Unusual transformations of polynuclear cobalt trimethylacetate complex in tetrahydrofuran on exposure to atmospheric oxygen. Synthesis and structure of the cobalt(III) complexes $[Co_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(OH)_2(\mu\text{-}OOCBu^t)_9]^+(OOCBu^t)^-(HOOCBu^t)$ and $Co_{14}(\mu_5\text{-}O)_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_{12}(OH)_4(\mu\text{-}OOCBu^t)_8(OOCBu^t)_{10}\cdot 2[\overline{OC(=O)C}_3H_6]\cdot 2[\overline{OC(H)(OH)C}_3H_6]$*

T. O. Denisova, M. A. Golubnichaya, and S. E. Nefedov★

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: snef@igic.ras.ru

Trimethylacetate complexes of transition metals attract considerable attention primarily as the starting compounds used for the synthesis of complexes having unique structures and possessing unusual physicochemical properties[1] as well as for the preparation of binuclear complexes modeling the active sites of natural metalloenzymes.[2] Earlier,[3] we have demonstrated that the reaction of atmospheric oxygen with one of such model compounds, *viz.*, $[Co_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4(MeCN)_2]^{2+}\cdot 2[OS(O)_2CF_3]^-$ (Hdmpz is 3,5-dimethylpyrazole), dissolved in anhydrous THF afforded the $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4]^{2+}\cdot 2[OS(O)_2CF_3]^-(thf)_2$ complex (**1**).

We found that the analogous reaction of the polynuclear cobalt complex, which was prepared by fusion of an aqueous cobalt(II) acetate with trimethylacetic acid,[4] in a THF solution gave rise to cobalt(III) compounds, *viz.*, the green-brown $[Co_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(OH)_2(\mu\text{-}OOCBu^t)_9]^+(OOCBu^t)^-(HOOCBu^t)\cdot 1.5Et_2O$ (**2**) and yellow-brown $Co_{14}(\mu_5\text{-}O)_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_{12}(OH)_4(\mu\text{-}OOCBu^t)_8(OOCBu^t)_{10}\cdot 2[\overline{OC(=O)C}_3H_6]\cdot 2[\overline{OC(H)(OH)C}_3H_6]$ complexes (**3**).

According to the X-ray diffraction data, the oxygen atoms belonging to the Co(1)O(2)Co(3)O(3) face of the central pseudocubane fragment $Co_4(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_2$ (Co...Co, 2.683(2)—2.843(2) Å; Co—μ_3-O, 1.856(6)—1.919(6) Å; Co—μ_3-O(H), 1.839(7)—1.862(7) Å) in the cation of complex **2** (Fig. 1) form bonds with two peripheral cobalt atoms (Co(5)—O(2), 1.946(5) Å; Co(6)—O(3), 1.892(6) Å). Each peripheral metal atom is additionally coordinated by three oxygen atoms. Two of these oxygen atoms belong to two bridging trimethylacetate anions, through which the peripheral metal atoms are linked to the Co(1) and Co(3) atoms (Co—O, 1.941(8)—1.950(8) Å), whereas the third oxygen atom belongs to the terminal trimethylacetate anion (Co(5)—O(21), 1.869(9) Å; Co(6)—O(23), 1.895(9) Å). Two other cobalt atoms of the Co_4O_4 fragment, which are not involved in the above-described binding, are also coordinated by the bridging trimethylacetate ligands located between the Co(4)...Co(1) and Co(2)...Co(3) atoms. Yet another bridging trimethylacetate anion also links the Co(2)...Co(4) atoms (Co—O, 1.896(9)—1.919(9) Å). In addition, each of these metal atoms is bound to the terminal hydroxy group (Co(2)—O(18), 1.922(9) Å; Co(4)—O(25), 1.961(9) Å). As a result, the peripheral Co^{III} atoms are in a distorted tetrahedral environment. Each Co^{III} atom involved in the pseudocubane fragment has a distorted octahedral environment.

It is this pseudocubane fragment that plays the major role in the formation of 14-nuclear complex **3**, whose structure was established by X-ray diffraction analysis (Fig. 2). In complex **3**, the Co_4O_4 pseudocubane fragments are linked in pairs *via* the shared Co(1)O(1) (Co(1a)O(1a)) edges to form two symmetrical Co_7O_7 fragments, which shared the Co(2) and Co(2a) atoms (Co...Co, 2.733(2)—2.833(2) Å). In both Co_7O_7 fragments, the O(1) and O(1a) atoms are μ_3-coordinated (Co—O, 1.903(5)—2.358(5) Å). The Co—O bonds with the tridentate-bridging O(7) and O(7a) atoms (1.847(5)—1.879(5) Å) are substantially shortened compared to the bonds between the Co atoms and the remaining tridentate-bridging oxygen atoms involved in the hydroxy groups (Co—O, 1.904(5)—2.247(6) Å). In addition,

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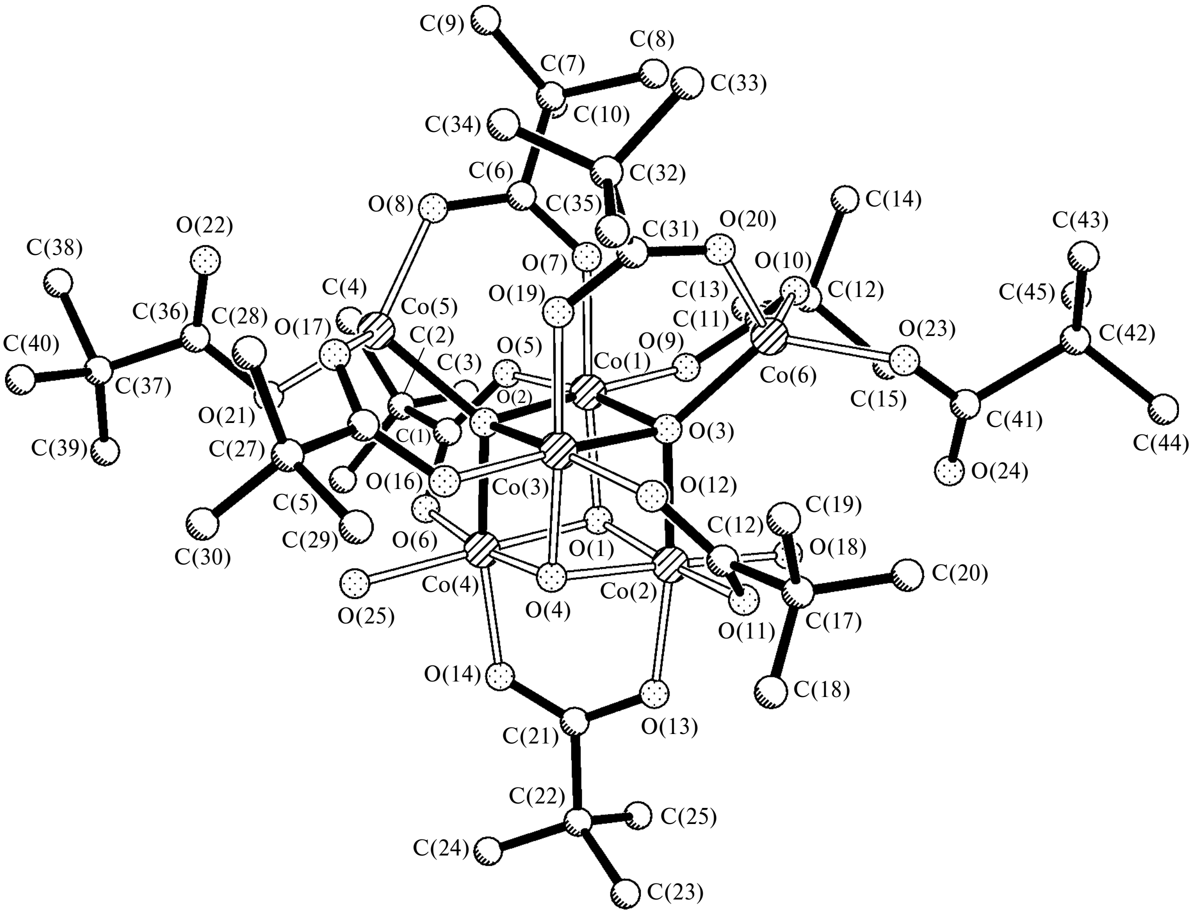

Fig. 1. Structure of the cation in complex **2**.

the bridging trimethylacetate anions are coordinated at the Co(1)Co(4) and Co(3)Co(6) edges of the pseudocubane fragments (Co—O, 1.888(7)—2.077(8) Å). The Co(3) and Co(5) atoms involved in two adjacent pseudocubane fragments are linked to the peripheral Co(7) atom (Co—O, 1.999(6)—2.072(6) Å) through the μ_3-OH group. The Co(7) atom is bound to two oxygen atoms of the bridging trimethylacetate anions coordinated to the Co(5) atom (Co—O, 2.018(7)—2.101(7) Å) and is coordinated by the terminal trimethylacetate (Co—O, 2.151(8) Å) and hydroxy (Co—O, 2.141(7) Å) groups. The Co(3) and Co(4) atoms of the Co_7O_7 fragment also have terminal OH groups (Co—O, 1.955(6) and 2.135(6) Å). The Co(6) atom of this fragment is coordinated by two terminal trimethylacetate anions (Co—O, 2.034(7) and 2.168(7) Å). As a result, each cobalt(III) atom in complex **3** is in a distorted octahedral environment.

It should be noted that oxidation of Co^{II} to Co^{III} led to a substantial shortening of the metal—metal and metal—oxygen distances (by 0.2—0.4 Å) compared to the distances in the cobalt(II) trimethylacetate clusters[5,6] analogously to that observed in the structurally similar dinuclear complexes $Co_2(\mu\text{-}OH_2)_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4[OS(O)_2CF_3]_2(thf)_2$ [7] and $Co_2(\mu\text{-}OH)_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4[OS(O)_2CF_3]_2(thf)_2$.[3]

Complex **3** is the first example of 14-nuclear cobalt complexes with carboxylate ligands. However, what is more important, the crystals of complex **3** contain two γ-butyrolactone molecules and two 2-hydroxytetrahydrofuran molecules of solvation. The latter are the decomposition products of 2-hydroperoxotetrahydrofuran,[8] which was generated in the coupled reaction of atmospheric oxygen with THF in the presence of Co^{II}. Earlier,[3] the formation of these products in the synthesis of complex **1** was detected by GLC-mass spectroscopy.

The resulting Co^{III} complexes are convenient starting compounds for the synthesis of dinuclear complexes, which model the active sites of metalloenzymes and contain metal in a high oxidation state.

All operations were carried out in anhydrous solvents under argon. 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 complexes. Atmospheric oxygen was bubbled through a violet solution of the polymeric cobalt complex (1 g) (insoluble in hexane and readily soluble in THF), which was

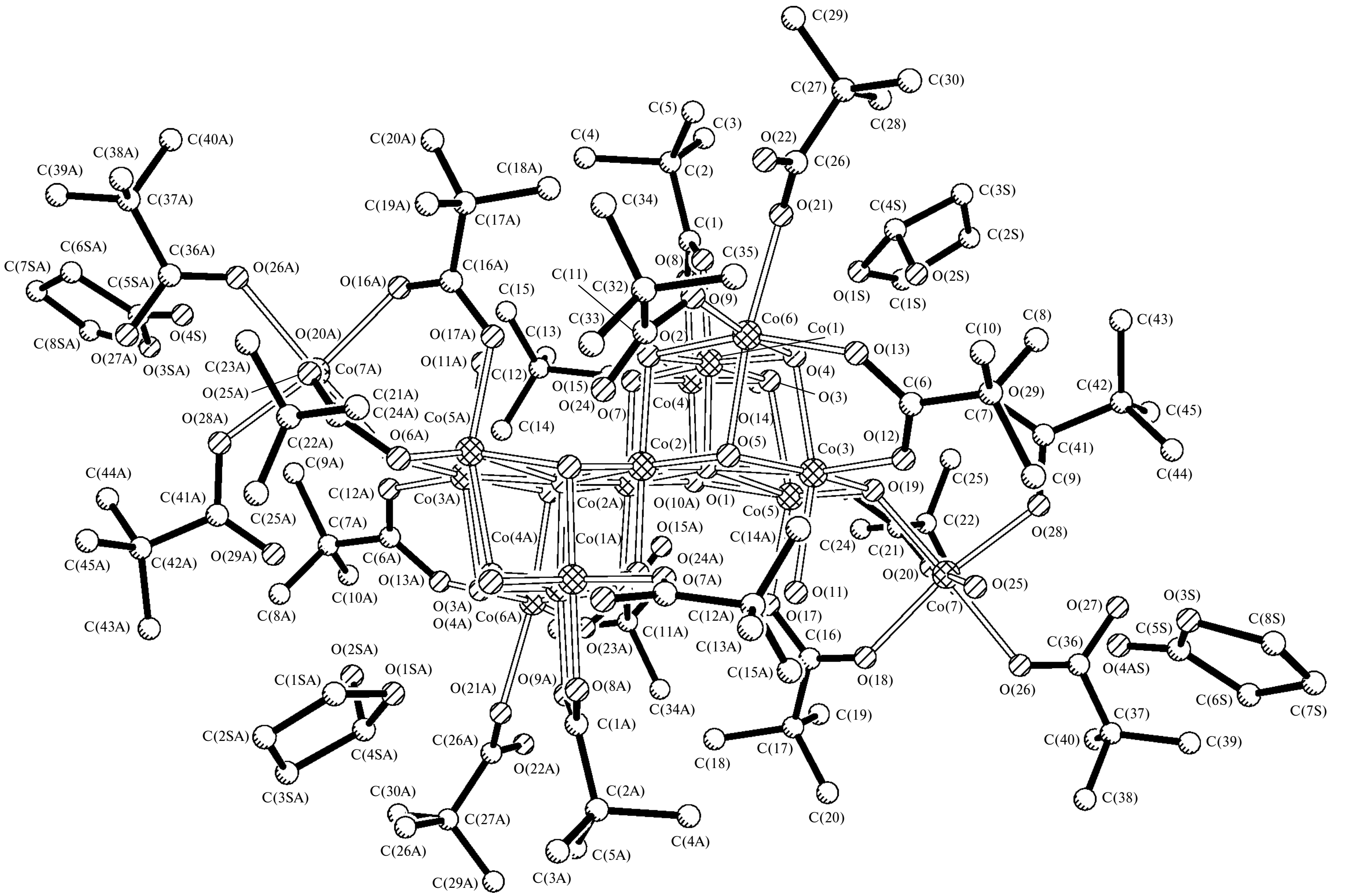

Fig. 2. Structure of complex 3.

prepared by fusion of cobalt(II) acetate tetrahydrate with pivalic acid,[4] in anhydrous THF (50 mL) for 30 min. Then the solvent was completely removed *in vacuo*. The dry brown-green residue was successively extracted with pentane (3×20 mL) (extract *A*) and diethyl ether (3×20 mL) (extract *B*), concentrated to 20 (*A*) and 15 mL (*B*), and kept at −18 °C for one day to prepare large prismatic crystals, which were separated from the solution by decantation, washed with cold hexane (−10 °C), and dried under a stream of argon at 20 °C.

Complex **2** was isolated from the extract *B* in a yield of 0.23 g. Found (%): C, 43.60; H, 7.01. $C_{61}H_{119}Co_6O_{29.5}$. Calculated (%): C, 43.65; H, 7.09. IR (ν/cm^{-1}): 3375 m.br, 2960 s, 2929 w, 2902 w, 2871 w, 1650 w, 1574 s, 1483 s, 1457 w, 1471 s, 1360 s, 1289 m, 1225 m, 1201 w, 1124 w, 937 w, 897 m, 867 m, 783 m, 765 w, 641 w, 610 s, 525 w, 433 w.

Complex **3** was isolated from the extract *A* in a yield of 0.29 g. Found (%): C, 38.19; H, 6.09. $C_{106}H_{206}Co_{14}O_{64}$. Calculated (%): C, 38.22; H, 6.19. IR (ν/cm^{-1}): 3442 s.br, 2959 s, 2927 s, 2872 w, 1676 w, 1592 s, 1483 s, 1459 m, 1412 s, 1361 s, 1224 s, 1119 w, 1031 m, 937 w, 893 m, 786 m, 640 w, 606 m, 541 w, 466 w, 411 w.

X-ray diffraction study. X-ray diffraction data were collected on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo-Kα radiation, graphite monochromator, ω scan technique, scan step was 0.3°, frames were exposed for 10 s, $2\theta_{max} = 50°$) according to standard procedures[9] at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, the Russian Academy of Sciences).

Complex 2. $M = 1677.08$, space group $P\bar{1}$, $a = 14.802(2)$, $b = 14.947(2)$, $c = 24.338(4)$ Å, $\alpha = 83.758(4)°$, $\beta = 77.558(3)°$, $\gamma = 63.044(3)°$ (112 K), $V = 4686.6(13)$ Å^3, $Z = 2$, 15044 measured reflections, of which 5251 independent reflections were with $F^2 > 2\sigma(I)$, $\rho_{calc} = 1.467$ g cm^{-3}, $\mu = 1.109$ cm^{-1}, $R_1 = 0.084$, $wR_2 = 0.192$.

Complex 3. $M = 3328.41$, space group $P2_1/n$, $a = 19.318(4)$, $b = 15.948(3)$, $c = 29.968(4)$ Å, $\beta = 97.961(4)°$ (112 K), $V = 9144(3)$ Å^3, $Z = 4$, 16038 measured reflections, of which 6388 independent reflections were with $F^2 > 2\sigma(I)$, $\rho_{calc} = 1.487$ g cm^{-3}, $\mu = 1.655$ cm^{-1}, $R_1 = 0.086$, $wR_2 = 0.204$.

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References

1. F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, *Advanced Inorganic Chemistry*, 6th Ed., John Wiley and Sons, Inc., 1999, 493.
2. S. J. Lippard and J. M. Berg, *Principles of Bioinorganic Chemistry*, *University Science Books*, Mill Valley, CA, 1994.
3. T. O. Denisova and S. E. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1551 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 1637].
4. A. A. Pasynskii, T. Ch. Idrisov, K. M. Suvorova, V. M. Novotortsev, V. V. Zelentsov, and V. T. Kalinnikov, *Dokl. Akad. Nauk SSSR,* 1975, **220**, 881 [*Dokl. Chem.*, 1975 (Engl. Transl.)].
5. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 409 [*Russ. Chem. Bull.*, 1999, **48**, 405 (Engl. Transl.)].
6. M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, L. T. Eremenko, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Zh. Neorg. Khim.,* 1999, **44**, 1479 [*Russ. J. Inorg. Chem.*, 1999, **44** (Engl. Transl.)].
7. T. O. Denisova and S. E. Nefedov, *Mendeleev Commun.*, 2003, 162.
8. V. Karnojitzki, *Les Peroxydes Organiques*, Hermann, Paris, 1958.
9. SMART (Control) and SAINT (Integration) Software, Version 5.0, Bruker AXS Inc., Madison, WI, 1997.

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