared to those found in complexes **I**–**III**, which is also related, most likely, to the formation in the crystal of a complicated network

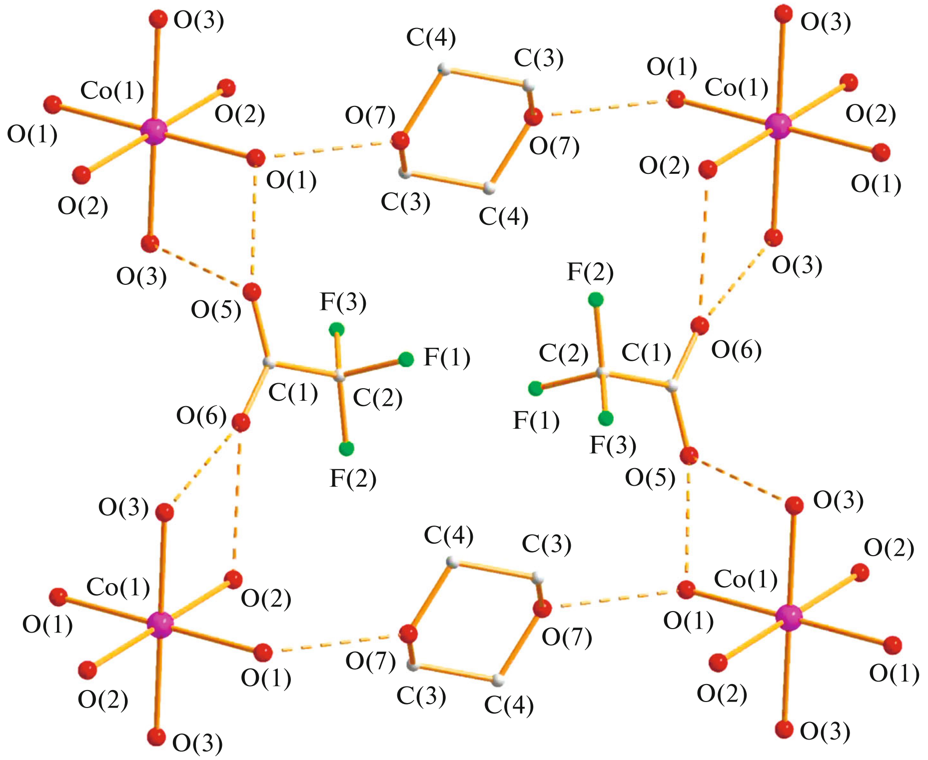

Fig. 5. Fragment of the packing of molecules of complex **II** in the crystal.

of intra- and intermolecular hydrogen bonds and to the presence of the solvate dioxane molecule (O(4)...O(5) 2.792 Å). All these factors result in the formation of the 3D polymer (Fig. 8).

The dissolution of complex **III** in the presence of pyrazole in boiling methylene dichloride followed by crystallization from a CH_2Cl_2–hexane mixture at 5°C gives orange single crystals of complex **V** (86% yield). In octahedral complex **V** (metal atom in the partial position), Co(II) is linked with four pyridinic nitrogen atoms of the heterocycles (Co–N(1) 2.0800(13), Co–N(3) 2.0893(14) Å) and two oxygen atoms of two trifluoroacetate anions (Co–O(1) 2.2327(13) Å) (Tables 1, 3; Fig. 9). Note that the metal–oxygen bonds are appreciably elongated compared to those found in the previously studied complexes, which is related, most likely, to steric contacts of pyrazole and trifluoromethyl substituents in the anions.

The hydrogen atoms of two pyrrole fragments of pyrazole form short intramolecular hydrogen bonds with the oxygen atoms of the anions (N(4)...O(2) 2.749 Å), and two other NH fragments form intramolecular bonds with the oxygen atoms of the solvate dioxane molecules (N(2)...O(3) 2.805 Å) to form 1D chains (Fig. 10).

The same octahedral complex **VI** (92% yield) is formed by the reaction of complex **I** with HPz in boiling methylene dichloride with the replacement of all water molecules by pyrazole. According to the XRD analysis of orange single crystals of complex **VI** (Tables 1, 3; Fig. 11), the metal atom is bound to four nitrogen atoms of coordinated pyrazoles (Co–N(1) 2.108(4), Co–N(3) 2.155(4) Å) and two oxygen atoms of the anions (Co–O(1) 2.142(3) Å). Slight differences in the metal–nitrogen distances are probably determined by the formation of various hydrogen bonds of the NH fragment with the oxygen atom of the anion. These bonds are intramolecular for the N(4) atom (N(4)...O(2) 2.739 Å), whereas for the N(2) atom they are intermolecular (N(2)...O(2) 2.805 Å) forming the crystal cell (Fig. 12). The coordinated pyrazole molecules are arranged at an angle of 97.8° relative to each other.

Note that the disorders of the fluorine atoms are eliminated when the structural experiment for complex **VI** is carried out at low temperatures, which results in the transition from the monoclinic to triclinic cell (Table 1) but, unlike complex **I**, the geometry of complex **VI** and the character of intermolecular and intramolecular hydrogen bonds remain substantially the same (Co–O(1) 2.1979(14), Co–N(1) 2.1043(16), Co–N(3) 2.1185(16), O(2)...N(4) 2.731, and O(2)...N(2) 2.893 Å, angle HPz/HPz 96.6°).

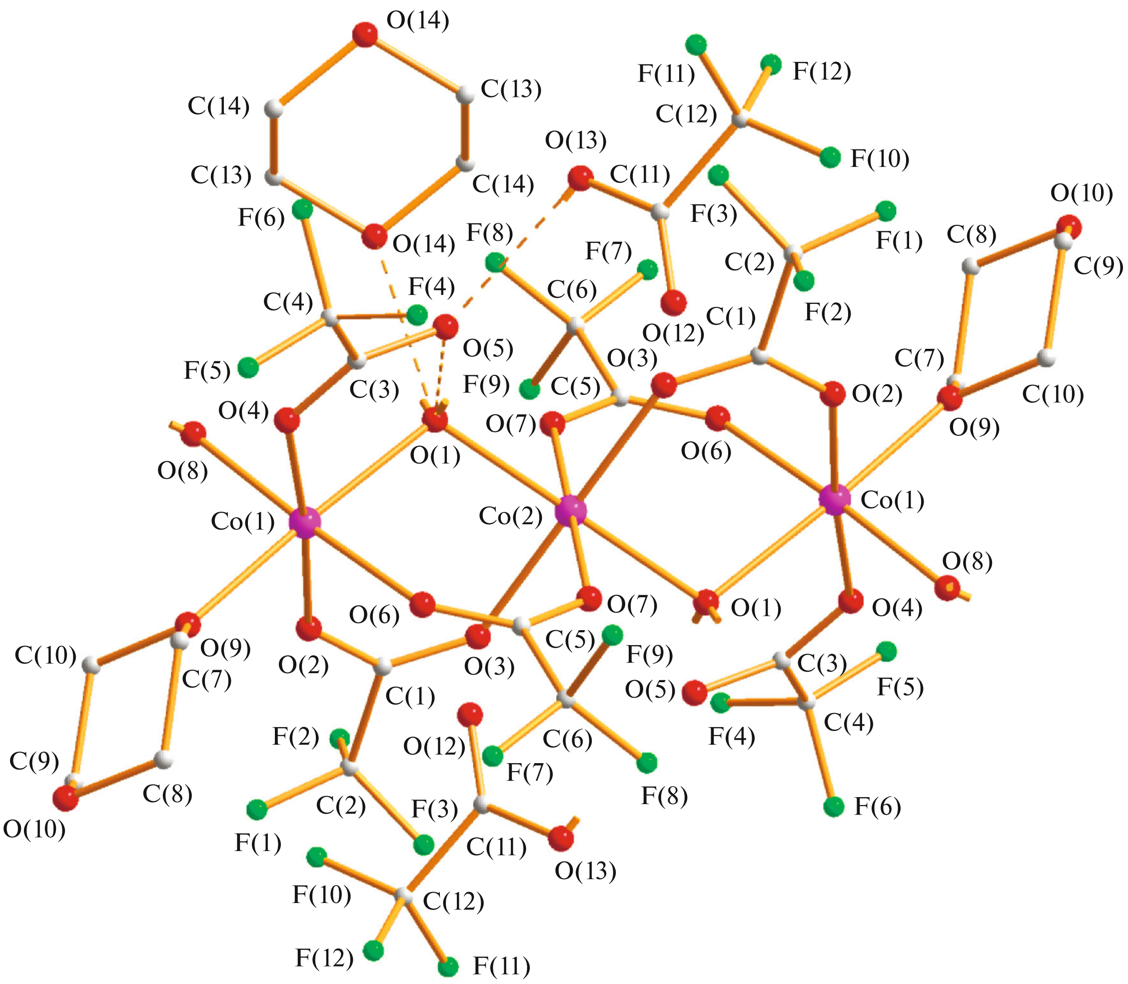

Fig. 6. Molecular structure of complex **III** (fluorine atoms F(4*A*)–F(9*A*) disordered with the multiplicity 0.8 : 0.2 are omitted).

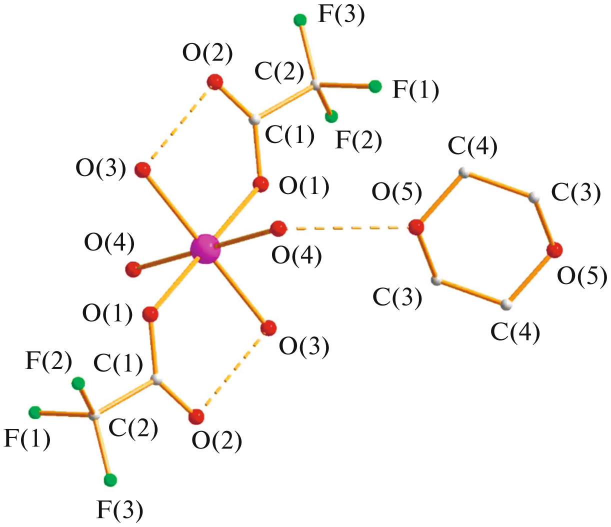

Fig. 7. Structure of complex **IV**. Fluorine atoms disordered with the multiplicity 0.5 : 0.5 are omitted.

Thus, it is shown by the present studies that the donor ability of bidentate 1,4-dioxane is insufficient for the direct coordination with the metal atom in the presence of water or pyrazole in the reaction solution. However, 1,4-dioxane plays a substantial role in the formation of the crystal cell forming polymers of various dimensionalities due to hydrogen bonds. It is known that 3,5-dimethylpyrazole is characterized by a diminished acidity of the NH proton and enhanced donor ability of the nitrogen atom of the pyridine type compared to unsubstituted HPz. Therefore, in the case of strong trifluoroacetic acid anions, the metal atom binds four pyrazole molecules. At the same time, in the reactions of Co(II) pivalate and benzoate, 3,5-dimethylpyrazole is deprotonated to form binuclear pyrazolate-bridged $[Co_2(\mu\text{-}Dmpz)_2(OOC^tBu)_2\text{-}(HDmpz)_2]$ [22, 23] and mononuclear $[(HDmpz)_2\text{-}Co(OOCPh)_2]$ [24] complexes. It should be mentioned that on going from room to low temperature trifluoroacetates undergo the transition accompanied by both a change in the hydro-

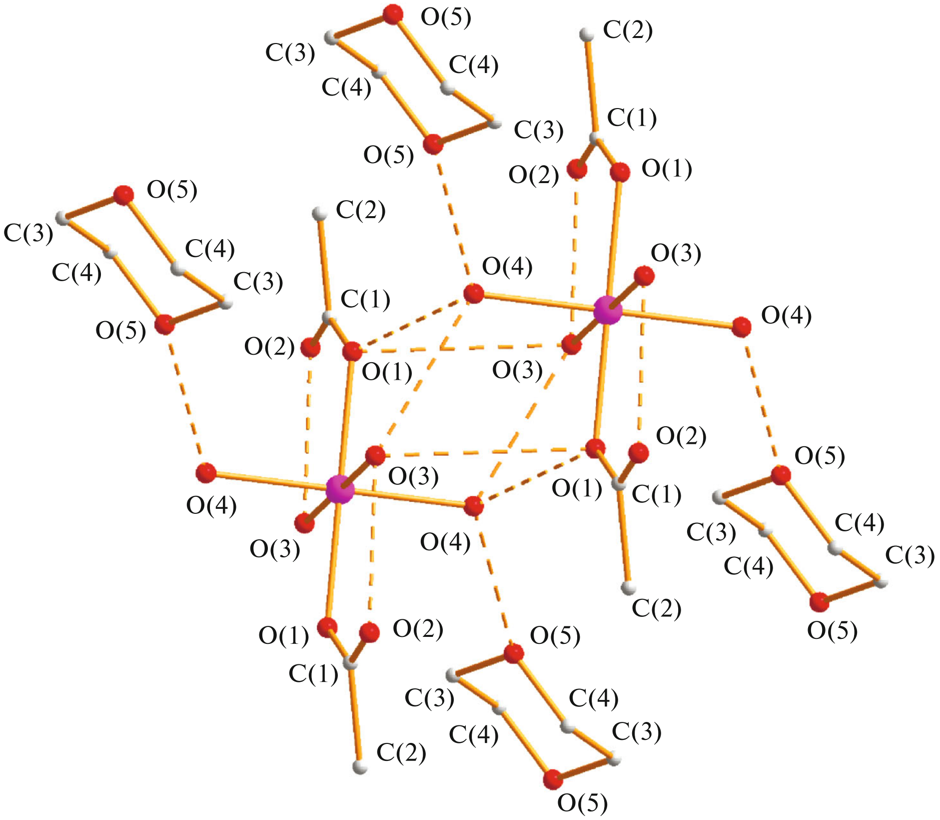

Fig. 8. Hydrogen bonds in the crystal of complex **IV** (O(3)...O(2) 2.790, O(3)...O(4) 2.961, O(3)...O(1) 2.904, and O(4)...O(1) 2.843 Å).

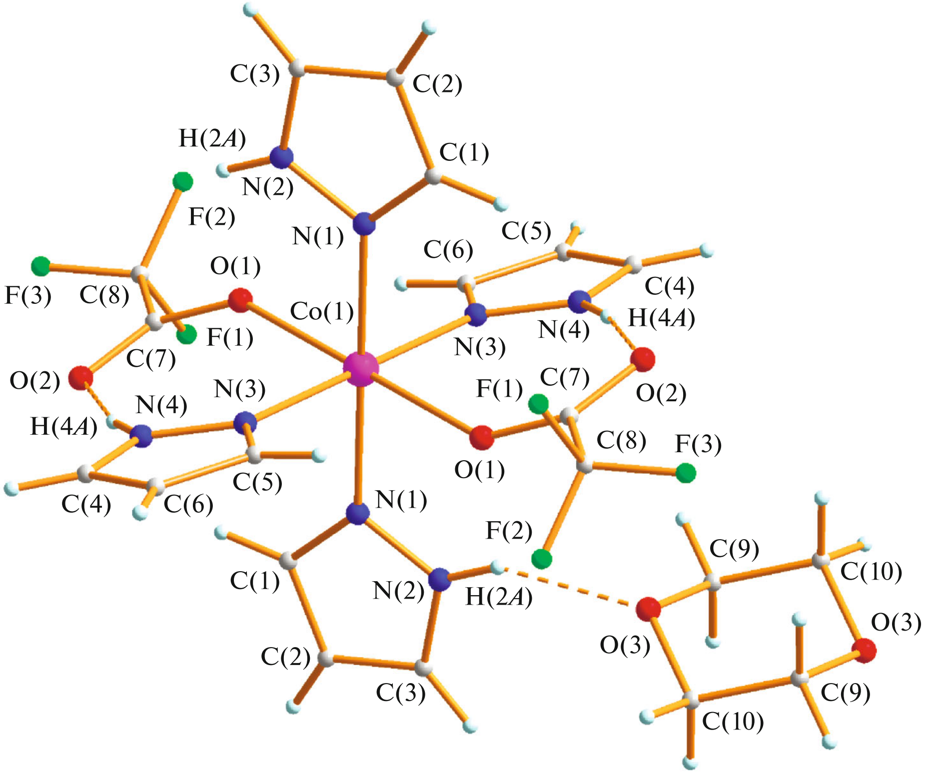

Fig. 9. Molecular structure of complex **V**.

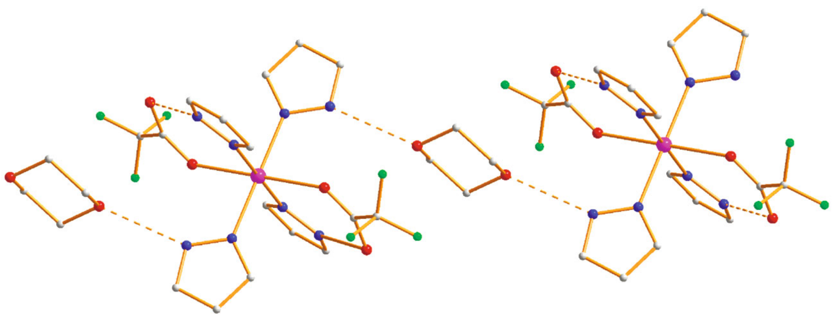

Fig. 10. Packing of molecules of complex **V** in the crystal (Co is violet, O is red, and N is blue).

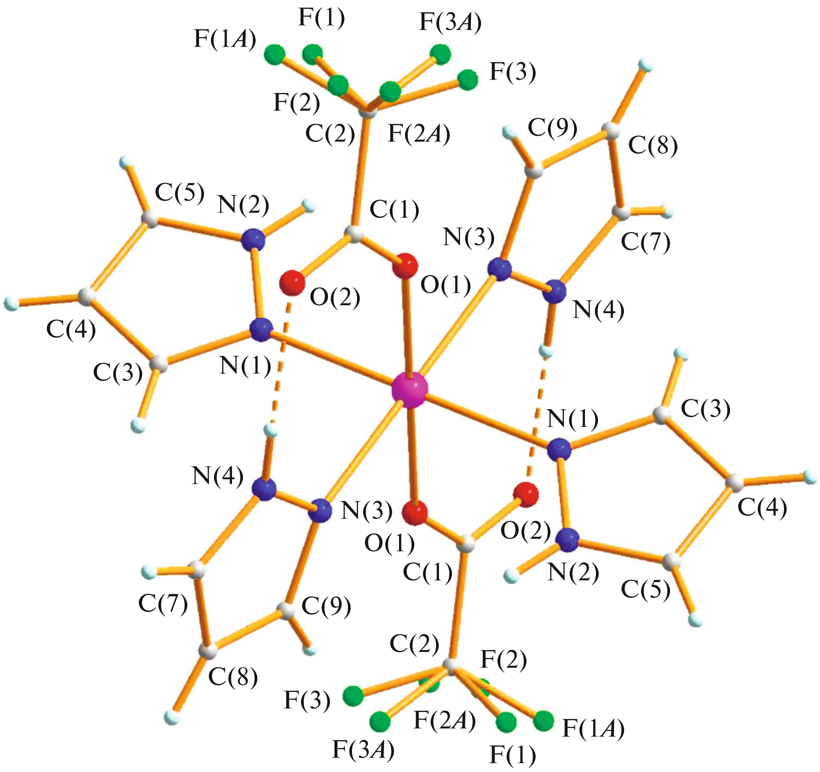

Fig. 11. Structure of complex **VI** at room temperature (fluorine atoms are disordered with the multiplicity 0.6 : 0.4).

gen bond network in the crystal packing of the complexes and disordering of the CF_3 substituent in the carboxylate anion and also, as found for complex **I**, a significant change in its geometry.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

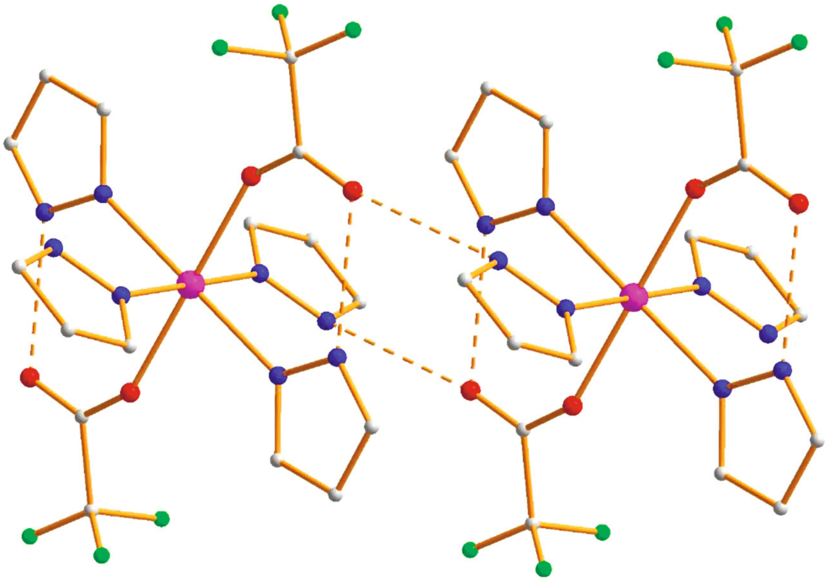

Fig. 12. Arrangement of molecules of complex **VI** in the crystal cell at room temperature (Co is violet, O is red, and N is blue).

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