

## Effect of the Nature of the Anion on the Composition and Structure of Cobalt Complex with Monoethanolamine

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**Abstract**—A number of products formed in reactions of cobalt(II) salts with monoethanolamine (HEtm) in a neutral medium were synthesized and studied. X-Ray diffraction study showed that the nitrate and acetate form the dimers  $[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3](\text{NO}_3)_3$  and  $[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3](\text{CH}_3\text{COO})_3 \cdot 8\text{H}_2\text{O}$ , respectively. In chloride solutions, cobalt is partially oxidized to give the trinuclear complex  $[\text{Co}^{\text{II}}\{\text{Co}^{\text{III}}(\text{Etm})_3\}_2]\text{Cl}_3 \cdot \text{H}_2\text{Etm} \cdot 2\text{H}_2\text{O}$ . The reaction of the chelate  $[\text{Co}(\text{Etm})_3] \cdot 3\text{H}_2\text{O}$  with nitric acid is accompanied by complete protonation of the coordinated aminoethanolate ions, and the reaction with formic acid involves complete replacement of the coordinated ligand by acid residue anions and water molecules to give the coordination polymer  $\{\text{Co}_2(\mu\text{-HCOO})_4(\text{H}_2\text{O})_4\}_n$ .

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Previously [1–3], we described the specific features of reactions of monoethanolamine with cobalt(II) chloride and sulfate. Our works and published sources [1–8] prove that the composition and structure of the resulting complex in these systems depends on the conditions of synthesis (metal : ligand ratio, nature of the salt anion, solvent, and pH) because monoethanolamine can be coordinated either in the molecular ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$  (HEtm)) or monodeprotonated ( $\text{Etm}^-$ ) form or in the chelating bridging fashion. It was shown [1] that the reaction of a methanol solution of cobalt(II) chloride with  $\beta$ -aminoethanol in the presence of potassium hydroxide (1 : 5 : 3 ratio) affords the chelate  $[\text{Co}(\text{Etm})_3] \cdot 3\text{H}_2\text{O}$  (**I**) in which all of the coordinated ligands are deprotonated at the hydroxy groups. Previously [3], we showed that depending on the solution pH, the reaction of HEtm with cobalt(II) sulfate yields various types of complexes. The complex  $[\text{Co}(\text{HEtm})_3](\text{SO}_4)(\text{HSO}_4) \cdot \text{H}_2\text{O}$  (**II**) in which the ligand is coordinated in the molecular form is isolated from neutral solutions. An identical complex cation is also present in  $[\text{Co}(\text{HEtm})_3]_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$  (**III**) resulting from the reaction of complex **I** with sulfuric acid. It was shown by X-ray diffraction that the acid residues in complex **III** are doubly deprotonated, whereas in compound **II**, half of the acid residues are monodeprotonated. The reaction of HEtm with  $\text{CoSO}_4$  in weakly alkaline medium (pH ~ 8) is accompanied by partial deprotonation of the ligand. Three protons are eliminated from two neutral complexes,

giving rise to the binuclear complex  $\{[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3]\}_2(\text{SO}_4)_3 \cdot 7.75\text{H}_2\text{O}$  (**IV**).

The purpose of this work is to study the effect of the nature of the cobalt(II) salt anion on the composition and the structure of the products formed in the reaction with HEtm in a neutral medium. Cobalt(II) nitrate, acetate, and chloride salts and KI and  $\text{NH}_4\text{CNS}$  were used. It was found that the nitrate and acetate form dimeric compounds,  $[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3](\text{NO}_3)_3$  (**V**) and  $[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3](\text{CH}_3\text{COO})_3 \cdot 8\text{H}_2\text{O}$  (**VI**), in which the coordination environment of cobalt is the same as found in complex **IV**. Note that in weakly alkaline medium, cobalt chloride forms the trinuclear complex  $[\text{Co}^{\text{II}}\{\text{Co}^{\text{III}}(\text{Etm})_3\}_2]\text{Cl}_3 \cdot \text{H}_2\text{Etm} \cdot 2\text{H}_2\text{O}$  (**VII**) [8].

The reaction of chelate **I** with nitric acid, as in the case of sulfuric acid [3], is accompanied by complete protonation of the coordinated aminoethanolate ions giving rise to the complex  $[\text{Co}(\text{HEtm})_3](\text{NO}_3)_3$  (**VIII**). An X-ray diffraction study of the reaction product of **I** with formic acid showed that it is an inorganic polymer described as  $[\text{Co}_2(\mu\text{-HCOO})_4(\text{H}_2\text{O})_4]_n$  (**IX**).

The reactivity of known salt forms of cobalt aminoethanolates was studied by examples of reactions with potassium iodide and ammonium thiocyanate.

### EXPERIMENTAL

The complexes were synthesized using reagent grade  $\beta$ -aminoethanol and cobalt(II) nitrate, acetate,

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and chloride. Cobalt was quantified by gravimetry, nitrogen was determined by the Dumas method, and the water content was found by thermogravimetry. Compounds **I**, **II**, **III**, and **IV** were prepared by known procedures [1, 2].

**Synthesis of V.**  $\beta$ -Aminoethanol (6 mL, 0.1 mol) was added dropwise with stirring to a solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (5.82 g, 0.02 mol) in an ethanol (30 mL) and  $\text{H}_2\text{O}$  (5 mL) mixture. The red needle crystals that precipitated after 2 days were filtered off and washed with ethanol and diethyl ether. Yield 81%.

For  $\text{C}_{12}\text{H}_{39}\text{N}_9\text{O}_{15}\text{Co}_2$

anal. calcd. (%): Co, 17.69; N, 18.89.

Found (%): Co, 17.47; N, 18.79.

**Synthesis of VI.**  $\beta$ -Aminoethanol (6 mL, 0.1 mol) was added dropwise with stirring to a solution of  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (4.98 g, 0.02 mol) in an ethanol (30 mL) and  $\text{H}_2\text{O}$  (5 mL) mixture. The red crystals that precipitated after 36 h were filtered off and washed with ethanol and diethyl ether. Yield 70%.

For  $\text{C}_{18}\text{H}_{64}\text{N}_6\text{O}_{20}\text{Co}_2$

anal. calcd. (%): Co, 14.71; N, 10.47;  $\text{H}_2\text{O}$ , 17.95.

Found (%): Co, 15.05; N, 10.38;  $\text{H}_2\text{O}$ , 16.80.

**Synthesis of VII.**  $\beta$ -Aminoethanol (6 mL, 0.1 mol) was added dropwise with stirring to a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (4.76 g, 0.02 mol) in an ethanol (30 mL) and  $\text{H}_2\text{O}$  (5 mL) mixture. The red crystals that precipitated after 36 h were filtered off and washed with ethanol and diethyl ether. Yield 74%.

For  $\text{C}_{14}\text{H}_{48}\text{N}_7\text{O}_9\text{Cl}_3\text{Co}_3$

anal. calcd. (%): Co, 23.87; N, 13.22;  $\text{H}_2\text{O}$ , 4.85.

Found (%): Co, 23.51; N, 13.04;  $\text{H}_2\text{O}$ , 4.70.

**Synthesis of VIII.** A methanol solution of nitric acid was added dropwise with stirring to complex **I** (1 g, 0.0034 mol) wetted by a smallest possible amount of methanol in the **I** :  $\text{HNO}_3$  ratio of 1 : 3 (0.29 mL of 54%  $\text{HNO}_3$  in 25 mL of methanol). Crystallization occurs for 5–7 days to give a 15–20% yield.

For  $\text{C}_6\text{H}_{21}\text{N}_6\text{O}_{12}\text{Co}$

anal. calcd. (%): Co, 13.78; N, 19.63.

Found (%): Co, 13.61; N, 19.29.

**Synthesis of IX.** A 20% solution of formic acid (2.2 mL) was added with continuous stirring to a solution containing compound **I** (1 g, 0.0034 mol). The red crystalline solid that precipitated after 5 days was filtered off and washed with ethanol and diethyl ether. Yield 41%.

For  $\text{C}_4\text{H}_{12}\text{O}_{12}\text{Co}_2$

anal. calcd. (%): Co, 31.89.

Found (%): Co, 30.96.

**Synthesis of  $[\text{Co}^{\text{II}}\{\text{Co}^{\text{III}}(\text{Etm})_3\}_2]\text{I}_2 \cdot 5.75\text{H}_2\text{O}$  (X).**

A saturated solution of KI was added to a solution of any of complexes **IV–VI** (0.005 mol) in water (15–20 mL) until a red microcrystalline precipitate started to form. The precipitate was filtered off and washed with ethanol and diethyl ether. Yield 70–76%.

For  $\text{C}_{12}\text{H}_{47.5}\text{N}_6\text{O}_{11.75}\text{I}_2\text{Co}_3$

anal. calcd. (%): Co, 19.79; N, 9.39;  $\text{H}_2\text{O}$ , 11.57.

Found (%): Co, 19.41; N, 9.24;  $\text{H}_2\text{O}$ , 11.30.

**Synthesis of  $[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3](\text{NCS})_3$  (XI).**

A saturated solution of  $\text{NH}_4\text{SCN}$  was added to a solution of any of complexes **IV–VI** (0.005 mol) in water (15–20 mL) until a blue microcrystalline precipitate started to form. The precipitate was filtered off and washed with ethanol and diethyl ether. Yield 70–80%.

For  $\text{C}_{15}\text{H}_{39}\text{N}_9\text{O}_6\text{S}_3\text{Co}_2$

anal. calcd. (%): Co, 18.01; N, 19.23.

Found (%): Co, 17.84; N, 19.15.

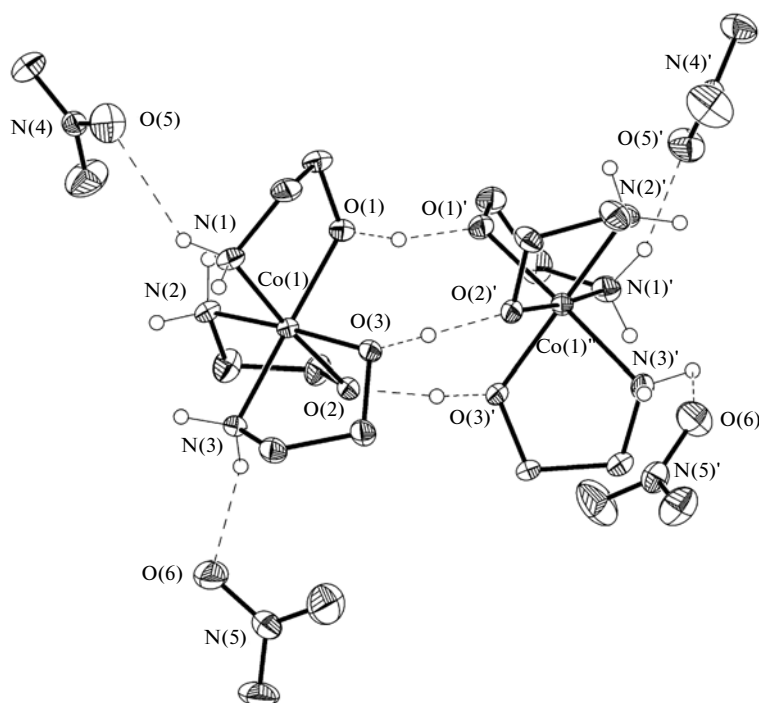
**Synthesis of  $\{[\text{Co}^{\text{III}}(\text{HEtm})_3][\text{Co}^{\text{III}}(\text{Etm})_3]\}_2[\text{Co}^{\text{II}}(\text{NCS})_6](\text{NCS})_2$  (XII).** A saturated solution of  $\text{NH}_4\text{SCN}$  was added to a solution of complex **VII** or **X** (0.005 mol) in water (15–20 mL) until a red microcrystalline precipitate started to form. The precipitate was filtered off and washed with ethanol and diethyl ether. Yield 60–65%.

For  $\text{C}_{32}\text{H}_{78}\text{N}_{20}\text{O}_{12}\text{S}_8\text{Co}_5$

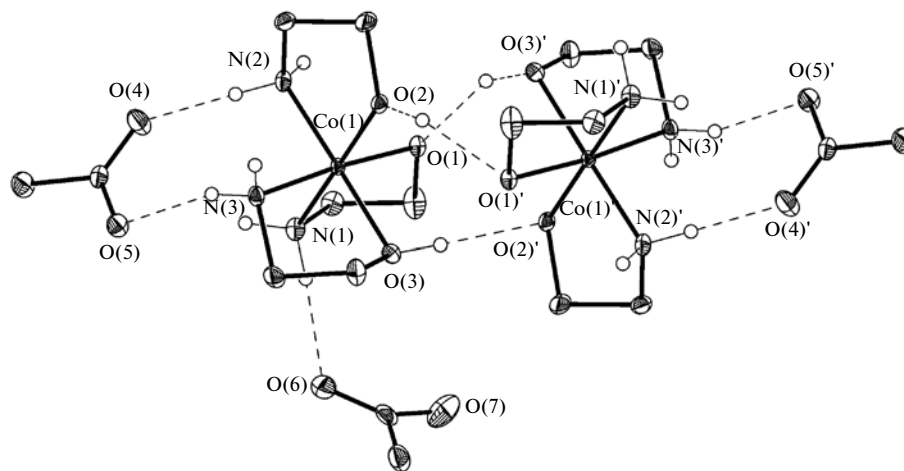
anal. calcd. (%): Co, 19.86; N, 18.85.

Found (%): Co, 18.61; N, 18.62.

**X-ray diffraction.** The experimental data for **V–X** and **XII** were collected at 100 K on a Bruker SMART-APEX II CCD diffractometer ( $\text{MoK}_\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ , graphite monochromator). The absorption corrections were applied empirically by the SADABS program. The structures were solved by the direct method and refined by the least-squares method in the full-matrix anisotropic mode for non-hydrogen atoms (SHELX-97). The hydrogen atom positions at the N and O atoms were found from difference Fourier maps and detailed considering the geometric parameters of hydrogen bonds (Table 1, 2). The position of other H atoms were calculated geometrically and refined isotropically in the “rigid body” model  $U_{\text{H}} = 1.2 U_{\text{eq}}$  of C atoms.



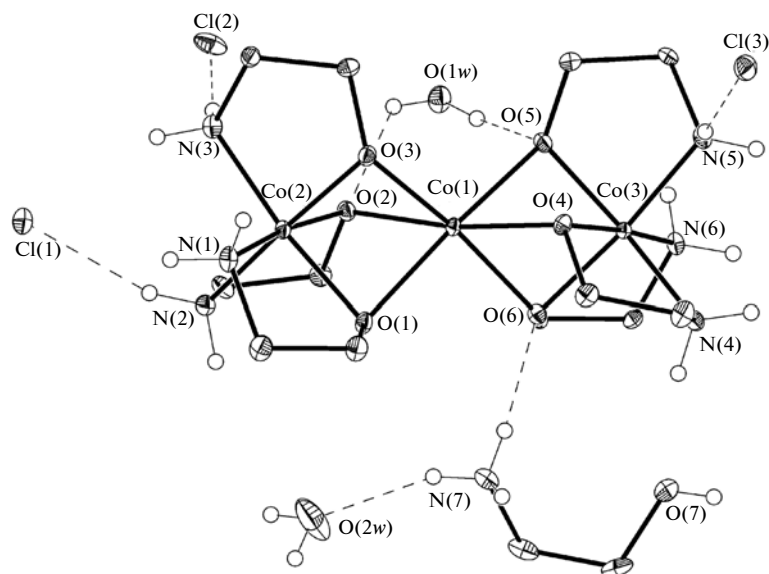
**Fig. 1.** Structure of the compound  $[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3](\text{NO}_3)_3$  (**V**); some interatomic distances:  $\text{Co}1-\text{O}1$ , 1.905(4);  $\text{Co}1-\text{O}2$ , 1.920(4);  $\text{Co}1-\text{O}3$ , 1.911(4);  $\text{Co}1-\text{N}1$ , 1.936(5);  $\text{Co}1-\text{N}2$ , 1.948(5);  $\text{Co}1-\text{N}3$ , 1.926(4) Å and bond angles:  $\text{O}1\text{Co}1\text{O}3$ ,  $92.0(2)^\circ$ ;  $\text{O}2\text{Co}1\text{N}1$ ,  $174.9(2)^\circ$ ;  $\text{O}1\text{Co}1\text{O}2$ ,  $90.0(2)^\circ$ ;  $\text{N}3\text{Co}1\text{N}1$ ,  $93.0(2)^\circ$ ;  $\text{O}3\text{Co}1\text{O}2$ ,  $90.7(2)^\circ$ ;  $\text{O}1\text{Co}1\text{N}2$ ,  $89.3(2)^\circ$ ;  $\text{O}1\text{Co}1\text{N}3$ ,  $176.6(2)^\circ$ ;  $\text{O}3\text{Co}1\text{N}2$ ,  $175.5(2)^\circ$ ;  $\text{O}3\text{Co}1\text{N}3$ ,  $85.3(2)^\circ$ ;  $\text{O}2\text{Co}1\text{N}2$ ,  $85.0(2)^\circ$ ;  $\text{O}2\text{Co}1\text{N}3$ ,  $92.1(2)^\circ$ ;  $\text{N}3\text{Co}1\text{N}2$ ,  $93.6(2)^\circ$ ;  $\text{O}1\text{Co}1\text{N}1$ ,  $85.0(2)^\circ$ ;  $\text{N}1\text{Co}1\text{N}2$ ,  $94.2(2)^\circ$ ;  $\text{O}3\text{Co}1\text{N}1$ ,  $90.2(2)^\circ$ .



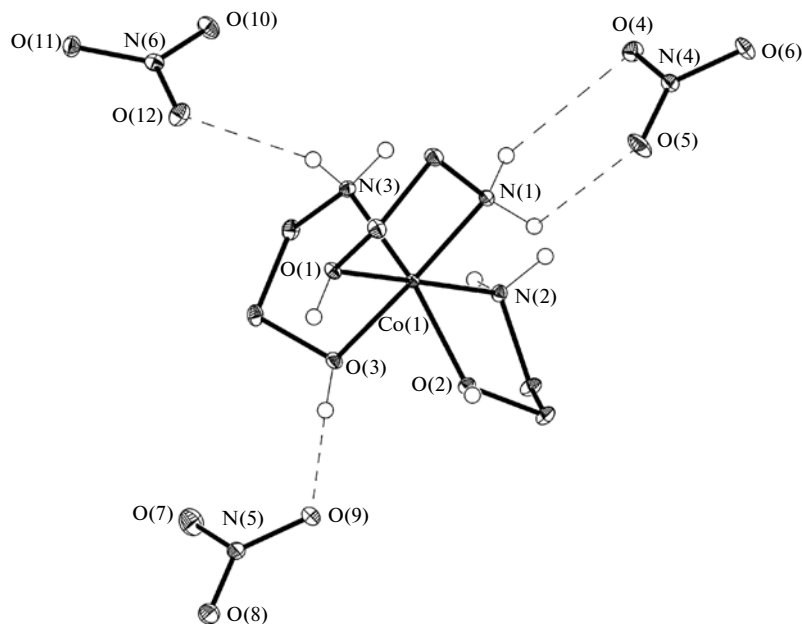
**Fig. 2.** Structure of the cation  $\{[\text{Co}(\text{HEtm})_3][\text{Co}(\text{Etm})_3]\}^{3+}$  and the hydrogen-bonded anions  $\text{CH}_3\text{COO}^-$  (**VI**); some interatomic distances:  $\text{Co}1-\text{O}1$ , 1.886(5);  $\text{Co}1-\text{O}2$ , 1.919(5);  $\text{Co}1-\text{O}3$ , 1.959(5);  $\text{Co}1-\text{N}1$ , 1.920(6);  $\text{Co}1-\text{N}2$ , 1.885(6);  $\text{Co}1-\text{N}3$ , 1.972(6) Å and bond angles:  $\text{O}1\text{Co}1\text{N}1$ ,  $87.2(2)^\circ$ ;  $\text{O}1\text{Co}1\text{N}2$ ,  $92.6(2)^\circ$ ;  $\text{O}1\text{Co}1\text{N}3$ ,  $175.5(2)^\circ$ ;  $\text{O}1\text{Co}1\text{O}2$ ,  $93.3(2)^\circ$ ;  $\text{O}1\text{Co}1\text{O}3$ ,  $91.6(2)^\circ$ ;  $\text{N}1\text{Co}1\text{O}3$ ,  $90.6(2)^\circ$ ;  $\text{N}1\text{Co}1\text{N}3$ ,  $90.1(3)^\circ$ ;  $\text{N}1\text{Co}1\text{O}2$ ,  $179.5(2)^\circ$ ;  $\text{O}2\text{Co}1\text{O}3$ ,  $89.6(2)^\circ$ ;  $\text{O}2\text{Co}1\text{N}3$ ,  $89.4(2)^\circ$ ;  $\text{O}3\text{Co}1\text{N}3$ ,  $84.7(2)^\circ$ ;  $\text{N}2\text{Co}1\text{O}2$ ,  $86.9(2)^\circ$ ;  $\text{N}2\text{Co}1\text{O}3$ ,  $174.7(2)^\circ$ ;  $\text{N}2\text{Co}1\text{N}1$ ,  $92.9(3)^\circ$ ;  $\text{N}2\text{Co}1\text{N}3$ ,  $91.2(3)^\circ$ .

The crystal data and X-ray experiment details for **V–X** and **XII** are summarized in Table 1 and the geometric parameters of hydrogen bonds (HBs) are in Table 2. The structures of complexes **V–X** and **XII** are shown in Figs. 1–7. The positional and thermal

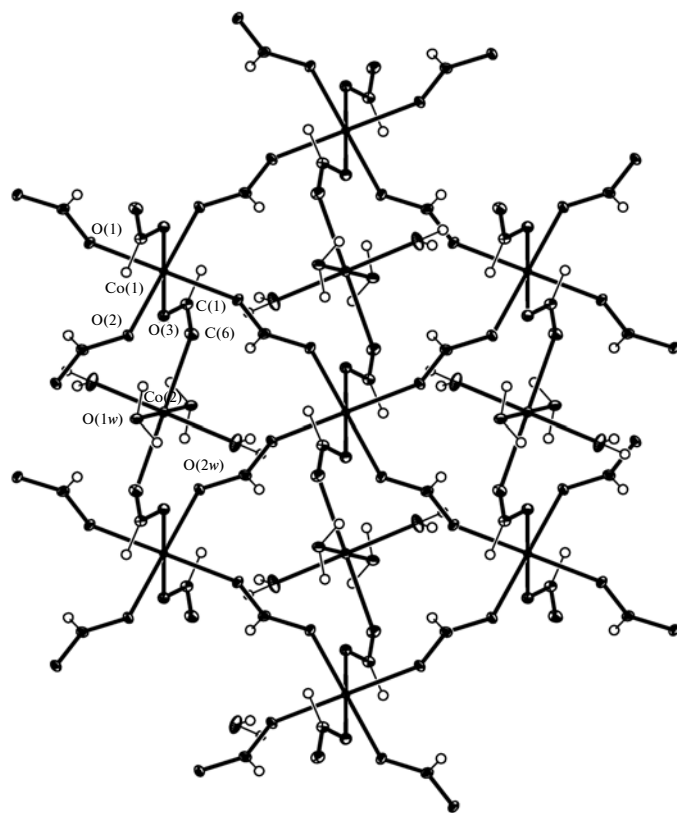
parameters of structures **V–X** and **XII** are deposited with the Cambridge Crystallographic Data Bank (nos. 861997–862003, respectively; deposit@ccdc.cam.ac.uk or [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).



**Fig. 3.** Structure of  $[\text{Co}^{\text{II}}\{\text{Co}^{\text{III}}(\text{Etm})_3\}_2]\text{Cl}_3 \cdot \text{H}_2\text{Etm} \cdot 2\text{H}_2\text{O}$  (**VII**); some interatomic distances: Co1–O1, 2.108(2); Co1–O4, 2.075(2); Co1–O2, 2.054(2); Co1–O5, 2.116(2); Co1–O3, 2.113(2); Co1–O6, 2.158(2); Co2–N1, 1.941(3); Co2–N6, 1.937(2); Co2–O1, 1.921(2); Co2–N2, 1.950(3); Co2–O2, 1.914(2); Co2–N3, 1.938(3); Co2–O3, 1.911(2); Co2–N4, 1.939(2); Co2–N1, 1.941(3); Co2–N5, 1.946(2); Co3–O4, 1.908(2); Co3–N4, 1.935(3); Co3–O5, 1.930(2); Co3–N5, 1.935(3); Co3–O6, 1.923(2); Co3–N6, 1.934(3) Å; and bond angles: O4Co1O1, 111.37(9)°; O2Co1O1, 77.66(9)°; O5Co1O6, 76.12(9)°; O2Co1O3, 77.38(9)°; O4Co1O3, 171.88(9)°; O1Co1O3, 76.26(9)°; O2Co1O4, 101.11(9)°; O2Co1O5, 172.68(9)°; O4Co1O5, 78.01(9)°; O1Co1O5, 95.82(9)°; O4Co1O6, 75.44(9)°; O1Co1O6, 168.5(1)°; O3Co1O6, 97.53(9)°; O3Co2O2, 85.9(1)°; O3Co2O1, 85.7(1)°; O2Co2O1, 85.8(1)°; O3Co2N3, 93.0(1)°; O2Co2N3, 87.0(1)°; O1Co2N3, 172.7(1)°; O3Co2N1, 173.1(1)°; N3Co2N1, 93.7(1)°; O3Co2N2, 87.7(1)°; O2Co2N2, 173.5(1)°; O1Co2N2, 92.7(1)°; N3Co2N2, 94.4(1)°; N1Co2N2, 93.1(1)°; O4Co3O6, 85.1(1)°; O4Co3O5, 86.8(1)°; O6Co3O5, 86.3(1)°; O4Co3N6, 174.1(1)°; O6Co3N6, 93.8(1)°; O5Co3N6, 87.3(1)°; O4Co3N5, 93.3(1)°; O6Co3N5, 87.6(1)°; O5Co3N5, 173.9(1)°; N6Co3N5, 92.4(1)°; O4Co3N4, 87.1(1)°; O6Co3N4, 172.1(1)°; O5Co3N4, 92.1(1)°; N6Co3N4, 93.8(1)°; N5Co3N4, 94.1(1)°.



**Fig. 4.** Structure of  $[\text{Co}(\text{HEtm})_3](\text{NO}_3)_3$  (**VIII**); some interatomic distances: Co1–O1, 1.948(1); Co1–O2, 1.922(1); Co1–O3, 1.921(8); Co1–N1, 1.931(1); Co1–N2, 1.926(1); Co1–N3, 1.927(1) Å; and bond angles: O3Co1O2, 86.09(4)°; O2Co1N2, 84.99(4)°; N2Co1N3, 93.95(4)°; N1Co1O1, 85.03(4)°; O2Co1N3, 170.80(4)°; O3Co1N1, 177.24(4)°; O2Co1N1, 95.65(4)°; N2Co1N1, 92.15(4)°; N3Co1N1, 93.51(4)°; O3Co1N2, 90.14(4)°; O3Co1O1, 92.79(4)°; O2Co1O1, 91.57(4)°; N2Co1O1, 175.33(4)°; N3Co1O1, 89.94(4)°; O3Co1N3, 84.78(4)°.



**Fig. 5.** Fragment of the crystal structure of  $[\text{Co}_2(\mu\text{-HCOO})_4(\text{H}_2\text{O})_4]_n$  (**IX**); some interatomic distances:  $\text{Co1-O1}^1$ , 2.094(2);  $\text{Co1-O2}$ , 2.065(2);  $\text{Co1-O3}$ , 2.13(2);  $\text{Co2-O6}$ , 2.145(2);  $\text{Co2-O1w}$ , 2.127(2);  $\text{Co2-O2w}$ , 2.042(2);  $\text{O2Co1O1}^1$ , 90.43(6) Å; and bond angles:  $\text{O2Co1O3}$ , 87.42(7)°;  $\text{O1}^1\text{Co1O3}$ , 86.42(7)°;  $\text{O2wCo2O1w}$ , 90.71(7)°;  $\text{O2wCo2O6}$ , 89.85(6)°;  $\text{O1wCo2O6}$ , 88.81(6)° ( $^1 - x + 2, y - 1/2, -z - 1/2$ ).

## RESULTS AND DISCUSSION

Compounds **V** and **VI** refer to the same type. The crystal structure is based on the dimeric cation in which two chemically equivalent units are connected by strong hydrogen bonds. The units  $\text{Co}(\text{Etm})_3$  are arranged in the head-to-head fashion, the  $\text{CoN}_3\text{O}_3$  coordination octahedron having a *fac*-configuration. The  $\text{O}\cdots\text{O}$  distances in the  $\text{O-H}\cdots\text{O}$  hydrogen bond are within 2.395–2.457 Å, which does not rule out the possibility of equally probable proton distribution on the donor and the acceptor.

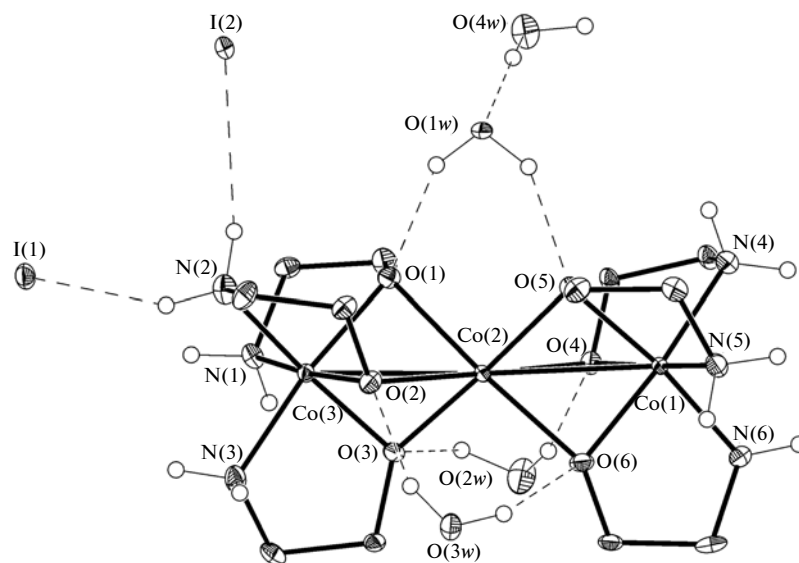
Upon the reaction of  $\beta$ -aminoethanol with cobalt(II) chloride in a neutral medium, we isolated trinuclear complex **VII** reported in [3] (obtained in weakly alkaline medium). These results indicate that the complexation is rather dictated by the nature of the anion of the initial salt and is less dependent on the pH of the reaction medium, as even in a neutral medium, the ligand is coordinated in the deprotonated form. The sulfate, nitrate, and acetate ions containing non-metal in the higher oxidation state and, hence, having oxidative properties, promote complete oxidation of  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  in the presence of air oxygen. In the case of chloride ions, this reaction occurs only partially,

and the isolated complex contains  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  in 1 : 2 ratio.

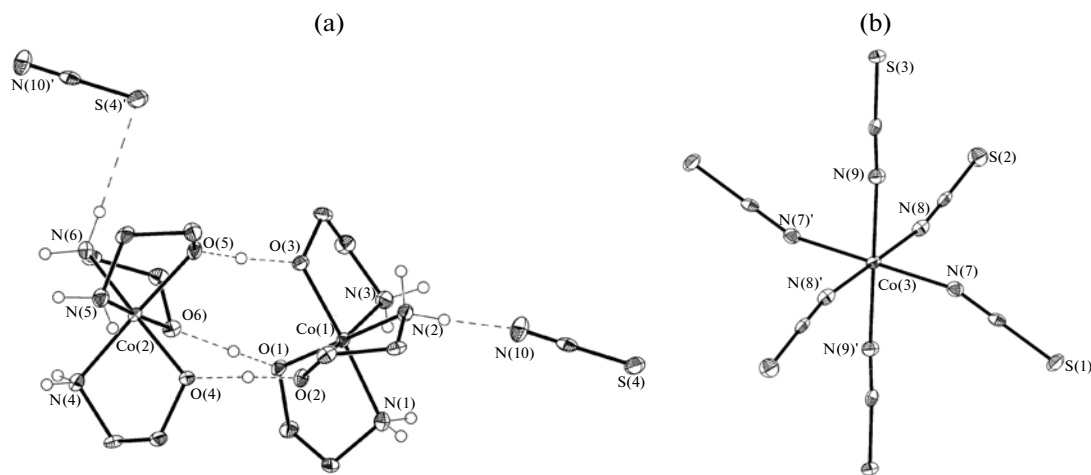
The replacement of sulfuric acid by nitric acid in the protonation of chelate **I** did not show considerable changes. The isolated complex **VIII** is mononuclear and is identical to complex **III**.

For comparative analysis, we studied the protonation reactions with organic acids (formic, acetic, oxalic, succinic, and adipic acids). It was noted that after addition of the corresponding acid, the violet-colored solution of cobalt(III) tris- $\beta$ -aminoethanolate turns red. Several days later, in the case of formic and acetic acids, a red microcrystalline solid precipitates from solutions, and solutions with a dicarboxylic acid (oxalic, succinic, and adipic) change the color once again to violet, and a mixture of the initial complex and the corresponding acid precipitates from the solution.

According to elemental analysis data, the compound obtained by the reaction of cobalt(III) tris- $\beta$ -aminoethanolate with formic acid contains no nitrogen. The IR spectrum exhibits no absorption bands for amino groups, but two absorption bands at 1570 and 1408  $\text{cm}^{-1}$  corresponding to the asymmetric and symmetric vibrations of carboxyl group are clearly seen.



**Fig. 6.** Structure of  $[\text{Co}^{\text{II}}\{\text{Co}^{\text{III}}(\text{Etm})_3\}_2]\text{I}_2 \cdot 5.75\text{H}_2\text{O}$  (**X**); some interatomic distances: Co1–O4, 1.926(3); Co1–O5, 1.913(3); Co1–O6, 1.916(3); Co1–N4, 1.950(4); Co1–N5, 1.933(4); Co1–N6, 1.946(4); Co2–O1, 2.133(3); Co2–O2, 2.048(3); Co2–O3, 2.131(3); Co2–O4, 2.096(3); Co2–O5, 2.091(3); Co2–O6, 2.140(3); Co3–O1, 1.925(3); Co3–O2, 1.894(3); Co3–O3, 1.917(3); Co3–N1, 1.946(4); Co3–N2, 1.941(4); Co3–N3, 1.938(4) Å; and bond angles: O4Co1N4, 87.5(1)°; O4Co1N5, 173.5(2)°; O4Co1N6, 91.2(2)°; O5Co1N6, 173.0(1)°; O5Co1O6, 85.7(1)°; O5Co1O4, 86.6(1)°; O5Co1N5, 87.5(1)°; O6Co1N5, 91.6(1)°; O6Co1O4, 85.5(1)°; O6Co1N6, 87.5(1)°; N5Co1N6, 94.4(2)°; O5Co1N4, 91.2(1)°; O6Co1N4, 172.4(2)°; N5Co1N4, 95.2(2)°; N6Co1N4, 95.3(2)°; O3Co2O5, 177.4(1)°; O3Co2O4, 102.4(1)°; O5Co2O4, 77.9(1)°; O3Co2O2, 77.1(1)°; O5Co2O2, 102.6(1)°; O4Co2O2, 178.6(1)°; O3Co2O1, 76.7(1)°; O5Co2O1, 100.7(1)°; O4Co2O1, 102.7(1)°; O3Co2O1, 75.9(1)°; O2Co2O6, 106.7(1)°; O5Co2O6, 76.0(1)°; O2Co2O6, 105.5(1)°; O4Co2O6, 76.0(1)°; O1Co2O6, 176.6(1)°; O1Co3N1, 87.49(14)°; O1Co3N2, 92.29(2)°; O1Co3N3, 172.48(2)°; O3Co3N1, 91.2(2)°; O3Co3N2, 173.8(2)°; O3Co3N3, 87.1(2)°; O3Co3O1, 85.6(1)°; O3Co3O2, 86.3(1)°; O2Co3O1, 86.1(1)°; O2Co3N1, 173.3(1)°; O2Co3N2, 87.8(1)°; O2Co3N3, 91.7(1)°; N2Co3N1, 94.6(2)°; N3Co3N1, 94.4(2)°; N3Co3N2, 94.8(2)°.



**Fig. 7.** Structure of (a) the cation  $\{\text{Co}^{\text{III}}(\text{HEtm})_3\}[\text{Co}^{\text{III}}(\text{Etm})_3]_2$  and (b) the anion  $[\text{Co}^{\text{II}}(\text{NCS})_6](\text{NCS})_2$  in **XII**; some interatomic distances: Co1–O1, 1.901(2); Co1–O2, 1.924(2); Co1–O3, 1.889(2); Co1–N1, 1.947(2); Co1–N2, 1.934(2); Co1–N3, 1.929(2); Co2–O4, 1.898(2); Co2–O5, 1.901(2); Co2–O6, 1.909(2); Co2–N6, 1.937(2); Co2–N4, 1.939(2); Co2–N5, 1.946(2); Co3–N7, 2.115(2); Co3–N8, 2.118(3); Co3–N9, 2.118(2) Å; and bond angles: O1Co1O2, 91.54(8)°; O1Co1N1, 85.24(9)°; O1Co1N2, 176.8(1)°; O1Co1N3, 89.03(9)°; O2Co1N1, 87.86(9)°; O2Co1N2, 85.39(9)°; O2Co1N3, 178.55(9)°; O3Co1O1, 91.07(8)°; O3Co1O2, 91.75(8)°; O3Co1N1, 176.28(9)°; O3Co1N2, 88.23(9)°; O3Co1N3, 86.90(9)°; N2Co1N1, 95.4(1)°; N3Co1N1, 93.5(1)°; N3Co1N2, 94.0(1)°; O4Co2O5, 92.13(8)°; O4Co2O6, 90.34(8)°; O4Co2N4, 85.68(9)°; O4Co2N5, 89.37(9)°; O4Co2N6, 175.60(9)°; O5Co2O6, 91.95(8)°; O5Co2N4, 177.81(9)°; O5Co2N5, 85.56(9)°; O5Co2N6, 87.37(9)°; O6Co2N4, 87.93(9)°; O6Co2N5, 177.5(1)°; O6Co2N6, 85.31(9)°; N4Co2N5, 94.6(1)°; N6Co2N4, 94.8(1)°; N6Co2N5, 94.9(1)°; N7Co3N8, 89.60(9)°; N7Co3N9, 93.11(9)°; N8Co3N9, 88.61(9)°.

Table 1. Crystallographic data and X-ray experiment and structure refinement details for compounds V–XII

Compound	V	VI	VII	VIII	IX	X	XII
<i>M</i>	667.38	802.61	741.73	428.22	185.00	894.65	1486.27
System	Trigonal	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P3_22_1$	$P\bar{1}$	$Cc$	$P2_1/c$	$P2_1/c$	$Cc$	$P\bar{1}$
<i>a</i> , Å	8.6508(2)	8.8002(5)	19.5340(4)	13.4437(7)	8.6634(3)	22.1674(6)	9.0647(3)
<i>b</i> , Å	8.6508(2)	10.8120(8)	11.5550(4)	13.6608(7)	7.1257(2)	8.6706(2)	12.0048(5)
<i>c</i> , Å	30.369(1)	11.2595(7)	14.4260(4)	8.8850(5)	9.2713(3)	14.9996(3)	14.8938(6)
$\alpha$ , deg	90	80.081(5)	90	90	90	90	110.507(2)
$\beta$ , deg	90	67.043(3)	118.252(2)	99.073(3)	97.404(3)	91.689(3)	93.633(2)
$\gamma$ , deg	120	66.313(4)	90	90	90	90	96.080(2)
<i>V</i> , Å <sup>3</sup>	1968.2(1)	903.2(1)	2868.2(1)	1611.3(2)	567.57(3)	2881.7(1)	1500.7(1)
<i>Z</i> ; $\rho$ (calcd.), g/cm <sup>3</sup>	3; 1.689	1; 1.476	4; 1.718	4; 1.765	4; 2.165	4; 2.062	1; 1.645
$\mu_{\text{Mo}}$ , mm <sup>-1</sup>	1.348	1.000	2.048	1.142	2.982	3.908	1.700
Crystal size, mm	$0.2 \times 0.2 \times 0.1$	$0.2 \times 0.14 \times 0.05$	$0.2 \times 0.18 \times 0.1$	$0.3 \times 0.25 \times 0.2$	$0.28 \times 0.2 \times 0.08$	$0.2 \times 0.15 \times 0.05$	$0.3 \times 0.2 \times 0.15$
Range of $\theta$ , deg	2.01–25.69	1.96–26.00	3.35–26.00	2.76–30.07	2.37–25.09	2.52–26.00	1.89–27.50
Range of indices	$-10 \leq h \leq 10$ , $-10 \leq k \leq 10$ , $-37 \leq l \leq 36$	$-10 \leq h \leq 10$ , $-13 \leq k \leq 13$ , $-13 \leq l \leq 13$	$-24 \leq h \leq 24$ , $-14 \leq k \leq 14$ , $-17 \leq l \leq 16$	$-18 \leq h \leq 18$ , $-19 \leq k \leq 19$ , $-12 \leq l \leq 12$	$-10 \leq h \leq 10$ , $-8 \leq k \leq 8$ , $-11 \leq l \leq 11$	$-27 \leq h \leq 27$ , $-10 \leq k \leq 10$ , $-18 \leq l \leq 18$	$-11 \leq h \leq 11$ , $-15 \leq k \leq 15$ , $-19 \leq l \leq 19$
The number of measured/independent reflections ( $R_{\text{int}}$ )	71648/2508 (0.0536)	25768/3543 (0.0718)	9091/5059 (0.0333)	54135/4710 (0.0403)	9099/887 (0.0475)	25098/5665 (0.0455)	48897/6879 (0.0912)
Flack parameter	0.525 (0.042)		0.032 (0.011)			-0.004 (0.016)	
The number of refined parameters	174	272	326	226	85	324	349
GOOF on $F_{hkl}^2$	1.028	1.067	1.053	1.041		1.051	1.020
$R(I > 2\sigma(I))$	$R_1 = 0.0517$ , $wR_2 = 0.1045$	$R_1 = 0.0490$ , $wR_2 = 0.1300$	$R_1 = 0.0259$ , $wR_2 = 0.0567$	$R_1 = 0.0237$ , $wR_2 = 0.0585$	$R_1 = 0.0228$ , $wR_2 = 0.0482$	$R_1 = 0.0251$ , $wR_2 = 0.0563$	$R_1 = 0.0404$ , $wR_2 = 0.0613$
$R$ (all data)	$R_1 = 0.0556$ , $wR_2 = 0.1064$	$R_1 = 0.0597$ , $wR_2 = 0.1340$	$R_1 = 0.0271$ , $wR_2 = 0.0574$	$R_1 = 0.0289$ , $wR_2 = 0.0609$	$R_1 = 0.0327$ , $wR_2 = 0.0499$	$R_1 = 0.0268$ , $wR_2 = 0.0571$	$R_1 = 0.0789$ , $wR_2 = 0.0671$
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ , e Å <sup>-3</sup>	0.450/-1.161	1.070/-0.527	0.374/-0.481	0.407/-0.405	0.231/-0.333	1.247/-0.495	0.620/-0.480

**Table 2.** Geometric parameters of the hydrogen bonds in **V–X** and **XII**

D–H...A contact	Distance, Å			DHA angle, deg
	D–H	H...A	D...A	
<b>V</b>				
O(3)–H...O(2) <sup>1</sup>	0.98	1.45	2.421(5)	170
O(1)–H...O(1) <sup>1</sup>	0.99	1.43	2.395(8)	163
N(3)–H...O(6)	0.90	2.18	3.037(7)	159
N(3)–H...O(6) <sup>2</sup>	0.90	2.20	3.079(7)	166
N(1)–H...O(5)	0.90	2.28	3.016(7)	138
N(1)–H...O(7) <sup>3</sup>	0.90	2.26	3.089(8)	153
N(2)–H...O(7) <sup>2</sup>	0.90	2.26	3.072(7)	150
* Symmetry codes: <sup>1</sup> $x - y, -y, -z + 1/3$ ; <sup>2</sup> $y + 1, x, -z$ ; <sup>3</sup> $x + 1, y + 1, z$ for <b>V</b> .				
<b>VI</b>				
O(2w)–H...O(5)	0.90	1.89	2.762(4)	163
O(2w)–H...O(6) <sup>1</sup>	0.90	1.85	2.750(4)	172
O(3w)–H...O(6)	0.90	1.88	2.754(4)	162
O(3w)–H...O(2w)	0.90	2.05	2.761(5)	135
N(3)–H...O(5) <sup>2</sup>	0.90	2.22	3.091(7)	162
N(3)–H...O(5)	0.90	2.01	2.879(7)	162
N(2)–H...O(4) <sup>3</sup>	0.90	2.11	2.960(7)	156
N(2)–H...O(4)	0.90	1.88	2.779(7)	172
O(2)–H...O(1) <sup>4</sup>	0.90	1.94	2.820(7)	165
O(1)–H...O(3) <sup>4</sup>	0.89	2.21	2.919(7)	137
O(3)–H...O(2) <sup>4</sup>	0.89	2.21	2.998(7)	147
* Symmetry codes: <sup>1</sup> $x + 1, -y + 1, -z + 2$ ; <sup>2</sup> $-x + 1, -y + 1, -z + 1$ ; <sup>3</sup> $x + 2, -y + 1, -z + 1$ ; <sup>4</sup> $x + 1, -y + 2, -z + 1$ for <b>VI</b> .				
<b>VII</b>				
N(2)–H...Cl(1)	0.90	2.48	3.338(3)	159
N(3)–H...Cl(2)	0.90	2.31	3.195(3)	169
N(3)–H...Cl(1)	0.90	2.45	3.299(3)	157
N(4)–H...O(7)	0.90	2.05	2.930(4)	166
N(4)–H...Cl(2) <sup>2</sup>	0.90	2.37	3.222(3)	159
N(5)–H...Cl(3)	0.90	2.38	3.227(3)	157
N(5)–H...Cl(2) <sup>2</sup>	0.90	2.69	3.486(3)	149
N(6)–H...Cl(3) <sup>3</sup>	0.90	2.49	3.242(3)	142
N(6)–H...Cl(2) <sup>2</sup>	0.90	2.39	3.253(3)	160
O(1w)–H...O(5)	0.89	1.83	2.704(3)	167
O(1w)–H...O(2)	0.74	2.36	2.875(3)	127
O(2w)–H...Cl(3) <sup>1</sup>	0.79	2.36	3.135(3)	169
O(2w)–H...Cl(2) <sup>4</sup>	0.90	2.23	3.119(3)	170
N(7)–H...O(6)	0.89	1.90	2.781(4)	172
N(7)–H...O(2w)	0.89	1.96	2.802(4)	158
O(7)–H...O(1w) <sup>2</sup>	0.80	1.93	2.701(3)	160
* Symmetry codes: <sup>1</sup> $-y + 2, z - 1/2$ ; <sup>2</sup> $x + 1/2, -y + 5/2, z + 1/2$ ; <sup>3</sup> $x, -y + 3, z - 1/2$ ; <sup>4</sup> $x + 1/2, -y + 3/2, z + 1/2$ for <b>VII</b> .				
<b>VIII</b>				
O(1)–H...O(6) <sup>2</sup>	0.80	1.81	2.587(1)	166
O(1)–H...N(4) <sup>2</sup>	0.80	2.62	3.379(1)	161
O(3)–H...O(9)	0.82	1.74	2.568(1)	176
N(1)–H...O(5) <sup>1</sup>	0.90	2.49	3.297(1)	149
N(1)–H...O(5)	0.90	2.63	3.179(1)	120
N(2)–H...O(11) <sup>5</sup>	0.90	2.04	2.902(1)	159
N(1)–H...O(12) <sup>4</sup>	0.90	2.22	3.013(1)	146
N(1)–H...O(4)	0.90	2.65	3.142(1)	115
N(3)–H...O(12)	0.90	2.17	2.957(1)	146
N(3)–H...O(11) <sup>4</sup>	0.90	1.99	2.869(1)	165
* Symmetry codes: <sup>1</sup> $-x + 2, -y, -z + 1$ ; <sup>2</sup> $x, y, z + 1$ ; <sup>3</sup> $x, y, z - 1$ ; <sup>4</sup> $x, -y + 1/2, z - 1/2$ ; <sup>5</sup> $-x + 1, y - 1/2, -z + 3/2$ for <b>VIII</b> .				



Table 2. (Contd.)

D–H...A contact	Distance, Å			DHA angle, deg
	D–H	H...A	D...A	
<b>IX</b>				
O(1w)–H...O(2) <sup>1</sup>	0.89	1.88	2.770(2)	176
O(1w)–H...O(3)	0.88	1.88	2.744(2)	166
O(2w)–H...O(1) <sup>1</sup>	0.90	1.87	2.757(2)	169
O(2w)–H...O(6) <sup>2</sup>	0.89	1.84	2.735(2)	175
* Symmetry codes: <sup>1</sup> –x + 2, –y + 1, –z; <sup>2</sup> –x + 1, y + 1/2, –z + 1/2 for <b>IX</b> .				
<b>X</b>				
N(1)–H...I(1)	0.92	2.76	3.615(4)	156
N(2)–H...I(2)	0.92	2.73	3.604(4)	160
N(2)–H...I(1)	0.92	2.92	3.673(4)	140
O(1w)–H...O(1)	0.90	1.96	2.779(4)	152
O(1w)–H...O(5)	0.90	1.98	2.782(4)	148
O(2w)–H...O(2)	1.02	2.24	3.016(5)	132
O(2w)–H...O(4)	0.96	1.91	2.832(4)	160
O(3w)–H...O(3)	0.89	2.03	2.853(4)	152
O(3w)–H...O(6)	0.89	2.10	2.917(4)	152
O(4w)–H...O(1w)	0.90	1.90	2.793(4)	170
O(4w)–H...O(2w) <sup>5</sup>	0.89	1.93	2.805(5)	166
N(3)–H...O(1w) <sup>2</sup>	0.92	2.06	2.923(5)	156
N(4)–H...O(3w) <sup>3</sup>	0.92	2.17	3.089(5)	174
N(5)–H...I(1) <sup>4</sup>	0.92	2.83	3.677(4)	153
* Symmetry codes: <sup>1</sup> x, y + 1, z + 1/2; <sup>2</sup> x, –y + 2, z + 1/2; <sup>3</sup> x, –y + 2, z – 1/2; <sup>4</sup> x + 1/2, y + 1/2, z; <sup>5</sup> x, –y + 1, z – 1/2 for <b>X</b> .				
<b>XII</b>				
O(1)–H...O(6)	1.03	1.40	2.429(3)	177
O(2)–H...O(4)	1.13	1.30	2.431(3)	175
O(5)–H...O(3)	1.12	1.31	2.414(3)	167
N(1)–H...S(2) <sup>1</sup>	0.90	2.70	3.520(2)	152
N(1)–H...S(3) <sup>1</sup>	0.90	2.82	3.687(2)	161
N(2)–H...N(10)	0.90	2.08	2.952(3)	162
N(4)–H...S(3) <sup>3</sup>	0.90	2.59	3.410(2)	152
N(4)–H...N(7)	0.90	2.19	3.028(3)	155
N(6)–H...S(3)	0.90	2.68	3.525(3)	157
N(6)–H...S(4) <sup>4</sup>	0.90	2.53	3.410(3)	165
N(5)–H...S(3)	0.90	2.68	3.517(3)	155
N(5)–H...S(1) <sup>5</sup>	0.90	2.78	3.578(3)	149
* Symmetry codes: <sup>1</sup> x, y – 1, z; <sup>2</sup> –x + 2, –y – 1, –z; <sup>3</sup> –x + 2, –y + 1, –z + 1; <sup>4</sup> x, y + 1, z; <sup>5</sup> x + 1, y, z for <b>XII</b> .				

This points to bidentate coordination of these groups to the central atom upon complete displacement of the aminoethanolate ions from the inner sphere of the initial complex. X-Ray diffraction study of this compound (**IX**) demonstrated that it is an inorganic polymer described as  $[\text{Co}_2(\mu\text{-HCOO})_4(\text{H}_2\text{O})_4]_n$ .

According to physicochemical analysis, the composition and structure of the complex formed in the reaction of chelate **I** with acetic acid are identical to those of compound **VI** (obtained by the direct reaction of monoethanolamine with cobalt acetate in neutral medium). Thus, in this case, the complex is only half protonated.

The reactivity of the known salt forms of cobalt aminoethanolate was studied in relation to the reac-

tions with potassium iodide and ammonium thiocyanate. The reactions of aqueous solutions of complexes **IV**, **V**, and **VI** with potassium iodide was accompanied by partial reduction of cobalt +3 to +2 and simultaneous deprotonation of the coordinated ligand to give compound **X**. Treatment with potassium hydroxide transforms this complex into **I**, while treatment with a sulfuring acid solution gives **III**.

The composition and structure of the products of reaction of complexes **II–VII** and **X** with ammonium thiocyanate depends on the composition of the initial compound. In the case of binuclear complexes **II–VI**, only double exchange reaction takes place accompanied by the formation of complex **XI** described in our earlier publication [5]. Meanwhile, treatment of an

aqueous solution of trinuclear compounds **VII** or **IX** with  $\text{NH}_4\text{SCN}$  induces changes in the cobalt(II) coordination polyhedron to give complex **XII**.

In conclusion note the following.

1. In nitrate and acetate solutions, the dimeric complex cation  $\{[\text{Co}^{\text{III}}(\text{HEtm})_3][\text{Co}^{\text{III}}(\text{Etm})_3]\}^{3+}$  with a cobalt oxidation number of +3 is formed.

2. In chloride solutions, cobalt is partly oxidized to give the trinuclear complex  $[\text{Co}^{\text{II}}\{\text{Co}^{\text{III}}(\text{Etm})_3\}_2]^{2+}$ .

3. Upon protonation of the  $[\text{Co}(\text{Etm})_3]$  chelate with nitric acid, the resulting complex cation,  $[\text{Co}^{\text{III}}(\text{HEtm})_3]^{3+}$ , retains the mononuclear structure.

4. The reaction of potassium iodide with the dimeric complex cation  $\{[\text{Co}^{\text{III}}(\text{HEtm})_3][\text{Co}^{\text{III}}(\text{Etm})_3]\}^{3+}$  results in partial reduction of cobalt(III) to cobalt(II) and deprotonation of the coordinated ligand HEtm to give trinuclear  $[\text{Co}^{\text{II}}\{\text{Co}^{\text{III}}(\text{Etm})_3\}_2]^{2+}$ .

5. The addition of a saturated solution of ammonium thiocyanate to the dimeric cation  $\{[\text{Co}^{\text{III}}(\text{HEtm})_3][\text{Co}^{\text{III}}(\text{Etm})_3]\}^{3+}$  does not induce a change in the cation structure, whereas treatment of a solution of  $[\text{Co}^{\text{II}}\{\text{Co}^{\text{III}}(\text{Etm})_3\}_2]^{2+}$  induces its decomposition to the dimeric cation

$\{[\text{Co}^{\text{III}}(\text{HEtm})_3][\text{Co}^{\text{III}}(\text{Etm})_3]\}^{3+}$  and the monomeric anion  $[\text{Co}^{\text{II}}(\text{NCS})_6]^{4-}$ , the isolated compound being  $\{[\text{Co}^{\text{III}}(\text{HEtm})_3][\text{Co}^{\text{III}}(\text{Etm})_3]\}_2[\text{Co}^{\text{II}}(\text{NCS})_6](\text{NCS})_2$ .

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