

## STRUCTURES OF STRONTIUM- AND BARIUM-DOMINANT COMPOUNDS THAT CONTAIN THE AUTUNITE-TYPE SHEET

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### ABSTRACT

Strontium and barium uranyl phosphate and uranyl arsenate hydrates have been synthesized by diffusion in gels (*SrUP11*,  $\text{Sr}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$ , *SrUAs11*,  $\text{Sr}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{11}$ , synthetic heinrichite,  $\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{10}$ , or by hydrothermal methods (synthetic meta-uranocircite I,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_7$ ), and their crystal structures have been determined. Single-crystal X-ray-diffraction intensity data were collected at room temperature using  $\text{MoK}\alpha$  radiation and a CCD-based area detector. The crystal structures of the four compounds were solved by direct methods and refined by full-matrix least-squares techniques on the basis of  $F^2$  for all unique reflections to agreement indices (*SrUP11*, *SrUAs11*, synthetic heinrichite and synthetic meta-uranocircite I)  $R1$  of 3.6, 5.2, 4.3 and 5.2%, respectively. These compounds contain the autunite-type sheet of composition  $[(\text{UO}_2)(\text{XO}_4)]^-$ ,  $\text{X} = \text{P}$  or  $\text{As}$ , which involves the sharing of equatorial vertices of uranyl square bipyramids with tetrahedra. The interlayer region contains cations and  $\text{H}_2\text{O}$  groups, and the sheets are linked by hydrogen bonding and through bonds from the interlayer cations to oxygen atoms of the sheets. *SrUP11* is orthorhombic, space group *Pnma*,  $a$  14.042(6),  $b$  21.008(9),  $c$  6.997(3) Å,  $V$  2064.1(15) Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}}$  3.269 g/mL. *SrUAs11* is orthorhombic, space group *Pnma*,  $a$  14.3778(6),  $b$  20.9611(9),  $c$  7.1703(3) Å,  $V$  2160.95(16) Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}}$  3.392 g/mL. These Sr compounds are isostructural with autunite,  $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$ . On this basis, uranospinite is predicted to be isostructural with autunite, and have the formula  $\text{Ca}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{11}$ , with expected crystal-data: orthorhombic, space group *Pnma*,  $a$  14.35,  $b$  20.66,  $c$  7.17 Å,  $V$  2125 Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}}$  3.3 g/mL. Synthetic heinrichite is monoclinic, space group *P2/c*,  $a$  7.1548(11),  $b$  7.1340(11),  $c$  21.290(3) Å,  $\beta$  104.171(5)°,  $V$  1053.6(3) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.579 g/mL. The unit cell of synthetic uranocircite,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$ , was measured from a crystal aggregate, but a structure refinement is not presented. Synthetic uranocircite is interpreted to be isostructural with heinrichite: monoclinic, space group *P2/c*,  $a$  7.01,  $b$  6.99,  $c$  21.2 Å,  $\beta$  103.9°,  $V$  1008.4 Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.45 g/mL. The structure of synthetic meta-uranocircite I was determined from a crystal twinned by pseudomerohedry, and is monoclinic, space group *P2<sub>1</sub>*,  $a$  6.943(2),  $b$  17.634(6),  $c$  6.952(2) Å,  $\beta$  90.023(7)°,  $V$  851.2(5) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.876 g/mL. Metaheinrichite is predicted to be isostructural with synthetic meta-uranocircite I, with the formula  $\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_7$ , and expected crystal-data: monoclinic, space group *P2<sub>1</sub>*,  $a$  7.08,  $b$  17.7,  $c$  7.09 Å,  $\beta$  90.02°,  $V$  889 Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  4.0 g/mL.

**Keywords:** autunite, heinrichite, metaheinrichite, uranocircite, meta-uranocircite I, meta-uranocircite II, uranospinite, uranyl phosphate, uranyl arsenate, crystal structure, gel synthesis, hydrothermal synthesis.

### SOMMAIRE

Nous avons synthétisé les phosphates et arsenates à uranyle hydratés de strontium et de barium soit par diffusion dans un gel (*SrUP11*,  $\text{Sr}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$ , *SrUAs11*,  $\text{Sr}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{11}$ , heinrichite synthétique,  $\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{10}$ , soit par voie hydrothermale (méta-uranocircite I synthétique  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_7$ ), et leurs structures cristallines ont été déterminées. Les données d'intensité en diffraction X ont été prélevées sur monocristaux à température ambiante avec rayonnement  $\text{MoK}\alpha$  et un détecteur à aire de type CCD. Les structures cristallines des quatre composés ont été résolues par méthodes directes et affinées par techniques de moindres carrés sur matrice entière en utilisant les facteurs  $F^2$  pour toutes les réflexions uniques, jusqu'à un résidu  $R1$  pour *SrUP11*, *SrUAs11*, heinrichite et méta-uranocircite I synthétiques de 3.6, 5.2, 4.3

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et 5.2%, respectivement. Ces composés contiennent le feuillet de type autunite, de composition  $[(\text{UO}_2)(\text{XO}_4)]^-$ ,  $X = \text{P}$  ou  $\text{As}$ , qui implique le partage des coins équatoriaux des pyramides carrées à uranyle avec des tétraèdres. La région interfoliaire contient des cations et des groupes  $\text{H}_2\text{O}$ , et ces feuillets sont interconnectés par liaisons hydrogène et par liaisons entre les cations interfoliaires et les atomes d'oxygène des feuillets. *SrUP11* est orthorhombique, groupe spatial *Pnma*,  $a$  14.042(6),  $b$  21.008(9),  $c$  6.997(3) Å,  $V$  2064.1(15) Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}}$  3.269 g/mL. *SrUAs11* est orthorhombique, groupe spatial *Pnma*,  $a$  14.3778(6),  $b$  20.9611(9),  $c$  7.1703(3) Å,  $V$  2160.95(16) Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}}$  3.392 g/mL. Ces composés de Sr possèdent la structure de l'autunite,  $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$ . Par conséquent, l'uranospinite aurait aussi cette structure, et aurait la formule  $\text{Ca}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{11}$ , et les données cristallographiques suivantes: orthorhombique, groupe spatial *Pnma*,  $a$  14.35,  $b$  20.66,  $c$  7.17 Å,  $V$  2125 Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}}$  3.3 g/mL. La heinrichite synthétique est monoclinique, groupe spatial *P2/c*,  $a$  7.1548(11),  $b$  7.1340(11),  $c$  21.290(3) Å,  $\beta$  104.171(5)°,  $V$  1053.6(3) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.579 g/mL. La maille élémentaire de l'uranocircite synthétique,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$ , a été mesurée à partir d'un agrégat polycristallin, mais sans affinement de la structure. La uranocircite synthétique serait isostructurale avec la heinrichite: monoclinique, groupe spatial *P2/c*,  $a$  7.01,  $b$  6.99,  $c$  21.2 Å,  $\beta$  103.9°,  $V$  1008.4 Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.45 g/mL. La structure de la méta-uranocircite I synthétique, déterminée à partir d'un cristal maclé par pseudomérodrie, est monoclinique, groupe spatial *P2<sub>1</sub>*,  $a$  6.943(2),  $b$  17.634(6),  $c$  6.952(2) Å,  $\beta$  90.023(7)°,  $V$  851.2(5) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.876 g/mL. La métaheinrichite serait isostructurale avec la méta-uranocircite I synthétique, de formule  $\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_7$ , et aurait les caractéristiques cristallographiques suivantes: monoclinique, groupe spatial *P2<sub>1</sub>*,  $a$  7.08,  $b$  17.7,  $c$  7.09 Å,  $\beta$  90.02°,  $V$  889 Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  4.0 g/mL.

(Traduit par la Rédaction)

**Mots-clés:** autunite, heinrichite, métaheinrichite, uranocircite, méta-uranocircite I, méta-uranocircite II, uranospinite, phosphate uranyle, arsenate uranyle, structure cristalline, synthèse par gel, synthèse hydrothermale.

## INTRODUCTION

Approximately forty mineral species of hydrated uranyl phosphates and arsenates contain the autunite-type sheet (Smith 1984, Burns 1999, Finch & Murakami 1999). The structures, compositions and stabilities of these minerals are of interest because of their environmental significance. They are widespread and abundant, and affect the mobility of uranium in phosphate-bearing systems such as uranium deposits (Murakami *et al.* 1997) and soils contaminated by actinides (Buck *et al.* 1996, Roh *et al.* 2000). Amongst the least soluble of these minerals is the barium uranyl phosphate hexahydrate meta-uranocircite II, with a mean  $\text{pK}_{\text{sp}}$  of 51.8, almost forty orders of magnitude lower than the solubility products of related uranyl phosphates (Vochten *et al.* 1992). In the natural oxidation of products of uranium mineralization (in the presence of Ba and phosphate), meta-uranocircite II has been found to immobilize U over long periods and thereby greatly attenuate migration of U into groundwater (Jerden & Sinha 2003, Jerden *et al.* 2003). As part of our ongoing research into the structures of uranyl phosphates and arsenates, we have synthesized Sr and Ba uranyl phosphate and uranyl arsenate compounds and report their crystal structures herein.

## PREVIOUS WORK

Although strontium is not an essential element of any uranyl mineral, with the possible exception of agrinierite,  $\text{K}_2(\text{Ca}_{0.65}\text{Sr}_{0.35})[(\text{UO}_2)_3\text{O}_3(\text{OH})_2]_2(\text{H}_2\text{O})_5$  (Cahill & Burns 2000), substantial Sr contents were noted in autunite (0.34–0.52 wt% SrO) and meta-autunite (1.38 wt% SrO) from the Mt. Spokane area, Washington, by

Leo (1960) and Volborth (1959), respectively. Synthetic strontium uranyl phosphates and arsenates with various states of hydration have been characterized by Weigel & Hoffmann (1976) and Chernorukov *et al.* (1996), and the structure of synthetic  $\text{Sr}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$ , *SrUAs8*, was presented by Pushcharovskii *et al.* (2003).

In contrast to the rarity of strontium in uranyl minerals, barium is an essential element in a dozen uranyl minerals (Gaines *et al.* 1997, Mandarin & Back 2004), of which the barium uranyl phosphates and arsenates that contain the autunite-type sheet are the most common species. In spite of a long history of investigation of these minerals, the literature is in many instances not in agreement about their characteristics, probably because of their ease of dehydration and rehydration under differing temperature and humidity conditions. For the system Ba–U–P–H<sub>2</sub>O, the early work was reviewed by Frondel (1958), and further descriptions were reported by Nuffield & Milne (1953), Donnay & Donnay (1955), Walenta (1963, 1965a), Weigel & Hoffmann (1976), and Chernorukov *et al.* (1997), whereas for the system Ba–U–As–H<sub>2</sub>O, data were presented by Gross *et al.* (1958), Walenta (1965a, b), Weigel & Hoffmann (1976), and Chernorukov *et al.* (1997). Infrared spectroscopic data for these minerals are presented by Čejka Jr. *et al.* (1984a, b, 1985), Čejka *et al.* (1985), and Čejka (1999). As a result of this work on barium-bearing autunite-type compounds, although their absolute states of hydration have not been completely certain, three separate hydrates of barium uranyl phosphate and two hydrates of barium uranyl arsenate are well established to occur in nature: uranocircite,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$ ,  $a$  7.0 Å,  $c$  20.5 Å; meta-uranocircite I,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$ ,  $a$  7.0,  $c$  17.6 Å; meta-uranocircite II,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_6$ ,  $a'$  7.0 Å (see below),  $c$  16.9 Å;

heinrichite,  $\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{10}$ ,  $a$  7.1,  $c$  20.6 Å; and metaheinrichite,  $\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$ ,  $a$  7.1,  $c$  17.7 Å. The states of hydration listed here are only approximate, as previous investigators are not in agreement on this point. In almost all cases, they assumed that the compounds are tetragonal (despite their biaxial optical properties), by analogy with other members of the autunite and meta-autunite groups.

Note that Walenta (1965a, b) reported a fourth higher hydrate in the system  $\text{Ba-U-P-H}_2\text{O}$ ,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{12}$ , with  $c$  22.6 Å, and referred to this compound as uranocircite I, reserving uranocircite II for the decahydrate,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$ . We have not followed this terminology because data for the dodecahydrate are incomplete, and evidence that it occurs in nature is lacking, in contrast to the three lower hydrates, for which we use the nomenclature: uranocircite, meta-uranocircite I, and meta-uranocircite II. The Commission on New Minerals and Mineral Names of the International Mineralogical Association does not appear to have made any recommendations with regard to the nomenclature of the barium uranyl phosphate and arsenate hydrates ([www.geo.vu.nl/~ima-cnmmn/](http://www.geo.vu.nl/~ima-cnmmn/)).

Khosrawan-Sazedj (1982) determined that meta-uranocircite II has monoclinic symmetry, and presented a refinement in the non-standard space-group  $P2_1/a$  with  $a$  9.789(3),  $b$  9.882(3),  $c$  16.868(3) Å,  $\gamma$  89.95°,  $R1 = 7.1\%$ . In this setting of the unit cell, the structure of meta-uranocircite II is pseudotetragonal, and this cell can be related to that given above by the matrix  $[\frac{1}{2}, \frac{1}{2}, 0/\frac{1}{2}, \frac{1}{2}, 0/001]$ . Zolensky (1983) disagreed (erroneously) that meta-uranocircite II is centrosymmetric, and refined its structure in a similar non-standard setting of space group  $P2_1$  ( $R1 = 7.2\%$ ), based upon the solution of Khosrawan-Sazedj (1982).

More recently, Barinova *et al.* (2003) have suggested a structure for meta-uranocircite I in a non-standard setting of space group  $P2_1$  with  $a$  6.965(3),  $b$  6.964(2),  $c$  17.65(1) Å,  $\gamma$  90°,  $R1 = 11.0\%$ . This refinement is not of ideal quality: the two Ba positions are half-occupied and too close to each other, seven of the eight symmetrically independent  $\text{H}_2\text{O}$  groups are partially occupied

(yielding a total of 6  $\text{H}_2\text{O}$  per formula unit), and the interatomic distances around the U and P positions are outside the normal ranges.

The only other known barium uranyl phosphate structure is that of the synthetic compound  $\text{Ba}_3[(\text{UO}_2)(\text{PO}_4)(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_{0.4}]$  (Guesdon & Raveau 1998). This structure was synthesized by hydrothermal techniques at 220°C and has a highly corrugated uranyl phosphate sheet that is not related to the other structures discussed herein.

## EXPERIMENTAL

### Synthesis of the crystals

Crystals of *SrUP11*,  $\text{Sr}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$ , *SrUAs11*,  $\text{Sr}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{11}$ , and synthetic heinrichite,  $\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{10}$ , were grown at room temperature over the course of months by slow diffusion of phosphoric acid or hydrogen arsenate, and uranyl nitrate into cation-bearing silica gels contained in U-shaped tubes (Table 1). The gels were formed by the hydrolysis of a mixture of tetramethoxysilane (TMOS) and aqueous solutions of metal nitrates or metal chlorides. This method was modified after Arend & Connelly (1982), Manghi & Polla (1983), Zolensky (1983), Perrino & LeMaster (1984), Robert & LeFauchaux (1988), and Henisch (1988).

Crystals of synthetic meta-uranocircite I,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_7$ , were obtained by hydrothermal reaction of 0.1017 g  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ , 0.1510 g  $\text{Ba}(\text{NO}_3)_2$ , 0.1160 g fluorapatite [ideally  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , from the Liscombe deposit, near Wilberforce, Ontario, Canada], 0.1459 g concentrated  $\text{HNO}_3(\text{aq})$  and 6 mL of ultrapure  $\text{H}_2\text{O}(l)$ . The reactants were weighed into a 23 mL Teflon-lined Parr acid-digestion vessel and held in a Fisher Isotemp oven at 60(1)°C for two weeks. The vessel was then removed and allowed to cool in air to room temperature.

### Single-crystal X-ray diffraction

For each of the four compounds, a suitable crystal was captured in a glass capillary 0.3–0.5 mm in diameter (Charles Supper Co.) with either diluted growth solution or Millepore-filtered ultrapure water (18 MΩ resistance) and immobilized with high-vacuum silicone grease (Dow Corning). Each encapsulated crystal was mounted on a Bruker PLATFORM three-circle X-ray diffractometer operated at 50 keV and 40 mA and equipped with a 4K APEX CCD detector with a crystal-to-detector distance of 4.7 cm. Data were collected at room temperature using graphite-monochromatized  $\text{MoK}\alpha$  X-radiation and frame widths of 0.3° in  $\omega$ . Details of the data acquisition and refinement parameters are provided in Table 2. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the program SAINT (Bruker 1998a), and

TABLE 1. SYNTHESSES BY DIFFUSION-IN-GEL METHODS

Compound	<i>SrUP11</i>	<i>SrUAs11</i>	Heinrichite
Gel	TMOS 0.1 M $\text{Sr}(\text{NO}_3)_2$	TMOS 0.1 M $\text{Sr}(\text{NO}_3)_2$	TMOS 0.03 M $\text{Ca}(\text{NO}_3)_2$
Left arm	0.1 M uranyl nitrate	0.1 M uranyl nitrate	0.1 M uranyl nitrate + 0.3 M $\text{BaCl}_2$ mixture
Right arm	0.1 M $\text{H}_3\text{PO}_4$	0.033 M $\text{H}_2\text{As}_2\text{O}_{10}$	0.033 M $\text{H}_2\text{As}_2\text{O}_{10}$
Time	4 months	4 months	2 months

Note: gel volumes are 11 mL (1 mL TMOS + 10 mL aqueous solution); arm volumes are 6 mL each. All solutions are aqueous. TMOS: tetramethoxysilane,  $(\text{CH}_3\text{O})_2\text{Si}$ .

the unit-cell dimensions were refined using least-squares techniques. Comparison of the intensities of equivalent reflections measured at different times during data acquisition showed no significant decay for any of the compounds.

Space group *Pnma* was assigned to *SrUP11* and *SrUAs11*, by analogy with the structure refinement of synthetic autunite,  $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$  (Locock & Burns 2003a). Systematic absences of reflections for synthetic heinrichite were consistent with space groups *Pn* and *P2/n* (alternative settings of space groups *Pc* and *P2/c*, respectively). The unit cell of synthetic heinrichite can be transformed between these settings by the matrix  $[100/010/101]$ . Systematic absences of reflections for meta-uranocircite I are consistent with space groups *P2<sub>1</sub>* and *P2<sub>1</sub>/m*, and assigning phases to a set of normalized structure-factors gave a mean value of  $|E^2 - 1|$  of 0.784, consistent with space group *P2<sub>1</sub>*. Trial solutions were obtained for both space groups, but reasonable

interatomic distances were obtained only in the case of *P2<sub>1</sub>*.

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-ray Crystallography, Vol. C* (Wilson 1992). The SHELXTL Version 5 series of programs was used for the solution and refinement of the crystal structures (Sheldrick 1998).

#### Refinement of the structures

All four structures were refined on the basis of  $F^2$  for all unique data. In the final cycle of each refinement, the mean parameter shift/esd was 0.000. As is common in heavy-atom structures, the location of each H atom in the unit cell was not determined for any of these compounds because of the minimal contribution of H atoms to the diffracted intensities.

The crystal structures of *SrUP11* and *SrUAs11* were refined using the non-H atom positions of Locock &

TABLE 2. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS

Compound	<i>SrUP11</i>	<i>SrUAs11</i>	Heinrichite	Meta-uranocircite I
<i>a</i> (Å)	14.042(6)	14.3778(6)	7.1548(11)	6.943(2)
<i>b</i> (Å)	21.008(9)	20.9611(9)	7.1340(11)	17.634(6)
<i>c</i> (Å)	6.997(3)	7.1703(3)	21.290(3)	6.952(2)
$\beta$ (°)	90	90	104.171(5)	90.023(7)
<i>V</i> (Å <sup>3</sup> )	2064.1(15)	2160.95(16)	1053.6(3)	851.2(5)
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>P2/c</i>	<i>P2<sub>1</sub></i>
<i>Z</i>	4	4	2	2
Chemical formula	$\text{Sr}[(\text{UO}_2)(\text{PO}_4)]_2$	$\text{Sr}[(\text{UO}_2)(\text{AsO}_4)]_2$	$\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2$	$\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2$
Formula weight <sup>1</sup>	1015.786	1103.681	1135.373	993.432
<i>F</i> (000) <sup>1</sup>	1832	1976	1004	872
$\mu$ (mm <sup>-1</sup> ) <sup>1</sup>	18.48	20.55	20.39	21.55
<i>D</i> <sub>calc</sub> (g/mL) <sup>1</sup>	3.269	3.392	3.579	3.876
Size (mm)	0.44 × 0.20 × 0.02	0.30 × 0.24 × 0.04	0.25 × 0.12 × 0.02	0.10 × 0.10 × 0.01
Color and habit	yellow plate	yellow plate	yellow plate	yellow plate
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Frame width (°), time (s)	0.3, 5	0.3, 20	0.3, 20	0.3, 60
Collection, hrs	sphere, 4	sphere, 15	sphere, 15	sphere, 45
$\theta$ range (°)	2.90 – 34.56	2.83 – 34.52	2.86 – 34.50	2.31 – 34.60
Data collected	<i>h</i> ± 22, <i>k</i> ± 33, <i>l</i> ± 11	<i>h</i> ± 22, <i>k</i> ± 33, <i>l</i> ± 11	<i>h</i> ± 11, <i>k</i> ± 11, <i>l</i> ± 33	<i>h</i> ± 10, <i>k</i> ± 27, <i>l</i> ± 11
Absorption <sup>2</sup>	plate (010) 3°	plate (010) 3°	plate (001) 3°	SADABS
Total refl.	37119	38284	18634	17488
Unique refl., <i>R</i> <sub>int</sub>	4461, 0.139	4631, 0.109	4364, 0.144	6856, 0.095
Unique $ F_o  \geq 4\sigma_F$	1853	2051	3298	4889
Extinction		0.0011(1)	0.0024(2)	
Parameters	134	76	124	124
$R1^3$ for $ F_o  \geq 4\sigma_F$	3.6	5.2	4.3	5.2
$R1^3$ all data, $wR2^4$	8.3, 12.8	8.3, 19.2	5.4, 10.4	8.7, 11.0
Weighting <i>a</i> , <i>b</i>	0.0545	0.1035	0.0487	0.0434
Goodness of fit	0.918	1.004	0.920	0.906
Mean shift/esd	0.000	0.000	0.000	0.000
Peaks ( <i>e</i> /Å <sup>3</sup> )	3.9, -2.3	9.9, -4.6	3.1, -4.8	6.6, -5.5

<sup>1</sup> Calculated with ideal occupancy of all atom positions. <sup>2</sup> Corrections for absorption are either semi-empirical (crystal modeled as a plate, rejecting data within 3° of the primary X-ray beam), or empirical (program SADABS, G. Sheldrick, unpubl.) based on the intensities of equivalent reflections. <sup>3</sup>  $R1 = [\sum |F_o| - |F_c|] / \sum |F_o| \times 100$ . <sup>4</sup>  $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5} \times 100$ ,  $w = 1 / [\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$ , and  $P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$ .

Burns (2003a) for autunite as a starting point. For *SrUP11*, a structure model including anisotropic displacement parameters for all atoms converged, and gave an agreement index (*R1*) of 3.6%, calculated for the 1853 observed unique reflections ( $|F_o| \geq 4\sigma_F$ ). The final value of  $wR_2$  was 12.8% for all data using the structure-factor weights assigned during least-squares refinement. In the case of *SrUAs11*, a structure model including anisotropic displacement parameters for U, As and Sr converged, and gave an agreement index (*R1*) of 5.2%, calculated for the 2051 observed unique reflections ( $|F_o| \geq 4\sigma_F$ ). The final value of  $wR_2$  was 19.2% for all data using the structure-factor weights assigned during least-squares refinement.

The structure of synthetic heinrichite was solved in space group *Pn* by direct methods and transformed to space group *P2/c* by the ADDSYM algorithm in the program PLATON (Le Page 1987, Spek 2003), as use of direct methods to solve the structure of heinrichite in *P2/n* yielded an inappropriate pseudosolution. A structure model including anisotropic displacement parameters for all non-H atoms converged, and gave an agreement index (*R1*) of 4.3%, calculated for the 3298 observed unique reflections ( $|F_o| \geq 4\sigma_F$ ). The final value of  $wR_2$  was 10.4% for all data using the structure-factor weights assigned during least-squares refinement.

The structure of synthetic meta-uranocircite I was solved in space group *P2<sub>1</sub>* by direct methods, and a structure model including anisotropic displacement parameters for U, P and Ba converged. Because synthetic meta-uranocircite I was solved in a non-centrosymmetric space-group, and is pseudo-orthorhombic, with a  $\beta$  angle close to 90° (Table 2), the inversion twin law  $[100/0\bar{1}0/00\bar{1}]$  and a pseudo-orthorhombic twin law  $[100/0\bar{1}0/00\bar{1}]$  were applied simultaneously, and the structure was refined according to published methods (Jameson 1982, Herbst-Irmer & Sheldrick 1998), yielding an agreement index (*R1*) of 5.2%, calculated for the 4889 observed unique reflections ( $|F_o| \geq 4\sigma_F$ ). The inversion and pseudo-orthorhombic twin scale-factors refined to 12(1)% and 70.7(1)%, respectively, consistent with asymmetrical distributions of the twin components. The final value of  $wR_2$  was 11.0% for all data using the structure-factor weights assigned during least-squares refinement. The refined solution obtained for synthetic meta-uranocircite I was checked with the ADDSYM algorithm in the program PLATON (Le Page 1987, Spek 2003); no higher symmetry was found. The structure refinement of synthetic meta-uranocircite I leads to the cell contents: Ba[(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>], with *Z* = 2 and *D*<sub>calc</sub> = 3.88 g/mL. Note that this hydration state differs from that reported by Barinova *et al.* (2003): Ba[(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>], and by Walenta (1965a): Ba[(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>], for meta-uranocircite I with the same unit-cell volume. No positions consistent with further H<sub>2</sub>O groups were found in the top 200 peaks of the final difference-Fourier map. The final structure-model was subjected to cavity analysis using the pro-

gram ATOMS (Dowty 2000). No cavity with a radius greater than 2.0 Å was found in the structure model, consistent with the lack of further H<sub>2</sub>O groups in this structure. The validity of the cavity analysis was established by examination of the structure model of synthetic meta-uranocircite I with the O(19)W position vacant. In this unoccupied case, analysis revealed a cavity with radius 2.48 Å at atom coordinates (*x*, *y*, *z*) 0.14, 0.92, 0.32, within 0.22 Å of the refined position of the O(19)W H<sub>2</sub>O group, thus supporting the reliability of this approach.

The positional parameters of atoms are given in Table 3 for *SrUP11*, Table 4 for *SrUAs11*, Table 5 for synthetic heinrichite, and Table 6 for synthetic meta-uranocircite I. Selected interatomic distances are listed in Table 7 for *SrUP11*, Table 8 for *SrUAs11*, Table 9 for synthetic heinrichite, and Table 10 for synthetic meta-uranocircite I. Anisotropic displacement parameters for these compounds, as well as observed and calculated structure-factors, are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

The structures of the related compounds Sr[(UO<sub>2</sub>)(AsO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>], *SrUAs8*, of cell dimensions 7.154(1), *b* 7.101(1), *c* 18.901(7) Å,  $\beta$  92.67(2)°, and meta-uranocircite II, Ba[(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>], have previously been reported in the literature (Pushcharovskii *et al.* 2003, Khosrawan-Sazedj 1982). However, *SrUAs8* was refined in the non-centrosymmetric space-group *Pc*, and meta-uranocircite II was reported in the non-standard space-group *P2<sub>1</sub>/a*, with  $\gamma = 89.95^\circ$ . Both structures were tested with the ADDSYM algorithm in the program PLATON (Le Page 1987, Spek 2003). The structure of *SrUAs8* was transformed to space group *P2/c*, which yielded improved interatomic distances: <U(1)–O<sub>ap</sub>> 1.79 Å, <U(1)–O<sub>eq</sub>> 2.27 Å, <As(1)–O> 1.68 Å, and <Sr(1)–O> 2.65 Å. The structure of meta-

TABLE 3. ATOM COORDINATES FOR Sr[(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>11</sub>]

<i>SrUP11</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
U(1)	0.1249(1)	0.5414(1)	0.7483(1)	0.012(1)
P(1)	0.1238(3)	0.5003(1)	0.2461(2)	0.014(1)
Sr(1) <sup>†</sup>	0.1247(1)	½	0.4687(1)	0.020(1)
O(1)	0.1239(7)	0.4567(3)	0.7473(5)	0.027(2)
O(2)	0.1220(7)	0.6260(3)	0.7428(5)	0.022(1)
O(3)	0.1251(5)	0.5437(2)	0.0698(7)	0.028(1)
O(4)	0.0363(5)	0.4583(5)	0.2434(5)	0.027(3)
O(5)	0.2109(5)	0.4556(5)	0.2533(5)	0.022(2)
O(6)	0.1205(5)	0.5453(2)	0.4214(7)	0.022(1)
O(7)W	0.7446(10)	½	0.2671(10)	0.039(3)
O(8)W	0.2405(4)	0.6593(3)	0.3450(13)	0.065(2)
O(9)W	0.0087(4)	0.6593(3)	0.3535(11)	0.059(2)
O(10)W	0.9982(9)	½	0.2630(9)	0.039(4)
O(11)W	0.1245(7)	¾	0.0660(11)	0.040(2)
O(12)W	0.1772(4)	0.3431(3)	0.4787(8)	0.051(2)
O(13)W	0.0720(4)	0.3433(3)	0.0189(8)	0.052(2)

*U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>*i*</sub> tensor.

<sup>†</sup> Occupancy refined to 79.5(3)%.



uranocircite II was reset in the standard space-group  $P2_1/c$ ; the matrix for transformation to the standard setting is  $[\bar{0}10/001/100]$ , yielding  $a$  9.882(3) Å,  $b$  16.868(3) Å,  $c$  9.789(3) Å,  $\beta$  90.05(2)°. Revised positional parameters of the atoms in *SrUAs8* and meta-uranocircite II are given in Tables 11 and 12, respectively.

Bond-valence sums at the non-H cation sites for the four compounds refined herein, and for *SrUAs8* and meta-uranocircite II, are presented in Table 13; they were calculated using the parameters of Burns *et al.* (1997) for sixfold coordinated  $U^{6+}$ , Brown & Altermatt (1985) for  $P^{5+}$ ,  $As^{5+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$ . The bond-valence sums are in good agreement with expected formal oxidation states, with the exception of the P(1) position of meta-uranocircite II (Khosrawan-Sazedj 1982), which is somewhat high (see note to Table 13).

TABLE 4. ATOM COORDINATES FOR  $Sr[(UO_2)(AsO_4)]_2(H_2O)_{11}$ 

<i>SrUAs11</i>	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
U(1)	0.1251(1)	0.5451(1)	0.7485(1)	0.014(1)
As(1)	0.1251(1)	0.5002(1)	0.2451(1)	0.016(1)
Sr(1) <sup>†</sup>	0.1249(1)	3/8	0.4820(2)	0.034(1)
O(1)	0.1256(4)	0.4605(4)	0.7488(4)	0.029(2)
O(2)	0.1263(3)	0.6304(3)	0.7420(4)	0.024(1)
O(3)	0.1284(3)	0.5488(3)	0.0634(11)	0.031(1)
O(4)	0.0326(5)	0.4503(3)	0.2426(4)	0.024(2)
O(5)	0.2170(6)	0.4532(3)	0.2515(5)	0.036(2)
O(6)	0.1224(3)	0.5487(2)	0.4298(10)	0.029(1)
O(7)W	0.7619(12)	1/4	0.2628(14)	0.109(6)
O(8)W	0.2418(4)	0.6621(4)	0.3670(9)	0.075(2)
O(9)W	0.0081(4)	0.6627(4)	0.3683(8)	0.072(2)
O(10)W	0.0049(7)	1/4	0.2577(7)	0.037(2)
O(11)W	0.1247(5)	3/8	0.0588(14)	0.047(2)
O(12)W	0.3209(4)	0.6587(4)	-0.0114(8)	0.073(2)
O(13)W	0.0710(4)	0.3409(4)	0.0103(8)	0.072(2)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_i$  tensor.

<sup>†</sup> Occupancy refined to 84.0(5)%.

TABLE 5. ATOM COORDINATES FOR  $Ba[(UO_2)(AsO_4)]_2(H_2O)_{10}$ 

Heinrichite	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
U(1)	0.2861(1)	0.7488(1)	0.0440(1)	0.013(1)
As(1)	0.2462(1)	0.2486(1)	0.0011(1)	0.014(1)
Ba(1)	1/2	-0.0417(1)	1/4	0.024(1)
O(1)	0.3520(7)	0.7528(4)	0.1308(2)	0.019(1)
O(2)	0.3200(6)	0.4323(5)	0.0502(2)	0.022(1)
O(3)	0.2436(6)	0.0635(5)	0.0497(2)	0.021(1)
O(4)	0.3966(6)	0.2112(6)	-0.0469(2)	0.019(1)
O(5)	0.0284(6)	0.2857(6)	-0.0477(2)	0.021(1)
O(6)	0.2234(7)	0.7473(5)	-0.0418(2)	0.024(1)
O(7)W	0.1406(7)	0.1012(7)	0.1747(3)	0.043(1)
O(8)W	0.7529(8)	-0.0049(7)	0.1623(3)	0.043(1)
O(9)W	0.5252(9)	0.3046(8)	0.1772(3)	0.048(1)
O(10)W	0.2806(7)	0.6324(8)	0.2615(3)	0.043(1)
O(11)W	0.0189(9)	0.5071(8)	0.3373(3)	0.051(2)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_i$  tensor.

## DESCRIPTION OF THE STRUCTURES

All four of the compounds investigated contain the well-known corrugated autunite-type sheet as originally described by Beintema (1938), formed by the sharing of vertices between uranyl square bipyramids and either phosphate or arsenate tetrahedra (Fig. 1), with composition  $[(UO_2)(PO_4)]^-$  or  $[(UO_2)(AsO_4)]^-$ .

TABLE 6. ATOM COORDINATES FOR  $Ba[(UO_2)(PO_4)]_2(H_2O)_9$ 

Meta-uranocircite I	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
U(1)	0.5350(1)	0.0711(1)	0.5464(1)	0.012(1)
U(2)	0.0412(1)	0.1665(1)	0.0404(1)	0.011(1)
Ba(1)	0.3984(2)	0.3399(1)	0.1804(2)	0.027(1)
P(1)	0.0362(7)	0.1180(4)	-0.4591(8)	0.013(1)
P(2)	0.5348(7)	0.1203(4)	0.0518(8)	0.013(1)
O(1)	0.5360(20)	0.1725(13)	0.5350(20)	0.026(4)
O(2)	0.0440(20)	0.0670(12)	0.0420(20)	0.020(3)
O(3)	0.4893(19)	0.0768(9)	0.8716(18)	0.019(3)
O(4)	0.5690(17)	0.0670(10)	0.2186(17)	0.013(3)
O(5)	0.2107(19)	0.0676(10)	-0.4911(19)	0.016(3)
O(6)	-0.2830(20)	0.1714(11)	0.0200(20)	0.021(3)
O(7)	-0.1406(18)	0.0700(9)	-0.4252(19)	0.019(3)
O(8)	0.0660(20)	0.1732(10)	-0.2850(20)	0.023(3)
O(9)	0.0062(19)	0.1716(9)	-0.6330(20)	0.020(3)
O(10)	0.3674(18)	0.1773(8)	0.0969(17)	0.013(3)
O(11)	0.5380(20)	-0.0295(9)	0.5616(19)	0.016(3)
O(12)	0.0480(20)	0.2694(9)	0.0400(20)	0.017(3)
O(13)W	0.2560(20)	0.3072(9)	0.5540(30)	0.040(4)
O(14)W	0.6930(20)	0.4329(9)	0.0570(30)	0.037(4)
O(15)W	0.7520(20)	0.3109(9)	0.3880(20)	0.033(4)
O(16)W	0.2420(30)	0.4226(10)	-0.1380(30)	0.042(4)
O(17)W	-0.0520(20)	-0.0803(9)	-0.2660(20)	0.030(3)
O(18)W	0.5800(30)	0.3029(10)	-0.1760(30)	0.044(5)
O(19)W	0.1390(30)	-0.0770(11)	-0.7100(30)	0.049(5)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_i$  tensor.

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR  $Sr[(UO_2)(PO_4)]_2(H_2O)_{11}$ 

U(1)-O(2)	1.778(6)	O(7)W-O(12)W	2.771(8)
U(1)-O(1)	1.779(6)	O(7)W-O(11)W	2.968(14)
U(1)-O(3)	2.250(5)		
U(1)-O(4)	2.264(7)	O(8)W-O(12)W	2.812(10)
U(1)-O(6)	2.289(5)	O(8)W-O(13)W	2.901(9)
U(1)-O(5)	2.306(8)		
<U(1)-O <sub>eq</sub> >	1.78	O(9)W-O(13)W	2.842(9)
<U(1)-O <sub>ap</sub> >	2.28	O(9)W-O(12)W	2.863(9)
O(2)-U(1)-O(1)	177.7(3)		
		O(10)W-O(13)W	2.798(8)
		O(10)W-O(11)W	2.875(14)
P(1)-O(4)	1.514(8)		
P(1)-O(3)	1.534(5)		
P(1)-O(5)	1.543(9)	O(11)W-O(10)W	2.875(14)
P(1)-O(6)	1.549(5)	O(11)W-O(7)W	2.968(14)
<P(1)-O>	1.54		
		O(12)W-O(7)W	2.771(8)
Sr(1)-O(10)W	2.550(10)	O(12)W-O(8)W	2.812(10)
Sr(1)-O(7)W	2.604(11)	O(12)W-O(9)W	2.863(9)
Sr(1)-O(9)W	2.632(6) × 2	O(12)W-O(5)	2.881(10)
Sr(1)-O(8)W	2.650(6) × 2		
Sr(1)-O(11)W	2.818(8)	O(13)W-O(10)W	2.798(8)
Sr(1)-O(2)	3.234(6) × 2	O(13)W-O(9)W	2.842(9)
<Sr(1)-O>	2.78	O(13)W-O(8)W	2.901(9)
		O(13)W-O(4)	2.925(11)

Both *SrUP11* and *SrUAs11* are isostructural with synthetic autunite (Locock & Burns 2003a). Their interlayers contain Sr coordinated by seven H<sub>2</sub>O groups with bond lengths in the range 2.45 to 3.04 Å (Tables 7, 8). The Sr sites are also located 3.1–3.2 Å from uranyl ion oxygen atoms of the sheets on either side, and thus serve to link the sheets directly (Fig. 2). The Sr positions in *SrUP11* and *SrUAs11* refined to 79.5(3)% and 84.0(5)% occupancy (Hawthorne *et al.* 1995), respectively; charge balance is interpreted to be maintained by oxonium, in analogy with chernikovite, H<sub>3</sub>O[(UO<sub>2</sub>)(PO<sub>4</sub>)](H<sub>2</sub>O)<sub>3</sub> (Atencio 1988, Morosin 1978a, b). Two additional H<sub>2</sub>O groups are located in the interlayer, where they are held in position only by hydrogen bonds. Although H positions were not determined in these two structures, a network of hydrogen bonds similar to that found in autunite is proposed on the basis of O...O interatomic distances in the range 2.7–3.0 Å (Tables 7, 8, Fig. 3), in accord with the usual D...A separations found for hydrogen bonds (Jeffrey 1997). Four interlayer H<sub>2</sub>O groups are linked by hydrogen bonding to form square planar sets. Hydrogen bonds extend from this set to acceptors in the sheets (the anions at the equatorial vertices of uranyl square bipyramids that are also shared with tetrahedra), and to interlayer H<sub>2</sub>O groups that are bonded to Sr (Fig. 3).

The interlayer of synthetic heinrichite contains Ba in ten-fold coordination by four symmetrically independent H<sub>2</sub>O groups and one oxygen atom from a uranyl ion (Fig. 4), with a mean Ba–O interatomic distance of 2.89 Å (Table 9). The uranyl arsenate sheets are linked

directly through the bonds from the apical oxygen atoms of the uranyl ion to the Ba position (Fig. 4). One symmetrically independent H<sub>2</sub>O group is held in position solely by hydrogen bonds. A possible network of hydrogen bonds (not illustrated) can be suggested on the basis of O...O interatomic distances in the range 2.7–

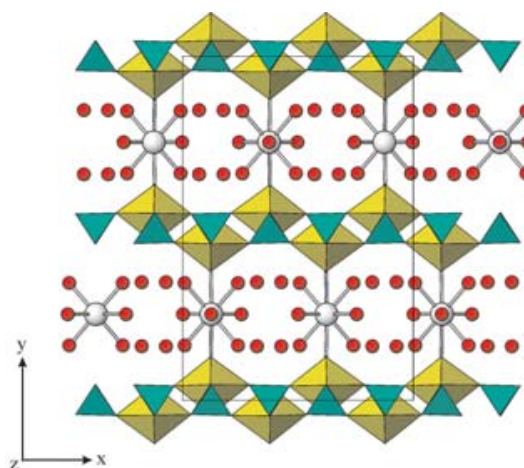


FIG. 2. The structure of *SrUP11*, projected along [001]. The uranyl polyhedra are shown in yellow, and the phosphate tetrahedra, in green. The Sr atoms are shown as large gray spheres, and the H<sub>2</sub>O groups are shown as small red spheres.

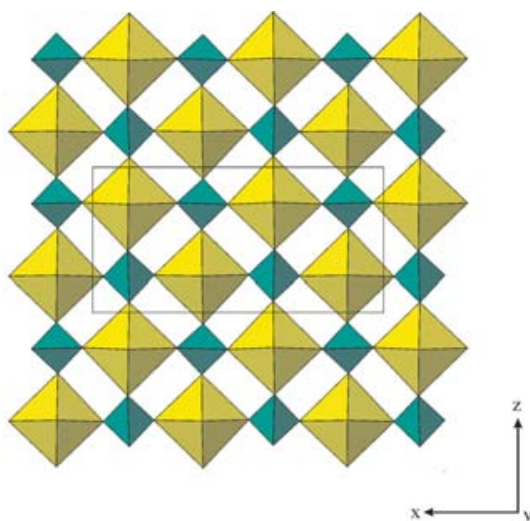


FIG. 1. The autunite-type sheet of *SrUP11*, Sr[(UO<sub>2</sub>)(PO<sub>4</sub>)]<sub>2</sub>(H<sub>2</sub>O)<sub>11</sub>, formed by the sharing of vertices between uranyl square bipyramids and phosphate tetrahedra.

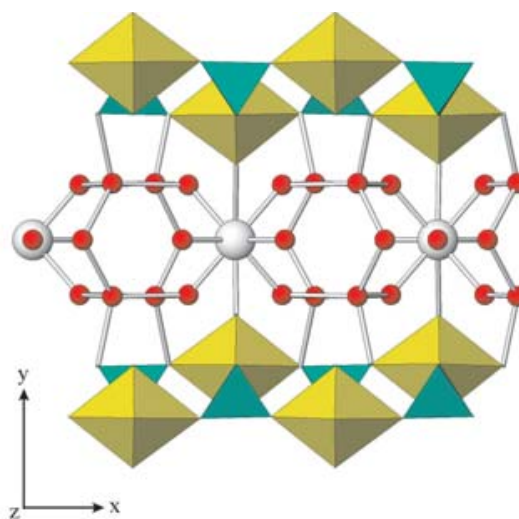


FIG. 3. Possible hydrogen bonding in a portion of the structure of *SrUP11*, projected along [001]. Sr–O bonds and donor–acceptor (O...O) distances of less than 3.0 Å are shown as rods. The legend is the same as in Figure 2.

3.1 Å (Table 9). Despite having been synthesized in a gel environment in which the nominal molar Ba:Ca ratio was 10:1, the synthetic heinrichite does not seem to have incorporated any significant amount of Ca into its structure; the occupancy of the Ba position refined to 100%.

The interlayer of synthetic meta-uranocircite I contains Ba in nine-fold coordination by six symmetrically independent H<sub>2</sub>O groups, two uranyl ion oxygen atoms, and one phosphate oxygen atom (Fig. 5), with a mean Ba–O interatomic distance of 2.87 Å (Table 10). The uranyl phosphate sheets are linked directly through the

bonds from the phosphate oxygen atom and the uranyl ion apical oxygen atom to the Ba position (Fig. 5). One symmetrically independent H<sub>2</sub>O group, O(19)W, is held in position solely by hydrogen bonds. A unique network of hydrogen bonds cannot be proposed for synthetic meta-uranocircite I on the basis of O...O interatomic distances, because of the excessive number of such distances in the range 2.6–3.1 Å. As in synthetic heinrichite, the Ba position in synthetic meta-uranocircite I refined to full occupancy, even though the nominal molar Ba:Ca ratio was 1:2 in the hydrothermal synthesis.

TABLE 8. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR Sr[(UO<sub>2</sub>)(AsO<sub>4</sub>)<sub>2</sub>](H<sub>2</sub>O)<sub>11</sub>

U(1)-O(1)	1.773(8)	O(7)W-O(11)W	2.823(15)
U(1)-O(2)	1.788(7)	O(7)W-O(12)W	2.887(11)
U(1)-O(3)	2.260(8)		
U(1)-O(4)	2.270(7)	O(8)W-O(13)W	2.882(9)
U(1)-O(5)	2.271(9)	O(8)W-O(12)W	2.943(9)
U(1)-O(6)	2.287(7)		
<U(1)-O <sub>ap</sub> >	1.78	O(9)W-O(12)W	2.881(9)
<U(1)-O <sub>ap</sub> >	2.27	O(9)W-O(13)W	2.944(8)
O(1)-U(1)-O(2)	178.35(17)		
		O(10)W-O(13)W	2.771(9)
As(1)-O(5)	1.649(8)	O(10)W-O(11)W	2.937(12)
As(1)-O(3)	1.654(7)		
As(1)-O(6)	1.670(7)	O(11)W-O(7)W	2.823(16)
As(1)-O(4)	1.692(7)	O(11)W-O(10)W	2.937(12)
<As(1)-O>	1.67		
		O(12)W-O(9)W	2.881(9)
Sr(1)-O(7)W	2.449(14)	O(12)W-O(7)W	2.887(11)
Sr(1)-O(9)W	2.615(7) × 2	O(12)W-O(8)W	2.943(9)
Sr(1)-O(8)W	2.626(7) × 2	O(12)W-O(5)	2.947(9)
Sr(1)-O(10)W	2.640(8)		
Sr(1)-O(11)W	3.035(10)	O(13)W-O(10)W	2.771(9)
Sr(1)-O(2)	3.124(6) × 2	O(13)W-O(8)W	2.882(9)
<Sr(1)-O>	2.76	O(13)W-O(4)	2.888(9)
		O(13)W-O(9)W	2.944(8)

TABLE 9. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR HEINRICHITE, Ba[(UO<sub>2</sub>)(AsO<sub>4</sub>)<sub>2</sub>](H<sub>2</sub>O)<sub>10</sub>

U(1)-O(6)	1.771(5)	O(7)W-O(8)W	2.825(7)
U(1)-O(1)	1.791(5)	O(7)W-O(3)	2.941(7)
U(1)-O(2)	2.271(4)		
U(1)-O(3)	2.273(4)	O(8)W-O(9)W	2.807(8)
U(1)-O(4)	2.274(4)	O(8)W-O(7)W	2.825(7)
U(1)-O(5)	2.284(4)		
<U(1)-O <sub>ap</sub> >	1.78	O(9)W-O(8)W	2.807(8)
<U(1)-O <sub>ap</sub> >	2.28	O(9)W-O(2)	2.890(7)
O(6)-U(1)-O(1)	179.19(17)		
		O(10)W-O(11)W	2.758(8)
As(1)-O(5)	1.669(4)	O(10)W-O(11)W	2.896(8)
As(1)-O(4)	1.677(4)		
As(1)-O(2)	1.680(4)	O(11)W-O(10)W	2.758(8)
As(1)-O(3)	1.681(4)	O(11)W-O(5)	2.847(7)
<As(1)-O>	1.68	O(11)W-O(10)W	2.896(8)
		O(11)W-O(7)W	3.100(8)
Ba(1)-O(10)W	2.849(5) × 2		
Ba(1)-O(7)W	2.864(5) × 2		
Ba(1)-O(1)	2.897(4) × 2		
Ba(1)-O(8)W	2.913(5) × 2		
Ba(1)-O(9)W	2.945(6) × 2		
<Ba(1)-O>	2.89		

TABLE 10. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR META-URANOCIRCITE I, Ba[(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>](H<sub>2</sub>O)

U(1)-O(11)	1.777(16)	P(1)-O(7)	1.509(15)
U(1)-O(1)	1.792(2)	P(1)-O(5)	1.520(16)
U(1)-O(7)	2.261(13)	P(1)-O(9)	1.548(16)
U(1)-O(5)	2.268(13)	P(1)-O(8)	1.566(17)
U(1)-O(3)	2.285(12)	<P(1)-O>	1.54
U(1)-O(4)	2.292(12)		
<U(1)-O <sub>ap</sub> >	1.78	P(2)-O(3)	1.502(15)
<U(1)-O <sub>ap</sub> >	2.28	P(2)-O(4)	1.511(15)
O(11)-U(1)-O(1)	178.8(6)	P(2)-O(6)	1.569(16)
		P(2)-O(10)	1.569(14)
		<P(2)-O>	1.54
U(2)-O(2)	1.76(2)		
U(2)-O(12)	1.814(16)	Ba(1)-O(14)W	2.758(16)
U(2)-O(6)	2.258(14)	Ba(1)-O(13)W	2.838(19)
U(2)-O(8)	2.273(14)	Ba(1)-O(17)W	2.848(16)
U(2)-O(9)	2.286(13)	Ba(1)-O(18)W	2.858(19)
U(2)-O(10)	2.306(12)	Ba(1)-O(16)W	2.866(19)
<U(2)-O <sub>ap</sub> >	1.79	Ba(1)-O(15)W	2.891(17)
<U(2)-O <sub>ap</sub> >	2.28	Ba(1)-O(12)W	2.905(15)
O(2)-U(2)-O(12)	178.1(5)	Ba(1)-O(10)	2.934(14)
		Ba(1)-O(11)	2.952(15)
		<Ba(1)-O>	2.87

TABLE 11. REVISED ATOM COORDINATES FOR Sr[(UO<sub>2</sub>)(AsO<sub>4</sub>)<sub>2</sub>](H<sub>2</sub>O)<sub>8</sub>

	x	y	z	U <sub>eq</sub>
U(1)	0.2536	0.2592	0.0499	0.016
As(1)	0.7439	0.2492	0.0007	0.017
Sr(1)	0	0.1687	1/4	0.026
O(1)	0.254	0.267	-0.045	0.014
O(2)	0.245	0.250	0.145	0.015
O(3)	0.938	0.296	0.050	0.021
O(4)	0.569	0.218	0.057	0.023
O(5)	0.776	0.057	-0.049	0.029
O(6)	0.695	0.424	-0.057	0.011
O(7)W	0.112	0.475	0.320	0.032
O(8)W	0.037	0.879	0.174	0.046
O(9)W	0.661	0.079	0.198	0.038
O(10)W	0.560	0.682	0.183	0.039

U<sub>eq</sub> is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor. Revised from Pushcharovskii *et al.* (2003). The origin was shifted to: 0.362, 0.001, 0.015 after transformation; revised space-group P2<sub>1</sub>/c, cell dimensions: a 7.154(1), b 7.101(1), c 18.901(7) Å, β 92.67(2)°.



## DISCUSSION

*Meta-uranocircite I, meta-uranocircite II, metaheinrichite*

Collection of preliminary X-ray data from an unencapsulated crystal of synthetic meta-uranocircite I revealed that the heat generated by absorption of the impinging X-ray beam caused the dehydration of the crystal to (presumably) meta-uranocircite II, in accord with the observations of Walenta (1965a, 1963). The change in structure from synthetic meta-uranocircite I,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_7$ , to meta-uranocircite II,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_6$ , involves the loss of one  $\text{H}_2\text{O}$  group *pfu* and only a slight decrease in interlayer spacing, from  $d_{020} = 8.82 \text{ \AA}$  to  $d_{020} = 8.43 \text{ \AA}$ , but entails considerable rearrangement of the interlayer contents, especially the Ba position (Fig. 5). In synthetic meta-uranocircite I, the Ba atoms lie in the same plane but are isolated from each other, with a minimum Ba–Ba distance of  $6.94 \text{ \AA}$ . In meta-uranocircite II, the Ba atoms are separated by a minimum distance of  $4.61 \text{ \AA}$ , and the coordination environments of the Ba atoms share two  $\text{H}_2\text{O}$  groups, forming a pair of edge-sharing  $\text{BaO}_9$  polyhedra (Fig. 3 of Khosrawan-Sazedj 1982).

On the basis of the similarity of the cell dimensions of synthetic meta-uranocircite I and metaheinrichite (Gross *et al.* 1958, Walenta 1965a, b 1963), it is likely that these species are isostructural. Metaheinrichite is predicted to have the formula  $\text{Ba}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_7$ , with expected crystal-data: monoclinic, space group  $P2_1$ ,  $a 7.08$ ,  $b 17.7$ ,  $c 7.09 \text{ \AA}$ ,  $\beta 90.02^\circ$ ,  $V 889 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} 4.0 \text{ g/mL}$ . Metaheinrichite probably also exhibits an inversion and pseudomorph twinning like that found in meta-uranocircite I. A lower hydrate in the system Ba–U–As– $\text{H}_2\text{O}$  analogous to meta-uranocircite II has not yet been described.

*Heinrichite and uranocircite*

Heinrichite was originally assumed by Gross *et al.* (1958) and Walenta (1965a, b) to be tetragonal, despite the observation of biaxial optical properties. The cell dimensions and density given by Walenta (1965a, b),  $a 7.13$ ,  $c 20.56 \text{ \AA}$ ,  $D_{\text{calc}} 3.61 \text{ g/mL}$ , are in fair agreement with the data presented herein for heinrichite, but set in space group  $P2/n$ :  $a 7.155(1)$ ,  $b 7.134(1)$ ,  $c 20.733(3) \text{ \AA}$ ,  $\beta 95.38(1)^\circ$ ,  $D_{\text{calc}} 3.58 \text{ g/mL}$ . Because of the identical chemical composition, and close resemblance of the cell dimensions, the synthetic material investigated here is presumed to be identical with natural heinrichite.

It did not prove possible to refine the structure of uranocircite to a satisfactory level of accuracy in the course of this study. Gel synthesis had been undertaken in the same manner as for heinrichite, but with the use of  $0.1 \text{ M}$  phosphoric acid instead of hydrogen arsenate. However, aggregates of synthetic uranocircite were refined rather than single crystals. The best crystal from

the synthesis was encapsulated and examined on a three-circle X-ray diffractometer, but proved not to be a single crystal. Figure 6 illustrates the difficulty in choosing a single crystal from this synthesis for X-ray study. Although under plane-polarized light a given crystal may appear ideal, under crossed-polarized illumination, the absence of consistent interference-colors and lack of uniform extinction are consistent instead with the presence of two (or more) crystals. The optical effects under crossed-polarized illumination from the intergrown crystals can be subtle and may be enhanced by the use of an anisotropic background (such as polystyrene) and an accessory plate.

Owing to the impracticality of determining the quality of the centering of a crystal aggregate encapsulated in a fluid-filled capillary, a refinement of the structure of synthetic uranocircite is not presented here. However, sufficient data were collected to establish the unit-cell dimensions. The orientation matrix of the dominant crystal component was resolved using GEMINI software (Bruker 1998b):  $a 7.01$ ,  $b 6.99$ ,  $c 20.7 \text{ \AA}$ ,  $\beta 95.3^\circ$ , space group  $P2/n$  (as corrections were not made for the degree of overlap of reflections from the intergrown crystals, estimates of uncertainty for the cell dimensions are not given). These dimensions are similar to the  $a$  and  $c$  dimensions of uranocircite given by Walenta (1963, 1965a), and to the cell of synthetic heinrichite in space group  $P2/n$  cited above, if allowance is made for changes in the cell dimensions resulting from the replacement of P for As. Although the refined structure of

TABLE 12. ATOM COORDINATES FOR META-URANOCIRCITE II IN THE CONVENTIONAL SETTING

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
U(1)	-0.50710(14)	-0.79811(8)	0.73137(14)	0.0146(3)
U(2)	-0.00705(14)	-0.69617(8)	0.72978(13)	0.0147(3)
Ba(1)	-0.82940(24)	-0.94228(15)	0.87402(27)	0.0348(6)
P(1)	-0.7622(8)	-0.7576(6)	0.4757(9)	0.018(3)
P(2)	-0.2579(8)	-0.7585(6)	0.4799(9)	0.018(3)
O(1)	-0.5174(20)	-0.9050(13)	0.7406(21)	0.025(5)
O(2)	-0.5096(21)	-0.6951(13)	0.7141(21)	0.023(5)
O(3)	-0.0114(22)	-0.5934(15)	0.7071(22)	0.035(6)
O(4)	-0.9919(21)	-0.8019(13)	0.7502(21)	0.022(5)
O(5)	-0.8583(20)	-0.8168(13)	0.4041(21)	0.023(5)
O(6)	-0.8420(23)	-0.7029(15)	0.5640(24)	0.038(6)
O(7)	-0.6630(20)	-0.8026(13)	0.5574(20)	0.022(5)
O(8)	-0.7014(23)	-0.7066(15)	0.3665(24)	0.038(6)
O(9)	-0.1591(25)	-0.7016(15)	0.5496(25)	0.042(8)
O(10)	-0.3621(21)	-0.7074(14)	0.4025(22)	0.029(6)
O(11)	-0.1823(22)	-0.8115(14)	0.3763(23)	0.033(6)
O(12)W	-0.3348(17)	-0.8109(11)	0.5834(18)	0.010(4)
O(13)W	-0.1185(21)	-0.9415(16)	0.9197(22)	0.038(6)
O(14)W	-0.8972(23)	-0.9462(17)	0.5905(25)	0.046(6)
O(15)W	-0.6089(29)	-0.9526(20)	0.0658(31)	0.073(9)
O(16)W	-0.6752(25)	-0.0513(18)	0.7361(27)	0.055(8)
O(17)W	-0.5784(24)	-0.9546(17)	0.4132(25)	0.047(6)
O(18)W	-0.2100(25)	-0.9637(17)	0.6508(27)	0.057(8)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Note:  $a 9.882(3)$ ,  $b 16.868(3)$ ,  $c 9.789(3) \text{ \AA}$ ,  $\beta 90.05(2)^\circ$ , space group  $P2_1/c$ ; revised from Khosrawan-Sazedj (1982).

synthetic uranocircite is not presented in this work, it is presumed to be isostructural with heinrichite because of the similarity of their cell dimensions, and the general isotypism of chemically similar uranyl phosphates and uranyl arsenates of the autunite and meta-autunite groups, *e.g.*, torbernite and zeunerite, metatorbernite and metazeunerite (Locock & Burns 2003b). As in synthetic heinrichite, the cell of uranocircite can be transformed by the matrix  $[100/0\bar{1}0/\bar{1}0\bar{1}]$  to the conventional setting in space group  $P2/c$ :  $a$  7.01,  $b$  6.99,  $c$  21.2 Å,  $\beta$  103.9°,  $V$  1008.4 Å<sup>3</sup>. By analogy with synthetic heinrichite, and in agreement with Walenta (1963, 1965a), the formula

TABLE 13. BOND-VALENCE SUMS FOR THE CATIONS (*vu*)

<i>SrUP11</i>		Heinrichite		<i>SrUAs8</i>	
U(1)	6.18	U(1)	6.18	U(1)	6.12
P(1)	5.00	As(1)	5.11	As(1)	5.06
Sr(1)	1.80	Ba(1)	1.94	Sr(1)	1.95
<i>SrUAs11</i>		Meta-uranocircite I		Meta-uranocircite II	
U(1)	6.20	U(1)	6.16	U(1)	6.24
As(1)	5.26	U(2)	6.12	U(2)	6.18
Sr(1)	1.90	P(1)	4.99	P(1) <sup>†</sup>	5.47
		P(2)	4.97	P(2)	4.92
		Ba(1)	1.86	Ba(1)	1.68

<sup>†</sup> Sum for P(1) is high because of the short average P(1)-O distance, 1.50(6) Å, but is acceptable, given the low precision of the refinement (Khosrawan-Sazedj 1982). Bond-valence sums were calculated assuming full occupancies of atom sites.

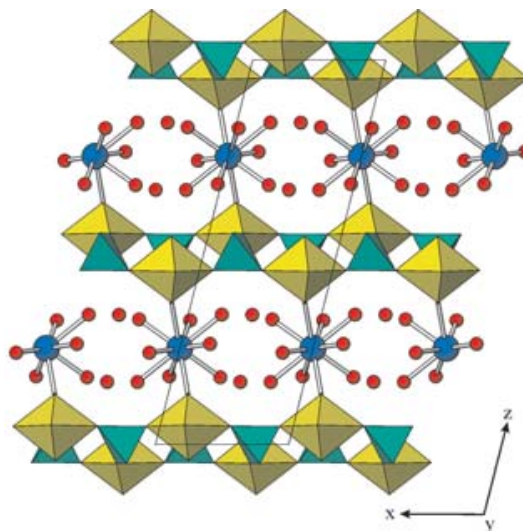


FIG. 4. The structure of heinrichite, projected along [010]. The uranyl polyhedra are shown in yellow, and the arsenate tetrahedra, in green. The Ba atoms are shown as large blue spheres, and the H<sub>2</sub>O groups are shown as small red spheres.

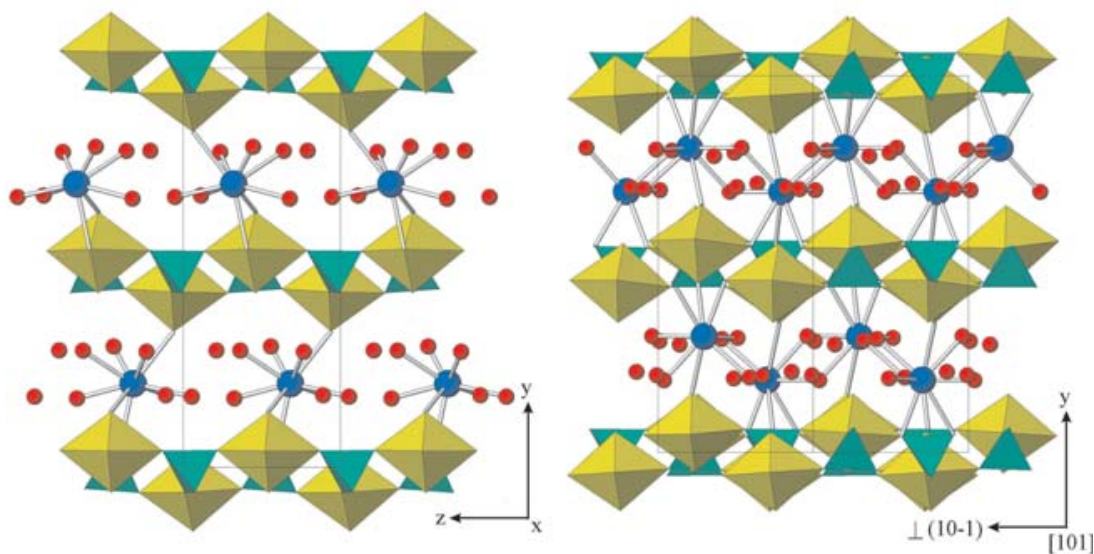


FIG. 5. Left: The structure of meta-uranocircite I, projected along [100]. Right: The structure of meta-uranocircite II, projected along [101] (after Khosrawan-Sazedj 1982). The uranyl polyhedra are shown in yellow, and the phosphate tetrahedra, in green. The Ba atoms are shown as large blue spheres, and the H<sub>2</sub>O groups are shown as small red spheres.

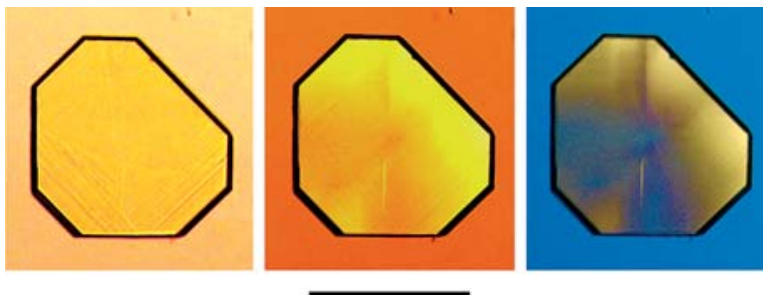


FIG. 6. Photomicrographs of a sample of synthetic uranocircite,  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$ , immersed in water and contained in a polystyrene Petri dish. Left: plane-polarized illumination. Center: crossed-polarized illumination. Right: crossed-polarized illumination with 530 nm accessory plate. Scale bar is 0.100 mm in length. The non-uniformity of the interference colors indicates that the sample is not a single crystal. The polystyrene gives rise to the unusual colors of the backgrounds under crossed-polarized light. Image contrast and brightness have been optimized for the purposes of display.

of synthetic uranocircite is  $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$ , with  $Z = 2$ , yielding  $D_{\text{calc}} = 3.45 \text{ g/mL}$ .

*Strontium: solid solution and uranospinite*

*SrUP11* and *SrUAs11* are isostructural with autunite (Locock & Burns 2003a), and thus the incorporation of Sr in solid solution in autunite and meta-autunite (Leo 1960, Volborth 1959) is readily explained. On the basis of the isotopy of *SrUP11* and *SrUAs11*, uranospinite is predicted to be isostructural with autunite, and to have the formula  $\text{Ca}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{11}$ . The cell dimensions of the Sr compounds change ( $a +0.34 \text{ \AA}$ ,  $b -0.05 \text{ \AA}$ ,  $c +0.17 \text{ \AA}$ ) with the substitution of As for P; therefore, crystal data for uranospinite may be estimated: orthorhombic, space group *Pnma*,  $a 14.35$ ,  $b 20.66$ ,  $c 7.17 \text{ \AA}$ ,  $V 2125 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} 3.3 \text{ g/mL}$ . The estimated unit-cell dimensions for uranospinite are in good agreement with the tetragonal subcells presented by Walenta (1965a,b) and Weigel & Hoffmann (1976):  $a 7.15\text{--}7.17$ ,  $c 20.61 \text{ \AA}$ .

Considerable efforts were made to synthesize uranospinite by diffusion-in-gel methods, but single crystals were not obtained. Although a number of apparent single crystals of uranospinite were examined on the three-circle X-ray diffractometer, these proved to have cell dimensions several times larger those reported by powder methods (*e.g.*, 41 to 83  $\text{\AA}$ ), and were interpreted to be crystal aggregates. The same effect was observed in an earlier synthesis of *SrUAs11*, for which the refined unit-cell was  $a 41.958(6)$ ,  $b 14.395(2)$ ,  $c 7.175(1) \text{ \AA}$ , and the structure solved in space group *Cmma* to an agreement index  $R1 = 3.5\%$ , with every second interlayer perfectly half-occupied but having twice as many independent positions of atoms. These

pseudosolutions and large unit-cell dimensions may be attributable to the tendency of autunite-group compounds to grow as subparallel aggregates along their basal surfaces, as illustrated in Figure 6. Evidently, some compounds with the autunite sheet are particularly gregarious, which greatly complicates the determination of their structures.

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