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Tetrapyridineplatinum(II) Carboxylates: Synthesis and Crystal Structure

I. A. Yakushev[a, *, **], M. Yu. Nesterenko[a, b], P. V. Dorovatovskii[c], A. B. Kornev[d], A. D. Maksimova[a, b], A. S. Popova[a, e], N. V. Cherkashina[a], A. V. Churakov[a], and M. N. Vargaftik[a]

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

[b] *Higher Chemical College of the Russian Academy of Sciences, Mendeleev University of Chemical Technology of Russia, Moscow, Russia*

[c] *National Research Center Kurchatov Institute, Moscow, Russia*

[d] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia*

[e] *Peoples' Friendship University of Russia, Moscow, Russia*

**e-mail: ilya.yakushev@igic.ras.ru*

***e-mail: cs68@mail.ru*

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Abstract—A series of mono- and bimetallic cation-anionic complexes based on the $[PtPy_4]^{2+}$ cation with different single-charge anions of carboxylic acids ($RCOO^-$) is synthesized and structurally characterized. A synthetic approach to the preparation of tetrapyridineplatinum complexes $[PtPy_4]^{2+}$ soluble in polar solvents from available reagents is developed. The reaction of tetrapyridineplatinum dichloride $[PtPy_4](Cl)_2$ with silver acetate or trifluoroacetate affords compounds $[PtPy_4](OOCMe)_2 \cdot 6H_2O$ (**I**) and $[PtPy_4](OOCCF_3)_2 \cdot 2H_2O$ (**II**) in the form of crystalline hydrates (CIF files CCDC nos. 2161100 and 2161101, respectively) in high yields. Other carboxylates can be prepared by the treatment of compound **I** with an excess of a stronger acid, for example, trifluoroacetic acid, with the formation of the corresponding complex trifluoroacetate $[PtPy_4](OOCCF_3)_2 \cdot 4CF_3COOH$ (**IIa**) (CIF file CCDC no. 2161102). Another method consists of the displacement of acetic acid with an excess of a lowly volatile acid, for example, pivalic acid, when $[PtPy_4](Piv)_2 \cdot 5HPiv$ (**III**) is formed from the acid melt, and solvatomorph $[PtPy_4](Piv)_2 \cdot 4HPiv \cdot 3C_6H_{12}$ (**IIIa**) (CIF files CCDC nos. 2161103 and 2161104, respectively) is formed in a cyclohexane medium. Heteroanionic heterometallic complex $[PtPy_4](OOCFc)(OOCMe)$ (**IV**) (CIF file CCDC no. 2161105) is shown to be formed by the reaction of complex **I** with ferrocenecarboxylic acid under mild conditions.

Keywords: platinum, cation-anionic complexes, crystalline hydrates, synthesis, X-ray diffraction analysis, crystal chemistry

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INTRODUCTION

The study and modification of coordination compounds of platinum and platinum group metals as a whole and their chemical and physicochemical properties are of interest due to potent value of these compounds for using as precursors of supported catalysts of cracking and reforming of oil fractions [1], for fine chemical synthesis [2, 3], due to biotherapeutic properties [4–7], and as sources of metal-containing ions in reaction mass spectrometry [8, 9].

In many cases, it is important that the synthesized compounds would not contain halides strongly bound to the metal center, which results in a broad use of acetylacetonates [10] or carboxylates of the corresponding metals for synthetic and catalytic applications [11]. However, unlike convenient and available for synthesis palladium acetate $[Pd_3(OOCMe)_6]$ [12, 13], the crystalline form of platinum(II) acetate [14–16] is a lowly soluble, poorly available, and chemically lowly inert compound, which restricts its use for synthetic purposes. Another possible starting compound, acetate platinum blue [17], is efficient in the synthesis of the heterometallic platinum complexes [18–20] and a series of cation-anionic and mononuclear complexes with chelating ligands, for instance, with 1,10-phenanthroline [21], but the synthesis of palladium blue is also difficult.

A possible approach that makes it possible to prepare stable containing no chlorine anions plati-

num(II) carboxylate complexes from available potassium tetrachloroplatinite $K_2[PtCl_4]$, which are highly soluble in polar solvents, for example, water or alcohols, can be the insertion of chemically stable aromatic N-donor ligands (e.g., pyridine (Py)) into the coordination sphere of platinum with the displacement of the strongly bound chloride anion to the outer sphere of the complex followed by binding with silver salts. The present work is devoted to the use of this approach and study of the properties of the synthesized carboxylates of the $[PtPy_4]^{2+}$ cation, including heterometallic carboxylates.

EXPERIMENTAL

The solvents used (pyridine, *n*-hexane, cyclohexane, and diethyl ether) were purified according to standard procedures [22]. Compounds $K_2[PtCl_4]$ (REAKHIM, Russia), silver acetate (MeCOOAg 99%, Sigma-Aldrich), silver trifluoroacetate (CF_3COOAg 98%, Sigma-Aldrich), pivalic acid (Me_3CCOOH 99%, Sigma-Aldrich), trifluoroacetic acid (CF_3COOH 99%, Sigma-Aldrich), and ferrocenecarboxylic acid (FcCOOH, 97%, Sigma-Aldrich) were used as received. The $[PtPy_4]Cl_2\cdot 3H_2O$ cationionic complex was synthesized according to a known procedure [23] and used for the synthesis of the complexes as the starting compound.

Elemental analysis was carried out on a EuroVector EA3000 automated C,H,N analyzer (Italy, 2008). IR spectra were recorded on a Bruker Alpha FTIR spectrometer by the attenuated total internal reflectance (ATR) method in a range of 4000–400 cm^{-1}.

Synthesis of $[PtPy_4](OOCMe)_2\cdot 6H_2O$ (I). A 250-mL beaker was filled with $[PtPy_4]Cl_2\cdot 3H_2O$ (700 mg, 1.2 mmol), and the contents was dissolved in water (40 mL). A weighed sample of silver acetate (400 mg, 2.4 mmol) was placed in a 250-mL beaker and dissolved in water (60 mL) on heating to 25°C. The resulting solution of silver acetate was filtered on a folded filter, and both solutions were mixed together. The formed finely crystalline precipitate of silver chloride was filtered off on a Schott filter. The filtrate was evaporated under reduced pressure to 2 mL and left for crystallization. The yield of transparent crystals of compound **I** was 720 mg (82%).

For $C_{24}H_{38}N_4O_{10}Pt$

Anal. calcd., %	C, 39.08	H, 5.19	N, 7.60
Found, %	C, 39.36	H, 4.71	N, 7.45

IR (ATR; ν, cm^{-1}): 2920 s, 2852 m, 1610 w, 1560 m, 1455 m, 1376 m, 1329 w, 1244 w, 1214 w, 1156 w, 1077 m, 1050 w, 1016 w, 949 w, 919 w, 768 m, 696 m, 617 m, 471 m.

Synthesis of $[PtPy_4](OOCCF_3)_2\cdot 2H_2O$ (II). Compound $[PtPy_4]Cl_2\cdot 3H_2O$ (70 mg, 0.120 mmol) was placed in a 25-mL beaker and dissolved in water (4 mL). A weighed sample of silver trifluoroacetate (40 mg, 0.240 mmol) was placed in a 25-mL beaker and dissolved in water (6 mL) on heating to 25°C. The resulting solution of silver trifluoroacetate was filtered on a folded filter to remove impurities, and both solutions were mixed. The formed precipitate of silver chloride AgCl was filtered off, and an aqueous solution of the complex was evaporated under reduced pressure to form a crystalline mixture. The yield of the product was 92 mg (98%).

For $C_{24}H_{24}N_4O_6F_6Pt$

Anal. calcd., %	C, 37.26	H, 3.13	N, 7.24
Found, %	C, 37.07	H, 3.42	N, 6.89

IR (ATR; ν, cm^{-1}): 3176 br.w, 3364 br.w, 3103 w, 3079 w, 3032 w, 1679 s, 1608 m, 1482 w, 1455 m, 1417 w, 1375 w, 1172 s, 1150 s.

Synthesis of $[PtPy_4](OOCCF_3)_2\cdot 4(OOCCF_3)$ (IIa). A weighed sample of complex **I** (74 mg, 0.1 mmol) was placed in a 25-mL round-bottom flask and dissolved in water (1 mL). A 50% solution of trifluoroacetic acid in water (3 mL) was poured to the obtained solution, and the mixture was heated in a steam bath with a reflux condenser for 1 h and evaporated to dryness. Then 100% trifluoroacetic acid (3 mL) was added followed by heating. A transparent solution formed due to the reaction was concentrated to 1 mL and left for crystallization. Colorless transparent crystals of compound **IIa** was decanted and washed with cold diethyl ether. The yield of compound **IIa** was 103 mg (86%).

For $C_{32}H_{24}N_4O_{12}F_{18}Pt$

Anal. calcd., %	C, 32.20	H, 2.03	N, 4.69
Found, %	C, 32.31	H, 2.10	N, 4.57

IR (ATR; ν, cm^{-1}): 1782 br.m, 1701 w, 1613 w, 1459 m, 1317 w, 1195 m, 1143 s, 1077 m, 1021 w, 787 m, 768 s, 693 s, 608 w, 591 w, 516 w, 475 w.

Synthesis of $[PtPy_4](OOCCMe_3)_2\cdot 5HPiv$ (III). A weighed sample of complex **I** (200 mg, 0.27 mmol) was placed in a 50-mL round-bottom flask, and pivalic acid (4 g, 39.16 mmol) was added. The reaction mixture was heated at 90°C in an oil bath for 2 h using magnetic stirring with a reflux condenser. A crystalline precipitate was formed on slow cooling of the pivalic acid melt. The precipitate was washed from a pivalic

acid excess by consecutive washing with *n*-hexane and cold diethyl ether. The yield of the product was 295 mg (89%).

For $C_{55}H_{88}N_4O_{14}Pt$

Anal. calcd., %	C, 53.95	H, 7.24	N, 4.56
Found, %	C, 53.81	H, 7.55	N, 4.36

IR (ATR; ν, cm^{-1}): 3101 w, 3034 w, 2958 w, 2930 w, 2869 w, 1733 w, 1701 m, 1665 w, 1611 m, 1562 m, 1479 m, 1458 w, 1391 w, 1279 w, 1184 m, 1149 m, 1078 m, 1018 m, 934 m, 885 m, 862 m, 774 m, 700 s, 603 m, 529 m, 521 m, 403 m.

Synthesis of $[PtPy_4](OOCCMe_3)_2 \cdot 4HPiv \cdot 3C_6H_{12}$ (IIIa). A weighed sample of complex **I** (150 mg, 0.2 mmol) was placed in a 50-mL round-bottom flask, and a solution of pivalic acid (102 mg, 1 mmol) in cyclohexane (10 mL) was added. The resulting solution was refluxed in an oil bath for 1 h, evaporated on a rotary evaporator until an oily liquid formed, and left for crystallization. After 2 days, large transparent crystals were observed, separated by decantation, and dried in an argon flow from a solvent excess. The yield of platy crystals was 210 mg (75%).

For $C_{68}H_{114}N_4O_{12}Pt$

Anal. calcd., %	C, 59.87	H, 8.03	N, 4.01
Found, %	C, 59.38	H, 8.42	N, 4.13

IR (ATR; ν, cm^{-1}): 2955 m, 2925 s, 2851 m, 1728 m, 1701 s, 1630 m, 1562 w, 1479 s, 1455 s, 1409 w, 1391 w, 1361 m, 1279 m, 1185 s, 1151 s, 1076 s, 936 w, 862 s, 797 s, 773 s, 754 s, 700 s, 662 w, 604 m, 584 w, 523 s, 475 w, 449 w, 405 m.

Synthesis of $[PtPy_4](OOCFc)(OOCMe) \cdot 6H_2O$ (IV). Ferrocenecarboxylic acid FcCOOH (40 mg, 0.173 mmol) was placed in a 50-mL beaker, and the contents was dissolved in methanol (13 mL). The resulting solution was filtered from insoluble impurities on a folded filter, and compound **I** (54 mg, 0.073 mmol) in methanol (20 mL) was added. The obtained solutions were mixed and filtered on a folded filter from possible mechanical impurities. Yellow crystals isolated upon slow dryness of the solution were decanted from the mother liquor, washed with *n*-hexane, and dried in air. The yield of the product was 24 mg (34%).

For $C_{33}H_{44}FeN_4O_{10}Pt$

Anal. calcd., %	C, 43.67	H, 4.89	N, 6.17
Found, %	C, 43.71	H, 4.69	N, 5.87

IR (ATR; ν, cm^{-1}): 3375 br.w, 3097 w, 1649 m, 1608 m, 1555 m, 1455 m, 1384 m, 1343 m, 1321 m, 1279 m, 1217 m, 1156 m, 1106 m, 1077 m, 1052 m, 1025 m, 933 m, 914 m, 821 m, 769 m, 739 m, 696 m, 597 m, 562 s.

X-ray diffraction (XRD). The XRD data for complex **I** were obtained on the Belok beamline at the Kurchatov synchrotron radiation source of the National Research Center Kurchatov Institute (Moscow, Russia) in the φ scan mode using a Rayonix SX165 CCD detector at 100 K (λ = 0.74500 Å) [24]. Unit cell parameters were determined and refined, reflections were integrated, and a reflection intensity absorption correction was applied using the XDS software [25].

The XRD data for complexes **II**–**IV** were obtained on a Bruker D8 Venture Photon diffractometer in the φ and ω scan modes at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) at 100 K (150 K for crystals of compound **IIa**) at the X-ray radiation wavelength λ = 0.71073 Å using an Incoatec IμS 3.0 microfocus X-ray radiation source. In the case of complex **III**, the experiment was carried out at λ = 1.54178 Å. Primary indexing, unit cell parameter refinement, and reflection integration were carried out using the Bruker APEX3 software [26]. A reflection intensity absorption correction was applied using the SADABS software [26].

The structures of complexes **I**–**IV** were solved by direct methods [27] and refined in the anisotropic approximation by least squares for F^2 for all non-hydrogen atoms [28] except for fluorine atoms in the lower disordering component of the CF_3 group of the trifluoroacetic acid molecule in complex **IIa** and partially occupied position of the cocrystallization pivalic acid molecule in complex **III**. The disordered positions of the atoms of the trifluoroacetate groups in complex **II** were refined using restraints imposed on the geometric parameters of the model (SADI rules), and the strongly disordered *tert*-butyl groups of the pivalate anions and neutral pivalic acid in complex **III** were refined using restraints on geometric parameters (SADI, DFIX, FLAT) and thermal shifts of atoms (SIMU, RIGU).

Hydrogen atoms were placed in the calculated positions and refined by the riding model with $U_{eq}(H) = 1.5U_{eq}(C)$ for the hydrogen atoms of the methyl groups and $1.2U_{eq}(C)$ for the hydrogen atoms of pyridine and cyclohexane. The positions of the hydrogen atoms of water, pivalic acid, and trifluoroacetic acid involved in hydrogen bond formation were revealed from the electron density map and refined in the isotropic approximation without geometric restraints in the case of

complexes **II** and **IIa** and using geometric restraints in the case of complexes **I**, **III**, **IIIa**, and **IV** (DFIX or SADI rules).

The calculations were performed using the SHELXTL software [28] in the OLEX2 visualization and data processing medium [29].

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2161100–2161105 for compounds **I**–**IV**, respectively) and are available at ccdc.cam.ac.uk/structures (deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The popular method for the synthesis of molecular [23], cation-ionic [30], and mono- and bimetallic [31] platinum complexes is the use of $K_2[PtCl_4]$ as the platinum source at the initial stages of the synthesis. At the same time, the common products of these reactions are the chlorine-containing complexes of the general structure $[PtL_2Cl_2]$, $[PtL_4](Cl)_2$, or $[Pt(LH)_2L_2]$ (in the case of the possible deprotonation of nitrogen-containing ligand LH), and these compounds can save as convenient "building blocks" for the preparation of heterometallic complexes [32]. The approaches to the preparation of the acetate and carboxylate systems as a whole and their chemical properties are less studied [33], although some noble metal carboxylates were shown to be capable of transferring to the gas phase [34] and the platinum complexes with pyridine are highly volatile [9], and the chemical nature and composition of the anion play an important role in the formation of metal-containing ions.

It is known that $K_2[PtCl_4]$ easily enters complex formation reactions with the N-donor ligands [23], which makes it possible to separate platinum from potassium at the first stage to obtain the platinum complexes of the cis structure, and the cation-anionic complex can be isolated at the second stage

$$K_2[PtCl_4] + 2Py \rightarrow [cis\text{-}Py_2PtCl_2] + 2KCl, \quad (1)$$

$$[cis\text{-}Py_2PtCl_2] + Py\,(exc.) \rightarrow [PtPy_4](Cl)_2. \quad (2)$$

Compound $[PtPy_4](Cl)_2$ is a convenient starting reagent for ion exchange reactions and substitution of chloride anions by other carboxylate (acetate or trifluoroacetate) anions using soluble silver salts MeCOOAg or CF_3COOAg, respectively

$$[PtPy_4](Cl)_2 + 2MeCOOAg \rightarrow [PtPy_4](OOCMe)_2 + 2AgCl. \quad (3)$$

Complex $[PtPy_4](OOCMe)_2$ (**I**) remains in the solution due to its high solubility and can be isolated by concentrating as crystals of hexahydrate $[PtPy_4](OOCMe)_2\cdot 6H_2O$ (Fig. 1). According to the XRD data, the crystals have the triclinic space group $P\bar{1}$, and the platinum atom Pt(1) lies on the inversion center.

As a whole, the structure is formed by discrete cations $[PtPy_4]^{2+}$ and acetate anions bound to the water molecules via hydrogen bonds that do not enter the nearest coordination environment of the platinum atoms: the shortest Pt(1)–O(1) distance to the oxygen atoms of the anion is 4.785(2) Å, which excludes any direct interaction between the central platinum atom of the cation and acetate anions. The cation itself exhibits the expected planar square environment of the platinum atoms and corresponding nitrogen atoms of coordinated pyridine with the Pt(1)–N interatomic distance equal to 2.020(2)–2.025(2) Å, which is characteristic of this cation [35]. The angle between the basal planes of the adjacent molecules of coordinated pyridine is 83.52(8)°, and the interplanar angles formed by four nitrogen atoms of the cation and pyridine planes N(1)C(1)C(2)C(3)C(4)C(5) and N(2)C(6)C(7)C(8)C(9)C(10) are 66.35(9)° and 72.23(9)°, respectively (detailed information about the interatomic distances and angles in the crystals of complexes **I**–**IV** is given in Tables 1–3). Water of crystallization forms numerous hydrogen bonds between both molecules of water itself and water molecules and acetate anions and separates the layers of cations and anions in the structure of complex **I** (Fig. 2), and the shortest distance between the platinum atoms of the adjacent cations is 8.6555(10) Å. The hydrogen bond parameters in the structures of compounds **I**–**IV** are given in Table 4.

Complex $[PtPy_4](OOCCF_3)_2\cdot 2H_2O$ (**II**) (Fig. 3) can be synthesized using a similar procedure by the exchange reaction with silver trifluoroacetate. As shown earlier, this complex can form platinum-containing cations in the gas phase upon thermolysis under the conditions of mass spectrometric experiment [9]. The complex was isolated in the solid phase as dihydrate $[PtPy_4](OOCCF_3)_2\cdot 2H_2O$ that crystallizes in the triclinic space group $P\bar{1}$ with the main geometric parameters of the cation close to those of acetate complex **I** (Tables 1–3).

The most distinction from the structure of complex **I** is the relatively short Pt(1)–O(1S) contact with an interatomic distance of 3.3315(11) Å between the platinum atom and neutral molecule of water of crystallization. This is less than the sum of the crystallographic van der Waals radii (3.60 Å) of platinum and oxygen of the water molecule (2.05 and 1.55 Å for Pt

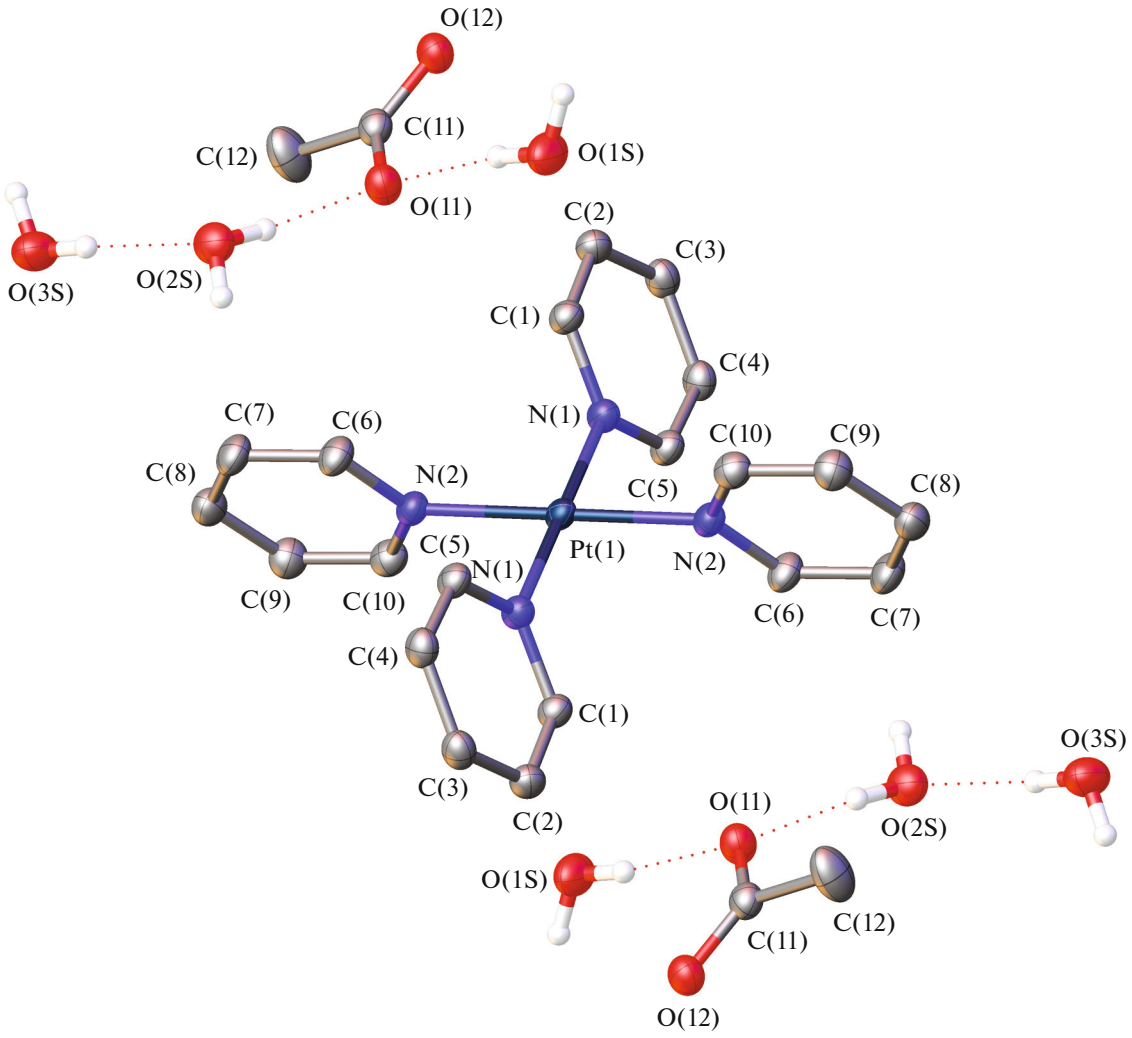

Fig. 1. Structure and numeration scheme of atoms in $[PtPy_4](OAc)_2 \cdot 6H_2O$ (**I**). Thermal parameters of atomic shifts are shown with 50% probability. Hydrogen atoms of methyl groups and pyridine are omitted.

and O, respectively) [36]. The oxygen atom enters into the direct coordination environment of platinum similarly to the chloride anions that occupy pseudo-axial positions in the platinum complexes with substituted pyridines [37].

The presented synthetic scheme of reactions (1)–(3) makes it possible to obtain trifluoroacetate or acetate with the tetrapyridineplatinum(II) cation, and other complexes can be synthesized from complex **I** by displacement with the stronger trifluoroacetic acid on heating. One of the expected products of the reaction of compound **I** with a strong acid under these conditions is mononuclear complex *trans*-$[Py_2Pt(OOCCF_3)_2]$. However, even after prolong heating, only one product $[PtPy_4](OOCCF_3)_2 \cdot 4CF_3COOH$ (**IIa**) (Fig. 4) was isolated from the reaction mixture as large colorless crystals. According to the XRD data, they crystallize in the monoclinic space group *C*2/*c*. Analogously to the structure of compound **II**, a shortened contact is observed between the platinum atom and oxygen atom of neutral crystallization trifluoroacetic acid: Pt(1)–O(11) with an interatomic distance of 3.327(2) Å. Very short (2.451(3) Å) hydrogen bonds O(12)–H(12)...O(22) were also found in the structure. They are additionally shortened probably due to the electrostatic interaction of the cation with the anion via the neutral trifluoroacetic acid molecule.

At the same time, the synthesis of other carboxylates via Scheme (1)–(3) is also difficult because of a low solubility of pivalates and other silver salts. Nevertheless, the corresponding complex pivalate $[PtPy_4](Piv)_2 \cdot 5HPiv$ (**III**) (Fig. 5), which is in fact a

Table 1. Crystallographic data and structure refinement parameters for complexes **I**–**IV**

Parameter	Value					
	I	**II**	**IIa**	**III**	**IIIa**	**IV**
Empirical formula	$C_{24}H_{38}N_4O_{10}Pt$	$C_{24}H_{24}N_4O_6F_6Pt$	$C_{32}H_{24}N_4O_{12}F_{18}Pt$	$C_{55}H_{88}N_4O_{14}Pt$	$C_{68}H_{114}N_4O_{12}Pt$	$C_{33}H_{44}FeN_4O_{10}Pt$
FW	737.67	773.56	1193.64	1224.38	1374.72	907.66
Color, habitus	Colorless, prism	Colorless, prism	Colorless, prism	Colorless, prism	Colorless, prism	Yellow, prism
Crystal sizes, mm	0.130 × 0.090 × 0.070	0.180 × 0.120 × 0.080	0.210 × 0.180 × 0.070	0.11 × 0.08 × 0.06	0.160 × 0.120 × 0.050	0.090 × 0.060 × 0.030
Temperature, K	100(2)	100(2)	150(2)	100(2)	100(2)	100(2)
Wavelength, Å	0.74500	0.71073	0.71073	1.54178	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space groups	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Cell parameters:						
a, Å	8.6555(10)	8.8531(10)	17.8771(7)	10.9121(4)	9.7905(4)	8.9771(3)
b, Å	8.8755(6)	8.9945(10)	8.8732(3)	30.9854(11)	10.9315(5)	23.0823(7)
c, Å	10.2893(12)	9.3613(10)	26.9228(10)	9.5472(3)	18.0503(8)	17.3209(5)
α, deg	102.117(19)	115.172(3)	90	90	72.6081(15)	90
β, deg	109.968(7)	90.525(3)	99.0870(10)	96.541(2)	74.7082(14)	101.5124(10)
γ, deg	91.651(4)	92.056(3)	90	90	82.7696(14)	90
V, Å^3	722.02(14)	673.96(13)	4217.1(3)	3207.05(19)	1775.92(14)	3516.89(19)
Z	1	1	4	2	1	4
ρ_{calc}, g/cm^3	1.697	1.906	1.880	1.268	1.285	1.714
μ, mm^{-1}	5.519	5.293	3.470	4.574	2.034	4.447
F(000)	368	376	2320	1272	724	1816
θ_{min}–θ_{max}, deg	2.640–31.009	2.303–30.757	2.307–30.557	2.852–66.754	1.955–27.446	2.134–30.569
Ranges of reflections indices	$-11 \le h \le 11$, $-12 \le k \le 12$, $-14 \le l \le 14$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-13 \le l \le 13$	$-25 \le h \le 25$, $-12 \le k \le 12$, $-38 \le l \le 38$	$-12 \le h \le 12$, $-36 \le k \le 36$, $-11 \le l \le 11$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-23 \le l \le 23$	$-12 \le h \le 12$, $-33 \le k \le 32$, $-24 \le l \le 24$
Measured reflections	16918	90781	32676	32911	34342	66794
Independent reflections (R_{int})	3916 (0.0187)	4219 (0.0392)	6464 (0.0348)	5654 (0.0447)	8126 (0.0514)	10773 (0.0436)
Reflections with $I > 2\sigma(I)$	3916	4219	4778	4796	8081	9172
Reflections/restraints/parameters	3916/6/198	6464/15/325		5654/224/412	8126/1/439	10773/11/461
GOOF	1.113	1.058	1.062	1.319	1.050	1.096
R factors for $I > 2\sigma(I)$	$R_1 = 0.0195$, $wR_2 = 0.0492$	$R_1 = 0.0098$, $wR_2 = 0.0256$	$R_1 = 0.0265$, $wR_2 = 0.0455$	$R_1 = 0.0552$, $wR_2 = 0.1155$	$R_1 = 0.0308$, $wR_2 = 0.0729$	$R_1 = 0.0312$, $wR_2 = 0.0629$
R factors for all reflections	$R_1 = 0.0195$, $wR_2 = 0.0492$	$R_1 = 0.0098$, $wR_2 = 0.0256$	$R_1 = 0.0465$, $wR_2 = 0.0495$	$R_1 = 0.0670$, $wR_2 = 0.1198$	$R_1 = 0.0313$, $wR_2 = 0.0731$	$R_1 = 0.0403$, $wR_2 = 0.0656$
Residual electron density (min/max), e Å^{-3}	−1.104/0.869	−0.793/0.771	−0.760/0.511	−0.544/1.165	−1.203/1.079	−1.489/1.019

Table 2. Selected interatomic distances and angles in the structures of complexes **I**–**IV**

Distances, Å	**I**	**II**	**IIa**	**III**	**IIIa**	Distances, Å	**IV**
Pt(1)–N(1)	2.020(2)	2.0232(9)	2.019(2)	2.010(5)	2.018(2)	Pt(1)–N(4)	2.017(2)
Pt(1)–N(1)$^{\#1}$	2.020(2)	2.0232(9)	2.019(2)	2.010(5)	2.018(2)	Pt(1)–N(1)	2.021(2)
Pt(1)–N(2)	2.025(2)	2.0218(9)	2.0181(19)	2.018(4)	2.017(2)	Pt(1)–N(3)	2.022(2)
Pt(1)–N(2)$^{\#1}$	2.025(2)	2.0218(9)	2.0182(19)	2.018(4)	2.017(2)	Pt(1)–N(2)	2.023(2)
Angles, deg						Angles, deg	
N(1)Pt(1)N(1)$^{\#1}$	180.0	180.00(5)	180.0	180.00(11)	180.0	N(4)Pt(1)N(1)	90.81(10)
N(1)Pt(1)N(2)	88.48(8)	91.83(4)	88.39(8)	89.70(18)	90.81(9)	N(4)Pt(1)N(3)	89.44(10)
N(1)$^{\#1}$Pt(1)N(2)	91.52(8)	88.17(4)	91.61(8)	90.29(18)	89.19(9)	N(1)Pt(1)N(3)	178.81(10)
N(1)Pt(1)N(2)$^{\#1}$	91.52(8)	88.17(4)	91.61(8)	90.29(18)	89.19(9)	N(4)Pt(1)N(2)	177.25(10)
N(1)$^{\#1}$Pt(1)N(2)$^{\#1}$	88.48(8)	91.83(4)	88.39(8)	89.70(18)	90.81(9)	N(1)Pt(1)N(2)	89.56(10)
N(2)Pt(1)N(2)$^{\#1}$	180.0	179.999(19)	180.0	180.0	180.0	N(3)Pt(1)N(2)	90.25(10)
Symmetry procedures	$-x+2$, $-y+1$, $-z+2$	$-x$, $-y+1$, $-z$	$-x+1$, $-y+1$, $-z+1$	$-x$, $-y+1$, $-z+1$	$-x+1$, $-y+1$, $-z+1$		

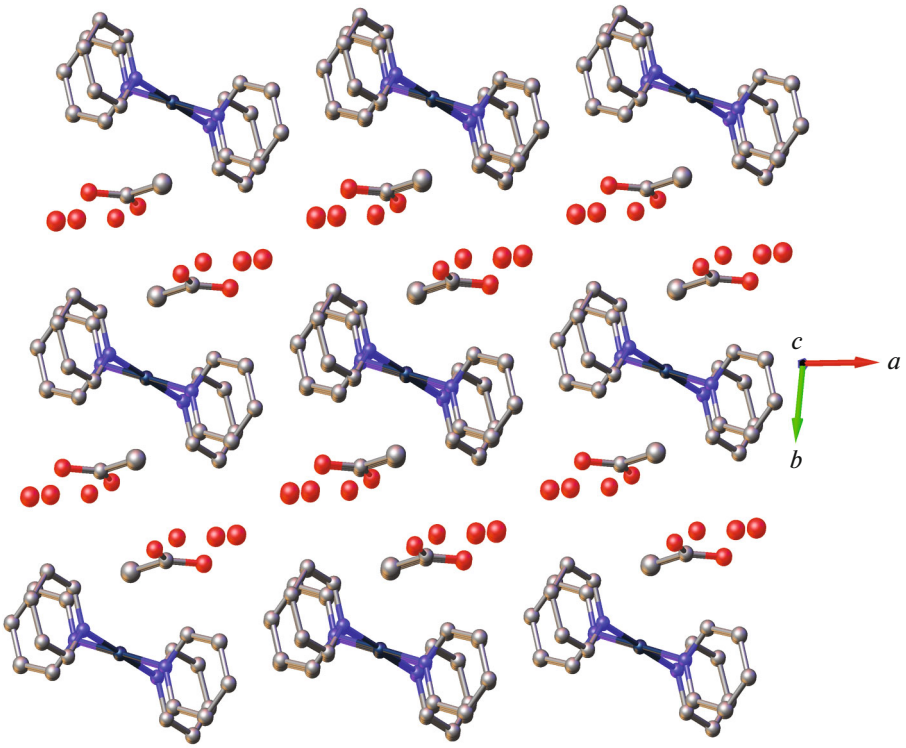

Fig. 2. Fragment of the crystal packing of complex **I** (view along with the *c* crystallographic axis).

Table 3. Selected torsion angles (φ) in the structures of complexes **I**–**IV**

Angle	φ, deg
I	
Pt(1)N(1)C(11)C(12)	178.18(18)
Pt(1)N(1) C(15)C(14)	−179.69(18)
Pt(1)N(2)C(21)C(22)	177.8(2)
Pt(1)N(2)C(25)C(24)	−179.02(19)
II	
Pt(1)N(1)C(11)C(12)	178.01(8)
Pt(1)N(1)C(15)C(14)	−177.69(9)
Pt(1)N(2)C(21)C(22)	177.53(8)
Pt(1)N(2)C(25)C(24)	−176.81(8)
IIa	
Pt(1)N(1)C(1)C(2)	−177.9(2)
Pt(1)N(1)C(5)C(4)	177.9(2)
Pt(1)N(2)C(6)C(7)	−177.1(2)
Pt(1)N(2)C(10)C(9)	176.6(2)
III	
Pt(1)N(1)C(1)C(2)	177.5(6)
Pt(1)N(1)C(5)C(4)	−177.9(5)
Pt(1)N(2)C(6)C(7)	178.9(5)
Pt(1)N(2)C(10)C(9)	−177.8(5)
IIIa	
Pt(1)N(1)C(1)C(2)	176.5(2)
Pt(1)N(1)C(5)C(4)	−177.0(2)
Pt(1)N(2)C(6)C(7)	175.7(2)
Pt(1)N(2)C(10)C(9)	−175.9(2)
IV	
Pt(1)N(1)C(1)C(2)	177.9(2)
Pt(1)N(1)C(5)C(4)	−177.7(2)
Pt(1)N(2)C(6)C(7)	179.3(2)
Pt(1)N(2)C(10)C(9)	−179.5(2)
Pt(1)N(3)C(11)C(12)	−179.1(2)
Pt(1)N(3)C(15)C(14)	179.2(2)
Pt(1)N(4)C(16)C(17)	−179.4(2)
Pt(1)N(4)C(20)C(19)	178.7(2)

cocrystallizate of $[PtPy_4](Piv)_2$ with pivalic acid, was prepared on heating in a high yield by the treatment of complex **I** with molten pivalic acid being less volatile and substantially weaker than acetic acid. A change in the reaction conditions, including the replacement of the solvent by cyclohexane inert toward the reagents and a decrease in the ratio of the starting complex and pivalic acid to 1 : 5, results in a change in the composition of the synthesized final complex $[PtPy_4](OOCCMe_3)_2 \cdot 4HPiv \cdot 3C_6H_{12}$ (**IIIa**) (Fig. 6), and a fraction of neutral pivalic acid is substituted by a cyclohexane molecule. Both complexes **III** and **IIIa** that crystallize in the monoclinic space groups $P2_1/c$ and $P\bar{1}$, respectively, include a similar structural motif of interaction of the $[PtPy_4]^{2+}$ cations, pivalic acid, and its anions. Each structure contains the neutral acid in the sphere of coordination interaction of the platinum atoms via the carbonyl oxygen atom O(11) at a Pt(1)–O(11) distance of 3.301(5)–3.322(2) Å, and the hydroxyl group O(12)–H(12) of the acid forms the O(12)–H(12)...O(21) hydrogen bond with the anion. In turn, one more pivalic acid molecule coordinates to each anion also due to the O(32)–H(32)...O(22) hydrogen bond, which predetermines the composition of cocrystallizate **III** and its solvatomorph **IIIa**.

Interestingly, attempts to insert metal-containing carboxylic acid (ferrocenecarboxylic) into the anionic moiety of the complex under mild conditions (without heating) via the interaction of complex **I** with an equimolar amount of FcCOOH resulted in the isolation of heteroanionic complex crystalline hydrate $[PtPy_4](FcCOO)(OOCMe) \cdot 6H_2O$ (Fig. 7), which is the product of displacement of one acetate anion and its replacement by the ferrocenecarboxylate ion. This highly soluble heterometallic compound crystallizes in the monoclinic space group $P2_1/n$, and all atoms of the independent part of the unit cell and its cationic moiety $[PtPy_4]^{2+}$ are in the general position, unlike all complexes considered above. The Pt(1)–O(1S) interatomic distance is 3.286(3) Å, which is somewhat less than those in compounds **I**–**III**. In the anionic moiety of the molecule, the acetate anion is located closer to the platinum atom than the ferrocenecarboxylate ion, whose metal center (Fe(1)), in turn, forms the heterometallic structure with three shortest interatomic distances Pt(1)–Fe(1) (6.2597(5), 6.5891(5), and 7.0083(5) Å).

Thus, the possibility of synthesizing the highly soluble Pt(II) complexes via the synthesis of the corresponding carboxylates was shown. The series of new coordination platinum compounds was synthesized: acetate $[PtPy_4](OOCMe)_2 \cdot 6H_2O$ (**I**), trifluoroacetate $[PtPy_4](OOCCF_3)_2 \cdot 2H_2O$ (**II**), pivalate

Table 4. Hydrogen bond parameters in compounds **I**–**IV**

D–H...A	Symmetry transform	Distance, Å			Angle DHA, deg
		D–H	H–A	D...A	
		I			
O(2S)–H(2S*A*)...O(1)		0.825(19)	1.90(2)	2.719(3)	174(4)
O(2S)–H(2S*B*)...O(1S)	$-x+2, -y+2, -z+2$	0.804(19)	1.95(2)	2.746(3)	173(4)
O(3S)–H(3S*B*)...O(2S)		0.816(19)	1.95(2)	2.766(3)	175(5)
O(3S)–H(3S*A*)...O(2)	$-x+2, -y+2, -z+1$	0.821(19)	1.920(19)	2.741(3)	178(5)
O(1S)–H(1S*A*)...O(1)		0.816(19)	1.88(2)	2.692(3)	171(5)
O(1S)–H(1S*B*)...O(3S)	$x-1, y, z$	0.816(19)	1.93(2)	2.744(3)	174(5)
		II			
O(1S)–H(1S*A*)...O(12)	$-x, -y, -z$	0.84(2)	1.93(2)	2.7544(14)	164(2)
O(1S)–H(1S*B*)...O(11)		0.80(2)	2.04(2)	2.7644(15)	150(2)
		IIa			
O(12)–H(12)...O(22)		1.08(5)	1.38(5)	2.451(3)	178(5)
O(32)–H(32)...O(21)		0.99(6)	1.65(6)	2.633(3)	170(5)
		III			
O(12)–H(12)...O(21)		0.846(14)	1.67(2)	2.501(6)	167(9)
O(32)–H(32)...O(22)		0.85(2)	1.72(3)	2.559(7)	172(12)
O(42)–H(42)...O(31)		0.84	2.21	2.903(15)	139.7
		IIIa			
O(12)–H(12)...O(21)		0.99(3)	1.52(4)	2.487(3)	165(5)
O(32)–H(32)...O(22)		0.99(3)	1.61(4)	2.574(3)	165(4)
		IV			
O(4S)–H(4S*B*)...O(2)	$x+1, y, z$	0.827(19)	1.97(2)	2.788(3)	172(4)
O(4S)–H(4S*A*)...O(5S)		0.821(19)	1.948(19)	2.767(3)	175(4)
O(5S)–H(5S*B*)...O(1)		0.807(19)	1.943(19)	2.748(3)	175(4)
O(5S)–H(5S*A*)...O(1*A*)		0.838(18)	1.94(2)	2.738(3)	158(4)
O(3S)–H(3S*B*)...O(2S)	$-x+1, -y+1, -z+1$	0.84	1.98	2.737(5)	149.3
O(3S)–H(3S*A*)...O(6S)	$x+1, y, z$	0.84	1.95	2.787(4)	172.0
O(2S)–H(2S*B*)...O(3S)		0.84	1.91	2.740(5)	170.5
O(2S)–H(2S*A*)...O(2*A*)		0.84	1.91	2.730(5)	165.9
O(1S)–H(1S*B*)...O(2)	$x+1, y, z$	0.840(19)	1.99(3)	2.772(3)	155(5)
O(1S)–H(1S*A*)...O(2*A*)		0.840(19)	1.95(2)	2.754(4)	160(5)
O(6S)–H(6S*B*)...O(1)		0.84	2.20	2.956(4)	149.8
O(6S)–H(6S*A*)...O(1*A*)		0.84	1.87	2.698(5)	168.6

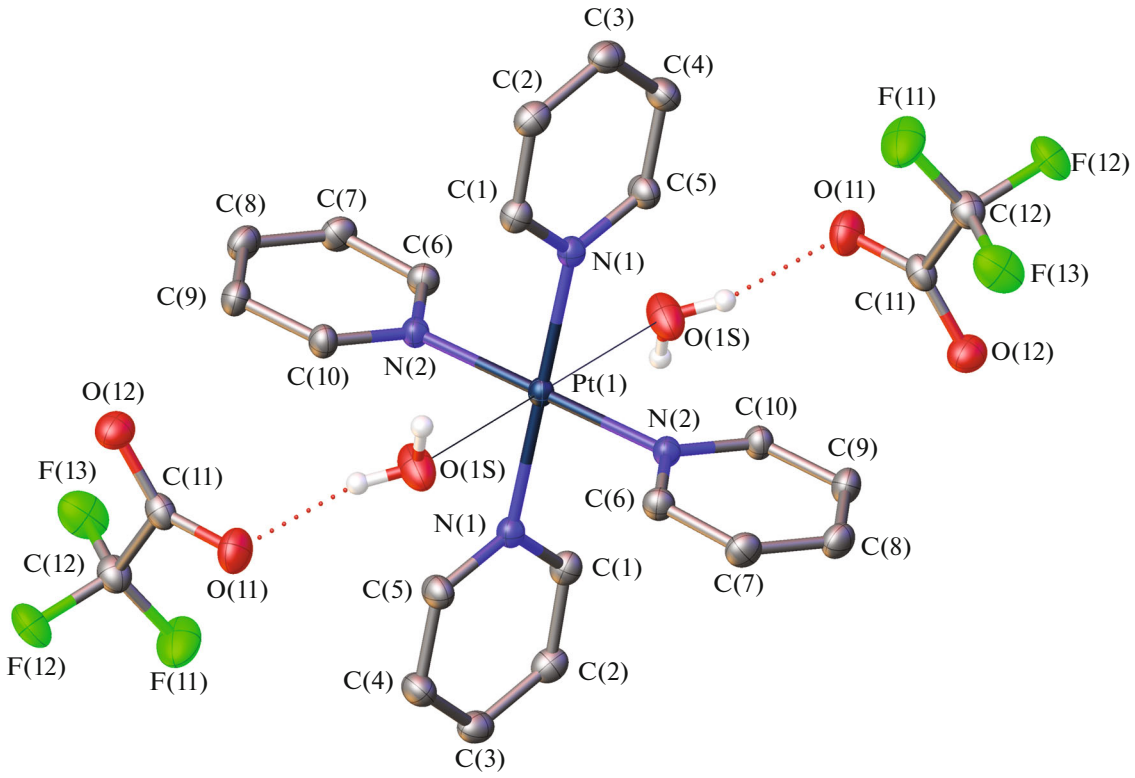

Fig. 3. Structure and numeration scheme of atoms in $[PtPy_4](OOCCF_3)_2 \cdot 2H_2O$ (**II**). Thermal parameters of atomic shifts are shown with 50% probability. Hydrogen atoms of pyridine are omitted.

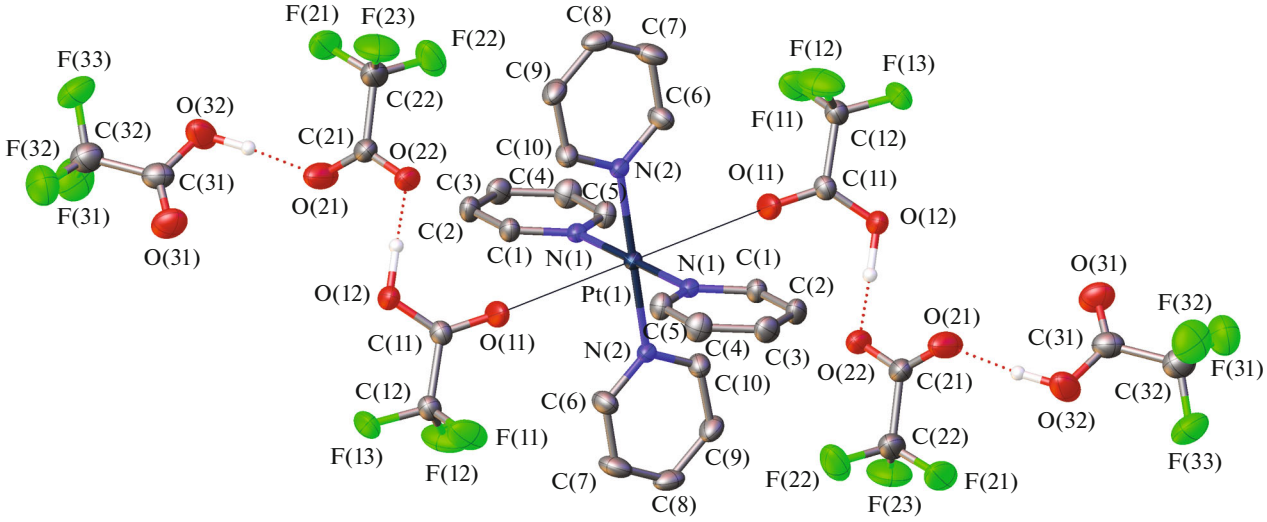

Fig. 4. Structure and numeration scheme of atoms in $[PtPy_4](OOCCF_3)_2 \cdot 4CF_3COOH$ (**IIa**). Thermal parameters of atomic shifts are shown with 50% probability. Hydrogen atoms of pyridine are omitted.

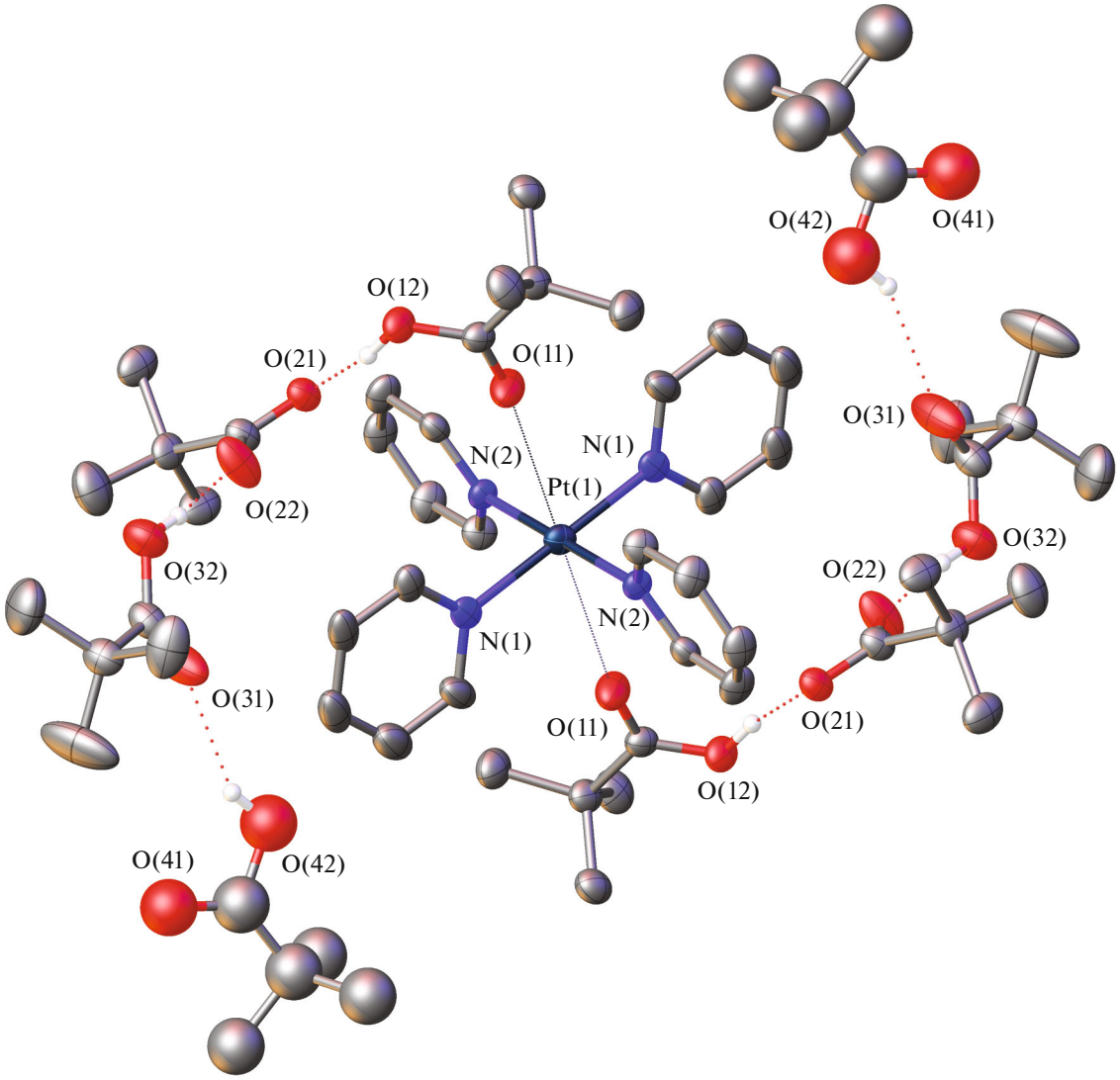

Fig. 5. Molecular structure and numeration scheme of heteroatoms in $[PtPy_4](Piv)_2 \cdot 5HPiv$ (**III**). Hydrogen atoms of methyl groups and pyridine are omitted. Thermal ellipsoids are given with 30% probability.

$[PtPy_4](Piv)_2 \cdot 5HPiv$ (**III**) and its solvatomorph $[PtPy_4](Piv)_2 \cdot 4HPiv \cdot 3C_6H_{12}$ (**IIIa**), and heteroanionic acetate ferrocenecarboxylate $[PtPy_4](OOCFc)(OOCMe) \cdot 6H_2O$ (**IV**). The crystal structures of the synthesized compounds were determined. The high resistance of the tetrapyridineplatinum complex cation to hydrolysis and action of strong organic acids was shown. The resistance to acids was shown for trifluoroacetic acid as an example, which completely displaces acetic acid from complex **I** to form solvatomorph $[PtPy_4](OOCCF_3)_2 \cdot 4CF_3COOH$ (**IIa**). Under milder conditions without additional heating, the exchange of the acetate ligands in complex **I** treated with ferrocenecarboxylic acid is incomplete and leads to the isolation of the $[PtPy_4](OOCFc)(OOCMe) \cdot 6H_2O$ heteroanionic bimetallic complex in the crystalline state, which can further be used for the preparation of supported heterometallic systems.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

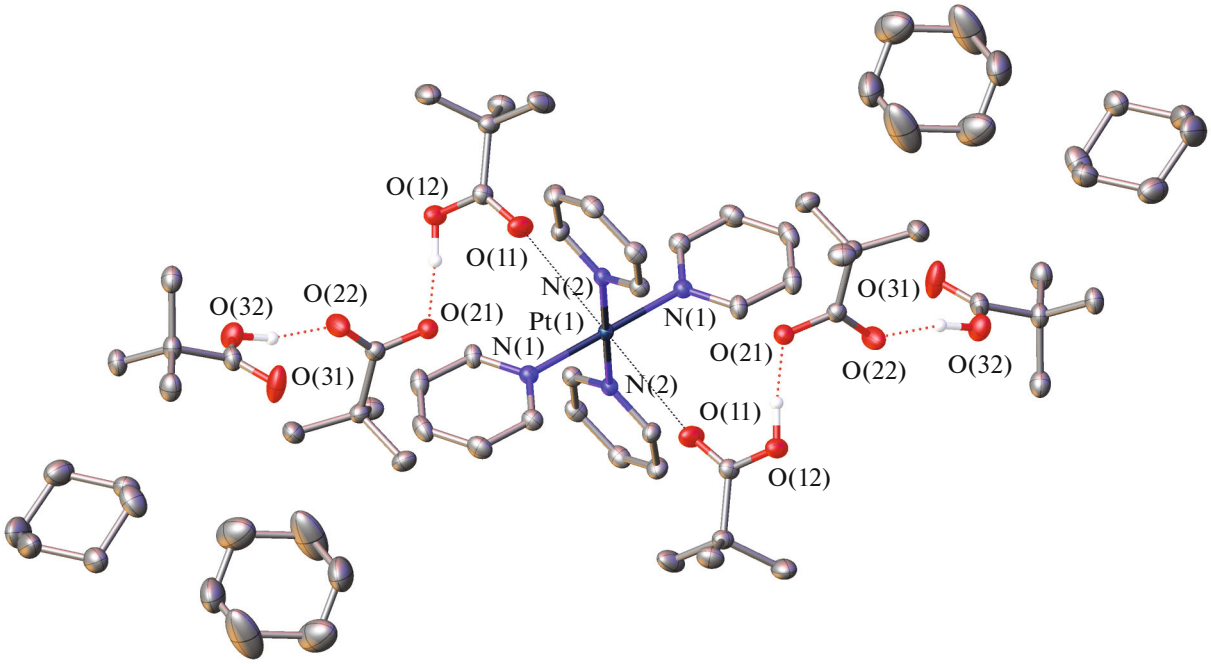

Fig. 6. Molecular structure and numeration scheme of heteroatoms in $[PtPy_4](OOCCMe_3)_2 \cdot 4HPiv \cdot 3C_6H_{12}$ (**IIIa**). Hydrogen atoms of methyl groups, pyridine, and cyclohexane are omitted. Thermal ellipsoids are given with 50% probability.

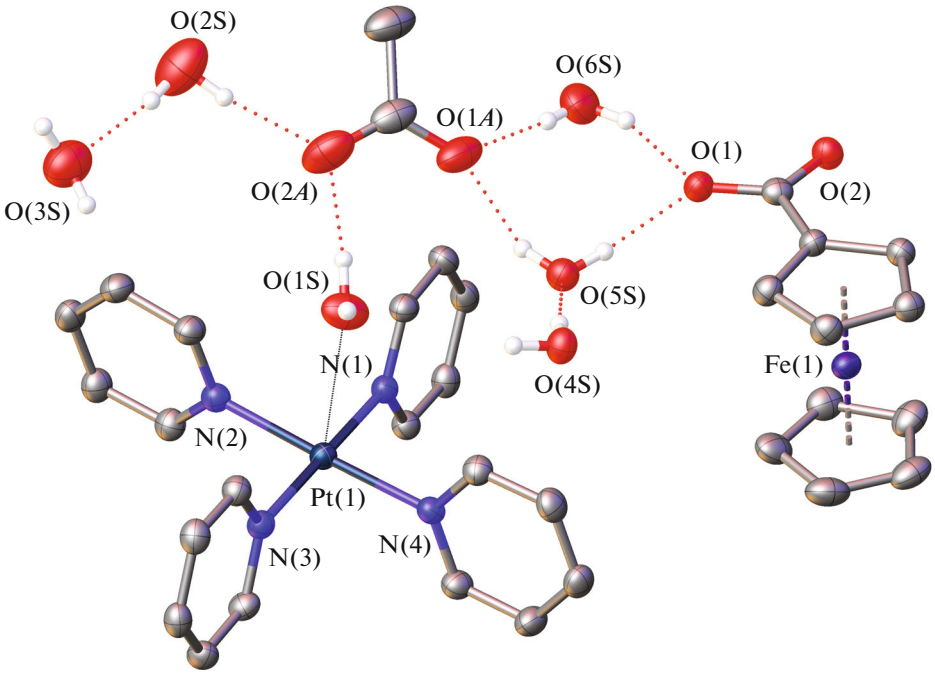

Fig. 7. Molecular structure and numeration scheme of heteroatoms in $[PtPy_4](FcCOO)(OOCMe) \cdot 6H_2O$. Hydrogen atoms of methyl groups and pyridine are omitted. Thermal ellipsoids are given with 50% probability.

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