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New polynuclear molecular ferromagnetic complex $\{Co_3((\eta^2\text{-}NH_2)_2C_6H_2Me_2)_2(\mu\text{-}OOCCMe_3)_2(\eta^1\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2(HOOCCMe_3)_2\}\{Co((\eta^2\text{-}NH_2)_2C_6H_2Me_2)_2(\eta^1\text{-}OOCCMe_3)_2\}$

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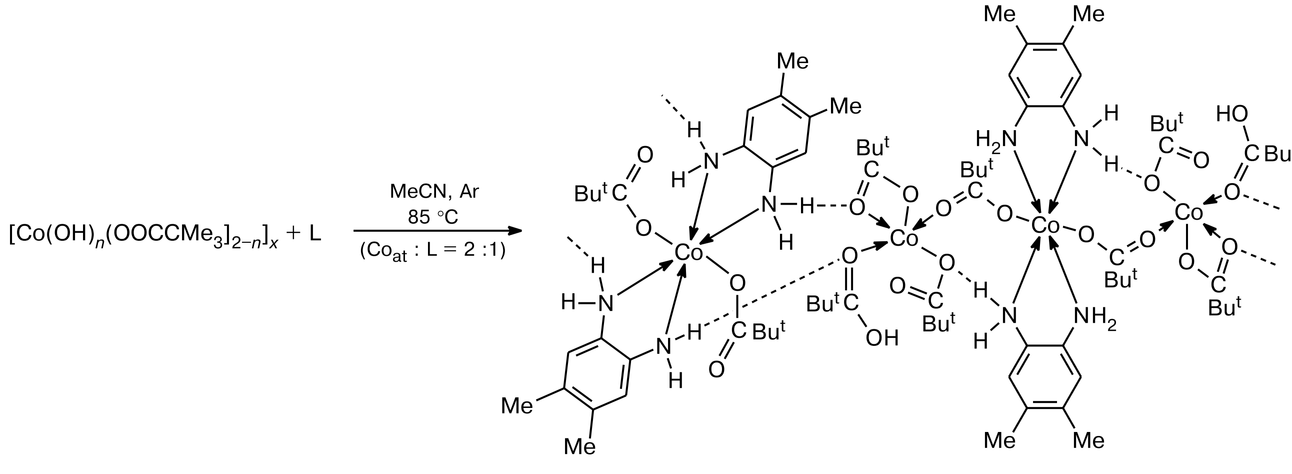
We found that the reaction of polymeric cobalt trimethylacetate[1] (prepared by melting of $Co(OOCCMe)_2 \cdot 4H_2O$ with trimethylacetic acid) with 1,2-diamino-4,5-dimethylbenzene (**L**) afforded the $\{Co_3((\eta^2\text{-}NH_2)_2C_6H_2Me_2)_2(\mu\text{-}OOCCMe_3)_2(\eta^1\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2(HOOCCMe_3)_2\}\{Co((\eta^2\text{-}NH_2)_2C_6H_2Me_2)_2(\eta^1\text{-}OOCCMe_3)_2\}$ complex (**1**), which exhibits properties of a molecular ferromagnetic material[2] at 5 K. The reaction was carried out under reflux in MeCN for 1 h in an argon stream using the the reactant ratio Co_{at} : **L** = 2 : 1 (Scheme 1).

According to the results of X-ray diffraction analysis, the crystal structure of **1** is built from one-dimensional chains consisting of the alternating mononuclear {Co} and trinuclear $\{Co_3\}$ fragments (Fig. 1). The cobalt atoms in the $\{Co_3\}$ fragment are located at nonbonded distances from each other (Co(1)...Co(2), 4.505(8) Å). In the $\{Co_3\}$ fragment, the coordination polyhedra about the peripheral cobalt atoms, *viz*., Co(2) and Co(2a), are tetragonal pyramids formed by the chelating carboxylate group (Co(2)—O(8), 2.031(8) Å; Co(2)—O(7), 2.308(8) Å), the terminal trimethylacetate anion (Co(2)—O(3), 1.98(7) Å), and the C=O groups of the acid coordinated through the oxygen atom (Co(2)—O(5), 2.024(8) Å). The central octahedrally coordinated Co(1) atom is bound to the Co(2) and Co(2a) atoms through the μ-$OOCCMe_3$ groups (Co(1)—O(1), 1.910(7) Å; Co(2)—O(2), 2.096(7) Å). The remaining four coordination sites are occupied by the N atoms of the amino groups of two chelate molecules **L** (Co(1)—N(1), 1.960(7) Å; Co(1)—N(2), 1.949(8) Å). The Co(3) atom in the {Co} fragment is octahedrally surrounded by two chelating molecules **L** located in the equatorial plane (Co(3)—N(3), 1.956(7) Å; Co(3)—N(4), 1.947(7) Å) and two axial trimethylacetate anions as ter-

Scheme 1



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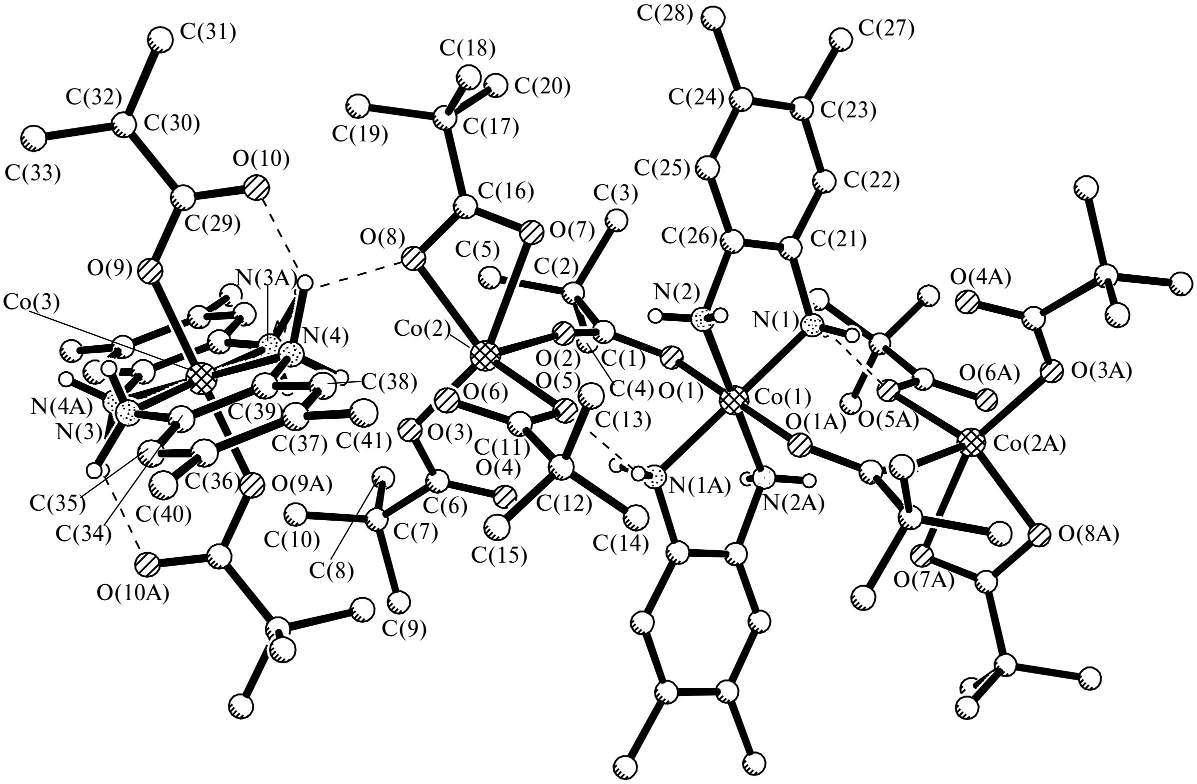

Fig. 1. Structure of complex **1**.

minal ligands (Co(3)—O(9), 1.896(7) Å). The distance between the Co(2) and Co(3) atoms is 5.146(7) Å. These fragments are linked in an infinite polymeric chain (along the *c* axis) through hydrogen bonds between the protons of the NH_2 groups of ligand **L** (in the monomeric fragments) and the O atoms of the chelating carboxylate anions as well as of the C=O groups of trimethylacetic acid coordinated to the Co(2) and Co(2a) atoms (in the trimeric fragments) (N(3)H(1)...O(8), 2.107(7) Å; N(4)H(1)...O(6), 1.997(5) Å) (Fig. 2).

Complex **1** exhibits unusual magnetic properties (Fig. 3). Its magnetic moment (per molecule) monotonically decreases from 11.22 to 8.63 μB in the range of 300—28 K, then increases to 9.6 μB at 20 K, and again decreases to 3.5 μB at 2 K. At 5 K, the hysteresis loop is observed with the coercive force of 2 kOe (Fig. 4).

The synthesis was carried out in an inert atmosphere using anhydrous acetonitrile. The IR spectra of the complexes were recorded on a Specord M80 instrument in KBr pellets. The magnetic susceptibility was measured in the International Cen-

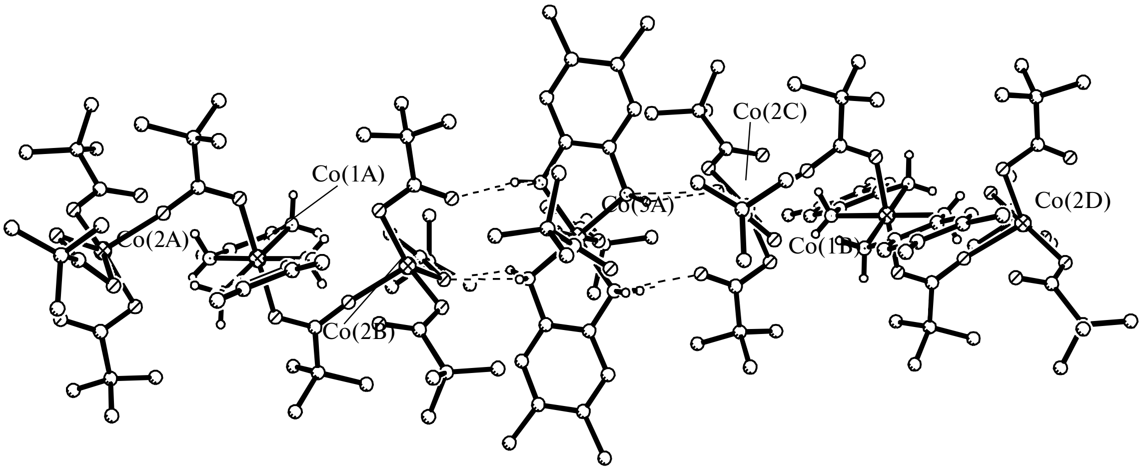

Fig. 2. Fragment of the supramolecular chain formed by the tetranuclear complexes.

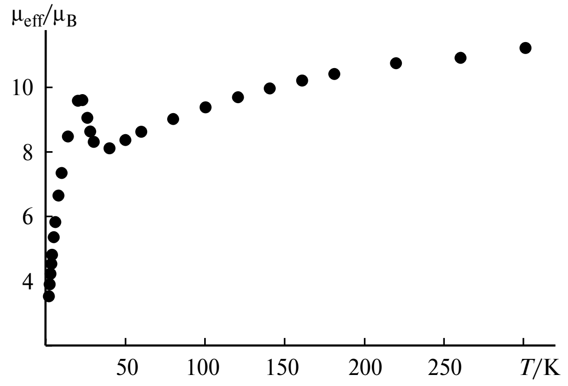

Fig. 3. Temperature dependence of the magnetic moment (μ_{eff}) for complex **1**.

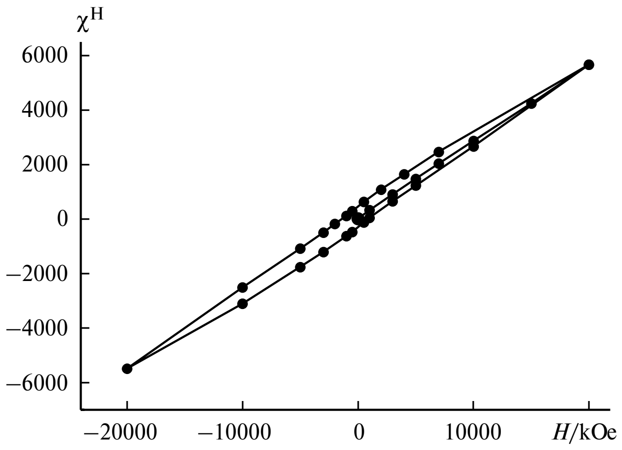

Fig. 4. Dependence of the magnetization of complex **1** on the magnetic field strength at 5 K.

ter of the Siberian Division of the Russian Academy of Sciences on a SQUID MPMS-59 Quantum Design magnetometer in the temperature range of 2—300 K.

[Bis(4,5-dimethyl-*ortho*-phenylenediamine)di(trimethylacetic acid)(hexatrimethylacetato)tricobaltate(II)][bis(4,5-dimethyl(*ortho*-phenylenediamine)di(trimethylacetato)cobaltate(II)], $\{Co_3((\eta^2\text{-}(NH_2)_2C_6H_2Me_2)_2(\mu\text{-}OOCCMe_3)_2(\eta^1\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2(HOOCCMe_3)_2\}\{Co((\eta^2\text{-}(NH_2)_2C_6H_2Me_2)_2(\eta^1\text{-}OOCCMe_3)_2\}$ (1). A mixture of the $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ polymer (0.5 g, 1.9 mmol) and 4,5-dimethyl-1,2-phenylenediamine (0.26 g, 1.8 mmol) in MeCN (50 mL) was stirred under argon at 80 °C for 1 h until the starting reagents were completely dissolved. The resulting dark-violet solution was concentrated to 30 mL and kept at room temperature for 3 weeks, after which the color of the solution changed from violet to brown. The red-brown crystals that precipitated were washed with cold MeCN and dried in an argon stream. Complex **1** was obtained in a yield of 0.44 g (50 %). Found (%): C, 55.2; H, 7.45; N, 7.51. $C_{86}H_{144}Co_4N_4O_{20}$. Calculated (%): C, 55.0; H, 7.68; N, 7.47. IR (KBr), μ/cm^{-1}: 3360 m, 3292 m, 2956 s, 2928 s, 2868 w, 1732 w, 1664 m, 1636 m, 1608 s, 1564 s, 1532 v.s, 1512 v.s, 1480 v.s, 1416 v.s, 1372 s, 1360 s, 1260 w, 1226 s, 1092 w, 1024 s, 944 m, 896 w, 860 w, 788 w, 608 w, 596 w, 472 w, 436 w, 420 w.

X-ray diffraction analysis was carried out in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences). Complex **1**, $C_{86}H_{144}Co_4N_4O_{20}$, M = 1873.84, space group $P\bar{1}$, a = 11.52(2) Å, b = 12.170(13) Å, c = 19.05(2) Å, α = 106.38(10)°, β = 107.40(13)°, γ = 91.30(10)°, V = 2428(5) Å^3, Z = 1, a total of 6512 reflections were measured, of which 5690 reflections were independent, R_1 = 0.0827, wR_1 = 0.2116.

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