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Synthesis and structure of the $Co_3(\mu,\eta^2\text{-}OOCBu^t)_2(\mu\text{-}OOCBu^t)_4(NEt_3)_2$ complex containing a linear metal core

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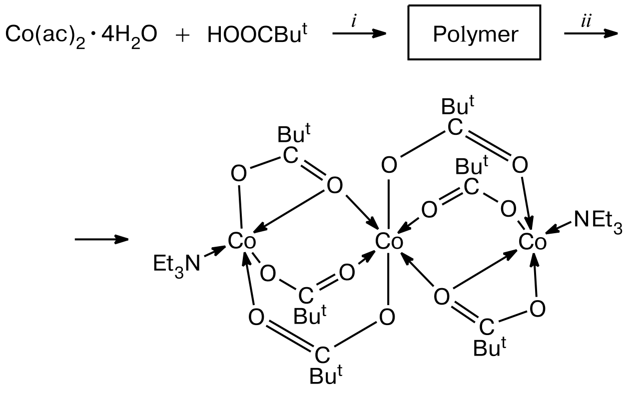
We found that a polymer, which was prepared by fusing cobalt acetate tetrahydrate with trimethylacetic acid,[1] reacted with an excess of triethylamine in hexane at room temperature to give the violet $Co_3(\mu,\eta^2\text{-}OOCBu^t)_2(\mu\text{-}OOCBu^t)_4(NEt_3)_2$ complex (**1**) in 76% yield.

According to the X-ray data, three Co^{II} atoms in molecule **1** (Fig. 1) are in line with each other and are located at a nonbonded Co...Co distance of 3.546 Å. The coordination environment about the central 19-electron cobalt atom is a distorted octahedron formed by six oxygen atoms four of which belong to four μ-bridging trimethylacetate groups (Co(2)—O(4) and Co(2)—O(4A), 2.067(2) Å; Co(2)—O(6) and Co(2)—O(6A), 2.087(2) Å). Two other oxygen atoms belong to two chelate-bridging trimethylacetate fragments untypical of this structural type.



1

i. Fusion at 150 °C. *ii.* Et_3N, hexane, 22 °C.

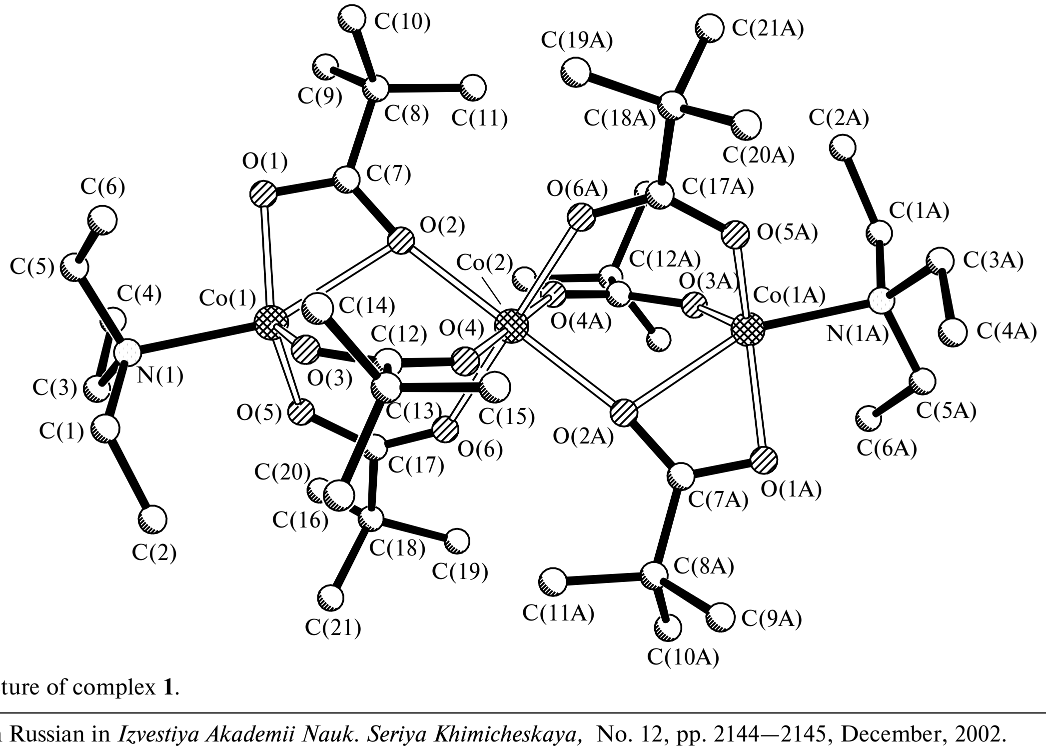


Fig. 1. Structure of complex **1**.

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These oxygen atoms are η^2-coordinated to two peripheral 17-electron cobalt atoms, which are in a distorted trigonal-bipyramidal environment completed with the nitrogen atom of the NEt_3 ligand (Co(2)—O(2) and Co(2)—O(2A), 2.108(2) Å; Co(1)—O(1), 2.014(2) Å; Co(1)—O(2), 2.316(2) Å; Co(1)—N(1), 2.130(2) Å). The nitrogen atoms of the NEt_3 ligands are at angles of 13.8° with respect to the Co(1)Co(2)Co(1A) line.

It should be noted that this reaction with polymeric nickel(II) trimethylacetate afforded only the binuclear complex $Ni_2(\mu\text{-}OOCBu^t)_4(NEt_3)_2$ adopting a Chinese-lantern conformation.[2]

All operations were carried out in air. The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets in the frequency range of 392—4000 cm^{-1}.

Synthesis of bis(triethylamine)tetra(μ-*O*,*O*′-trimethylacetato)di(μ,η²-*O*′,*O*,*O*′-trimethylacetato)tricobalt(II), $Co_3(\mu,\eta^2\text{-}OOCBu^t)_2(\mu\text{-}OOCBu^t)_4(NEt_3)_2$ (1). A solution of triethylamine (5 mL, 39.6 mmol) in hexane (20 mL) was added with stirring (~20 °C) to the solid cobalt polymer (1 g, 3.8 mmol with respect to $Co(OOCBu^t)_2$), which was prepared by fusing cobalt acetate tetrahydrate with trimethylacetic acid.[1] The violet-blue solution that formed after 2 min was concentrated to 5 mL and kept at −18 °C for one day. The resulting large violet prismatic crystals were separated from the solution by decantation, washed with cold hexane (−10 °C), and dried under a stream of argon at room temperature.

The yield was 0.95 g (0.96 mmol, 76%). Found (%): C, 49.91; H, 8.24. $Co_3C_{42}H_{84}O_{12}N_2$. Calculated (%): C, 49.95; H, 8.32.

IR (ν/cm^{-1}) (KBr): 3300 w.br, 2976 m, 2956 m, 2924 m, 2864 w, 1600 s, 1536 s, 1452 s, 1372 s, 1324 s, 1228 s, 1176 m, 1100 w, 936 w, 912 w, 896 m, 808 w, 788 m, 752 m, 616 m, 548 w, 496 w, 476 w, 436 m.

X-ray diffraction study. The X-ray diffraction data were collected in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector according to a standard procedure[3] (λMo radiation, graphite monochromator, 110 K, ω scan technique, scan step was 0.3°, time of exposure was 30 s, $2\theta_{max} = 60°$). For complex **1**: $C_{21}H_{42}Co_{1.5}NO_6$, $M = 492.95$, space group *Pbca*, $a = 14.4787(8)$ Å, $b = 16.5647(9)$ Å, $c = 22.0891(12)$ Å, $V = 5297.7(5)$ Å^3 (110 K), $Z = 8$, $\rho_{calc} = 1.236$ g cm^{-3}, $\mu = 9.81$ cm^{-1}, 78628 measured reflections of which 7728 independent reflections were with $F^2 > 2\sigma(I)$, $R_1 = 0.0576$, $wR_2 = 0.1252$.

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