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Synthesis and structure of the binuclear and mononuclear complexes $Co_2(\mu\text{-}OH_2)_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4[OS(O)_2CF_3]_2\cdot 2THF$ and $Co(Hdmpz)_2(MeCN)_2(OH_2)_2[OS(O)_2CF_3]_2\cdot THF$ (Hdmpz = 3,5-dimethylpyrazole)

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The reaction of $Co_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4(MeCN)_2[OS(O)_2CF_3]_2$ (Hdmpz = 3,5-dimethylpyrazole) with water in THF at room temperature gave the binuclear and mononuclear complexes $Co_2(\mu\text{-}OH_2)_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4[OS(O)_2CF_3]_2\cdot 2THF$ and $Co(Hdmpz)_2(MeCN)_2(OH_2)_2[OS(O)_2CF_3]_2\cdot THF$, which were characterised using X-ray diffraction analysis.

Binuclear transition metal complexes incorporating $M_2(\mu\text{-}OOCR)_2$-$(\mu\text{-}OH_2)$ fragments are considered as synthetic analogues of the reactive part of natural metal-based enzymes.[1–3] The synthesis and structural and physico-chemical characterization of these model complexes is an important task of modern coordination chemistry. The primary goal of this modelling is the simulation of separate steps of naturally occurring catalytic reactions with the isolation of their intermediate products.

Previously, we found that the dissolution of one of these model compounds, *viz*., the $Co_2(\mu\text{-}OOCBu^t)_2(\mu\text{-}OH_2)[\eta\text{-}OS(O)_2CF_3]_2$-$(Hdmpz)_4\cdot THF$ complex, in MeCN at room temperature unexpectedly results in the loss of the bridging water molecule to give $Co_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4(MeCN)_2[OS(O)_2CF_3]_2$ complex **1**[4] containing terminal 3,5-dimethylpirazole (Hdmpz) molecules; these molecules formally simulate the imidazole fragments of the terminal histidine molecules found, *e.g.*, in the reactive part of nickel-containing urease.[5]

Here we report the reaction products of complex **1** with water, which is undoubtedly one of the most important natural reagents.

The reaction of compound **1** with an excess of H_2O in THF at room temperature resulted in the red binuclear complex $Co_2(\mu\text{-}OH_2)_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4[OS(O)_2CF_3]_2\cdot 2THF$ **2** (11% yield) and the yellowish orange mononuclear complex $Co(Hdmpz)_2(MeCN)_2(OH_2)_2[OS(O)_2CF_3]_2\cdot THF$ **3** (9% yield) (Scheme 1).[†]

According to X-ray diffraction data,[‡] each cobalt atom in the cation of complex **2** (Figure 1) is bound to four oxygen atoms: two of these atoms belong to bridging water molecules [Co–O 2.229(4), 2.239(3) Å, Co(1)–O(3)–Co(1A) 89.15(14)°] and the other two atoms belong to bridging pivalate anions [Co–O 2.049(4), 2.057(4) Å]. This results in the almost planar eight-membered metal-containing ring CoOCOCoOCO. The distorted octahedral environment of the 19-electron metal(II) atoms is complemented by two nitrogen atoms of the terminal Hdmpz molecules [Co–N 2.086(5), 2.092(4) Å].

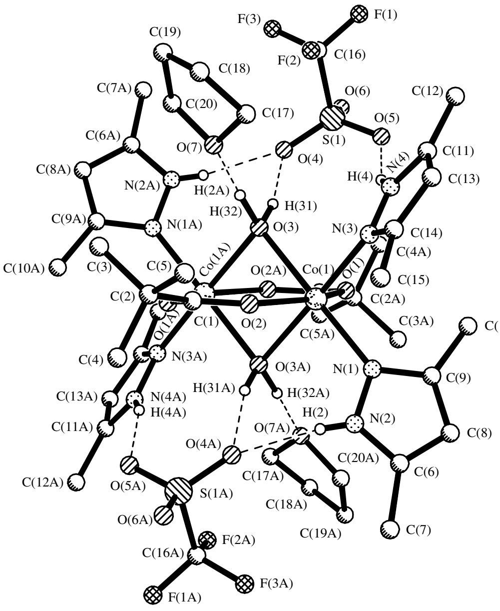


Figure 1 Structure of complex **2**.

[†] The $Co_2(\mu\text{-}OOCBu^t)_2(Hdmpz)_4(MeCN)_2[\eta\text{-}OS(O)_2CF_3]_2$ complex (0.3 g, 0.25 mmol) was dissolved in 10 ml of THF containing 0.05 ml (2.8 mmol) of water. The resulting crimson-red solution was concentrated to 5 ml and kept for one day at –15 °C. The red crystals of complex **2** formed were separated by decantation from the mother liquor, washed with hexane and dried at room temperature in a stream of argon.

Hexane (2 ml) was added to the mother liquor, which was then kept for a day at –15 °C. The resulting yellowish orange crystals of complex **3** were separated by decantation from the solution, washed with cold hexane and dried at room temperature in a stream of argon. The yield of compound **2** was 0.036 g (11%). IR (KBr, ν/cm^{-1}): 3496 (br. s), 3408 (br. s), 2960 (br. m), 2926 (m), 2875 (w), 1760 (w), 1732 (w), 1716 (w), 1668 (w), 1644 (m), 1580 (m), 1548 (m), 1520 (m), 1504 (m), 1480 (m), 1372 (m), 1360 (w), 1276 (s), 1252 (s), 1168 (s), 1044 (s), 1032 (s), 800 (m), 660 (w), 640 (w), 624 (w), 520 (w), 435 (w). Found (%): C, 40.52; H, 5.87. Calc. for $Co_2C_{40}H_{70}F_6N_8O_{14}S_2$ (%): C, 40.60; H, 5.91.

The yield of compound **3** was 0.020 g (9%). IR (KBr, ν/cm^{-1}): 3520 (br. s), 3404 (br. s), 1664 (m), 1616 (w), 1568 (m), 1276 (s), 1236 (s), 1176 (s), 1044 (s), 800 (w), 656 (w), 568 (w), 520 (m), 428 (w), 408 (w). Found (%): C, 32.43; H, 4.62. Calc. for $CoC_{20}H_{34}F_6N_6O_9S_2$ (%): C, 32.45; H, 4.59.

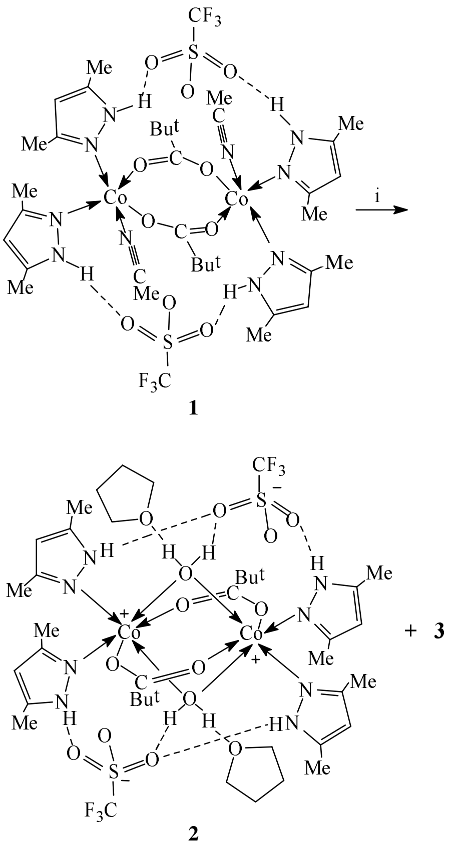
[‡] The X-ray diffraction study was carried out at the Centre for Structural Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, RAS) using standard techniques[7] on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector [λ(MoKa) = 0.71072 Å, graphite monochromator, ω-scanning, scanning step of 0.4°, frame measurement time of 20 s, $2\theta_{max} = 50°$].

For **2**: $C_{40}H_{70}Co_2F_6N_8O_{14}S_2$, $M = 1183.02$, monoclinic, space group $P2_1/n$, $a = 12.6677(16)$, $b = 15.236(3)$ and $c = 14.2869(18)$ Å, $\beta = 97.267(1)°$ (120 K), $V = 2725.3(6)$ Å^3, $Z = 2$, 17441 measured reflections including 4769 independent reflections with $F^2 > 2\sigma(I)$, $d_{calc} = 1.436$ g cm^{-3}, $\mu = 7.68$ cm^{-1}, $R_1 = 0.0592$, $wR_2 = 0.1254$.

For **3**: $C_{20}H_{34}CoF_6N_6O_9S_2$, $M = 739.58$, monoclinic, space group $C2_1/c$, $a = 23.674(3)$, $b = 11.8605(18)$ and $c = 12.1748(18)$ Å, $\beta = 108.551(3)°$ (120 K), $V = 3240.9(8)$ Å^3, $Z = 4$, 9321 measured reflections including 2835 independent reflections with $F^2 > 2\sigma(I)$, $d_{calc} = 1.516$ g cm^{-3}, $\mu = 7.46$ cm^{-1}, $R_1 = 0.0763$, $wR_2 = 0.1882$.

The hydrogen atoms of the bridging and terminal water molecules in complexes **2** and **3** and NH fragments were located by electron density difference syntheses and refined isotropically. The positions of the other hydrogen atoms were calculated geometrically. The fluorine and oxygen atoms in complex **3** are disordered with respect to two positions with multiplicities of 0.5 and 0.5 or 0.7 and 0.3, respectively. The atomic positions of the solvate THF molecule in complex **3** are disordered and occupy two positions with populations of 0.5. The C3S (C3SA) atoms belong to both disordered THF molecules.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 217808 and 217809. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2003.



Scheme 1 *Reagents and conditions*: i, H_2O (excess), THF, 22 °C.

Note that two outer-sphere triflate anions are located unusually close to the metal atoms (Co$\cdots$S 5.263 Å; in compound **1**, it is 4.998 Å). This probably results from the formation of short bonds between two oxygen atoms in the anions with hydrogen atoms of the NH fragments of terminal pyrazoles, which are coordinated by different metal atoms of the binuclear fragment [O(4)–H(2A) 2.105 Å, O(4)$\cdots$N(2) 2.827 Å, O(5)–H(4) 2.094 Å, O(5)–N(4) 2.847 Å], and with one hydrogen atom of the bridging water molecule [O(4)–H(31) 1.911 Å, O(4)$\cdots$O(3) 2.763 Å]. In addition, the lattice cell of complex **2** contains two solvate molecules of THF [Co$\cdots$O(7) 4.216, 4.238 Å], which form even shorter bonds with the other hydrogen atoms of the bridging water molecules [O(7)–H(32) 1.544 Å, O(1)$\cdots$O(7) 2.629 Å].

As a result, the metal atoms in the complex obtained are arranged at a nonbonding Co$\cdots$Co distance of 3.136(1) Å, which is much shorter than the metal–metal distance observed in complex **1** [Co$\cdots$Co 3.490(1) Å] containing two bridging pivalate anions and no bridging water molecules, which possess a shrinking effect.[4]

Note that the synthesised complexes containing the $\mathrm{M_2(\mu\text{-}OOCR)_2(\mu\text{-}OH_2)_2}$ fragment have not been known before in inorganic chemistry; recently, the synthesis and structure of $\mathrm{Co_2(\mu\text{-}OOCR)_2(\mu\text{-}OH_2)_2(OOCR)_2L_2}$ complexes, where R = = 2,6-di(*p*-tolyl)benzoate and L = Py, THF or *N*,*N*′-dibenzylethylenediamine, were reported.[6] Although these complexes contain sterically hindered carboxylate anions, the metal–metal distances in them are 3.052–3.068 Å, which are shorter than those in compound **2**. This is probably due to the formation of short intramolecular bonds between hydrogen atoms of the bridging water molecule and oxygen atoms of the two terminal carboxylate anions present in the compounds, whereas the cation of complex **2** has no intramolecular hydrogen bonds.

The formation of a short hydrogen bond between the hydrogen atoms of the water molecule and the oxygen or nitrogen atoms of the substrate molecule can be the first step (possibly, the key step) of processes that occur in the coordination environment of the reactive part of natural metal-containing enzymes.

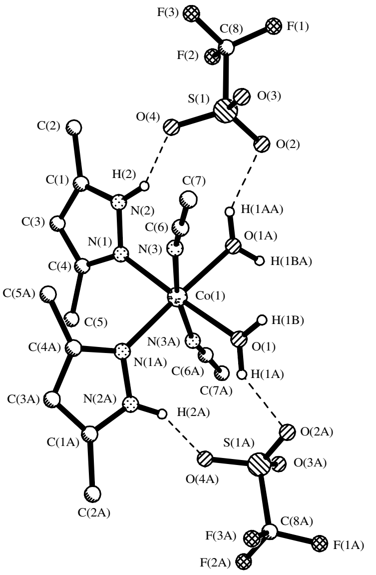


Figure 2 Structure of complex **3**.

The second reaction product is the ionic mononuclear complex $\mathrm{Co(Hdmpz)_2(MeCN)_2(OH_2)_2[OS(O)_2CF_3]_2{\cdot}THF}$ **3**, which can be a disproportionation product of compound **1**. According to X-ray diffraction data,[‡] the cobalt(II) atom in the cation of complex **3** (Figure 2) is in a distorted octahedral environment consisting of four nitrogen atoms, two of which belong to two acetonitrile molecules arranged axially [Co–N 2.130(4) Å], while the two others belong to pyrazole molecules [Co–N 2.092(4) Å].

Equatorial positions are also occupied by two oxygen atoms of terminal water molecules [Co–O 2.096(4) Å], which are *trans* located with respect to the nitrogen atoms of the coordinated pyrazole molecules. The oxygen atoms of the two symmetrically arranged outer-sphere triflate anions in complex **3** form short bonds with the hydrogen atoms of the NH fragment of pyrazoles [O(4)–H(2) 2.133 Å, O(4)$\cdots$N(2) 2.849 Å] and with one hydrogen atom of water molecules [O(2)–H(1AA) 2.081 Å, O(2)$\cdots$O(1) 2.813 Å]. The second hydrogen atom of each water molecule is bound with an oxygen atom of the triflate anion in another complex molecule [H(1B)–O(3′) 1.802 Å, O(1)$\cdots$O(3′) 2.750 Å].

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