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COORDINATION COMPOUNDS

Synthesis and Structure of New Pt(IV) Perfluorocarboxylate Complexes and Their Reactivity with Respect to Alkanes and Cycloalkanes

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Abstract—New Pt(IV) perfluorocarboxylate complexes of the composition $[Pt(R_FCOO)_4]_n$ and $M_2[Pt(R_FCOO)_6]$ ($R_F = CF_3$, C_2F_5; M = Li, Na, K, Rb, Cs, NMe_4) have been synthesized and studied. These complexes are strong oxidizing agents capable of oxidizing alkanes in trifluoroacetic acid under mild conditions to form trifluoroacetic acid esters and acting as catalysts for the oxidative trifluoroacetoxylation of alkanes, cycloalkanes, and framework compounds. They can also be used as starting compounds for the synthesis of other perfluorocarboxylate complexes of platinum in various oxidation states. The structure of $(NMe_4)_2[Pt(CF_3COO)_6] \cdot 6CF_3COOH$ has been determined by X-ray diffraction.

Keywords: platinum, perfluorocarboxylates, oxidation, alkanes, cycloalkanes

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Platinum(II) and platinum(III) acetate complexes were studied in detail [1–4]; however, among platinum perfluorocarboxylate complexes, Pt(II) trifluoroacetate has been the only compound studied by X-ray diffraction. The structure of Pt(II) trifluoroacetate ($Pt_4(CF_3COO)_8$) was determined as early as in 1994 [5]. It was prepared when a mixture of $Na_2[Pt(OH)_6]$, trifluoroacetic acid, and formic acid was continuously heated at 72°C until traces of metallic platinum appeared. Apparently, as a result of the acid–base reaction, an intermediate product is first formed, trifluoroacetate Pt(IV) complex, which is then reduced to the final product. Indeed, it was found by ^{195}Pt NMR spectroscopy that a solution of hydroxo complex $H_2[Pt(OH)_6]$ in anhydrous CF_3COOH contains Pt(IV) trifluoroacetate *cis*-$Pt(CF_3COO)_4(H_2O)_2$ and complex ions $[Pt(CF_3COO)_5(H_2O)]^-$ and $[Pt(CF_3COO)_3(H_2O)_3]^+$ [6]. We succeeded in isolating individual Pt(IV) perfluorocarboxylate complexes from the reaction products of Pt(IV) hydroxo complexes with an excess of lower perfluorocarboxylic acids in the absence of a reducing agent in accordance with the equations:

$$K_2[Pt(OH)_6] + 6R_FCOOH$$
$$= K_2[Pt(R_FCOO)_6] + 6H_2O,$$
$$H_2[Pt(OH)_6] + 4R_FCOOH$$
$$= [Pt(R_FCOO)_4]_n + 6H_2O\ (R_F = CF_3, C_2F_5),$$
$$[Pt(R_FCOO)_4]_n + 2nR_FCOOM$$
$$= nM_2[Pt(R_FCOO)_6]\ (M = Li, Na, Rb, Cs, NMe_4).$$

EXPERIMENTAL

Hydroxo complexes $K_2[Pt(OH)_6]$ and $H_2[Pt(OH)_6]$ were obtained according to [7] and [8], respectively. Glacial acetic acid (chemically pure grade, Russian State Standard, Khimmed) and perfluorocarboxylic acids CF_3COOH (99%, Alfa Aesar GmbH, Germany) and C_2F_5COOH (97%, Feinchemikalien und Forschungsbedarf GmbH, Germany) were used. Alkali metal perfluorocarboxylates were prepared by the reaction between the corresponding M_2CO_3 carbonate (chemically pure grade, Russian State Standard) and R_FCOOH acids. Tetramethylammonium trifluoroacetate was obtained when an aqueous solution of tetramethylammonium hydroxide (REAKHIM, USSR) was allowed to react with

CF_3COOH and the crystalline salt precipitated when using acetone.

Elemental analysis of the prepared compounds on carbon, hydrogen, and nitrogen was carried out on an EA3000 CHN analyzer (Eurovector, EU). The platinum content was determined gravimetrically after the reduction of the complexes in a solution using hydrogen. The attenuated total reflection (ATR) IR spectra of the prepared compounds in the range of 4000–500 cm^{-1} were recorded on a Nikolet spectrophotometer (France) equipped with an ATR attachment. The mass spectra of the complexes in solutions were obtained by the electrospray ionization method using a Shimadzu LCMS-2020 mass spectrometer (Shimadzu Scientific Instruments, Kyoto, Japan). Samples were dissolved in acetonitrile dried over 4 Å molecular sieves (J.T. Baker, Phillipsburg, USA) immediately prior to analysis or in glacial acetic acid (Sigma-Aldrich, ACS reagent) to achieve a concentration of ~0.1 mg/mL. Using a microsyringe, solutions of the complexes were injected directly into the mass spectrometer. The temperature of the evaporator was 150°C; that of the connecting line was 200°C. Nitrogen was used to spray the solution and dry it (1.5 and 10 L/min, respectively). The ionization voltage is 3.0 kV for positive ions and –3.0 kV for negative ions. The range of mass spectra is 200–2000 *m*/*z*. The Shimadzu LabSolutions software was used to analyze the obtained results.

The ^{1}H, ^{13}C, ^{19}F, and ^{195}Pt NMR spectra were recorded on a Bruker AVANCE III 500 MHz high-resolution spectrometer (Germany) with operating frequencies of 500, 126, 471, and 108 MHz, respectively. All spectra were recorded from solutions in CD_3CN at 22 ± 10°C. The chemical shift scale for ^{1}H and ^{13}C NMR spectra was calibrated using solvent signals ($\delta(CD_2HCN) = 1.94$ ppm for ^{1}H, $\delta(CD_3CN) = 1.32$ ppm for ^{13}C); that for ^{19}F NMR spectra was calibrated using an internal standard ($\delta(C_6F_6) = -162.2$ ppm).

X-ray diffraction was performed on a Bruker SMART APEX II diffractometer at 173 K using MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å). The data were corrected for absorption based on equivalent reflections [9]. The structure was solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation on F^2 for all non-hydrogen atoms [10]. All $-CF_3$ groups are rotationally disordered in three or four positions and were refined with the restrictions imposed on the C–F and F···F distances. All hydrogen atoms were located in calculated positions and refined using the "rider" model. Crystals $C_{32}H_{30}F_{36}N_2O_{24}Pt$ (FW = 1705.67) are trigonal, $a = 15.0054(5)$ Å, $c = 47.414(2)$ Å, $V = 9245.6(6)$ Å^3, space group $R\text{-}3c$, $Z = 6$, $\rho = 1.838$ g/cm^3, $F(000) = 4980$, $\mu(MoK_\alpha) = 2.457$ mm^{-1}. Number of reflections collected, 30187; unique, 2484; $R_{int} = 0.0283$. The final divergence factors are: $R1 = 0.0440$, $wR2 = 0.1680$ for 1997 reflections with $I > 2\sigma(I)$ and 0.0516, 0.1787 for all data for 274 parameters.

Crystallographic data were deposited with the Cambridge Structural Database (CCDC no. 1029288). The X-ray diffraction studies were carried out at the Shared Facility Center of the Kurnakov Institute.

The organic products of alkane oxidation in reactions involving Pt(IV) trifluoroacetate complexes were identified on an Agilent 6890-series chromatomass spectrometer (USA) equipped with a mass-selective detector 5973 without prior isolation of the complexes from the mixture.

Synthesis of Pt(IV) Perfluorocarboxylate Complexes

$K_2[Pt(CF_3COO)_6]$. Crystalline potassium hydroxoplatinate $K_2[Pt(OH)_6]$ (0.3753 g, 1 mmol) was heated in a round-bottom flask with reflux contained trifluoroacetic acid (10 mL) for 15 min. The precipitate of the hydroxo compounds completely dissolved at boiling to form a yellow-orange solution. Most of trifluoroacetic acid was evaporated from the solution in a vacuum of 30 Torr at 60°C; remaining acid was removed from the resulting orange "oil" when dried in a vacuum desiccator. A solid yellow substance is obtained in vacuum over KOH, whose composition corresponds to the formula $K_2[Pt(CF_3COO)_6]$. The yield was quantitative.

For $K_2[Pt(CF_3COO)_6]$ anal. calcd. (%): C, 15.14; Pt, 20.51.

Found (%): C, 15.38; Pt, 20.39.

The ATR-IR spectrum is presented in Table 1; the mass spectrum (electrospray ionization in MeCN) is shown in Table 2.

^{1}H NMR (500 MHz, CD_3CN, 23°C, $\delta(CD_2\underline{H}CN) = 1.94$, ppm): δ 10.72 ($CF_3COO\underline{H}$). ^{13}C NMR (126 MHz, CD_3CN, 23°C, $\delta(\underline{C}D_3CN) = 1.32$, ppm): 162.8 (m; $^{2}J(^{13}C,^{19}F) = 37.9$ Hz, $^{2}J(^{13}C,^{195}Pt) = 21.1$ Hz; $\underline{C}OOPt$); 159.6 (q; $^{2}J(^{13}C,^{19}F) = 40.2$ Hz; $\underline{C}OOH$); 116.4 (q; $^{1}J(^{13}C,^{19}F) = 286.5$ Hz; $\underline{C}F_3COOH$); 112.9 (m; $^{1}J(^{13}C,^{19}F) = 289.5$ Hz, $^{3}J(^{13}C,^{195}Pt) = 68.1$ Hz; $\underline{C}F_3COOPt$). ^{19}F NMR (471 MHz, CD_3CN, 23°C, $\delta(C_6F_6) = -162.2$): δ –72.05 (m; $^{4}J(^{19}F,^{195}Pt) = 10.6$ Hz; $C\underline{F}_3COOPt$); –74.55 (s; $C\underline{F}_3COOH$). ^{195}Pt NMR (108 MHz, CD_3CN, 23°C): δ 3780.

$[Pt(CF_3COO)_4]_n$. Platinum dioxide hydrate $PtO_2 \cdot nH_2O$ ($H_2Pt(OH)_6$) precipitated from an aqueous solution was thoroughly washed with methyl acetate or acetone and dried in vacuum over KOH. Platinum dioxide hydrate $PtO_2 \cdot nH_2O$ without the excess adsorbed water (0.280 g, 1 mmol) was heated in a round-bottom flask with trifluoroacetic acid (10 mL) for 15 min. The precipitate of the hydroxo compound almost completely dissolved at boiling to form a yellow-orange solution; a small amount of the precipitate was removed by filtration through a porous glass filter.

Table 1. ATR-IR spectra of Pt(IV) complexes

Compound	$\nu_{as}(COO^-)$, cm^{-1}	$\nu_s(COO^-)$, cm^{-1}	$\nu(C-F)$, cm^{-1}
$Li_2[Pt(CF_3COO)_6]$	1679, 1629	1405	1143
$Li_2[Pt(C_2F_5COO)_6]$	1683, 1640	1390	1315, 1213, 1183,1148, 1132
$K_2[Pt(CF_3COO)_6]$	1729, 1703	1379	1130
$K_2[Pt(C_2F_5COO)_6]$	1732, 1706	1370	1314, 1214, 1183, 1026
$Na_2[Pt(CF_3COO)_6]$	1730, 1648	1378	1138
$Na_2[Pt(C_2F_5COO)_6]$	1732, 1660	1372	1318,1215, 1150, 1130
$Rb_2[Pt(CF_3COO)_6]$	1729, 1712	1379	1127
$Rb_2[Pt(C_2F_5COO)_6]$	1730, 1718	1370	1316, 1212, 1148, 1028
$Cs_2[Pt(CF_3COO)_6]$	1729, 1676	1376	1136
$Cs_2[Pt(C_2F_5COO)_6]$	1732, 1684	1371	1315, 1214, 1150, 1030
$(NMe_4)_2[Pt(CF_3COO)_6]$	1722, 1698	1390	1143
$(NMe_4)_2[Pt(C_2F_5COO)_6]$	1725, 1670	1418	1314, 1216, 1152, 1026
$Pt(CF_3COO)_4$	1680	1394	1140
$Pt(C_2F_5COO)_4$	1706, 1608	1370	1317, 1213, 1180, 1149, 1029

Most of trifluoroacetic acid was removed from the solution in a vacuum of 30 Torr at 60°C; remaining acid was removed from the resulting orange "oil" when dried in a vacuum desiccator. An orange solid is obtained in vacuum over KOH, whose composition corresponds to the formula $Pt(CF_3COO)_4$. The yield was quantitative.

For $Pt(CF_3COO)_4$ anal. calcd. (%): C, 14.83; Pt, 30.14.

Found (%): C, 15.18; Pt, 30.39.

The ATR-IR spectrum is presented in Table 1; the mass spectrum (electrospray ionization in MeCN) is shown in Fig. 2.

The mass spectrum containing ions with two and three platinum atoms indicates the oligomeric structure of compound $[Pt(CF_3COO)_4]_n$, $n \geq 3$.

Compound $Pt(C_2F_5COO)_4$ was prepared by an analogous synthetic procedure.

$(NMe_4)_2[Pt(CF_3COO)_6]$. Weighed samples of $Pt(CF_3COO)_4$ (0.200 g) and $[NMe_4]OCOCF_3$ (0.230 g) were dissolved in CF_3COOH (5 mL) under reflux when heating to ~100°C. The resulting pale yellow solution slightly suspended was filtered through a porous glass filter and most of the acid was removed in vacuum at 60°C. Remaining acid was removed when keeping the obtained viscous "oil" in a vacuum desiccator over KOH. A yellow hygroscopic solid was obtained whose composition corresponds to the formula $(NMe_4)_2[Pt(CF_3COO)_6]$. Yield, 95%. The compound is soluble in methyl acetate and nitromethane and insoluble in chloroform. The ATR-IR spectrum is given in Table 1; the mass spectrum (electrospray ionization in MeCN) is shown in Table 2. Single crystals suitable for X-ray diffraction were obtained from a solution in trifluoroacetic acid standing in a refrigerator; the obtained data confirmed the expected structure of the compound: the molecule consists of the $[Pt(CF_3COO)_6]^-$ octahedral anion and two cations. Other complexes of the composition $M_2[Pt(CF_3COO)_6]$, where M = K, Na, Li, Rb, and Cs, were obtained by a similar method.

$K_2[Pt(C_2F_5COO)_6]$. Crystalline potassium hydroxoplatinate $K_2[Pt(OH)_6]$ (0.1640 g, 0.44 mmol) was heated to boiling in a round-bottomed flask with pentafluoropropionic acid (10 mL) for 30 min. The precipitate of the hydroxo compound was completely dissolved during the reaction to form a yellow-brown solution. Most of the pentafluoropropionic acid was released from the solution in a vacuum at 60°C. The obtained "oil" was dissolved in perfluorobenzene (10 mL); the solvent was released in vacuum at 60°C. Remaining acid was removed from the resulting solid when dried in a vacuum desiccator. In vacuum over KOH, a yellow-orange compound of the composition $K_2[Pt(C_2F_5COO)_6]$ was obtained. The yield is quantitative (0.4100 g). After reprecipitation from ether-pentane (1 : 1) and drying in a vacuum, the product was obtained as a yellow powder.

For $K_2[Pt(C_2F_5COO)_6]$ anal. calcd. (%): C, 17.26; Pt, 15.59.

Found (%): C, 17.86; Pt, 15.39.

The ATR-IR spectrum is given in Table 1; the mass spectrum (electrospray in MeCN) is shown in Table 2. When stored in air, the product without changing its color gradually hydrolyzes to form $K_2[PtO(C_2F_5COO)_4]$,

Table 2. Mass spectra of compounds obtained by electrospray in acetonitrile

Compound	FW, formula unit, and ion charge
$Pt(CF_3COO)_4$	664, $Pt(CF_3COO)_4(OH)^-$ 682, $Pt(CF_3COO)_4(H_2O)(OH)^-$ 778, $Pt(CF_3COO)_5(H_2O)^-$ 1215, $Pt_2(CF_3COO)_7(OH)_2^-$ 1365, $Pt_2(CF_3COO)_8(H_2O)_3(OH)^-$ 1592, $Pt_3(CF_3COO)_8(H_2O)(OH)_5^-$ 1595, $Pt_3(CF_3COO)_8(H_2O)_4(OH)_2^-$ 1689, $Pt_3(CF_3COO)_8(H_2O)_2(OH)_3^-$
$Pt(C_2F_5COO)_4$	882, $Pt(C_2F_5COO)_4(OH)(H_2O)^-$ 1028, $Pt(C_2F_5COO)_5(H_2O)^-$
$K_2Pt(CF_3COO)_6$	1931, $K_3Pt(CF_3COO)_6(MeCN)^+$ 912, $KPt(CF_3COO)_6^-$ 1064, $K_2Pt(CF_3COO)_7^-$
$K_2Pt(C_2F_5COO)_6$	556, $Pt(OH)(C_2F_5COO)_2^+$ 864, $Pt(C_2F_5COO)_4(OH)^-$ 1212, $KPt(C_2F_5COO)_6^+$ 1769, $KPt_2(OH)_2(C_2F_5COO)_7(MeCN)^-$
$[NMe_4]_2Pt(CF_3COO)_6$	1095, $[NMe_4]_3Pt(CF_3COO)_6(MeCN)^+$ 664, $Pt(CF_3COO)_4(OH)^-$ 947, $[NMe_4]Pt(CF_3COO)_6^-$

which is converted to the starting compound when dissolved in pentafluoropropionic acid.

Cyclohexane, adamantane, and *n*-alkanes were oxidized under the action of Pt(IV) trifluoroacetate in sealed glass ampoules containing 20 mg of Pt(IV) trifluoroacetate, 0.40 mL of CF_3COOH, and 40–50 mg of the corresponding hydrocarbons at 100°C for 0.5–2 h. Catalytic oxidation of hydrocarbons was carried out in sealed glass ampoules with pertrifluoroacetic acid; the latter was prepared in situ when trifluoroacetic anhydride was allowed to react with 50% H_2O_2 when cooling. $K_2[Pt(CF_3COO)_6]$ or $[Pt(CF_3COO)_4]_n$ (20 mg) and a hydrocarbon (50 mL) were added to a mixture of pertrifluoroacetic and trifluoroacetic acids (0.40 mL). The ampoule was sealed and allowed to stand at 20°C for 16–24 h. At room temperature, the contents of the ampoules gradually became single-phase without stirring: the hydrocarbon layer in the ampoule became thinner and disappeared completely in 17–24 h because of alkane oxidation to form secondary alkyl trifluoroacetates (the latter dissolved in trifluoroacetic acid). At the same time, the catalytically active Pt(IV) complex was not degraded; the solution remained its light yellow color. In the reaction mixture, the mass spectrometry method detected the same products as found in the reactions of stoichiometric oxidation of alkanes under the action of Pt(IV) compounds and traces of the initial alkanes.

RESULTS AND DISCUSSION

Pt(IV) hydroxo complexes $K_2[Pt(OH)_6]$ (**I**) and $H_2[Pt(OH)_6]$ (**II**) (often referred to as $PtO_2 \cdot 4H_2O$) easily dissolve in boiling trifluoroacetic acid to form yellow-orange solutions; after removing the acid by heating in vacuum, orange compounds $K_2[Pt(CF_3COO)_6]$ (**IIIa**) and $[Pt(CF_3COO)_4]_n$ (**IVa**) were prepared. The resulting complexes are stable at 20°C but hygroscopic. They dissolve in polar solvents (perfluorocarboxylic and carboxylic acids, acetonitrile, methyl acetate, and acetone) being stable only in some of them.

Similar reactions were carried out with perfluoropropionic acid at a temperature of 70°C; as a result, orange complexes $[Pt(C_2F_5COO)_4]_n$ (**IVb**) and $K_2[Pt(C_2F_5COO)_6]$ (**IIIb**) were isolated. Compound **IIIb** was found to be photosensitive. Perfluorobutyrate Pt(IV) complexes could not be isolated in solid form from the reaction mixture after treating Pt(IV) hydroxo complexes with *n*-perfluorobutyric acid because they are easily decomposed. Under the action of methyl acetate, alcohol or diethyl ether, all these compounds are reduced to the "platinum blues," perfluorocarboxylate platinum compounds in a mixed oxidation state of +3.

All Pt(IV) compounds obtained and their reduced products can be used to obtain other Pt(IV) perfluorocarboxylate complexes. The interaction of **IV** with alkali metal and tetramethylammonium trifluoroacetates in CF_3COOH afforded complexes $M_2[Pt(CF_3COO)_6]$ (**IIIc–IIIf**, M = Li, Na, Rb, Cs, respectively) and crystalline complex $(NMe_4)_2[Pt(CF_3COO)_6] \cdot 6CF_3COOH$ (**IIIg**):

$$\left[Pt(CF_3COO)_4\right]_n + 2CF_3COOM = M_2\left[Pt(CF_3COO)_6\right].$$

Complex $K_2[Pt(CF_3COO)_6] \cdot 2CF_3COOH$ was studied by ^1H, ^{13}C, ^{19}F, and ^{195}Pt NMR spectroscopies. The spectra confirm the chemical structure and high purity of the complex obtained.

In the ^1H NMR spectra, one broad singlet at 10.72 ppm is observed belonging to the acidic protons of residual CF_3COOH. The ^{13}C and ^{19}F spectra contain signals of carbon and fluorine atoms belonging to the same type of trifluoroacetate groups and participating in the spin-spin interaction with ^{19}F and ^{195}Pt atoms and signals of free trifluoroacetic acid. The presence of ^{13}C–^{195}Pt and ^{19}F–^{195}Pt magnetic interactions confirm that trifluoroacetate groups are in the inner sphere of the complex anion. In the ^{195}Pt NMR spectrum, the signal found at 3780 ppm is in the region characteristic of Pt^{4+}, but not for platinum in other oxidation states [11].

Solutions of $K_2[Pt(CF_3COO)_6] \cdot 2CF_3COOH$ in acetonitrile-d_3 remained stable for several days, while solutions of $(NMe_4)_2[Pt(CF_3COO)_6] \cdot 6CF_3COOH$ in the same solvent decomposed quickly (probably because of oxidation of the organic cation), which did not allow us to study them by NMR spectroscopy.

The interaction between **IV** and pyridine (**L**) or *o*-phenanthroline (**L₂**) yielded orange complexes $PtL_2(CF_3COO)_4$:

$$Pt(CF_3COO)_4 + L \rightarrow PtL_2(CF_3COO)_4.$$

Complex **IIIa** reacts with hydrochloric acid to form poorly soluble potassium hexachloroplatinate:

$$K_2\left[Pt(CF_3COO)_6\right] + 6HCl = K_2\left[PtCl_6\right] + 6CF_3COOH.$$

The compounds obtained were studied by chemical analysis, ATR-IR spectroscopy (Table 1), NMR spectroscopy, and mass spectroscopy obtained by electrospray ionization in solutions (Table 2). The polymeric nature of **IV** is confirmed by the mass spectra recorded in acetonitrile. The structure of **IIIc** was determined by X-ray diffraction (Fig. 1).

Table 3. Binding energies in inorganic platinum compounds

Compound	$E_b(Pt4f_{7/2})$, eV
K_2PtF_6	77.8
K_2PtCl_6	75.7
$K_2Pt(OH)_6$	75.3
$K_2Pt(CF_3COO)_6$	79.2
$[Pt(CF_3COO)_4]_n$	79.6
$Pt(CF_3COO)_3$	78.0
$Pt_4(CF_3COO)_8$	73.9

The structure contains cations NMe^{4+}, anions $Pt(O_2CCF_3)_6^{2-}$, and solvate CF_3CO_2H molecules. The cation is located on a third-order axis. The Pt atom occupies a special position of $\bar{3}$; therefore, only one carboxylate ligand is crystallographically independent. The metal atom has a slightly distorted octahedral coordination. Carboxylate ligands are monodentate and form almost ideal angles Pt(1)O(1)C(1) 122.6(3)°. Noncoordinated O(2) atoms are involved in relatively strong hydrogen bonds with solvate CF_3CO_2H molecules forming supramolecular dianion $[Pt(O_2CCF_3)_6 \cdot 6CF_3CO_2H]^{2-}$ (Fig. 1). The trifluoromethyl groups of the ligands are rotationally disordered in four positions with a population ratio of 0.40/0.37/0.13/0.10. The trifluoromethyl groups of solvate acid are also disordered in three positions with a population ratio of 0.39/0.34/0.27. As far as we know, compound **III** is the first example of a Pt(IV) homoleptic carboxylate complex.

X-ray electron spectroscopy was first used to determine the oxidation state of platinum in the compounds prepared. According to the obtained data, the oxidation state of platinum in complexes **III** and **IV** is +4, whereas in platinum blues of composition $Pt(R_FCOO)_3$ it is close to +3 (Fig. 2).

Figure 2 shows the $Pt4f_{7/2}$ photoelectron spectra of the samples studied; Table 3 presents data on the binding energies, from which, according to [12], it follows that the Pt atoms are both in the Pt(IV) and in the Pt(III) states, which is the result of a partial decomposition of the compound under the action of X-rays during spectra recording.

The obtained Pt(IV) complexes are promising because they not only allow to prepare new platinum perfluorocarboxylate complexes but also can be used in the oxidative functionalization of RH alkanes in solutions of Pt(II) and Pt(IV) complexes (Shilov reaction). In aqueous solutions of chloro-complexes, this reaction affords alkyl chlorides RCl and alcohols ROH

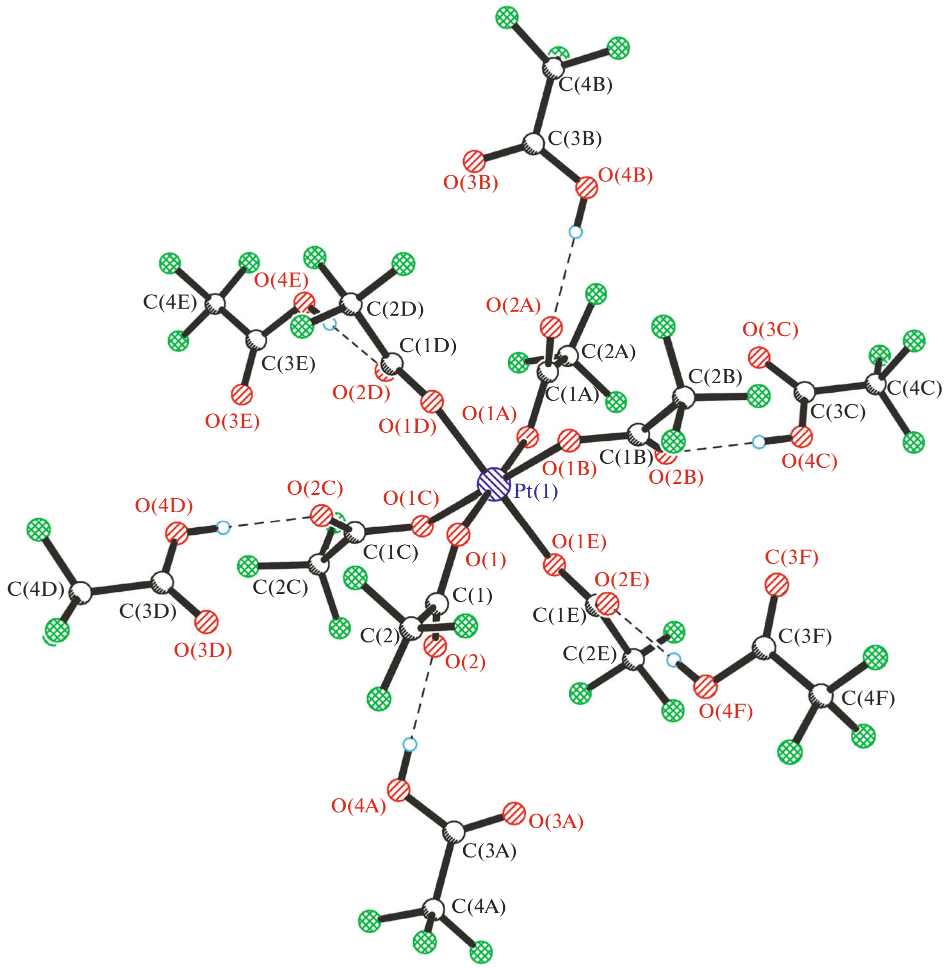

Fig. 1. Dianion $[Pt(O_2CCF_3)_6 \cdot 6CF_3CO_2H]^{2-}$ in **III**. Only the major components of the disordered CF_3 groups are shown. Hydrogen bonds are shown by dotted lines. Selected bond lengths and angles: O(1)–C(1) 1.291(5), O(2)–C(1) 1.205(5) Å, OPtO 82.4(2)° and 97.6(2)°, C(1)O(1)Pt(1) 122.6(3)°, and O(2)···O(4A) 2.689(6) Å.

[13], whereas in aqueous CF_3COOH it results in a mixture of alkyl chlorides, alcohols, and alkyl trifluoroacetates $ROCOCF_3$ [14]. In the presence of *p*-benzoquinone and $CuCl_2$, the catalytic oxidation of alkanes slowly proceeds [15]. Replacing the relatively inert platinum chloro-complexes with labile trifluoroacetate in this reaction should lead to an increase in the reaction rate and preparation of alkyl trifluoroacetates as the main products. Unlike alcohols, alkyl trifluoroacetates are resistant to further oxidation; the CF_3COO group is used in organic chemistry to esterify hydroxyl groups of alcohols preventing from oxidation [16]. The preparation of aliphatic alcohols by hydrolysis of trifluoroacetic acid esters formed during the catalytic oxidation of alkanes has clear advantages over the hydrolysis of alkyl chlorides formed by direct chlorination of alkanes or in the course of the Shilov reaction with the participation of platinum chloro-complexes.

Our experiments showed that under soft conditions Pt(IV) trifluoroacetate complexes easily oxidize saturated alkanes of normal structure as well as cycloalkanes and adamantane in CF_3COOH to form the corresponding trifluoroacetates. A mixture of trifluoroacetates of secondary alcohols is formed from normal hydrocarbons, cyclohexyl trifluoroacetate—from cyclohexane, and 1-adamantyl trifluoroacetate—from adamantane. In the course of the reaction, Pt(IV) complexes are reduced to complexes in the mixed oxidation state of platinum, presumably +3, and the solutions darken.

In the presence of trifluorone acetic acid and $K_2[Pt(CF_3COO)_6]$ or $[Pt(CF_3COO)_4]_n$, the oxidation reaction of cyclohexane and *n*-alkanes (*n*-pentane, *n*-hexane, *n*-heptane, etc.) proceeds catalytically to form the corresponding trifluoroacetates. It is noteworthy that, unlike the original Shilov’ reaction, no trifluoroacetates of primary alcohols are among the products of the oxidation of *n*-alkanes. It is known that the activation of the C–H bond of alkanes in the

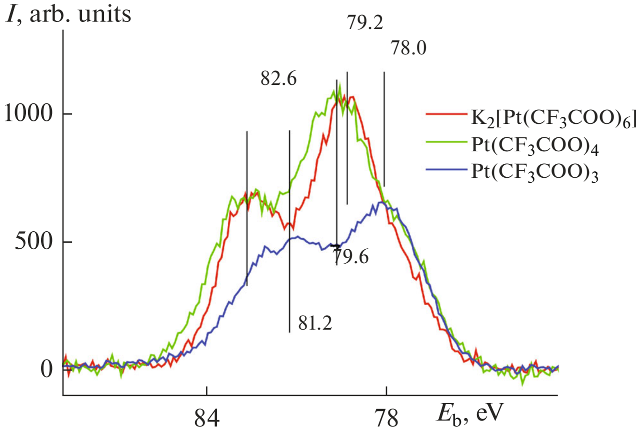

Fig. 2. Pt4*f* photoelectron spectra of the samples studied.

Shilov's reaction occurs when Pt(II) chlorocomplexes participate, whereas Pt(IV) complexes are oxidizing agents. Obviously, under our conditions, the mechanism of the reaction between complexes and hydrocarbons is different from the mechanism of the Shilov's reaction, since no Pt(II) complexes form in the reaction mixture.

CONCLUSIONS

The obtained results indicate the high reactivity of the obtained Pt(IV) compounds with respect to inert hydrocarbons such as alkanes. These compounds can be applied in organic synthesis for introducing the CF_3COO substituent instead of the hydrogen atom of the secondary and tertiary carbon atoms of alkanes, cycloalkanes, and frame compounds like adamantane.

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REFERENCES

1. M. A. A. F. Carrondo and A. C. Skapski, Acta Crystallogr., Sect. B **34**, 1857 (1978).
2. M. A. A. F. Carrondo and A. C. Skapski, Acta Crystallogr., Sect. B **34**, 3576 (1978).
3. R. I. Rudyi, N. V. Cherkashina, G. Ya. Mazo, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 754 (1980).
4. T. G. Appleton, K. A. Byriel, J. M. Garrett, et al., Inorg. Chem. **34**, 5646 (1995).
5. N. V. Gerbeleu, G. A. Timko, K. M. Indrichan, et al., Koord. Khim. **20**, 846 (1994).
6. D. R. Bedgood, Jr., PhD Thesis in chem. (Montana Wtate Univ., Bozeman, Montana, 1991).
7. *Synthesis of Platinum-Group Metal Complexes. Handbook*, Ed. by I. I. Chernyaev (Nauka, Moscow, 1964) [in Russian].
8. *Handbuch der praeparativen anorganischen Chemie*, Ed. by G. Brauer (Ferdinand Enke, Stuttgart, 1975–1981; Mir, Moscow, 1985).
9. G. M. Sheldric, SADABS. Program for Scaling and Correction of Area Detector Data (Univ. of Göttingen, Göttingen, 1997).
10. G. M. Sheldrick, Acta Crystallogr., Sect. A **64**, 112 (2008).
11. B. M. Still, P. G. Anil Kumar, J. R. Aldrich-Wright, et al., Chem. Soc. Rev. **36**, 665 (2007).
12. V. I. Nefedov, *X-ray Electron Spectroscopy of Chemical Compounds* (Khimiya, Moscow, 1984) [in Russian].
13. N. F. Gol'dshleger, V. V. Es'kova, A. E. Shilov, et al., Zh. Fiz. Khim. **46**, 1353 (1972).
14. V. V. Es'kova, A. E. Shilov, and A. A. Shteinman, Kinet. Katal. **13**, 534 (1972).
15. N. F. Gol'dshleger, V. V. Lavrushko, and A. P. Khrushch, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2174 (1976).
16. *Protective Groups in Organic Chemistry*, Ed. by J. F. W. McOmie (Plenum, 1973; Mir, Moscow, 1976).

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