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Dedicated to the memory of Academician Il'ya Iosifovich Moiseev

Ligand Exchange and Pyrazole Deprotonation in the Reaction of Trinuclear Palladium(II) Acetate with Binuclear Zinc Pivalate Pyrazole Pyrazolate

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Abstract—The reaction of Pd$_3$(OOCMe)$_6$ with Zn$_2$(μ-Dmpz)$_2$(HDmpz)$_2$(OOC^{t}Bu)$_2$ (HDmpz is 3,5-dimethylpyrazole) in dichloromethane at room temperature induces ligand exchange, accompanied by deprotonation of zinc-coordinated pyrazole to give heterocarboxylate 1D coordination polymer [Zn$_2$(μ-OOCMe)(μ-OOC^{t}Bu)$_3$]$_n$ (**I**) and 1,4-dioxane-solvated trinuclear complex Pd$_3$(μ-Dmpz)$_6$·C$_4$H$_8$O$_2$ (**II**). Compounds **I** and **II** were studied by chemical analysis, IR spectroscopy, and X-ray diffraction (CIF files CCDC no. 2076508 (**I**) and no. 2076509 (**II**) respectively).

Keywords: trinuclear palladium(II) pyrazolate, pyrazolate, palladium(II), zinc, pivalate acetate coordination polymer, ligand exchange, pyrazole deprotonation, 3,5-dimethylpyrazole, synthesis, X-ray diffraction

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INTRODUCTION

Ligand exchange reactions are rather traditional for coordination chemistry. In the first approximation, the reaction route and the composition of the final products are dictated by the Pearson's hard–soft acid–base theory [1, 2].

At the same time, ligand exchange reactions may occur via proton transfer giving new types of anions and accompanied by the release of a more stable base with a proton into the reaction solution. In particular, pyrazole and its analogues can bind to metals via the pyridine nitrogen atom giving an anion upon deprotonation of the pyrrole NH group. The formation of the anion results in a bridging position of the diatomic three-electron-donating pyrazolate anion, thus forming bi- and polynuclear complexes and clusters. These compounds have been obtained for virtually all 3*d* metals, namely, binuclear M$_2$(μ-Dmpz)$_2$(HDmpz)$_2$(OOCR)$_2$ (M = Zn, Cu, Co) [3] and polynuclear metallacycles [Zn$_4$(μ-Dmpz)$_6$(μ-OH)$_2$]$_2$ and [Zn$_4$(μ-Dmpz)$_6$(μ-OH)$_2$]$_4$ [4]; Cu$_8$(μ-Dmpz)$_8$(μ-OH)$_8$ [5], {Cu(μ-OH)(μ-Pz)}$_n$ (n = 6, 8, 9, 12, 14) [6, 7], {Cu(μ-OH)(μ-Pz)}$_n$ (n = 28, 31) [8]; (Bu$_4$N)$_2$[Ni$_8$(μ$_4$-OH)$_6$(μ-Pz)$_{12}$](CH$_8$CN)$_4$ [9]; (Bu$_4$N)$_2$-[Co$_3^{\text{III}}$(μ$_3$-O)(μ-4-NO$_2$–Pz)$_6$(NO$_2$)$_3$] [10], Co$_4^{\text{II}}$(μ$_4$-O)(μ-Dmpz)$_6$ [11], (Bu$_4$N)$_2$[Co$^{\text{III}}$(μ-OH)(μ-4-NO$_2$–Pz)(μ-Dmpz)]$_{10}$(NO$_2$)$_2$ [10]; (Bu$_4$N)$_2$[Co$^{\text{III}}$(μ-OH)(μ-4-NO$_2$–Pz)(μ-Dmpz)]$_{12}$(NO$_2$)$_2$ [10]; cubane Fe$_4$O$_4$-based iron(III) complexes Fe$_8$(μ$_4$-O)$_4$(μ-Pz)$_{12}$Cl$_4$ [12] and Fe$_8$(μ$_4$-O)$_4$(μ-Pz)$_{12}$X$_4$ (Pz = 4-Cl–Pz, 4-Me–Pz; X = Br) [13]; and manganese(III) complexes based on the cubane motif: Mn$_8$(μ$_3$-O)$_4$(μ-Pz)$_8$(μ-OMe)$_4$(OMe)$_4$ [14]. It is also noteworthy that there are several examples in which the pyrazolate anion forms Pt(II)-based heterometallic clusters: Pt$_2$Ag$_4$(μ-Cl)$_2$(μ-Ph$_2$Pz)$_6$, Pt$_2$Ag$_2$Cl$_2$(μ-Ph$_2$Pz)$_4$(Ph$_2$PzH)$_2$, Pt$_2$Cu$_2$Cl$_2$(μ-Ph$_2$Pz)$_4$(Ph$_2$PzH)$_2$, [Pt$_2$Ag$_4$(μ-Cl)(μ-Dmpz)(μ-Ph$_2$Pz)$_6$, Pt$_2$Ag$_4$(μ-Dmpz)$_2$-(μ-Ph$_2$Pz)$_6$ [15], and Pt$_2$M$_4$(μ-Dmpz)$_8$ (M = Ag, Cu) [16].

This communication reports the structure of the products formed in the reaction between palladium acetate and binuclear zinc pyrazolate pyrazole pivalate, accompanied by ligand exchange and deprotonation of pyrazole.

EXPERIMENTAL

The initial complexes were prepared by reported procedures [17, 18].

Synthesis of {[Zn$_2$(μ-OOC^{t}Bu)$_3$](μ-OOCMe)}$_n$ (I) and Pd$_3$(μ-Dmpz)$_6$·C$_4$H$_8$O$_2$ (C$_4$H$_8$O$_2$ = 1,4-dioxane) (II).

A colorless solution of $Zn_2(\mu\text{-Dmpz})_2\text{-}(HDmpz)_2\text{-}(OOC^tBu)_2$ (0.64 g, 0.089 mm) in dichloromethane (5 mL) was slowly added dropwise to an orange solution of palladium acetate (0.2 g, 0.089 mm) in dichloromethane (5 mL). The resulting mixture was magnetically stirred at room temperature for 1 h. The color of the solution gradually changed from orange to yellow. Hexane (3 mL) and one drop of each of benzene and 1,4-dioxane were added to the resulting solution. The solution was concentrated to 5 mL with heating in a water jet pump vacuum and kept in a refrigerator at 5°C for 2 days. The colorless and straw-colored crystals thus formed were separated from the mother liquor by decanting, washed with cold benzene (2 × 5 mL) and hexane (5 mL), and dried in an argon flow.

Large colorless (**I**) and straw-colored (**II**) crystals were physically separated from the mixture under a microscope. The yield was 0.12 g (28%).

For $C_{17}H_{30}O_8Zn_2$ (**I**)

Anal. calcd., %	C, 41.40	H, 6.13
Found, %	C, 40.75	H, 6.21

IR (ν, cm^{-1}): 3434 w, 2964 m, 2920 m, 1629 m, 1582 s, 1562 vs, 1557 vs, 1485 s, 1428 s, 1301 w, 1228 m, 1049 w, 897 w, 789 w, 764 w, 726 w, 648 w, 606 w, 574 w, 518 w, 476 w. The yield was 0.09 g (32%).

For $C_{34}H_{44}N_{12}OPd_3$ (**II**)

Anal. calcd., %	C, 42.41	H, 4.64	N, 17.58
Found, %	C, 42.24	H, 4.55	N, 17.44

IR (ν, cm^{-1}): 2996 m, 2820 m, 1992 br.w, 1682 m, 1570 s, 1552 s, 1483 m, 1444 m, 1308 w, 1228 m, 860 m.

IR spectra were measured on a Perkin-Elmer Spectrum 65 FTIR spectrophotometer in the attenuated total reflectance (ATR) mode in the frequency range of 400–4000 cm^{-1}.

X-ray diffraction study of **I** and **II** was carried out by the standard procedure on a Bruker SMART Apex II automated diffractometer equipped with a CCD array detector (MoK_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scan mode). The structures were refined using the SHELXTL PLUS program package (PC version) [19–22]. The crystallographic data and structure refinement details for **I** and **II** are given in Table 1 and the bond lengths and bond angles are summarized in Table 2.

The structural data for the complexes are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2076508 (**I**) and no. 2076509 (**II**); http://www.ccdc.cam.ac.uk/).

RESULTS AND DISCUSSION

It was shown that palladium(II) acetate reacts with $Zn_2(\mu\text{-Dmpz})_2(HDmpz)_2(OOC^tBu)_2$ in dichloromethane at room temperature to give the following complexes: colorless 1D coordination polymer (CP) $\{[Zn_2(\mu\text{-}OOC^tBu)_3](\mu\text{-OOCMe})]\}_n$ (**I**, 28% yield) and trinuclear pyrazolate-bridged complex $Pd_3(\mu\text{-Dmpz})_6 \cdot C_4H_8O_2$ (**II**, 32% yield). The results are in fairly good agreement with Pearson's hard–soft acid–base theory: the soft Pd^{2+} cation binds to the soft $Dmpz^-$ anion, while the intermediate Zn^{2+} ion binds to hard $OOCR^-$ [2]. Note, however, that the reaction is accompanied by deprotonation of pyrazole; the hydrogen atom binds to the carboxylate anion, which gives rise to an equilibrium in the solution, because of similar acidity characteristics of the resulting acids (R = Me, ^{t}Bu; pK_a = 4.76, 5.05 at 25°C in H_2O, respectively [23]).

According to X-ray diffraction data, in the CP of complex **I** (Tables 1, 2), the binuclear $Zn_2(\mu\text{-}OOC^tBu)_3$ moieties (Zn...Zn 3.211(1) Å) containing three pivalate bridges (Zn–O, 1.913(9)–1.952(9) Å) are linked into a polymer via acetate bridges (Z–O, 1.941(8)–1.942(8) Å), with the metal atom being located in a distorted tetrahedral environment. Note that the closely spaced dimers in the polymer are arranged at an angle of 85.9°, each being parallel to the next nearest one (Figs. 1, 2). The distance between the metal atoms of the adjacent dimers in the 1D chain is 4.455 Å, while the distance between the closely spaced metal atoms of the neighboring layers is 8.774 Å.

It is noteworthy that the 1D CPs containing $Zn_2(\mu\text{-OOCR})_3$ moieties linked by the $OOCR^-$ bridges have already been known. However, unlike those in **I**, they are all formed by identical carboxylate anions. For example, CPs with R = Ph [24], *iso*-Pr [25], Mes [26], $CH_2{}^tBu$ [25], CF_3 [27], and 2-Cl–Ph [28] were obtained.

The trinuclear pyrazolate-bridged complex $Pd_3(\mu\text{-Dmpz})_6$ (**II**) is formed as the second reaction product. According to X-ray diffraction data, the three metal atoms in **II** (Tables 1, 2) are located at the Pd(1)...Pd(2) distances of 2.9766(6) and Pd(2)...Pd(2) distances of 3.0059(10) Å and are connected in pairs by two Dmpz bridges (Pd(1)–N(1), 2.026(4); Pd(1)–N(3), 2.010(4); Pd(2)–N(2), 1.970(4); Pd(2)–N(4), 1.962(4); Pd(2)–N(5), 1.957(4); Pd(2)–N(6), 1.960(4) Å). Finally, each metal atom has a square planar environment composed of four nitrogen atoms that belong to the bridging anions (Fig. 3). The geometry of the obtained pyrazolate **II** differs little from those of known trinuclear Pd_3 complexes with pyrazolate bridges containing different substituents R in the anions. Using $PdCl_2(CH_3CN)_2$, HPz, 4-MePz, $Pd(HPz)_4Cl_2$, and triethylamine in acetonitrile, the following complexes were obtained and structurally

Table 1. Crystallographic parameters and structure refinement details for **I** and **II**

Parameter	Value	
	I	**II**
Molecular formula	$C_{17}H_{30}O_8Zn_2$	$C_{34}H_{44}N_{12}OPd_3$
M	493.15	956.01
Color	Colorless	Straw-colored
T, K	150(2)	150(2)
System	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Ibam*
a, Å	9.644(6)	24.7898(15)
b, Å	12.911(7)	15.6505(10)
c, Å	19.776(11)	19.320(2)
α, deg	90	90
β, deg	98.511(9)	90
γ, deg	90	90
V, Å^3	2435(2)	7495.7(11)
Z	4	8
ρ(calcd.), mg/m^3	1.345	1.694
μ, mm^{-1}	2.003	1.469
F(000)	1024	3824
Crystal size, mm	0.20 × 0.18 × 0.16	0.26 × 0.24 × 0.22
θ Range of scanning, deg	2.08–26.00	2.61–28.00
Ranges of reflection indices	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-24 \leq l \leq 24$	$-32 \leq h \leq 32$, $-20 \leq k \leq 19$, $-25 \leq l \leq 25$
Number of reflections	18069	33616
Number of unique reflections (R_{int})	4758 (0.1590)	4634 (0.0366)
GOOF	1.233	1.095
R ($I > 2\sigma(I)$)	$R_1 = 0.0997$, $wR_2 = 0.2230$	$R_1 = 0.0494$, $wR_2 = 0.1520$
R (for all reflections)	$R_1 = 0.2233$, $wR_2 = 0.2697$	$R_1 = 0.0590$, $wR_2 = 0.1688$
Electron density (max/min), e Å^{-3}	1.521/–1.086	1.614/–2.054

characterized: $Pd_3(\mu\text{-Pz})_6$ (Pd...Pd, 3.0270(4), 3.0607(4), 3.0460(3) Å; Pd–N, 1.985(3)–2.020(3) Å); $Pd_3(\mu\text{-Pz})_6 \cdot 2MeCN$ (Pd...Pd, 3.0293(4), 3.0559(3), 3.0560(3) Å; Pd–N, 2.011(3)–2.024(3) Å); and $Pd_3(\mu\text{-4-MePz})_6 \cdot 2MeCN$ (in two independent molecules) (Pd...Pd, 3.0486(4)–3.0727(4); Pd–N, 1.999(3)–2.029(3) Å) [29]. It was shown that the reaction of *cis*-$PdCl_2(3\text{-Ph–PzH})_2$ with a stoichiometric amount of Et_3N gives the trinuclear complex $Pd_3(\mu\text{-3-Ph–Pz})_4(3\text{-Ph–Pz–H})_2Cl_2$ (Pd...Pd, 3.95 Å) in the first stage. The subsequent addition of a base gives the triangle $Pd_3(\mu\text{-3-Ph–Pz})_6$ (Pd...Pd, 2.997(1), 3.079(1), 3.087(1) Å; Pd–N, 1.963(9)–2.027(8) Å) [30]. In the case of complex **II**, due to the presence of two electron-donating methyl groups, i.e., for the Dmpz$^-$ base, which is the strongest among the considered compounds, the Pd...Pd and Pd–N distances are markedly shortened.

According to the proposal of Raphael G. Raptis [30], comparison of the chemical behaviors and geometric details of three-electron-donating diatomic pyrazolate anions and triatomic carboxylate anions in similar polynuclear complexes and clusters showed for $Pd_3(\mu\text{-OOCR})_6$: R = Me (Pd...Pd, 3.105(1)–3.203(1) Å; Pd–O, 1.973(9)–2.014(9) Å [31]; R = Et (Pd...Pd, 3.135(1)–3.191(1) Å; Pd–O$_{\text{mean}}$, 1.993(9) Å) [32]; R = ^{t}Bu (Pd...Pd, 3.131(1)–3.132(1) Å; Pd–O$_{\text{mean}}$, 1.980(8) Å) [32–34]; R = CF_3 (Pd...Pd, 3.244(1)–3.266(1) Å; Pd–O, 1.980(8) Å), and R = 2,4,6-$C_6H_2(CH_3)_3$ (Pd...Pd, 3.131(1)–3.132(1) Å; Pd–

Table 2. Selected bond lengths (Å) and bond angles (deg.) in complex **I***

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(2)–O(1)	1.930(9)	Zn(2)–O(3)	1.930(8)
Zn(2)–O(7)	1.941(8)	Zn(2)–O(5)	1.952(9)
Zn(1)–O(6)	1.913(9)	Zn(1)–O(2)	1.920(8)
Zn(1)–O(4)	1.927(8)	Zn(1)–O(8)$^{\#1}$	1.942(8)
O(8)–Zn(1)$^{\#2}$	1.942(8)		
		II	
Pd(1)–N(3)	2.010(4)	Pd(1)–N(3)$^{\#1}$	2.010(4)
Pd(1)–N(1)$^{\#1}$	2.026(4)	Pd(1)–N(1)	2.026(4)
Pd(1)–Pd(2)$^{\#1}$	2.9766(6)	Pd(1)–Pd(2)	2.9766(6)
Pd(2)–N(5)	1.957(4)	Pd(2)–N(6)	1.960(4)
Pd(2)–N(4)	1.962(4)	Pd(2)–N(2)	1.970(4)
Pd(2)–Pd(2)$^{\#1}$	3.0059(10)	N(1)–N(2)	1.348(5)
N(3)–N(4)	1.373(5)	N(5)–N(5)$^{\#1}$	1.342(10)
N(6)–N(6)$^{\#1}$	1.369(10)		
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Zn(2)O(3)	121.4(4)	O(1)Zn(2)O(7)	109.9(4)
O(3)Zn(2)O(7)	106.1(4)	O(1)Zn(2)O(5)	106.4(4)
O(3)Zn(2)O(5)	107.0(4)	O(7)Zn(2)O(5)	104.9(4)
O(6)Zn(1)O(2)	114.3(4)	O(6)Zn(1)O(4)	115.6(4)
O(2)Zn(1)O(4)	113.5(4)	O(6)Zn(1)O(8)$^{\#1}$	102.6(3)
O(2)Zn(1)O(8)$^{\#1}$	105.5(4)	O(4)Zn(1)O(8)$^{\#1}$	103.3(4)
C(1)O(1)Zn(2)	137.5(9)	C(1)O(2)Zn(1)	129.3(9)
C(6)O(3)Zn(2)	136.7(9)	C(6)O(4)Zn(1)	126.6(8)
C(11)O(5)Zn(2)	132.3(11)	C(11)O(6)Zn(1)	136.6(11)
C(16)O(7)Zn(2)	109.8(7)	C(16)O(8)Zn(1)$^{\#2}$	132.0(8)
		II	
N(3)Pd(1)N(3)$^{\#1}$	93.0(2)	N(3)Pd(1)N(1)$^{\#1}$	172.99(15)
N(3)$^{\#1}$Pd(1)N(1)$^{\#1}$	83.97(15)	N(3)Pd(1)N(1)	83.97(15)
N(3)$^{\#1}$Pd(1)N(1)	172.98(15)	N(1)$^{\#1}$Pd(1)N(1)	98.3(2)
N(3)Pd(1)Pd(2)$^{\#1}$	107.57(11)	N(3)$^{\#1}$Pd(1)Pd(2)$^{\#1}$	64.49(11)
N(1)$^{\#1}$Pd(1)Pd(2)$^{\#1}$	65.41(11)	N(1)Pd(1)Pd(2)$^{\#1}$	110.36(11)
N(3)Pd(1)Pd(2)	64.49(11)	N(3)$^{\#1}$Pd(1)Pd(2)	107.57(11)
N(1)$^{\#1}$Pd(1)Pd(2)	110.36(11)	N(1)Pd(1)Pd(2)	65.41(11)
Pd(2)$^{\#1}$Pd(1)Pd(2)	60.65(2)	N(5)Pd(2)N(6)	84.66(18)
N(5)-Pd(2)N(4)	96.32(17)	N(6)Pd(2)N(4)	170.53(18)
N(5)Pd(2)N(2)	178.22(18)	N(6)Pd(2)N(2)	94.37(17)
N(4)Pd(2)N(2)	84.39(16)	N(5)Pd(2)Pd(1)	112.60(14)
N(6)Pd(2)Pd(1)	103.20(13)	N(4)Pd(2)Pd(1)	67.70(11)
N(2)Pd(2)Pd(1)	66.14(11)	N(5)Pd(2)Pd(2)$^{\#1}$	64.84(14)
N(6)Pd(2)Pd(2)$^{\#1}$	65.33(14)	N(4)Pd(2)Pd(2)$^{\#1}$	106.54(11)
N(2)Pd(2)Pd(2)$^{\#1}$	113.39(12)	Pd(1)Pd(2)Pd(2)$^{\#1}$	59.673(10)

* Symmetrical codes used to generate equivalent atoms: $^{\#1}$ $-x + 1/2$, $y + 1/2$, $-z + 1/2$; $^{\#2}$ $-x + 1/2$, $y - 1/2$, $-z + 1/2$ (**I**); $^{\#1}$ x, y, $-z + 1$ (**II**).

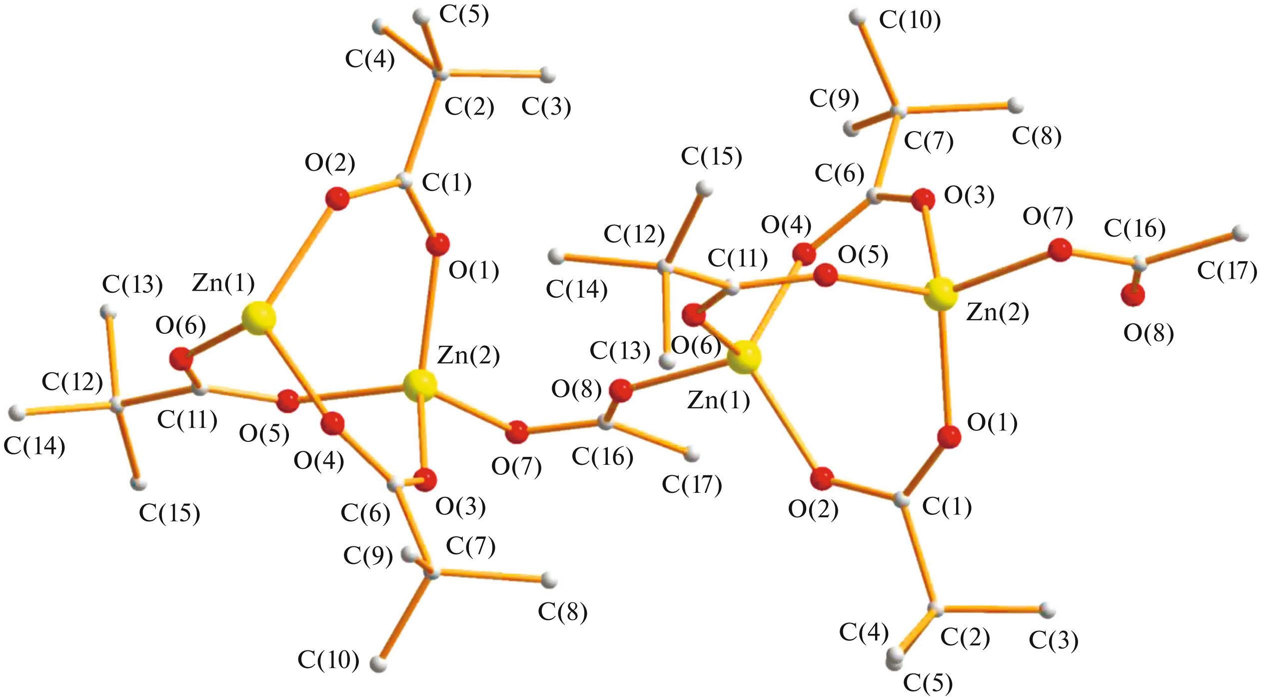


Fig. 1. Structure of complex **I**.

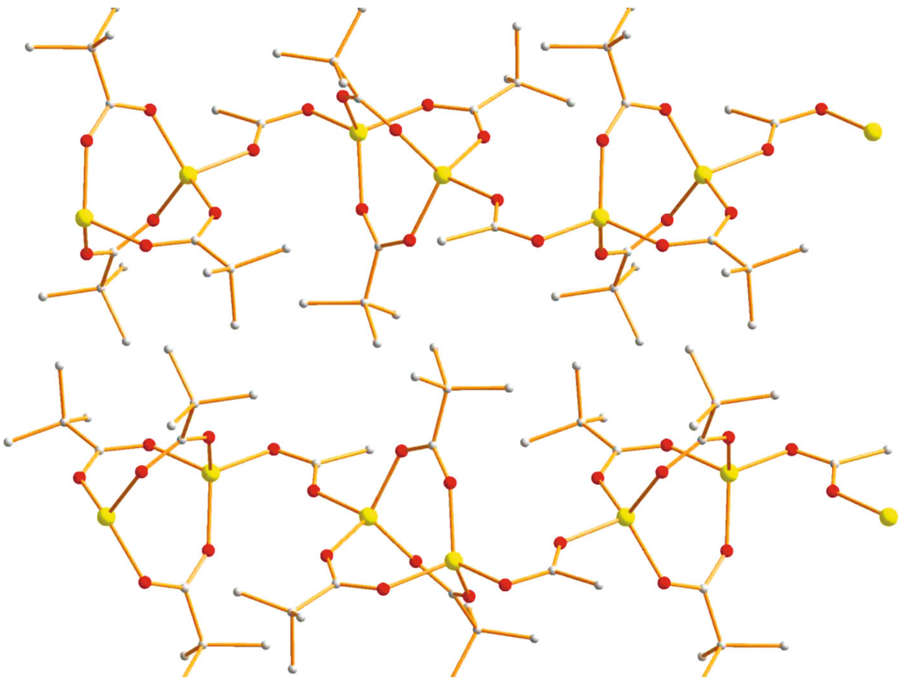


Fig. 2. Fragment of packing of 1D polymer **I** in the crystal.

O_{mean}, 1.980(8) Å) [32]; R = CH_2Cl (Pd...Pd, 3.2036(9), 3.1588(9), 3.2311(9) Å; Pd–O, 1.987(6)–2.015(6) Å) [34]; R = *cyclo*-C_6H_{11} (Pd...Pd, 3.1350(3), 3.2166(4), 3.2166(4) Å; Pd–O, 1.9809(19)–1.987(2) Å) [34].

Thus, as in pyrazolates, the trend of dependence of Pd...Pd and Pd–O bond lengths on the electronic nature of the substituent R in the carboxylate anion is also retained for palladium(II) carboxylates. The Pd...Pd bond lengths formed by triatomic bridges

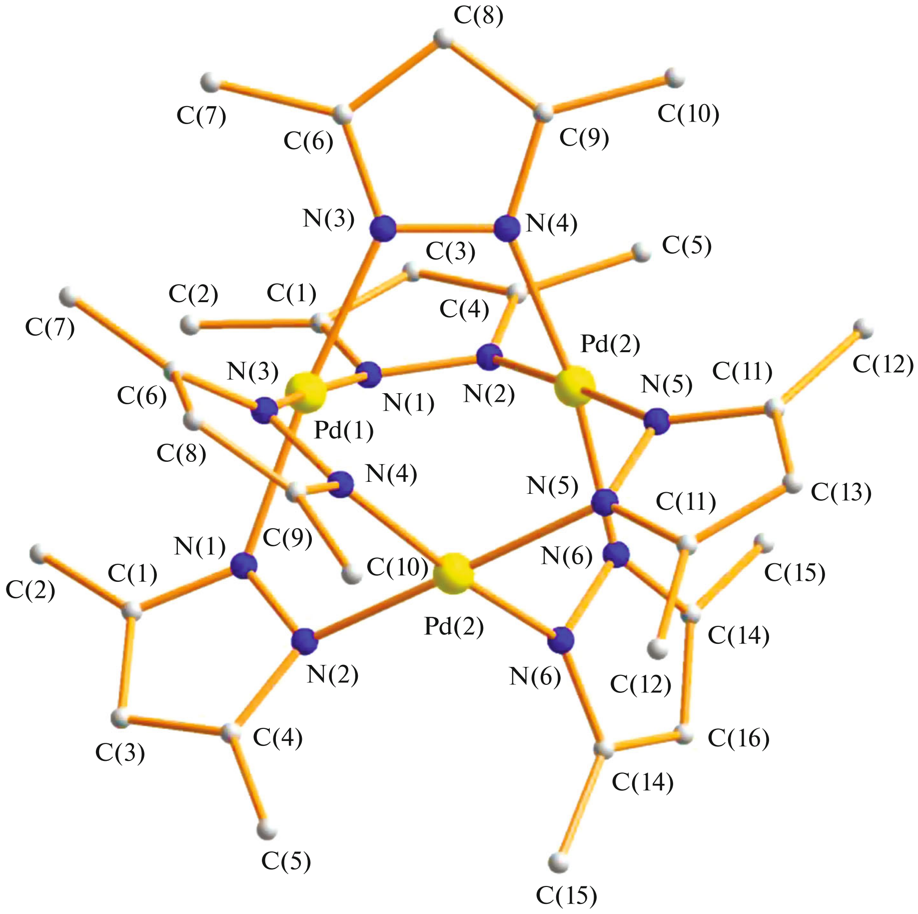
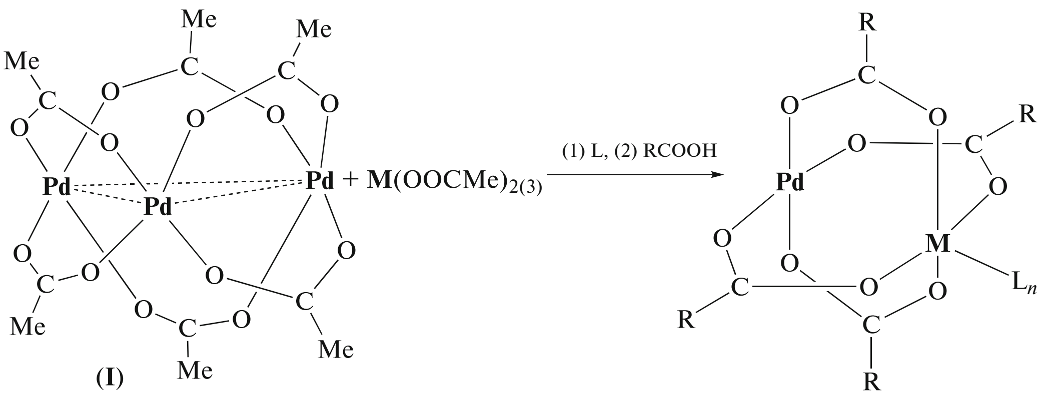


Fig. 3. Structure of complex **II**.

are, on average, somewhat longer in carboxylates than in pyrazolates, while the Pd–O bond lengths are either equal or are somewhat shorter in carboxylates.

It is noteworthy that previously, reactions of trinuclear palladium(II) acetate with transition and rare earth metal carboxylates were studied in detail in the laboratory of Academician I. I. Moiseev. The chemists synthesized a broad range of Chinese lantern-shaped heterobimetallic palladium(II) acetate and pivalate complexes (Scheme 1) [35–43]:



Scheme 1.

Note, however, that reactions of this type involving trinuclear Pd(II) pyrazolate-bridged complex have not yet been studied.

Thus, we demonstrated that reactions of palladium(II) acetate with binuclear zinc pyrazole pyrazolate pivalate not only involve ligand exchange, but are also accompanied by deprotonation of the coordinated pyrazole, thus giving trinuclear palladium(II) pyrazolate complex and unusual heterocarboxylate 1D linear zinc-containing coordination polymer.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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