# Synthesis, structure, and magnetic properties of the cobalt(II) 1,3,5-benzenetricarboxylate layered coordination polymer*

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The reaction of $Co(NO_3)_2 \cdot 6H_2O$ with 1,3,5-benzenetricarboxylic acid ($H_3$btc, trimesic acid) in DMF at 100 °C afforded the coordination polymer $[Co_3(dmf)_6(btc)(Hbtc)(H_2btc)] \cdot 9H_2O$ (**1**) (dmf is *N*,*N*′-dimethylformamide, DMF). According to the X-ray diffraction study, the metal-organic coordination polymer is composed of planar honeycomb (6,3) networks, in which the organic benzenetricarboxylate anions and the inorganic $Co^{2+}$ cations play a role of three-connected nodes. Disordered water molecules are intercalated between the layers. A study of the magnetic properties showed the presence of a weak antiferromagnetic coupling between the $Co^{2+}$ ions ($S = {}^3/_2$).

**Key words:** cobalt, coordination polymers, network structures, X-ray diffraction study, magnetic properties, antiferromagnetic coupling.

Coordination polymers are ordered metal-organic structures composed of metal cations linked together by organic bridging ligands. Due to a great diversity of both organic and inorganic building blocks, there is a huge number of possible structures of coordination polymers, which offer scope for the design of various materials with desired structures and properties.[1,2] The chemistry of coordination polymers is progressing rapidly due to the possible application of these compounds in the catalysis,[3,4] for the separation and purification,[5,6] for the design of nonlinear optical materials,[7] and for the synthesis of new compounds undergoing a magnetic phase transition at high temperatures (critical temperature, $T_c$).[8,9] The formation of layered or framework structures is a necessary condition for the magnetic phase transition to the ferromagnetic state.[10] In addition, it is necessary to use bridging ligands with conjugated bonds for efficient coupling between the magnetic spins in solids. For example, the paramagnetic centers of 3d metals in compounds of the Prussian Blue family are linked together by cyanide bridges to form framework polymer structures. The temperatures $T_c$ for these materials are as high as 315 K,[11] which allows their use for the design of thermomagnetic switches or devices for solar energy absorption.[10] In recent years, various cyanide ligands, azides, nitrogen-containing aromatic ligands, or carboxylates have been primarily used for the design of hybrid metal-organic compounds with interesting magnetic properties.[2] In the present study, we carried out the solvothermal synthesis of the new layered coordination polymer $[Co_3(dmf)_6(btc)(Hbtc)(H_2btc)] \cdot 9H_2O$ and investigated its structure and magnetic properties. In this compound, the metal-organic framework is composed of $Co^{II}$ cations linked together by 1,3,5-benzenetricarboxylate ligands.

## Results and Discussion

Cobalt(II) benzenetricarboxylate was synthesized as crimson-colored plate-like crystals by heating $Co(NO_3)_2 \cdot 6H_2O$ and $H_3$btc in DMF at 100 °C for two days. The structure and composition of the crystalline compound $[Co_3(dmf)_6(btc)(Hbtc)(H_2btc)] \cdot 9H_2O$ (**1**) were determined by X-ray diffraction and confirmed by elemental analysis. The color of compound **1** is in good agreement with the octahedral coordination of the cobalt atoms, which was confirmed by the X-ray diffraction data (Table 1). Compound **1** crystallizes in the trigonal space group $R\bar{3}c$ and belongs to layered coordination polymers. The coordination unit consists of the cobalt atom in a distorted octahedral environment (Fig. 1, *a*). The Co—O distances in the coordination octahedron are typical of doubly charged octahedral cobalt cations (Table 2).

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**Table 1.** Crystallographic data and the X-ray data collection and refinement statistics for compound **1**

| Parameter | Value |
|---|---|
| Molecular formula | $C_{45}H_{72}Co_3N_6O_{33}$ |
| Molecular weight | 1401.88 |
| Crystal system | Trigonal |
| Space group | $R\bar{3}c$ |
| $a$/Å | 16.6290(3) |
| $b$/Å | 16.6290 |
| $c$/Å | 42.040(2) |
| $V$/Å$^3$ | 10067.7(6) |
| $Z$ | 6 |
| $\rho_{calc}$/g cm$^{-3}$ | 1.387 |
| $\mu$/cm$^{-3}$ | 0.821 |
| $2\theta_{max}$/deg | 50 |
| Temperature/K | 90.0(2) |
| Number of measured/ independent/observed ($I > 2\sigma(I)$) reflections | 23436/1980/1727 |
| $R_{int}$ | 0.0545 |
| Crystal dimensions/mm | 0.21×0.16×0.01 |
| Number of variables | 161 |
| Method of refinement | Full-matrix Least-squares based on $F^2$ |
| $R_1$ ($I > 2\sigma(I)$) | 0.1000 |
| $wR_2$ (based on all reflections) | 0.2563 |
| GOOF (based on all reflections) | 1.225 |
| Residual electron density (max/min), e Å$^3$ | −1.158/1.354 |

**Table 2.** Selected bond lengths ($d$) and bond angles (ω) in the structure of compound **1**

| Parameter | Value |
|---|---|
| Bond | $d$/Å |
| Co(1)—O(1) | 2.037(6) |
| Co(1)—O(3) | 2.136(5) |
| Co(1)—O(1DA) | 2.209(19) |
| Co(1)—O(1DB) | 1.989(13) |
| O(1)—C(1) | 1.212(9) |
| O(2)—C(1) | 1.247(8) |
| C(1)—C(2) | 1.501(9) |
| C(2)—C(3) | 1.380(9) |
| O(3)—C(4) | 1.251(6) |
| C(4)—C(5) | 1.503(12) |
| C(5)—C(6) | 1.384(6) |
| Angle | ω/deg |
| O(1)—Co(1)—O(1)* | 107.7(3) |
| O(1)—Co(1)—O(3) | 95.5(2) |
| O(3)*—Co(1)—O(3) | 61.5(3) |
| O(1DA)*—Co(1)—O(1DA) | 165.5(9) |
| O(1DB)*—Co(1)—O(1DB) | 154.5(9) |
| O(1DB)*—Co1—O(1DA) | 166.7(6) |

* The symmetry code is $2/3 + y$, $4/3 - x + y$, $-2/3 - z$.

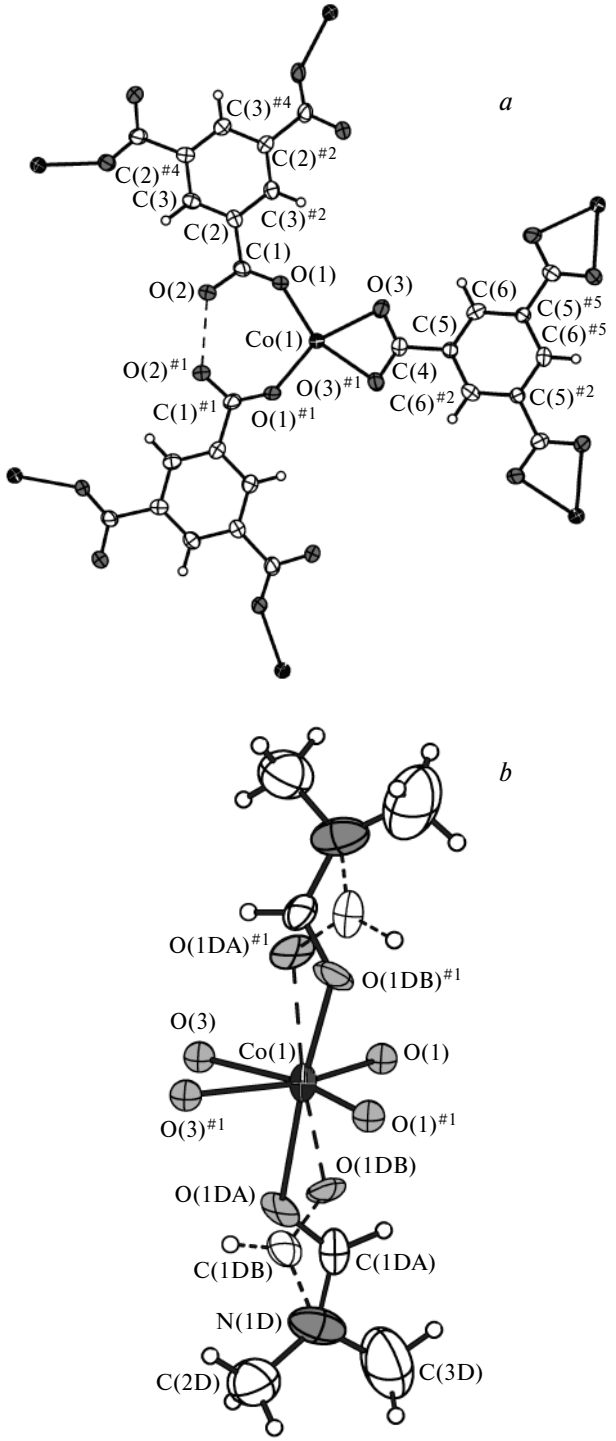


**Fig. 1.** Atomic numbering scheme in the structure of **1** and the coordination environment of the cobalt atom: the top view (*a*) and the side view (*b*). (*a*) The O...H—O hydrogen bond (2.398(8) Å) is indicated by a dashed line; the dmf ligands are omitted. (*b*) The second position of the disordered dmf molecule is indicated by dashed lines. The symmetry codes: (#1) $2/3 + x - y$; $4/3 - y$; $-1/6 - z$, (#2) $2 - x + y$; $2 - y$; $z$; (#3) $2 - y$; $1 + x - y$; $z$; (#4) $1 - x + y$; $2 - x$; $z$; (#5) $2 - x + y$, $2 - x$, $z$.

An analysis of the data from the Cambridge Structural Database (CSD) showed that the Co(octahedron)—O bond lengths in the known structures have a bimodal distribution with the characteristic distance ranges of 1.850—1.950 (for $Co^{3+}$) and 1.950—2.200 Å (for $Co^{2+}$). The oxidation state +2 of the metal atoms in compound **1** is additionally confirmed by the magnetic measurements (see below). The apical positions in the octahedron are occupied by the oxygen atoms of two coordinated dmf molecules. Both dmf molecules are disordered over two positions (see Fig. 1, *b*). There are two crystallographically independent benzenetricarboxylate anions, **A** and **B**, per asymmetric unit (Fig. 2). The equatorial positions in the octahedron of the $Co^{2+}$ cation are occupied by four oxygen atoms belonging to one anion **A** and two anions **B**, each anion being, in turn, coordinated to three cobalt atoms. Therefore, the $Co^{2+}$ cations and the benzenetricarboxylate cations play a role of three-connected nodes giving rise to polymer networks having a slightly distorted honeycomb structure (Fig. 2). Each COO group of the anion **A** is chelated to the metal atom, and, consequently, this anion is fully deprotonated (**A** = $btc^{3-}$). Each COO group of the anion **B** is coordinated in a monodentate fashion. The oxygen atoms, which are not involved in the coordination, are located at a very short distance (O...O, 2.398(8) Å), which is evidence that there is a hydrogen bond between these atoms. Taking into account the symmetry equivalence, half of the anions **B** are statistically protonated: 2**B** = $btc^{3-}$ + $H_3btc$ or $Hbtc^{2-}$ + + $H_2btc^{-}$. Since the position of the hydrogen atom was not located, these types of protonation cannot be distinguished. According to the stoichiometry, there are one anion **A** and two anions **B** per three cobalt ions in the structure of **1**. Hence, based on the crystallographic data, the formula of the neutrally charged layer can be written as $[Co_3(dmf)_6(btc)_2(H_3btc)]$ or $[Co_3(dmf)_6(btc)(Hbtc)(H_2btc)]$. According to the data from the Cambridge Structural Database,[12] the O...O distances in 12 known structures of carboxylate complexes, in which the uncoordinated oxygen atoms of two carboxyl ligands are at a short distance, vary from 2.409 to 2.568 Å. Therefore, the O...O distance in compound **1** (2.398(8) Å) is the shortest among the known O...O distances in this type of compounds.

In the crystal structure, the layers are packed so that the disordered coordinated dmf molecules of one layer ($L^1$) are located in cavities between the coordinated dmf molecules of another layer ($L^2$). The layers $L^1$ and $L^2$ are related to each other by a center of inversion. These layers alternate along the *c* axis of the trigonal unit cell of **1** as ($L^1L^2L^1L^2L^1L^2$), the layers being shifted with respect to each other (Fig. 3). The distances between the adjacent layers are ~7 Å. The water solvent molecules are intercalated between the layers (three solvent molecules per cobalt atom). It is difficult to determine the positions of the oxygen atoms because of the high crystallographic symmetry. The structural features of compound **1** agree well with those of the $[Co_3(H_2O)_6(btc)(Hbtc)(H_2btc)] \cdot 2H_2O$ compound (space group $P6_522$). However, these compounds differ in the mutual arrangement of the neu-

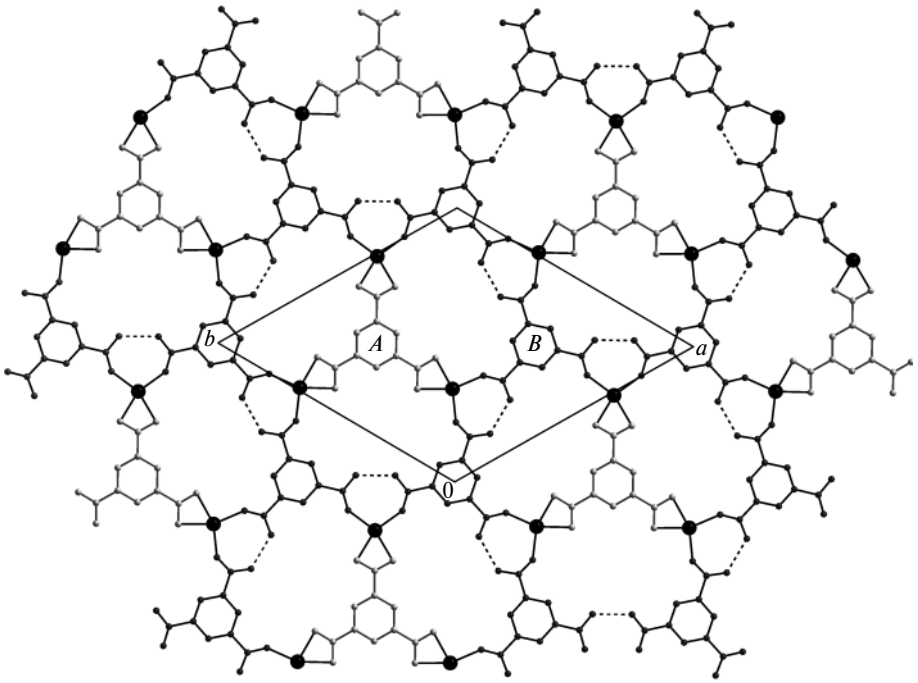


**Fig. 2.** Fragment of the hexagonal layer $[Co_3(btc)(Hbtc)(H_2btc)]$ with distorted honeycomb topology in the structure of **1**. The O...H—O hydrogen bonds are indicated by dashed lines. The **A**- and **B**-type trimesic acid ligands are pale and dark, respectively.

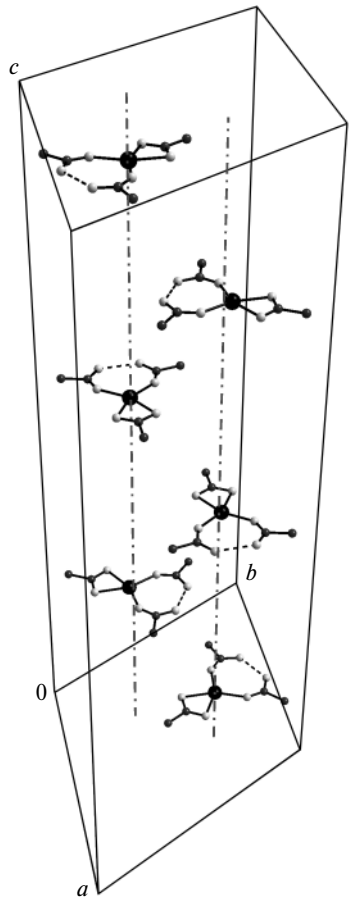


**Fig. 3.** Alternation of layers in the structure of **1**. For each layer, only one $Co^{2+}$ cation and the nearest coordination environment ($COO^-$ groups) are shown. The dmf ligands are omitted. The O...H—O hydrogen bonds are indicated by dashed lines. The alternation of the Co atoms between the adjacent $L^1L^2L^1L^2L^1L^2$ layers in the trigonal rhombohedral unit cell occurs along the dashed-and-dotted arbitrary lines.

tral layers $[Co_3(H_2O)_6(btc)(Hbtc)(H_2btc)]$, because the layers in the latter compound are related by screw axes $6_5$.[13] This compound was synthesized by the hydrothermal reaction of $CoCl_2$ with $H_3btc$ in water. As a consequence, a considerable difference between $[Co_3(H_2O)_6(btc)(Hbtc)(H_2btc)]\cdot 2H_2O$ and **1** is that the former compound contains terminal $H_2O$ ligands smaller in size than the dmf ligands in the structure of **1**, resulting in the decrease in the interlayer distances (3.4 Å in $[Co_3(H_2O)_6(btc)(Hbtc)(H_2btc)]\cdot 2H_2O$) and, consequently, in the decrease in the number of water molecules intercalated between the layers. Therefore, the interlayer distances in the $[Co_3(L)_6(btc)(Hbtc)(H_2btc)]$-type structures can be controlled by performing the reactions of cobalt salts with trimesic acid in the presence of other monodentate ligands (L).

The magnetic measurements for $[Co_3(dmf)_6(btc)(Hbtc)(H_2btc)]\cdot 9H_2O$ (**1**) were carried out in the temperature range 2—300 K. The effective magnetic moment was calculated from the molar magnetic susceptibility by the equation $\mu_{eff} = 2.828\cdot(\chi_m T)^{1/2}$. The temperature dependences of the inverse magnetic susceptibility $\chi_m^{-1}$ and the effective magnetic moment are presented in Fig. 4. In the temperature range of 50—300 K, the plot of $\chi_m^{-1}$ *vs.* $T$ follows the Curie—Weiss law. The calculated Weiss constant ($\theta = -19.2$ K) may be indicative of the weak antiferromagnetic nature of the spin-spin coupling between the $Co^{2+}$ atoms in the structure of **1**, so that the population of high-spin states gradually increases with increasing temperature of samples.[14] However, an analogous dependence can be observed also for isolated $Co^{2+}$ centers due to the contribution of the spin-orbital couplings, which are typical of this cation, to the ground state. The Curie constant $C = 3.06$ cm$^3$ K mol$^{-1}$ agrees well with other experimental data for the octahedral $Co^{2+}$ cation.[15,16] The effective magnetic moment of **1** gradually decreases with decreasing temperature throughout the temeprature range. It should be noted that the magnetic moment $\mu_{eff}$ changes only slightly in the range of 100—300 K and changes more strongly at temperatures below 5 K (see Fig. 4). The magnetic moment $\mu_{eff} = 4.77\ \mu_B$ at $T = +300$ K is typical of the $Co^{2+}$ cation in the high-spin state $S = {}^3/_2$.

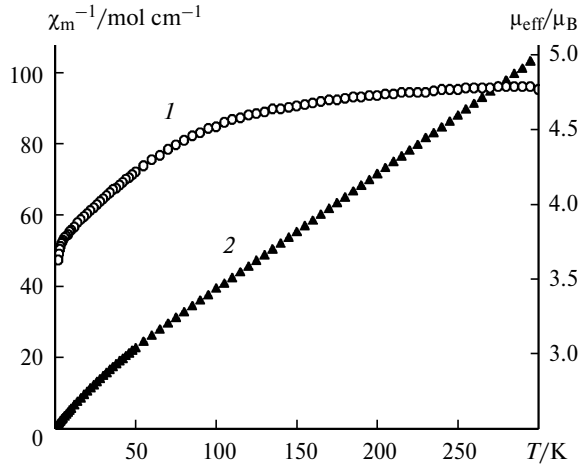


**Fig. 4.** Temperature dependences of the effective magnetic moment $\mu_{eff}$ (*1*) and the inverse molar magnetic susceptibility $\chi_m^{-1}$ (*2*) for compound **1**.

## Experimental

The starting compounds, *viz.*, $Co(NO_3)_2\cdot 6H_2O$, $H_3btc$, and DMF, of at least analytical grade were used without additional purification. The elemental microanalysis was carried out in the Laboratory of Microanalysis of the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The X-ray diffraction study was carried out on a Bruker Nonius X8Apex single-crystal diffractometer equipped with a 4 K CCD detector. The IR spectra were

recorded on a Scimitar FTS 2000 instrument in KBr pellets. The magnetic measurements were performed on a Quantum Design MPMS SQUID instrument in the temperature range of 2—300 K under a magnetic field of 0.5 T. The diamagnetic correction was applied with the use of the Pascal constants.

**Catena-[($\mu_3$-dihydro-1,3,5-benzenecarboxylato)-($\mu_3$-hydro-1,3,5-benzenecarboxylato)-($\mu_3$-1,3,5-benzenecarboxylate)hexadimethylformamidetricobalt] nanohydrate, $[Co_3(dmf)_6(btc)(Hbtc)(H_2btc)]\cdot 9H_2O$ (1).** A solution of $Co(NO_3)_2\cdot 6H_2O$ (15 mg, 51 μmol) and $H_3btc$ (10 mg, 48 μmol) in DMF (2.5 mL) was sealed in a glass tube and heated at 100 °C for 1 day. After cooling, the tube was opened (*Caution! An increased pressure can arise!*). The crimson-colored crystalline precipitate was filtered off, washed with DMF (2×3 mL) and diethyl ether (2×2 mL), and dried in air. The yield was 10 mg (43%). Found (%): C, 41.51; H, 4.60; N, 6.73. $[Co_3(dmf)_6(btc)(Hbtc)(H_2btc)]\cdot 9H_2O$. Calculated (%): C, 41.78; H, 4.67; N, 6.50. IR (KBr), $\nu/cm^{-1}$: 3362 (m), 2942 (w), 2887 (w), 2813 (w), 1656 (s), 1628 (s), 1580 (m), 1498 (w), 1437 (s), 1372 (s), 1253 (w), 1108 (m), 1062 (w), 936 (w), 870 (w), 767 (m), 718 (m), 683 (w), 572 (w), 462 (w), 462 (w), 419 (w).

**X-ray diffraction study.** The structure of compound **1** was established by X-ray diffraction. The X-ray diffraction data were collected on a four-circle automated Bruker X8APEX diffractometer equipped with a CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at $T = 90$ K. The crystallographic data and the X-ray data collection and refinement statistics are given in Table 1. The semiempirical absorption correction was applied based on the intensities of equivalent reflections with the use of the SADABS program.[17] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms using the SHELXTL program package.[18] The hydrogen atoms were positioned geometrically and refined. The water solvent molecules were not located because of their strong disorder. To increase the accuracy of the structure determination, the electron density peaks located in the cavities between the layers were approximated by neon atoms taking into account the equality of the number of electrons in Ne atoms and $H_2O$ molecules. The occupancies of the positions of these atoms were refined with fixed $U_{iso} = 0.05$ Å$^{-2}$ and were fixed in the subsequent refinement of isotropic displacement parameters. The relatively high $R$ factor (10.00%) is associated with a low quality of the plate-like crystals. The crystals are highly prone to the formation of intergrowths along large faces, which made it impossible to cleave intergrowths. This crystal shape is in good agreement with the layered structure of compound **1**. Selected bond lengths are given in Table 2.

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