Oxidation of cobalt atoms accompanied by formation of hydroxo bridges in binuclear complexes as analogs of active sites of metalloenzymes. Synthesis and structure of the complex $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OOCBu^t)_2(PirH)_4][OS(O)_2CF_3]_2(thf)_2$ (PirH = 3,5-dimethylpyrazole)

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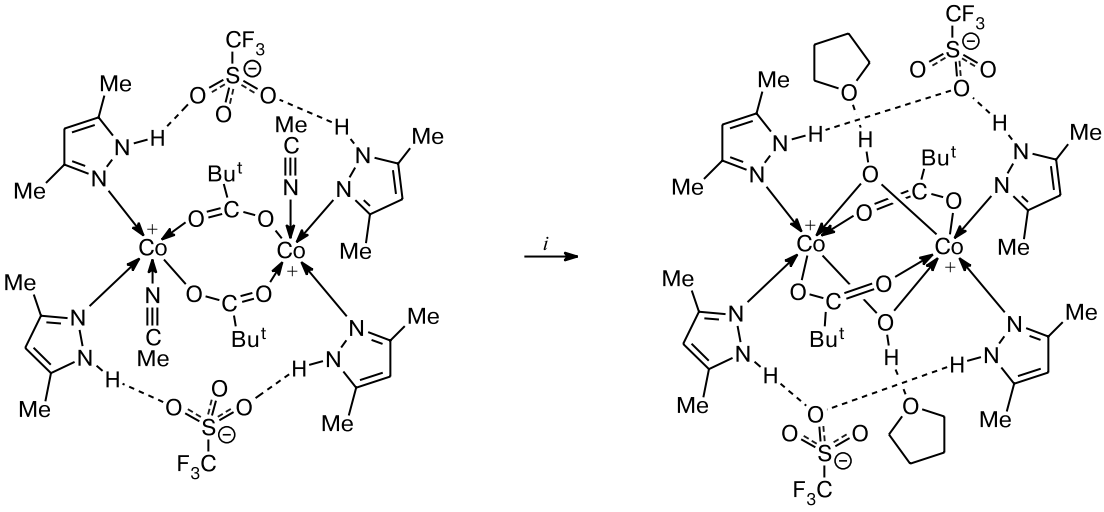
It is well known that the $M_2(\mu\text{-}OOCR)_2$ fragment is present in active centers of many metalloenzymes responsible for different chemical processes in nature (redox reactions, oxygen transport, peptide bond hydrolysis, fixation and transformations of small molecules, *etc.*).[1—4] The synthesis of binuclear transition metal complexes with bridging carboxylate anions and studies of their structures and chemical and physical properties are important problems of modern coordination chemistry, because these compounds are potential models of metal-containing fragments of natural enzymes.

Earlier,[5] we have demonstrated that dissolution of one of such model compounds, *viz.*, the complex $[Co_2(\mu\text{-}OOCBu^t)_2(PirH)_4(MeCN)_2][OS(O)_2CF_3]_2$ (**1**), in THF in the presence of H_2O (2 mol) afforded the complex $[Co_2(\mu\text{-}OH_2)_2(\mu\text{-}OOCBu^t)_2(PirH)_4][OS(O)_2CF_3]_2(thf)_2$ (**2**)[6] containing two bridging H_2O molecules and 3,5-dimethylpyrazole molecules (PirH), which formally serve as models of the imidazole fragments of the terminal histidines. The latter were found, for example, in the active site of nickel urease.[7,8]

In the present study, we describe the product of the reaction of complex **1** with dioxygen.

The reaction of complex **1** with O_2 in THF at room temperature (1 h) gave rise to the green-brown complex $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OOCBu^t)_2(PirH)_4][OS(O)_2CF_3]_2(thf)_2$ (**3**) in 79% yield.

According to the results of X-ray diffraction analysis, the Co...Co distance between two cobalt(III) atoms in complex **3** (Fig. 1) is nonbonded (2.655(1) Å) and the Co atoms are linked *via* two trimethylacetate bridges (Co(1)—O(1), 1.913(4) Å; Co(1)—O(2), 1.928(4) Å) and two hydroxo bridging ligands (Co(1)—O(3), 1.860(4) Å; Co(1A)—O(3), 1.876(4) Å).



1 **3**

i. O_2, THF, 22 °C

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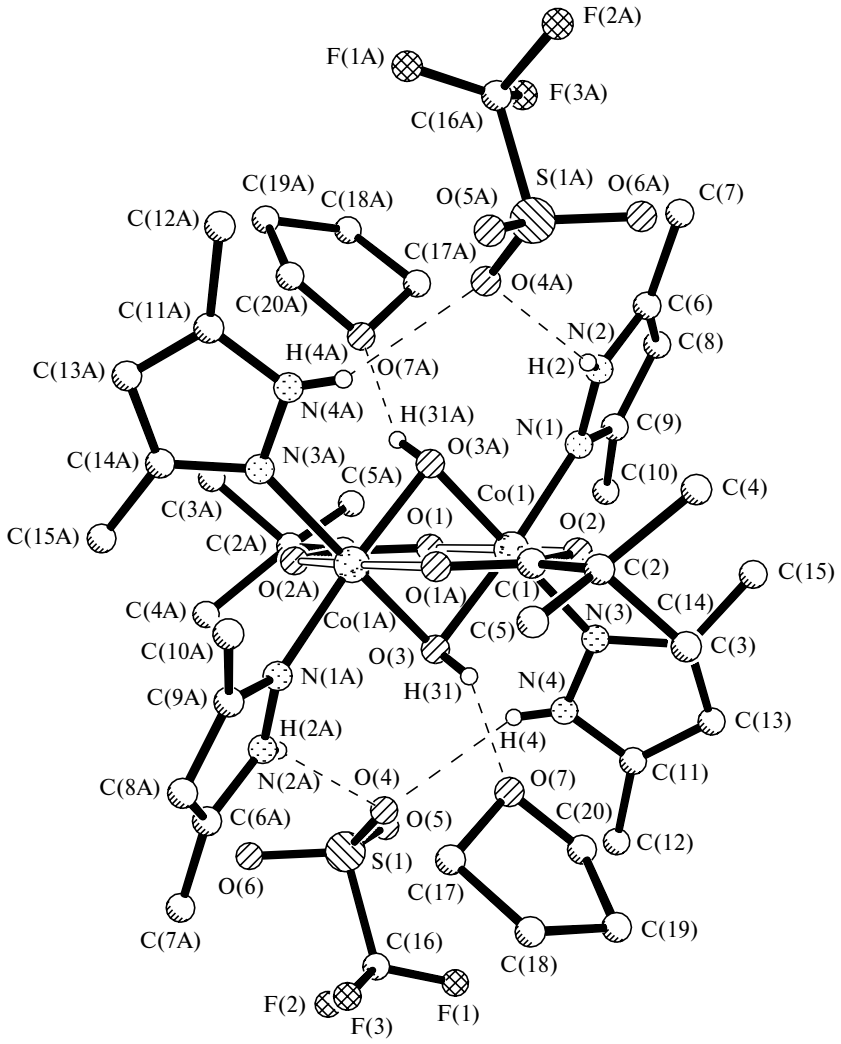

Fig. 1. Structure of complex **3**.

The distorted octahedral coordination environment about each 18-electron metal atom is completed with two pyrazole molecules (Co(1)—N(1), 1.937(5) Å; Co(1)—N(3), 1.938(5) Å). In the crystal unit cell, there are two THF molecules of solvation, whose oxygen atoms are involved in a short bond with the hydrogen atoms of the bridging hydroxo groups (O(7)—H(31), 1.921 Å; O(7)...O(3), 2.673 Å). The O(4) atom of the outer-sphere triflate anion also forms short hydrogen bonds with the H atoms of the NH fragments of the pyrazole ligands (O(4)—H(2), 2.539 Å; O(4)...N(2), 3.114 Å; O(4)—H(4), 2.363 Å; O(4)...N(4), 3.037 Å).

The geometry of complex **3** surprisingly resembles that of complex **2** (Fig. 2) prepared earlier.[6] The latter Co^{II}-containing complex also has THF molecules of solvation and outer-sphere triflate anions. However, only water molecules serve as bridging ligands in complex **2**.

A comparison of the structures of complexes **2** and **3** demonstrates that the change in the oxidation state of the cobalt atoms and in the nature of the bridging ligand causes substantial changes in the bond lengths in the complexes. The M—O and M—N bonds in molecule **3** are shortened compared to those in molecule **2** (in **2**: Co(1)—O(1), 2.049(3) Å; Co(1)—O(2), 2.057(3) Å; Co(1)—N(1), 2.086(4) Å; Co(1)—N(3), 2.092(4) Å). The metal—metal distance is also shortened in **3** by 0.48 Å (3.136(1) Å in molecule **2**). In addition, the character of intermolecular and interionic hydrogen bonding also changes. Thus, the oxygen atom of the THF molecule in complex **2** is located closer to the hydrogen atom of the bridging water molecule (O(7)—H(32), 1.544 Å; O(7)...O(3), 2.628 Å), and the triflate anions are rotated so that two oxygen atoms of the anions are involved in hydrogen bonding. By contrast to complex **2**, the THF molecules of solvation in complex **3** are located at a closer distance from the cobalt atom (Co...O(7) are 4.216 and 3.859 Å in **2** and **3**, respectively), whereas the triflate anions are more remote from the cobalt atom (Co(1)...S(1)

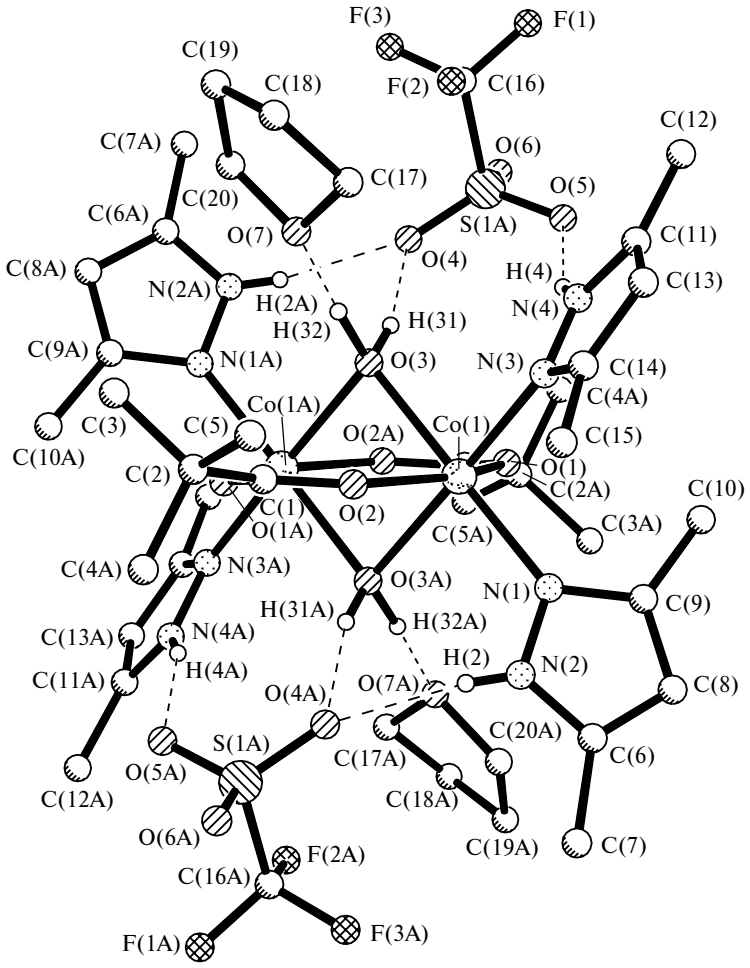

Fig. 2. Structure of complex **2**.

are 5.264 and 5.608 Å in **2** and **3**, respectively). Apparently, these characteristic features of the structure of **3** are associated with the presence of the steric contacts of the triflate anions and THF molecules of solvation with the coordinated 3,5-dimethylpyrazole molecules.

The formation of short hydrogen bonds in complexes **2** and **3** regardless of the oxidation state of the metal atoms is, apparently, the first step of fixation of electron-donating molecules at the metal center. Recently, an analogous decrease in the metal—metal distances and bond lengths has been observed on going from the Co^{II} complex $Co_2(\mu\text{-}OOCR)_2(\mu\text{-}OH_2)_2(OOCR)_2L_2$ (**4**) to the Co^{III} complex $Co_2(\mu\text{-}OOCR)_2(\mu\text{-}OH)_2(OOCR)_2L_2$ (**5**), where R = 2,6-di(*p*-tolyl)benzoate, L = py (Co...Co, 3.0562(2) Å (**4**), 2.6802(2) Å (**5**); $Co—O_{(\mu\text{-}O)}$, 2.223(2)—2.343(2) Å (**4**), 1.858(2)—1.865(2) Å (**5**); Co—O, 2.022(2)—2.059(2) Å (**4**), 1.906(2)—1.948(2) Å (**5**)). However, these complexes contain not only bridging but also terminal carboxylate ligands and are devoid of THF molecules of solvation.[9]

Compound **3** was immediately produced in the reaction of complex **1** with pre-synthesized 2-hydroperoxotetrahydrofuran in THF at room temperature, whereas complex **1** was not oxidized with oxygen even upon heating. Apparently, complex **3** is a product of the coupled reaction of dioxygen with THF, which proceeds on complex **1** and can give rise to hydroxy fragments.

All operations were carried out in an argon stream. The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets in the frequency range of 392—4000 cm^{-1}. The GLC-MS analysis was carried out on an Automass 150 instrument (Delsi Nermag, France) equipped with a 0.25 mm×25 m capillary column with 0.3 μm OV101 (helium as carrier gas, 0.6 atm; injector temperature 250 °C, divider 1 : 40, volume of the sample 0.2 μL, initial column temperature 50 °C (2 min), temperature programming to 250 °C at a rate of 10 °C min^{-1}, interface temperature 250 °C). The electron-impact mass spectra (70 eV) were measured at a temperature of the ion source of 100 °C.

Tetrakis(3,5-dimethylpyrazole)-μ-bis(μ-*O*,*O*′-trimethylacetato)-μ-bis(hydroxo)dicobalt(II) di(triflate) solvate with ditetrahydrofuran, $Co_2(\mu\text{-}OH)_2(\mu\text{-}OOCBu^t)_2(PirH)_4[OS(O)_2CF_3]_2(thf)_2$ (3). ***A.*** Oxygen was bubbled through a violet-blue solution of the complex $[Co_2(\mu\text{-}OOCBu^t)_2(PirH)_4(MeCN)_2][OS(O)_2CF_3]_2$ (0.5 g,

0.46 mmol) in freshly distilled THF (10 mL) at ~20 °C for 30 min. The resulting green-brown solution was concentrated to 5 mL and kept at −15 °C for two days. The green-brown crystals that precipitated were separated from the solution by decantation, washed with cold hexane, and dried in an argon stream. According to the GLC-mass spectrometric data, the resulting solution contained ~0.4% of butyrolactone and 0.7% of 2-hydroxotetrahydrofuran. The yield of **3** was 0.43 g (0.36 mmol, 79%). Found (%): C, 40.65; H 5.73. $C_{40}H_{68}Co_2N_8O_{14}F_6S_2$. Calculated (%): C, 40.68; H, 5.8. IR (KBr, ν/cm^{-1}): 3474 s.br, 3413 s.br, 3276 s.br, 2979 s, 2934 s, 2878 m, 1637 w, 1617 m, 1575 s, 1503 s, 1406 m, 1366 w, 1352 m, 1291 s, 1256 s, 1176 m, 1063 w, 1031 s, 805 w, 779 w, 637 m, 517 w.

B. The initial 3,5-dimethylpyrazole complex $[Co_2(\mu\text{-}OOCBu^t)_2(PirH)_4(MeCN)_2][OS(O)_2CF_3]_2$ (0.1 g) was dissolved in THF (10 mL) containing approximately 0.1% of 2-hydroperoxotetrahydrofuran (according to GLC-mass spectrometric data; was identified based on the total concentration of the products of decomposition of butyrolactone and 2-hydroxotetrahydrofuran), which was prepared by bubbling O_2 through anhydrous THF followed by storage of the solution in the light for one day.[10] The solution immediately turned green-brown. The yield of complex **3** was 0.093 g (89%).

X-ray diffraction study. X-ray diffraction data were collected at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, the Russian Academy of Sciences) according to standard procedures[11] 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 30 s, $2\theta_{max}$= 50°). Complex **3**: $C_{40}H_{68}Co_2F_6N_8O_4S_2$, M = 1181.00, space group $\bar{P}1$, a = 10.581(4) Å, b = 10.655(4) Å, c = 13.084(5) Å, α = 68.186(7)°, β = 80.196(8)°, γ = 72.368(7)° (153 K), V = 1303.6(8) Å^3, Z = 1, 6243 measured reflections of which 4375 independent reflections were with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.504 g cm^{-3}, μ = 8.06 cm^{-1}, R_1 = 0.0658, wR_2 = 0.1524.

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