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Volatile Fluorinated Trimethylplatinum(IV) β-Diketonates with Pyridine: Synthesis, Properties, and Structure

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Abstract—Volatile fluorinated trimethylplatinum(IV) β-diketonates with pyridine $(CH_3)_3Pt(CH_3{-}CO{-}CH{-}CO{-}CF_3)Py$ (**I**) and $(CH_3)_3Pt(CF_3{-}CO{-}CH{-}CO{-}CF_3)Py$ (**II**) obtained from trifluoroacetylacetone and hexafluoroacetylacetone were studied. The synthesis, elemental analysis data, and IR spectra were described. X-Ray diffraction analysis was performed and the crystal structure was determined; the geometric characteristics of complexes **I** and **II** were obtained. Both structures are monomeric molecular structures. The molecules in the crystal are connected only by weak van der Waals forces. The coordination polyhedron of platinum in **I** and **II** is a slightly distorted octahedron. The shortest Pt···Pt distances are 6.639 Å (for **I**) and 6.254 Å (for **II**). The average P–O, Pt–N, and P–C distances are 2.157, 2.182, and 2.030 Å, respectively. The deviations of the bond angles at Pt atoms from ideal values of 90° do not exceed 4.8°.

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The modern trends in the development of high technology are tightly connected with ever increasing requirements to the composition and structure of novel functional materials. The nanostructures and nanolayers based on platinum metals find wide use in various fields of microelectronics, catalysis, etc. [1, 2]. Metal-Organic Chemical Vapor Deposition ((MOCVD) is one of the methods suitable for forming materials with specified functional properties [3,4].

Among the known volatile Pt(IV) compounds used in CVD processes to obtain platinum coatings, platinum(IV) complexes with β-diketones should be mentioned first. Usually, platinum(IV) trialkyl compounds, most often, the most stable trimethylplatinum iodide $(CH_3)_3PtI$, are used as the starting compounds [5]. Previously, it was known from the literature that trimethylplatinum(IV) forms dimeric complexes with β-diketones given by $[Me_3Pt(R{-}CO{-}CH{-}CO{-}R)]_2$, where R is a simple alkyl radical ranging from CH_3 to C_5H_{11} [6, 7]. For example, in the $[(CH_3)_3Pt(Acac)]_2$ dimer, acetylacetone is a tridentate ligand having, apart from the two donor oxygen atoms, the third donor atom, namely, the middle ring carbon atom, giving the bridging Pt–C_γ bond, which forms the dimer. Due to low volatility, dimers of this type are less suitable for CVD application than monomeric trimethylplatinum β-diketonates. It is known that introduction of CF_3 groups into chelating ligands facilitates the volatility of complexes [8]. Before our studies, fluorinated trimethylplatinum β-diketonates were not reported in the literature. We were the first to synthesize [9–11] volatile trimethylplatinum(IV) chelates based on various fluorinated β-diketones and their adducts with donor ligands. These works were concerned with the conditions of synthesis, spectral characteristics, and the thermal stability of the complexes. It was noted that trimethylplatinum(IV) compounds are more volatile than analogous platinum(II) β-diketonates, which we had thoroughly studied. From the structural standpoint, fluorinated β-diketonates of trimethylplatinum(IV) had not been studied before. However, establishing the relationship between the composition, structure, and thermal properties of these compounds allows one to simplify the selection of the most suitable precursors for CVD applications. Analysis of the published data and the data from Cambridge Crystallographic Data Centre (CCDC) confirm the lack of structural studies of platinum(IV) compounds of this type having practically valuable properties.

As a continuation of our systematic research into "composition–structure–property" relationships of volatile β-diketonates of noble metals, here we describe the synthesis and X-ray diffraction study of the crystal structure of volatile fluorinated β-diketonates of trimethylplatinum(IV) with pyridine: $CH_3)_3Pt(CH_3{-}CO{-}CH{-}CO{-}CF_3)Py$ (**I**) and $CH_3)_3Pt(CF_3{-}CO{-}CH{-}CO{-}CF_3)Py$ (**II**). These compounds were obtained from trifluoroacetylacetone and hexafluoroacetylacetone, respectively.

EXPERIMENTAL

As the starting platinum(IV) compound, $(CH_3)_3PtI$ (**III**) was used.

Synthesis of III. First, the Grignard reagent CH_3MgI was obtained from Mg powder (1.32 g, 55 mmol) and CH_3I (7.81 g, 55 mmol) in 50 mL of anhydrous diethyl ether, then 60 mL of dry benzene was added. Finely ground Na_2PtCl_6 (1 g, 11 mmol), which was thoroughly pre-dehydrated in vacuum, was quickly added at –20°C in an inert gas stream to the vigorously stirred solution. The reaction mixture was stirred in a constant inert gas stream for 2 h at 0°C; the mixture gradually turned dark brown. The complex was isolated from the reaction mixture into ice water slightly acidified with HCl. The organic layer was separated and the aqueous layer was repeatedly extracted with hexane. The resulting compound was isolated by evaporation of the solvent. Yield 0.61 g (75%). The crystals of **III** are orange-colored, air stable, insoluble in water but readily soluble in organic solvents.

Synthesis of I and II. Fluorinated trimethylplatinum(IV) β-diketonates with pyridine were synthesized by the following procedure. Complex **III** (1 g, 2.8 mmol) was dissolved in 50 mL of benzene. A solution of the potassium salt of the corresponding ligand (5.6 mmol) in 20 mL of 96% ethanol was added to the orange solution, and dry AgF (2.8 mmol) was added. The reaction mixture was stirred at 40–50°C until the solution became colorless and AgI and KF precipitated. The precipitate was filtered off, the solution was evaporated to dryness, the dry residue was dissolved in chloroform, dry pyridine (5.6 mmol) was added, and the solution was refluxed for 1 h. The solvent and the excess of pyridine were evaporated on a water bath at reduced pressure. The dry residue was extracted with hexane. The product isolated from hexane was purified by sublimation under reduced pressure. The yields of complexes **I** and **II** are 90–92%.

Compound **I** is a light yellow crystalline solid (mp = 40–41°C).

For $C_{13}H_{18}F_3NO_2Pt$

anal. calcd., %:	C, 33.0;	H, 3.8;	F,12.0;	N, 3.0.
Found, %:	C, 33.1;	H, 3.6;	F, 12.3;	N, 3.2.

IR spectrum of **I** (ν, cm^{-1}): 3078, 2961, 2902, 2815,1617, 1516, 1474, 1449, 1364, 1287, 1137, 1068, 863, 781, 754, 692, 615,492,422.

Compound **II** is a light green crystalline solid (mp = 54–56°C).

For $C_{13}H_{15}F_6NO_2Pt$

anal. calcd., %:	C 29.6;	H 2.8;	F 21.7;	N 2.6.
Found, %:	C 29.7;	H 2.6;	F 21.5;	N 2.3.

IR spectrum of **II** (ν, cm^{-1}): 3080, 2963, 2898, 2816, 1638, 1607,1559, 1533, 1469, 1427, 1260, 1153, 1090, 803, 758, 680, 584, 486, 401.

The IR spectra of complexes **I** and **II** in the region of 400–4000 cm^{-1} were recorded on a Scimitar FTS-2000 spectrometer (KBr pellets).

X-Ray diffraction. The single crystals of compounds **I** and **II** were prepared from their solutions in hexane at 0°C. The unit cell parameters and the experimental intensities for crystal structure solution were measured on a Bruker-Nonius X8Apex four-circle automated diffractometer (two-coordinate CCD detector, MoK_α radiation, λ = 0.71073 Å, graphite monochromator, φ- and ω scan mode). The structures **I** and **II** were solved by the direct method and refined in the full-matrix anisotropic approximation. The hydrogen atoms were specified geometrically and included in the refinement in the anisotropic approximation together with non-hydrogen atoms.

The crystallographic characteristics and X-ray experiment details are presented in Table 1, the interatomic distances and bond angles are in Table 2. All calculations were performed using the SHELX-97 program package (Bruker AXS Inc., 2004) [12]. The X-ray diffraction patterns of **I** and **II** were fully indexed based on the single crystal investigation data. The atom coordinates and other parameters of **I** and **II** are deposited with the Cambridge Crystallographic Data Centre (nos. 792536 for I and 791909 for II); deposit@ccde.cam.ac.uk.

RESULTS AND DISCUSSION

As the starting compounds for the synthesis of volatile platinum(IV) β-diketonates, we chose the most stable trimethylplatinum iodide **III**. This complex was first obtained [5] in a yield of not more than 20% by the reaction of the Grignard reagent CH_3MgI with $PtCl_4$. Later, the synthetic routes to **III** from various chloro derivatives of platinum(IV) complexes were studied [13]. However, the highest yield (52–55%) was attained in the reaction of Na_2PtCl_6 with Grignard reagent [14]. As a result of numerous experiments, we improved this method for the synthesis of **III**. We changed the order of mixing the reactants: the platinum salt thoroughly pre-dehydrated in vacuum was added to the Grignard reagent rather than *vice versa*. The optimal reactant and solvent ratios and the reaction temperature and time regimes were selected. Thus, this method of the synthesis allowed the yield of

Table 1. Crystallographic data and X-ray experiment details for complexes **I** and **II**

Parameter	Value	
	I	II
M	472.37	526.35
T, K	273(2)	150(2)
System	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a, Å	7.4618(3)	9.7564(3)
b, Å	17.5425(6)	16.9091(6)
c, Å	11.4282(4)	21.4192(6)
α, deg	90	69.9360(10)
β, deg	93.9130(10)	89.1770(10)
γ, deg	90	81.646(2)
V, Å^3	1492.45(9)	3281.50(18)
Z	4	8
ρ(calcd.), g/cm^3	2.102	2.131
μ_{Mo}, mm^{-1}	9.434	8.619
$F(000)$	896	1984
Crystal size, mm	0.02 × 0.02 × 0.02	0.28 × 0.04 × 0.04
Measurement range, θ, deg	2.93–36.28.	1.90–30.51.
Range of indices	$-11 \leq h \leq 12$, $-29 \leq k \leq 16$, $-18 \leq l \leq 14$	$-13 \leq h \leq 13$, $-24 \leq k \leq 24$, $-29 \leq l \leq 30$
I_{hkl} measured	18449	34834
I_{hkl} independent	7121 ($R_{int} = 0.0200$)	19704 ($R_{int} = 0.0226$)
Number of reflections with $I_{hkl} > 2\sigma(I)$	15657	6173
Number of refined parameters	841	253
GOOF for F^2_{hkl}	1.057	1.024
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0183$, $wR_2 = 0.0387$	$R_1 = 0.0280$, $wR_2 = 0.0596$
R factor (all reflections)	$R_1 = 0.0242$, $wR_2 = 0.0397$	$R_1 = 0.0432$, $wR_2 = 0.0596$
Residual electron density (max/min), e/Å^3	1.598/–0.938	1.368/–1.012

Table 2. Bond lengths and bond angles in complexes **I** and **II** (the mean values are in parentheses)

Bond	I	II
	d, Å	
Pt–CH$_3$	2.025(2)–2.036(2) ⟨2.030⟩	2.022(4)–2.038(4) ⟨2.030⟩
Pt–O	2.153(1), 2.157(1) ⟨2.155⟩	2.153(3)–2.168(2) ⟨2.161⟩
Pt–N	2.184(1)	2.165(3)–2.197(3) ⟨2.181⟩
N–C	1.342(2), 1.349(2) ⟨1.346⟩	1.334(4)–1.342(4) ⟨1.376⟩
C–C	1.378(3)–1.387(3) ⟨1.383⟩	1.352(8)–1.385(5) ⟨1.376⟩
O–C	1.259(2), 1.273(2)	1.249(4)–1.261(4) ⟨1.255⟩
C–Cγ	1.426(2), 1.379(2)	1.384(5)–1.402(5) ⟨1.394⟩
C–C$_{Me}$	1.500(2), 1.531(2)	1.522(5)–1.533(5) ⟨1.528⟩
C–F	1.332(2)–1.342(2) ⟨1.338⟩	1.244(7)–1.327(5) ⟨1.302⟩
Angle	ω, deg	
OPtO	88.81(5)	85.23(9)–93.69(8) ⟨89.46⟩

III to be increased to 75%. A study of the structure of **III** was reported [15].

While using fluorinated β-diketones for the synthesis of trimethylplatinum chelates, we expected the formation of dimeric chelates similar, for example, to trimethylplatinum acetylacetonate $[(CH_3)_3Pt(Acac)]_2$, as the trifluoromethyl group should not create steric hindrance for the dimer formation [16]. However, it was found in the experiments that fluorinated β-diketones do not form dimeric complexes. An obligatory condition for the formation of a monomeric fluorinated β-diketonate of trimethylplatinum is the presence of donor molecule, for example, H_2O, in the reaction medium. This molecule occupies the sixth coordination site of platinum in the monomeric β-diketonate complex. This is why we failed to obtain fluorinated β-diketonates of trimethylplatinum in anhydrous solvents. Upon the addition of some water in the reaction medium (it is sufficient to use 96% ethanol), monomeric fluorinated complexes containing a water molecule are formed. Thus, fluorinated β-diketonates of trimethylplatinum do nor form dimers through Pt–C_γ bonding, as has been the case for trimethylplatinum chelates with phenyl or alkyl substituents in the β-diketonate ligand. Apparently, the increase in the electronegativity of the terminal β-diketonate radical entails the growth of the positive charge of the ligand γ-C atom and, hence, the probability of formation of the Pt–C_γ bond decreases, thus enabling binding of platinum to other donor molecules. Note that water adds to the chelate complex molecule only in the case of fluorinated β-diketones. Pyridine, which is a stronger base, easily displaces water from these monomeric complexes. Note also that initially, we used only the potassium salts of ligands (KL_F) for the synthesis of fluorinated β-diketonates. In this case, the yield of the target products did not exceed 50%.

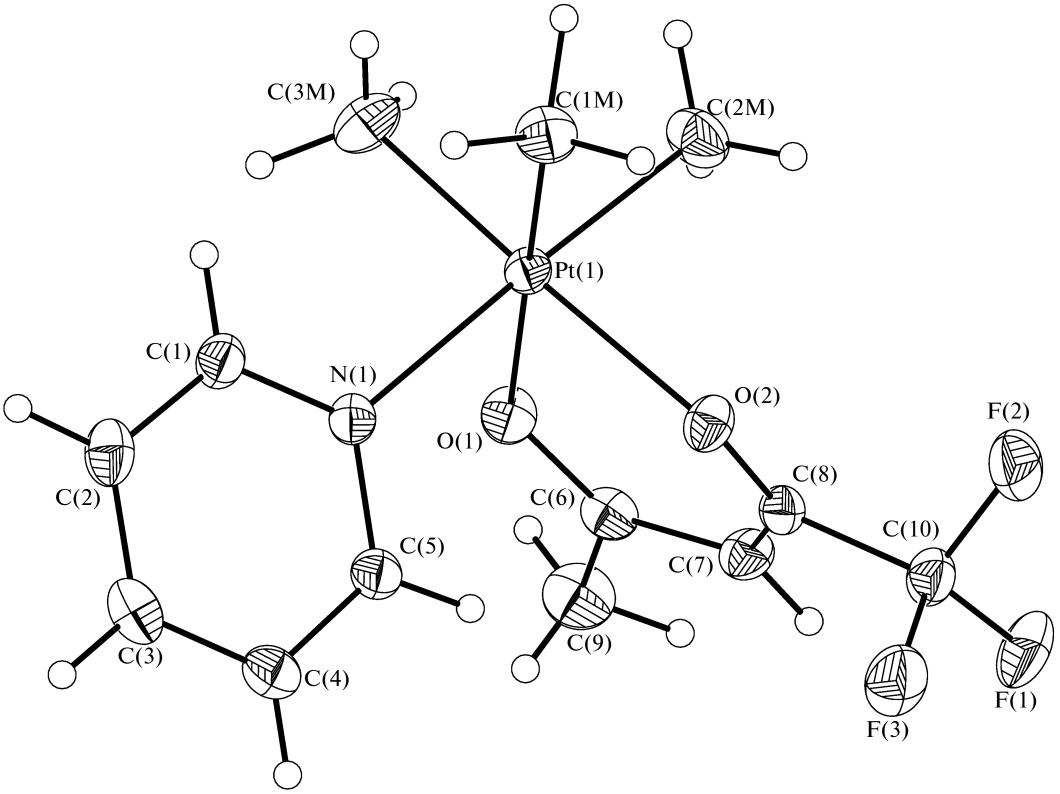

Fig. 1. Structure of the complex Pt(CH_3-CO-CH-CO-CF_3)Py (**I**).

By using silver ions, we were able to prepare fluorinated β-diketonates of trimethylplatinum(IV) in up to 92% yield.

The IR spectra of **I** and **II** confirm the chelate type of platinum bonding to β-diketone. The C–H and Pt–CH_3 stretching vibrations occur at 3000–2800 cm^{-1}. Characteristic C–O and C–C vibrations of the chelate ring occur at 1650–1450 cm^{-1}. The (Pt–C) vibrations account for the less intense bands at 500–600 cm^{-1} [17]. The bands at 400–1800 cm^{-1} for pyridine vibrations are difficult to analyze due to the large number of absorption bands corresponding to the chelate ring. The weak bands at 3078 cm^{-1} (for **I**) and 3080 cm^{-1} (for **II**) were assigned to pyridine =C–H stretching bands [18].

The molecular structure of compound **I** consists of neutral complexes $(CH_3)_3$Pt(tfac)Py (Fig. 1). The platinum atom is coordinated by two oxygen atoms of the unsymmetric ligand, by the pyridine nitrogen atom, and by three three methyl carbon atoms. The PtC_3NO_2 coordination unit is a slightly distorted octahedron. The Pt–O_{mean} distance is 0.029 Å shorter than the Pt–N_{mean} distance. The Pt–CH_3 bonds are 2.030 Å and the chelate OPtO bond angle is 88.8°. Two triangular faces (C_3 and O_2N) of the platinum octahedron are nearly parallel, the angle between their planes being 1.8°. In the β-diketonate ligand, the differences between O–C, C–Cγ, and C–C_{Me}bond lengths on the side of different substituents are 0.014, 0.047, and 0.031 Å, respectively. In the CF_3 group, the C–F_{mean} distance is 1.34 Å. The folding angle of the chelate ring along the O···O line reaches 14.7°, the intramolecular F(1)···H_γ contact is 2.39 Å. The mean C–N and C–C bond lengths in the pyridine molecule are 1.34 and 1.38 Å, respectively. The angle between the normals to the Py and β-diketonate ligand planes is 91°.

The packing of structural units in the crystal of **I** along the *x* axis is shown in Fig. 2. The complex molecules are packed in the crystal with minimum Pt···Pt distances of 6.639–7.462 Å. The H···F intermolecular contacts are 2.65–2.86 Å long.

The structure of compound **II** is also molecular, being composed of neutral $(CH_3)_3$Pt(Hfac)Py complexes. The structure comprises four crystallographically independent complexes with similar structures. The Pt coordination polyhedra are slightly distorted octahedra. The structure of one of the complexes **II** is shown in Fig. 3. The mean Pt–O, Pt–N, and Pt–CH_3 bond lengths are 2.160, 2.181, and 2.030 Å, respectively. The deviations of the *cis* bond angles at Pt from the ideal values of 90° do not exceed 4.8°. The planes of two triangular faces of the Pt octahedra are nearly

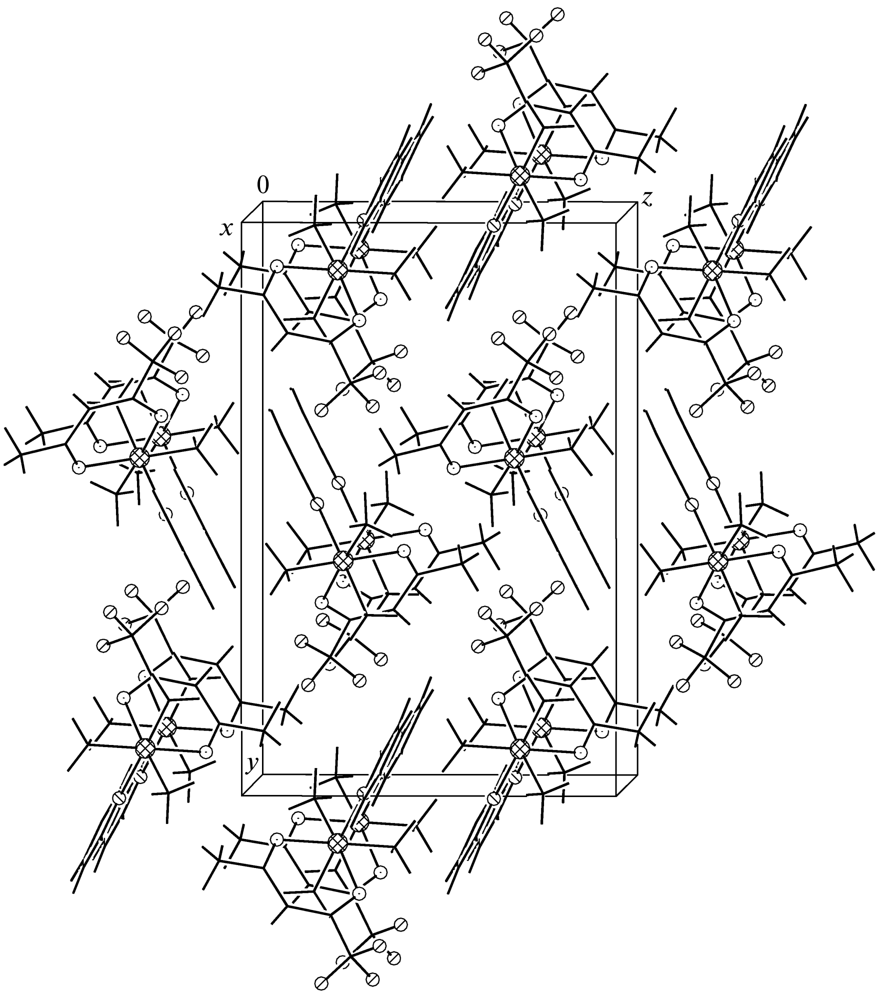

Fig. 2. Packing of the complexes in structure **I** along the *x* axis.

parallel, the dihedral angles not exceeding 2.4°. In the symmetric ligand of this complex, the mean O–C, C–Cγ, C–C_{Me}, and C–F bond lengths are 1.255, 1.394, 1.528, and 1.302 Å, respectively. The mean value for the chelate OPtO angle is 89.46°. The folding angles of the chelate rings at the O···O lines are 4.0°–8.2°. All intramolecular F···H_γ contacts in complex **II** are ~2.3 Å. The average bond lengths of the pyridine molecule in structure **II** are the same as in **I**. The angle between the normals to the pyridine and β-diketonate ligand planes is 72.7°–90°.

The projection of structure **II** onto the *xy* plane is shown in Fig. 4. The structure is layered, F and H atoms of the terminal substituents being located on the layer surfaces. The minimum values for the intermolecular F···F, F···H, and H···H contacts are 2.87 Å, 2.58 Å, and 2.38 Å. The shortest Pt···Pt distances between the centers of the complexes are in the range from 6.254 to 6.517 Å.

Thus, our study dealing with the synthesis of trimethylplatinum(IV) compounds showed that fluorinated β-diketones do not form dimeric complexes. A condition for the formation of monomeric complexes is the presence of a donor molecule in the reaction mixture able to occupy the sixth coordination site at the platinum atom. An X-ray diffraction study of volatile trimethylplatinum(IV) complexes with fluorinated β-diketones was carried out for the first time. The crystal structures and the geometric characteristics of complexes **I** and **II** were determined. Both structures are molecular and monomeric, the molecules in the crystal being linked by only weak van der Waals forces. The platinum coordination polyhedron is a slightly distorted octahedron; the shortest Pt···Pt distances are 6.639 Å (for **I**) and 6.254 Å (for **II**). The mean Pt–O, Pt–N, and Pt–C bond lengths are 2.157, 2.182, and 2.030 Å.

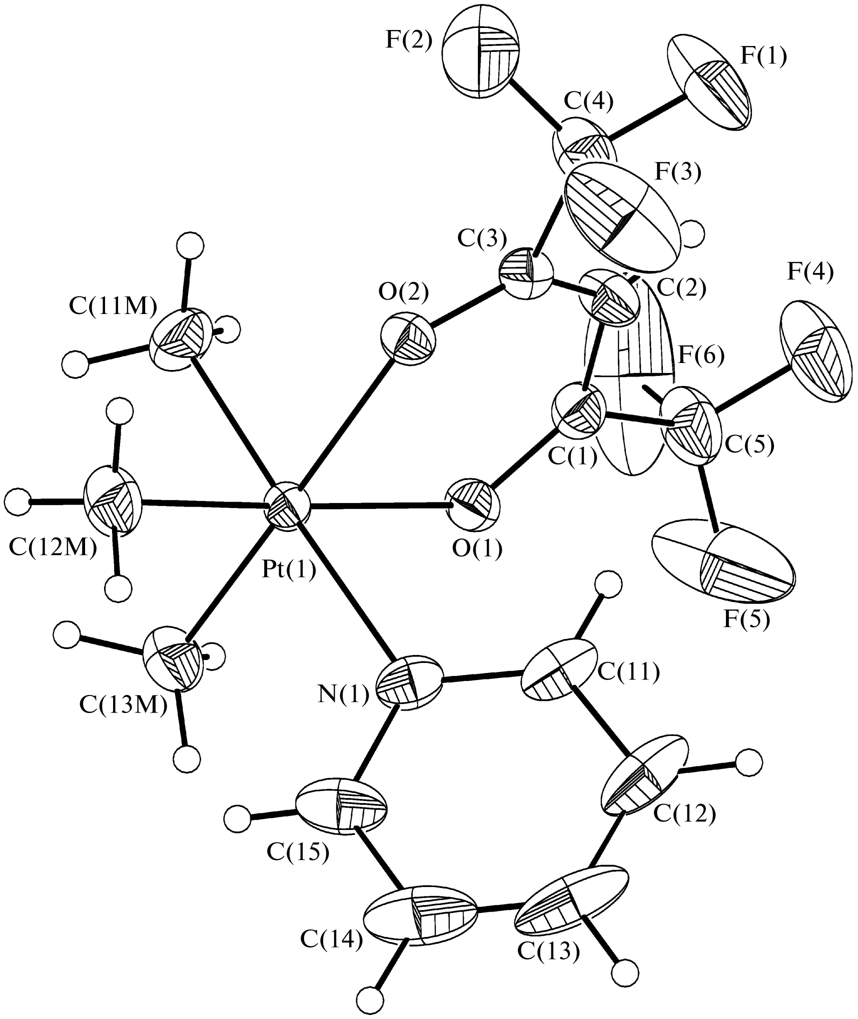

Fig. 3. Structure of the complex $(CH_3)_3Pt(CF_3\text{-}CO\text{-}CH\text{-}CO\text{-}CF_3)Py$ (**II**).

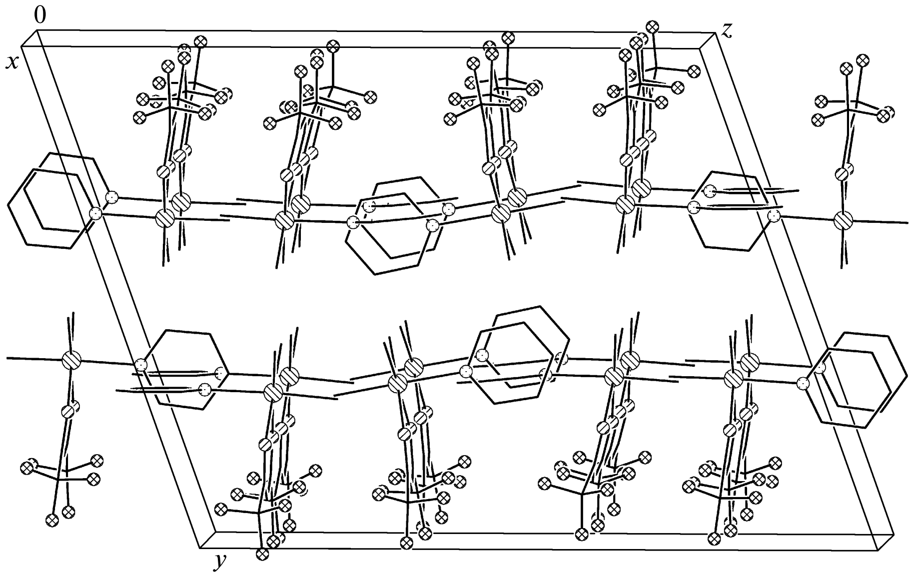

Fig. 4. Projection of structure **II** onto the *xy* plane.

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