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LETTERS TO THE EDITOR

Synthesis of a New Tetranuclear Cobalt(III) Trifluoroacetate Complex $[Co_4(\mu_3\text{-}O)_4(\mu\text{-}O_2CCF_3)_2(C_5H_5N)_8](ClO_4)_2$

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As noted in [1], trifluoroacetate complexes of many *d* elements are active catalysts of hydrocarbon functionalization owing to the capability of these complexes to activate C–H and C=C bonds. In particular, Vargaftik *et al*. [2, 3] revealed unique activity of cobalt(III) trifluoroacetate as a catalyst of oxidation with oxygen in trifluoroacetic acid of even such inert substrates as methane and other lower alkanes. However, no assumptions were made on the structure of this compound.

To determine the structure of cobalt(III) trifluoroacetate, we isolated its derivative with a heterocyclic amine, as suggested in [4] for "cobalt(III) acetate."

The complex $[Co_4(\mu_3\text{-}O)_4(\mu\text{-}O_2CCF_3)_2(C_5H_5N)_8]\cdot(ClO_4)_2$ crystallizes in the monoclinic system, space group $P2_1/c$; a 12.727(8), b 21.432(9), c 19.393(9) Å; β 90.18(4)°, Z 4; R 5.10%.

The main fragment of the molecular structure of the complex cation is the tetranuclear "cubane" core $Co_4(\mu_3\text{-}O)_4$, in which the cobalt atoms located on opposite edges of the Co_4O_4 cube are linked in pairs with bridging trifluoroacetate ligands. The octahedral surrounding of the metal atoms is completed with two pyridine molecules coordinated with each cobalt atom. Thus, the idealized symmetry of the cation is D_{2d}. It is important that the unit cell contains no molecules of solvation, which is untypical of other cobalt(III) carboxylate complexes studied by single crystal X-ray diffraction [5, 6]. This compound is the first structurally characterized cobalt(III) carboxylate with the carboxylate ligands containing electron-withdrawing groups.

Octapyridinebis(μ-trifluoroacetato)tetrakis(μ_3-oxo)tetracobalt(III) perchlorate. A 2.0-g portion of "cobalt(III) acetate" prepared as described in [4] was dissolved in 80 ml of trifluoroacetic acid, after which the solvent was evaporated in a dry air flow. The olive green amorphous residue was dried in a vacuum desiccator over KOH, after which it was dissolved in 60 ml of methanol, and 1.6 g of $NaClO_4$ and 2.0 g of pyridine were added. The brown finely crystalline precipitate that formed within 5–8 h was filtered off, washed with methanol and diethyl ether, and dried in a stream of dry air. Larger dark brown crystals of the complex, suitable for X-ray structural analysis, were isolated from the filtrate after 24 h. The total yield was 44% (based on Co^{3+}). The complex is soluble in acetonitrile, acetone, and methanol and insoluble in hexane and diethyl ether. Found, %: C 39.0; H 3.02; Co 17.5; N 8.14. $C_{44}H_{40}Cl_2Co_4F_6N_8O_{16}$. Calculated, %: C 38.93; H 2.97; Co 17.37; N 8.25.

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