ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2010, Vol. 55, No. 9, pp. 1398–1401. © Pleiades Publishing, Ltd., 2010.
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COORDINATION COMPOUNDS

Synthesis and Structure of the Pyrazolate-Bridged Cobalt(II) Benzoate $Co_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCPh)_2$

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Received January 14, 2010

Abstract—The reaction between $Co(Hdmpz)_2(OOCPh)_2$ and cobalt acetate hydrate leads to the deprotonation of coordinated pyrazole and formation of pyrazolate-bridged $Co_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCPh)_2$ binuclear complex. The structure of the complex was determined by X-ray crystallography.

DOI: 10.1134/S003602361009010X

The composition and structure of the products of reactions between transition-metal carboxylates $M_2(\mu\text{-OOCR})_4L_2$ or $M_3(\mu\text{-OOCR})_6L_2$ (M = Zn, Cu, Ni, Co; R = Bu^t, Me, Ph; L = NEt_3, $OC(R')OHNEt_3$ (R' = Me, Ph)) and 3,5-dimethylpyrazole (Hdmpz), including the reactions that lead to the formation of pyrazolate-bridged complexes as a result of deprotonation, depend on the transition-metal nature, reaction conditions, and also on the donor ability of the R substituent in the carboxylate anion [1–8].

For example, the reaction between cobalt(II) pivalate $Co_3(\mu\text{-OOCBu}^t)_6(NEt_3)_2$ containing donor tert-butyl substituents in the carboxylate anion and Hdmpz at room temperature under mild conditions was shown to lead to deprotonation of pyrazole and formation of a pyrazolate-bridged dimer $Co_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCBu^t)_2$ [1, 2]. After substitution of less donor methyl substituents for tert-butyl in the initial carboxylate, the analogous reaction yields the trinuclear complex $Co_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$ [6, 7]. Lastly, the same reaction of $Co_3(\mu\text{-OOCPh})_6[OC(Ph)OHNEt_3]_2$ with the acceptor phenyl substituent occurs without deprotonation of pyrazole, and the monomer $Co(Hdmpz)_2(OOCPh)_2$ is formed [8].

In this work, we report on the synthesis of binuclear pyrazolate-bridged cobalt(II) benzoate structurally similar to $M_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCR)_2$ (M = Zn; R = Bu^t, Me, Ph; M = Co; R = Bu^t) complexes.

EXPERIMENTAL

All procedures relating to the synthesis and isolation of complexes were carried out in a pure argon atmosphere with the use of dry solvents.

IR spectra were recorded as KBr pellets on a Nexus-Nicolet spectrophotometer in the range of 400–4000 cm^{-1}.

Synthesis of $Co_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCPh)_2$ (1). To a solution of 0.1 g (0.2 mmol) of $Co(Hdmpz)_2(OOCPh)_2$ in 10 mL of *o*-xylene, cobalt acetate hydrate (0.05 g, 0.2 mmol) was added. The mixture was stirred at 140°C for 3 h. The resulting solution was separated from the precipitate by filtration and kept at +5°C for several days. The violet crystals formed were isolated from the mother liquor by decantation, washed with hexane, and dried in an argon flow. Yield, 0.018 g (12%).

For $Co_2C_{34}H_{40}N_8O_4$ anal. calcd (%): C, 54.97; H, 5.43; N, 15.09.

Found (%): C, 54.89; H, 4.97; N, 15.13.

IR (KBr, ν, cm^{-1}): 3700 w, 2924 w, 2852 w, 2368 w, 2336 m, 1664 w, 1604 m, 1552 s, 1524 m, 1448 w, 1388 s, 1296 m, 1184 w, 1048 s, 1016 w, 968 w, 832 w, 792 w, 720 s, 676 m, 620 w, 448 m, 352 w, 392 w, 320 w.

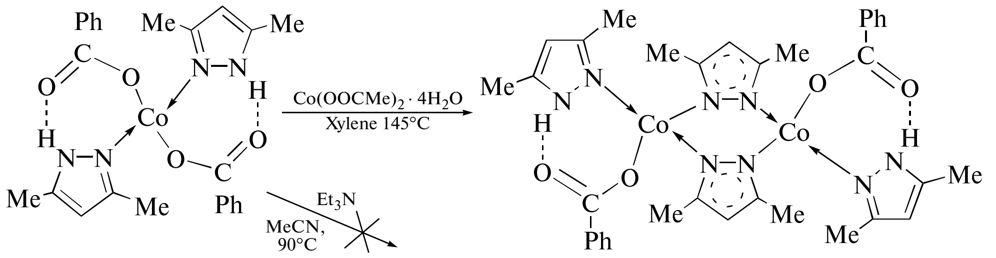
X-ray diffraction studies were performed by a standard procedure on an automated Bruker SMART Apex II diffractometer equipped with a CCD detector (λMo, graphite monochromator, ω scan). The structures were solved with the use of SHELXTL PLUS (PC version) and refined with SHELXTL-97 [9, 10]. Crystal data obtained for **1** ($C_{34}H_{40}Co_2N_8O_4$, FW = 742.60) were as follows: space group $P2(1)/c$, a = 8.198(4) Å, b = 16.118(9) Å, c = 14.108(7) Å, β = 105.174(19)°, V = 1799.2(15) $Å^3$ (at 296(2) K), Z = 2, a total of 14468 reflections, 3532 independent reflections with $F^2 > 2\sigma(I)$, ρ_{calcd} = 1.371 g/cm^3, μ = 0.970 cm^{-1}, R_1 = 0.0798, wR_2 = 0.1364.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic parameters ($Å^2 \times 10^3$) for complex **1**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
Co(1)	840(2)	1027(1)	361(1)	60(1)	C(6)	4610(14)	851(6)	1333(7)	78(3)
N(1)	116(8)	222(4)	1233(6)	60(2)	C(7)	4515(14)	–72(6)	1266(9)	122(4)
N(2)	601(8)	549(4)	–928(6)	60(2)	C(8)	5943(14)	1353(8)	1779(9)	101(4)
N(3)	3248(9)	1325(4)	972(5)	65(2)	C(9)	5400(14)	2155(8)	1701(8)	85(3)
N(4)	3768(10)	2112(5)	1225(5)	71(2)	C(10)	6222(13)	2981(7)	2046(7)	111(4)
O(1)	–581(7)	1997(4)	208(4)	75(2)	C(11)	–292(14)	2766(6)	165(7)	67(3)
O(2)	1121(8)	3104(4)	410(5)	91(2)	C(12)	–1819(12)	3309(5)	–197(6)	57(2)
C(1)	186(11)	318(6)	2179(8)	62(2)	C(13)	–1630(13)	4139(5)	–336(7)	74(3)
C(2)	840(12)	1109(6)	2697(7)	92(3)	C(14)	–3034(16)	4638(6)	–667(7)	87(3)
C(3)	1696(14)	1742(5)	–1679(7)	103(4)	C(15)	–4608(16)	4310(7)	–865(8)	100(4)
C(4)	871(12)	912(6)	–1739(8)	68(3)	C(16)	–4814(13)	3487(7)	–710(8)	91(3)
C(5)	405(12)	379(7)	–2516(7)	75(3)	C(17)	–3407(14)	2980(6)	–384(7)	80(3)

RESULTS AND DISCUSSION

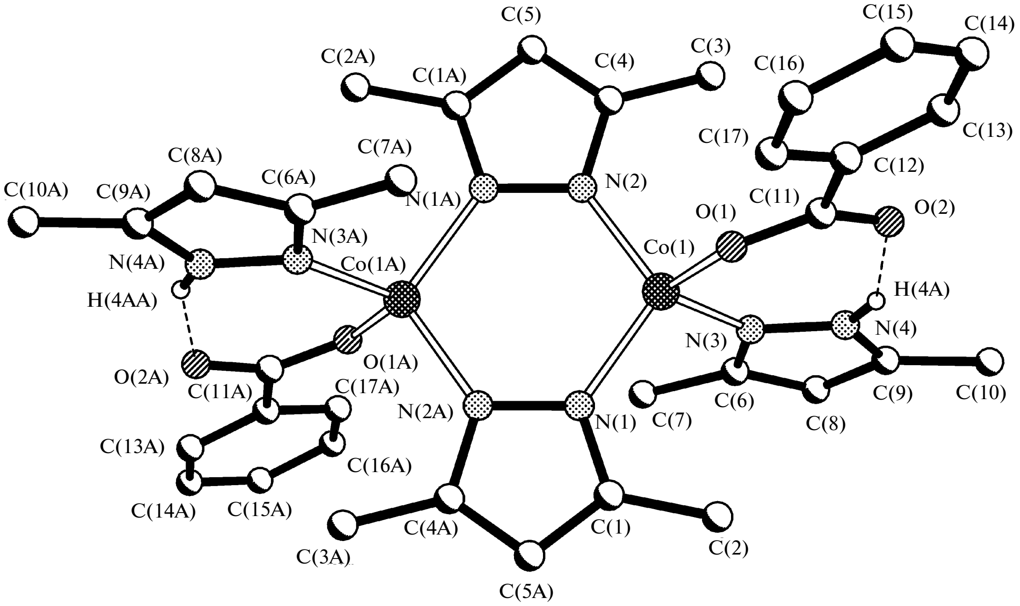
The reaction of cobalt acetate hydrate with mononuclear pyrazole benzoate Co(Hdmpz)$_2$(OOCPh)$_2$ in boiling *o*-xylene was found to result in deprotonation of coordinated pyrazole and formation of a pyrazolate-bridged dimer Co$_2$(μ-dmpz)$_2$(Hdmpz)$_2$(OOCPh)$_2$ (**1**). Yield, 52%.



Noteworthy, cobalt acetate hydrate acts as a deprotonating agent in this case, whereas the reaction does not occur in the presence of a strong base (triethylamine) in boiling acetonitrile [8].

According to the X-ray diffraction data, two cobalt atoms in **1** (figure; Tables 1, 2), which are at a nonbonding Co···Co distance of 3.6283(9) Å, are linked only by nitrogen atoms of two bridging pyrazolate ligands (Co(1)–N(1), 1.983(8) Å; Co(1)–N(2), 1.938(7) Å) formed as a result of deprotonation of 3,5-dimethylpyrazole. Each metal atom is bound to a nitrogen atom of the terminal pyrazole molecule (Co–N, 1.995(7) Å) and oxygen atom of the terminal benzoate anion (Co–O, 1.928(6) Å). As a result, the binuclear complex is formed, where each cobalt(II) atom is electron deficient (15 electrons) and has a distorted tetrahedral environment.

A comparison of the geometry of **1** with the geometry of the binuclear pyrazolate-bridged pivalate Co$_2$(μ-dmpz)$_2$(Hdmpz)$_2$(OOCBu^t)$_2$ (**2**) has shown that replacement of the acceptor phenyl substituent by the donor tert-butyl that virtually does not influence the



Structure of complex **I**.

metal–metal distance, however the distances metal–nitrogen in **1** become nonequivalent and shorter than the equalized distances in **2** (Co–N, 1.999(2) and 1.996(1) Å). The bond lengths of the terminal pyrazole molecules and benzoate anions are somewhat lengthened (in **2**, Co–N is 2.015(2) Å and Co–O is 1.942(1) Å).

Table 2. Selected bond lengths (*d*) and bond angles (ω) for complex **1**

Bond	*d*, Å	Bond	*d*, Å
Co(1)–O(1)	1.928(6)	Co(1)–N(2)	1.938(7)
Co(1)–N(1)	1.983(8)	Co(1)–N(3)	1.995(7)
N(1)–C(1)	1.329(10)	N(1)–N(2)#1	1.394(8)
N(2)–C(4)	1.354(10)	N(2)–N(1)#1	1.393(8)
N(3)–C(6)	1.339(11)	N(3)–N(4)	1.355(8)
N(4)–C(9)	1.333(10)	O(1)–C(11)	1.266(10)
O(2)–C(11)	1.244(10)		
Angle	ω, deg	Angle	ω,deg
O(1)Co(1)N(2)	107.9(3)	O(1)Co(1)N(1)	109.3(3)
N(2)Co(1)N(1)	110.4(3)	O(1)Co(1)N(3)	110.7(3)
N(2)Co(1)N(3)	110.3(3)	N(1)Co(1)N(3)	108.2(3)
C(1)N(1)N(2)#1	108.5(7)	C(1)N(1)Co(1)	127.3(6)
N(2)#1N(1)Co(1)	124.2(6)	C(4)N(2)Co(1)	128.5(6)
N(1)#1N(2)Co(1)	125.1(6)	C(6)N(3)Co(1)	131.2(7)
N(4)N(3)Co(1)	123.2(6)	C(11)O(1)Co(1)	133.2(7)

Symmetry code: #1 –*x*, –*y*, –*z*.

As distinct from the electron-deficient cobalt(II) atom, in structurally similar pyrazolate-bridged complexes of tetrahedral electron-saturated zinc (18 electrons) $Zn_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCR)_2$ (R = Bu^t, Me, Ph), no definite dependence on the nature of the substituent of the carboxylate anion is observed, though the metal–metal distances are considerably shortened compared with those in **1** and **2**:

R source	M···M, Å	M–μ-N, Å	$M–N_{Hdmpz}$, Å	$M–O_{OOCR}$, Å
Bu^t [2]	3.5821(6)	1.981(2)–1.988(2)	2.030(2)	1.940(1)
Me [7]	3.593(1)	1.976(7)–1.985(6)	2.023(6)	1.949(5)
Ph [7]	3.5827(8)	1.960(4)–1.971(3)	2.008(3)	1.944(2)

Therefore, our studies have shown that cobalt acetate hydrate can be a deprotonating agent for the Hdmpz molecules coordinated in the cobalt pyrazole benzoate, which leads to formation of pyrazolate-bridged binuclear cobalt benzoate.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 08-03-01063, 08-03-90455), the Council for Grants of the President of the Russian Federation (the Program for Support of Leading Scientific Schools of Russia; grant no. NSh-1764.2003.03), and the Presidium and the Division of Chemistry and Materials Science of the Russian Academy of Sciences (programs “Theoretical and Experimental Investigations of the Nature of the Chemical Bond and the Mechanisms of Important

Chemical Reactions and Processes" and "Targeted Synthesis of Inorganic Compounds and Design of Functional Materials").

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