

STRUCTURE AND PROPERTIES OF THE VOLATILE ISOMERS OF BIS(1,1,1-TRIFLUORO-5,5- DIMETHYLHEXANE-2,4-DIONATO) OF PLATINUM(II)

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In the work, isomeric complexes of platinum(II) with the $(\text{ptac})^{-1}$ pivaloyltrifluoroacetate ion $(\text{Pt}((\text{CH}_3)_3\text{CO}-\text{CH}-\text{CO}-\text{CF}_3)_2)$ are studied. The synthesis and chromatographic separation of $\text{Pt}(\text{ptac})_2$ isomers are described, TGA data for the separated isomers are given, and the crystal structures of the solid phases are studied. The *cis*- $\text{Pt}(\text{ptac})_2$ complex crystallizes in the space group *P*-1, $a = 10.7091(4)$ Å, $b = 12.7787(6)$ Å, $c = 16.0154(8)$ Å, $\alpha = 92.389(2)^\circ$, $\beta = 90.868(2)^\circ$, $\gamma = 112.1260(10)^\circ$, $V = 2027.39(16)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.918$ g/cm³. The *trans*- $\text{Pt}(\text{ptac})_2$ complex crystallizes in the space group *C*2/*m*, $a = 13.3235(5)$ Å, $b = 8.5515(3)$ Å, $c = 9.6694(3)$ Å, $\beta = 118.5880(10)^\circ$, $V = 967.38(6)$ Å³, $Z = 2$, $d_{\text{calc}} = 2.010$ g/cm³. The structures of the complexes are molecular, the Pt atom has a square coordination of four oxygen atoms of two ligands; for *cis*- $\text{Pt}(\text{ptac})_2$, the Pt–O_{av} distance is 1.968 Å, for *trans*- $\text{Pt}(\text{ptac})_2$ it is 1.980 Å.

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Modern high-tech trends are inextricably linked to constantly rising requirements to the composition and structure of new functional materials. Nanostructures and nanolayers based on platinum metals are promising materials for electrodes in medicine and microelectronics, integrated circuits, microheaters, temperature detectors, catalysts, and so on [1-5]. One of the most widespread methods to obtain platinum films is metal-organic chemical vapor deposition (MOCVD) using volatile β -diketonates of platinum [6-8]. The formation of functional layers occurs by the decomposition of the initial compound (precursor) vapor on the support surface. The precursor type affects the film characteristics and the temperature modes of its deposition. The important characteristics of these compounds such as the volatility and thermal stability depend on the composition and structure of initial β -diketone. Therefore, the study of the composition and structural features of volatile platinum β -diketonates based on the asymmetric β -diketones is relevant. Our previous experiment on the direct measurement of the pressure of saturated vapor for the *cis*- and *trans*-isomers of the platinum(II) complex with the $\text{Pt}(\text{tfac})_2$ trifluoroacetylacetate ion revealed a significant difference in the volatility of the *cis*- and *trans*-isomers [9], which is probably associated with different packing of isomer molecules in the crystal lattice. It is natural to suppose that the symmetric *trans*-isomer has a closer molecular packing as compared to the *cis*-form giving an increased lattice energy and, consequently, a lower volatility, which we later confirmed by the results of our single crystal XRD study of the *cis*- and *trans*-isomers of $\text{Pt}(\text{tfac})_2$ [10].

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The continuation of our work on the study of volatile platinum(II) β -diketonates based on asymmetric fluorinated β -diketones is the investigation of the structure of the platinum complex with the pivaloyltrifluoroacetate ion: $\text{Pt}[\text{C}(\text{CH}_3)_3\text{CO-CH-CO-CF}_3]_2$ (hereinafter, $\text{Pt}(\text{ptac})_2$). The preparation of this complex and its physicochemical and thermal characteristics we described in [11]. Here, we describe the synthesis of $\text{Pt}(\text{ptac})_2$, the chromatographic separation of the *cis*- and *trans*-complexes, report the TGA data for the separated isomeric phases and the results of their crystal chemical study, which was performed for the first time.

EXPERIMENTAL

Synthesis of the $\text{Pt}(\text{ptac})_2$ complex. K_2PtF_6 salt was used as a precursor. In the first stage, Pt(IV) reduces to Pt(II) in ethanol in a perchloric acid solution with the formation of the Pt(II) aqua ion [11]. The addition of a slight excess of pivaloyltrifluoroacetone (Hptac) to the obtained solution with a subsequent increase in pH to 5 by the KOH solution with stirring leads to the formation of a yellow $\text{Pt}(\text{ptac})_2$ precipitate from the solution. The filtered precipitate was dried and purified by sublimation in vacuum ($P = 10^{-2}$ Torr, $T = 200$ °C); the yield of the sublimated product was 85%. The crystals are yellow, $T_{\text{melt}} = 164$ °C. Found, %: C 33.9, H 3.5, F 19.6. For $\text{C}_{16}\text{H}_{20}\text{F}_6\text{O}_4\text{Pt}$ calculated, %: C 33.7, H 3.4, F 19.5.

IR study of the sublimated product (carried out on a Scimitar FTS-2000 spectrometer in a range 400-4000 cm^{-1} , KBr pellet): $\nu(\text{C-H})$ 2979, 2939, 2878; $\nu(\text{C=O+C=C})$ 1580, 1536, 1512, 1435; $\nu(\text{H-C-H})$ 1396, 1369; 1312; $\nu(\text{C-F})$ 1256, 1196, 1160; $\nu(\text{Pt-O})$ 861, 806.730, 623, 500, 398. Complication of the structure of the complex due to the asymmetry of the ligand used results in the appearance of additional bands in the Pt-O bond vibration region [12], since in this case the spectrum is the sum of the spectra for a mixture of the *cis*- and *trans*-isomers.

Powder XRD study was carried out on a DRON-3M diffractometer ($R = 192$ mm, $\text{CuK}\alpha$ radiation, Ni filter, scintillation detector with an amplitude discrimination in the 2θ angle range from 5° to 50° at room temperature). The experimental diffraction pattern of the sublimated $\text{Pt}(\text{ptac})_2$ product given in Fig. 1 evidences that it is not a single phase.

Separation of the isomeric phases of the sublimated $\text{Pt}(\text{ptac})_2$ complex was performed on a chromatographic column, SiO_2 support, a hexane/benzene solvent mixture in the 3:1 ratio used as the eluent. *cis*- $\text{Pt}(\text{ptac})_2$ elutes first from the column and then *trans*- $\text{Pt}(\text{ptac})_2$. The isolated isomeric forms of the complex are very soluble in chloroform, benzene, hexane and less soluble in alcohol.

Single crystals of the *cis*- and *trans*-isomers for the XRD analysis were grown by slow crystallization from an alcohol solution at room temperature; they crystallize as yellow transparent prisms; the crystals of the *cis*-isomer are more

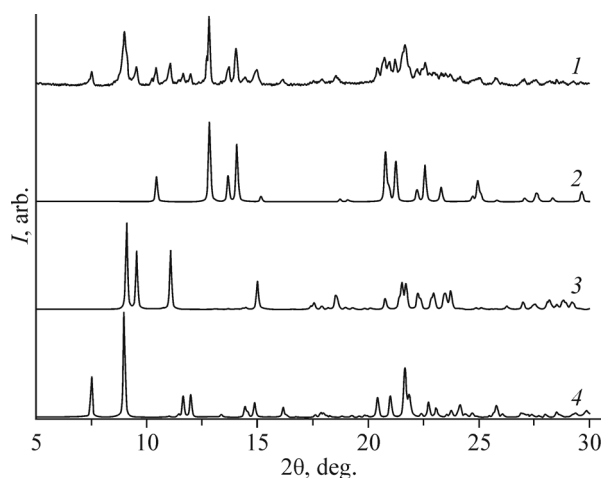


Fig. 1. Diffraction pattern of the sublimated product $\text{Pt}(\text{ptac})_2$ (1) in comparison with the calculated diffraction patterns of three phases: *cis* (2), *trans* (3), *mix* (4).

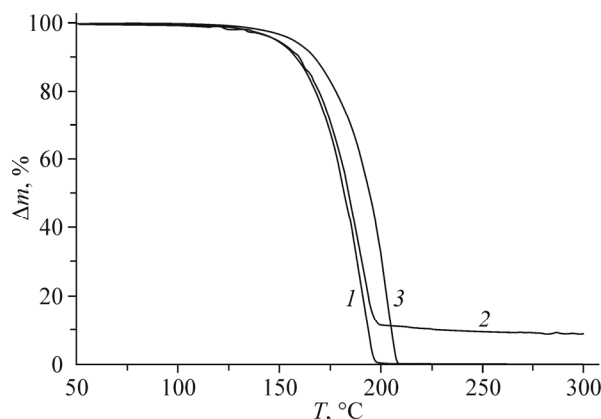


Fig. 2. Thermogravimetric curves of the compounds: *mix*-Pt(ptac)₂ (1), *cis*-Pt(ptac)₂ (2), *trans*-Pt(ptac)₂ (3).

isometric. From a heptane solution, the crystals of a new phase, *mix*-Pt(ptac)₂, were obtained, which is a solid solution of the isomers in the *cis*–*trans* ratio of 2:1. Single crystals of all phases melt without decomposition: for *cis*-Pt(ptac)₂ $T_{\text{melt}} = 163\text{ }^{\circ}\text{C}$, for *trans*-Pt(ptac)₂ $T_{\text{melt}} = 182\text{ }^{\circ}\text{C}$, for *mix*-Pt(ptac)₂ $T_{\text{melt}} = 168\text{ }^{\circ}\text{C}$.

Thermal study of the Pt(ptac)₂ isomeric phases was performed on a NETZSCH TG 209 F1 device: a temperature range 20–350 °C, helium atmosphere, gas flow rate 30 ml/min, heating rate 10 deg/min, a 5–6 mg portion, a standard open crucible. Nearly quantitative weight loss of all compounds under the measurement conditions occurs in a range 150–210 °C (Fig. 2). In the thermogravimetric experiment, the *cis*-Pt(ptac)₂ complex passes to the gas phase with partial decomposition: its weight loss is ~90%. *Cis*-Pt(ptac)₂ and *mix*-Pt(ptac)₂ pass to the gas phase almost in the same temperature range and their volatility is somewhat higher than that of *trans*-Pt(ptac)₂.

Single crystal XRD study. The unit cell parameters and experimental intensities to determine the crystal structures were measured at room temperature on an automated Bruker-Nonius X8 Apex four-circle diffractometer equipped with a two-dimensional detector (MoK_α radiation, graphite monochromator). The structures were solved by the standard heavy atom method and refined in the anisotropic/isotropic (for H) approximation; the positions of the hydrogen atoms of the CH₃ groups were calculated geometrically. The crystallographic characteristics of the studied compounds, the parameters of the experiment and structure refinement are given in Table 1; interatomic distances and bond angles are listed in Table 2. All calculations were performed using the SHELX-97 software [13]. The coordinates of the basic atoms have been deposited with the Cambridge Structural Database (CCDC) under numbers: 1424 107 for the *cis*-Pt(ptac)₂ phase, 1424 105 for the *trans*-Pt(ptac)₂ phase, 1424 106 for the *mix*-Pt(ptac)₂ phase; see deposit@ccde.cam.ac.uk.

DESCRIPTION OF CRYSTAL STRUCTURES. CONCLUSIONS

Structure of *cis*-Pt(ptac)₂ is molecular formed of isolated complexes whose structure with atomic numbering is given in Fig. 3. The crystals are triclinic; the structure contains two crystallographically independent complexes having different orientations in the unit cell. The Pt atom has a square coordination of four oxygen atoms of two ligands; the Pt–O distances and the chelate O–Pt–O bond angles are in the ranges of 1.940–1.985 Å and 94.8–95.6°; their average values are 1.968 Å and 95.0° respectively. The maximum difference in the O–C bond lengths is only 0.03 Å; the average C–Cγ bond lengths from the side of different substituents are 1.42 (CH₃) Å and 1.36 (CF₃) Å. In the CF₃ groups, the average C–F bond length is 1.30 Å. The molecules of the complexes (excluding terminal substituents) are almost planar; the metal ring bend angles along the O...O line do not exceed 2.4°; the intramolecular F...Hγ contacts are estimated as 2.32 Å. The angle between the normals to the coordination square planes of different complexes is 68.5°. The packing of molecules along the *X* axis is shown in Fig. 4 *a*. The Pt(1) and Pt(2) complexes are packed in infinite stacks with the Pt...Pt distance of 5.018–5.534 Å (Fig. 4 *b*); the other Pt...Pt distances in the structure are >9.890 Å. The slope angles of the coordination squares to

TABLE 1. Crystallographic Data and Conditions of the Diffraction Experiment for *cis*-Pt(ptac)₂, *trans*-Pt(pta)₂, and *mix*-Pt(ptac)₂ Crystalline Phases

Parameter	<i>cis</i> -Pt(ptac) ₂	<i>trans</i> -Pt(ptac) ₂	<i>mix</i> -Pt(ptac) ₂
Chemical formula	C ₁₆ H ₂₀ F ₆ O ₄ Pt	C ₁₆ H ₂₀ F ₆ O ₄ Pt	C ₁₆ H ₂₀ F ₆ O ₄ Pt
Formula weight	585.41	585.41	585.41
Temperature, K	296(2)	296(2)	296(2)
Crystal symmetry	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>m</i>	<i>P</i> -1
<i>a</i> , Å	10.7091(4)	13.3235(5)	9.9249(8)
<i>b</i> , Å	12.7787(6)	8.5515(3)	12.2193(9)
<i>c</i> , Å	16.0154(8)	9.6694(3)	12.8075(9)
α , deg	92.389(2)		74.966(3)
β , deg	90.868(2)	118.5880(10)	84.223(3)
γ , deg	112.1260(10)		85.916(3)
Volume, Å ³	2027.39(16)	967.38(6)	1490.81(19)
<i>Z</i>	4	2	3
<i>d</i> _{calc} , g/cm ³	1.918	2.010	1.956
Absorption coefficient, mm ⁻¹	6.991	7.326	7.131
<i>F</i> (000)	1120	560	840
Crystal size, mm	0.05×0.03×0.01	0.10×0.08×0.05	0.20×0.15×0.15
θ range, deg	1.27–31.71	4.30–33.89	3.46–34.63
<i>h</i> , <i>k</i> , <i>l</i> limits	−10 ≤ <i>h</i> ≤ 15, −17 ≤ <i>k</i> ≤ 18, −23 ≤ <i>l</i> ≤ 22	−19 ≤ <i>h</i> ≤ 19, −9 ≤ <i>k</i> ≤ 13, −12 ≤ <i>l</i> ≤ 14	−14 ≤ <i>h</i> ≤ 15, −16 ≤ <i>k</i> ≤ 17, −17 ≤ <i>l</i> ≤ 12
<i>I</i> _{<i>hkl</i>} meas. / <i>I</i> _{<i>hkl</i>} indep.	24384 / 11130 [<i>R</i> (int) = 0.0360]	6458 / 1830 [<i>R</i> (int) = 0.0232]	22229 / 8700 [<i>R</i> (int) = 0.0362]
<i>GOOF</i> on <i>F</i> _{<i>hkl</i>} ²	1.274	1.082	1.130
<i>R</i> (<i>I</i> > 2 σ _{<i>I</i>})	<i>R</i> ₁ = 0.0573, <i>wR</i> ₂ = 0.1380	<i>R</i> ₁ = 0.0173, <i>wR</i> ₂ = 0.0430	<i>R</i> ₁ = 0.0529, <i>wR</i> ₂ = 0.1384
<i>R</i> (<i>I</i> _{meas})	<i>R</i> ₁ = 0.0803, <i>wR</i> ₂ = 0.1433	<i>R</i> ₁ = 0.0173, <i>wR</i> ₂ = 0.0430	<i>R</i> ₁ = 0.0675, <i>wR</i> ₂ = 0.1441
Residual electron density (max / min), e/Å ³	2.767 / −1.539	0.993 / −0.637	6.158 / −1.461

TABLE 2. Main Interatomic Distances *d* (Å) and Bond Angles ω (deg) for the Studied Pt(pta)₂ Complexes

Complex	<i>cis</i> -Pt(pta) ₂	<i>trans</i> -Pt(pta) ₂	<i>mix</i> -Pt(pta) ₂	
			<i>cis</i> -Pt(pta) ₂	<i>trans</i> -Pt(pta) ₂
Pt–O(CF ₃)	1.940–1.985 ⟨1.972⟩	1.979	⟨1.988⟩	1.972
Pt–O(Bu ^{<i>t</i>})	1.952–1.974 ⟨1.965⟩	1.981	⟨1.981⟩	1.980
O–C(CF ₃)	1.272–1.292 ⟨1.281⟩	1.274	⟨1.274⟩	1.266
O–C(Bu ^{<i>t</i>})	1.273–1.301 ⟨1.287⟩	1.269	⟨1.248⟩	1.265
C–C γ (CF ₃)	1.328–1.376 ⟨1.356⟩	1.369	⟨1.368⟩	1.375
C–C γ (Bu ^{<i>t</i>})	1.396–1.435 ⟨1.419⟩	1.415	⟨1.425⟩	1.407
C–F	⟨1.29⟩	⟨1.282⟩	⟨1.29⟩	⟨1.28⟩
O–Pt–O	94.8–95.6 ⟨95.1⟩	95.0	⟨95.2⟩	94.6

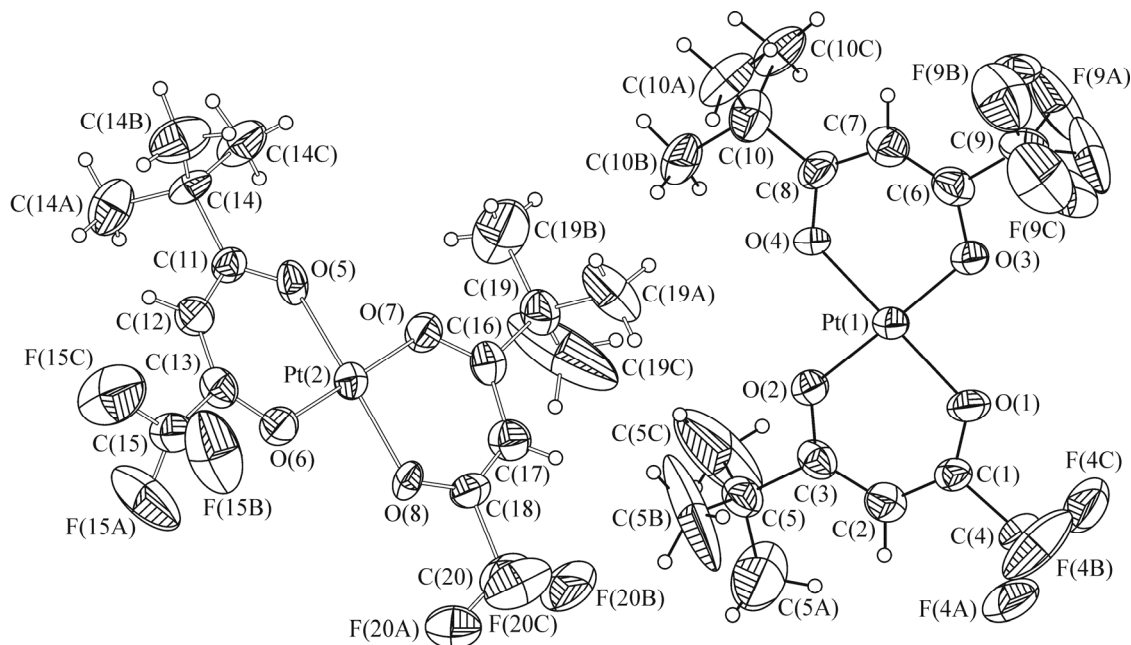


Fig. 3. Molecular structure in the *cis*-Pt(ptac)₂ phase with atomic numbering.

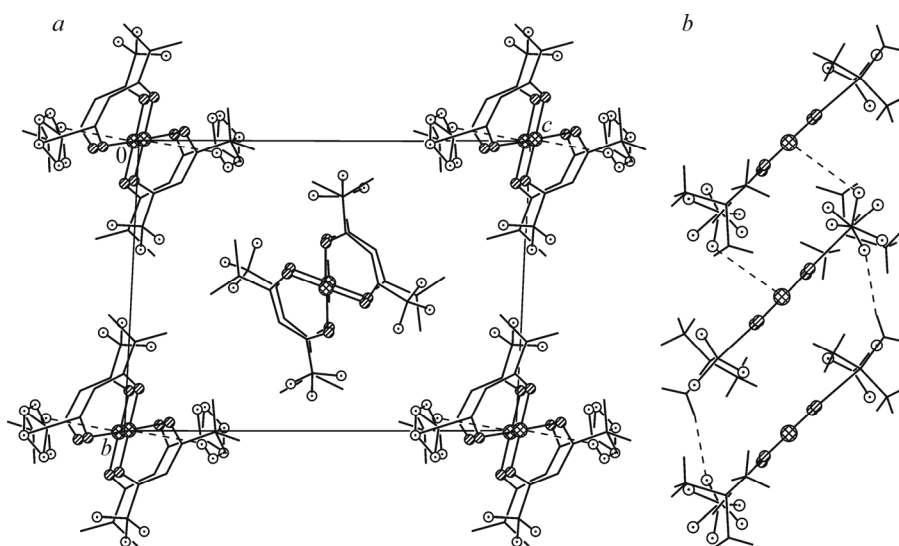


Fig. 4. Packing of molecules in the *cis*-Pt(ptac)₂ phase along the *X* axis (*a*) and the stack of Pt(1) complexes (*b*).

the stack axes are $\sim 42^\circ$. In a stack, the platinum coordination is completed to pyramidal by contacts with the CF_3 group of the neighboring complex at the Pt...F distance of 3.58 Å. The intermolecular F...F and F...H interactions in the crystal have the shortest estimates of 3.05 Å and 2.48 Å.

Structure of *trans*-Pt(ptac)₂ is formed of isolated centrosymmetric complexes lying on the mirror plane *m*; the structure of the molecule of the complex with atomic numbering is shown in Fig. 5 *a*. The coordination square is [PtO₄]; the Pt–O bond lengths from the side of different substituents are almost equal and are 1.980 Å; the chelate O–Pt–O angle is 95.0°. The maximum difference of 0.05 Å occurs in the O–C bonds; the average C–F and C–C bond lengths in the ligand substituents are 1.282 Å and 1.526 Å. The packing of molecules in the crystal along the *Y* axis is given in Fig. 5 *b*. In the structure, the complexes have the same orientation; each molecule is surrounded by six neighbors at the Pt...Pt distances of 7.916–8.552 Å. The shortest F...F, F...H intermolecular contacts have lower estimates of 2.86 Å and 2.50 Å. The crystals of

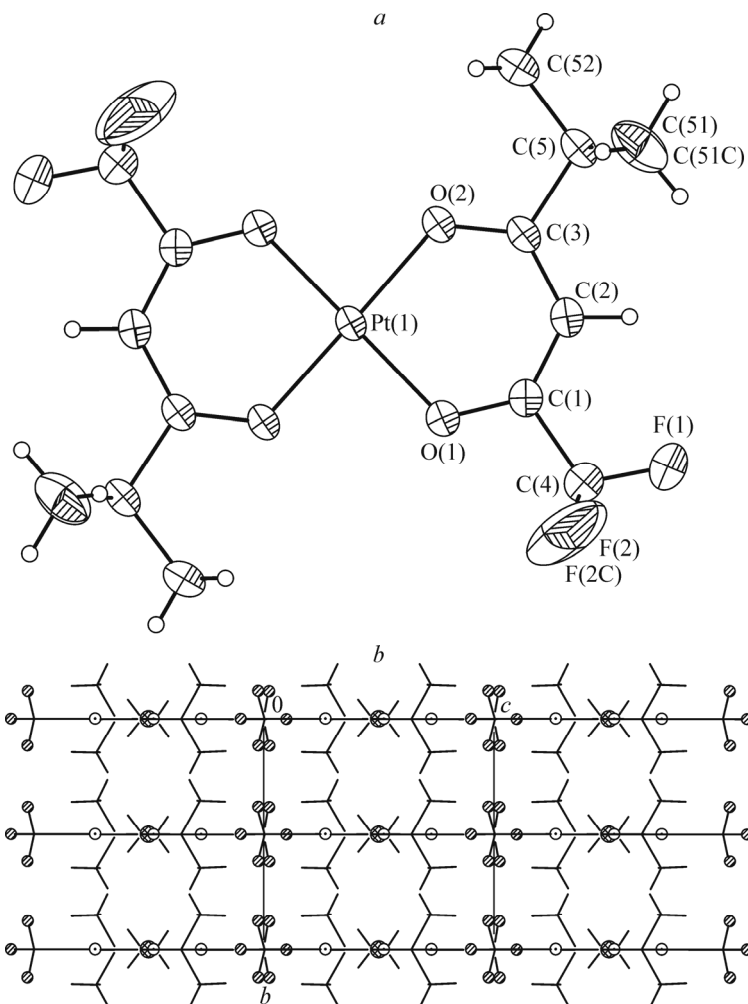


Fig. 5. Structure of complexes in the *trans*-Pt(ptac)₂ phase (a) and the packing of molecules in the crystal along the *Y* axis (b).

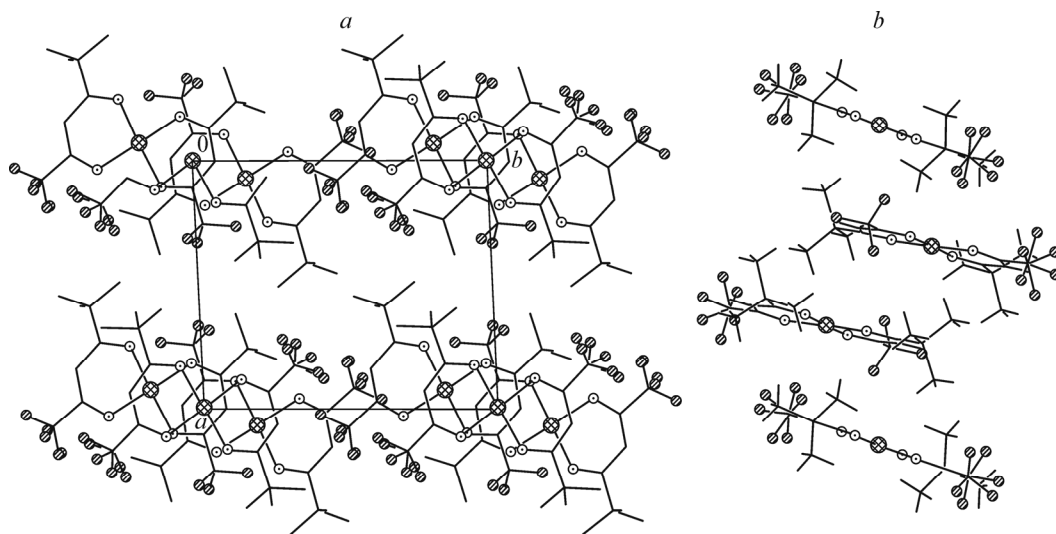


Fig. 6. Packing of molecules of the *cis*- and *trans*-isomers in the *mix*-Pt(ptac)₂ phase along the *Z* axis (a); mutual orientation of the Pt(1) and Pt(2) complexes in the structure (b).

the *cis*- and *trans*-isomers have different structural characters; the calculated density of the *trans*-isomer is larger than that of the *cis*-isomer by 0.09 g/cm³.

Structure of *mix*-Pt(ptac)₂ is a mixture of the *cis*–*trans* isomers in the 2:1 ratio. The compound crystallizes in the triclinic crystal symmetry; the structure is molecular formed of monomeric complexes whose structure is shown in Fig. 6 *a*; the *trans*-complex is centrosymmetric. The covalent Pt–O bond lengths vary in a range 1.972–1.991 Å; their average values are 1.984 Å for the *cis*-isomer and 1.976 Å for the *trans*-isomer. The chelate O–Pt–O angles are 95.2° and 94.6° respectively. The packing of the complexes along the *Z* axis is given in Fig. 6 *b*. The isomers are packed in infinite corrugated stacks with the Pt...Pt distances of 5.32 Å and 5.50 Å.

From the single crystal data, we calculated the theoretical diffraction patterns for all crystalline phases of Pt(ptac)₂ and compared them with the experimental diffraction pattern of the sublimated product in which all isolated phases of the Pt(ptac)₂ isomers are present (Fig. 1).

Therefore, this paper reports the single crystal XRD study of solid phases of the Pt(ptac)₂ isomeric complexes, which was performed for the first time. The crystal structures of the *cis*- and *trans*-isomers and their mixed phase were determined. From the TGA data it follows that the isomeric complexes have very similar thermal characteristics. The observed small difference in the volatility of the complexes is likely to be due to the different packing of molecules of the isomers in the crystal lattice. It can be supposed that the less volatile *trans*-isomer of Pt(ptac)₂, which has a greater X-ray density and the uniform intermolecular environment, is characterized by a greater energy of the crystal lattice.

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REFERENCES

1. D. J. Comstock, S. T. Christensen, J. W. Elam, M. J. Pellin, and M. C. Hersam, *Adv. Funct. Mater.*, **20**, 3099–3126 (2010).
2. A. Cowley, *Platinum Met. Rev.*, **55**, No. 2, 98–120 (2011).
3. C. Schoßler, A. Kaya, J. Kretz, M. Weber, and H. W. P. Koops, *Microelectron. Eng.*, **30**, 471–494 (1996).
4. B. M. Kuchumov, T. P. Koretskaya, Y. V. Shevtsov, et al., *ESC Transactions*, **25**, No. 8, 909–916 (2009).
5. I. K. Igumenov, G. I. Zharkova, I. A. Baidina, P. A. Stabnikov, et al., *Electrochem. Soc. Proc.*, **2005-09**, 675–682 (2005).
6. N. V. Gelfond, P. S. Galkin, I. K. Igumenov, et al., *J. Phys. IV France.*, **11**, 593–599 (2001).
7. R. V. Garcia and T. Goto, *Mater. Trans.*, **44**, No. 9, 1717–1728 (2003).
8. C. Thurier and P. Doppelt, *Coord. Chem. Rev.*, **252**, 155–169 (2008).
9. G. I. Zharkova, I. K. Igumenov, and S. V. Zemskov, *Koord. Khim.*, **9**, No. 6, 845–850 (1983).
10. G. I. Zharkova, I. A. Baidina, R. A. Stabnikov, and I. K. Igumenov, *J. Struct. Chem.*, **47**, No. 4, 716–725 (2006).
11. G. I. Zharkova, I. K. Igumenov, S. V. Tkachev, and S. V. Zemskov, *Koord. Khim.*, **8**, No. 1, 74–81 (1982).
12. G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **7**, No. 3, 433–440 (1967).
13. APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11) and SHELXTL (Version 6.12), *Bruker Advanced X-ray Solutions*, Bruker AXS Inc, Madison, Wisconsin, USA (2004).