

Original paper

Synthesis and Crystal Structure of the New Uranyl Carbonate $(\text{NH}_4, \text{Na})_4[\text{UO}_2(\text{CO}_3)_3]$, and its relation to Čejkaite[#]

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[#] In the memory of Ing. Jiří Čejka, DrSc. (1929–2025), who has left a bright trace and rich legacy in mineralogy, structural chemistry and spectroscopy of uranium compounds



Single crystals of a new uranyl carbonate $(\text{NH}_4, \text{Na})_4[\text{UO}_2(\text{CO}_3)_3]$ (**1**) have been prepared by evaporation at room temperature from aqueous solution. The structure was solved by direct methods [orthorhombic, *Cmcm*, $a = 15.712(3)$, $b = 9.039(2)$, $c = 8.915(3)$ Å, $V = 1266.2(6)$ Å³ and $Z = 4$] and refined to $R_1 = 0.0314$ ($wR_2 = 0.0704$). The crystal structure of the novel compound is based on pseudo-layered complex built by $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$ uranyl tricarbonate clusters (UTC) linked together through Na^+ and NH_4^+ ions. Such layered complexes of UTC are typical for a number of uranyl compounds of both natural and synthetic origin, including čejkaite. However, the relative arrangement of layers in **1** is distinct due to the specific interlayer content and can be described as a novel polytype.

Keywords: uranyl, carbonate, čejkaite, crystal structure, X-ray diffraction, structural complexity

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1. Introduction

Carbonate salts of uranium are of great interest and are being broadly studied due to their abundance and thermodynamic stability in environmental conditions (Axelrod et al. 1951; Ondruš et al. 1997; Finch and Murakami 1999; Plášil et al. 2015; Lussier et al. 2016). Uranyl carbonate phases form in nature as the result of primary uranium mineral alteration by atmospheric and groundwater enriched with CO_2 (Clark et al. 1995; Stefaniak et al. 2009; Plášil 2014), which comes from the dissolution of host carbonate rocks. In addition, uranyl carbonate phases were detected as secondary alteration products that were formed on a surface of highly radioactive Chernobyl “lavas” (Teterin et al. 1994; Burakov et al. 1996). Investigation of synthetic uranyl carbonate phases is also of great importance, since it can shed light on environmental processes and conditions at which minerals form. Recently, an overview of the crystal structures of natural and synthetic uranyl carbonates has been prepared (Gurzhiy et al. 2021). The structures of synthetic analogues of natural uranyl carbonates suggest that most of the uranyl carbonate minerals were formed under ambient conditions that do not require heating of aqueous solutions, as it was suggested in the case of other U-bearing phases like uranyl molybdates or vanadates (Kuporev et al. 2024, 2025). Uranyl carbonates, whose structures are based on the

uranyl tricarbonate clusters, are among the most common phases of both natural and synthetic origin. These include, for example, such minerals as agricolaite (Skála et al. 2011), čejkaite (Plášil et al. 2013) and grimselite (Plášil et al. 2012). Crystal structures of these minerals and related synthetic compounds, although quite different, have many similarities that allow one to consider them as polytypes. Polytypism is a feature of the existence of different sequences of crystallographically similar layers stacking, which is common to layered species, and uranyl minerals dominantly possess layer topologies.

Herein we report on the synthesis, spectroscopy studies and structure description of the novel uranyl carbonate compound $(\text{NH}_4, \text{Na})_4[\text{UO}_2(\text{CO}_3)_3]$ (**1**), the chemical composition and structural architecture of which is closely related to natural phases. The paper also discusses the structural features of compounds, whose structures are based on layers formed by uranyl tricarbonate clusters.

2. Experimental

2.1. Synthesis

Uranyl acetate dihydrate $((\text{UO}_2)(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, 99%, Vekton), sodium chloride (NaCl, 99%, Vekton)

Tab. 1 Crystallographic data and refinement parameters for **1**.

| <i>Crystallographic data</i> | |
|---|--|
| Chemical formula | (NH ₄) _{2.7} Na _{1.3} [UO ₂ (CO ₃) ₃] |
| Crystal system, space group | Orthorhombic, <i>Cmcm</i> |
| <i>M_r</i> | 542.02 |
| Temperature (K) | 296.15 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 15.712(3), 9.039(2), 8.915(3) |
| α , β , γ (°) | 90 |
| <i>V</i> (Å ³) | 1266.2(6) |
| <i>Z</i> | 4 |
| <i>Data collection parameters</i> | |
| Radiation type | MoK α |
| μ (mm ⁻¹) | 13.002 |
| Diffractometer | XtaLAB Synergy-S |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 6696, 808, 742 |
| <i>R_{int}</i> | 0.0742 |
| <i>Refinement Parameters</i> | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.0314, 0.0704, 1.083 |
| No. of reflections | 808 |
| No. of parameters | 60 |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 1.540, -0.820 |
| <i>ICSD</i> | 2519626 |

and ammonium carbonate ((NH₄)₂CO₃, 99%, Vekton) were used as received, and were dissolved in 4 ml distilled water in a molar ratio of 1 : 4 : 6. The solution was left to evaporate in a watch glass at room temperature and translucent yellow square lamina crystals of **1** were detected after 3 days. The pH of the solution was in the range of 7 to 8.

Tab. 2 Selected bond length and angles in the structure of **1**: bond lengths, Å; angles, °. The most likely H-bonds are marked in italic.

| Bond | | H-bond (<i>D</i> -H... <i>A</i>) | <i>D</i> -H | H... <i>A</i> | <i>D</i> ... <i>A</i> | < <i>DHA</i> |
|--------------------------|---------------|---------------------------------------|-------------|---------------|-----------------------|--------------|
| U1-O1 _{Ur} | 1.787(7) × 2 | <i>NI-H1A...O1</i> | 0.97(2) | 2.48(18) | 3.212(8) | 132(18) |
| U1-O2 | 2.428(6) × 2 | <i>NI-H1A...O1_{Ur}</i> | 0.97(2) | 2.5(2) | 3.182(8) | 129(19) |
| U1-O3 | 2.436(6) × 2 | | | | | |
| U1-O4 | 2.426(6) × 2 | <i>NI-H1B...O4</i> | 0.97(2) | 2.33(14) | 3.158(8) | 142(17) |
| <U1-O _{eq} > | 2.43 | <i>NI-H1B...O5</i> | 0.97(2) | 2.57(16) | 3.339(9) | 136(17) |
| | | NI-H1A...O3 | 0.97(2) | 2.61(16) | 3.389(10) | 137(18) |
| C1-O1 | 1.162(19) | | | | | |
| C1-O2 | 1.341(12) × 2 | <i>NI-H1C...O4</i> | 0.97(2) | 2.53(15) | 3.225(9) | 129(14) |
| C2-O3 | 1.277(10) | <i>NI-H1C...O5</i> | 0.97(2) | 2.42(11) | 3.240(11) | 141(14) |
| C2-O4 | 1.295(11) | NI-H1C...N1 | 0.97(2) | 2.45(16) | 3.058(15) | 120(13) |
| C2-O5 | 1.242(10) | | | | | |
| | | <i>NI-H1D...O5</i> | 0.97(2) | 2.30(11) | 3.008(9) | 129(11) |
| Na1(N1)-O5 | 3.008(9) | <i>NI-H1D...O2</i> | 0.97(2) | 2.59(12) | 3.259(9) | 126(10) |
| Na1(N1)-O4 | 3.158(8) | NI-H1D...N1 | 0.97(2) | 2.45(11) | 3.184(16) | 132(11) |
| Na1(N1)-O1 _{Ur} | 3.182(8) | | | | | |
| Na1(N1)-O1 | 3.212(8) | | | | | |
| Na1(N1)-O4 | 3.225(9) | | | | | |
| Na1(N1)-O5 | 3.240(11) | | | | | |
| Na1(N1)-O2 | 3.259(9) | | | | | |
| Na1(N1)-O5 | 3.339(9) | | | | | |
| <Na1(N1)-O> | 3.203 | | | | | |

2.2. Chemical analysis

The chemical analyses of several crystals of **1**, preliminarily checked using a single crystal X-ray diffractometer, were performed using a Hitachi S-3400N scanning electron microscope equipped with an Oxford EDX spectrometer, with an acquisition time of 30 s per point in energy dispersive mode (acceleration voltage 15 kV). No other elements with atomic numbers higher than that of oxygen, except for Na and U were detected. Analytical calculations; atomic ratio from structural data: Na 1.3, U 1.0; found by EDX: Na 1.35, U 0.95.

2.3. Single-crystal X-ray diffraction

Single crystal of **1** was selected under a microscope, placed in an oil-based cryoprotectant, and mounted on acryloop. Diffraction data have been collected at room temperature using a Rigaku XtaLAB Synergy-S X-ray diffractometer operated with a monochromated

microfocus MoK α tube PhotonJet-S ($\lambda = 0.71073$ Å) at 50 kV and 1.0 mA, and equipped with a HyPix 6000HE hybrid photon-counting detector. *CrysAlisPro* software [1] was used for integration and correction of diffraction data for polarization, background and Lorentz effects. The unit-cell parameters (Tab. 1) were refined using the least-squares techniques. The structure was solved by a dual-space algorithm and refined with *SHELX* programs (Sheldrick 2015a, b), incorporated in the *OLEX2* program package (Dolomanov et al. 2009). Selected bond lengths are listed in Tab. 2. The final model included coordinates and anisotropic displacement parameters for all non-H atoms. Positions of H

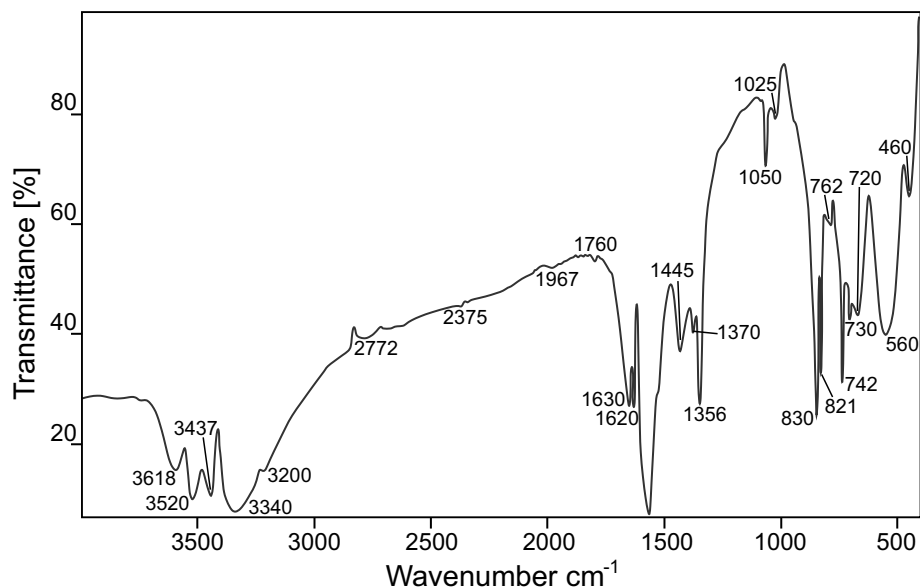


Fig. 1 – IR transmission spectrum of **1**.

atoms were localized from difference Fourier maps and were included in the refinement with bond length restraints and individual isotropic displacement parameters. Ammonium and Na^+ cations occupy the same crystallographic site in the structure of **1** with an electron density of *c.a.* $8.5 \text{ e}/\text{\AA}^3$, which allows assignment (N/Na) of individual site occupancy factors (s.o.f.) equal to 0.67/0.33, and total s.o.f. equal to 1.0, which results in the ratio of $(\text{NH}_4)_{2.7}\text{Na}_{1.3}$ per formula unit (*pfu*). This model seems most probable, given the absence of other cations according to the EDX data. It is of interest that in all other known uranyl minerals that contain both Na^+ and NH_4^+ , distinct coordination and large size difference of these ions split them into different sites, but the structure built by *čejkaite*-type layers can adapt to it and accommodate both sorts of ions in a single site. Water molecules should not be regarded within the model since *čejkaite* and related minerals are anhydrous, and also due to the need to maintain charge balance of the structure; H_3O^+ cations cannot be considered as well because of an alkaline reaction environment. It should be noted that EDX data have shown slight differences in Na content (0.8–1.4 p.f.u.), which demonstrates the possibility of variable composition of crystals within the single synthesis. Moreover, the highest values for Na corresponded to the best quality crystals, while low Na contents corresponded to fine crystalline masses. Due to this, we suggest generalizing the formulae of the compound **1** to be written as $(\text{NH}_4, \text{Na})_4[\text{UO}_2(\text{CO}_3)_3]$ instead of $(\text{NH}_4)_{2.7}\text{Na}_{1.3}[\text{UO}_2(\text{CO}_3)_3]$. Supplementary crystallographic data were deposited in the Inorganic Crystal Structure Database (ICSD) and can be obtained by quoting the CSD 2519626 via www.ccdc.cam.ac.uk/structures/ (see Supplementary Materials).

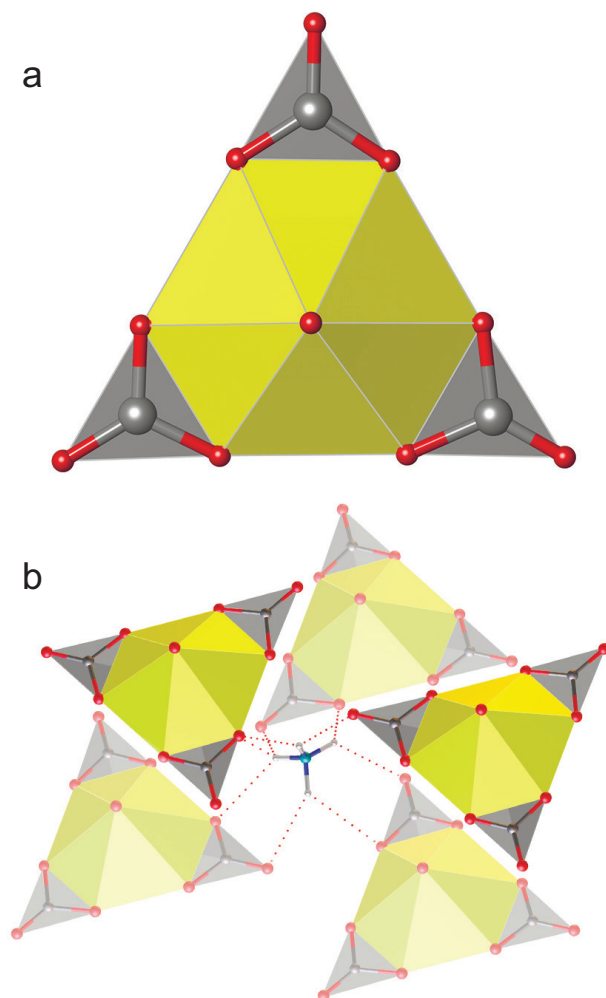


Fig. 2 – Uranyl tricarbonate cluster (**2a**); coordination of (Na, NH_4)-site in the structure of **1** (**2b**). Legend: U = yellow, O = red, C = grey, N(Na) = cyan, H = white, H-bonds = dashed red lines.

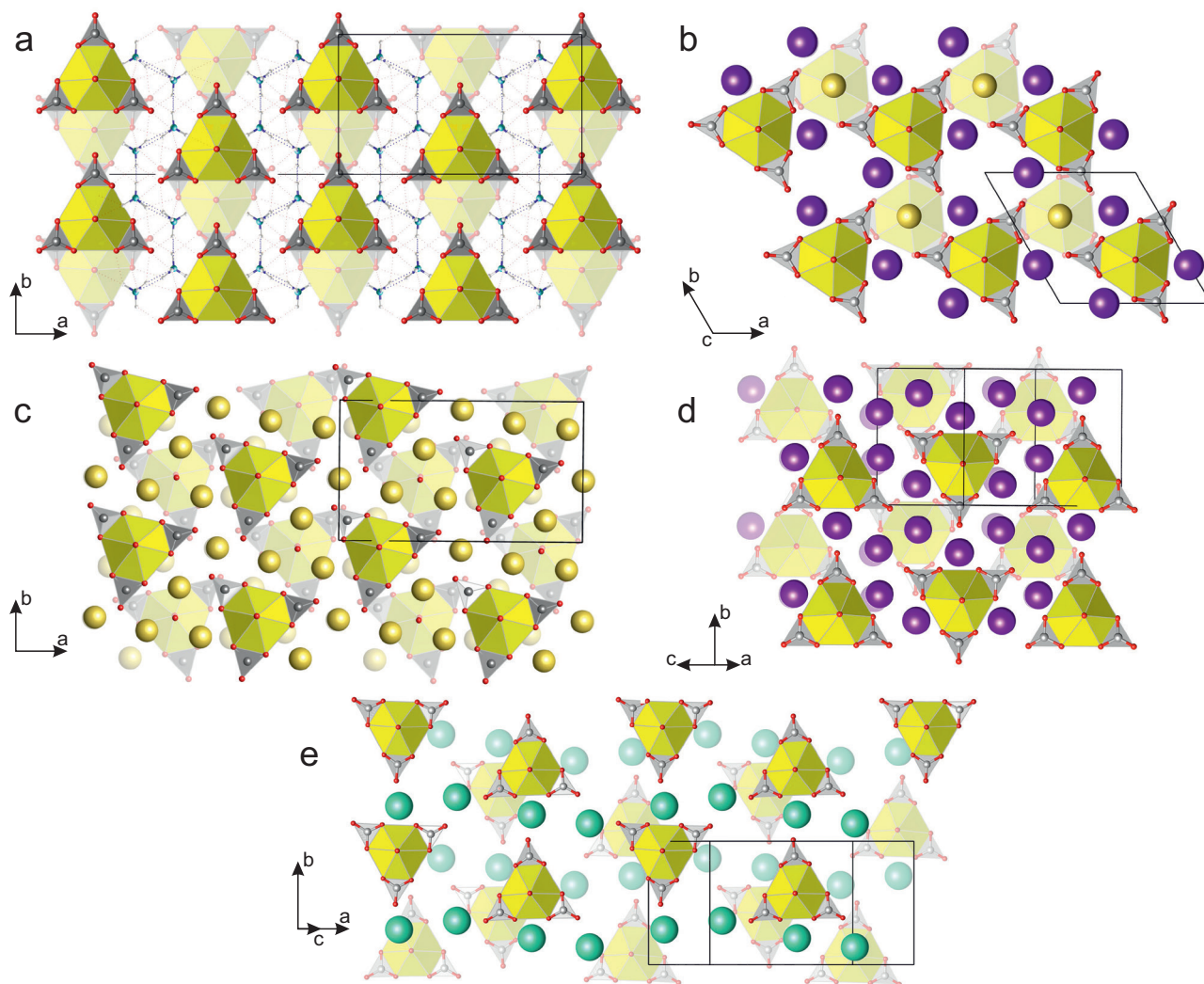


Fig. 3 – The crystal structures of **1–13** projected perpendicular to the layers of uranyl tricarbonate clusters: (a) – **1**, (b) – **2, 3**, (c) – **4, 5, 6**, (d) – **7, 8, 9, 10, 11, 12** (e) – **13**. Legend: see Fig. 2; Na = yellow, K = purple, Cs = aqua; UTC of the adjacent layers are shaded.

2.4. Infrared Spectroscopy

To record the Infrared (IR) absorption spectra, a powdered sample of **1** was ground with KBr and pressed into transparent pellets. The measurements were carried out on a Bruker Vertex 70 spectrometer in Attenuated Total Reflection mode in the region of 4000–300 cm^{-1} . Band assignments follow the interpretations provided by Gurzhiy et al. (2025) and Rofail (1994).

The region of 3150–3350 cm^{-1} corresponds to N–H asymmetric stretching vibrations ν_3 , while bands observed at 1620–1630 and a strong band at 1445 cm^{-1} are attributed to deformation vibrations ν_2 of NH_4^+ and H–N–H bending modes (ν_4), respectively. The band around 2800 cm^{-1} correspond to nonaxial ν_1 valence vibrations of NH_4^+ . Weak combination or overtone bands related to water may appear in the spectral region of 1700–2500 cm^{-1} . Bands at 1050 and 1025 are ν_2 vibra-

tions of CO_3^{2-} groups. Two bands at 730 and 720 are attributed to ν_3 vibrations of CO_3^{2-} groups. Bands at 830 and 821 cm^{-1} are assigned to the ν_3 antisymmetric stretching frequencies of UO_2^{2+} (Fig. 1). IR absorbance features in the 3400–3620 cm^{-1} region correspond to O–H stretching vibrations ν_3 , which come from the H_2O molecules sorbed on the surface of crystals, as well as water captured in the form of inclusions during crystal growth.

3. Results and Discussion

3.1. Crystal Structure

The crystal structure of **1** contains one structurally non-equivalent U^{6+} cation, which is strongly bonded to two O atoms in a linear manner forming a uranyl

Tab. 3 Crystallographic characteristics of natural and synthetic compounds related to **1**.

| No | Chemical composition / Mineral name | Sp. Gr. | <i>a</i> (Å) / α (°) | <i>b</i> (Å) / β (°) | <i>c</i> (Å) / γ (°) | < <i>M-O</i> > (Å) | Ref.* | |
|-----------|---|-------------------|-----------------------------|----------------------------|-----------------------------|-------------------------------------|--------------------------------------|------------|
| 1 | $(\text{NH}_4, \text{Na})_4[\text{UO}_2(\text{CO}_3)_3]$ | <i>Cmcm</i> | 15.712(3) / 90 | 9.039(2) / 90 | 8.915(3) / 90 | N1(Na1) Na1 Na2 Na3 Na4 | 3.23 2.48 3.39 2.47 2.47 | 1 2 |
| 2 | $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ / <i>čejkaite</i> | <i>Cc</i> | 9.2919(8) / 90 | 16.0991(11) / 91.404(5) | 6.4436(3) / 90 | Na1 Na2 Na3 Na4 | 2.44 2.49 2.39 | 3,4 |
| 3 | $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ | <i>P\bar{3}c</i> | 9.3417(6) / 90 | 9.3417(6) / 90 | 12.824(1) / 120 | K Na | 2.93 2.60 | 5 |
| 4 | $\text{K}_3\text{Na}(\text{UO}_2)(\text{CO}_3)_3$ | <i>P\bar{6}2c</i> | 9.29(2) / 90 | 9.29(2) / 90 | 8.26(2) / 120 | K Na | 2.83 2.62 | 6 |
| 5 | $\text{K}_3\text{Na}(\text{UO}_2)(\text{CO}_3)_3(\text{H}_2\text{O})$ / <i>grimselite</i> | <i>P\bar{6}2c</i> | 9.3000(1) / 90 | 9.3000(1) / 90 | 8.2940(2) / 120 | Rb Na | 2.95 2.60 | 7 |
| 6 | $\text{Rb}_6\text{Na}_2((\text{UO}_2)(\text{CO}_3)_3)_2(\text{H}_2\text{O})$ / Rb analogue of <i>grimselite</i> | <i>P\bar{6}2c</i> | 9.4316(7) / 90 | 9.4316(7) / 90 | 8.3595(8) / 120 | K1 K2 | 2.86 2.90 | 8 |
| 7 | $\text{K}_4(\text{UO}_2)(\text{CO}_3)_3$ / <i>agricolaite</i> | <i>C2/c</i> | 10.2380(2) / 90 | 9.1930(2) / 95.108(2) | 12.2110(3) / 90 | K1 K2 | 2.92 2.91 | 9, 10 |
| 8 | $\text{K}_4\text{UO}_2(\text{CO}_3)_3$ | <i>C2/c</i> | 10.247(3) / 90 | 9.202(2) / 95.11(2) | 12.226(3) / 90 | Rb1 Rb2 | 3.04 3.02 | 11 |
| 9 | $\text{Rb}_4\text{UO}_2(\text{CO}_3)_3$ | <i>C2/c</i> | 10.778(5) / 90 | 9.381(2) / 94.42(3) | 12.509(3) / 90 | Cs1 Cs2 | 3.21 3.19 | 12 |
| 10 | $\text{Cs}_4(\text{UO}_2)(\text{CO}_3)_3$ | <i>C2/c</i> | 11.5131(9) / 90 | 9.6037(8) / 93.767(2) | 12.9177(10) / 90 | N1 N2 | 2.86 3.01 | 13 |
| 11 | $(\text{NH}_4)_4(\text{UO}_2)(\text{CO}_3)_3$ | <i>C2/c</i> | 10.679(4) / 90 | 9.373(2) / 96.43(2) | 12.850(3) / 90 | Tl1 Tl2 | 3.02 3.03 | 14 |
| 12 | $\text{Tl}_4((\text{UO}_2)(\text{CO}_3)_3)$ | <i>C2/c</i> | 10.684(2) / 90 | 9.309(2) / 94.95(2) | 12.726(3) / 90 | Cs1 Cs2 Cs3 Cs4 | 3.29 3.26 3.28 3.28 | 15 |
| 13 | $\text{Cs}_4(\text{UO}_2)(\text{CO}_3)_3(\text{H}_2\text{O})_6$ | <i>P2_1/n</i> | 11.1764(4) / 90 | 9.5703(4) / 96.451(2) | 18.5756(7) / 90 | | | |

*: 1 – this work; 2 – Plášil et al. 2013; 3 – Císařová et al. 2001; 4 – Li et al. 2001; 5 – Li and Burns 2001; 6 – Plášil et al. 2012; 7 – Kubatko and Burns 2004; 8 – Skála et al. 2011; 9 – Anderson et al. 1980; 10 – Han et al. 1990; 11 – Chemorukov et al. 2005; 12 – Krivovichev and Burns 2004; 13 – Serezhkin et al. 1983; 14 – Mereiter 1986; 15 – Charushnikova et al. 2016

cation $[\text{O}\equiv\text{U}\equiv\text{O}]^{2+}$ (*Ur*). In the equatorial plane, *Ur* is surrounded by six O atoms that belong to three bidentate carbonate groups, which results in the formation of a hexagonal bipyramidal polyhedra of U, and consequent arrangement of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ uranyl tricarbonate cluster (UTC) as the main building block of the structure of **1** (Fig. 2a).

UTC are arranged in layers parallel to the (001) plane. Within the layer, clusters are tightly packed, where each cluster has six neighbors (Fig. 3a). All UTC clusters within the layer are co-directed, and adjacent layers are rotated by 180° around the [001] and shifted by the $[0 \frac{1}{2} \frac{1}{2}]$. Ammonium and Na^+ cations are arranged in the interlayer space. Thus, the crystal structure of **1** with a certain tolerance for the absence of displacement of each second layer along [100] can be described as hexagonal closest packing (alternation stacking of two tightly packed layers), in which NH_4^+ and Na^+ ions occupy all tetrahedral voids (Fig. 2b).

3.2. Polytypism

Such layered tightly packing arrangement of UTC clusters is typical for the large family of natural and synthetic compounds (Tab. 3) such as *čejkaite*, $\text{Na}_4[(\text{UO}_2)(\text{CO}_3)_3]$ (Plášil et al. 2013), *grimselite*, $\text{K}_3\text{Na}[(\text{UO}_2)(\text{CO}_3)_3]$ (Li and Burns 2001; Plášil et al. 2012), etc. All known crystal structures based on $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ layered complexes of tightly packed UTC can be divided into 4 nominal “structural” groups according to their unit-cell metrics and symmetry (Tab. 3): *čejkaite*, *agricolaite*, *grimselite* and $\text{Cs}_4(\text{UO}_2)(\text{CO}_3)_3(\text{H}_2\text{O})_6$. Compounds of the *čejkaite* (**2,3**) and *agricolaite* (**7–12**) “structural” groups are mostly monoclinic and anhydrous. Compounds of the *grimselite* “structural” group (**4–6**) are hexagonal and can be both hydrated and anhydrous. The only structure of the fourth type is the monoclinic hydrated synthetic compound $\text{Cs}_4(\text{UO}_2)(\text{CO}_3)_3(\text{H}_2\text{O})_6$ (**13**). Compound **1** is the first structure

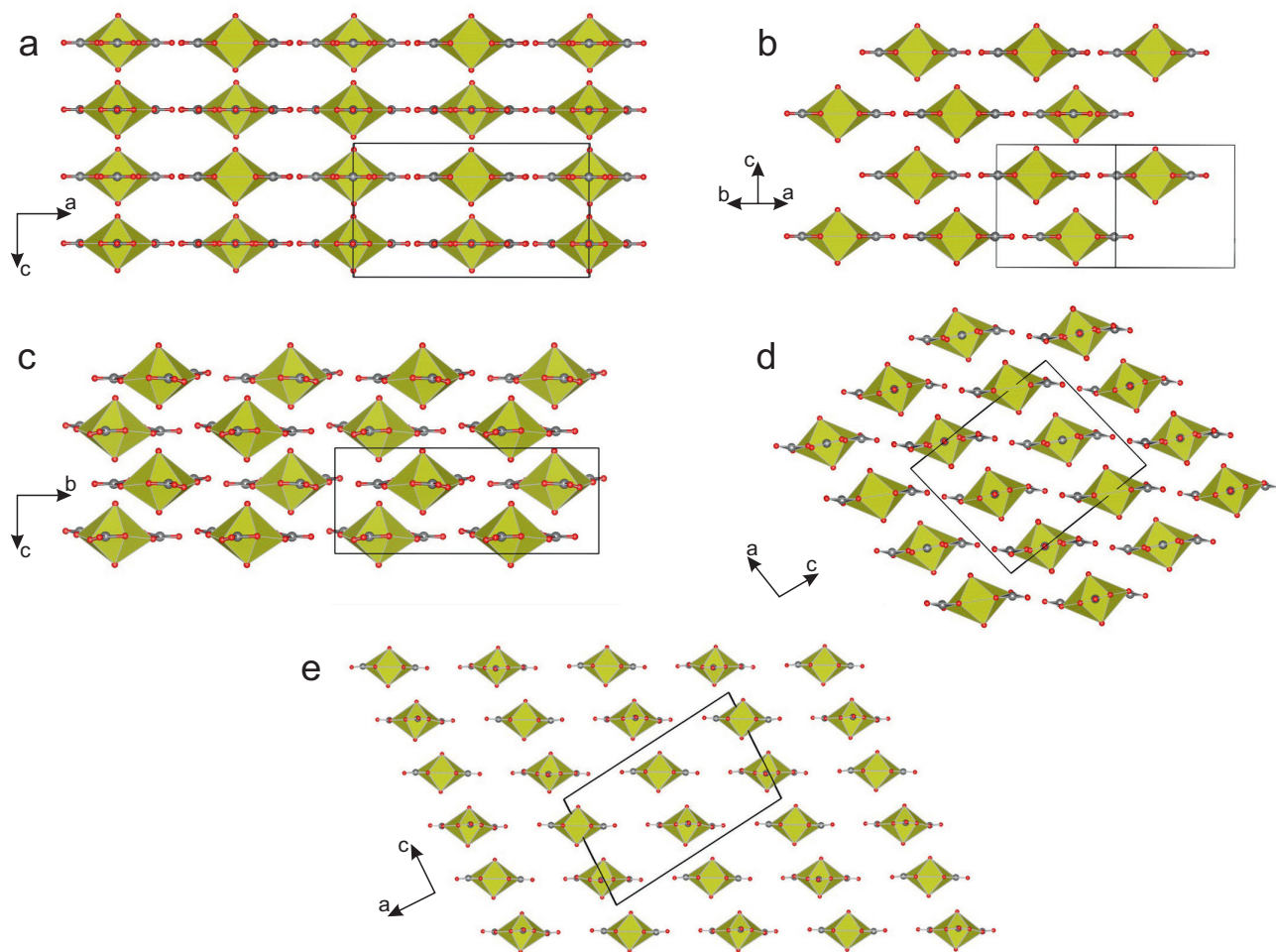


Fig. 4 – The crystal structures of **1–13** projected along the layers of uranyl tricarbonate clusters: (a) – **1**, (b) – **2, 3**, (c) – **4, 5, 6**, (d) – **7, 8, 9, 10, 11, 12** (e) – **13**. Legend: see Fig. 2

of this family, which crystallizes in the orthorhombic space group, and belongs to the distinct fifth type of layer arrangement.

All compounds except for **13** have similar alternation of layers—displacement of each second layer, which allows one to describe these structures in terms of double layer or hexagonal closest packing (Fig. 4a–d), while the structure of compound **13** is more consistent with the description of four-layer closest packing (Fig. 4e), when considering its layers perpendicular to [102]. Although the mutual arrangement of layers is quite similar among each group, the structures of all thirteen compounds under consideration differ significantly in detail.

Thus, crystal structures of compounds of the čejkaite group (**2,3**) are based on layered complexes that are arranged parallel to the (001) plane (Fig. 4b). UTC clusters within the layer are co-directed, and adjacent layers are rotated by c.a. 30° and shifted by $[\frac{1}{2} \ 0 \ \frac{1}{2}]$ (Fig. 3b). It is worth noting that a compound with the

same composition $\text{Na}_4[(\text{UO}_2)(\text{CO}_3)_3]$ was described as an alteration product formed on the surface of Chernobyl “lavas” (Teterin et al. 1994; Burakov et al. 1996). However, it is not clear to which structural type (**2** or **3**) this phase belongs. In the structures of grimselite group members (**4–6**), UTC clusters are arranged co-directed within the layers parallel to (0001). The direction of UTC is maintained in adjacent layers, which are shifted by $[\frac{2}{3} \ \frac{1}{3} \ \frac{1}{2}]$ (Figs 3c, 4c). In the structures of agricolaite-group minerals and synthetic compounds (**7–12**) (Krivovichev and Burns 2004), UTC complexes are organized into layers parallel to (101), and individual uranyl tricarbonate clusters are not co-directed, but arranged in a herringbone-like pattern within these layers (Figs 3d, 4d). Adjacent layers are shifted by $[\frac{1}{2} \ \frac{1}{2} \ 0]$. The same pattern is created by UTC in the structure of **13**, and the complexes are arranged in layers parallel to the (201) plane (Fig. 3e). UTC clusters in neighbor layers are rotated by c.a. 60° and shifted by $[\frac{1}{2} \ \frac{1}{4} \ 0]$ (Fig. 4e).

Tab. 4 Structural complexity parameters (in bits/atom and bits/unit cell)

| № | Chemical composition / Mineral name | Closest U···U contact | V , Å ³ | Complexity of the U–CO ₃ substructure | | Complexity of the entire structure | |
|----|---|-----------------------|----------------------|--|---------|------------------------------------|---------|
| 1 | (NH ₄ ,Na) ₄ [UO ₂ (CO ₃) ₃] | 5.490(1) | 1266.2 | 3.107 | 93.207 | 3.644 | 255.050 |
| 2 | Na ₄ (UO ₂)(CO ₃) ₃ / <i>čejkaite</i> | 6.202(1) | 963.6 | 3.907 | 117.207 | 4.248 | 161.420 |
| 3 | Na ₄ (UO ₂)(CO ₃) ₃ | 6.204(1) | 969.18 | 2.639 | 158.335 | 3.049 | 231.750 |
| 4 | K ₃ Na(UO ₂)(CO ₃) ₃ | 6.769(11) | 617.37 | 2.506 | 75.168 | 2.891 | 109.870 |
| 5 | K ₃ Na(UO ₂)(CO ₃) ₃ (H ₂ O) / <i>grimselite</i> | 6.784(1) | 621.24 | 2.506 | 75.168 | 3.197 | 140.670 |
| 6 | Rb ₆ Na ₂ ((UO ₂)(CO ₃) ₃) ₂ (H ₂ O) / Rb analogue of <i>grimselite</i> | 6.864(1) | 643.99 | 2.506 | 75.168 | 3.197 | 140.670 |
| 7 | K ₄ (UO ₂)(CO ₃) ₃ / <i>agricolaite</i> | 6.880(1) | 1144.71 | 3.107 | 93.207 | 3.406 | 129.420 |
| 8 | K ₄ UO ₂ (CO ₃) ₃ | 6.886(1) | 1146.57 | 3.107 | 93.207 | 3.406 | 129.420 |
| 9 | Rb ₄ UO ₂ (CO ₃) ₃ | 7.412(1) | 1261 | 3.107 | 93.207 | 3.406 | 129.420 |
| 10 | Cs ₄ (UO ₂ (CO ₃) ₃) | 7.363(1) | 1425.2 | 3.107 | 93.207 | 3.406 | 129.420 |
| 11 | (NH ₄) ₄ (UO ₂ (CO ₃) ₃) | 7.105(1) | 1278.12 | 3.107 | 93.207 | 4.215 | 295.050 |
| 12 | Tl ₄ ((UO ₂)(CO ₃) ₃) | 7.085(1) | 1260.97 | 3.107 | 93.207 | 3.406 | 129.420 |
| 13 | Cs ₄ (UO ₂ (CO ₃) ₃ (H ₂ O)) ₆ | 5.708(1) | 1974.29 | 3.907 | 234.413 | 5.209 | 771.000 |

3.3. The Role of Interstitial Cation

Having observed the crystal chemistry of nearly all alkaline cations in these phases, as well as ions similar to them in functionality, it could be assumed that the structural type will depend on the ionic radius of the element located between the layers of UTC clusters. However, such a direct relationship is not observed. In the discussed set, the most representative compounds are those containing Na and K, and they belong to various structural types. At the same time, correlation with the distance between UTC clusters in adjacent layers, which can be estimated by the distance between the central U atoms, is observed. Considering an average effective radius of the interlayer cation (considering their proportional contribution), the direct tendency for the U···U distance to increase with increasing effective radius is observed for all compounds, except for the structures of **1** and **13**, for which a significant decrease in the shortest contact is observed (Tab. 4, Fig. 5a). This observation is in even more contrast to the highest values of $\langle M-O \rangle$ bonds for interlayer cations for these two structures (Tab. 3). However, it should be noted that in these two cases, short contacts between UTC clusters from neighbour layers is compensated by increasing the distance between the clusters within the layer, while in other structures the difference is less significant (5.490(1)/9.064(1), 5.708(1)/9.570(1) and 6.880(1)/8.372(1) Å for **1**, **13** and **7**, respectively).

3.4. Structural Complexity

Recently developed (Krivovichev 2012, 2016, 2025) and implemented in several papers (Gurzhiy et al. 2021;

Durova et al. 2023; Kuporev et al. 2024, 2025), the information-based structural complexity approach can help reveal crystal-chemical features that are not obvious from the standard description. Structural complexity is estimated as the Shannon information content per atom (I_G) and per unit cell ($I_{G, total}$), and calculated parameters for the structures **1–13** are listed in Tab. 4.

Structural complexity parameters of compounds under consideration have positive correlation with unit-cell volume (Fig. 5b, c), according to which the structures of **1–13** can be divided into four groups. The lowest unit-cell volumes as well as the lowest complexity parameters belong to the compounds of the *grimselite* group. Next considered are compounds of the *čejkaite* group, the variation in complexity for which turns out to be quite significant, with almost the same unit-cell volume due to differences in symmetry of compounds **2** and **3**. Next, the region that includes all compounds of the *agricolaite* group, as well as compound **1** can be identified. The cesium uranyl carbonate hexahydrate **13** has the largest unit-cell volume among all compounds, and also has the most structural complexity, which is explained by the large number of additional atoms in the form of H₂O molecules compared to other structures. The complexity of the entire structure of compounds **1–13** is mainly determined by the contribution of the uranyl-bearing substructure (Tab. 4, Fig. 5b). It is of interest that the complexity of the uranyl carbonate layered complexes in the structure of **1** is the same as for compounds of the *agricolaite* group (Tab. 4, Fig. 5b), despite their differences in symmetry and unit-cell metrics. In general, structural complexity measures are consistent with the

general trend that more complex structures may form as transition phases before (or between) structures with less structural information. For example, the formation of metastable phase **13** was detected before phase **10** (Krivovichev and Burns 2004). However, it is currently impossible to draw additional correlations between the structural complexity and thermodynamic parameters for compounds under consideration. For instance, there is a low number of known synthetic compounds in the

čejkaite and grimselite groups, while for the agricolaite group, the temperature range is quite wide (from room temperature up to +130 °C).

4. Conclusions

In this paper, we report for the first time on the synthesis and structural studies of the novel uranyl carbonate of sodium and ammonium $(\text{NH}_4\text{Na})_4[\text{UO}_2(\text{CO}_3)_3]$ (**1**). Despite the high topological similarity of the structure of **1** with compounds of the čejkaite group, its structural complexity parameters demonstrate the informational identity of compound **1** with compounds of the agricolaite group. Thus, it can be assumed that the compound obtained herein, and its structural type can be considered an intermediate of čejkaite and agricolaite, or represents a transitional configuration between these groups of compounds in general. It is also reasonable to expect the discovery of mineral phases similar to **1**, particularly in geological conditions rich in organic matter or with active biological processes (Gurzhiy et al. 2025).

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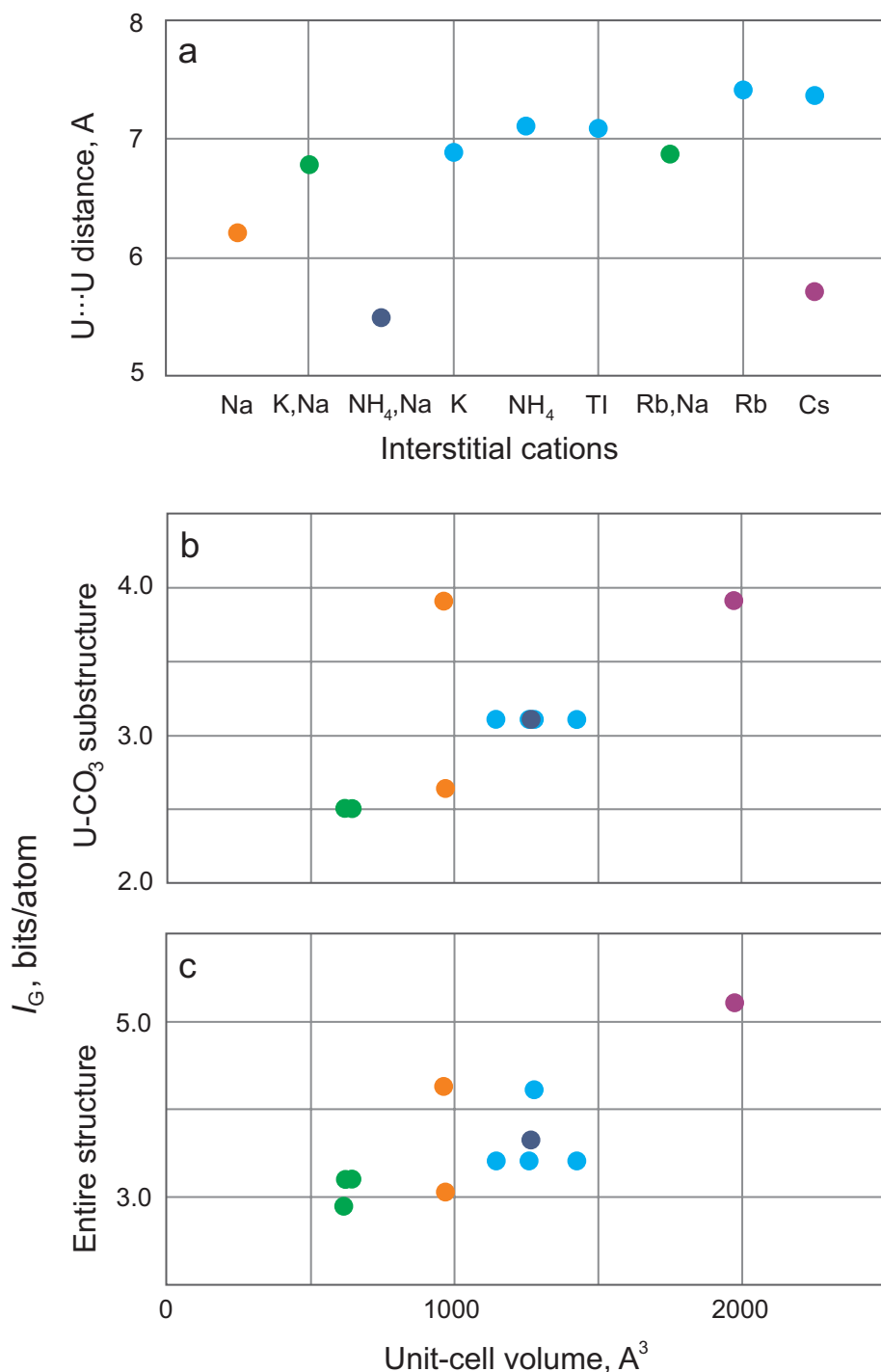


Fig. 5 – Correlation graphs of: (a) the closest U...U distance in adjacent layers in the structures of **1–13**, depending on the effective ionic radii of the interstitial cation; complexity of uranyl carbonate structural unit (b) and complexity of the entire structure (bits per atom) depending on the unit-cell volume of **1–13**. Legend: compound **1** = blue, **2–3** = orange, **4–6** = green, **7–12** = light blue, **13** = violet; values for effective ionic radii are taken from (Gagné, Hawthorne 2015; Sidey 2016; Hawthorne, Gagné 2024).

00083). XRD studies have been performed at the X-ray Diffraction Centre of St. Petersburg State University.

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