Crystalline and Molecular Structure of Diaquadinitratouranyl Dihydrate $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

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Abstract—Single crystals of previously unknown diaquadinitratouranyl dihydrate $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (I) were obtained by evaporation of aqueous solution of $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ containing nitric acid in air at ambient temperature. The structure of the complex was studied by X-ray diffraction analysis. Crystals are monoclinic, $a = 7.6820(15) \text{ Å}$, $b = 9.887(2) \text{ Å}$, $c = 7.1990(14) \text{ Å}$, $\beta = 105.08(3)^\circ$, space group $P2_1/c$, $Z = 2$, $V = 527.95(18) \text{ Å}^3$. Structural units of crystal are neutral centrosymmetrical molecular complexes $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ and crystal water molecules united by a hydrogen bond system. Certain structural and spectral characteristics of new complex I and known diaquadinitratouranyl complexes were compared.

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Diaquadinitratouranyl complex $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ and its hydrates $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot n(\text{H}_2\text{O})(n = 1, 4)$ (containing crystal water molecules along with coordinated molecules) are known for a long time [1].

The formation of these compounds and $\text{UO}_2(\text{NO}_3)_2 \cdot 3(\text{HNO}_3)$ was established in the studies of solubility in a triple system $\text{UO}_2(\text{NO}_3)_2\text{─HNO}_3\text{─H}_2\text{O}$ at 30.2 and 49.1°C [2]. The results reported in [2] indicate that nitric acid content affects the formation of hydrate compounds in solution: the higher its concentration, the smaller number of water molecules incorporated into hydrate.

To date, the structure of crystals is established for complexes $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ [3], $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ [4], and $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ [5] as solid phases in a $\text{UO}_2(\text{NO}_3)_2\text{─HNO}_3\text{─H}_2\text{O}$ system and for two polymorphous modifications of $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ [6, 7] prepared under another conditions.

Complex $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ is a common structural fragment of all compounds, U atom in the complex coordinates in equatorial plane two bidentate cyclic nitratog groups and two water molecules, CN of $\text{UO}_2^{2+}$ is 6 [3–7]. In the structures of all compounds, except for one polymorphous modification $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ [7], similar ligands are coordinated in the trans position toward each other. Outer-sphere water molecules are held together in the structure of hydrate compounds by hydrogen bonds (HB). The type of HB, the character of their distribution, and strength in the structure II were determined in [5]; HB in monohydrate complexes either not revealed or determined with insufficient accuracy [4, 6, 7].

We isolated crystals of previously unknown diaquadinitratouranyl dihydrate $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (I) by evaporation of aqueous solution of compound II containing nitric acid in air at ambient temperature.

The aim of this work is to study the structure of compound I by X-ray diffraction analysis.

EXPERIMENTAL

Chemical used in the work were diaquadinitratouranyl tetrahydrate II of reagent grade, concentrated nitric acid ($d = 1.4$) of analytical grade, and distilled water. Uranyl nitrate was analyzed, recrystallized from 18% nitric acid, dried, and analyzed again.

Synthesis of I. Fifteen milliliters of concentrated nitric acid was added to 93.00 g of II, additional 90 mL of water heated to ~30°C was then added in small portions at constant stirring. The resultant solution contained 35.77, 6.72, and 57.51 wt% of $\text{UO}_2(\text{NO}_3)_2$, $\text{HNO}_3$, and $\text{H}_2\text{O}$, respectively. The solution was allowed to evaporate (without stirring) in air at ambient temperature and atmospheric pressure. On the fourth day, rather large yellow cubic crystals deposited from the solution, while small greenish yellow prismatic crystals formed on the surface of the solution. The solution was continued to evaporate for additional 6 days. Then, the crystals from the surface of the solution were removed by decantation, and the precipitate
of the large crystals was separated by filtration from the mother liquor, dried in a vacuum desiccators over KOH until constant weight, and analyzed by procedure [8].

For \([\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\) anal. calcd. (%): UO\(^{2+}\), 57.93; N, 6.01; H, 1.73.

Found (%): UO\(^{2+}\), 58.02; N, 6.10; H, 1.78.

The mother liquor after separation of \(\text{I}\) was continued to evaporate until precipitate formation. The analysis results for this precipitate and crystals removed from the surface of the crystallization solution coincided and corresponded to the composition of the initial compound \(\text{II}\).

For \([\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\) anal. calcd. (%): UO\(^{2+}\), 53.78; N, 5.58; H, 2.41.

Found (%): UO\(^{2+}\), 53.90; N, 5.67; H, 2.45.

\([\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\) (\(\text{IV}\)) result from dehydration of \(\text{II}\) over 96% and 63% sulfuric acid, respectively [9]. The complexes were synthesized to make more accurate their spectral characteristics [10, 11].

X-ray diffraction study of compound I. Experimental intensities were obtained on an Enraf-Nonius CAD4 automated diffractometer at 293 K (MoK\(_\alpha\) radiation, graphite monochromator, \(\lambda = 0.71073 \text{ Å}\), \(\omega\) scan mode) for a faceted cubic pale yellow single crystal of \(\text{I}\) with dimensions 0.06 \(\times\) 0.05 \(\times\) 0.05 mm. Absorption was taken into account by semiempirical method from equivalents. Computations and structure refinement were made using SHELXTL software package [12]. The structure was solved by heavy atom method. Anisotropic refinement for all non-hydrogen atoms was performed by full-matrix least squares on \(F^2\). Hydrogen atoms were added in ideal positions and refined using a riding model. Experiment characteristics and crystallographic data are presented in Table 1, selected bond distances and valence angles are given in Table 2, geometrical parameters of HB are shown in Table 3.

IR spectra (400–4000 cm\(^{-1}\)) with different recording scale were registered on an IR–75 spectrophotometer and a Nicolet Nexus Fourier-transform IR spectrometer (resolution 4 cm\(^{-1}\), 32 scans). Samples were triturated in Nujol and hexachlorobutadiene. Assignment of vibration frequencies was carried out with