Letters to the Editor

Unusual thermal dimerization of thrimethylacetate cobalt complexes. Synthesis and structure of $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{12}$

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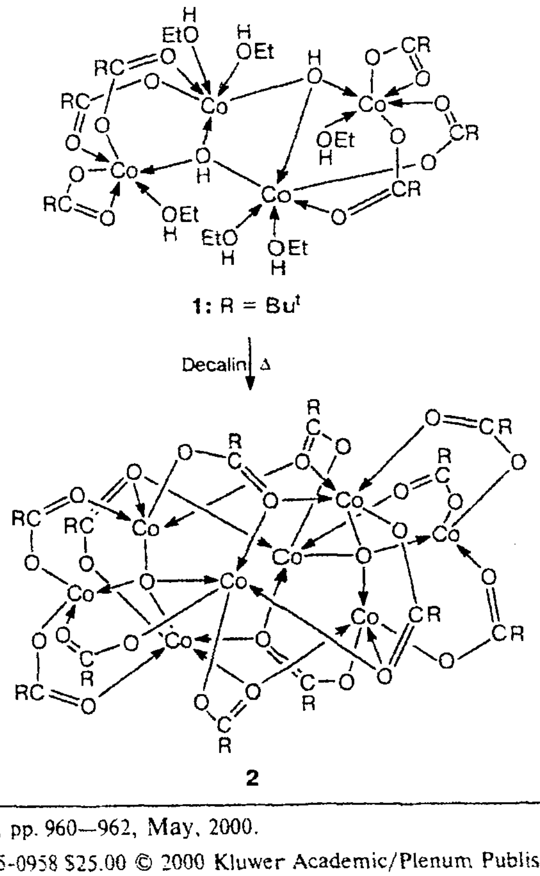
Dissolution of the violet polymer prepared by fusion of aqueous cobalt acetate and pivalic acid at 165 °C in ethanol afforded the red tetranuclear complex $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(EtOH)_6$ (**1**) in high yield.[1]

We found that heating of complex **1** in decalin (2 h, 170 °C) afforded the blue product $Co_8(\mu_4\text{-}O)_2(\mu_n\text{-}OOCCMe_3)_{12}$ (**2**), where $n = 2$ or 3, in 75% yield

According to the data of X-ray diffraction analysis (crystals of **2**, at 200 K, cubic system, space group *Pa*3, $a = 20.1464(2)$ Å, $V = 8177.0(16)$ Å^3, $Z = 4$, $R_1 = 0.0495$ for 1641 independent reflections with $I > 4\sigma$); the Co^{II} atoms in two symmetrical $Co(\mu\text{-}OOCCMe_3)_3(\mu_4\text{-}O)Co_3(\mu\text{-}OOCCMe_3)_3$ fragments of cluster **2** (Fig. 1) are located at nonbonding distances (Co(1)...Co(2) 3.057(1) Å, Co(1)—Co(1A) 3.338(1) Å, Co(1)—Co(1B) 3.338(1) Å, Co(1)—Co(1C) 3.925(1) Å, Co(1)—Co(1D) 3.295(1) Å, Co(1)—Co(1E) 4.690(1) Å). The μ_4-bridging oxygen atoms occupy the centers of the Co_4O tetrahedra (Co(1)—O(1) 1.966(1) Å, Co(2)—O(1) 1.984(1) Å) in which all adjacent cobalt atoms are linked to one another through the μ-bridging pivalate ligands (Co(1)—O(3) 1.974(3) Å, Co(1)—O(4) 2.093(3) Å, Co(1)—O(5) 2.212(3) Å, Co(2)—O(2) 1.942(1) Å). Three of these pivalate groups act as tridentate ligands due to additional coordination of the oxygen atom of the carboxylate ligand to one of the cobalt atoms of the adjacent fragment (Co—O 2.019(3) Å). These six carboxylate groups link two $Co(\mu\text{-}OOCCMe_3)_3(\mu_4\text{-}O)Co_3$ fragments to form



1: R = Bu^t

2

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 960—962, May, 2000.

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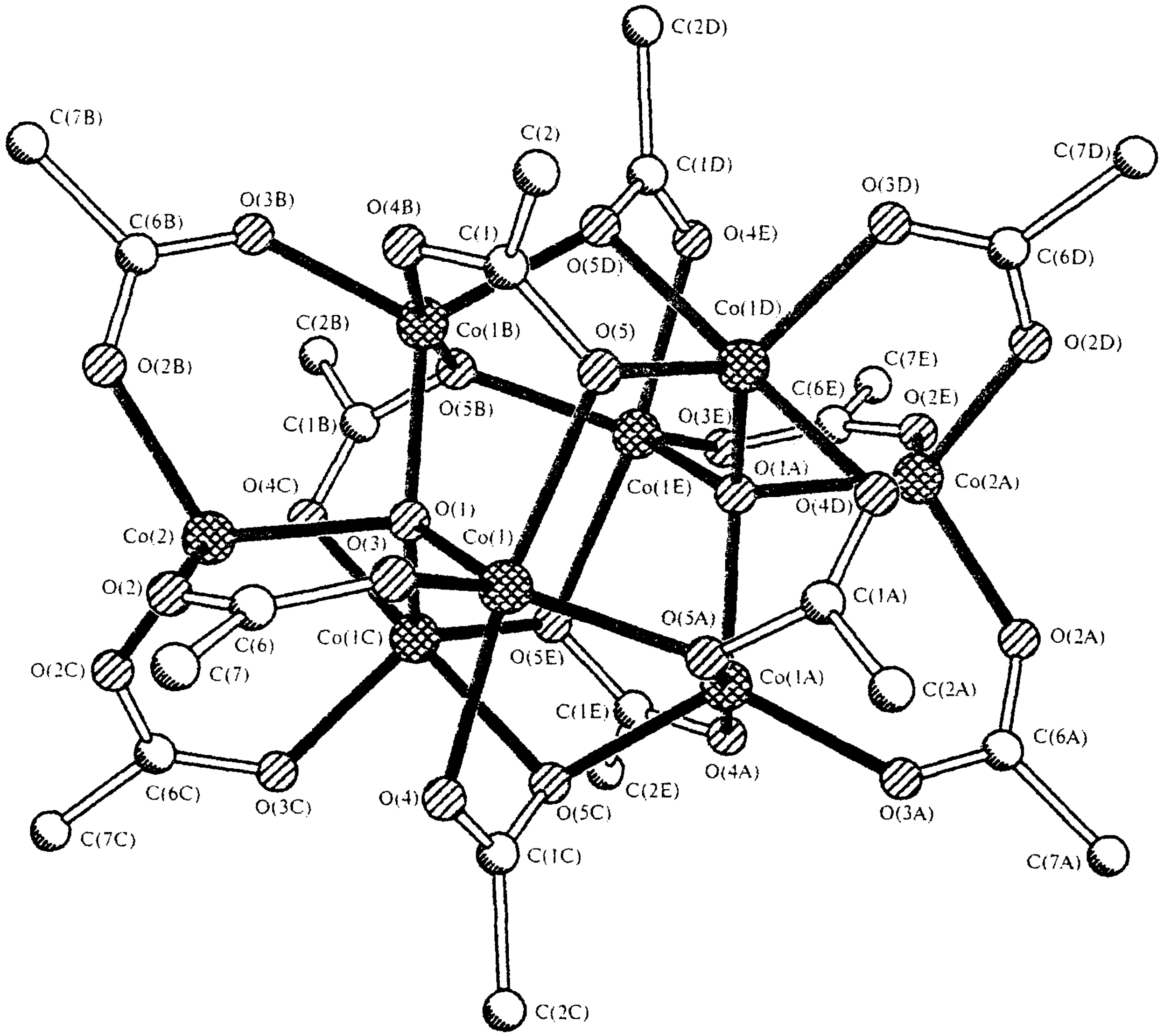

Fig. 1. Structure of bis(μ_4-oxo)hexahis(μ_3-pivalato)hexakis(μ_2-pivalato)octacobalt(II) (**2**) (the methyl substituents of the Bu^t fragments are omitted).

octanuclear complex **2**. The peripheral Co(2) and Co(2A) atoms, which are not involved in these interactions, are in a tetrahedral environment and the coordination environments about the remaining six cobalt atoms (Co(1)—Co(1E)) are distorted trigonal pyramids.

In a certain approximation, "enlarging" of complex **1**, which occurred upon thermolysis, can be considered as a model of the initial stages of the thermally initiated conversion of $Co(OH)_2$ into CoO. Unlike the Co and μ_4-O atoms in the structure of **2**, each atom of the CoO core is six-coordinate. In this connection, it is of interest to compare the electrophysical characteristics of cluster **2** and bulkier oligomers with those of CoO. The results of this comparison will be published elsewhere.

X-ray diffraction analysis was carried out at the Center for X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences).

This work was financially supported by the Ministry of Science and Technical Policy (Grant 9.3.05), the Russian Foundation for Basic Research (Project Nos. 99-03-33091 and 99-03-32805), and INTAS (Grant 97-30344).

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Received February 11, 2000