

# New Complexes of Tris(2-aminoethanolato-O,N)cobalt(III) Sulfates: Synthesis and Structure

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**Abstract**—The reaction of  $[\text{Co}(\text{Etm})_3] \cdot 3\text{H}_2\text{O}$  (**I**) with sulfuric acid affords  $[\text{Co}(\text{HEtm})_3]_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$  (**II**). The change in the synthesis procedure (the direction interaction of cobalt(II) sulfate with  $\beta$ -aminoethanol (HEtm)) makes it possible to isolate  $[\text{Co}(\text{HEtm})_3](\text{SO}_4)(\text{HSO}_4) \cdot \text{H}_2\text{O}$  (**III**) and  $\{[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3]\}_2(\text{SO}_4)_3 \cdot 7.75\text{H}_2\text{O}$  (**IV**). The X-ray diffraction analyses of compounds **II–IV** show that all of them are of the ionic type. In compounds **II** and **III**, the ionic structure consists of the  $[\text{Co}(\text{HEtm})_3]_{3+}$  cations and sulfate anions in a ratio of 2 : 3 and 1 : 2, respectively. The basic difference in compounds **II** and **III** is the different degrees of deprotonation of the acid residues. In complex **II**, two  $\text{SO}_4^{2-}$  anions are doubly deprotonated. In complex **III**, of the four anions found in the independent part of the unit cell of the sulfate anion two anions are monodeprotonated. In structure **IV**, two crystallographically independent complexes  $[\text{Co}(\text{HEtm})_3]^{3+}$  and  $[\text{Co}(\text{Etm})_3]$  are joined into a dimer through the O–H...O hydrogen bonding.

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## INTRODUCTION

Transition metal complexes with chelating bidentate N,O ligands are of considerable interest for coordination chemistry. Octahedral complexes are formed at a metal to ligand ratio of 1 : 3. They formed a basis for studying an important aspect of theoretical chemistry, namely, the geometric isomerism phenomenon, because complex formation under certain conditions produces both facial (*fac*, 1, 2, 3) and meridional (*mer*, 1, 2, 6) isomers.

$\beta$ -Aminoethanol  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$  (**HEtm**) is a promising ligand for the synthesis of such complexes. Its complexes with Co(III) were synthesized for the first time in [1]. A specific feature of the HEtm ligand is the mobile proton of its alcohol group. During deprotonation the Etm<sup>–</sup> ligand can act as a monoanion, whereas in the case of the neutral ligand, its existence as an  $\text{H}_3\text{N}^+-\text{CH}_2-\text{CH}_2-\text{O}^-$  zwitterion cannot be excluded.

The system of two geometric isomers in  $[\text{Co}(\text{Etm})_3] \cdot n\text{H}_2\text{O}$  was studied rather completely by NMR spectroscopy and X-ray diffraction analysis [2–8]. In all cases, the  $\beta$ -aminoethanolate ions act as bidentate ligands. An analysis of published data [9] shows that three main structural types were found in addition to the cited above hydrate forms for the complexes synthesized by the reactions of monoethanolamine with cobalt salts. The cation-anionic form is presented, in particular, by the compounds  $[\text{Co}(\text{HEtm})_2(\text{Etm})][\text{Co}(\text{HEtm})(\text{Etm})_2](\text{ClO}_4)_3 \cdot 0.5\text{H}_2\text{O}$  [10, 11],  $[\text{Co}^{\text{III}}\text{Ni}^{\text{II}}(\text{Etm})_3(\text{HEtm})_3]_2$  [12], and  $[\text{Co}(\text{HEtm})_3](\text{NCS})_3$  [13]. The cation-anionic form can

exist as linear trinuclear clusters containing the  $\{\text{Co}^{\text{III}}, \text{Co}^{\text{II}}, \text{Co}^{\text{III}}\}^{2+}$  cations in which the alcohol groups of the ligand act as bridges [14–16]. The solvates are known in which  $\text{H}_2\text{O}$  in the outer sphere is replaced by other solvents, particularly, propanol and acetone [7].

We systematically studied the reaction products of  $\beta$ -aminoethanol with bivalent cobalt sulfate, nitrate, acetate, and chloride to reveal more completely the influence of the nature of the anion, its electronic and geometric features, specifics of the medium, and other parameters on the generation of the salt form. In this work, we present the data on the synthesis (under different conditions) and structures of the reaction products of  $[\text{Co}(\text{Etm})_3] \cdot 3\text{H}_2\text{O}$  (**I**) with sulfuric acid and of cobalt(II) sulfate with  $\beta$ -aminoethanol:  $[\text{Co}(\text{HEtm})_3]_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$  (**II**),  $[\text{Co}(\text{HEtm})_3](\text{SO}_4)(\text{HSO}_4) \cdot \text{H}_2\text{O}$  (**III**), and  $\{[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3]\}_2(\text{SO}_4)_3 \cdot 7.75\text{H}_2\text{O}$  (**IV**).

## EXPERIMENTAL

Cobalt(II) sulfate and  $\beta$ -aminoethanol (reagent grade) were used for the synthesis of complexes **I–IV**. The cobalt content was determined gravimetrically, the nitrogen content was found by the Dumas method, and water was determined thermogravimetrically.

Complex **I** was synthesized from cobalt(II) chloride using a described procedure [4].

**Synthesis of complex II.** A methanolic solution of sulfuric acid was poured dropwise with stirring to com-

**Table 1.** Crystallographic data and parameters of X-ray diffraction experiments for complexes **II–IV**

Parameter	<b>II</b>	<b>III</b>	<b>IV</b>
FW	844.62	906.66	1390.51
Temperature, K	100(2)	100(2)	100(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P6cc$
$a, b, c, \text{Å}$	8.0469(3), 8.4932(3), 12.6962(6)	8.994(5), 13.724(5), 13.729(5)	12.4037(5), 12.4037(5), 22.4752(12)
$\alpha, \beta, \gamma, \text{deg}$	84.950(2), 83.463(3), 66.420(2)	81.839(5), 74.070(5), 86.671(5)	90, 90, 120
$V, \text{Å}^3$	789.23(6)	1612.7(12)	2994.6(2)
$Z$	1	2	2
$\rho_{\text{calcd}}, \text{g/cm}^3$	1.777	1.867	1.542
$\mu, \text{mm}^{-1}$	1.345	1.391	1.285
$F(000)$	442	944	1463
$\theta$ range, deg	2.62–25.69	1.50–26.00	3.75–25.71
Index range	$-9 \leq h \leq 9, -10 \leq k \leq 10, -5 \leq l \leq 15$	$-11 \leq h \leq 11, -16 \leq k \leq 16, -16 \leq l \leq 16$	$-15 \leq h \leq 15, -15 \leq k \leq 15, -27 \leq l \leq 27$
$I_{hkl}$ of measured/ $I_{hkl}$ of independent reflections	29519/2991 ( $R_{\text{int}} = 0.0448$ )	40271/6325 ( $R_{\text{int}} = 0.0430$ )	72342/1915 ( $R_{\text{int}} = 0.0659$ )
Number of refined parameters	237	434	97
Goodness-of-fit for $F^2_{hkl}$	1.050	1.029	1.045
$R$ factor ( $I > 2\sigma(I)$ )	$R_1 = 0.0316, wR_2 = 0.0712$	$R_1 = 0.0556, wR_2 = 0.1315$	$R_1 = 0.0716, wR_2 = 0.1577$
$R(I_{\text{meas}})$	$R_1 = 0.0350, wR_2 = 0.0725$	$R_1 = 0.0639, wR_2 = 0.1347$	$R_1 = 0.0776, wR_2 = 0.1607$
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}, e \text{ Å}^{-3}$	0.57/–0.395	1.648/–0.821	0.754/–0.827

plex **I** (2.93 g, 0.01 mol) wetted with a minimum amount of methanol at complex **I** to  $\text{H}_2\text{SO}_4$  ratios of 1 : 0.5, 1 : 1, and 1 : 1.5. In all cases, the product crystallized for 10–15 days, and the yield was 15–20%. The elemental analysis data indicate the identical composition of the isolated products.

For  $\text{C}_{12}\text{H}_{50}\text{Co}_2\text{N}_6\text{O}_{22}\text{S}_3$  anal. calcd. (%): Co, 13.98; N, 9.95;  $\text{H}_2\text{O}$ , 8.53.

Found (%): Co, 14.04; N, 9.86;  $\text{H}_2\text{O}$ , 8.50.

**Synthesis of complex III.**  $\beta$ -Aminoethanol (6 ml, 0.1 mol) was added dropwise with stirring to  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (5.62 g, 0.02 mol) dissolved in an aqueous-ethanol mixture (20 ml of ethanol and 10 ml of  $\text{H}_2\text{O}$ ). After 2 days, precipitated red needle-like crystals of compound **III** were filtered off and washed with ethanol and ether. The yield was 65%.

For  $\text{C}_{12}\text{H}_{48}\text{Co}_2\text{N}_6\text{O}_{24}\text{S}_4$  anal. calcd. (%): Co, 13.02; N, 9.27;  $\text{H}_2\text{O}$ , 3.97.

Found (%): Co, 13.15; N, 9.38;  $\text{H}_2\text{O}$ , 4.10.

Complex **IV** was synthesized analogously to complex **II** with the only difference that an ethanolic solution containing KOH (2.8 g, 0.05 mol) was added to the solution obtained by the interaction of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  with monoethanolamine. The red-violet crystals of compound **IV** precipitated during 3 days. The yield was 50%.

For  $\text{C}_{24}\text{H}_{93.50}\text{Co}_4\text{N}_{12}\text{O}_{31.75}\text{S}_3$  anal. calcd. (%): Co, 16.98; N, 12.09;  $\text{H}_2\text{O}$ , 10.04.

Found (%): Co, 16.46; N, 11.89;  $\text{H}_2\text{O}$ , 10.00.

**X-Ray diffraction analysis.** The experimental intensities for compounds **II–IV** were obtained at 100 K (monochromatized  $\text{MoK}_\alpha$  radiation) on an X8 APEXII CCD diffractometer. The crystals were placed at a distance of 40 cm from the CCD chamber. The total observed reflections were 1840, 1790, and 2230 frames for complexes **II**, **III**, and **IV**, respectively. The detection time for each frame was 30 s, and the scan ranges were  $1^\circ$ . The data were processed using the SAINT program package [17]. Structures **II–IV** were solved by direct methods and refined in the anisotropic variant for all non-hydrogen atoms. The hydrogen atoms of the water molecules and hydroxy groups of the ligands were objectively found from the difference Fourier syntheses and included into the refinement in the idealized positions. The positions of other hydrogen atoms were geometrically calculated. All calculations were performed by the SHELXS-97 [18] and SHELXL-93 [19] program packages. The characteristics of the X-ray diffraction experiments and the refinement details for structures **II**, **III**, and **IV** are given in Table 1.

Additional parameters were deposited with the Cambridge Structural Database (no. 703954 for **IV** and no. 703956 for **III**).

## RESULTS AND DISCUSSION

In the hydrate form of molecular compound **I**, the  $\text{Etm}^-$  ligand in the deprotonated form can stepwise add a proton due to the interaction with acids to form three protonation products, depending on the complex to  $[\text{H}^+]$  ratio. However, regardless of the pH value of the medium, the same compound **II** is formed due to the protonation of compound **I** by sulfuric acid. Since the crystallization process is prolonged, the formation of both mono- and diprotonated anionic species,  $[\text{Co}(\text{Etm})_2(\text{HEtm})]^+$  and  $[\text{Co}(\text{Etm})(\text{HEtm})_2]^{2+}$ , in the solution cannot be excluded. These species are unstable and transformed into the completely protonated product.

The interaction of cobalt(II) sulfate with  $\beta$ -aminoethanol in a neutral medium affords complex **III** in which all the three HEtm ligands are neutral. When this reaction is carried out in a weakly alkaline medium (pH  $\sim$ 8), the HEtm ligand is partially deprotonated. During this process, three protons are abstracted from two neutral complexes to form binuclear complex **IV**. All ligands are deprotonated with the further increase in the pH value of the reaction mixture to form inner-sphere complex **I**.

The X-ray diffraction analyses of compounds **II** and **III** showed their anionic structures consisting of the  $[\text{Co}(\text{HEtm})_3]^{3+}$  cations and sulfate anions in a ratio of 2 : 3 in complex **II** and 1 : 2 in complex **III**. Note that 50% of the acid residues in compound **III** are partially depro-

tonated. Compound **IV** has the composition  $\{[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3]\}_2(\text{SO}_4)_3 \cdot 7.75\text{H}_2\text{O}$ .

The independent part of the unit cell of compound **II** (Fig. 1) corresponds to the  $[\text{Co}(\text{HEtm})_3] 1.5(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ . One of the  $\text{SO}_4$  groups is centrosymmetric and disordered. In the  $[\text{Co}(\text{HEtm})_3]^{3+}$  complex cation, the neutral  $\beta$ -aminoethanol molecules are coordinated according to the 1,2,3-N,O type. The average distances are  $\text{Co}-\text{N} = 1.923 \text{ \AA}$  and  $\text{Co}-\text{O} = 1.930 \text{ \AA}$  (Table 2). Three metallocycles have somewhat asymmetric *gauche* conformation. As a whole, the geometric parameters of compound **II** are close to those found in complexes **V** [11], **VI** [7], and *fac*- $[\text{Co}(\text{Etm})_3] \cdot 5.44\text{H}_2\text{O}$  [8]. In crystal **II**, the structural units are joined into a three-dimensional framework through a system of hydrogen bonds (Table 3).

The fragment of the structure of compound **III** and the numeration of atoms in the independent cell are shown in Fig. 2. The structures of the 1,2,3- $[\text{Co}(\text{HEtm})_3]^{3+}$  complex cation in compounds **II** and **III** are identical. The average interatomic distances in complex **III** ( $\text{Co}-\text{N} 1.920$ ,  $\text{Co}-\text{O} 1.937 \text{ \AA}$ ) (Table 2) coincide within  $3\sigma$  with those found for compound **II** and other analogous complexes.

The basic difference between complexes **II** and **III** is the different degrees of deprotonation of the acid residues. In complex **II**, two  $\text{SO}_4^{2-}$  anions are doubly deprotonated, whereas in complex **III** two of the four sulfate

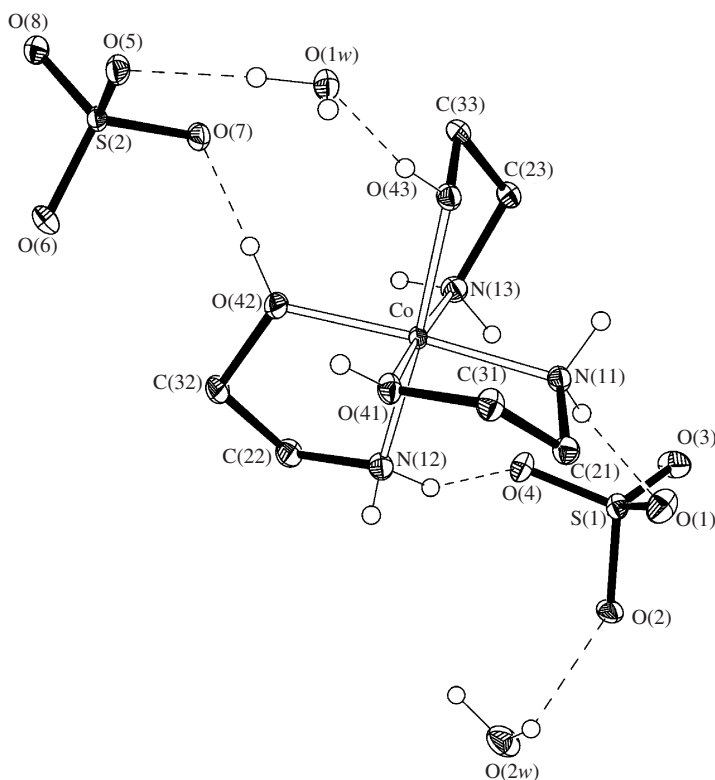


Fig. 1. Crystallographically independent part of the unit cell in structure **II**.

**Table 2.** Bond lengths and bond angles in structures **II–IV**\*

Bond	<i>d</i> , Å	Angle	$\omega$ , deg
<b>II</b>			
Co–N(11)	1.927(2)	O(41A)Co(A)N(11A)	84.65(9)
Co–N(12)	1.922(2)	O(41A)Co(A)N(12A)	90.24(9)
Co–N(13)	1.922(2)	O(41A)Co(A)N(13A)	175.31(9)
Co–O(41)	1.936(2)	O(42A)Co(A)N(11A)	174.09(1)
Co–O(42)	1.917(2)	O(42A)Co(A)N(12A)	84.60(9)
Co–O(43)	1.938(2)	O(42A)Co(A)N(13A)	94.46(1)
C21–N(11)	1.490(4)	O(43A)Co(A)N(11A)	90.27(9)
C22–N(12)	1.485(4)	O(43A)Co(A)N(12A)	175.62(9)
C23–N(13)	1.490(4)	O(43A)Co(A)N(13A)	85.74(9)
C31–O(41)	1.445(3)	O(41A)Co(A)O(42A)	89.68(9)
C32–O(42)	1.445(3)	O(41A)Co(A)O(43A)	91.95(8)
C33–O(43)	1.452(3)	O(42A)Co(A)O(43A)	91.62(8)
C21–C(31)	1.499(4)	N(11A)Co(A)N(12A)	93.70(1)
C22–C(32)	1.511(4)	N(11A)Co(A)N(13A)	91.27(1)
C23–C(33)	1.501(4)	N(12A)Co(A)N(13A)	92.33(1)
<b>III</b>			
Co(A)–N(11A)	1.910(4)	O(41A)Co(A)N(11A)	84.78(2)
Co(A)–N(12A)	1.929(4)	O(41A)Co(A)N(12A)	173.90(2)
Co(A)–N(13)	1.920(4)	O(41A)Co(A)N(13A)	93.44(2)
Co(A)–O(41A)	1.912(3)	O(42A)Co(A)N(11A)	89.57(2)
Co(A)–O(42A)	1.925(3)	O(42A)Co(A)N(12A)	84.56(2)
Co(A)–O(43A)	1.956(3)	O(42A)Co(A)N(13A)	175.52(2)
Co(B)–N(11B)	1.920(4)	O(43A)Co(A)N(11A)	175.90(2)
Co(B)–N(12B)	1.933(4)	O(43A)Co(A)N(12A)	89.02(2)
Co(B)–N(13B)	1.914(4)	O(43A)Co(A)N(13A)	84.45(2)
Co(B)–O(41B)	1.899(3)	O(41A)Co(A)O(42A)	89.35(1)
Co(B)–O(42B)	1.954(3)	O(41A)Co(A)O(43A)	91.44(1)
Co(B)–O(43B)	1.938(3)	O(42A)Co(A)O(43A)	91.98(1)
C(21A)–N(11A)	1.496(6)	N(11A)Co(A)N(12A)	94.92(2)
C(22A)–N(12A)	1.483(6)	N(11A)Co(A)N(13A)	94.17(2)
C(23A)–N(13A)	1.484(6)	N(12A)Co(A)N(13A)	92.65(2)
C(31A)–O(41A)	1.460(6)	O(41B)Co(B)N(11B)	84.76(1)
C(32A)–O(42A)	1.440(5)	O(41B)Co(B)N(12B)	175.01(2)
C(33A)–O(43A)	1.447(6)	O(41B)Co(B)N(13B)	92.50(2)
C(21A)–C(31A)	1.512(7)	O(42B)Co(B)N(11B)	90.55(2)
C(22A)–C(32A)	1.497(6)	O(42B)Co(B)N(12B)	83.79(1)
C(23A)–C(33A)	1.497(6)	O(42B)Co(B)N(13B)	175.25(2)
C(21B)–N(11B)	1.492(6)	O(43B)Co(B)N(11B)	175.84(2)
C(22B)–N(12B)	1.480(6)	O(43B)Co(B)N(12B)	89.96(1)
C(23B)–N(13B)	1.486(6)	O(43B)Co(B)N(13B)	85.30(2)
C(31B)–O(41B)	1.436(6)	O(41B)Co(B)O(42B)	91.51(1)
C(32B)–O(42B)	1.443(6)	O(41B)Co(B)O(43B)	91.91(1)
C(33B)–O(43B)	1.452(6)	O(42B)Co(B)O(43B)	92.03(1)
C(21B)–C(31B)	1.516(6)	N(11B)Co(B)N(12B)	93.57(2)
C(22B)–C(32B)	1.484(7)	N(11B)Co(B)N(13B)	92.34(2)
C(23B)–C(33B)	1.509(6)	N(12B)Co(B)N(13B)	92.26(2)
<b>IV</b>			
Co(A)–N(11A)	1.96(1)	O(41A)Co(A)N(11A)	85.3(4)
Co(A)–O(41A)	1.934(9)	O(41A)Co(A)N(11A) <sup>1</sup>	88.4(4)
Co(B)–N(11B)	1.92(1)	O(41A)Co(A)N(11A) <sup>2</sup>	177.8(4)
Co(B)–O(41C)	1.92(1)	O(41A)Co(A)O(41A)	92.7(3)
C(21A)–C(31A)	1.49(2)	N(11A)Co(A)N(11A)	93.6(4)
C(22A)–C(32A)	1.51(1)	O(41B)Co(B)N(11B)	83.8(4)
		O(41B)Co(B)N(11B) <sup>1</sup>	172.6(4)
		O(41B)Co(B)N(11B) <sup>2</sup>	91.7(4)
		O(41B)Co(B)O(41B)	88.8(3)
		N(11B)Co(B)N(11B)	95.7(4)

\* Symmetric transformations of equivalent atoms: <sup>1</sup>  $-x + y + 1, -x + 1, z$ ; <sup>2</sup>  $-y + 1, x - y, z$ .**Table 3.** Geometric characteristics of hydrogen bonding in structure **II**\*

D–H...A	Distance, Å			Angle D–H...A, deg
	D–H	H...A	D...A	
N(11)–H...O(1) <sup>2</sup>	0.92	1.99	2.864(5)	158
N(11)–H...O(2) <sup>5</sup>	0.92	2.20	3.009(4)	146
N(11)–H...O(6) <sup>4</sup>	0.92	1.97	2.882(3)	170
N(12)–H...O(4) <sup>2</sup>	0.92	2.05	2.897(5)	152
N(12)–H...O(3) <sup>5</sup>	0.92	2.03	2.903(5)	158
N(12)–H...O(8) <sup>2</sup>	0.92	2.02	2.851(3)	149
N(13)–H...O(4) <sup>2</sup>	0.92	2.04	2.896(5)	153
N(13)–H...O(2) <sup>5</sup>	0.92	2.10	2.929(5)	150
N(13)–H...O(2w)	0.92	1.91	2.785(6)	158
N(13)–H...O(3w)	0.92	2.15	3.039(6)	162
O(41)–H...O(5) <sup>3</sup>	0.81	1.76	2.558(3)	170
O(42)–H...O(7)	0.87	1.64	2.507(4)	179
O(43)–H...O(1w)	0.87	1.66	2.518(3)	168
O(1w)–H...O(5)	0.89	1.80	2.692(3)	177
O(1w)–H...O(6) <sup>3</sup>	0.89	1.80	2.691(3)	177

\* Symmetric transformations of equivalent atoms: <sup>1</sup>  $2 - x, -y, 1 - z$ ; <sup>2</sup>  $-1 + x, y, z$ ; <sup>3</sup>  $1 - x, 1 - y, -z$ ; <sup>4</sup>  $x, -1 + y, z$ ; <sup>5</sup>  $1 - x, -y, -z$ .

anions are monodeprotonated, which corresponds to the  $\{[\text{Co}(\text{HEtm})_3]_2(\text{SO}_4)_2(\text{HSO}_4)_2 \cdot 2\text{H}_2\text{O}\}$  composition.

A chain of three sulfuric acid residues joined by the hydrogen bond is observed in crystal **III** (Fig. 2, Table 4). This chain is the predominant packing fragment. As in compound **II**, the H-bonded three-dimensional framework is formed in crystal **III**.

According to the X-ray diffraction data, the composition of compound **IV** can be formulated as  $\{[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3]_2(\text{SO}_4)_3 \cdot 7.75\text{H}_2\text{O}\}$ , confirming the assumption of the partial deprotonation of the HETm ligand in the case when the synthesis is carried out at an elevated pH of the medium. In structure **IV**, two crystallographically independent complexes are joined



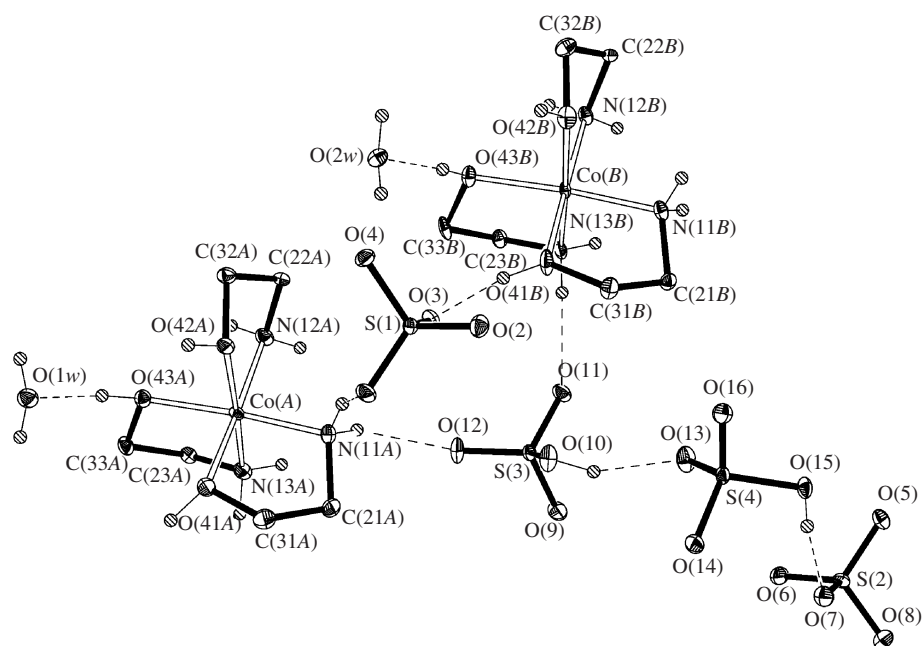


Fig. 2. Crystallographically independent part of the unit cell in structure III.

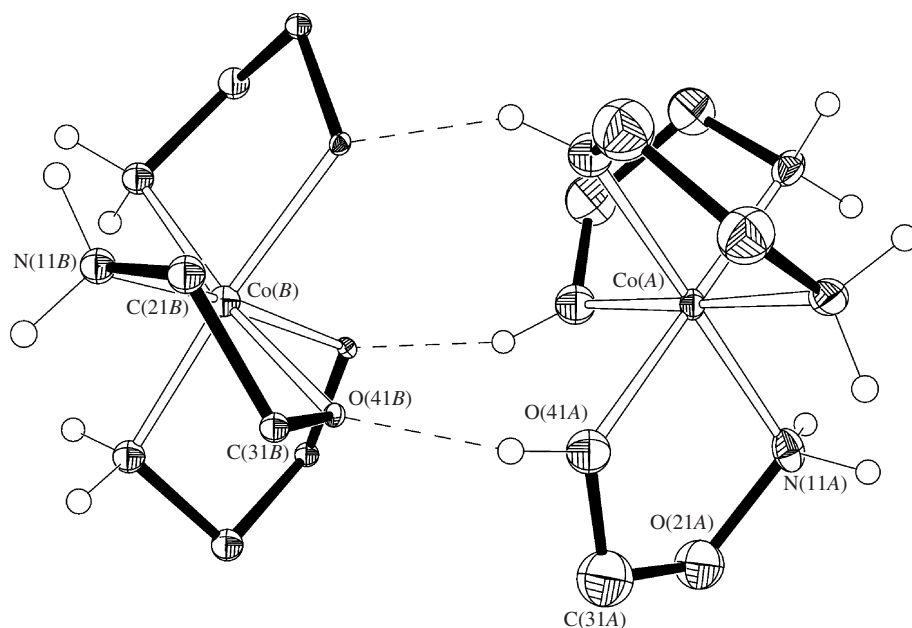


Fig. 3. Structure of two independent coordination molecules joined by hydrogen bonds in structure IV.

into a dimer through the O–H···O hydrogen bonding (O···O 2.419(7) Å) (Fig. 3). The protons near the alcohol groups of molecule A presented in Fig. 3 are equally distributed between complexes A and B. Two complexes are conjugated according to the “head-to-head” principle. The formation of the hydrogen bonding system is rather typical of the tris-complexes of monoethanolamine with cobalt(III). This interaction is organized, as a rule,

according to the “head-to-tail” principle. We observed such cases in the hydrate complexes of the *fac*- and *mer*-isomers of  $[\text{Co}(\text{Etm})_3] \cdot \text{H}_2\text{O}$  [8]. However, in this case, the donor–acceptor distances (O···O) range from 2.829 to 2.947 Å. The intrinsic symmetry of the Co(III) complexes in compound IV is  $C_3$ . The Co–N and Co–O distances in compound IV (Table 2) are 1.940 and 1.924 Å, respectively. The Co–O bonds in compound IV are

**Table 4.** Geometric characteristics of hydrogen bonding in structure **III**\*

D–H...A	Distance, Å			Angle D–H...A, deg
	D–H	H...A	D...A	
N(11A)–H...O(1)	0.90	2.18	2.946(6)	143
N(11A)–H...O(12)	0.90	2.10	2.844(6)	139
N(12A)–H...O(2) <sup>2</sup>	0.90	1.97	2.841(6)	161
N(12A)–H...O(16) <sup>3</sup>	0.90	2.07	2.952(6)	166
N(13A)–H...O(14) <sup>3</sup>	0.90	2.00	2.894(6)	171
N(13A)–H...O(14)	0.90	2.06	2.946(6)	169
O(41A)–H...O(7)	0.93	1.65	2.561(5)	167
O(42A)–H...O(4) <sup>1</sup>	0.92	1.61	2.524(5)	174
O(43A)–H...O(1 <sub>w</sub> )	0.99	1.55	2.530(5)	169
N(11B)–H...O(5) <sup>4</sup>	0.90	2.06	2.862(6)	148
N(11B)–H...O(11) <sup>5</sup>	0.90	2.25	3.084(6)	153
N(12B)–H...O(6) <sup>6</sup>	0.90	1.93	2.816(6)	166
N(12B)–H...O(9) <sup>5</sup>	0.90	1.96	2.820(6)	159
N(13B)–H...O(11) <sup>5</sup>	0.90	2.11	2.956(5)	157
N(13B)–H...O(11)	0.90	2.03	2.909(5)	164
O(41B)–H...O(3)	0.90	1.70	2.475(5)	143
O(42B)–H...O(8) <sup>1</sup>	0.92	1.72	2.629(6)	172
O(43B)–H...O(2 <sub>w</sub> )	0.90	1.64	2.525(5)	167
O(10)–H...O(13) <sup>7</sup>	0.90	1.77	2.615(6)	155
O(1 <sub>w</sub> )–H...O(2) <sup>1</sup>	0.99	1.72	2.702(6)	174
O(1 <sub>w</sub> )–H...O(8)	0.83	1.90	2.713(6)	168
O(2 <sub>w</sub> )–H...O(4)	0.90	1.85	2.718(5)	164
O(2 <sub>w</sub> )–H...O(6) <sup>1</sup>	0.90	1.80	2.696(5)	178

\* Symmetric transformations of equivalent atoms: <sup>1</sup>  $-x, 1-y, -z$ ; <sup>2</sup>  $-1+x, y, z$ ; <sup>3</sup>  $-x, 1-y, 1-z$ ; <sup>4</sup>  $1+x, -1+y, z$ ; <sup>5</sup>  $1-x, -y, 1-z$ ; <sup>6</sup>  $x, -1+y, z$ ; <sup>7</sup>  $1-x, 1-y, 1-z$ .

**Table 5.** Geometric characteristics of hydrogen bonding in structure **IV**\*

D–H...A	Distance, Å			Angle D–H...A, deg
	D–H	H...A	D...A	
O(41A)–H...O(41B) <sup>2</sup>	0.87	1.66	2.424(1)	145
N(11A)–H...O(1)	0.90	1.93	2.84(2)	178
N(11A)–H...O(2)	0.90	2.18	3.03(2)	157
O(41B)–H...O(41A) <sup>1</sup>	0.86	1.62	2.424(1)	153
N(11B)–H...O(1) <sup>4</sup>	0.90	2.07	2.96(2)	167
N(11B)–H...O(4) <sup>3</sup>	0.90	2.06	2.81(2)	140

\* Symmetric transformations of equivalent atoms: <sup>1</sup>  $1-x+y, 1-x, z$ ; <sup>2</sup>  $1-y, x-y, z$ ; <sup>3</sup>  $1-x, -x+y, -1/2+z$ ; <sup>4</sup>  $1-y, 1-x, -1/2+z$ .

shortened compared to those in complexes **II** and **III** due, most likely, to the deprotonation of the alcohol groups.

Crystal **IV** is interestingly organized. The [Co(HEtm)<sub>3</sub>][Co(Etm)<sub>3</sub>] dimers in the direction of the *z* axis alternate in the direction of three *z* axes with the disordered SO<sub>4</sub><sup>2-</sup> groups and are connected with them through the N–H...O bonds (Table 5). The packing of the dimer molecules results in the channel structure (Figs. 4a and 4b). The axis of the channels filled with the disor-

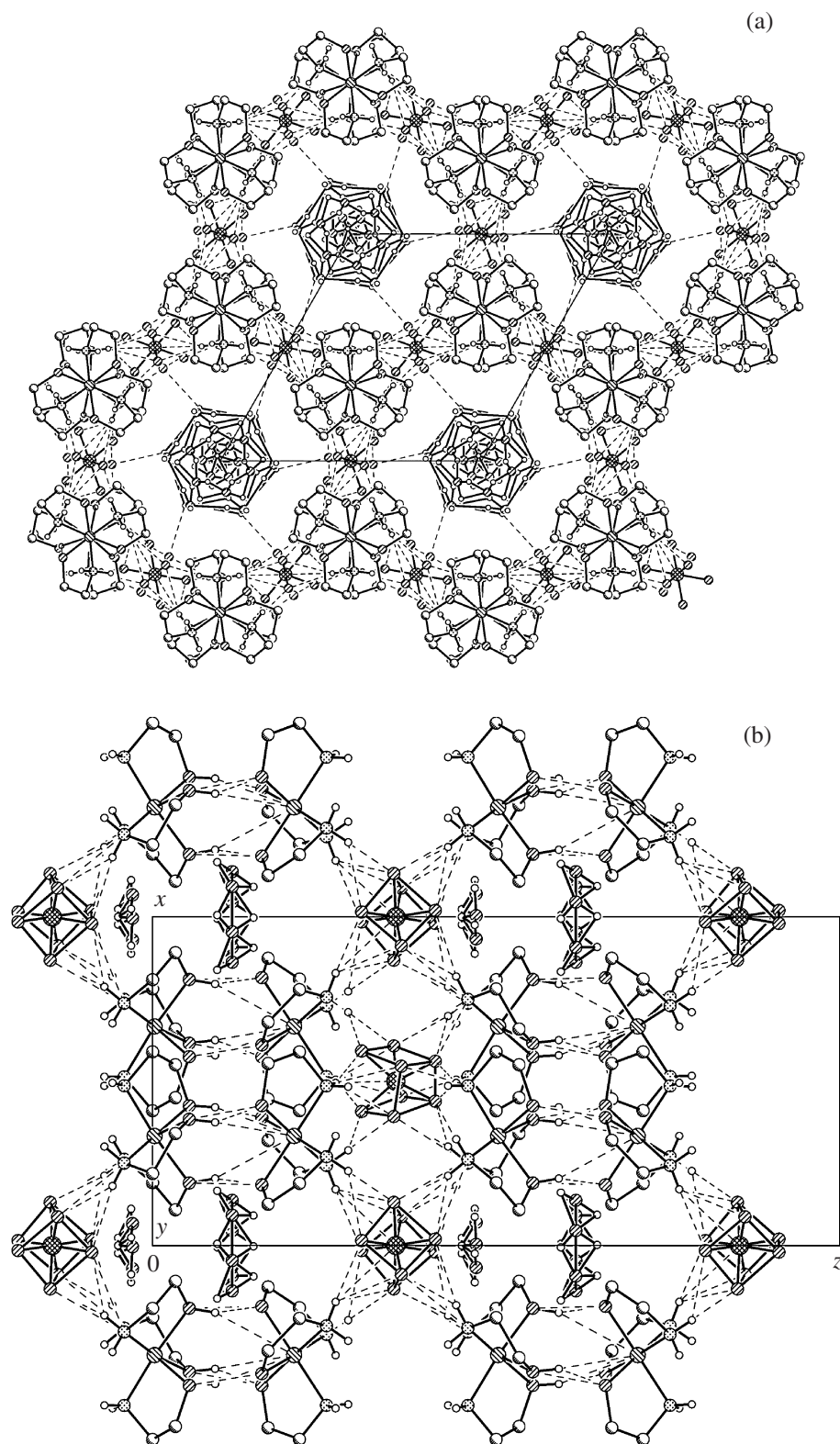


Fig. 4. Projections of crystal structure IV along the (a) z and (b) y axes.

dered water molecules is directed along the  $z$  axis of the crystal.

The data presented in this work show that the pH of the medium during the synthesis and a change in the course of the chemical reactions make it possible to monitor and control the type of the structure and the distribution of hydrogen atoms in it.

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