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Effect of the Nature of Haloacetic Acids on the Type of Morpholine Complexes Formed. Crystal Structure of the First Palladium Tetracarboxylate with Monocarboxylic Acid: Morpholinium Tetrakis(trifluoroacetato)palladate(II), $(O(CH_2CH_2)_2NH_2)_2[Pd(CF_3COO)_4]$

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Abstract—The effect of the nature of halogen-substituted carboxylic acids RCOOH, where R is $ClCH_2$, Cl_2CH, Cl_3C, or F_3C, on the complexation of palladium halocarboxylates with morpholine C_4H_9NO was investigated. Reactions with $ClCH_2COOH$ and $Cl_2CHCOOH$ gave binuclear complexes $[(C_4H_9NO)_2Pd_2(\mu\text{-}OOCR)_2(OOCR)_2]$ with palladium-coordinated morpholine, whereas reactions with Cl_3CCOOH and F_3CCOOH afforded the first tetra(halocarboxylate) palladium complexes with protonated morpholine as the cation, $(C_4H_{10}NO)_2[Pd(RCOO)_4]$. The acid–base balance of morpholine and halocarboxylic acid was the key factor determining the composition of the resulting complexes. For the formation of palladium tetra(halocarboxylates) with morpholine, the difference between the morpholine and acid pK_a values should be not lower than 7.63. X-ray diffraction studies were carried out for the first tetra(halocarboxylate) palladium complex with a monocarboxylic acid $(C_4H_{10}NO)_2[Pd(OOCCF_3)_4 \cdot 2H_2O]$ (**I**) and for *trans*-$[(C_4H_9NO)_2Pd(OOCCH_2Cl)_2 \cdot 2H_2O]$ (**II**), *trans*-$[(C_4H_9NO)_2Pd(OOCCHCl_2)_2]$ (**III**), and *trans*-$[(C_4H_9NO)_2Pd(OOCCF_3)_2 \cdot 2H_2O]$ (**IV**) (CIF files CCDC nos. 1008564, 1894300, 1008566, and 1894299, respectively).

Keywords: palladium monochloroacetates, trifluoroacetates, trichloroacetates with a protonated or coordinated morpholine molecule, selection criteria for acids and bases, structures

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INTRODUCTION

The antitumor properties of cisplatin (*cis*-$Pt(NH_3)_2Cl_2$) were discovered more than 50 years ago [1]. Until now, only three Pt(II) compounds have found use in cancer therapy, namely, cisplatin and two its carboxylate analogues, carboplatin and oxaliplatin, which provide not only high antitumor action, but also a variety of side effects. Meanwhile, it was noted that going from compounds with chloride ions (cisplatin) to compounds with carboxylate ions (carboplatin and oxaliplatin) is accompanied by a decrease in toxicity [2–10]. In subsequent years, there has been search for compounds with antitumor activity among other platinum group metals. However, none of the compounds possessed antitumor activity comparable with the activity of platinum(II) compounds used in the cancer therapy [11–20]. As a result of studying the physicochemical and pharmacological properties of representatives of various classes of palladium compounds, we distinguished the compounds $(AmH_n)_k[PdCl_4]$ with protonated amines (Am) [21]. In the most widely studied group of compounds of this class, that is, cation–anion palladium complexes with protonated morpholine derivatives, some mononuclear morpholinium $(C_4H_{10}NO)_2[PdCl_4]$ or methylmorpholinium $(C_5H_{14}NO)_2[PdCl_4]$) derivatives were found to have antitumor activity equal to or exceeding that of cisplatian and much lower toxicity [22–25]. For further investigations along this line, of obvious interest is the synthesis of carboxylate analogues of the indicated chloride complexes. The conditions of formation of the cation–anion palladium carboxylate complexes with a protonated morpholine molecule, whose pK_a is 8.33, were investigated using halogen-substituted acetic acids RCOOH (R = $ClCH_2$, Cl_2CH, Cl_3C, F_3C), with pK_a values being 2.87–0.0.

This paper describes the synthesis of several palladium complexes with halogen-substituted acetate anion and morpholine and identifies the factor determining the type of the resulting complexes. Depending on pK_a of halocarboxylic acid, these are either binuclear amino complexes $[(C_4H_9NO)_2Pd_2(\mu\text{-}OOCR)_2(OOCR)_2]$ (R = $ClCH_2$, Cl_2CH) with a palladium-coordinated morpholine molecule or mononuclear complexes $(C_4H_{10}NO)_2[Pd(RCOO)_4]$ (R = Cl_3C–, F_3C–) with a protonated morpholine molecule as the counter-ion. It is noteworthy that only one platinum metal tetracarboxylate has been reported in the literature, namely, platinum tetrapivalate $K_2[Pt((CH_3)_3CCO_2)_4]$, which was obtained in a low yield under fairly specific conditions [26].

EXPERIMENTAL

The palladium complexes with the above-indicated acids were synthesized starting from $Pd_3(\mu\text{-}MeCO_2)_6$, obtained by the procedure we developed [27]. Crystalline $Pd_3(\mu\text{-}ClCH_2CO_2)_6$ was prepared by the reported procedure [28]. Palladium mono-, di-, and trihaloacetates were obtained using $ClCH_2COOH$, $Cl_2CH\text{-}COOH$, and Cl_3CCOOH (Sigma-Aldrich), F_3COOH (reagent grade, Khimmed), and morpholine C_4H_9NO (Fluka). Commercial organic solvents—benzene, dichloromethane, diethyl ether, and hexane (Acros)—were used.

Synthesis of $[(C_4H_9NO)_2Pd_2(\mu\text{-}OOCCH_2Cl)_2\text{-}(OOCCH_2Cl)_2]$ (I). $Pd_3(CH_3COO)_6$ (0.150 g, 0.6 mmol) was added to a 90% solution of $ClCH_2COOH$ (1.8 g in 2 mL of water). The reaction mixture was stirred at 55°C until the starting compounds completely dissolved (for 30 min). Then morpholine (0.180 mL, 2 mmol) was added to the filtered solution. The synthesis was conducted at room temperature for 4 h until a precipitate formed. The light brown precipitate was collected on a filter, washed with water, and dried at 100°C to a constant weight. The yield was 25% based on palladium used.

For $C_{16}H_{26}N_2O_{10}Cl_4Pd_2$

Anal. calcd., %	C, 25.32	H, 3.43	N, 3.69
Found, %	C, 25.87	H, 4.28	N, 3.03

IR (ν, cm^{-1}): 1643, 1589, 1350 $\nu_{as}(COO^-)$, 1350, 1408 $\nu_s(COO^-)$, 3093 $\nu(NH_{coord})$.

When the synthesis was carried out in 20% acid, the same product was formed.

Synthesis of *trans*-$[(C_4H_9NO)_2Pd(OOCCH_2Cl)_2]$ (II). $Pd_3(OOCCH_2Cl)_6$ (0.147 g, 0.5 mmol) was dissolved in benzene (20 mL), and morpholine (0.087 mL, 1 mmol) was added. The synthesis was conducted with continuous stirring at room temperature for 24 h, then the reaction mixture was concentrated on a rotary evaporator to ~5 mL. The addition of hexane (20 mL) gave a light yellow precipitate, which was collected on a filter, washed with hexane (3 × 10 mL), and dried in a vacuum of 93 Pa to a constant weight. The yield was 72% based on the palladium used. From the mother liquor, a single crystal of *trans*-$[(C_4H_9NO)_2Pd(OOCCH_2Cl)_2 \cdot 2H_2O]$ **(IIa)** was grown.

For $C_{12}H_{22}N_2O_6Cl_2Pd$ **(II)**

Anal. calcd., %	C, 30.82	H, 4.74	N, 5.99
Found, %	C, 31.21	H, 5.44	N, 5.95

IR (ν, cm^{-1}): 1642 $\nu_{as}(COO^-)$, 1349 $\nu_s(COO^-)$, 3203 $\nu(NH_{coord})$.

Synthesis of $[(C_4H_9NO)_2Pd_2(\mu\text{-}OOCCHCl_2)_2\text{-}(OOCCHCl_2)_2]$ (III). $Pd_3(CH_3COO)_6$ (0.331 g, 0.5 mmol) was dissolved in $Cl_2CHCOOH$ (20 mL) with continuous stirring during 1 h at 30°C. Morpholine (0.253 g, 3 mmol) was added to the filtered solution and the mixture was stirred for 6 h at 35–40°C until a precipitate formed. The light brown precipitate was collected on a filter, washed with water (3 × 5 mL), kept over KOH, dried at 80°C to a constant weight, and recrystallized from CH_2Cl_2. When the synthesis was carried out in 20% $Cl_2CHCOOH$, the product was similar to that obtained in 100% $Cl_2CH\text{-}COOH$. The yield was 45% based on palladium used.

For $C_{16}H_{22}N_2O_{10}Cl_8Pd_2$

Anal. calcd., %	C, 21.38	H, 2.47	N, 3.13	Pd, 23.68
Found, %	C, 21.33	H, 2.52	N, 3.03	Pd, 23.57

IR (ν, cm^{-1}): 1669, 1610 $\nu_{as}(COO)$; 1349, 1401 $\nu_s(COO)$; 3133 $\nu(NH_{coord.})$.

Synthesis of *trans*-$[(C_4H_9NO)_2Pd(OOCCHCl_2)_2]$ (IV). A mixture of *trans*-$(C_4H_9ON)_2PdCl_2$ (0.202 g, 0.6 mmol) and $AgOOCCHCl_2$ (0.271 g, 1.2 mmol) was stirred in benzene (30 mL) for 3 h, then the resulting AgCl was filtered off, and the solution was concentrated to dryness on a rotary evaporator. The residue was dissolved in diethyl ether (20 mL) and concentrated to dryness. The product was recrystallized from benzene and dried at 80°C to a constant weight. The yield was 40% based on palladium used.

For $C_{12}H_{20}N_2O_6Cl_4Pd$

Anal. calcd., %	C, 26.87	H, 3.74	N, 5.23	Pd, 19.84
Found, %	C, 27.78	H, 4.07	N, 6.10	Pd, 18.75

IR (ν, cm^{-1}): 1663, 1649 $\nu_{as}(COO^-)$; 1349, 1327 $\nu_s(COO^-)$, 3211, 3185 $\nu(NH_{coord.})$.

Synthesis of $(C_4H_{10}NO)_2[Pd(OOCCCl_3)_4]$ (V). $Pd_3(CH_3COO)_6$ (0.200 g, 0.3 mmol) was dissolved in a 75% aqueous solution of Cl_3CCOOH (4.57 g in 1.5 mL of water) with stirring during 1 h at 30°C. Morpholine (0.154 g, 1.8 mmol) was added to a filtered solution and the mixture was stirred for 6 h at 35–40°C. The resulting fine light brown precipitate was collected on a filter, washed with water (4 × 5 mL), kept over KOH, and dried at 80°C to a constant weight. The yield was 66% based on palladium used.

For $C_{16}H_{20}O_{10}N_2Cl_{12}Pd$

Anal. calcd., %	C, 20.62	H, 2.17	N, 3.01	Pd, 11.42
Found, %	C, 20.78	H, 2.07	N, 3.10	Pd, 10.95

IR (ν, cm^{-1}): 1687, 1647 $\nu_{as}(COO^-)$; 1335, 1330 $\nu_s(COO^-)$; 3149, 3057 $\nu\left(NH_2^+\right)$; 1587 $\delta\left(NH_2^+\right)$.

Synthesis of *trans*-[$(C_4H_9NO)_2Pd(OOCCCl_3)_2$] (VI). A mixture of *trans*-$(C_4H_9ON)_2PdCl_2$ (0.260 g, 0.75 mmol) and $AgOOCCHCl_3$ (0.402 g, 1.5 mmol) in benzene (30 mL) was stirred for 3 h and filtered to remove AgCl. The filtrate was concentrated to dryness on a rotary evaporator. The residue was dissolved in diethyl ether (20 mL) and the solution was concentrated to dryness. The product was recrystallized from benzene and dried at 80°C to a constant weight. The yield was 32% based on palladium used.

For $C_{12}H_{18}O_6N_2Cl_6Pd$

Anal. calcd., %	C, 23.81	H, 3.00	N, 4.63	Pd, 17.58
Found, %	C, 24.48	H, 3.76	N, 4.29	Pd, 18.15

IR (ν, cm^{-1}): 1672 $\nu_{as}(COO^-)$; 1309 $\nu_s(COO^-)$; 3133 $\nu(NH_{coord.})$.

Synthesis of $(C_4H_{10}NO)_2[Pd(OOCCF_3)_4]$ (VII). $Pd_3(CH_3COO)_6$ (0.448 g, 2 mmol) was dissolved in F_3CCOOH (20 mL) at 55°C. The reaction mixture was filtered to remove Pd metal. Morpholine (0.35 mL, 4 mmol) (per Pd atom) was added to the resulting solution. The synthesis was conducted with stirring at room temperature for 1 h. The reaction mixture was concentrated to ~5 mL on a rotary evaporator, diethyl ether (15 mL) was added, and the mixture was concentrated on a rotary evaporator. This procedure was repeated two more times until a light yellow precipitate formed; the precipitate was collected on a filter, washed with diethyl ether, and dried in vacuo to a constant weight. The yield was 58% based on palladium used. The synthesis in dilute (20%) CF_3COOH also gave compound **VII**. A single crystal of $(C_4H_{10}NO)_2[Pd(OOCCF_3)_4]$ for X-ray diffraction was grown from the mother liquor.

For $C_{16}H_{20}N_2O_{10}F_{12}Pd$

Anal. calcd., %	C, 26.22	H, 2.73	N, 3.81
Found, %	C, 27.05	H, 2.09	N, 4.40

IR (ν, cm^{-1}): 1691, 1667 $\nu_{as}(COO^-)$, 1411 $\nu_s(COO^-)$, 3112, 3035 $\nu\left(NH_2^+\right)$, 1557 $\delta\left(NH_2^+\right)$.

Synthesis of *trans*-[$(C_4H_9NO)_2Pd(OOCCF_3)_2$] (VIII) $PdCl_2$ (0.177 g, 1 mmol) and $AgCF_3COO$ (0.44 g, 2 mmol) were placed in a round-bottom flask, and toluene (20 mL) was added. The synthesis was conducted in the dark at room temperature for 24 h. Then the reaction mixture was filtered, and morpholine (0.180 mL, 2 mmol) was added to the resulting solution. The synthesis was conducted for 2 h. The light gray precipitate thus formed was collected on a filter, washed with hexane (3 × 10 mL), and dried in vacuo to a constant weight. The yield was 45% based on palladium used. The mother liquor obtained after separation of the precipitate was concentrated on a rotary evaporator to give an oil, which was dissolved in 15 mL of CH_2Cl_2. A single crystal of *trans*-[$(C_4H_9NO)_2Pd(OOCCF_3)_2 \cdot 2H_2O$] (**VIIIa**) suitable for X-ray diffraction was selected from the crystalline mass formed in the solution.

For $C_{12}H_{18}N_2O_6F_6Pd$ (**VIII**)

Anal. calcd., %	C, 28.45	H, 3.56	N, 5.53
Found, %	C, 27.49	H, 4.36	N, 5.40

IR (ν, cm^{-1}): 1659 $\nu_{as}(COO^-)$, 1431 $\nu_s(COO^-)$, 3183 $\nu(NH_{coord.})$.

Analysis for C, H, N was carried out on a Carlo Erba Instruments CHNS OEA 1108 analyzer. Palladium was quantified by the gravimetric method. The IR spectra of crystalline samples and solutions were measured in the 4000–550 cm^{-1} range in the ATR mode using a NEXUS NICOLET Fourier transform spectrometer (one-beam, scanning, with a CsI beam splitter and a TGS-CsI detector, 0.1% photometric accuracy, and 2 cm^{-1} resolution) equipped with a MIRacle attachment (PIKE Technologies) with a diamond crystal. The crystalline samples were directly deposited on the diamond crystal without additional sample preparation procedure.

X-ray diffraction. The experimental data for compounds **IIa**, **IV**, **VII**, and **VIIIa** were collected on a Bruker SMART APEX II automated diffractometer (MoK_α radiation (λ = 0.71073 Å, graphite monochromator) in the ω-scan mode. The absorption corrections were based on intensity measurements for equivalent reflections [29]. The structures were solved by direct methods and refined by the full-matrix anisotropic least-squares method on F^2 for all non-hydrogen atoms (SHELXTL) [30]. The crystal of **IIa** was a pseudo-merohedral twin with the 1 0 1 0 1 0 0 0 –1 twinning matrix and the component ratio of 0.965(1)/0.035(1). In **VII** and **VIIIa**, the trifluoromethyl groups are rotationally disordered with occupancy ratios of 0.62/0.38 and 0.40/0.38/0.22 (for **VII**) and 0.48/0.34/0.19 (for **VIIIa**). In structures **IIa**, **VII**,

Table 1. Crystallographic data and structure refinement details for compounds **IIa**, **IV**, **VII**, and **VIIIa**

Parameter	Value			
	IIa	**IV**	**VII**	**VIIIa**
Molecular formula	$C_{12}H_{26}N_2O_8Cl_2Pd$	$C_{12}H_{20}N_2O_6Cl_4Pd$	$C_{16}H_{20}N_2O_{10}F_{12}Pd$	$C_{12}H_{22}N_2O_8F_6Pd$
M	503.65	536.50	734.74	542.72
Crystal size, mm	0.20 × 0.20 × 0.04	0.35 × 0.20 × 0.15	0.22 × 0.20 × 0.08	0.40 × 0.40 × 0.35
System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$Pbca$
Temperature, K	160	150	173	230
Unit cell parameters				
a, Å	9.8233(15)	12.2919(4)	9.3775(9)	6.1596(4)
b, Å	16.363(3)	33.5948(9)	14.7100(14)	16.8732(11)
c, Å	6.1975(10)	19.4777(6)	19.0247(18)	18.9401(12)
β, deg	107.809(2)	106.257(1)	96.794(1)	90
V, Å^3	948.4(3)	7721.6(4)	2605.9(4)	1968.5(2)
Z	2	16	4	4
ρ(calcd.), g/cm^3	1.764	1.846	1.873	1.831
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	1.301	1.545	0.850	1.040
F(000)	512	4288	1456	1088
θ range, deg	1.24–26.99	1.63–29.00	2.16–27.00	2.41–27.99
Number of reflections	7011	93262	19790	16547
Number of unique reflections (R_{int})	2057 (0.0264)	20442 (0.0286)	5666 (0.0320)	2368 (0.0241)
Number of refined parameters	128	901	463	154
R_1 for $I > 2\sigma(I)$	0.0245	0.0515	0.0438	0.0442
wR_2 (all data)	0.0626	0.1247	0.1141	0.1066
GOOF on F^2	1.092	1.096	1.04	1.082
$\Delta\rho_{\mathrm{min}}/\Delta\rho_{\mathrm{max}}$, e/Å^3	–0.664/0.528	–2.472/4.858	–0.826/1.216	–0.783/0.978

and **VIIIa**, the hydrogen atoms attached to carbon were placed into calculated positions and refined in the riding model, whereas the "active" hydrogen atoms (ammonium and water) were located objectively and their positional parameters were refined. For compound **IV**, all hydrogen atoms were placed into calculated positions and refined using the riding model.

The crystallographic data and X-ray experiment and structure refinement details are summarized in Table 1. The structures of **IIa**, **IV**, **VII**, and **VIIIa** are deposited with the Cambridge Crystallographic Data Centre (nos. 1008564, 1894300, 1008566, and 1894299, respectively) [31]. X-ray diffraction measurements were performed at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

RESULTS AND DISCUSSION

In the first stage of preparing morpholonium tetraacetato palladate, the reaction of $Pd_3(CH_3COO)_6$ with morpholine in 90% acetic acid was used. However, the reaction gave the palladium amino complex *trans*-$[(C_4H_9NO)_2Pd(OOCCH_3)_2]$ [32]. This was due to fragmentation of the starting trinuclear palladium acetate in the concentrated acid in the presence of morpholinium acetate formed in the reaction. Our results of examination of the UV/Vis spectra of the reaction mixture are consistent with the data reported previously [33]. Detailed investigation of the reaction of $Pd_3(CH_3COO)_6$ with CH_3COONa and CH_3COOLi in acetic acid [33] demonstrated that the first step of palladium acetate depolymerization gives binuclear complexes $Na_2[Pd_2(CH_3COO)_6]$ and $Li_2[Pd_2(CH_3COO)_6]$, which are then converted to monomers $Na_2[Pd(CH_3COO)_4]$ and $Li_2[Pd(CH_3COO)_4]$. However, in the case of formation of cation–anion complexes, in which cations are represented by protonated nitrogen-containing ligands $(AmH)_2[(Pd(RCOO)_4]$, the formation of the final products is complicated by the possible deprotonation of onium cations, coordination of two Am molecules to palladium, and formation of *trans*-diamino complexes *trans*-$[(Am)_2Pd(OOCR)_2]$. Thus, the Anderson rearrangement being accomplished [34] is displacement of inner-sphere anionic ligands by amine molecules formed in the reaction. The author [34] noted that the rate of transformations involved in the Anderson rearrangement is determined, first, by the basicity of the protonated ligand and, second, by the nature of the acid residue, which accepts the proton detached from the onium ligand. In [32], we attempted to prepare morpholinium complexes with the $[Pd(CH_3COO)_4]^{2-}$ anion. The reaction gave only mononuclear *trans*-$[(C_4H_9NO)_2Pd(OOCCH_3)_2]$. It was found that protonation of morpholine with acetic acid to give the tetraacetate anion is impossible in the Pd–morpholine ($pK_a = 8.33$)–acetic acid ($pK_a = 4.56$) system, where $\Delta pK_a = 3.77$.

In this study, to elucidate the factors determining the possibility of formation of morpholinium tetracarboxylato-palladates, we chose a series of halogenated acetic acids RCOOH, with pK_a being in the range from 2.45 ($R = ClCH_2$) to 0.0 ($R = F_3C$) [33]. This is much lower than pK_a of acetic acid, which may result in the required increase in the pK_a difference between morpholine and the acid (Δ). The reactions of palladium halocarboxylates with morpholine were practically performed in two steps. The first one was the formation of palladium halocarboxylates in solutions upon the replacement of the acetate group in $Pd_3(CH_3COO)_6$ by the corresponding haloacetate groups without separation of the resulting $Pd_3(RCOO)_6$ to the solid phase. The synthesis of solid complexes $Pd_3(ClCH_2COO)_6$, $Pd_3(Cl_3CCOO)_6$, and $Pd_3(F_3CCOO)_6$ by a similar reaction was reported in our previous publication [28], together with the synthesis of $Pd_3(Cl_2CHCOO)_6$, which is also a trinuclear complex according to elemental analysis and IR spectroscopy data. The second step of the synthesis, that is, the reaction of palladium halocarboxylates with morpholine, was carried out in aqueous solutions of RCOOH ($R = ClCH_2$ or Cl_3C) or in concentrated acids ($R = Cl_2CH$ and F_3C) at a Pd : morpholine ratio of 1 : 2 with expectation to obtain $(AmH)_2[Pd(RCOO)_4]$. The study showed that reactions of morpholine with palladium mono- and di-chloroacetates afford binuclear amino complexes **I** and **III** containing both bridging and terminal carboxylate groups and palladium-coordinated morpholine. The structures of **I** and **III** were established relying on elemental analysis and IR spectroscopy data.

The IR spectra of **I** and **III** contain stretching bands for the coordinated NH groups of morpholine at 3093 cm^{-1} (for **I**) and 3133 cm^{-1} (for **III**). The asymmetric carboxylate modes of **I** and **III** are manifested at 1589 and 1610 cm^{-1}, while the symmetric carboxylate vibrations are observed at 1408 and 1401 cm^{-1}, respectively. The splitting Δ between the ν_{as} and ν_s modes in **I** and **III** is 181 and 209 cm^{-1}. According to [35], this corresponds to a bridging position of these groups in **I** and **III**. Meanwhile, the bands for asymmetric modes of another group occur at 1643 cm^{-1} (**I**) and 1669 (**III**) cm^{-1}, while the symmetric modes are manifested at 1350 cm^{-1} (**I**) and 1349 (**III**) cm^{-1}. The splitting Δ between these bands is 293 cm^{-1} (**I**) and 320 cm^{-1} (**III**), which implies a monodentate coordination of these carboxyl groups. To confirm the positions of bands of the terminal groups in **I** and **III**, mononuclear complexes **II** and **IV** with terminal carboxylate groups were prepared.

Complex **II** was obtained in benzene by the reaction of $Pd_3(OOCCH_2Cl)_6$ with morpholine. Complex **IV** was formed only in the reaction of $(C_4H_9NO)_2PdCl_2$, which we synthesized, with silver dichloroacetate. An increase in the Pd : morpholine ratio from 1 : 2 to 1 : 4 in the synthesis of **III** did not lead to cleavage of carboxylate bridges giving a mononuclear complex identical to **IV**. If the reaction mixture for the synthesis of **III** was kept at room temperature for 6 months in the presence of morpholine remaining in the reaction mixture, the formation of **III** was followed by its monomerization to give a mononuclear complex identical to **IV**.

The ν_{as} and ν_s modes of the terminal carboxylate groups of **II** occur at 1642 and 1349 cm^{-1}, respectively. The splitting between ν_{as} and ν_s for complex **II** (293 cm^{-1}) attests to the terminal position of these carboxylate groups in **II**, which coincides with similar characteristics of **I**. In the IR spectrum of **IV**, two $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands were detected, in particular, 1662, 1649 and 1349, 1327 cm^{-1}. The splitting between ν_{as} and ν_s for complex **IV** (293 and 222 cm^{-1}) is characteristic of terminal carboxylate groups. The IR spectrum of **IV** also exhibits two NH bands (at 3211 and 3185 cm^{-1}), which supports the data about more complex interaction between the carboxylate groups and protons of coordinated morpholine molecules. The obtained IR spectroscopy data for **IIa** and **IV** were confirmed by X-ray diffraction analysis of these complexes. Consideration of X-ray diffrac-

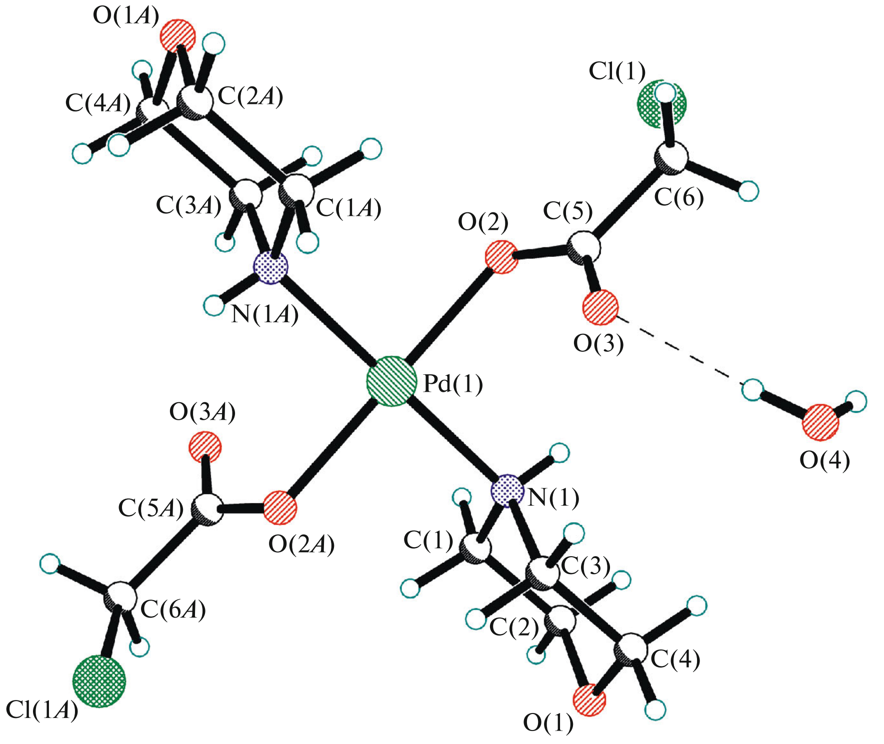

Fig. 1. Molecular structure of complex **IIa**.

tion data of palladium morpholine complexes with monochloroacetic (**IIa**) and dichloroacetic (**IV**) acids also included data for the palladium morpholine complex with trifluoroacetic acid (**VIIIa**), which is structurally similar to **IIa**.

Compounds **IIa**, **IV**, and **VIIIa** are the molecular complexes $Pd[-O-C(=O)-R]_2[\leftarrow NH(CH_2CH_2)_2-O]_2$ (R = CH_2Cl, $CHCl_2$, CF_3) (Figs. 1–3). In all three cases, the central palladium atom has a traditional square coordination with the *trans*-arrangement of morpholine ligands. Complexes **IIa** and **VIIIa** are located at the crystallographic inversion centers, while four independent molecules in **IV** occupy general positions. The interligand *trans*-angles at the palladium atom are in the 173.2(1)°–180° range, while *cis*-angles vary in the 88.9(1)°–91.1(1)° range. The deviations of Pd atoms from the N_2O_2 equatorial plane of ligands do not exceed 0.04 Å. Generally, the molecular geometry of these two compounds is close to that we found previously for the "parent" *trans*-$[(C_4H_9NO)_2Pd(OOCCH_3)_2] \cdot 2H_2O$ (**IX**) [28] (Table 2). It is noteworthy that with increasing electronegativity of the substituent R in the series of closely related complexes **IX** → **IIa** → **IV** → **VIIIa**, the Pd ← N distances tend to increase and the C–O(Pd) distances tend to decrease, whereas the Pd–O bond length does not undergo systematic changes. In molecules **IIa**, **VIIIa**, and **IX**, the carbonyl oxygen atoms are located on both sides of the N_2O_2 plane of the ligands due to the presence of the inversion center, whereas in all four molecules of structure **IV**, all oxygen atoms are located on one side of this plane. This

Table 2. Selected bond lengths (Å) in structures **IIa**, **IV**, **VII**, and **VIIIa**

Bond	**IX** (R = CH_3)	**IIa** (R = CH_2Cl)	**IV** (R = $CHCl_2$)	**VIIIa** (R = CF_3)	**VII**
Pd–N	2.047(4)	2.048(2)	2.047(3)–2.074(3)	2.057(3)	
Pd–O	2.017(3)	2.0303(16)	2.018(3)–2.027(2)	2.016(3)	1.989(3)– 2.009(3)
C–O	1.272(5)	1.267(3)	1.260(5)–1.283(4)	1.260(5)	1.263(5)–1.274(5)
C=O	1.238(6)	1.243(3)	1.215(4)–1.224(5)	1.220(5)	1.210(5)–1.223(5)

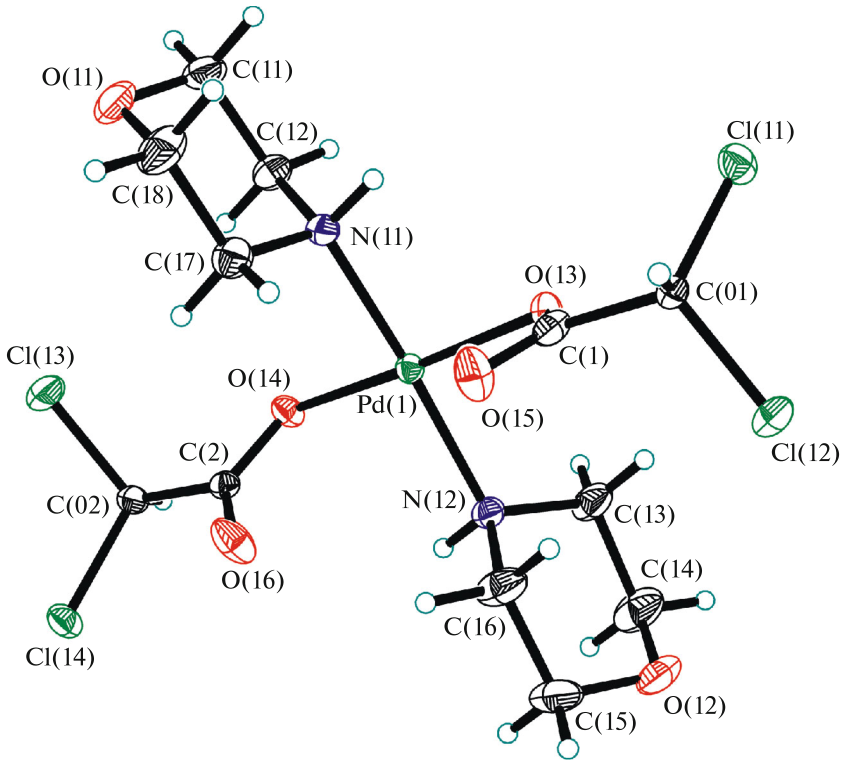

Fig. 2. Structure of one of the four crystallographically independent molecules in compound **IV**.

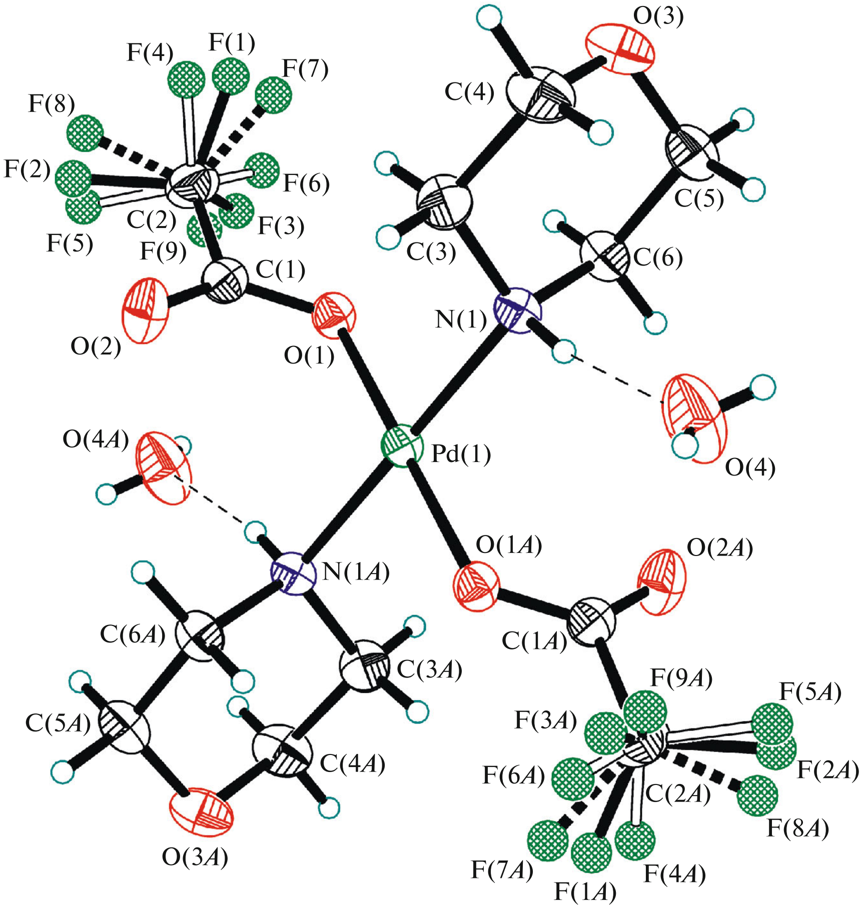

Fig. 3. Molecular structure of complex **VIIIa**.

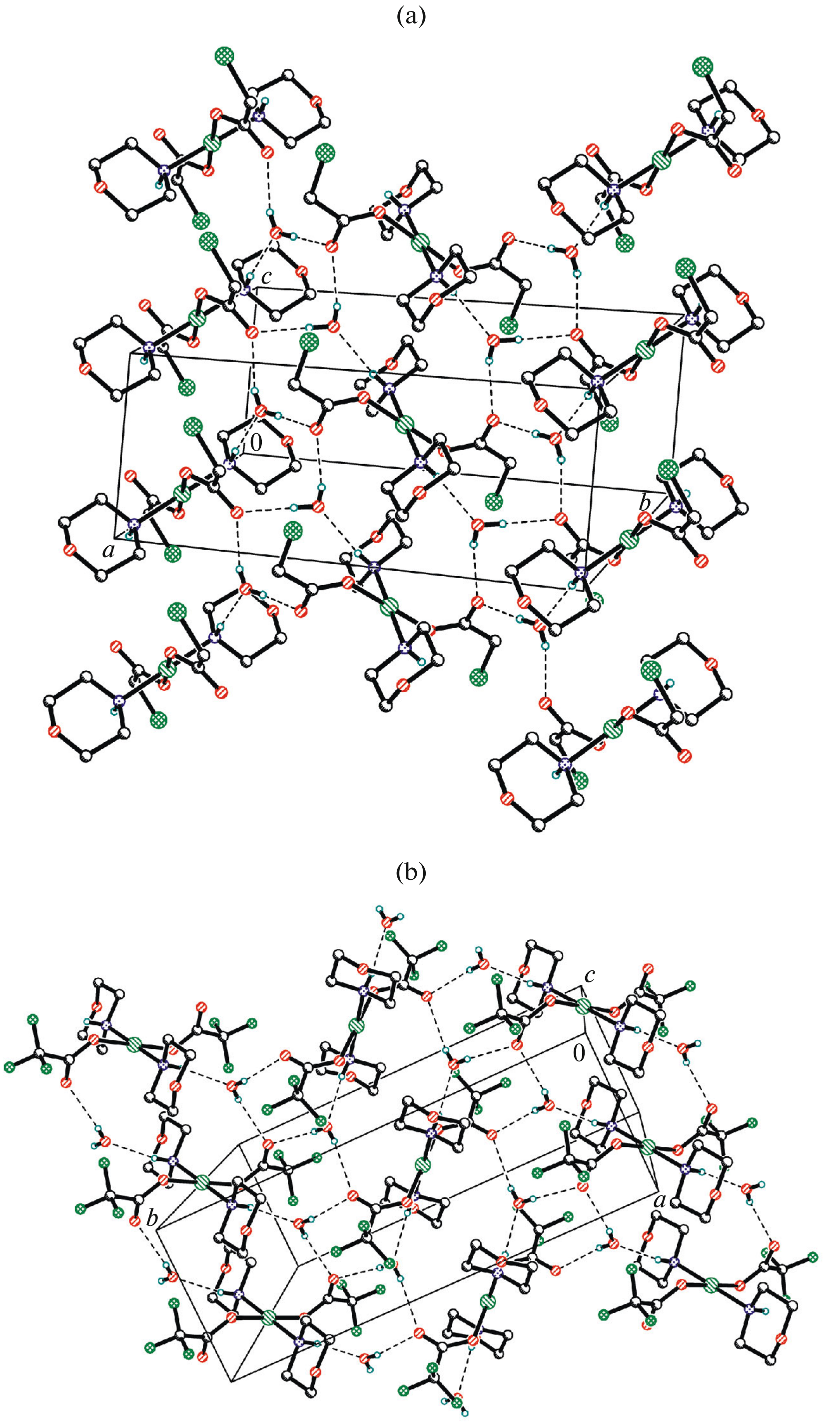

Fig. 4. Hydrogen-bonded layers in the crystals of (a) **IIa** and (b) **VIIIa**.

may be caused by the absence of solvate molecules in **IV**, as opposed to **IIa** and **VIIIa**.

In structures **IIa** and **VIIIa**, all amine hydrogen atoms of the morpholine ligands are involved in hydrogen bonds with hydrate water molecules (Fig. 4). In **IV**, all hydrogen atoms form hydrogen bonds with both chlorine atoms, OH···Cl (3.583–3.961Å), and oxygen atoms of the carboxylate ligands of neighboring molecules, OH···O (2.834–2.919 Å). As a result, intricate 3D networks of hydrogen bonds are formed in these compounds.

As shown by investigations, mononuclear morpholinium carboxylate complexes $(AmH)_2$-$[(Pd(RCOO)_4]$ may form only in reactions with tri-

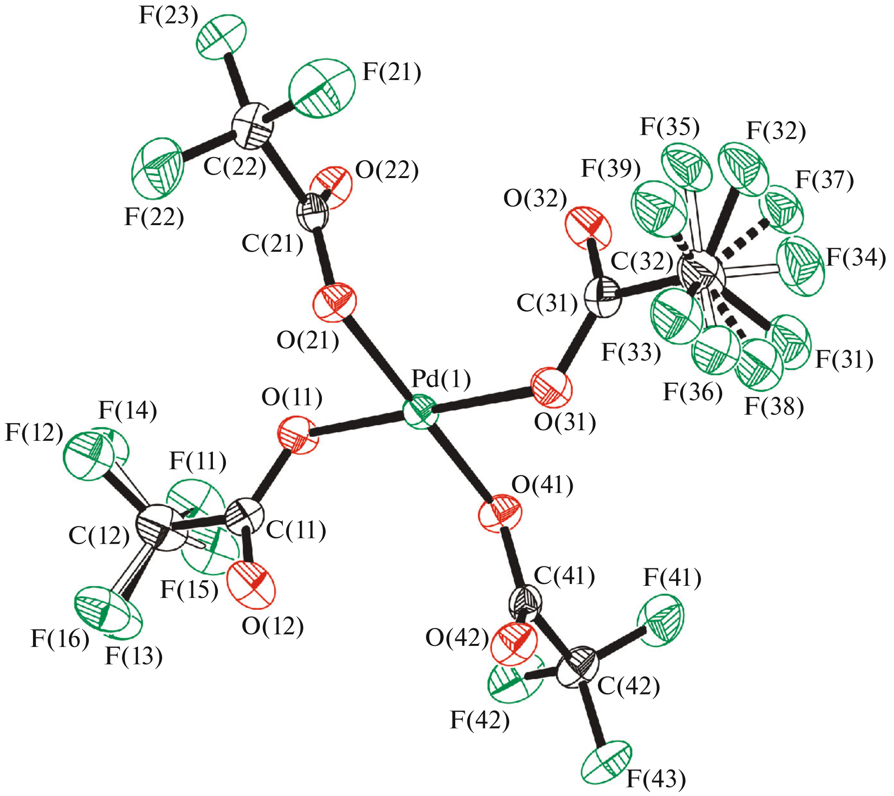

Fig. 5. Structure of the anion in **VII**.

chloroacetic ($pK_a = 0.66$) or trifluoroacetic ($pK_a = 0.0$) acids. The IR spectra of **V** and **VII** exhibit each two $\nu_{as}(COO^-)$ bands at 1687 and 1645 cm^{-1} and two $\nu_s(COO^-)$ bands at 1335 and 1300 cm^{-1} (Δ = 352 and 345 for **V**) and, respectively, at 1691, 1667, and 1411 cm^{-1} (Δ = 280 and 256 for **VII**), and also two bands corresponding to $\nu_{as}(NH_2^+)$ modes for 3149 and 3057 cm^{-1} (for **V**); 3112 and 3035 cm^{-1} (for **VII**). The presence of two carboxylate bands in the spectra of **V** and **VII** attests to non-equivalence of two pairs of carboxylate groups in the $[(Pd(RCOO)_4]^{2-}$ anion, since only one *trans*-located pair can be hydrogen bonded (via the O···HN bond) to two morpholinium cations. The obtained results indicate that the structures of **V** and **VII** are identical. To confirm the assignment of frequencies of the terminal carboxylate groups in **V** and **VII**, mononuclear aminate complexes **VI** and **VIII** were synthesized. The IR spectra of these complexes exhibit single $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands, which are located at 1672 and 1309 cm^{-1} (for **VI**) and 1659 and 1431 cm^{-1} (for **VIII**).

A study of the structure of the first palladium complex containing the tetracarboxylate anion $[Pd(O_2CCF_3)_4]^{2-}$ (**VII**) demonstrated that the central palladium atom of the $[Pd(O_2CCF_3)_4]^{2-}$ anion has a nearly regular square geometry with *cis*-angles ranging from 88.3(1)° to 91.6(1)° (Fig. 5). Two carbonyl oxygen atoms are located on one side of the O_4 base plane of the ligands, while the other two carbonyl oxygen atoms are on the other side. Only two carboxylate branches of the $[Pd(O_2CCF_3)_4]^{2-}$ anion are hydrogen-bonded to the morpholinium cations. Apparently, this gives rise to two pairs of Pd–O, C–O(Pd), and C=O bonds in the carboxylate ligands of **VII**, which is in line with IR spectroscopy data. In **VII**, the Pd–O bonds are shorter and C–O(Pd) bonds are longer than those in **VIIIa** (Table 2). The morpholinium cations in **VII** have a chair geometry, with their both amine hydrogen atoms being involved in hydrogen bonds with not only the carbonyl oxygen atoms of the anions, but also with the oxygen atoms of the neighboring morpholinium cations (Fig. 6).

As far as we know, **VII** is the first compound in the anion of which Pd atom coordinates four acid residues of the monocarboxylic trifluoroacetic acid.

Thus, this study showed that palladium complexes with tetracarboxylate anions $(C_4H_9NO)_2[Pd(OOCR)_4]$ and morpholinium can be prepared using halocarboxylic acids RCOOH (R = CF_3COO^- and CCl_3COO^-) if the ΔpK_a is higher than 7.63. For smaller ΔpK_a values, e.g., in the reactions with RCOOH (R = $ClCH_2COO^-$ and Cl_2CHCOO^-), binuclear complexes $[(C_4H_9NO)_2Pd_2(\mu\text{-}OOCR)_2$-

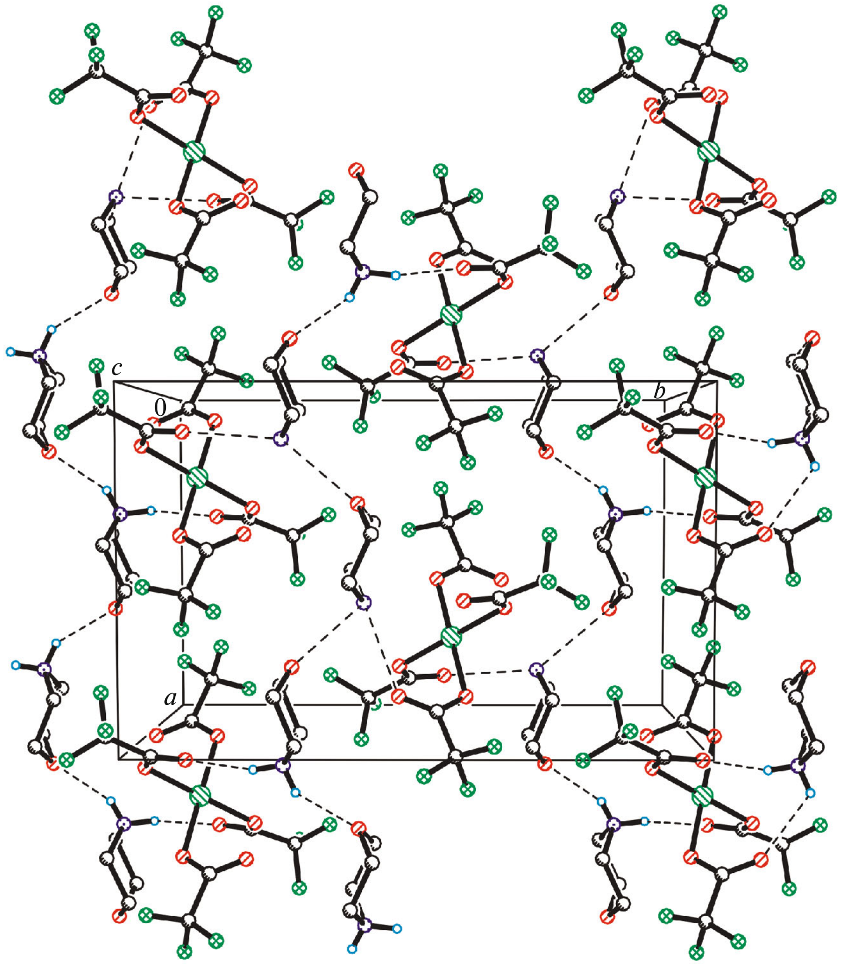

Fig. 6. Hydrogen-bonded layers in the crystal of **VII**.

$(OOCR)_2]$ with palladium-coordinated morpholine molecules are formed.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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