

## SYNTHESIS, PHYSICO-CHEMICAL ANALYSIS AND CRYSTAL STRUCTURE OF 3,5-DINITROBENZOATE OF URANIUM U(VI)

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**Abstract.** A new complex of U(VI) was synthesized and studied by physicochemical methods, and the crystal molecular structures were deciphered. It was found that the central atom of U(VI) is coordinated by the carboxyl groups of the ligand according to the chelate type. The coordination number of the central atom of U(VI) is eight and is carried out with the help of four oxygen atoms of two carboxyl groups, two atoms of oxygen from two molecules of water and two oxygen atoms of the uranyl cation-UO<sub>2</sub>.

**Keywords:** Complex of 3,5 dinitrobenzoic acid, Uranium complexes, Chelate type coordination, Coordination number eight.

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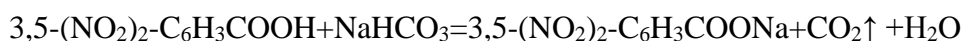
### 1. Introduction

The mononuclear complexes of uranyl, which U(VI) atom has hexagonal – bipyramidal coordination, are one of the most common types of carboxylate complexes of uranyl (Carter *et al.*, 2018; Jian *et al.*, 2012; Mougel *et al.*, 2010). Synthesized and deciphered the crystal structures of uranyl U(VI) benzoate, which the central U atom is coordinated by the carboxyl group of the ligand according to the chelate type (Deltel & Cahil, 2011; Carter *et al.*, 2019).

Furthermore, synthesized and studied the structure of halogens derivatives of benzoic acid (Deltel *et al.*, 2011; Serezhkin *et al.*, 2019). In addition, the structures of p – nitrobenzoate of U(VI) were investigated and it was found that the central atom U(VI) is coordinated by anions of p – nitrobenzoic acid according to the chelate type. The coordination number of the metal is eight (Serezhkin *et al.*, 2019). Having two nitro groups in the meta position in the benzene ring and exhibiting the meta effect, the crystal and molecular structures of metals Ce (III), and Cu (II) complex of 3,5–dinitrobenzoic acid were synthesized and studied (Tahir *et al.*, 1996). There is a lack of information in the literature about 2,5 – dinitrobenzoate of U(VI). In the present study, single crystals are treated, and the structures of the new complex are deciphered.

### 2. Experimental methods

The studied complex was synthesized in the following way. First, sodium salt of 3,5-dinitrobenzoic acid was obtained using the following reactions:



2.34 g (0.02 mole) of sodium 3,5-dinitrobenzoate is dissolved in hot (50-60 °C) distilled water, and a hot solution of 0.231 g (0.01 mole) salt  $\text{UO}_2(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ . The solution is filtered and left at room temperature. After a few days yellow lamellar crystals fall out. The resulting crystalline compounds are dried in a desiccator over anhydrous  $\text{CaCl}_2$ . Element analysis was performed using a Costech ECS 4010 CHNSO devise.

Found %: C – 23.29 H – 1.52, N – 7.58



Coled %: C – 23.07, H – 4.37, N – 7.69

In the current study, only commercially available reagent-grade chemicals were used. Infrared spectra were measured on a Perkin-Elmer spectrophotometer (100PT-TR) using KBr pallets in the range of 450-4000-  $\text{cm}^{-1}$ .

Thermal analysis was perfected by the NETZSCH STA-409 Pd PG-derivatograph. The DTA, FG, and DTG curves were taken in a static air atmosphere at an increasing heating rate of 10 °C/min from 20 to 800 °C by using platinum crucibles.

A suitable crystal was selected on a X<sub>ta</sub>LAB AFC11(RINC): quarter-chi single diffractometer. The crystal was kept at 294 K during data collection using Olex 2 (Dolomanov *et al.*, 2009). The structure was studied with the Shelx T (Sheldrick *et al.*, 2015; Bourhis *et al.*, 2015). The results obtained were analyzed and information about the structure was obtained. Information about the structural parameters of the objects of study is given in Tables 1, 2, 3 and 4.

**Table 1.** Crystal data and structure refinement for  $\text{UO}_2(\text{II})$

CCDC	2190646	Theta range for data collection	3.543 to 32.662°
Empirical formula	$\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_{16}\text{U}$	Index ranges	-30 ≤ h ≤ 30, -10 ≤ k ≤ 10, -21 ≤ l ≤ 21
Formula weight	728.29	Reflections collected	32143
Temperature	100.0(2) K	Independent reflections	1766 [R(int) = 0.0317]
Wavelength	0.71073 Å	Completeness to theta = 25.242°	97.2 %
Crystal system	Orthorhombic	Absorption correction	Semi-empirical from equivalents
Space group	$C_{mca}$	Max. and min. transmission	0.752 and 0.166
Unit cell dimensions	$a = 20.0510(3)$ Å $b = 6.60100(10)$ Å $c = 14.4184(2)$ Å $\alpha = \beta = \gamma = 90^\circ$	Refinement method	Full-matrix least-squares on $F^2$
Volume	$1908.37(5)$ Å <sup>3</sup>	Data / restraints / parameters	1766 / 0 / 89
Z	4	Goodness-of-fit on $F^2$	1.023
Density (calculated)	$2.535 \text{ Mg/m}^3$	Final R indices [I > 2σ(I)]	R1 = 0.0324, wR2 = 0.0820
Absorption coefficient	$8.607 \text{ mm}^{-1}$	R indices (all data)	R1 = 0.0331, wR2 = 0.0832
F(000)	1368		
Crystal size	$0.21 \times 0.18 \times 0.03 \text{ mm}^3$		

**Table 2.** Fractional atomic coordinates and equivalent isotropic displacement parameters for Ni\_p\_nitro BK piraz  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor

Atoms	<i>a</i> / <i>x</i>	<i>b</i> / <i>x</i>	<i>c</i> / <i>z</i>	$U_{(eq)}$
U(1)	0.5000	0.5000	0.5000	0.022(1)
O(1)	0.5000	0.2338(7)	0.4930(1)	0.030(1)
O(2)	0.3885(2)	0.4980(1)	0.4239(2)	0.028(1)
O(3)	0.1732(1)	0.6776(2)	0.2740(1)	0.030(1)
O(4)	0.847(1)	0.5309(3)	0.3291(2)	0.034(1)
O(5)	0.5000	0.5279(5)	0.3304(3)	0.037(1)
N(1)	0.1429(1)	0.5849(2)	0.3344(1)	0.025(1)
C(1)	0.3573(3)	0.5000	0.5000	0.024(1)
C(2)	0.2830(3)	0.5000	0.5000	0.023(1)
C(3)	0.2485(1)	0.5386(3)	0.4177(1)	0.024(1)
C(4)	0.1792(1)	0.5377(3)	0.4202(1)	0.024(1)
C(5)	0.1425(3)	0.5000	0.5000	0.024(1)

**Table 3.** Bond lengths, Å

U(1)-O(1)	1.760(5)	O(3)-N(1)	1.2253(18)	C(2)-C(3)#3	1.398(3)
U(1)-O(5)	2.453(4)	O(4)-N(1)	1.224(3)	C(3)-C(4)	1.390(3)
U(1)-O(2)#1	2.490(3)	O(5)-H(5A)	0.94(4)	C(3)-H(3)	0.9500
U(1)-O(2)#2	2.490(3)	N(1)-C(4)	1.469(2)	C(4)-C(5)	1.388(4)
U(1)-O(2)#3	2.490(3)	C(1)-O(2)#3	1.264(4)	C(5)-C(4)#3	1.388(4)
U(1)-O(2)	2.490(3)	C(1)-C(2)	1.488(8)	C(5)-H(5)	0.9500
O(2)-C(1)	1.264(4)	C(2)-C(3)	1.398(3)		

**Table 4.** Angles, °

O(1)#1-U(1)-O(1)	180.0	O(5)-U(1)-O(2)	63.95(7)	C(3)-C(2)-C(1)	119.7(2)
O(1)-U(1)-O(5)#1	88.98(10)	O(2)#1-U(1)-O(2)	180.00(6)	C(4)-C(3)-C(2)	118.2(3)
O(1)-U(1)-O(5)	91.02(10)	O(2)#2-U(1)-O(2)	127.70(14)	C(4)-C(3)-H(3)	120.9
O(5)#1-U(1)-O(5)	180.0	C(1)-O(2)-U(1)	93.6(3)	C(2)-C(3)-H(3)	120.9
O(1)-U(1)-O(2)#1	91.75(4)	U(1)-O(5)-H(5A)	124(2)	C(5)-C(4)-C(3)	123.6(3)
O(5)-U(1)-O(2)#1	116.05(7)	O(4)-N(1)-O(3)	125.01(17)	C(5)-C(4)-N(1)	118.3(2)
O(5)-U(1)-O(2)#2	63.95(7)	O(4)-N(1)-C(4)	117.61(18)	C(3)-C(4)-N(1)	118.13(18)
O(1)-U(1)-O(2)#3	91.75(4)	O(3)-N(1)-C(4)	117.37(14)	C(4)#3-C(5)-C(4)	115.9(4)
O(5)-U(1)-O(2)#3	116.05(7)	O(2)-C(1)-O(2)#3	120.6(5)	C(4)#3-C(5)-H(5)	122.0
O(1)-U(1)-O(2)	88.25(4)	O(2)-C(1)-C(2)	119.7(3)	C(4)-C(5)-H(5)	122.0
O(5)#1-U(1)-O(2)	116.05(7)	C(3)-C(2)-C(3)#3	120.5(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,y,z #3 x,-y+1,-z+1.

### 3. Results and Discussion

In the IR spectra of 3,5-dinitrobenzoate U(VI), absorption bands are observed in the region of  $1608\text{ cm}^{-1}$ , corresponding to the asymmetric vibrations of the carboxylic group and band in the region of  $1463\text{ cm}^{-1}$  corresponding to the symmetric of the carboxylic group. The difference between these frequencies determines type of coordination of carboxyl groups:  $\Delta\nu = (\nu_{asym}\text{COO}) - (\nu_{sym}\text{COO}) = 1608\text{ cm}^{-1} - 1463\text{ cm}^{-1} = \Delta\nu = 145\text{ cm}^{-1}$  shows the bidentate nature of the carboxyl group.

The absorption bands in the region of  $1358\text{ cm}^{-1}$ ,  $825\text{ cm}^{-1}$ ,  $560\text{ cm}^{-1}$  refer to the connection aromatic –  $\text{NO}_2$  coordinated  $\text{H}_2\text{O}$ , and Me – O group, respectively (Fig.1).

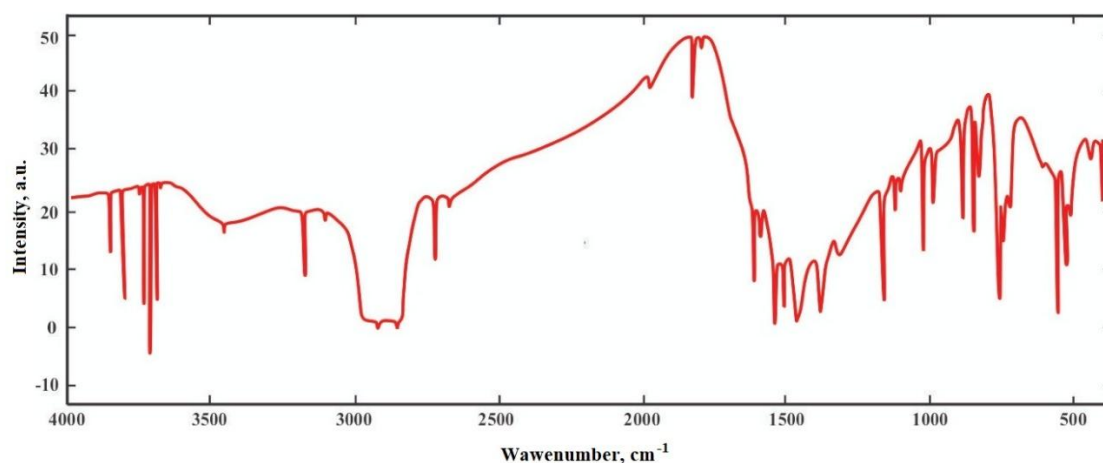


Fig.1. IR spectra of 3,5 – dinitrobenzoate of U(VI)

Thermogravimetric analysis of the complex shows that thermal decomposition occurs in four stages (Fig. 2).

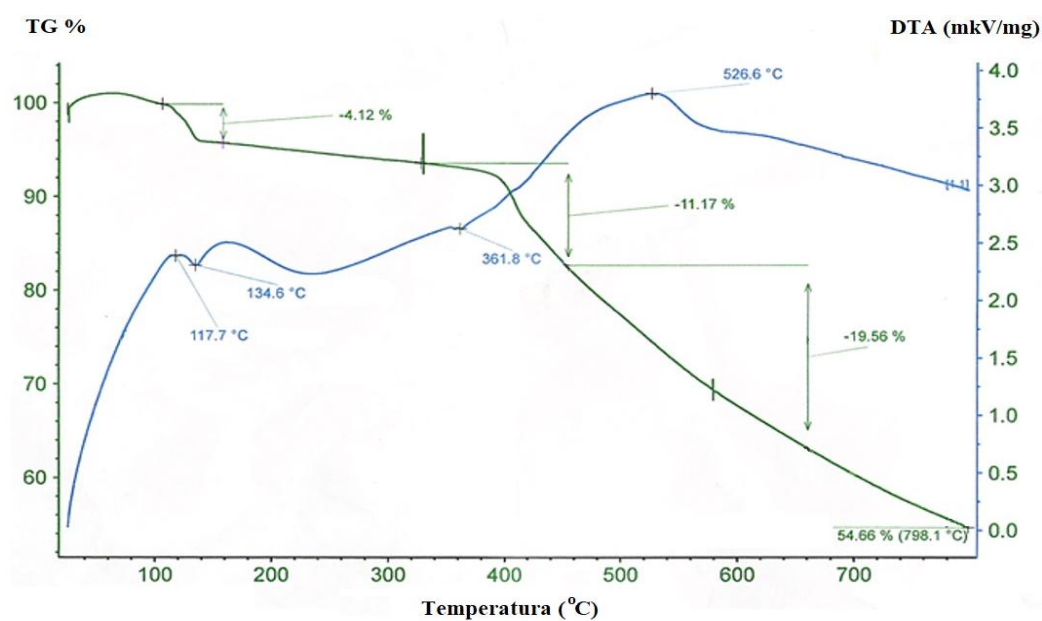


Fig. 2. Thermogram of 3,5 - dinitrobenzoate complex of U(VI)

The first stage corresponds to a temperature range of 117.7 – 134.6 °C accompanied by deep exothermic effects, which corresponds to the removal of coordinating water molecules.

The second stage is observed in the temperature range of 134.6 – 361.8 °C, along with deep endothermic effects, which indicates a stable dimeric molecule of the complex.

Third stage of thermolysis process at the temperature range of 361.8 – 526.6 °C is related to the destruction of the complex. In addition, the organic part of the complex burns out at this stage. The end product of thermolysis is uranium carbonate.

The crystal structure of the U(VI) complex is shown in Fig. 3.

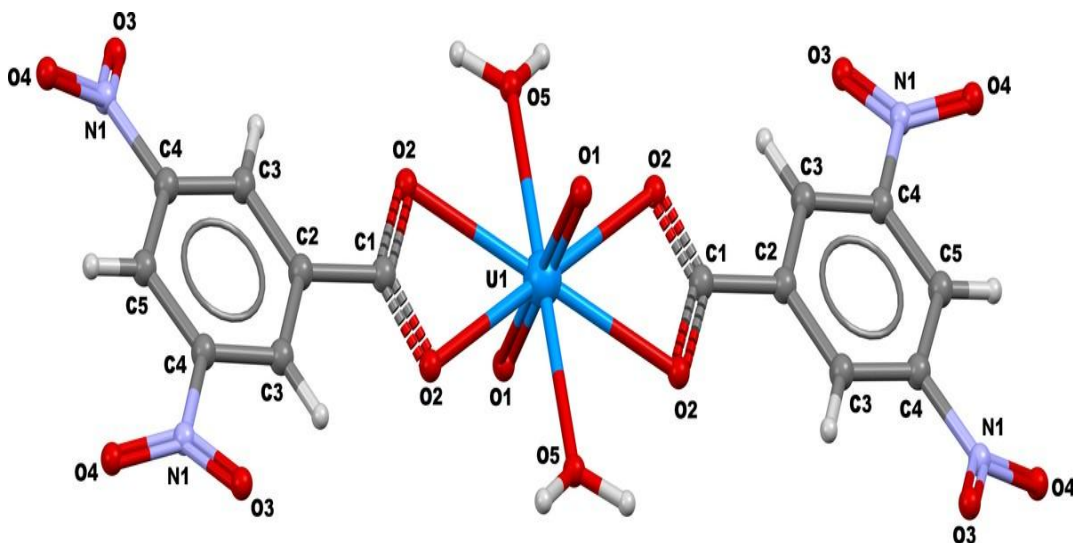


Fig.3. Crystal structure of complexes of U(VI) with 3,5–dinitrobenzoate

As can be seen from Fig. 3, the central atom U is coordinated by two oxygen atoms of the carboxyl group  $U(1) - O(1) = 1.760 \text{ \AA}$ ,  $U(1) - O(2) = 2.490 \text{ \AA}$ . Two water molecules are coordinated to uranium cations by donor oxygen atoms and add to its coordination number eight. Distance  $U - H_2O = 2.490 \text{ \AA}$ . The C – C distance in benzene is equal to an average of  $1.39 \text{ \AA}$  and corresponds to that in other derivatives of benzoic acid.

The C – NO<sub>2</sub> distance is  $1.469 \text{ \AA}$  and corresponds to other complexes of 3,5 - dinitrobenzoic acid [Sheldrick *et al*].

#### 4. Conclusions

Have been synthesized and studied a new complexes of uranium U(VI) with 3,5 dinitrobenzoate. The crystal structure of the complex was determined and it was found that the central atom of U(VI) is coordinated by the carboxyl groups of the ligand according to the chelate type. The structure of the complexes was also characterized by infrared (IR) spectroscopy and thermogravimetric (TGA) analysis. It was found that the difference between frequencies of the characteristic bands in the IR spectra shoves the bidentate nature of the carboxyl group. TGA analysis shows that the complex of uranium with 3,5 dinitrobenzoate undergoes thermal degradation in 4 stages, which is accompanied by various endothermic, exothermic effects, and thermolysis processes.

## References

- Carter, K.P., Kalaj, M., Keerodje, A., Cahil, C.L. (2018). Probing hydrogen and halogen-oxo interactions in uranyl coordination polymers: a combined crystallographic and computational study. *CrystEngComm*, 20, 4916-4921.
- Jian, L.W., Zhao, Y.D. Shi, B.D., Yong, H.X. (2012). Article Syntheses, structures, and fluorescent properties of two uranium coordination polymers with carboxylic acids. *Journal of Coordination Chemistry*, 65, 3546-3555.
- Mougel, V., Biswas, B., Pecaut J., Mazzanti M. (2010). New insights into the acid mediated disproportionation of pentavalent uranyl. *Chemical Communications*, 46(45), 8648-8650.
- Deifel, N.P., Cahill, C.L. (2011). Combining coordination and supramolecular chemistry for the formation of uranyl-organic hybrid materials. *Chemical Communications*, 47, 6114-6119.
- Carter, K.P., Kalaj, M., Kerridge, A., Cahil, C.L. (2018). Probing hydrogen and halogen-oxo interactions in uranyl coordination polymers: a combined crystallographic and computational study. *CrystEngComm*, 20, 4916-4925.
- Serezhkin, V.N., Grigor'ev, M.S., Fedoseev, A.M., Budantseva, N.A., Serezhkina L.B. (2019). Synthesis and structure of U(VI), Np(VI), and Pu(VI) 2-fluorobenzoates. *Radiochemistry*, 61, 293-299.
- Tahir, N.M., Ülkü, D., Movsumov, E.M. (1996). Structure of cesium 3,5 nitrobenzoate dihidrat. *Acta Crystallographica Section C*, 52, 1449-1451.
- Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A., & Puschmann, H. (2009). OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography*, 42(2), 339-341.
- Sheldrick, G.M. (2015). SHELXT– Integrated space- group and crystal- structure determination. *Acta Crystallographica. Section A, Foundations and Advances*, 71, 1, 3-8.
- Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment – Olex2 dissected. *Acta crystallographica. Section A, Foundations and Advances*, 71(1), 59-75.