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Synthesis, Crystal Structure, and Hirshfeld Surface Analysis of Hexachloroplatinate and Tetrachlorouranate of 3-Carboxypyridinium—Halogen Bonds and π -Interactions vs. Hydrogen Bonds

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Abstract: This work aimed to synthesize new platinum and uranium compounds with nicotinic acid. In this article we describe the synthesis of two new anionic complexes $(\text{HNic})_2[\text{PtCl}_6]$ and $(\text{HNic})_2[\text{UO}_2\text{Cl}_4]$ using wet chemistry methods. The structure of the obtained single crystals was established by single-crystal X-ray diffraction. The Hirshfeld surface analysis of the obtained complexes and their analogue $(\text{HNic})_2[\text{SiF}_6]$ was carried out for the analysis of intermolecular interactions. Hydrogen bonds ($\text{H}\cdots\text{Hal}/\text{Hal}\cdots\text{H}$ and $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$) make the main contribution to intermolecular interactions in all compounds. Other important contacts in cations in all compounds are $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ and $\text{C}\cdots\text{Hal}/\text{Hal}\cdots\text{C}$; in anions $\text{H}\cdots\text{Hal}/\text{Hal}\cdots\text{H}$. The Pt-containing complex has a halogen- π interaction and halogen bonds, but Si-containing complex has a π - π stacking interaction; these types of interactions are not observed in the U-containing compound.

Keywords: X-ray diffraction analysis; Hirshfeld surface analysis; nicotinic acid; platinum; uranium; π -interactions; halogen bonds; hydrogen bonds

1. Introduction

The synthesis and investigation of structural features of biomolecular *f*-element compounds are of great fundamental and practical interest in various fields including medicine, radioecology, and toxicology. In our work, we pay attention to niacin, also known as nicotinic acid or vitamin B₃, which plays a significant role in cellular energy metabolism [1]. Since nicotinic acid contains not only a carboxyl group but also a nitrogenous heterocycle, it has great potential to form compounds with metals using various mechanisms. One of the mechanisms is realized through non-covalent interactions between the metal atom and the nitrogen atom or π -electron density of the ring [2]. Weak non-covalent interactions are important for the design, operation, and efficiency of molecular sensors and switches [3,4]. These contacts include anion- π interaction (including the usual anion- π , anion- π -cation and anion- π - π interactions) as well as π -stacking, or cation- π -interactions. Since interactions of this type provide rapid association-dissociation between molecules, they are of great importance in the formation of biological self-assembling systems and pharmaceuticals [5].

Previous works have noted the role of intermolecular hydrogen bonds (HB) and π - π interactions in cocrystallization [6] and self-association [7,8] for nicotinic acid and its derivatives. The use of nicotinic acid in organic frameworks with various metals is also based on various non-valent interactions [9,10]. Tetranuclear and hexanuclear platinum-containing metallocycles based on non-covalent interactions are known [11]. Nicotinic

acid metal complexes show various biological activities (antimicrobial, anti-inflammatory, analgesic, anti-tubercular, anticancer, etc.) [12].

Organic platinum compounds (dichlorodiammineplatinum, diammineplatinum, etc.) are used as cytostatics in the treatment of various forms of cancer [13,14]. Currently, a search is underway for new platinum compounds for use in medicine, including the use of nicotinic acid [15,16].

The coordination chemistry of *f*-elements, especially their halogen derivatives, makes it possible to form many intermolecular interactions. This opens up a large range of functionalities for such compounds. In [4], the platinum complexes [(tBu₂bpy)Pt(C≡CAr)₂] (tBu₂bpy = 4,4'-bis-tert-butyl-2,2'-bipyridine, Ar = 4-pyridyl, 1; 3-pyridyl, 2; 2-pyridyl, 3; 4-ethynylpyridyl, 4; 2-thienyl, 5; pentafluorophenyl, 6) were synthesized and the following types of interactions have been described: C-H...π (C≡C), C-H...N(py), Cl...Cl, and C-H...F-C.

The study of uranium compounds with biomolecules is important in toxicology for detecting their toxic effects in cells [17]. In radioecology, the study of various uranium compounds with biologically active molecules is important for assessing possible mechanisms of uranium immobilization in the environment in plants, algae, fungi, and microorganisms. Previously, we have shown the effect of uranium immobilization due to carbonyl groups of o-polysaccharide bacteria living in uranium-contaminated groundwater [18]. In [19], uranium complexes with nicotinic acid in solutions were observed, and their formation constants were determined. The formation of uranium complexes with nicotinic acid has also been shown in [20].

Numerous works have noted the ability of uranium-containing compounds to participate in intermolecular interactions [21–24]. Thus, the complexes of uranyl cation with 4-halopyridinium ions (Hal = Cl, Br, I) can be divided into two categories based on the different modes of hydrogen bonding and halogen–halogen interactions present in the crystal structures [25].

Besides its involvement in nuclear energy, organic complexes of uranium are used in photoluminescence [26], magnetism [27], and catalytic [28,29].

In the major part of known Pt and U compounds with nicotinic acid, this acid enters into the coordination sphere of central atoms to form M-N or M-O coordination bonds. Thus, we aimed to obtain compounds of Pt(IV) and U(VI) with nicotinic acid in cationic form and to describe the crystal structure and intermolecular interactions.

2. Materials and Methods

2.1. Materials

Complexes 1 and 2 were synthesized using hexachloroplatinic (IV) acid hexahydrate (H₂PtCl₆ × 6H₂O, ~40% Pt), hydrochloric acid (HCl, 12.5 M), and nicotinic acid (C₆H₅NO₂ > 98%) all being ACS reagent grade chemicals purchased from Sigma-Aldrich (St. Louis, Missouri, United States) and used without additional purification. Uranyl acetate dihydrate (UO₂(CH₃COO)₂ × 2H₂O > 99%) was purchased from PA “IZOTOP”. (Moscow, Russia) To prepare the solutions, twice-distilled water was used, whose electric resistance was not less than 18 MOhm cm.

2.2. Synthesis of Complexes bis(3-pyridinecarboxylic Acid) Hexachloroplatinate, (HNic)₂[PtCl₆] (I)

In a 10 mL two-neck flask equipped with a thermometer and a reflux condenser, 10 mg of nicotinic acid was dissolved in 5 mL of 0.1 M HCl at room temperature. After dissolving all the nicotinic acid, 0.1 mL of an aqueous solution of 0.7 mol/L platinumic acid was added to the flask. The mixture was stirred for 5 min at room temperature, then the temperature was raised to 70 °C and held for 15 min. The resulting solution was cooled to room temperature without stopping stirring the flask, then removed the return condenser and thermometer; the flask with the solution was transferred to a vacuum desiccator and left for 12 h over anhydrous Mg(ClO₄)₂. The resulting yellow needles were washed with two 5 mL portions

of cold methanol and dried in an oil pump vacuum at room temperature. The yield was 81% for nicotinic acid. ($M_r = 654 \text{ g/mol}$).

2.3. Synthesis of Complexes bis(3-pyridinecarboxylic Acid) Uranile Tetrachloride, $(\text{HNic})_2[\text{UO}_2\text{Cl}_4]$ (II)

In a 10 mL two-necked flask equipped with a thermometer and a reflux condenser, 10 mg of nicotinic acid was dissolved in 2 mL of 0.1 M HCl. After dissolving all the nicotinic acid, 3 mL of a 0.01 M solution of uranyl acetate in 0.1 M HCl was added. The solution was stirred at room temperature for 5 min, then the mixture's temperature was gradually raised to 70 °C and held for 10 min. The resulting solution was cooled to room temperature without stopping stirring the flask, then removed the return condenser and thermometer; the flask with the solution was transferred to a vacuum desiccator and left for 12 h over anhydrous $\text{Mg}(\text{ClO}_4)_2$. The resulting yellow fluorescent crystals were washed with 5 mL of cold methanol and dried in vacuo at room temperature. The yield was 97% for nicotinic acid.

The precipitate **I** obtained was characterized by X-ray powder diffraction analysis; the diffraction pattern (Figure S1) was in a good agreement with the theoretical one and does not contain peaks corresponding to the starting substances. For compound **II**, the amount of the precipitate was insufficient for X-ray powder analysis. Some good crystals were selected for single-crystal X-ray diffraction studies.

2.4. Powder XRD Analysis

X-ray phase analysis was performed on a PANalytical AERIS diffractometer (Malvern, Worcestershire, United Kingdom; Almelo, Netherlands) with a Cu anode (40 kV). The analysis was performed over a 2 θ angle range from 3 to 70°.

2.5. Single-Crystal XRD Analysis

The crystal structure of all synthesized substances was determined by X-ray structural analysis using an automatic four-circle area-detector diffractometer Bruker KAPPA APEX II (Billerica, MA, USA) with $\text{MoK}\alpha$ radiation at a temperature of 100 and 296 K (for **I**) and 100 K (for **II**). The cell parameters were refined over the entire data set and data reduction by using SAINT-Plus software [30]. Absorption corrections were introduced using the SADABS program [31]. The structures were solved directly with the *SHELXS97* [32] and refined by *SHELXL-2018/3* [33]. The N- and C-bound hydrogen atoms were placed at calculated positions. The O-bound H atoms were located from different Fourier maps and refined with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O})$]. The hydrogen atoms of the OH groups in **I** were disordered over two positions with occupancies close to 0.5 (in final refinement, the occupancies were fixed at 0.5 at both temperatures). Tables and pictures for structures were generated by Olex2 [34].

Crystal data, data collection, and structure refinement details are summarized in Table 1. All other crystallographic parameters of structures **I** and **II** are indicated in Tables S1–S10. The atomic coordinates were deposited at the Cambridge Crystallographic Data Centre [35], CCDC № 2145387–2145389 for **I** at 296 K, at 100 K, and **II**, respectively. The Supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 30 January 2022).

Table 1. Crystal data and structure refinement for structures I and II.

	I		II
Empirical formula	C ₁₂ H ₁₂ N ₂ O ₄ Cl ₆ Pt	C ₁₂ H ₁₂ N ₂ O ₄ Cl ₆ Pt	C ₁₂ H ₁₂ N ₂ O ₆ Cl ₄ U
Formula weight	656.03	656.03	660.07
Temperature/K	296(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	9.0534(3)	8.9552(14)	6.6653(2)
<i>b</i> /Å	9.4852(3)	9.4270(16)	18.4856(5)
<i>c</i> /Å	11.9423(3)	11.8579(19)	7.4266(2)
α /°	90	90	90
β /°	110.521(1)	110.400(8)	95.0330(10)
γ /°	90	90	90
Volume/Å ³	960.45(5)	938.3(3)	911.52(4)
<i>Z</i>	2	2	2
<i>Z'</i>	0.5	0.5	0.5
ρ_{calc} /g/cm ³	2.268	2.322	2.405
μ /mm ^{−1}	8.159	8.352	9.521
<i>F</i> (000)	620.0	620.0	612.0
Crystal size/mm ³	0.2 × 0.18 × 0.1	0.32 × 0.12 × 0.1	0.16 × 0.14 × 0.06
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 Θ range for data collection/°	8.194 to 59.998	8.44 to 59.988	8.182 to 70
Index ranges	−11 ≤ <i>h</i> ≤ 12, −12 ≤ <i>k</i> ≤ 13, −16 ≤ <i>l</i> ≤ 16	−12 ≤ <i>h</i> ≤ 12, −13 ≤ <i>k</i> ≤ 13, −16 ≤ <i>l</i> ≤ 16	−8 ≤ <i>h</i> ≤ 10, −29 ≤ <i>k</i> ≤ 29, −11 ≤ <i>l</i> ≤ 11
Reflections collected	10,006	14,377	18,010
Independent reflections	2794 [<i>R</i> _{int} = 0.0205, <i>R</i> _{sigma} = 0.0201]	2735 [<i>R</i> _{int} = 0.0559, <i>R</i> _{sigma} = 0.0416]	4002 [<i>R</i> _{int} = 0.0283, <i>R</i> _{sigma} = 0.0253]
Data/restraints/parameters	2794/2/122	2735/2/121	4002/0/115
Goodness-of-fit on <i>F</i> ²	1.048	1.030	1.284
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0160, <i>wR</i> ₂ = 0.0372	<i>R</i> ₁ = 0.0235, <i>wR</i> ₂ = 0.0529	<i>R</i> ₁ = 0.0310, <i>wR</i> ₂ = 0.0546
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0234, <i>wR</i> ₂ = 0.0404	<i>R</i> ₁ = 0.0323, <i>wR</i> ₂ = 0.0568	<i>R</i> ₁ = 0.0398, <i>wR</i> ₂ = 0.0562
Largest diff. peak/hole/e Å ^{−3}	0.78/−0.69	0.82/−1.21	1.47/−2.32

3. Results and Discussion

3.1. Structural Description

Both compounds crystallize in the space group *P*2₁/*n* with two formula units in the unit cell. The asymmetric units are illustrated in Figure 1. Platinum and uranium atoms are in special positions two *a* and 2 *b*, respectively. In both compounds, the platinum and uranium atoms are octahedrally coordinated. Pt—Cl distances are changed from 2.3090(8) Å to 2.3180(8) Å in I at 100 K, and the average distance is 2.313 Å, which can be seen from Table 2. With the increase in temperature to 296 K, this distance slightly increases and amounts to 2.317 Å. At both temperatures, the Cl—Pt—Cl angles in I are close to 90° (Table 2).

Table 2. Selected geometric parameters (Å, °) for I.

100 K				296 K	
Pt1—Cl1	2.3180(8)	Cl2—Pt1—Cl3	90.89(3)	Pt1—Cl1	2.3220(6)
Pt1—Cl2	2.3090(8)	Cl2—Pt1—Cl1	89.06(3)	Pt1—Cl3	2.3139(5)
Pt1—Cl3	2.3107(8)	Cl3—Pt1—Cl1	90.43(3)	Pt1—Cl2	2.3144(5)

Figure 1. Molecular structure of **I** (a) and **II** (b) at 100 K, including atom labeling. Only one position of the disordered H-atom of the carboxyl group is shown in **I**. Displacement ellipsoids are drawn at the 50% probability level.

Uranyl tetrachloride forms a bipyramid. The average U—Cl distance in **II** is 2.658 Å, which is slightly shorter than in previous works in the CSD, where it was 2.67 Å. The U—O distance is 1.780(2) Å, which is longer than the average distance at 100 K in CSD, where it was 1.772 Å. This may be due to the participation of the oxygen atom of the anion in H-bonds. The angles Cl—U—Cl and O—U—Cl are close to 90°, as shown in Table 3. The position of the protonated oxygen atom in **I** and **II** is different relative to the nitrogen atom of the six-membered ring (torsion angles C4—C3—C7—O2(3) are −28.85° in **I** and −162.50° in **II**).

Table 3. Selected geometric parameters (Å, °) for **II**.

U1—O1	1.780(2)	O1—U1—Cl1	89.81(8)
U1—Cl1	2.6461(8)	O1—U1—Cl2	89.86(8)
U1—Cl2	2.6694(7)	O1—U1—Cl1	89.81(8)

The hydrogen bond system of **I** is shown in Figure 2a. In **I**, one bifurcate hydrogen bond O2—H2B...Cl1ⁱ and O2—H2B...Cl3ⁱ [symmetry code: (i) $-x+1, -y+1, -z+2$] is formed (Table 4). The strongest hydrogen bond is formed by N1—H1A with O1ⁱⁱⁱ of another cation with an N...O distance of 2.728(4) Å [symmetry code: (iii) $x-1/2, -y+3/2, z-1/2$]. In **II**, one bifurcate hydrogen bond is also formed (Figure 2b). N1—H1A forms a bifurcate H-bond with Cl2ⁱ and O2ⁱⁱ [symmetry codes: (i) $x+1, y, z+1$; (ii) $x, y, z+1$]. In both compounds, the CH groups of the six-membered rings form weak H-bonds of the C—H...Cl type, which provide additional bonding of cations and anions in the compounds, such as in [36,37]. In **I**, only one C—H...Cl bond is formed, in **II** three (Table 5), but two of them in **II** are weaker than in **I**.

Table 4. Hydrogen-bond geometry for **I** at 100 K (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O2—H2B...Cl1 ⁱ	0.85(2)	2.70(5)	3.486(3)	155(10)
O2—H2B...Cl3 ⁱ	0.85(2)	2.79(8)	3.401(3)	131(9)
O2—H2C...Cl3 ⁱⁱ	0.86(2)	2.61(4)	3.413(3)	155(8)
N1—H1A...O1 ⁱⁱⁱ	0.88	1.87	2.728(4)	163.0
C2—H2A...Cl1 ^{iv}	0.95	2.66	3.500(3)	148.0

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x-1/2, -y+1/2, z+1/2$; (iii) $x-1/2, -y+3/2, z-1/2$; (iv) $-x+1/2, y+1/2, -z+3/2$.

Figure 2. View showing the hydrogen and halogen bonds in **I** (a) [Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x-1/2, -y+1/2, z+1/2$; (iii) $x-1/2, -y+3/2, z-1/2$; (iv) $3/2-x, 1/2+y, 3/2-z$.] and hydrogen bonds in **II** (b) [Symmetry codes: (i) $x+1, y, z+1$; (ii) $x, y, z+1$]. Both positions of the disordered hydrogen atom of carboxyl group in **I** are shown.

Table 5. Hydrogen-bond geometry for **II** (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O1	0.857(3)	2.287(2)	3.125(3)	165.7(2)
N1—H1A...Cl2 ⁱ	0.88	2.81	3.380(3)	123.9
N1—H1A...O2 ⁱⁱ	0.88	2.00	2.721(3)	138.3
C2—H2A...Cl2 ⁱⁱⁱ	0.95	2.69	3.611(3)	163.4
C5—H5A...Cl2 ^{iv}	0.95	2.82	3.543(3)	133.8
C6—H6A...Cl1 ^v	0.95	2.67	3.411(3)	135.4

Symmetry codes: (i) $x+1, y, z+1$; (ii) $x, y, z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+1/2, -y+3/2, z+1/2$; (v) $-x+3/2, y+1/2, -z+3/2$.

The crystal packing in **I** can be represented as cationic and anionic layers parallel to the plane (−101) (Figure 3a). The cations in the layers are linked by hydrogen bonds of the N—H...O type and are connected to the anionic layers by hydrogen bonds of the O—H...Cl type. Anions in **I** are interconnected by halogen bonds Cl2...Cl3^v with a distance of 3.2074(12) Å [symmetry code: (v) $3/2-x, 1/2+y, 3/2-z$], as in [38]. The crystal packing in **II** can also consist of cationic and anionic layers parallel to the plane (010). In this case, cations interact with anions and other cations, but anions do not interact, unlike in **I**.

Figure 3. Crystal packing of **I** (a), showing the layers parallel to the plane (−101) with hydrogen and halogen bonds between them, and **II** (b), showing the layers parallel to plane (010) with hydrogen bonds between them.

In the earlier research works only one compound of singly protonated nicotinic acid with an octahedral anion was found, bis(3-carboxypyridinium) hexafluorosilicate (**III**) [39]. In [39], hexafluorosilicate was also added to nicotinic acid by hydrogen bonds. Compound **III**, like ours, crystallizes in $P2_1/n$ sp. gr. However, other layers are formed in **III**, in

which the anions do not interact with each other and in which there are no halogen bonds. However, in **III**, layers are stabilized due to the presence of π -stacking interaction between the rings, which is absent in **I** and **II**.

It has been established from the literature data that, upon interaction with nicotinic acid, platinum usually participates in Pt–N bonds and is attached directly to the nitrogen atom of the six-membered ring, as in [40,41]. Only one uranium-containing compound with nicotinic acid is known [42].

3.2. Hirshfeld Surface Analysis

Hirshfeld surface (HS) analysis was proposed as a new means of separating space in molecular crystals. The Hirshfeld surface covers the molecule and determines the volume of space in which the electron density of the promolecule exceeds the density of all neighboring molecules [43]. Fingerprint plots are a convenient way of summarizing the intermolecular contacts present in crystals, decomposing this fingerprint plot into features to identify specific interactions. This method can be used to analyze π - π stacking interactions [44], halogen and hydrogen bonds [45,46], and other weak non-covalent interactions [47,48].

The Crystal Explorer 21 [49] program was used to analyze the crystal and Hirshfeld surface analysis interactions. The donor-acceptor groups are visualized using a standard (high) surface resolution and d_{norm} surfaces, as illustrated in Figure 4. Red spots on the surface of the d_{norm} plot indicate intermolecular contacts involving the hydrogen and halogen bonds. The brightest red spots correspond to the strongest hydrogen bond N—H $\cdots$ O in both compounds and O—H $\cdots$ O in **II** (Figure 4). Weaker red spots correspond to bonds O—H $\cdots$ Cl in **I** and C—H $\cdots$ Cl for cations in both compounds. For the anion, red spots on the surface d_{norm} correspond to hydrogen bonds in **I** and **II**, and halogen bonds in **I**.

Figure 4. Hirshfeld surface mapper over d_{norm} for (a) cation and (b) for anion to visualize the interactions in compound **I** and in **II** (c).

π -stacking interactions are absent in **I** and **II**, which can be seen from the absence of characteristic red and blue triangles on the shape-index surface (Figure 5).

Figure 5. Hirshfeld surface mapper shape-index of cation in **I** (a) and **II** (b).

On the Hirshfeld surface d_{norm} above the six-membered ring, a weak red spot corresponds to the C...Cl interaction, which is also seen from the bright red spot on the shape index surface. The C6...Cl distance in **I** is 3.299 Å, which is shorter than the sum of the van der Waals radii of C and Cl. The distance between the center of the ring and the chlorine atom Cl1 in **I** at 100 K is 3.431 Å (3.489 Å at 296 K), and the angle α (Figure 6) is 70.97° (70.92° at 296 K). This contact can be called an anion- π interaction since the distance between the center of the ring and the anion is less than 5 Å, and the angle α is greater than 50° [3,50,51].

Figure 6. View showing halogen- π interactions in the structure **I** at 100 K (a) and "spacefill" image (b).

Since there are analogies with (HNic)₂[SiF₆], the Hirshfeld surfaces were also constructed and compared for this derivative of the nicotinium cation. Fingerprint plots for compounds **I–III** are shown in Figures S1–S6 and can be used to highlight specific short interactions. Separately, 2D branchings for cations and anions were built. It should be noted that the shape of fingerprint graphs for different types of contacts in compounds **I–III** is different. For example, the O...H/H...O hydrogen bonds, although there are two elongated peaks in **I** and **II**, they are sharper in **I** than in **II**, and in **III** they look like something in between. In this case, all contacts occupy approximately the same position on the fingerprint plots. The different anionic geometry can explain the different shapes of the fingerprint graphs in the compounds and the substitution of chlorine atoms by other atoms.

The temperature changes do not introduce significant changes in the percentage contribution of each type of contacts in cation **I**, as shown in Figure 7. In all compounds in cations, the main contribution to intermolecular interactions is made by hydrogen bonds (contacts H...Hal/Hal...H and O...H/H...O). The van der Waals interactions H...H and C...H/H...C also play an essential role in the cations of all compounds. The total contribution of hydrogen bonds of the type H...Hal/Hal...H and O...H/H...O in cations

in **I** and **II** is the same and is approximately 50%. However, the proportion of van der Waals interactions changes from **I** to **II**. The share of $H\cdots H$ decreases, while the share of $C\cdots H/H\cdots C$, on the contrary, increases. The proportion of contacts of the $C\cdots Cl/Cl\cdots C$ type decreases, which in compound **I** is explained by the presence of the anion– π interaction. The replacement of the anion leads to an increase in the proportion of $H\cdots Hal/Hal\cdots H$ and $O\cdots H/H\cdots O$ contacts in the cation in compound **III** compared to **I** and **II**.

Figure 7. Percentage contributions to the Hirshfeld surface area for the various close intermolecular contacts for cations in **I–III**.

In the anions in compound **I**, a temperature change also does not affect the fraction of intermolecular interactions (Figure 8). In the transition from **I** to **II** in anions, the proportion of hydrogen bonds in the total increases. In **II**, the ratio of $C\cdots Cl/Cl\cdots C$ and $Cl\cdots Cl$ interactions strongly decreases, which, as noted above, is due to the absence of anion– π interaction and halogen bonds in **II**. The replacement of a chlorine atom by fluorine leads to an increase in the proportion $H\cdots Hal/Hal\cdots H$, which may not all be called hydrogen bonds [52], but the virtual absence of other types of interactions. This may be because fluorine is not characterized by the formation of both hydrogen bonds and different types of non-valent interactions.

Figure 8. Percentage contributions to the Hirshfeld surface area for the various close intermolecular contacts for anions in **I–III**.

4. Conclusions

Although the compounds are similar (the same cation and octahedral or pseudooctahedral anion) and crystallize in the same space group, the compounds are not isostructural. They form a different system of hydrogen bonds and packing. For the first time, uranium

and platinum compounds with protonated nicotinic acid were obtained, in which there are no M-N or M-O coordination bonds. These compounds are stabilized by classical hydrogen bonds of the N-H...Cl/O and O-H...Cl/O types, as well as by nonclassical C-H...Cl hydrogen bonds, halogen bonds, and π -anionic interactions in (HNic)₂[PtCl₆]. In (HNic)₂[UO₂Cl₄], the structure is stabilized by N-H...Cl/O and O-H...Cl/O hydrogen bonds. Replacement of the anion in (HNic)₂[SiF₆] leads to the formation of another type of packing.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst12020271/s1>, Figure S1. Experimental and theoretical powder XRD spectra of I at 296 K. Figure S2. The 2D fingerprint plots of interatomic interactions for cation in I at 100 K show the percentages of contacts contributed to the total Hirshfeld surface area of the molecules. Figure S3. The 2D fingerprint plots of interatomic interactions for cation in II at 100 K show the percentages of contacts contributed to the total Hirshfeld surface area of the molecules. Figure S4. The 2D fingerprint plots of interatomic interactions for cation in III at 100 K show the percentages of contacts contributed to the total Hirshfeld surface area of the molecules. Figure S5. The 2D fingerprint plots of interatomic interactions for anion in I at 100 K show the percentages of contacts contributed to the total Hirshfeld surface area of the molecules. Figure S6. The 2D fingerprint plots of interatomic interactions for anion in II at 100 K show the percentages of contacts contributed to the total Hirshfeld surface area of the molecules. Figure S7. The 2D fingerprint plots of interatomic interactions for anion in III at 100 K show the percentages of contacts contributed to the total Hirshfeld surface area of the molecules. Table S1. Bond lengths for I at 100 K. Table S2. Bond angles for I at 100 K. Table S3. Torsion angles for I at 100 K. Table S4. Bond lengths for I at 296 K. Table S5. Bond angles for I at 296 K. Table S6. Hydrogen bonds for I at 296 K. Table S7. Torsion angles for I at 296 K. Table S8. Bond lengths for II at 100 K. Table S9. Bond angles for II at 100 K. Table S10. Torsion angles for II at 100 K.

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