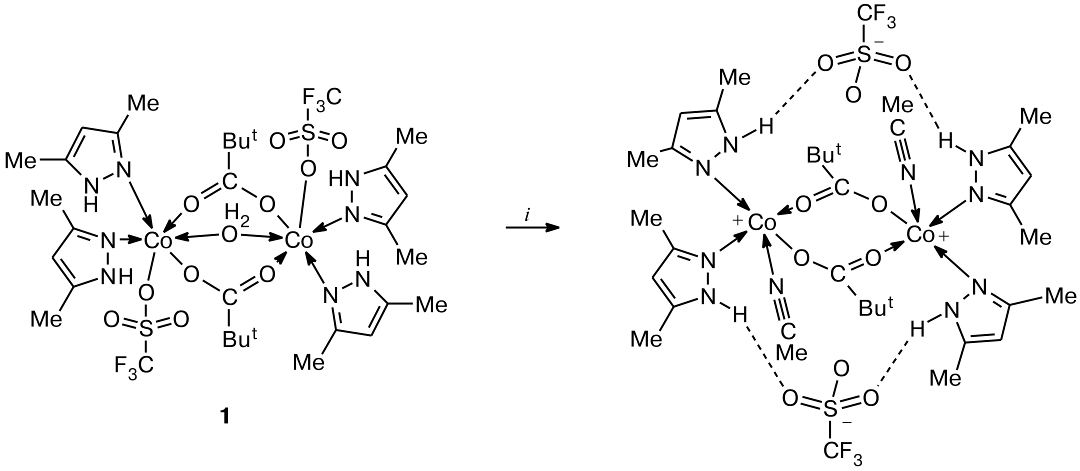
Letters to the Editor

Easy elimination of bridging water molecule from a binuclear cobalt(II) complex. Synthesis and structure of the $[Co_2(\mu\text{-}OOCBu^t)_2(PirH)_4(MeCN)_2][OS(O)_2CF_3]_2$ complex (PirH is 3,5-dimethylpyrazole)

T. O. Denisova 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

Earlier,[1] we have reported the synthesis of the $Co_2(\mu\text{-}OOCBu^t)_2(\mu\text{-}OH_2)[\eta\text{-}OS(O)_2CF_3]_2(PirH)_4$ complex (**1**) containing triflate anions σ-bound to the Co^{II} atom. It is known[2] that these anions are very labile and can be displaced to the outer sphere even under the action of acetonitrile. We found that dissolution of complex **1** in MeCN



1

2

i. MeCN, 22 °C.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 982—984, April, 2003.

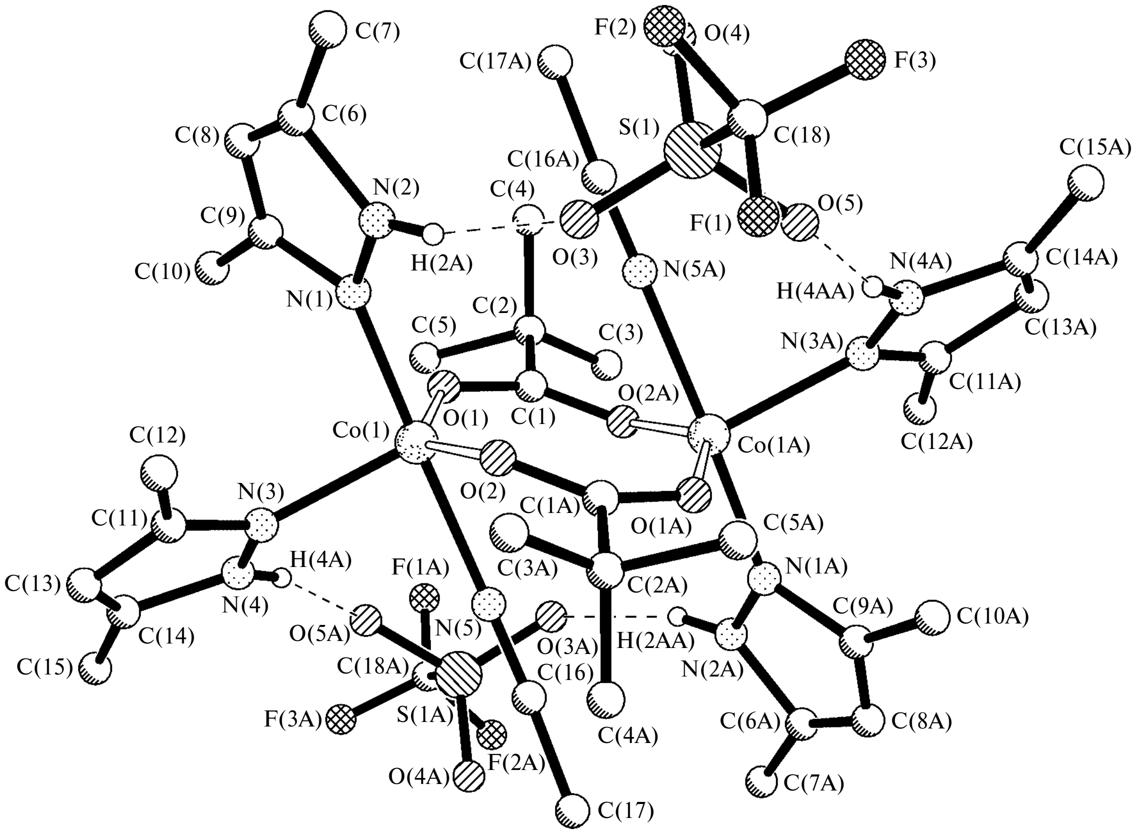


Fig. 1. Structure of complex **2**.

at room temperature afforded the pink binuclear ionic complex $[Co_2(\mu\text{-}OOCBu^t)_2(PirH)_4(MeCN)_2][OS(O)_2CF_3]_2$ (**2**) in 72% yield.

According to the results of X-ray diffraction analysis, two cobalt atoms in the cation of complex **2** (Fig. 1) are at a nonbonded distance (Co...Co, 3.490(1) Å) and are linked by only two trimethylacetate bridges (Co—O, 1.955(8) Å). The Co(1) and Co(1A) atoms are located at a distance of 0.37 Å above and below the O(1)C(1)O(2A)O(1A)C(1A)O(2) plane (planar to within 0.003 Å). In addition, each cobalt atom is coordinated by three nitrogen atoms belonging to two terminal pyrazole molecules (Co—N, 1.988(7) and 2.001(7) Å) and the acetonitrile molecule (Co—N, 2.121(8) Å). As a result, the metal atoms are in a trigonal-bipyramidal environment and have 17 valence electrons each. It should be noted that complex **2** does not contain a bridging water molecule, and the acetonitrile molecules are in *trans* orientations with respect to the metal—metal line.

Such an easy (at room temperature) elimination of the bridging water molecule, which is present in most of nickel(II) and cobalt(II) trimethylacetate complexes of the general formula $L_4M_2(\mu\text{-}OOCBu^t)_2(OOCBu^t)_2(\mu\text{-}OH_2)$ (**3**) (L is a nitrogen-containing base) was observed for the first time. For analogous processes to occur, for example, in complexes of type **3** (with L = py), either prolonged heating in xylene or toluene (for the nickel or cobalt complexes, respectively) or thermolysis of the solid complex *in vacuo* at high temperature is required.[3,4]

It should be noted that the outer-sphere triflate anions form very short hydrogen bonds with the hydrogen atoms of the NH groups of the terminal pyrazole ligands (O(3)—H(2A), 2.064 Å; O(5)—H(4A), 1.874 Å). Because of this, the size of complex **2** is only slightly larger than that of the initial complex **1**.

Presumably, taking into account that transition metal carboxylates are analogs of natural enzymes,[5] the observed elimination of the bridging water molecule under mild conditions, which is not accompanied by substantial changes in the volume and structure of the molecule, takes place in the course of processes occurring in enzymes.

All operations were carried out 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 tetrakis(3,5-dimethylpyrazole)bis(acetonitrile)-μ-bis(μ-O,O′-trimethylacetato)dicobalt(II) ditriflate, $[Co_2(\mu\text{-}OOCBu^t)_2(PirH)_4(MeCN)_2][OS(O)_2CF_3]_2$ (2). The $Co_2(\mu\text{-}OOCBu^t)_2(\mu\text{-}H_2O)[\eta\text{-}OS(O)_2CF_3]_2(PirH)_4$ complex (0.25 g, 2.4 mmol) was dissolved in acetonitrile (3 mL) at room temperature. The resulting crimson-red solution was kept at −15 °C for one day. The pink crystals that formed were separated from the solution by decantation, washed with hexane, and dried at ~22 °C under a stream of argon. The yield was 0.19 g (72%). Found (%): C, 39.72; H 5.11. $Co_2C_{36}H_{56}O_{10}N_{10}F_6S_2$. Calculated (%): C, 39.85; H, 5.16. IR (KBr), ν/cm^{-1}: 3104 m br, 3319 m br, 3229 m br, 3152 w, 3049 w, 2988 w, 2972 m, 2932 w, 2875 w, 1664 w, 1576 s, 1564 s, 1488 m, 1424 m, 1364 w, 1356 w, 1288 s, 1248 s, 1224 m, 1168 s, 1052 m, 1028 s, 808 m, 788 m, 748 w, 680 w, 660 w, 636 m, 516 w, 440 w.

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[6] on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo radiation, graphite monochromator, ω scan technique, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max} = 50°$). Complex **2**: $C_{36}H_{56}Co_2F_6N_{10}O_{10}S_2$, M = 1084.88, at 112 K space group $P2_1/c$, a = 10.268(2) Å, b = 17.269(3) Å, c = 13.141(3) Å, β = 95.01(2)°, V = 2321.2(8) Å^3, Z = 2, a total of 6401 reflections were measured, of which 1018 reflections were independent with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.552 g cm^{-3}, μ = 8.93 cm^{-1}, R_1 = 0.1051, wR_2 = 0.2386.

This study was financially supported by the Ministry of Industry, Science, and Technology of the Russian Federation (State Agreement 41.002.11.1402), the Russian Foundation for Basic Research (Project Nos. 02-03-32454, 03-03-06264, and 00-15-97429), and the Foundation for Support of National Science.

References

1. T. O. Denisova and S. E. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 739 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 775].
2. F. A. Cotton, G. Wilkincon, C. A. Murillo, and M. Bochmann, *Advanced Inorganic Chemistry*, 6th Ed., John Wiley and Sons Inc., 1999, 493.
3. 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.)].
4. 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.)].
5. R. H. Holm, P. Kennepohl, and E. I. Solomon, *Chem. Rev.*, 1996, **96**, 2239.
6. *SMART (Control) and SAINT (Integration) Software, Version 5.0*, Bruker AXS Inc., Madison, WI, 1997.

Received March 4, 2003