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Deprotonation of 3,5-Bis(trifluoromethyl)pyrazole in the Presence of $[Phen_2Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCMe)_2(OOCMe)_2]$

M. A. Uvarova[a], * **and S. E. Nefedov**[a], †

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*

**e-mail: yak_marin@mail.ru*

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Abstract—The reactions of 3,5-bis(trifluoromethyl)pyrazole ($(CF_3)_2PzH$) with the binuclear complex $[Phen_2Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCMe)_2(OOCMe)_2]$ were studied. The reaction in dichloromethane under mild conditions gave the complex $[Co_2(Phen)_2(\mu\text{-}H_2O)(\mu\text{-}OOCMe)_2(OOCMe)_2]((CF_3)_2PzH)_4$ (**I**). Refluxing of **I** in *ortho*-xylene resulted in deprotonation of pyrazole giving two mononuclear complexes: pyrazolate $[Co(Phen)_2(H_2O)(OOCMe)]((CF_3)_2Pz)$ (**II**) and pyrazolate acetate $[Co(Phen)_2((CF_3)_2Pz)_2]$ (**III**). Compounds **I–III** were studied by X-ray diffraction (CCDC nos. 2159355–2159357), IR spectroscopy, and elemental analysis. The thermal behavior of **I** was investigated by TGA.

Keywords: 3,5-bis(trifluoromethyl)pyrazole, pyrazolates, crystal structure, cobalt carboxylates

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INTRODUCTION

The chemistry of pyrazole and its analogues is a relevant and promising trend of modem coordination chemistry. This is due to the fact that the molecule of pyrazole contains two chemically different nitrogen atoms, pyridine and pyrrole ones. Owing to the lone pair of the pyridine nitrogen atom, pyrazole can be coordinated to a metal, while the pyrrole moiety can be deprotonated to give the pyrazolate anion with delocalized electron density [1, 2]. The deprotonation of pyrazole and analogous molecules by transition metal carboxylates affords pyrazolate-bridged complexes of various dimensionality. The composition and structure of the products of these reactions are determined, first of all, by the transition metal nature, the donor properties of the anion present in the initial complex, the reaction conditions (solvent polarity, temperature, etc.), and also by the nature of substituents in the pyrazole molecule. Metal pyrazolates thus formed can be considered as building blocks for the synthesis of homo- and heterometal clusters with interesting physicochemical properties [3–7].

Previously it was found that reactions of cobalt and zinc carboxylates with 3,5-dimethylpyrazole (HDmpz) at room temperature are accompanied by deprotonation of pyrazole to give pyrazolate-bridged complexes [8–16].

Meanwhile, 3,5-dimethylpyrazole is not deprotonated in the reactions with cobalt carboxylates (pivalate, acetate, benzoate) containing N-donor phenanthroline or bipyridine [17]. The replacement of the electron-donating methyl substituents in the pyrazole molecule by electron-withdrawing CF_3 groups considerably enhances the pyrazole acidity, which facilitates the formation of the pyrazolate anion [18–22].

This study deals with the major products formed in the reaction of the binuclear complex $[Phen_2Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCMe)_2(OOCMe)_2]$ [24] with 3,5-bis(trifluoromethyl)pyrazole under various conditions.

EXPERIMENTAL

The complexes were synthesized in air using commercial solvents, which were used as received: dichloromthane (special-purity grade, Khimmed), hexane (special-purity grade, Khimmed), and *ortho*-xylene (special-purity grade, Khimmed). Commercially available chemicals were used: 3,5-bis(trifluoromethyl)pyrazole (98%, Acros), cobalt acetate trihydrate (95%, Acros). The complex $[Phen_2Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCMe)_2(OOCMe)_2]$ was prepared by a known procedure [24].

Elemental analysis was carried out on a Carlo Erba EA 1108 automatic C,H,N-analyzer. IR spectra were measured on a Perkin-Elmer Spectrum 65 Fourier transform IR spectrometer by the attenuated total reflectance (ATR) method in the 400–4000 cm^{-1} frequency range [25].

The thermal behavior of **I** was studied by simultaneous thermal analysis (STA) in an argon atmosphere,

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† Deceased.

while simultaneously recording thermogravimetric (TG), differential thermogravimetric (DTG), and differential scanning calorimetric (DSC) curves. The measurements were performed on a STA 449 F1 Jupiter instrument (NETZSCH) in aluminum crucibles covered by lids with holes to ensure a vapor pressure of 1 atm during thermal decomposition of samples. The samples were heated to 200°C at a heating rate of 10°C/min. The sample mass was 20 mg. The accuracy of temperature measurement was ±0.7°C, that for mass change was $\pm 1 \times 10^{-2}$ mg. For recording TG, DTG, and DSC curves, a correction file was used, as well as temperature and sensitivity calibrations for the specified temperature program and heating rate.

Synthesis of $[Co_2(Phen)_2(\mu\text{-}H_2O)(\mu\text{-}OOCMe)_2(OOCMe)_2]((CF_3)_2PzH)_4$ (I). $[Phen_2Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCMe)_2(OOCMe)_2]$ (0.09 g, 0.26 mmol) was added to a solution of $(CF_3)_2PzH$ (0.2 g, 1.04 mmol) in dichloromthane (10 mL). The resulting pink solution was stirred at room temperature for 0.5 h, hexane (5 mL) was added, and the mixture was kept at 5°C for 24 h. The needle pink crystals thus formed were isolated by decantation and dried in an argon flow at room temperature. The yield was 0.26 g (65%).

For $C_{52}H_{38}N_{12}O_9F_{24}Co_2$

Anal. calcd., %	C, 40.32	H, 2.47	N, 10.85
Found, %	C, 39.78	H, 2.58	N, 10.82

IR (ν, cm^{-1}): 3439 w, 3148 w, 2928 w, 2695 w, 1614 s, 1574 m, 1428 s, 1344 m, 1331 m, 1258 s, 1229 m, 1165 m, 1138 s, 1068 m, 1024 w, 971 m, 912 w, 867 w, 846 m, 824 w, 773 w, 755 w, 728 m, 661 m, 642 w, 617 w, 466 m, 421 w.

Synthesis of $[Co(Phen)_2(H_2O)(OOCMe)]((CF_3)_2Pz)$ (II) and $[Co(Phen)_2((CF_3)_2Pz)_2]$ (III). *Method I.* Complex **I** (0.2 g, 0.13 mmol), ground preliminarily to a powder, was heated in a furnace to 200°C and kept for 3 h. The solid residue was weighed and dissolved in dichloromthane (20 mL), hexane (5 mL) was added, and the mixture was kept at 5°C for 24 h. Pink (**II**) and orange (**III**) crystals were isolated from the solution by decantation, washed with hexane, and separated under a microscope. The yield of **II** was 0.015 g (18%) and the yield of **III** was 0.045 g (46%).

Method II. Complex **I** was dissolved in *ortho*-xylene (20 mL) and the solution was stirred for 3 h at 144°C. The resulting orange solution was concentrated to 10 mL and kept for 24 h at 5°C. The pink (**II**) and orange (**III**) crystals were isolated from the solution by decantation, washed with hexane, and separated under a microscope.

The yield of **II** was 0.032 g (36%).

For $C_{31}H_{22}N_6O_3F_6Co$

Anal. calcd., %	C, 53.23	H, 3.11	N, 12.01
Found, %	C, 52.18	H, 3.28	N, 12.52

IR (ν, cm^{-1}): 3429 w.br, 3059 w, 1626 w, 1580 w, 1517 m, 1426 m, 1344 w, 1255 s, 1204 w, 1146 m, 1107 s, 996 s, 867 w, 844 m, 797 w, 753 w, 727 s, 641 w, 470 w, 421 w.

The yield of **III** was 0.022 g (22%).

For $C_{34}H_{18}N_8F_{12}Co$

Anal. calcd., %	C, 49.47	H, 2.20	N, 13.57
Found, %	C, 50.12	H, 2.38	N, 12.82

IR (ν, cm^{-1}): 3421 m.br, 3058 w, 1625 w, 1565 m, 1516 m, 1425 s, 1404 m, 1337 w, 1253 s, 1204 w, 1146 m, 1105 s, 991 m, 850 m, 793 w, 727 m, 655 m, 642 w, 470 w, 423 w.

X-ray diffraction analysis of complexes **I**–**III** was carried out at 296 K on a Bruker Apex II DUO diffractometer (CCD detector, MoK_α, $\lambda = 0.71073$ Å, graphite monochromator). The structures were solved using the ShelXT program [26–30] and refined by the full-matrix least squares in the anisotropic approximation using the Olex2 program for non-hydrogen atoms. Crystallographic data and refinement parameters are given in Table 1. Selected bond lengths and bond angles for the complexes are summarized in Table 2.

The full sets of X-ray diffraction data for complexes **I**–**III** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2159355–2159357, respectively; deposit@ccdc.cam.uk).

RESULTS AND DISCUSSION

The reaction of the known complex $[Phen_2Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCMe)_2(OOCMe)_2]$ with 3,5-bis(trifluoromethyl)pyrazole ($(CF_3)_2PzH$) in dichloromthane at room temperature and at 1 : 2 reactant ratio gave pink single crystals of the unusual intermediate $[Phen_2Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCMe)_2(OOCMe)_2]((CF_3)_2PzH)_4$ (**I**) (65% yield), in which four pyrazole molecules were hydrogen-bonded to four oxygen atoms of the acetate anions (Fig. 1).

This coordination mode of pyrazole leads to a pronounced decrease in the non-bonding distance between metal atoms linked by a bridging water molecule (Co–O, 2.092(4), 2.128(5)Å) and two bridging acetate anions (2.007(4)–2.103(5)Å) to 3.4458(9) Å. The octahedral environment of cobalt(II) atoms is completed by two nitrogen atoms of coordinated phenanthroline (Co–N, 2.103(5)–2.121(6) Å) and the

Table 1. Crystallographic data and structure refinement details for **I–III**

Parameter	Value		
	I	**II**	**III**
Molecular formula	$C_{52}H_{38}N_{12}O_9F_{24}Co_2$	$C_{31}H_{22}N_6O_3F_6Co$	$C_{34}H_{18}N_8F_{12}Co$
M	1548.80	699.47	825.49
Temperature, K	296	296	150(2)
Color	Pink	Pink	Orange
System	Monoclinic	Triclinic	Triclinic
Space group	Pn	$P\bar{1}$	$P\bar{1}$
a, Å	19.751(6)	9.393(2)	9.7874(14)
b, Å	7.566(2)	10.939(3)	12.6286(18)
c, Å	21.497(6)	16.051(4)	16.664(2)
α, deg	90	72.421(7)	96.198(2)
β, deg	108.149(4)	76.483(8)	104.183(2)
γ, deg	90	80.234(7)	102.278(2)
V, Å^3	3052.6(15)	1519.9(7)	1923.2(5)
Z	2	2	2
d(calcd) (mg/m^3)	1.685	1.528	1.426
μ, mm^{-1}	0.682	0.645	0.539
F(000)	1552.0	710.0	826.0
Crystal size, mm	0.12 × 0.1 × 0.06	0.1 × 0.1 × 0.05	0.15 × 0.15 × 0.07
Data collection range θ, deg	4.896–56	4.77–58	5.164–55.998
Ranges of reflection indices	$-26 \le h \le 23$, $-9 \le k \le 9$, $-28 \le l \le 28$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-21 \le l \le 21$	$-12 \le h \le 12$, $-16 \le k \le 16$, $-22 \le l \le 22$
Number of measured reflections	19601	16444	19756
Number of unique reflections (R_{int})	12125 (0.1016)	7961 (0.0276)	9190 (0.0483)
GOOF	0.922	1.028	0.932
R ($I > 2\sigma(I)$)	$R_1 = 0.0629$, $wR_2 = 0.1102$	$R_1 = 0.0504$, $wR_2 = 0.1314$	$R_1 = 0.0536$, $wR_2 = 0.1128$
R (for all reflections)	$R_1 = 0.1824$, $wR_2 = 0.1508$	$R_1 = 0.0705$, $wR_2 = 0.1452$	$R_1 = 0.1221$, $wR_2 = 0.1397$
Electron density (max/min), e Å^{-3}	0.46/–0.54	1.12/–0.51	0.24/–0.27

Table 2. Selected bond lengths (Å) and bond angles (deg) in complexes **I**–**III**

Bond	*d*, Å	Bond	*d*, Å
I			
Co(1)–O(1)	2.121(16)	Co(2)–O(1)	2.075(16)
Co(1)–O(6)	2.096(14)	Co(2)–O(8)	2.169(13)
Co(1)–O(4)	2.0.69(14)	Co(2)–O(3)	2.077(12)
Co(1)–N(1)	2.101(18)	Co(2)–O(5)	2.038(12)
Co(1)–O(2)	2.033(13)	Co(2)–N(3)	2.108(16)
Co(1)–N(2)	2.183(16)	Co(2)–N(4)	2.092(17)
II			
Co(1)–O(1)	2.0861(17)	Co(1)–N(4)	2.167(2)
Co(1)–O(3)	2.0707(18)	Co(1)–N(5)	2.140(2)
Co(1)–N(3)	2.1475(19)	Co(1)–N(6)	2.138(2)
III			
Co(1)–N(3)	2.138(2)	Co(1)–N(6)	2.200(3)
Co(1)–N(8)	2.190(3)	Co(1)–N(5)	2.182(2)
Co(1)–N(1)	2.153(2)	Co(1)–N(7)	2.193(2)
Angle	ω, deg	Angle	ω, deg
I			
Co(2)O(1)Co(1)	110.4(2)		
II			
O(1)Co(1)N(3)	92.67(7)	O(3)Co(1)N(5)	174.15(7)
O(1)Co(1)N(4)	168.81(7)	O(3)Co(1)N(6)	96.41(7)
O(1)Co(1)N(5)	88.81(7)	N(3)Co(1)N(4)	77.47(8)
O(1)Co(1)N(6)	95.01(8)	N(5)Co(1)N(3)	97.95(7)
O(3)Co(1)O(1)	91.68(7)	N(5)Co(1)N(4)	87.34(7)
O(3)Co(1)N(3)	87.85(7)	N(6)Co(1)N(3)	171.09(8)
O(3)Co(1)N(4)	93.22(7)	N(6)Co(1)N(4)	94.44(8)
III			
N(3)Co(1)N(8)	171.24(10)	N(1)Co(1)N(8)	85.40(9)
N(3)Co(1)N(1)	101.57(9)	N(1)Co(1)N(6)	170.34(9)
N(3)Co(1)N(6)	86.55(9)	N(1)Co(1)N(5)	97.92(9)
N(3)Co(1)N(5)	94.06(9)	N(1)Co(1)N(7)	94.34(9)
N(3)Co(1)N(7)	98.04(9)	N(1)Co(1)N(8)	90.20(9)
N(8)Co(1)N(6)	87.05(9)	N(5)Co(1)N(6)	76.08(10)
N(8)Co(1)N(7)	75.94(9)	N(5)Co(1)N(7)	160.69(9)

oxygen atoms of the terminal acetate anions (Co–O, 2.103(7), 2.158(7) Å). The four coordinated pyrazole molecules form short hydrogen bonds with the oxygen atoms of the bridging and terminal acetate anions (N...O, 2.659–2.987 Å).

It may be expected that a minor heating of complex **I** would result in proton transfer to acetate anions, thus giving four molecules of acetic acid, which is relatively weak in comparison with $(CF_3)_2PzH$. Indeed, according to thermogravimetric data, decomposition starts at a temperature of approximately 80°C and is accompanied by a decrease in the complex mass by 34.5% (Fig. 2). This mass loss corresponds to the removal of two pyrazole molecules and two acetic acid molecules, which can be detected in the mass spectra of the gas phase upon thermolysis. The preparative heating of single crystals of the intermediate up to 200°C leads to decrease in the mass observed in the thermogravimetric measurements, and dissolution of the dry residue in a dichloromethane–hexane mixture followed by crystallization gives pink crystals of the complex $[Co(Phen)_2(OOCMe)(OH_2)]((CF_3)_2Pz)$ (**II**) (18% yield) (Fig. 3) and yellow-orange crystals of the pyrazolate complex $[Co(Phen)_2((CF_3)_2Pz)_2]$ (**III**) (46% yield) (Fig. 4).

It is noteworthy that complexes **II** and **III** are also formed upon refluxing of **I** in *o*-xylene in 36 and 22% yields, respectively.

Thus, thermal degradation of intermediate **I** is accompanied by disproportionation with phenanthroline transfer to the electron-deficient cobalt(II) atom. In complex **II**, one acetate anion is replaced by a pyrazolate anion, and hence, the cobalt atom is surrounded by two phenanthroline molecules, an acetate anion, and a water molecule ($Co–N_{Phen}$, 2.1380(19)–2.166(2); Co–O, 2.0867(17); $Co–O_w$, 2.0701(18); O(3)...N(1), 2.724 Å). The pyrazolate anion is hydrogen-bonded to oxygen of the cobalt-coordinated water molecule (NH...O, 2.7229(27) Å). Hydrogen bonds are also formed between the coordinated water molecule and the acetate oxygen atom (OH...O, 2.6341(29) Å).

In complex **III**, all acetate anions are replaced by pyrazolate anions, and cobalt occurs in an octahedral environment of six nitrogen atoms belonging to two pyrazolate anions and two phenanthroline molecules ($Co–N_{Phen}$, 2.184(3)–2.196(3); $Co–N_{Pz}$, 2.142(3), 2.156(3) Å).

Thus, the obtained complexes are the products of stepwise deprotonation of 3,5-bis(trifluoromethyl)pyrazole in the presence of $Phen_2Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCMe)_2(OOCMe)_2$. Under mild conditions, deprotonation does not take place, but intermediate **I** is formed; meanwhile, at high temperature, acetic acid

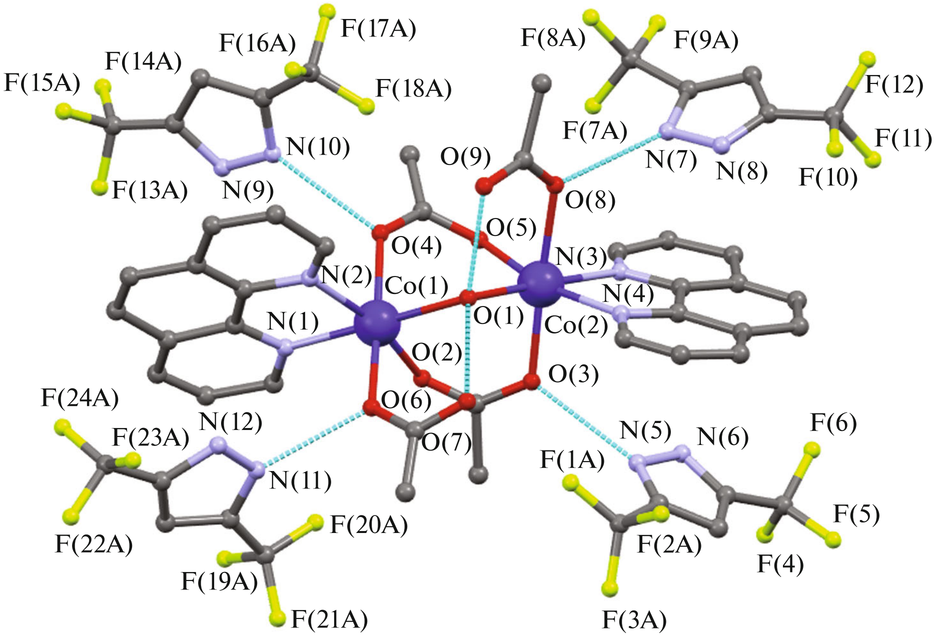

Fig. 1. Structure of complex **I**.

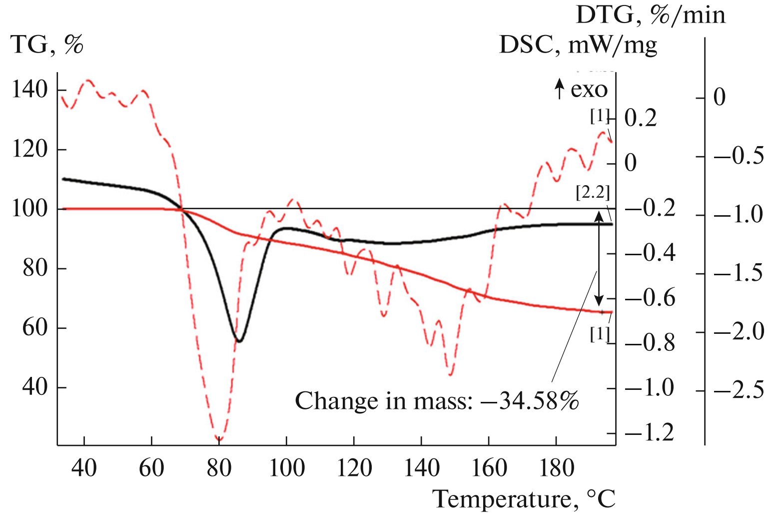

Fig. 2. TG, DTG, and DSC curves for complex **I**.

is removed to give pyrazolate acetate (**II**) and pyrazolate (**III**) complexes.

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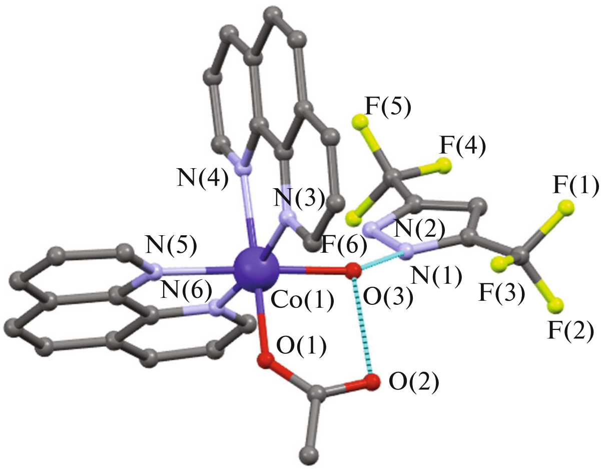

Fig. 3. Structure of complex **II**.

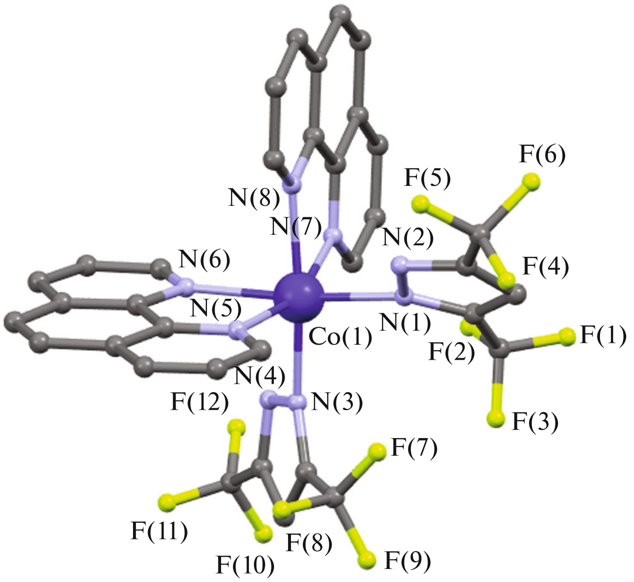

Fig. 4. Structure of complex **III**.

General and Inorganic Chemistry, Russian Academy of Sciences, in the field of fundamental research.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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