Synthesis, structure, and protonation of an unusual electron-deficient complex $Co_2(\mu\text{-Pir})_2(OOCCMe_3)_2(PirH)_2$ (PirH is 3,5-dimethylpyrazole) with bridging pyrazolate ligands*

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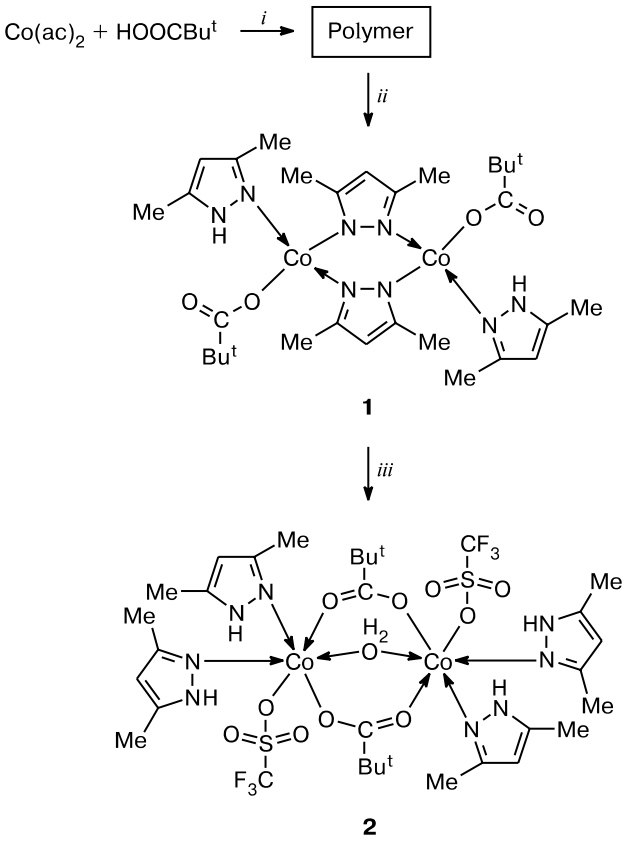
We found that the reaction of a polymeric cobalt(II) complex, which was prepared by melting cobalt(II) acetate tetrahydrate with trimethylacetic acid,[1] with 3,5-dimethylpyrazole (PirH) ($Co(OOCBu^t)_2$: PirH = 1 : 2) in refluxing *o*-xylene afforded the violet $Co_2(\mu\text{-Pir})_2(OOCCMe_3)_2(PirH)_2$ complex (**1**, 53% yield).



i. Melting at 150 °C. *ii*. 3,5-Dimethylpyrazole, *o*-xylene, reflux. *iii*. HO_3SCF_3, THF, 22 °C.

According to the results of X-ray diffraction analysis (Fig. 1), the Co...Co distance in complex **1** is nonbonded (3.629(1) Å) and the Co atoms are linked only *via* the N atoms of two bridging pyrazolate ligands (Co(1)—N(3), 1.990(1) Å; Co(1)—N(4), 1.994(1) Å) generated through deprotonation of the 3,5-dimethylpyrazole molecule. Each metal atom is coordinated by the nitrogen atom of the terminal pyrazole molecule (Co—N, 2.013(2) Å) and the oxygen atom of the terminal trimethylacetate anion (Co—O, 1.941(2) Å). This gives rise to an unusual binuclear complex in which each cobalt(II) atom is electron-deficient (15 electrons) and is in a distorted tetrahedral environment.

It should be emphasized that the oxygen atom of the terminal trimethylacetate anion forms a short intramolecular hydrogen bond (1.856 Å) with the hydrogen atom of the NH fragment of the coordinated pyrazole molecule.

Complex **1** is readily protonated under mild conditions (THF, room temperature) by the reaction with trifluoromethanesulfonic acid containing 0.5—2% of H_2O to give the $Co_2(\mu\text{-}OOCBu^t)_2(\mu\text{-}OH_2)[\eta\text{-}OS(O)_2CF_3]_2(PirH)_4 \cdot THF$ complex (**2**, 35% yield). According to the results of X-ray diffraction analysis (Fig. 2), one of the N atoms of each bridging pyrazolate fragment adds the H atom, so that each cobalt atom is coordinated by two terminal PirH molecules (Co—N, 2.085(5) and 2.114(5) Å). The terminal trimethylacetate anions serve as bridges (Co—O, 2.028(4) and 2.058(4) Å). In addition, each cobalt atom is coordinated by the triflate anion (Co—O, 2.221(5) Å). The distorted octahedral environment about each metal atom is completed with the oxygen atom of the bridging H_2O molecule (Co—O, 2.191(4) Å). As a result, interaction between the 19-electron Co^{II} atoms is nonbonded (Co...Co, 3.662(1) Å).

The crystal structure contains the THF molecule of solvation. Its oxygen atom forms intermolecular hydrogen bonds (2.137 Å) with the hydrogen atoms of the bridging water molecule of complex **2**. The hydrogen atoms of the NH fragments of the coordinated pyrazole molecules form short bonds with the noncoordinated oxygen atoms of the triflate anion (H(2A)—O(2), 1.878 Å, H(4)—O(3), 1.974 Å). Apparently, it is this distribution of the hydrogen bonds that leads to an increase in the Co...Co dis-

* Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

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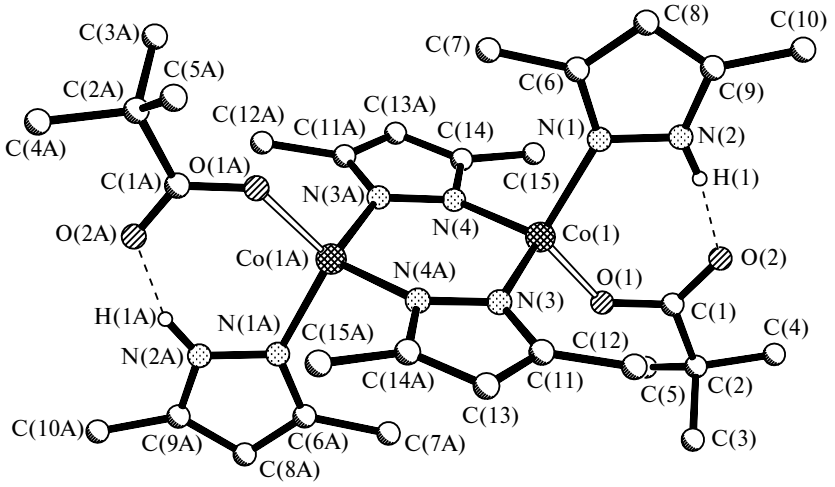

Fig. 1. Structure of complex **1**.

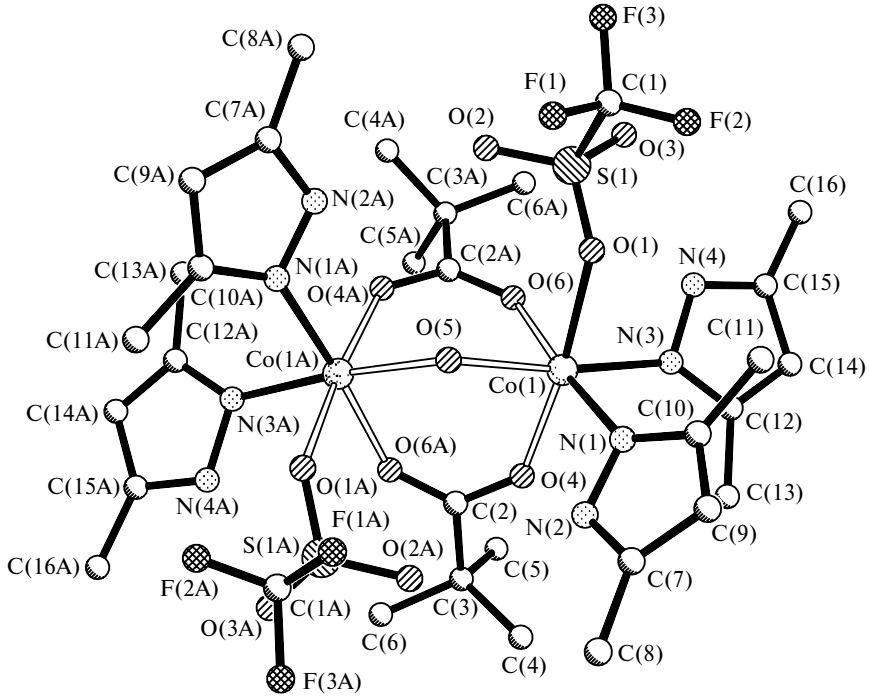

Fig. 2. Structure of complex **2**.

tance by 0.1 Å compared to the distance (Co...Co, 3.569(1) Å) observed in the $Co_2(\mu\text{-}OOCBu^t)_2(\mu\text{-}OH_2)(OOCBu^t)_2(py)_4$[2] complex, which has an analogous structure but possesses short intramolecular contacts between the oxygen atoms of the terminal trimethylacetate anions and the H atoms of the bridging H_2O molecule (O—H, 2.123 Å).

To summarize, it was found that the coordinated pyrazole molecule can be reversibly deprotonated. This is of importance for an understanding of the mechanism of action of metalloenzymes whose active site containes the imidazole fragment of the terminal histidine molecule[3] and for which binuclear transition metal carboxylate complexes serve as models.[4]

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

Bis(3,5-dimethylpyrazole)bis(trimethylacetato)-bis(μ-*N*,*N*′-3,5-dimethylpyrazolato)dicobalt(II), $Co_2(\mu\text{-}Pir)_2(OOCCMe_3)_2(PirH)_2$ (1). 3,5-Dimethylpyrazole (0.27 g, 2.73 mmol) was added to a suspension of the polymeric Co^{II} complex (0.37 g, 1.36 mmol with respect to $Co(OOCBu^t)_2$), which was prepared by melting cobalt acetate tetrahydrate with trimethylacetic acid[1] in refluxing *o*-xylene (20 mL). The resulting mixture was refluxed for 0.5 h. The violet solution was fil-

tered, concentrated to 10 mL, and kept at −5 °C for 2 days. The prismatic crystals that formed were separated from the solution by decantation, washed with cold hexane, and dried under a stream of argon at ~20 °C. The yield was 0.5 g (0.71 mmol, 53%). Found (%): C, 49.91; H 8.24. $C_{30}H_{48}Co_2N_8O_4$. Calculated (%): C, 49.95; H, 8.32. IR (KBr, ν/cm^{-1}): 3226 w.br, 2968 m, 2920 m, 2872 m, 1664 w, 1600 m, 1568 m, 1552 s, 1524 s, 1480 s, 1400 s, 1352 s, 1324 m, 1296 m, 1220 m, 1140 m, 1088 w, 1044 s, 1016 w, 888 w, 792 w, 776 m, 744 w, 612 m, 572 w, 432 m.

Tetra(3,5-dimethylpyrazole)bis(triflato)-μ-bis(μ-O,O′-trimethylacetato)-μ-aquadicobalt(II) tetrahydrofuran solvate, $Co_2(\mu\text{-}OOCBu^t)_2(\mu\text{-}OH_2)[\eta\text{-}OS(O)_2CF_3]_2(PirH)_4\cdot THF$ (2). Trifluoromethanesulfonic acid (0.11 mL) containing 0.5—2% of water was added to a solution of $Co_2(\mu\text{-}Pir)_2(OOCCMe_3)_2(PirH)_2$ (**1**) (0.45 g, 6.34 mmol) in THF (15 mL) and the reaction mixture was stirred at ~20 °C for 1 h. The red-brown solution that formed was concentrated to 5 mL and kept at −5 °C for two days. The red prismatic crystals that precipitated were separated from the solution by decantation, washed with hexane, and dried at ~20 °C under a stream of argon. The yield was 0.25 g (0.24 mmol, 35%). Found (%): C, 52.94; H 6.51. $Co_2C_{34}H_{46}O_{11}N_8F_6S_2$. Calculated (%): C, 53.01; H, 6.45. IR (KBr, ν/cm^{-1}): 3398 s.br, 2960 m, 2932 m, 2872 w, 1660 w, 1598 s, 1580 s, 1484 m, 1420 s, 1372 w, 1360 w, 1292 m, 1236 s, 1224 s, 1180 m, 1096 w, 1040 m, 1024 s, 888 w, 812 m, 808 w, 788 m, 680 w, 660 w, 636 m, 512 w, 424 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[5] on a Siemens P3/PC diffractometer (for **1**) (μ(Mo-Kα) radiation, λ = 0.71074 Å, θ-2θ scan technique, $2\theta_{max} = 56°$) and a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (for **2**) (λMo, graphite monochromator, ω scan technique, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max} = 50°$). Complex **1**: $C_{30}H_{48}Co_2N_8O_4$, M = 702.62, space group $P2_1/n$, a = 9.368(2) Å, b = 9.472(2) Å, c = 20.603(4) Å, β = 100.21(2)° (293 K), V = 1799.2(7) Å^3, Z = 4, a total of 4176 reflections were measured of which 3936 reflections were independent with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.297 g cm^{-3}, μ = 9.65 cm^{-1}, R_1 = 0.0394, wR_2 = 0.0835. Complex **2**: $C_{24}H_{39.33}Co_{1.33}F_4N_{5.33}O_8S_{1.33}$, M = 727.93, space group $I\bar{4}2d$, a = 19.0293(10) Å, b = 19.0293(10) Å, c = 26.962(2) Å, V = 9763.4(11) Å^3 (120 K), Z = 12, a total of 21777 reflections were measured of which 4319 were independent with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.486 g cm^{-3}, μ = 8.51 cm^{-1}, R_1 = 0.0569, wR_2 = 0.1280.

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