

DIVALENT TRANSITION METALS AND MAGNESIUM IN STRUCTURES THAT CONTAIN THE AUTUNITE-TYPE SHEET

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ABSTRACT

Compounds that contain the autunite-type sheet and divalent cations (Mg, Mn, Fe, Co, Ni) in their interlayers have been synthesized by diffusion in gels or by hydrothermal methods, and their crystal structure determined. Data on single-crystal X-ray diffraction intensities were collected at room temperature using MoK α radiation and a CCD-based area detector. The autunite-type sheet has the composition [(UO₂)(XO₄)]⁻, X = P or As, and involves the sharing of equatorial vertices of uranyl square bipyramids with phosphate or arsenate tetrahedra. The interlayer region contains H₂O groups and cations in octahedral coordination. The sheets are linked by hydrogen bonding and through bonds from the interlayer cations to oxygen atoms of the sheets. The structural roles of the interlayer cations in determining the symmetries and hydration states observed are discussed. Three different hydration states are observed, and these have characteristic symmetries and basal *d*-values: dodecahydrates are triclinic (pseudomonoclinic), basal spacing ~11 Å; decahydrates are monoclinic (pseudo-orthorhombic and commonly twinned), basal spacings ~10 Å, and octahydrates are triclinic, basal spacings of ~8.7 Å. Each hydration state corresponds to a different structure-type; the H₂O of hydration of these compounds does not vary in the same fashion as the H₂O content of zeolites, but rather is required to maintain the integrity of the hydrogen-bonding network. Changes in hydration state, whether through dehydration or rehydration, give rise to separate structures. Crystallographic data: Mn[(UO₂)(AsO₄)₂(H₂O)₁₂]: triclinic *P* $\bar{1}$, *a* 7.1359(11), *b* 7.1439(11), *c* 11.3616(17) Å, α 81.592(3)°, β 81.639(3)°, γ 88.918(3)°, *R*1 = 3.3%; Co[(UO₂)(AsO₄)₂(H₂O)₁₂] (*i.e.*, synthetic "kirchheimerite"): triclinic *P* $\bar{1}$, *a* 7.1552(5), *b* 7.1586(5), *c* 11.2912(8) Å, α 81.487(2)°, β 81.410(2)°, γ 88.891(2)°, *R*1 = 5.1%; Mg[(UO₂)(AsO₄)₂(H₂O)₁₂] (*i.e.*, synthetic nováčekite I): triclinic *P* $\bar{1}$, *a* 7.1594(5), *b* 7.1610(5), *c* 11.3146(7) Å, α 81.391(2)°, β 81.177(1)°, γ 88.884(1)°, *R*1 = 4.3%; Ni[(UO₂)(AsO₄)₂(H₂O)₁₂]: triclinic *P* $\bar{1}$, *a* 7.1523(3), *b* 7.1583(3), *c* 11.2564(5) Å, α 81.549(1)°, β 81.356(1)°, γ 88.916(1)°, *R*1 = 2.7%; Ni[(UO₂)(PO₄)₂(H₂O)₁₂]: triclinic *P* $\bar{1}$, *a* 6.9962(15), *b* 7.0012(15), *c* 11.171(2) Å, α 81.591(4)°, β 82.189(4)°, γ 88.721(4)°, *R*1 = 3.2%; Mn[(UO₂)(PO₄)₂(H₂O)₁₀]: monoclinic *I*2/m, *a* 6.9656(4), *b* 20.3768(13), *c* 6.9775(4) Å, β 91.019(1)°, *R*1 = 2.7%; Co[(UO₂)(PO₄)₂(H₂O)₁₀]: monoclinic *P*2₁/n, *a* 6.9490(5), *b* 19.9348(16), *c* 6.9620(5) Å, β 90.440(2)°, *R*1 = 5.1%; Ni[(UO₂)(PO₄)₂(H₂O)₁₀]: monoclinic *P*2₁/n, *a* 6.9506(4), *b* 19.8215(11), *c* 6.9711(4) Å, β 90.418(1)°, *R*1 = 3.1%; Mg[(UO₂)(AsO₄)₂(H₂O)₁₀] (*i.e.*, synthetic nováčekite II): monoclinic *P*2₁/n, *a* 7.1328(11), *b* 20.085(3), *c* 7.1569(11) Å, β 90.585(3)°, *R*1 = 8.5%; Mn[(UO₂)(AsO₄)₂(H₂O)₈]: triclinic *P* $\bar{1}$, *a* 7.2244(5), *b* 9.9170(8), *c* 13.337(1) Å, α 75.012(2)°, β 84.136(2)°, γ 81.995(2)°, *R*1 = 2.8%; Fe[(UO₂)(AsO₄)₂(H₂O)₈] (*i.e.*, synthetic metakahlerite): triclinic *P* $\bar{1}$, *a* 7.2072(3), *b* 9.8242(4), *c* 13.2708(6) Å, α 75.370(1)°, β 84.024(1)°, γ 81.839(1)°, *R*1 = 2.9%; Co[(UO₂)(AsO₄)₂(H₂O)₈] (*i.e.*, synthetic metakirchheimerite): triclinic *P* $\bar{1}$, *a* 7.1955(3), *b* 9.7715(4), *c* 13.2319(6) Å, α 75.525(1)°, β 84.052(1)°, γ 81.661(1)°, *R*1 = 2.5%.

Keywords: autunite, bassettite, kahlerite, kirchheimerite, lehnerite, metakahlerite, metakirchheimerite, metalodèveite, metanováčekite, metasaléeite, nováčekite I, nováčekite II, saléeite, uranyl phosphate, uranyl arsenate, crystal structure, gel synthesis, hydrothermal synthesis.

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SOMMAIRE

Nous avons synthétisé des composés contenant le feuillet de type autunite et des cations bivalents (Mg, Mn, Fe, Co, Ni) en position interfoliaire, par diffusion dans des gels ou bien par voie hydrothermale, et nous en avons déterminé la structure cristalline. Nous avons prélevé les données d'intensités en diffraction X sur monocristaux à température ambiante en utilisant un rayonnement $\text{MoK}\alpha$ et un détecteur à aire de type CCD. Le feuillet de type autunite possède une composition $[(\text{UO}_2)(\text{XO}_4)]^-$, $X = \text{P}$ ou As ; il y a un partage des coins équatoriaux des bipyramides carrées à uranyle avec les tétraèdres de phosphate ou d'arsenate. La région interfoliaire contient des groupes H_2O et des cations en coordinence octaédrique. Ces feuillets sont liés par liaisons hydrogène et par liaisons entre les cations interfoliaires et les atomes d'oxygène des feuillets. Nous évaluons les rôles structuraux dans la détermination des symétries et des degrés d'hydratation. Il y a trois degrés d'hydratation; chacun possède une symétrie et une valeur de l'espacement interfoliaire caractéristiques. Les dodécahydrates sont tricliniques (pseudomonocliniques), espacement interfoliaire ~ 11 Å; les décahydrates sont monocliniques (pseudo-orthorhombiques et généralement maclés), espacement interfoliaire ~ 10 Å, et les octahydrates sont tricliniques, espacement interfoliaire d'environ 8.7 Å. Chaque degré d'hydratation correspond à un type de structure différent; le nombre de groupes de H_2O ne varie pas de la même manière que dans un zéolite, mais est nécessaire pour conserver l'intégrité du réseau de liaisons hydrogène de ces composés. Un changement du degré d'hydratation, soit par déshydratation ou par réhydratation, donne lieu à des transformations structurales. Données cristallographiques: $\text{Mn}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$: triclinique $P\bar{1}$, a 7.1359(11), b 7.1439(11), c 11.3616(17) Å, α 81.592(3)°, β 81.639(3)°, γ 88.918(3)°, $R1 = 3.3\%$; $\text{Co}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$ (i.e., "kirchheimerite" synthétique): triclinique $P\bar{1}$, a 7.1552(5), b 7.1586(5), c 11.2912(8) Å, α 81.487(2)°, β 81.410(2)°, γ 88.891(2)°, $R1 = 5.1\%$; $\text{Mg}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$ (i.e., nováčekite I synthétique): triclinique $P\bar{1}$, a 7.1594(5), b 7.1610(5), c 11.3146(7) Å, α 81.391(2)°, β 81.177(1)°, γ 88.884(1)°, $R1 = 4.3\%$; $\text{Ni}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$: triclinique $P\bar{1}$, a 7.1523(3), b 7.1583(3), c 11.2564(5) Å, α 81.549(1)°, β 81.356(1)°, γ 88.916(1)°, $R1 = 2.7\%$; $\text{Ni}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{12}$: triclinique $P\bar{1}$, a 6.9962(15), b 7.0012(15), c 11.171(2) Å, α 81.591(4)°, β 82.189(4)°, γ 88.721(4)°, $R1 = 3.2\%$; $\text{Mn}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$: monoclinique $I2/m$, a 6.9656(4), b 20.3768(13), c 6.9775(4) Å, β 91.019(1)°, $R1 = 2.7\%$; $\text{Co}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$: monoclinique $P2_1/n$, a 6.9490(5), b 19.9348(16), c 6.9620(5) Å, β 90.440(2)°, $R1 = 5.1\%$; $\text{Ni}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$: monoclinique $P2_1/n$, a 6.9506(4), b 19.8215(11), c 6.9711(4) Å, β 90.418(1)°, $R1 = 3.1\%$; $\text{Mg}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{10}$ (i.e., nováčekite II synthétique): monoclinique $P2_1/n$, a 7.1328(11), b 20.085(3), c 7.1569(11) Å, β 90.585(3)°, $R1 = 8.5\%$; $\text{Mn}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$: triclinique $P\bar{1}$, a 7.2244(5), b 9.9170(8), c 13.337(1) Å, α 75.012(2)°, β 84.136(2)°, γ 81.995(2)°, $R1 = 2.8\%$; $\text{Fe}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$ (i.e., métakahlerite synthétique): triclinique $P\bar{1}$, a 7.2072(3), b 9.8242(4), c 13.2708(6) Å, α 75.370(1)°, β 84.024(1)°, γ 81.839(1)°, $R1 = 2.9\%$; $\text{Co}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$ (i.e., métakirchheimerite synthétique): triclinique $P\bar{1}$, a 7.1955(3), b 9.7715(4), c 13.2319(6) Å, α 75.525(1)°, β 84.052(1)°, $R1 = 2.5\%$.

Mots-clés: autunite, bassetite, kahlerite, kirchheimerite, lehnerite, métakahlerite, métakirchheimerite, métalodévite, métanováčekite, métasaléeite, nováčekite I, nováčekite II, saléeite, phosphate uranylé, arsenate uranylé, structure cristalline, synthèse par gel, synthèse hydrothermale.

INTRODUCTION

Compounds that contain the autunite-type sheet comprise one of the two major structural divisions of uranyl phosphate and uranyl arsenate minerals (the phosphuranylite group being the other), and together consist of approximately forty mineral species (Smith 1984, Finch & Murakami 1999, Burns 1999). The corrugated autunite-type sheet has the composition $[(\text{UO}_2)(\text{XO}_4)]^-$, $X = \text{P}$ or As , and involves the sharing of equatorial vertices of uranyl square bipyramids with phosphate or arsenate tetrahedra; it was first described by Beintema (1938). The structure of autunite *sensu stricto*, $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$, recently has been determined (Locock & Burns 2003a). The interlayer region contains cations and H_2O groups, and the sheets are linked by hydrogen bonding and through bonds from the interlayer cations to oxygen atoms of the sheets.

Amongst compounds that contain the autunite-type sheet, the members containing first-row divalent transition metals and structurally related magnesium-dominant members compose the largest category, with at least fourteen mineral species described (e.g., Gaines *et al.* 1997, Mandarino & Back 2004). However, with the

exception of the copper-bearing species (torbernite, zeunerite, metatorbernite and metazeunerite), these minerals are relatively rare. The copper-bearing species also differ in the details of their structures because of a pronounced Jahn–Teller effect (Eby & Hawthorne 1993), and have been discussed previously (Locock & Burns 2003b). The results reported herein pertain to compounds that contain divalent interlayer cations: Mg and the first-row transition metals Mn, Fe, Co and Ni.

PREVIOUS WORK

The minerals that contain the autunite-type sheet and divalent transition metals or magnesium and relevant synthetic compounds for which X-ray-diffraction patterns are available in the 2001 Release of the Powder Diffraction File (PDF) of the International Centre for Diffraction Data are listed in Table 1. All of these have nominal stoichiometry $M[(\text{UO}_2)(\text{XO}_4)]_2(\text{H}_2\text{O})_n$, where $M = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Mg^{2+} , Ni^{2+} , or Zn^{2+} , $X = \text{P}$ or As , and $4 \leq n \leq 12$. Both the uranyl phosphates and the uranyl arsenates may be divided into three classes, on the basis of their basal d -values: $d \approx 8.5$ Å ($n \approx 8$, range of $7 \leq n \leq 10$), $d \approx 10$ Å ($n \approx 10$, range of $4 \leq n \leq 10$), and

$d \sim 11 \text{ \AA}$ ($n \approx 12$, range of $9.5 \leq n \leq 12$). The apparent states of hydration of the compounds in Table 1 (the chemical formulas are from the PDF entries) are only in approximate agreement with this tripartite classification. Despite a considerable history of investigation: bassettite (Hallimond 1915), kahlerite (Meixner 1953), lehnerite (Mücke 1988), metakahlerite and metakirchheimerite (Walenta 1958, Nabar & Iyer 1977, Vochten 1984, Vochten & Goeminne 1984, Vochten *et al.* 1986), metalodèveite (Agrinier *et al.* 1972, Nabar & Iyer 1977), metanováčekite (Donnay & Donnay 1955), metasaléite (Mrose 1950), nováčekite (Frondel 1951, Stern & Annell 1954, Huang 1956, Elton *et al.* 1994), saléite (Thoreau & Vaes 1932, Frondel 1951, Piret & Deliens 1980, Miller & Taylor 1986, Suzuki *et al.* 1998), and *UM1997-41* (Nabar & Iyer 1977, Vochten 1984, Ondruš *et al.* 1997), there is no consensus in the literature with regard to the compositions and physical properties of these compounds, probably because of their ease of dehydration and rehydration under differing conditions of temperature and humidity. In addition to problems of hydration state, the pseudosymmetry common in this group of compounds, coupled with the preferred orientation induced by their platy morphologies,

have almost certainly complicated accurate determination of their crystal symmetries by powder X-ray diffraction. In most cases, previous investigators have interpreted the compounds to be tetragonal (despite their biaxial optical properties), by analogy with other members of the autunite and meta-autunite groups (*e.g.*, Pozas-Tormo *et al.* 1986). It is notable that the majority of the X-ray-diffraction patterns presented for these compounds are of questionable quality, as assessed by the International Centre for Diffraction Data (Table 1).

Mineral nomenclature

The Commission on New Minerals and Mineral Names of the International Mineralogical Association has not reached decisions with regard to the nomenclature of these minerals (www.geo.vu.nl/~ima-cnmmn/), with the exception of the acceptance of metalodèveite, which was originally reported to have the chemical formula $\text{Zn}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{8-12}$ (Agrinier *et al.* 1972), and lehnerite, $\text{Mn}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$ (Mücke 1988).

In a series of papers on the secondary uranium minerals of the Black Forest, Walenta (1958, 1964, 1965b, 1977), and Walenta & Wimmenauer (1961) established that there are three natural autunite-type hydrates of magnesium uranyl arsenate: the dodecahydrate, nováčekite I; the decahydrate, nováčekite II, and the octahydrate, metanováčekite. The uranyl arsenate octahydrates of Fe and Co, respectively metakahlerite and metakirchheimerite, were also found in the Black Forest as minerals, but their corresponding dodecahydrates kahlerite and "kirchheimerite" were only found as synthetic products (Walenta 1964). Note that on the basis of the similarity of their optical properties, the kahlerite of Meixner (1953) is equivalent to the metakahlerite of Walenta (1965a). However, both kahlerite and metakahlerite were found in an assemblage of supergene alteration phases in a context of uranium mineralization in Scotland by Braithwaite & Knight (1990).

Miller & Taylor (1986) determined, on the basis of material from the Ranger I mine, Northern Territory, Australia, that saléite is monoclinic (in agreement with Piret & Deliens 1980), with formula $\text{Mg}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$, and presented a refinement in the standard space-group $P2_1/c$, with a 6.951(3), b 19.947(8), c 9.864(4) Å, β 135.17(2)°, $R1 = 5.3\%$. The setting of this unit cell can be changed by the matrix [100/010/101] to the alternative space-group $P2_1/n$, with a 6.951(3), b 19.947(8), c 6.977(4) Å, β 90.55(2)°, to emphasize its pseudo-orthorhombic nature. The matrix [100/101/010] may be used to transform the original cell to a non-standard pseudotetragonal setting: a 6.951(3), b 6.977(4), c 19.947(8) Å, γ 90.55(2)° (see also Piret & Deliens 1980). The pseudosymmetry of saléite helps to explain previous assignments of tetragonal symmetry to this mineral (Mrose 1950, Frondel 1951, 1958, Walenta 1965a, Vochten & Van Springel 1996).

TABLE 1. BASAL SPACINGS OF DIVALENT TRANSITION METAL AND MAGNESIUM URANYL PHOSPHATES AND URANYL ARSENATES

Mineral	Chemical Formula	PDF #	Q	CS	d (Å)	hkl
lehnerite	$\text{Mn}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$	46-1372	M		8.56	020
bassettite	$\text{Fe}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$	07-0288	?	M	8.59	020
	$\text{Co}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_7$	35-0318	A		8.55	001
metasaléite	$\text{Mg}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$	41-1389	?	T	8.84	002
	$\text{Mn}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{9.5}$	40-0607	?	T	10.46	002
	$\text{Co}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_9$	40-0606	?	T	10.05	002
saléite	$\text{Mg}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_9$	29-0874	?	T	9.79	002
saléite	$\text{Mg}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$	08-0313	?	T	9.85	002
saléite, ferroan	$(\text{Mg,Fe})[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_4$	50-1585	?	T	9.96	002
	$\text{Ni}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_7$	35-0317	A		9.87	001
	$\text{Zn}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{9.5}$	40-0604	?	T	10.01	002
	$\text{Ni}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{9.5}$	40-0605	?	T	11.04	002
metakahlerite	$\text{Fe}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$	17-0151	?	T	8.86	001
metakirchheimerite	$\text{Co}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$	39-0201	?	T	8.56	002
metakirchheimerite	$\text{Co}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$	12-0586	?	T	8.78	002
metanováčekite	$\text{Mg}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$	17-0152	?	T	8.52	001
<i>UM1997-41</i>	$\text{Ni}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_7$	51-1481	?	T	8.55	002
	$\text{Ni}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$	39-0202	?	T	8.43	002
	$\text{Zn}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$	39-0203	?	T	8.35	002
metalodèveite	$\text{Zn}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{10}$	25-1239	?	T	8.66	002
nováčekite II	$\text{Mg}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{10}$	17-0148	?	T	10.00	002
nováčekite II	$\text{Mg}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{10}$	08-0286	?	T	10.20	002
kahlerite	$\text{Fe}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$	17-0145	?	T	11.10	002
"kirchheimerite"	$\text{Co}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$	17-0149	?	T	11.10	002
nováčekite I	$\text{Mg}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$	17-0147	?	T	10.90	002

NOTE: PDF # = Powder Diffraction File entry number, data from Release 2001; Q = quality assessed by the International Centre for Diffraction Data (ICDD), ? indicates questionable quality; CS = crystal system (A: triclinic, M: monoclinic, T: tetragonal); d = basal d -spacing; *UM* = unnamed mineral species. The term "kirchheimerite" has not been approved as the name of a mineral species by the International Mineralogical Association's Commission on New Minerals and Mineral Names.

Although not widely accepted as a separate mineral species, metasaléite was proposed for the lower hydrate of saléite by Mrose (1950), who described material from the Democratic Republic of Congo with the chemical formula $Mg[(UO_2)(PO_4)]_2(H_2O)_8$. Powder-diffraction data for metasaléite from Brazil were given by Cassedanne *et al.* (1986), PDF 41–1389, and metasaléite has been found in central Portugal (Pinto *et al.* 2001).

In this report, we concentrate on the crystal structures of compounds with the autunite-type sheet and interlayers that contain divalent transition metals (Mn, Fe, Co, Ni) or Mg, and how the symmetries of these compounds vary with their hydration states and the nature of the interlayer cations. Despite the existence of metalodévit, data for zinc compounds are not presented here, because of the repeated failure to grow crystals of sufficient quality and stability for room-temperature crystallographic investigations. Of the thirty possible compounds (five cations * three hydration states * two occupants of the tetrahedra), structures are presented for twelve. For simplicity, the compounds investigated are subsequently referred to by italicized abbreviations rather than mineral names or chemical formulas: *MnUAs12* = $Mn[(UO_2)(AsO_4)]_2(H_2O)_{12}$; *CoUAs12* = $Co[(UO_2)(AsO_4)]_2(H_2O)_{12}$ (*i.e.*, “kirchheimerite”); *MgUAs12* = $Mg[(UO_2)(AsO_4)]_2(H_2O)_{12}$ (*i.e.*, synthetic nováčekite I); *NiUAs12* = $Ni[(UO_2)(AsO_4)]_2(H_2O)_{12}$; *NiUP12* = $Ni[(UO_2)(PO_4)]_2(H_2O)_{12}$; *MnUP10* = $Mn[(UO_2)(PO_4)]_2(H_2O)_{10}$; *CoUP10* = $Co[(UO_2)(PO_4)]_2(H_2O)_{10}$; *NiUP10* = $Ni[(UO_2)(PO_4)]_2(H_2O)_{10}$; *MgUAs10* = $Mg[(UO_2)(AsO_4)]_2(H_2O)_{10}$ (*i.e.*, synthetic nováčekite II); *MnUAs8* = $Mn[(UO_2)(AsO_4)]_2(H_2O)_8$; *FeUAs8* = $Fe[(UO_2)(AsO_4)]_2(H_2O)_8$ (*i.e.*, synthetic metakahlerite); *CoUAs8* = $Co[(UO_2)(AsO_4)]_2(H_2O)_8$ (*i.e.*, synthetic metakirchheimerite).

EXPERIMENT

Crystal synthesis

Crystals of eight of the compounds (Table 2) were grown over weeks to months by slow diffusion of phosphoric acid or hydrogen arsenate, and uranyl nitrate into

cation-bearing silica gels contained in U-shaped tubes. Although most gel syntheses were undertaken at room temperature, *CoUAs12* was grown under refrigerated conditions ($\sim 5^\circ\text{C}$), following the approach of Berman (1957). The gels were formed by the hydrolysis of a mixture of tetramethoxysilane (TMOS) and aqueous solutions of metal nitrates or metal chlorides (Table 2), with the exception of *NiUP10*, which was synthesized with 1:1 water:methanol solutions in order to access the intermediate hydration state (*via* the lowered dielectric constant of the fluid mixture). The gel-growth method was modified after Arend & Connelly (1982), Manghi & Polla (1983), Zolensky (1983), Perrino & LeMaster (1984), Robert & LeFauchoux (1988), and Henisch (1988).

Crystals of *MnUAs8*, *FeUAs8* and *CoUAs8* were obtained by conventional mild hydrothermal syntheses (Table 3), in which the reactants were weighed directly into 23 mL Teflon-lined Parr acid-digestion vessels; the unstirred mixtures were heated in Fisher Isotemp ovens. The products were washed with ultrapure water upon removal from the vessels.

The crystal of *MgUAs10* from which the structure was determined was formed by the dehydration under

TABLE 2. SYNTHESSES BY DIFFUSION-IN-GEL METHODS

Compound	<i>MnUAs12</i>	<i>CoUAs12</i>	<i>MgUAs12</i>	<i>NiUAs12</i>
Gel	TMOS	TMOS	TMOS	TMOS
	0.3 M MnCl ₂	0.3 M CoCl ₂	0.1 M MgCl ₂	0.1 M NiSO ₄
Left arm	0.1 M U-NO ₃	0.1 M U-NO ₃	0.1 M U-NO ₃	0.1 M U-NO ₃
	0.03 M	0.03 M	0.03 M	0.03 M
Right arm	H ₃ As ₃ O ₁₀	H ₃ As ₃ O ₁₀	H ₃ As ₃ O ₁₀	H ₃ As ₃ O ₁₀
Temperature	22°C	5°C	22°C	22°C
Time	4 months	6 months	1 month	8 months

Compound	<i>NiUP12</i>	<i>MnUP10</i>	<i>CoUP10</i>	<i>NiUP10</i>
Gel	TMOS	TMOS	TMOS	TMOS
	0.1 M NiSO ₄	0.1 M MnCl ₂	0.1 M CoCl ₂	0.3 M NiCl ₂ *
Left arm	0.1 M U-NO ₃	0.1 M U-NO ₃	0.1 M U-NO ₃	0.1 M U-NO ₃ *
Right arm	0.1 M H ₃ PO ₄	0.1 M H ₃ PO ₄	0.1 M H ₃ PO ₄	0.1 M H ₃ PO ₄ *
Temperature	22°C	22°C	22°C	22°C
Time	4 months	1 month	2 weeks	2 months

NOTE: U-NO₃ = uranyl nitrate hexahydrate, TMOS = tetramethoxysilane, (CH₃O)₄Si. Gels are 10% TMOS, 90% aqueous solution (by volume), and average 11 mL; arm volumes are 6 mL each. *All solutions used in the crystallization of *NiUP10* were based on 1:1 water:methanol mixtures (by volume).

TABLE 3. SYNTHESSES BY HYDROTHERMAL METHODS

Compound	<i>MnUAs8</i>	<i>FeUAs8</i>	<i>CoUAs8</i>
Reagents	0.0698 g MnCl ₂ (H ₂ O) ₄	0.0703 g FeCl ₂ (H ₂ O) ₄	0.0788 g CoCl ₂ (H ₂ O) ₆
	3.0 mL 0.1 M U-acetate	3.0 mL 0.1 M U-acetate	3.0 mL 0.1 M U-acetate
	3.0 mL 0.033 M H ₃ As ₃ O ₁₀	3.0 mL 0.033 M H ₃ As ₃ O ₁₀	3.0 mL 0.033 M H ₃ As ₃ O ₁₀
Temperature program: start 50°C, ramp at 6°C/hour to 220°C, hold at 220°C for 24 hours, cool at 6°C/hour to 56°C, remove to air and cool to room temperature.			

NOTE: U-acetate = uranyl acetate dihydrate. Upon removal, products were washed with ultrapure water.

ambient conditions of a gel-grown crystal of *MgUAs12*. Surprisingly, despite the strain induced by dehydration, this crystal proved of sufficient quality to collect a hemisphere of diffraction data, before the heat load generated by the absorption of the primary X-ray beam caused further dehydration; diffraction data collected subsequently could no longer be indexed, nor could the sample be described as a single crystal.

Single-crystal X-ray diffraction

For each of the twelve compounds, a suitable 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. The crystals were either fixed to a glass fiber with two-part epoxy, or encapsulated in a glass capillary 0.3–0.5 mm in diameter (Charles Supper Co.) with Millepore-filtered ultrapure water (18 M Ω resistance) and immobilized with high-vacuum silicone grease (Dow Corning). Data were collected at room temperature using graphite-monochromatized MoK α X-radiation and frame widths of 0.3° in ω . Details of the data acquisition and refinement parameters are provided in Table 4. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the program SAINT (Bruker 1998), corrections for absorption were made with the programs XPREP and SADABS, and 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.

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).

Structure solution and refinement

The lack of systematic absences of reflections for *MnUAs12*, *CoUAs12*, *MgUAs12*, *NiUAs12*, and *NiUP12* are consistent with space groups *P1* and $\bar{P}1$. These structures were solved by Patterson or direct methods, and were refined on the basis of F^2 for all unique data in space group $\bar{P}1$. Structure models, including anisotropic displacement-parameters for all non-H atoms (*MnUAs12*, *NiUAs12*, *NiUP12*), or for non-O atoms (*CoUAs12*, *MgUAs12*), converged. The agreement indices ($R1$), calculated for the observed unique reflections ($|F_o| \geq 4\sigma_F$) of these refinements, range from 2.7 to 5.1%. For the structures of *NiUAs12* and *NiUP12*, possible positions of H atoms were located in difference-Fourier maps, calculated following refinement of the models. Their positions were refined with

the restraint that O–H bond-lengths be $\sim 0.96(2)$ Å and with fixed isotropic displacement-parameters. These refinements provided crystal-chemically reasonable H-bonding networks. In the other three dodecahydrates, the location of each H atom was not determined.

The unit cells of the five triclinic dodecahydrates exhibit severe pseudosymmetry; their cells can be transformed to pseudomonoclinic *C*-centered cells with the matrix $[\bar{1}\bar{1}0/\bar{1}\bar{1}0/001]$. For *MnUAs12*, this procedure yields the cell: a 10.192, b 10.002, c 11.362 Å, α 90.04°, β 101.79°, γ 89.94°. Solutions and refinements were attempted in space groups *C2*, *Cm* and *C2/m*, but in these space groups, the interlayer contents were disordered. For all five structures, the triclinic model was checked with the ADDSYM algorithm in the program PLATON (Le Page 1987, Spek 2003); no higher symmetry was found.

Systematic absences of reflections for *MnUP10* are consistent with space groups *I2*, *Im* and *I2/m* (alternative settings of *C2*, *Cm* and *C2/m*, respectively). The unit cell of *MnUP10* can be transformed between these settings by the matrix $[\bar{1}\bar{1}0/\bar{1}\bar{1}0/001]$. Intensity data for *CoUP10*, *NiUP10* and *MgUAs10* are consistent with space group *P2₁/n* (alternative setting of *P2₁/c*). The cells of these three compounds can be transformed between these settings by the matrix $[100/\bar{0}\bar{1}0/\bar{1}0\bar{1}]$. The crystal structures of all four compounds were solved by direct methods (in *I2/m* or *P2₁/n*) and were refined on the basis of F^2 for all unique data in the settings with β close to 90°, in order to facilitate models that involve twinning by pseudomerohedry. Structure models including anisotropic displacement-parameters for all non-H atoms (*CoUP10*, *NiUP10*, *MgUAs10*), or for non-O atoms (*MnUP10*), converged. The agreement indices ($R1$), calculated for the observed unique reflections ($|F_o| \geq 4\sigma_F$) of these refinements, range from 2.7 to 8.5%. Because these compounds are pseudo-orthorhombic (Table 4), with β angles close to 90°, the twin law $[100/\bar{0}\bar{1}0/001]$ was applied, and the structures were refined according to published methods (Jameson 1982, Herbst-Irmer & Sheldrick 1998). The twin scale-factors refined to 2.6(4)% for *MnUP10*, 0.36(3)% for *NiUP10*, and 0.9(1)% for *MgUAs10*, consistent with highly asymmetrical distributions of the twin components. The twin scale-factor for *CoUP10* refined to zero, and the twin law was omitted from this refinement. The location of each H atom in these structures was not determined. The structure model for *MgUAs10* is not of desirable quality: R_{int} is 16.4% and the agreement index $R1$ is 8.5%. It is likely that strain was imparted to the crystal because of its formation by dehydration from *MgUAs12* (and possibly because of the ongoing heat-load from the primary X-ray beam), and that this has affected its quality (mosaic spread).

The lack of systematic absences of reflections for *MnUAs8*, *FeUAs8*, and *CoUAs8* are consistent with space groups *P1* and $\bar{P}1$. These structures were solved by Patterson methods, and were refined on the basis of

TABLE 4. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS

Compound	Mn[UO ₂ AsO ₄] ₂ (H ₂ O) ₁₂	Co[UO ₂ AsO ₄] ₂ (H ₂ O) ₁₂	Mg[UO ₂ AsO ₄] ₂ (H ₂ O) ₁₂	Ni[UO ₂ AsO ₄] ₂ (H ₂ O) ₁₂	Ni[UO ₂ PO ₄] ₂ (H ₂ O) ₁₂	Mn[UO ₂ PO ₄] ₂ (H ₂ O) ₁₀
<i>a</i> (Å)	7.1359(11)	7.1552(5)	7.1594(5)	7.1523(3)	6.9962(15)	6.9656(4)
<i>b</i> (Å)	7.1439(11)	7.1586(5)	7.1610(5)	7.1583(3)	7.0012(15)	20.3768(13)
<i>c</i> (Å)	11.3161(17)	11.2912(8)	11.3146(7)	11.2564(5)	11.171(2)	6.9775(4)
<i>α</i> (°)	81.592(3)	81.487(2)	81.391(2)	81.591(4)	81.591(4)	90
<i>β</i> (°)	81.639(3)	81.410(2)	81.177(1)	81.556(1)	82.189(4)	91.019(1)
<i>γ</i> (°)	88.918(3)	88.891(2)	88.884(1)	88.916(1)	88.721(4)	90
<i>V</i> (Å ³)	566.88(15)	565.56(7)	566.76(7)	563.57(4)	536.27(19)	990.21(10)
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>I</i> 2/m
<i>Z</i>	1	1	1	1	1	2
Formula weight	1093.015	1093.010	1058.382	1092.770	1004.874	965.088
<i>F</i> (000)	491	493	478	494	458	870
<i>μ</i> (mm ⁻¹)	17.79	18.01	17.29	18.17	16.18	17.20
<i>D</i> _{calc} (g/mL)	3.190	3.209	3.101	3.220	3.112	3.237
Size (mm)	0.20 x 0.20 x 0.02	0.16 x 0.08 x 0.02	0.10 x 0.10 x 0.02	0.25 x 0.14 x 0.02	0.26 x 0.20 x 0.02	0.28 x 0.20 x 0.04
Color and habit	yellow plate	orange plate	yellow plate	yellow-green plate	yellow-green plate	yellow plate
Crystal mount	glass capillary	glass capillary	glass capillary	glass capillary	glass capillary	glass capillary
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Width (°), time (s)	0.3, 20	0.3, 20	0.3, 20	0.3, 15	0.3, 5	0.3, 5
Collection, hours	sphere, 16	sphere, 16	sphere, 16	sphere, 12	sphere, 4	sphere, 4
<i>θ</i> range (°)	2.88–34.49	2.88–34.54	2.88–34.53	2.88–34.47	2.88–34.56	3.09–34.49
Data collected	h±11, k±11, l±17	h±11, k±11, l±17	h±11, k±11, l±17	h±11, k±11, l±17	h±10, k±31, l±11	h±10, k±31, l±11
Absorption /	plate (001) 3°	plate (001) 3°	plate (001) 3°	plate (001) 3°	plate (001) 3°	plate (010) 3°
Total reflections	10438	10506	10548	10280	9990	9050
Unique refl., <i>R</i> _{int}	4548, 0.068	4538, 0.093	4562, 0.070	4518, 0.080	4310, 0.084	2101, 0.097
Unique <i>F</i> _o ≥ 4 $σ$ _{<i>F</i>}	3736	3471	3452	4017	3942	2017
Twin matrix	133	73	73			[100/0-10/00-1]
Twin proportion (%)	3.3	5.1	4.3	169	169	2.6(4)
Parameters	4.5, 6.5	6.8, 11.1	6.1, 9.1	3.2	3.2	60
<i>R</i> ¹ for <i>F</i> _o ≥ 4 $σ$ _{<i>F</i>}	0.0160	0.0414	0.0331	0.0097	0.0097	2.7
<i>R</i> ¹ all data, <i>wR</i> ₂ ³	0.896	0.914	0.878	3.1, 6.0	3.5, 7.7	2.8, 6.7
Goodness of fit	0.000	0.000	0.000	0.0097	0.0355	0.0301, 0.377
Mean shift/esd	3.3, -2.9	8.4, -2.3	6.1, -2.5			0.0107(5)
Peaks (e/Å ³)			nováčekite I			1.066
Mineral name						0.000
						2.5, -1.7

TABLE 4. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS (continued)

Goodness of fit	0.932	1.010	1.010	0.932	1.010	1.066
Mean shift/esd	2.7, -2.1	2.7, -2.1	2.7, -2.1	2.7, -2.1	2.7, -2.1	2.7, -2.1
Peaks (e/Å ³)	3.7, -3.5	3.7, -3.5	3.7, -3.5	3.7, -3.5	3.7, -3.5	3.7, -3.5

NOTE: ¹ Corrections for absorption are semi-empirical (crystal modelled as a plate, rejecting data within 3° of the primary X-ray beam). ² $R1 = [\sum |F_o| - |F_c|] / \sum |F_o| \times 100$. ³ $wR2 = [\sum [w(F_o^2 - F_c^2)]^2]^{0.5} \times 100$. $w = 1/(\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P)$, and $P = 1/3 \max(0, F_o^2 + 2/3 F_c^2)$. The term "kirchheimerite" has not been approved as the name of a mineral species by the International Mineralogical Association Commission on New Minerals and Mineral Names.

NOTE: ¹ Corrections for absorption are semi-empirical (crystal modelled as a plate, rejecting data within 3° of the primary X-ray beam). ² $R1 = [\sum |F_o| - |F_c|] / \sum |F_o| \times 100$. ³ $wR2 = [\sum [w(F_o^2 - F_c^2)]^2]^{0.5} \times 100$. $w = 1/(\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P)$, and $P = 1/3 \max(0, F_o^2 + 2/3 F_c^2)$. The term "kirchheimerite" has not been approved as the name of a mineral species by the International Mineralogical Association Commission on New Minerals and Mineral Names.

TABLE 4 (continued)

Compound	Co[UO ₂ PO ₄] ₂ (H ₂ O) ₁₀	Ni[UO ₂ PO ₄] ₂ (H ₂ O) ₁₀	Mg[UO ₂ AsO ₄] ₂ (H ₂ O) ₁₀	Mn[UO ₂ AsO ₄] ₂ (H ₂ O) ₈	Fe[UO ₂ AsO ₄] ₂ (H ₂ O) ₈	Co[UO ₂ AsO ₄] ₂ (H ₂ O) ₈
<i>a</i> (Å)	6.9490(5)	6.9506(4)	7.1328(11)	7.2244(5)	7.2072(3)	7.1955(3)
<i>b</i> (Å)	19.9348(16)	19.8215(11)	20.085(3)	9.9170(8)	9.8242(4)	9.7715(4)
<i>c</i> (Å)	6.9620(5)	6.9711(4)	9.0	13.337(1)	13.2708(6)	13.2319(6)
<i>α</i> (°)	90	90	90	75.012(2)	75.370(1)	75.525(1)
<i>β</i> (°)	90	90.440(2)	90.585(3)	84.136(2)	84.024(1)	84.052(1)
<i>γ</i> (°)	90	90	90	81.995(2)	81.839(1)	81.661(1)
<i>V</i> (Å ³)	964.40(12)	960.39(9)	1025.3(3)	911.83(12)	897.68(7)	889.08(7)
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
<i>Z</i>	2	2	2	2	2	2
Formula weight	969.084	968.844	1022.351	1016.954	1017.861	1020.949
<i>F</i> (000)	874	876	916	902	904	906
<i>μ</i> (mm ⁻¹)	17.87	18.06	19.10	22.09	22.55	22.88
<i>D</i> _{calc} (g/mL)	3.337	3.350	3.312	3.704	3.766	3.814
Size (mm)	0.15 × 0.15 × 0.02	0.10 × 0.10 × 0.02	0.15 × 0.08 × 0.02	0.24 × 0.10 × 0.06	0.28 × 0.06 × 0.04	0.36 × 0.25 × 0.04
Color and habit	orange plate	yellow-green plate	yellow plate	yellow plate	yellow-brown plate	orange plate
Crystal mount	glass capillary	glass fibre	glass fibre	glass fibre	glass fibre	glass fibre
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Width (°), time (s)	0.3, 90	0.3, 25	0.3, 30	0.3, 8	0.3, 20	0.3, 10
Collection, hours	hemisphere, 36	sphere, 20	hemisphere, 12	sphere, 7	sphere, 16	sphere, 8
θ range (°)	3.10 – 34.48	2.92 – 34.50	2.85 – 34.54	1.58 – 34.49	1.59 – 34.53	1.59 – 34.54
Data collected	-10 ≤ <i>h</i> ≤ 9, -31 < <i>k</i> ≤ 29, <i>l</i> ± 10	-10 ≤ <i>h</i> ≤ 11, <i>k</i> ± 30, <i>l</i> ± 11	-8 ≤ <i>h</i> ≤ 11, -31 < <i>k</i> ≤ 25, <i>l</i> ± 11	h ± 11, <i>k</i> ± 15, <i>l</i> ± 21	h ± 11, <i>k</i> ± 15, <i>l</i> ± 21	h ± 11, <i>k</i> ± 15, -20 ≤ <i>l</i> ≤ 21
Absorption /	face-indexed	plate (010) 3°	ellipsoid	SADABS	SADABS	plate (011) 3°
Total reflections	10667	17633	10393	18592	7209, 0.058	16412
Unique refl., <i>R</i> _{int}	3924, 0.084	3938, 0.062	4010, 0.164	7396, 0.043	5638	7141, 0.090
Unique <i>F</i> _o ≥ 4σ _{<i>F</i>}	2756	3264	2352	5908	227	6041
Twin matrix		[100/0-10/00-1]	[100/0-10/00-1]		227	227
Twin proportion (%)		0.36(3)	0.9(1)		16549	16412
Parameters	124	125	125		7209, 0.058	
<i>R</i> ¹ for <i>F</i> _o ≥ 4σ _{<i>F</i>}	5.1	3.1	8.5		2.9	2.5
<i>R</i> ¹ all data, <i>wR</i> ₂ ²	7.6, 13.5	3.8, 8.0	12.3, 21.9	3.5, 6.4	3.9, 6.1	3.0, 6.5
Weighting <i>a, b</i>	0.0724	0.0444	0.100	0.0243	0.0084	0.0
Goodness of fit	0.994	0.983	0.968	0.0042(1)	0.895	0.00045(10)
Mean shift/σ _d	0.000	0.000	0.000	0.000	0.000	0.000
Peaks (e/Å ³)	16.5*, -4.0	8.6*, -2.1	6.5, -7.9	2.6, -2.3	3.4, -1.8	1.7, -2.1
Mineral name		nováčekite II		metakalerite	metakalerite	metakirchheimerite

NOTE: ¹ Corrections for absorption are either semi-empirical (crystal modelled as a plate, rejecting data within 3° of the primary X-ray beam), or empirical (program SADABS, G. Sheldrick, unpublished) based on the intensities of equivalent reflections. ² $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \times 100$, ³ $wR2 = \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2}]^{0.5} \times 100$, $w = 1/(\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P)$, and $P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$.

TABLE 4 (continued)

Compound	Co[UO ₂ PO ₄] ₂ (H ₂ O) ₁₀	Ni[UO ₂ PO ₄] ₂ (H ₂ O) ₁₀	Mg[UO ₂ AsO ₄] ₂ (H ₂ O) ₁₀
<i>a</i> (Å)	6.9490(5)	6.9506(4)	7.1328(11)
<i>b</i> (Å)	19.9348(16)	19.8215(11)	20.085(3)
<i>c</i> (Å)	6.9620(5)	6.9711(4)	9.0
<i>α</i> (°)	90	90	90
<i>β</i> (°)	90	90.440(2)	90.585(3)
<i>γ</i> (°)	90	90	90
<i>V</i> (Å ³)	964.40(12)	960.39(9)	1025.3(3)
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2	2	2
Formula weight	969.084	968.844	1022.351
<i>F</i> (000)	874	876	916
<i>μ</i> (mm ⁻¹)	17.87	18.06	19.10
<i>D</i> _{calc} (g/mL)	3.337	3.350	3.312
Size (mm)	0.15 × 0.15 × 0.02	0.10 × 0.10 × 0.02	0.15 × 0.08 × 0.02
Color and habit	orange plate	yellow-green plate	yellow plate
Crystal mount	glass capillary	glass fibre	glass fibre
Temperature (K)	293(2)	293(2)	293(2)
Width (°), time (s)	0.3, 90	0.3, 25	0.3, 30
Collection, hours	hemisphere, 36	sphere, 20	hemisphere, 12
θ range (°)	3.10 – 34.48	2.92 – 34.50	2.85 – 34.54
Data collected	-10 ≤ <i>h</i> ≤ 9, -31 < <i>k</i> ≤ 29, <i>l</i> ± 10	-10 ≤ <i>h</i> ≤ 11, <i>k</i> ± 30, <i>l</i> ± 11	-8 ≤ <i>h</i> ≤ 11, -31 < <i>k</i> ≤ 25, <i>l</i> ± 11
Absorption /	face-indexed	plate (010) 3°	ellipsoid
Total reflections	10667	17633	10393
Unique refl., <i>R</i> _{int}	3924, 0.084	3938, 0.062	4010, 0.164
Unique <i>F</i> _o ≥ 4σ _{<i>F</i>}	2756	3264	2352
Twin matrix		[100/0-10/00-1]	[100/0-10/00-1]
Twin proportion (%)		0.36(3)	0.9(1)
Parameters	124	125	125
<i>R</i> ¹ for <i>F</i> _o ≥ 4σ _{<i>F</i>}	5.1	3.1	8.5
<i>R</i> ¹ all data, <i>wR</i> ₂ ²	7.6, 13.5	3.8, 8.0	12.3, 21.9
Weighting <i>a, b</i>	0.0724	0.0444	0.100
Goodness of fit	0.994	0.983	0.968
Mean shift/σ _d	0.000	0.000	0.000
Peaks (e/Å ³)	16.5*, -4.0	8.6*, -2.1	6.5, -7.9
Mineral name		nováčekite II	

NOTE: ¹ Corrections for absorption are either semi-empirical (crystal modelled as either a plate with rejection of data within 3° of the primary X-ray beam, or as an ellipsoid), or face-indexed analytical. ² $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \times 100$, ³ $wR2 = \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2}]^{0.5} \times 100$, $w = 1/(\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P)$, and $P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$. *See footnotes to Tables 11 and 12, respectively.

TABLE 5. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *MnUAs12*

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
U(1)	0.2325(1)	0.7301(1)	0.0793(1)	0.013(1)
As(1)	0.7491(1)	0.7545(1)	0.0011(1)	0.013(1)
Mn(1)	—	—	—	0.030(1)
O(1)	0.5475(5)	0.6950(5)	0.0935(4)	0.021(1)
O(2)	0.9152(5)	0.7765(5)	0.0883(3)	0.020(1)
O(3)	0.7273(5)	0.9558(4)	-0.0909(4)	0.021(1)
O(4)	0.8084(5)	0.5869(4)	-0.0854(3)	0.021(1)
O(5)	0.2723(5)	0.7682(5)	-0.0784(4)	0.024(1)
O(6)	0.1889(5)	0.6874(5)	0.2380(4)	0.024(1)
O(7)W	-0.2884(7)	0.7053(6)	0.5258(5)	0.041(1)
O(8)W	0.3030(8)	0.7250(6)	0.4527(4)	0.045(1)
O(9)W	-0.0307(6)	0.2901(6)	0.3035(4)	0.040(1)
O(10)W	0.5765(7)	-0.0576(6)	0.6893(4)	0.039(1)
O(11)W	0.6313(7)	0.5003(7)	0.3161(4)	0.041(1)
O(12)W	-0.1988(7)	0.9405(6)	0.3135(5)	0.042(1)

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

TABLE 6. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *CoUAs12*

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
U(1)	0.2303(1)	0.7325(1)	0.0800(1)	0.013(1)
As(1)	0.7462(1)	0.7511(1)	-0.0018(1)	0.014(1)
Co(1)	0	0	—	0.027(1)
O(1)	0.5439(8)	0.7736(8)	0.0918(6)	0.020(1)
O(2)	0.9138(8)	0.6921(8)	0.0854(6)	0.021(1)
O(3)	0.8082(8)	0.9535(8)	-0.0961(6)	0.020(1)
O(4)	0.7233(8)	0.5849(8)	-0.0891(6)	0.022(1)
O(5)	0.2718(7)	0.7767(7)	-0.0804(5)	0.017(1)
O(6)	0.1866(8)	0.6878(8)	0.2412(6)	0.023(1)
O(7)W	-0.1942(10)	0.7926(10)	0.4744(7)	0.035(2)
O(8)W	0.2179(10)	0.8124(10)	0.4548(7)	0.038(2)
O(9)W	0.5592(10)	0.9241(10)	0.3134(7)	0.038(2)
O(10)W	0.5606(11)	-0.3020(11)	0.6825(8)	0.042(2)
O(11)W	0.7930(10)	0.4656(10)	0.3068(7)	0.041(2)
O(12)W	0.0022(10)	0.1310(10)	0.3218(7)	0.038(2)

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

F^2 for all unique data in space group $P\bar{1}$. Structure models including anisotropic displacement-parameters for all atoms converged. The agreement indices ($R1$), calculated for the observed unique reflections ($|F_o| \geq 4\sigma_F$) of these refinements, range from 2.5 to 2.9%. The location of each H atom in these structures was not determined. The unit cells of the octahydrates can be transformed by the matrix $[100/0\frac{1}{2}\bar{1}/0^3/0^3/2\frac{1}{2}]$ to yield *A*-centered triclinic cells whose dimensions (but not angles) are reminiscent of the tetragonal meta-autunite group compounds (Locock *et al.* 2004). For *CoUAs8*, this procedure yields: a 7.196, b 7.175, c 17.524 \AA , α 84.67°, β 80.77°, γ 89.92°.

The positional parameters and equivalent isotropic displacement-parameters of atoms are given in Tables 5 to 16: *MnUAs12*, *CoUAs12*, *MgUAs12*, *NiUAs12*, *NiUP12*, *MnUP10*, *CoUP10*, *NiUP10*, *MgUAs10*, *MnUAs8*, *FeUAs8*, and *CoUAs8*, respectively. Selected interatomic distances of *MnUAs12*, *CoUAs12*, and

TABLE 7. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *MgUAs12*

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
U(1)	0.7322(1)	0.2300(1)	0.0798(1)	0.012(1)
As(1)	0.7509(1)	0.7457(1)	-0.0015(1)	0.012(1)
Mg(1)	0	0	—	0.028(1)
O(1)	0.7759(6)	0.2688(6)	-0.0797(4)	0.011(1)
O(2)	0.6863(7)	0.1871(7)	0.2401(5)	0.021(1)
O(3)	0.7726(7)	0.5427(7)	0.0922(5)	0.019(1)
O(4)	0.6926(7)	0.9131(7)	0.0864(5)	0.021(1)
O(5)	0.5854(7)	0.7254(7)	-0.0894(5)	0.020(1)
O(6)	0.9546(7)	0.8049(7)	-0.0959(5)	0.019(1)
O(7)W	0.8013(8)	-0.1966(8)	0.4748(6)	0.034(1)
O(8)W	0.1286(9)	0.0028(9)	0.3236(6)	0.039(2)
O(9)W	0.8163(9)	0.2132(9)	0.4508(6)	0.039(2)
O(10)W	0.4675(9)	0.7906(9)	0.3071(6)	0.040(2)
O(11)W	0.0789(9)	0.4415(9)	0.6868(6)	0.039(2)
O(12)W	0.3002(9)	0.4404(9)	0.3149(6)	0.041(2)

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

TABLE 8. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *NiUAs12*

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
U(1)	0.2301(1)	0.7327(1)	0.0802(1)	0.013(1)
As(1)	0.7458(1)	0.7511(1)	-0.0018(1)	0.014(1)
Ni(1)	0	0	—	0.025(1)
O(1)	0.5437(4)	0.7756(5)	0.0926(3)	0.022(1)
O(2)	0.9133(4)	0.6899(5)	0.0869(3)	0.023(1)
O(3)	0.8065(4)	0.9530(4)	-0.0956(3)	0.021(1)
O(4)	0.7231(4)	0.5848(4)	-0.0894(3)	0.022(1)
O(5)	0.2711(4)	0.7764(5)	-0.0806(3)	0.028(1)
O(6)	0.1858(4)	0.6878(5)	0.2424(3)	0.024(1)
O(7)W	-0.1892(5)	0.7975(6)	0.4726(3)	0.033(1)
O(8)W	0.2148(5)	0.8173(6)	0.4544(3)	0.035(1)
O(9)W	0.0034(5)	0.1287(6)	0.3253(3)	0.040(1)
O(10)W	0.4404(5)	0.0746(6)	0.6835(4)	0.037(1)
O(11)W	0.7893(6)	0.4653(6)	0.3082(4)	0.040(1)
O(12)W	0.4374(5)	0.3013(6)	0.3187(4)	0.042(1)
H(1)	-0.3020(60)	0.7770(100)	0.4410(60)	0.050
H(2)	-0.1970(90)	0.8940(70)	0.4070(40)	0.050
H(3)	0.2020(90)	0.7560(90)	0.3860(40)	0.050
H(4)	0.3160(60)	0.8980(80)	0.4170(50)	0.050
H(5)	-0.0310(90)	0.2530(40)	0.2970(60)	0.050
H(6)	0.0700(80)	0.1060(100)	0.2500(30)	0.050
H(7)	0.4470(90)	0.1080(100)	0.7600(30)	0.050
H(8)	0.4330(90)	-0.0560(30)	0.7140(60)	0.050
H(9)	0.8360(80)	0.5430(70)	0.2340(30)	0.050
H(10)	0.8100(90)	0.5440(90)	0.3670(50)	0.050
H(11)	0.5580(50)	0.3570(90)	0.3180(60)	0.050
H(12)	0.3470(80)	0.3720(80)	0.2750(50)	0.050

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor. U_{eq} of H atoms constrained during refinement.

MgUAs12 are given in Table 17, those of *NiUAs12* and *NiUP12* are in Table 18, those of *MnUP10*, *CoUP10*, *NiUP10* and *MgUAs10* are in Table 19, and selected interatomic distances for *MnUAs8*, *FeUAs8* and *CoUAs8* are given in Table 20. Anisotropic displacement-parameters, and observed and calculated structure-factors for these compounds, are available from the

Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Bond-valence sums at the non-H cation sites for the twelve compounds are listed in Table 21, and were calculated using the parameters of Burns *et al.* (1997) for sixfold-coordinated U^{6+} , Brown & Altermatt (1985) for P^{5+} , As^{5+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Mg^{2+} , and Ni^{2+} . The bond-valence sums are in good agreement with expected formal oxidation states for all of the compounds.

DESCRIPTION OF THE STRUCTURES

All twelve 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 $[(UO_2)(AsO_4)]^-$.

The five triclinic dodecahydrates, *MnUAs12*, *CoUAs12*, *MgUAs12*, *NiUAs12*, and *NiUP12*, are isostructural. Their interlayers contain a divalent metal cation in distorted octahedral coordination by H_2O

TABLE 9. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *NiUP12*

	x	y	z	U_{eq}
U(1)	-0.2646(1)	0.7316(1)	0.0729(1)	0.011(1)
P(1)	0.2493(1)	0.7536(1)	0.0019(1)	0.012(1)
Ni(1)	0	—	—	0.023(1)
O(1)	0.0599(4)	0.7039(5)	0.0866(4)	0.020(1)
O(2)	0.4087(4)	0.7690(5)	0.0827(3)	0.020(1)
O(3)	-0.3056(5)	0.6880(5)	0.2359(3)	0.020(1)
O(4)	0.2311(5)	0.9453(5)	-0.0818(3)	0.019(1)
O(5)	0.2993(5)	0.5939(5)	-0.0789(4)	0.020(1)
O(6)	-0.2246(6)	0.7717(5)	-0.0887(3)	0.028(1)
O(7)W	0.1300(7)	0.5052(7)	0.3234(4)	0.036(1)
O(8)W	-0.2068(7)	0.3103(6)	0.4708(4)	0.032(1)
O(9)W	0.1896(7)	0.2801(6)	0.5438(4)	0.034(1)
O(10)W	0.4728(6)	0.2917(7)	0.3046(5)	0.035(1)
O(11)W	0.9245(6)	0.0609(7)	0.3113(5)	0.035(1)
O(12)W	0.3075(7)	0.9332(7)	0.3185(5)	0.040(1)
H(1)	0.1390(110)	0.1550(60)	0.5740(80)	0.050
H(2)	-0.2730(100)	0.2050(80)	0.5180(70)	0.050
H(3)	0.2560(60)	0.4500(110)	0.3170(90)	0.050
H(4)	0.2650(100)	0.3110(120)	0.6030(60)	0.050
H(5)	0.8680(110)	0.0710(120)	0.2370(40)	0.050
H(6)	-0.1500(110)	0.2480(110)	0.4040(50)	0.050
H(7)	0.5600(90)	0.3280(110)	0.2310(40)	0.050
H(8)	0.3600(110)	0.8850(120)	0.2460(50)	0.050
H(9)	0.0460(60)	0.0370(120)	0.2680(70)	0.050
H(10)	0.5600(100)	0.2830(120)	0.3640(60)	0.050
H(11)	0.3740(100)	0.0530(60)	0.2990(80)	0.050
H(12)	0.0510(100)	0.5470(120)	0.2610(60)	0.050

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor. U_{eq} of H atoms constrained during refinement.

TABLE 10. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *MnUP10*

	x	y	z	U_{eq}
U(1)	0	0.2091(1)	—	0.013(1)
P(1)	0	0.2482(1)	0	0.016(1)
Mn(1)	0	0	0	0.042(1)
O(1)	0	0.1209(2)	—	0.024(1)
O(2)	0	0.2966(2)	—	0.027(1)
O(3)	0.0371(5)	0.2035(1)	0.1743(5)	0.023(1)
O(4)	0.3264(5)	0.2075(1)	0.5354(5)	0.023(1)
O(5)W	0.2991(7)	0.4203(3)	0.4268(7)	0.055(1)
O(6)W	0.1116(16)	0	-0.2925(16)	0.087(3)
O(7)W	0.0542(9)	0.4151(4)	0.7897(9)	0.072(2)

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

TABLE 11. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *CoUP10*

	x	y	z	U_{eq}
U(1)	0.4503(1)	0.2083(1)	0.9805(1)	0.009(1)
Co(1)	0	—	0	0.023(1)
P(1)	0.9484(3)	0.2515(1)	0.9779(3)	0.011(1)
O(1)W	0.5941(14)	0.0035(4)	0.2187(13)	0.039(2)
O(2)	0.4074(10)	0.2015(4)	0.3070(9)	0.019(1)
O(3)	0.4862(10)	0.2042(4)	0.6538(9)	0.019(1)
O(4)	0.1247(8)	0.2082(4)	-0.0614(10)	0.018(1)
O(5)	0.7790(9)	0.2047(4)	0.0213(10)	0.018(1)
O(6)	0.4545(10)	0.2975(4)	0.9848(9)	0.022(1)
O(7)	0.4463(9)	0.1193(4)	0.9789(9)	0.020(1)
O(8)W	0.2295(12)	0.5714(4)	0.0721(12)	0.031(2)
O(9)W	0.8283(12)	0.5817(4)	0.9404(12)	0.032(2)
O(10)W	0.0229(12)	0.0837(5)	0.7426(13)	0.038(2)
O(11)W	0.9350(18)	0.0739(6)	0.1491(17)	0.066(4)

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor. The largest residual peak in the difference Fourier map is at x 0.6541, y 0.2084, z 0.0672, height 16.5 $e/\text{\AA}^3$; the nearest atoms are: O(5) 0.93 \AA , U(1) 1.53 \AA , P(1) 2.31 \AA . The next largest peak has height 4.6 $e/\text{\AA}^3$. See text for discussion.

TABLE 12. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *NiUP10*

	x	y	z	U_{eq}
U(1)	0.0517(1)	0.2083(1)	0.5219(1)	0.009(1)
Ni(1)	0	0	0	0.020(1)
P(1)	-0.4457(2)	0.2518(1)	0.5258(2)	0.011(1)
O(1)	0.3784(5)	0.2080(2)	0.5691(6)	0.020(1)
O(2)	0.0149(6)	0.2037(2)	0.8497(5)	0.017(1)
O(3)	0.0968(6)	0.2011(2)	0.1961(5)	0.018(1)
O(4)	0.0565(5)	0.1181(2)	0.5252(5)	0.019(1)
O(5)W	0.2264(6)	0.0680(2)	0.0675(6)	0.028(1)
O(6)W	-0.0886(6)	0.0047(2)	0.2778(6)	0.030(1)
O(7)W	-0.0244(6)	0.4169(2)	0.2589(6)	0.034(1)
O(8)W	0.0670(9)	0.4276(3)	0.8545(8)	0.051(1)
O(9)	0.0463(5)	0.2978(2)	0.5182(5)	0.019(1)
O(10)	-0.2746(5)	0.2045(2)	0.4879(6)	0.018(1)
O(11)W	-0.1718(6)	0.0812(2)	-0.0588(6)	0.029(1)

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor. The largest residual peak in the difference Fourier map is at x 0.8461, y 0.2083, z 0.4238, height 8.6 $e/\text{\AA}^3$; the nearest atoms are: O(10) 0.96 \AA , U(1) 1.58 \AA , P(1) 2.32 \AA . The next largest peak has height 2.9 $e/\text{\AA}^3$. See text for discussion.

groups of three unique O positions (Fig. 2), with bond lengths in the range 2.04–2.20 Å (Tables 17, 18). Three additional symmetrically independent H₂O groups are held in these structures only by hydrogen bonds (Fig. 3). Hydrogen positions were located only in *NiUAs12* and *NiUP12*, but the proposed hydrogen-bond networks are presumed to be applicable to all five structures. Hydrogen bonds link the interstitial H₂O groups with the H₂O group at the apex of the octahedron into approximately square-planar sets. Hydrogen bonds extend from these sets to the anions at the equatorial vertices of uranyl square bipyramids, which also are shared with tetrahedra, and to the H₂O groups at the equatorial positions of the octahedra (Fig. 3).

Unlike the primitive structures of the other decahydrates presented herein, *MnUP10* is body-centered. In its interlayer, Mn is in nearly regular octahedral coordination with two symmetrically unique H₂O groups with equivalent bond-lengths of 2.20 Å (Table 19, Fig. 4). There is one symmetrically independent H₂O group, O(7), held in the structure only by hydrogen bonding (Table 10). Although H positions were not determined in this structure, a network of hydrogen bonds is proposed on the basis of O...O interatomic distances in the range 2.7–3.2 Å, in accord with the usual donor to acceptor (D...A) separations found for hydrogen bonds (Jeffrey 1997), and is illustrated in Figure 5. Hydrogen bonds from the interstitial H₂O group, O(7), link two Mn(H₂O)₆ octahedra through the O(5) and O(6) positions, and two further hydrogen bonds extend to acceptors within the uranyl phosphate sheet (an apical O atom

of the uranyl ion, and an equatorial O atom that is shared with phosphate). Hydrogen bonds also extend from the O(5) position to the O atoms of the phosphate tetrahedra that are shared with the uranyl square bipyramids

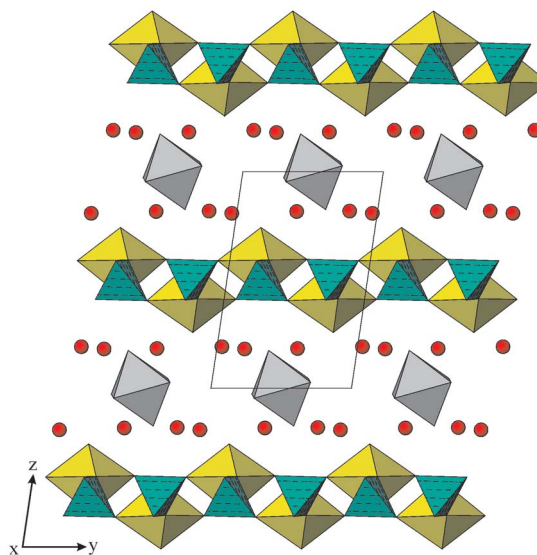


FIG. 2. The structure of *NiUAs12*, projected along [100]. Uranyl polyhedra are yellow, arsenate tetrahedra are green and stippled, nickel-based octahedra are gray, and H₂O groups are shown as red spheres.

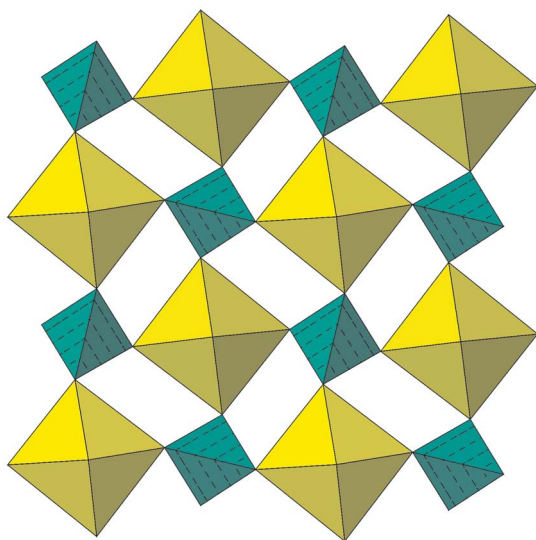


FIG. 1. The autunite-type sheet in *NiUAs12*, projected perpendicular to (001). The uranyl polyhedra are yellow, and the arsenate tetrahedra are green and stippled.

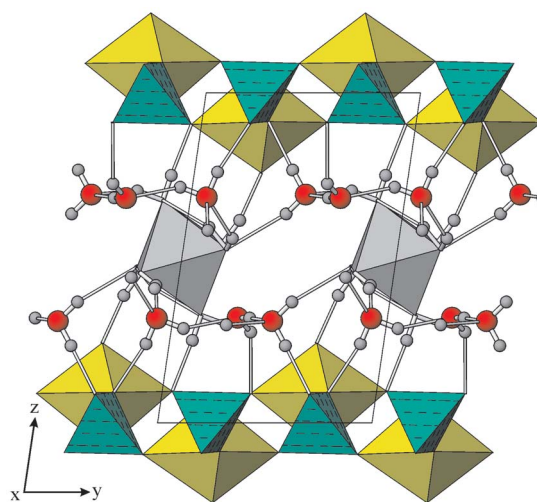


FIG. 3. Hydrogen bonding in the structure of *NiUAs12*, projected along [100]. Hydrogen atoms are shown as gray spheres, O–H bonds as thick short rods, and H...O bonds as thin long rods.

(Fig. 5). The separation distance between equivalent O(7) positions is 4.1 Å, and so these atoms are not connected to each other by hydrogen bonds.

The structures of the decahydrates *CoUP10*, *NiUP10* and *MgUAs10* were refined in space group $P2_1/n$, and

TABLE 13. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *MgUAs10*

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
U(1)	0.0592(1)	0.2044(1)	0.0227(1)	0.015(1)
As(1)	-0.4395(2)	0.2511(1)	0.0263(2)	0.016(1)
Mg(1)	—	—	0	0.033(2)
O(1)	-0.2585(15)	0.2000(5)	-0.0214(15)	0.018(2)
O(2)	0.0561(17)	0.2922(6)	0.0168(16)	0.026(3)
O(3)	-0.4844(16)	0.3008(6)	-0.1584(14)	0.020(2)
O(4)	-0.6280(20)	0.2020(6)	0.0780(20)	0.034(3)
O(5)	-0.3940(15)	0.3040(6)	0.2065(15)	0.021(2)
O(6)	0.0614(14)	0.1161(5)	0.0261(13)	0.015(2)
O(7)W	-0.3320(20)	0.5798(6)	0.0700(19)	0.035(3)
O(8)W	-0.4100(20)	0.5039(6)	-0.2700(20)	0.041(3)
O(9)W	-0.7218(19)	0.5677(7)	-0.0720(20)	0.040(3)
O(10)W	-0.5240(20)	0.0816(8)	0.2670(20)	0.045(4)
O(11)W	-0.4190(40)	0.0739(11)	-0.1570(30)	0.099(9)

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

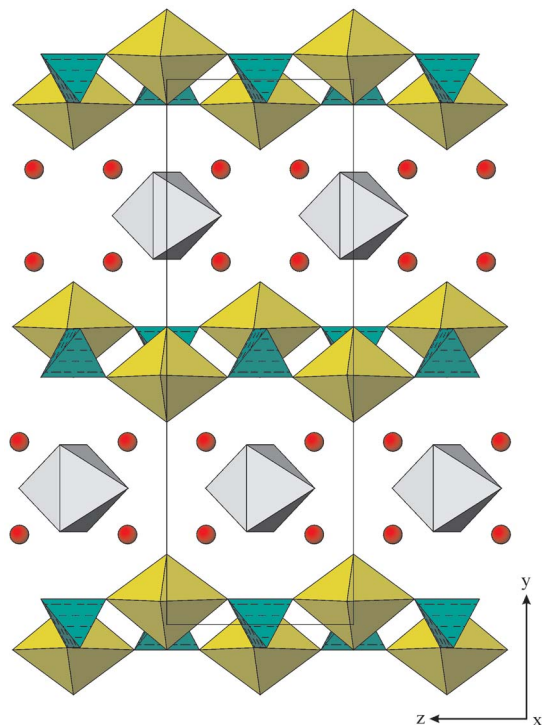


FIG. 4. The structure of *MnUP10*, projected along [100]. Uranyl polyhedra are yellow, phosphate tetrahedra are green and stippled, manganese-based octahedra are gray, and H_2O groups are shown as red spheres.

TABLE 14. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *MnUAs8*

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
U(1)	0.2347(1)	0.6923(1)	0.4009(1)	0.010(1)
U(2)	0.2282(1)	0.2001(1)	-0.0914(1)	0.011(1)
As(1)	0.2519(1)	0.8720(1)	0.1202(1)	0.011(1)
As(2)	0.2465(1)	0.3776(1)	-0.3724(1)	0.012(1)
Mn(1)	0.3228(1)	0.3606(1)	0.2594(1)	0.021(1)
O(1)	0.2618(4)	0.0445(3)	0.0669(2)	0.020(1)
O(2)	0.1977(4)	0.8337(3)	0.4631(2)	0.018(1)
O(3)	0.1903(4)	0.3384(3)	-0.0263(2)	0.019(1)
O(4)	0.0876(4)	0.8121(3)	0.0685(2)	0.019(1)
O(5)	0.4586(4)	0.7772(3)	0.0993(2)	0.021(1)
O(6)	0.4546(4)	0.2828(3)	-0.3884(2)	0.021(1)
O(7)	0.0823(4)	0.3133(3)	-0.4212(2)	0.019(1)
O(8)	0.2589(5)	0.5472(3)	-0.4367(2)	0.021(1)
O(9)	0.1992(4)	0.8550(3)	0.2485(2)	0.021(1)
O(10)	0.2710(4)	0.5463(3)	0.3388(2)	0.022(1)
O(11)	0.2681(4)	0.0629(3)	-0.1579(2)	0.023(1)
O(12)	0.1922(4)	0.3710(3)	-0.2455(2)	0.019(1)
O(13)W	0.4133(5)	0.1781(4)	0.1957(3)	0.035(1)
O(14)W	0.5745(5)	0.2911(4)	0.3405(3)	0.041(1)
O(15)W	0.1727(6)	0.2279(5)	0.3884(3)	0.042(1)
O(16)W	0.0703(6)	0.4317(4)	0.1795(3)	0.045(1)
O(17)W	0.4782(6)	0.4847(4)	0.1300(3)	0.045(1)
O(18)W	0.9578(6)	0.0906(4)	0.2978(4)	0.043(1)
O(19)W	0.7827(6)	0.2786(5)	0.1153(4)	0.055(1)
O(20)W	0.3758(8)	0.0068(5)	0.5937(5)	0.079(2)

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

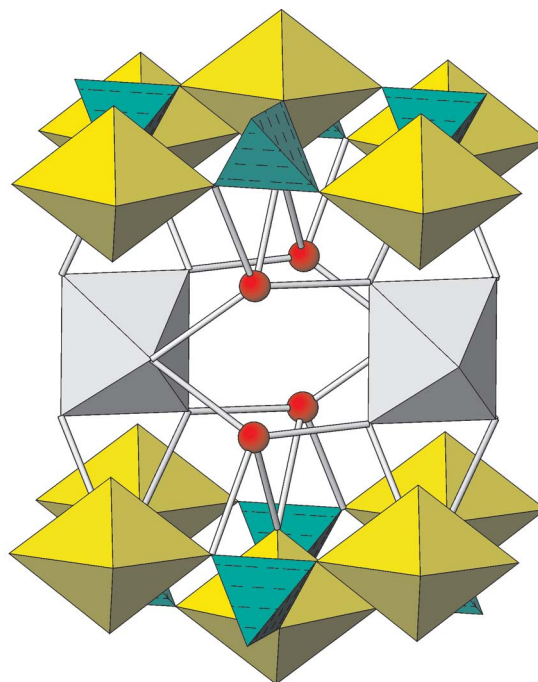


FIG. 5. Hydrogen bonding in the structure of *MnUP10*. Donor-acceptor (O...O) interatomic distances are shown as rods.

TABLE 15. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *FeUAs8*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
U(1)	0.2344(1)	0.6930(1)	0.4008(1)	0.011(1)
U(2)	0.2282(1)	0.2010(1)	-0.0914(1)	0.012(1)
As(1)	0.2515(1)	0.8716(1)	0.1200(1)	0.012(1)
As(2)	0.2464(1)	0.3780(1)	-0.3726(1)	0.013(1)
Fe(1)	0.3267(1)	0.3607(1)	0.2603(1)	0.020(1)
O(1)	0.2620(5)	0.0461(3)	0.0676(2)	0.021(1)
O(2)	0.1963(4)	0.8344(3)	0.4628(2)	0.018(1)
O(3)	0.1887(4)	0.3399(3)	-0.0260(2)	0.020(1)
O(4)	0.0873(4)	0.8121(4)	0.0673(2)	0.020(1)
O(5)	0.4588(4)	0.7762(4)	0.1009(2)	0.021(1)
O(6)	0.4542(4)	0.2815(4)	-0.3873(2)	0.021(1)
O(7)	0.0825(4)	0.3152(4)	-0.4231(2)	0.020(1)
O(8)	0.2609(5)	0.5491(3)	-0.4359(2)	0.022(1)
O(9)	0.1960(5)	0.8553(4)	0.2483(2)	0.022(1)
O(10)	0.2716(5)	0.5464(3)	0.3381(2)	0.023(1)
O(11)	0.2683(5)	0.0625(4)	-0.1576(2)	0.026(1)
O(12)	0.1888(5)	0.3717(4)	-0.2456(2)	0.021(1)
O(13)W	0.4113(5)	0.1800(4)	0.1965(3)	0.032(1)
O(14)W	0.5697(6)	0.2896(4)	0.3425(3)	0.039(1)
O(15)W	0.1766(6)	0.2338(4)	0.3847(3)	0.040(1)
O(16)W	0.0833(6)	0.4329(4)	0.1799(3)	0.041(1)
O(17)W	0.4786(6)	0.4803(4)	0.1349(3)	0.041(1)
O(18)W	0.9628(6)	0.0959(4)	0.2973(3)	0.038(1)
O(19)W	0.7833(6)	0.2812(5)	0.1159(3)	0.054(1)
O(20)W	0.3666(7)	0.0073(5)	0.5924(4)	0.064(2)

U_{eq} is defined as one third of the orthogonalized *U_{ij}* tensor.

TABLE 16. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR *CoUAs8*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
U(1)	0.2351(1)	0.6933(1)	0.4006(1)	0.011(1)
U(2)	0.2266(1)	0.2022(1)	-0.0912(1)	0.012(1)
As(1)	0.2522(1)	0.8715(1)	0.1199(1)	0.012(1)
As(2)	0.2457(1)	0.3786(1)	-0.3723(1)	0.012(1)
Co(1)	0.3278(1)	0.3616(1)	0.2616(1)	0.019(1)
O(1)	0.2615(4)	0.0460(3)	0.0666(2)	0.020(1)
O(2)	0.1954(4)	0.8364(3)	0.4625(2)	0.020(1)
O(3)	0.1858(4)	0.3420(3)	-0.0251(2)	0.021(1)
O(4)	0.0887(4)	0.8111(3)	0.0662(2)	0.020(1)
O(5)	0.4600(4)	0.7745(3)	0.1012(2)	0.023(1)
O(6)	0.4538(4)	0.2796(3)	-0.3858(2)	0.021(1)
O(7)	0.0811(4)	0.3161(3)	-0.4241(2)	0.020(1)
O(8)	0.2616(4)	0.5495(3)	-0.4361(2)	0.020(1)
O(9)	0.1953(4)	0.8556(3)	0.2480(2)	0.021(1)
O(10)	0.2741(4)	0.5461(3)	0.3378(2)	0.023(1)
O(11)	0.2679(4)	0.0632(3)	-0.1585(2)	0.026(1)
O(12)	0.1860(4)	0.3728(3)	-0.2451(2)	0.020(1)
O(13)W	0.4113(4)	0.1813(3)	0.1984(2)	0.030(1)
O(14)W	0.5648(4)	0.2890(3)	0.3408(3)	0.034(1)
O(15)W	0.1777(5)	0.2376(4)	0.3830(3)	0.037(1)
O(16)W	0.0892(5)	0.4297(4)	0.1824(3)	0.040(1)
O(17)W	0.4805(5)	0.4778(3)	0.1402(3)	0.042(1)
O(18)W	0.9642(5)	0.0982(4)	0.2950(3)	0.037(1)
O(19)W	0.7774(5)	0.2778(5)	0.1189(3)	0.050(1)
O(20)W	0.3609(6)	0.0056(4)	0.5907(3)	0.058(1)

U_{eq} is defined as one third of the orthogonalized *U_{ij}* tensor.

TABLE 17. SELECTED INTERATOMIC DISTANCES (\AA) AND ANGLES ($^\circ$) FOR *MnUAs12*, *CoUAs12* AND *MgUAs12*

<i>MnUAs12</i>		<i>CoUAs12</i>		<i>MgUAs12</i>	
U(1)-O(5)	1.755(4)	U(1)-O(5)	1.772(6)	U(1)-O(1)	1.764(5)
U(1)-O(6)	1.766(4)	U(1)-O(6)	1.783(6)	U(1)-O(2)	1.774(5)
U(1)-O(2)	2.272(3)	U(1)-O(4)	2.279(6)	U(1)-O(5)	2.278(5)
U(1)-O(4)	2.278(3)	U(1)-O(2)	2.279(6)	U(1)-O(4)	2.281(5)
U(1)-O(1)	2.283(3)	U(1)-O(3)	2.290(6)	U(1)-O(6)	2.283(5)
U(1)-O(3)	2.293(3)	U(1)-O(1)	2.295(6)	U(1)-O(3)	2.291(5)
<U(1)-O _{ap} >	1.76	<U(1)-O _{ap} >	1.78	<U(1)-O _{ap} >	1.77
<U(1)-O _{eq} >	2.28	<U(1)-O _{eq} >	2.29	<U(1)-O _{eq} >	2.28
O(5)-U(1)-O(6)	178.7(2)	O(5)-U(1)-O(6)	179.5(3)	O(1)-U(1)-O(2)	179.0(2)
As(1)-O(3)	1.669(3)	As(1)-O(2)	1.672(6)	As(1)-O(4)	1.676(5)
As(1)-O(4)	1.669(3)	As(1)-O(4)	1.678(6)	As(1)-O(5)	1.682(5)
As(1)-O(2)	1.675(4)	As(1)-O(1)	1.680(6)	As(1)-O(3)	1.685(5)
As(1)-O(1)	1.675(3)	As(1)-O(3)	1.690(6)	As(1)-O(6)	1.690(5)
<As(1)-O>	1.67	<As(1)-O>	1.68	<As(1)-O>	1.68
Mn(1)-O(11)W	2.161(4) x 2	Co(1)-O(12)W	2.088(8) x 2	Mg(1)-O(8)W	2.063(7) x 2
Mn(1)-O(8)W	2.175(5) x 2	Co(1)-O(8)W	2.093(7) x 2	Mg(1)-O(9)W	2.065(7) x 2
Mn(1)-O(7)W	2.204(5) x 2	Co(1)-O(7)W	2.132(7) x 2	Mg(1)-O(7)W	2.100(6) x 2
<Mn(1)-O>	2.18	<Co(1)-O>	2.10	<Mg(1)-O>	2.08

differ from the structure of *MnUP10* mainly in the arrangement of their interlayer contents. The divalent cations are in distorted octahedral coordination; there are three symmetrically independent H₂O groups, with bond lengths ranging from 2.04 to 2.19 Å (Table 19, Fig. 6). There are two symmetrically independent H₂O groups held in the structure only by hydrogen bonding. Although H positions were not determined in these structures, a network of hydrogen bonds is proposed on the basis of O...O interatomic distances in the range 2.7–3.2 Å, and is illustrated in Figure 7. Hydrogen bonds from the interstitial H₂O groups bridge the interlayer octahedra, extend to acceptors (anions of tetrahedra) in the sheet, and connect the two interstitial H₂O groups together (separation distance 2.9 Å). Hydrogen bonds also extend from the H₂O groups coordinating the metal cations to acceptors in the sheet (the apical O atoms of the uranyl ion, and the equatorial O atoms that are shared with tetrahedra).

The octahydrates *MnUAs8*, *FeUAs8* and *CoUAs8* are all isostructural. Whereas in the dodecahydrates and decahydrates the divalent cations are in octahedral coordination with H₂O groups and are linked to the sheets only by hydrogen bonds, in the octahydrates, the divalent cation octahedra are connected directly to the sheet by the O(10) atom of the U(1) uranyl ion (Fig. 8). The remaining five vertices of the octahedra are symmetrically unique H₂O groups. The octahedra are distorted, with the bond to O(10) being about 0.1–0.2 Å longer than the bonds to the other five ligands (Table 20). Similarly, the U(1)–O(10) bond in these structures is longer than the other three uranyl ion bonds by 0.04–0.05 Å. There are three symmetrically independent H₂O groups held in the structure only by hydrogen bonding. Although H positions were not determined in these structures, a network of hydrogen bonds is proposed on the basis of O...O interatomic distances in the range 2.7–3.2 Å. Hydrogen bonds link the interstitial H₂O groups with the H₂O group at the apex of the octahedron into

TABLE 18. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR *NiUAs12* AND *NiUP12*

<i>NiUAs12</i>		D-H		H...A		D-H...A
U(1)-O(5)	1.771(3)	O(7)W-H(1)	0.95	H(1)...O(10)W	2.00	134
U(1)-O(6)	1.788(3)	O(7)W-H(2)	0.94	H(2)...O(9)W	2.23	130
U(1)-O(4)	2.280(3)	O(8)W-H(3)	0.96	H(3)...O(6)	1.78	168
U(1)-O(2)	2.280(3)	O(8)W-H(4)	0.95	H(4)...O(10)W	1.92	148
U(1)-O(3)	2.290(3)	O(9)W-H(5)	0.94	H(5)...O(11)W	1.97	150
U(1)-O(1)	2.297(3)	O(9)W-H(6)	0.94	H(6)...O(3)	1.93	176
<U(1)-O _{ap} >	1.78	O(10)W-H(7)	0.94	H(7)...O(1)	1.97	170
<U(1)-O _{eq} >	2.29	O(10)W-H(8)	0.95	H(8)...O(12)W	2.03	140
O(5)-U(1)-O(6)	179.3(1)	O(11)W-H(9)	0.95	H(9)...O(2)	1.84	176
		O(11)W-H(10)	0.96	H(10)...O(7)W	2.32	163
As(1)-O(4)	1.679(3)	O(12)W-H(11)	0.96	H(11)...O(11)W	1.82	177
As(1)-O(3)	1.682(3)	O(12)W-H(12)	0.96	H(12)...O(4)	2.20	137
As(1)-O(1)	1.683(3)					
As(1)-O(2)	1.684(3)	Ni(1)-O(9)W	2.042(4) x 2	Ni(1)-O(7)W	2.088(4) x 2	
<As(1)-O>	1.68	Ni(1)-O(8)W	2.054(3) x 2	<Ni(1)-O>	2.06	
<i>NiUP12</i>						
U(1)-O(6)	1.770(4)	O(7)W-H(12)	0.96	H(12)...O(1)	2.09	142
U(1)-O(3)	1.787(4)	O(7)W-H(3)	0.95	H(3)...O(10)W	1.86	167
U(1)-O(2)	2.285(3)	O(8)W-H(2)	0.94	H(2)...O(12)W	1.92	141
U(1)-O(5)	2.287(3)	O(8)W-H(6)	0.95	H(6)...O(11)W	1.81	161
U(1)-O(4)	2.297(3)	O(9)W-H(1)	0.95	H(1)...O(11)W	1.86	156
U(1)-O(1)	2.298(3)	O(9)W-H(4)	0.95	H(4)...O(3)	1.86	152
<U(1)-O _{ap} >	1.78	O(10)W-H(10)	0.95	H(10)...O(8)W	2.18	167
<U(1)-O _{eq} >	2.29	O(10)W-H(7)	0.96	H(7)...O(5)	1.86	172
O(6)-U(1)-O(3)	179.3(1)	O(11)W-H(5)	0.96	H(5)...O(4)	1.97	171
		O(11)W-H(9)	0.95	H(9)...O(12)W	2.07	134
P(1)-O(4)	1.533(4)	O(12)W-H(11)	0.95	H(11)...O(10)W	1.84	164
P(1)-O(1)	1.535(3)	O(12)W-H(8)	0.95	H(8)...O(2)	2.09	167
P(1)-O(2)	1.542(3)					
P(1)-O(5)	1.542(4)	Ni(1)-O(7)W	2.053(4) x 2	Ni(1)-O(8)W	2.075(4) x 2	
<P(1)-O>	1.54	Ni(1)-O(9)W	2.058(4) x 2	<Ni(1)-O>	2.06	

NOTE: Uncertainties in H interatomic distances constrained to 0.02 Å. O-H...O angles rounded to the nearest degree. For hydrogen bonding, D = donor O atom, A = acceptor O atom.

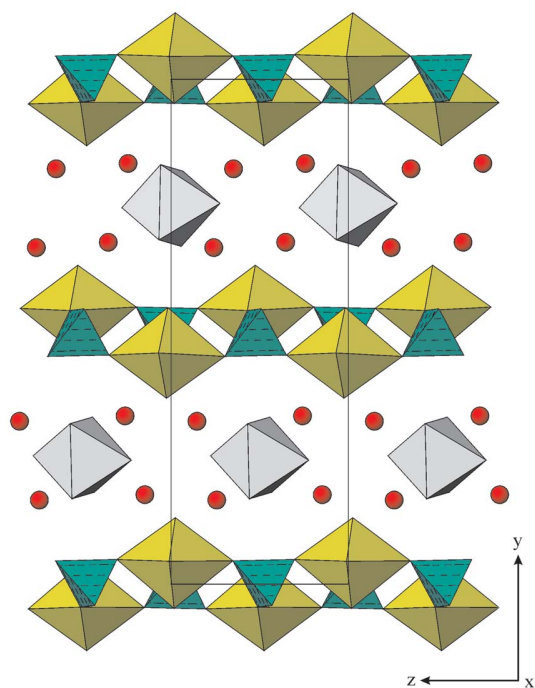


FIG. 6. The structure of *NiUP10*, projected along [100]. Uranyl polyhedra are yellow, phosphate tetrahedra are green and stippled, nickel-based octahedra are gray, and H₂O groups are shown as red spheres. The orientations of the interlayer octahedra and H₂O groups differ from the structure of *MnUP10* presented in Figure 4.

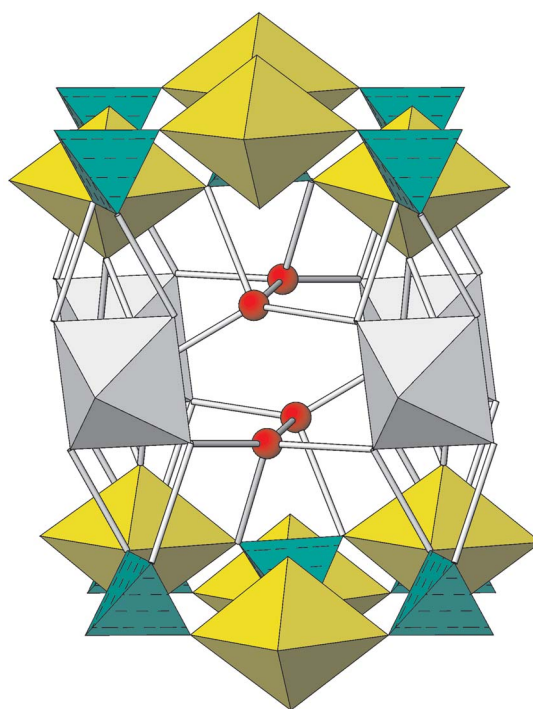


FIG. 7. Hydrogen bonding in the structure of *NiUP10*. Donor-acceptor (O...O) interatomic distances are shown as rods.

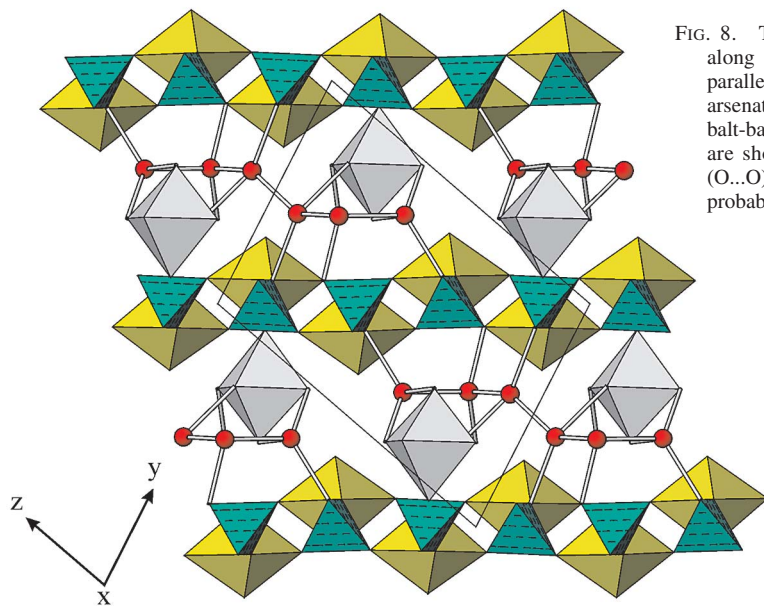


FIG. 8. The structure of *CoUAs8*, projected along [100]. The uranyl arsenate sheets are parallel to (011). Uranyl polyhedra are yellow, arsenate tetrahedra are green and stippled, cobalt-based octahedra are gray, and H₂O groups are shown as red spheres. Donor-acceptor (O...O) distances (<3.0 Å) corresponding to probable hydrogen bonds are shown as rods.

TABLE 19. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR *MnUP10*, *CoUP10*, *NiUP10*, AND *MgUAs10*

<i>MnUP10</i>	<i>CoUP10</i>		<i>NiUP10</i>		<i>MgUAs10</i>		
U(1)-O(2)	1.784(5)	U(1)-O(7)	1.774(7)	U(1)-O(9)	1.776(4)	U(1)-O(2)	1.765(12)
U(1)-O(1)	1.796(5)	U(1)-O(6)	1.779(7)	U(1)-O(4)	1.787(4)	U(1)-O(6)	1.774(10)
U(1)-O(4)	2.283(4)	x 2 U(1)-O(4)	2.279(6)	U(1)-O(10)	2.280(4)	U(1)-O(4)	2.265(15)
U(1)-O(3)	2.294(3)	x 2 U(1)-O(3)	2.292(6)	U(1)-O(1)	2.292(4)	U(1)-O(1)	2.287(11)
<U(1)-O _{ap} >	1.79	U(1)-O(2)	2.299(6)	U(1)-O(3)	2.299(4)	U(1)-O(5)	2.297(11)
<U(1)-O _{eq} >	2.29	U(1)-O(5)	2.301(6)	U(1)-O(2)	2.303(4)	U(1)-O(3)	2.309(10)
O(2)-U(1)-O(1)180	<U(1)-O _{ap} >	1.78	<U(1)-O _{ap} >	1.78	<U(1)-O _{ap} >	1.77	
	<U(1)-O _{eq} >	2.29	<U(1)-O _{eq} >	2.29	<U(1)-O _{eq} >	2.29	
	O(7)-U(1)-O(6)	179.4(3)	O(9)-U(1)-O(4)	179.8(2)	O(2)-U(1)-O(6)	179.4(5)	
P(1)-O(4)	1.533(3)	x 2 P(1)-O(4)	1.525(7)	P(1)-O(1)	1.531(4)	As(1)-O(3)	1.685(10)
P(1)-O(3)	1.538(3)	x 2 P(1)-O(3)	1.531(7)	P(1)-O(2)	1.535(4)	As(1)-O(1)	1.686(11)
<P(1)-O>	1.54	P(1)-O(5)	1.533(7)	P(1)-O(3)	1.538(4)	As(1)-O(5)	1.699(10)
		P(1)-O(2)	1.539(7)	P(1)-O(10)	1.539(4)	As(1)-O(4)	1.709(15)
		<P(1)-O>	1.53	<P(1)-O>	1.54	<As(1)-O>	1.69
Mn(1)-O(6)W	2.197(12)	x 2 Co(1)-O(9)W	2.060(8)	x 2 Ni(1)-O(6)W	2.039(4)	x 2 Mg(1)-O(8)W	2.042(16)
Mn(1)-O(5)W	2.198(5)	x 4 Co(1)-O(1)W	2.071(9)	x 2 Ni(1)-O(11)W	2.043(4)	x 2 Mg(1)-O(7)W	2.058(12)
<Mn(1)-O>	2.20	Co(1)-O(8)W	2.193(8)	x 2 Ni(1)-O(5)W	2.123(4)	x 2 Mg(1)-O(9)W	2.145(14)
		<Co(1)-O>	2.11	<Ni(1)-O>	2.07	<Mg(1)-O>	2.08

TABLE 20. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR *MnUAs8*, *FeUAs8* AND *CoUAs8*

<i>MnUAs8</i>	<i>FeUAs8</i>		<i>CoUAs8</i>		
U(1)-O(2)	1.783(3)	U(1)-O(2)	1.762(3)	U(1)-O(2)	1.765(3)
U(1)-O(10)	1.823(3)	U(1)-O(10)	1.813(3)	U(1)-O(10)	1.809(3)
U(1)-O(9)	2.257(3)	U(1)-O(9)	2.253(3)	U(1)-O(9)	2.250(3)
U(1)-O(6)	2.277(3)	U(1)-O(6)	2.276(3)	U(1)-O(8)	2.273(3)
U(1)-O(8)	2.278(3)	U(1)-O(8)	2.278(3)	U(1)-O(6)	2.274(3)
U(1)-O(7)	2.285(3)	U(1)-O(7)	2.283(3)	U(1)-O(7)	2.276(3)
<U(1)-O _{ap} >	1.80	<U(1)-O _{ap} >	1.79	<U(1)-O _{ap} >	1.79
<U(1)-O _{eq} >	2.27	<U(1)-O _{eq} >	2.27	<U(1)-O _{eq} >	2.27
O(2)-U(1)-O(10)179.25(12)	O(2)-U(1)-O(10)179.29(14)	O(2)-U(1)-O(10)179.51(11)			
U(2)-O(3)	1.781(3)	U(2)-O(3)	1.770(3)	U(2)-O(3)	1.774(3)
U(2)-O(11)	1.784(3)	U(2)-O(11)	1.774(4)	U(2)-O(11)	1.777(3)
U(2)-O(1)	2.284(3)	U(2)-O(4)	2.280(3)	U(2)-O(1)	2.271(3)
U(2)-O(4)	2.287(3)	U(2)-O(1)	2.282(3)	U(2)-O(4)	2.276(3)
U(2)-O(5)	2.294(3)	U(2)-O(5)	2.286(3)	U(2)-O(5)	2.287(3)
U(2)-O(12)	2.312(3)	U(2)-O(12)	2.309(3)	U(2)-O(12)	2.301(3)
<U(2)-O _{ap} >	1.78	<U(2)-O _{ap} >	1.77	<U(2)-O _{ap} >	1.78
<U(2)-O _{eq} >	2.29	<U(2)-O _{eq} >	2.29	<U(2)-O _{eq} >	2.28
O(3)-U(2)-O(11)179.30(13)	O(3)-U(2)-O(11)179.68(14)	O(3)-U(2)-O(11)179.52(12)			
As(1)-O(4)	1.677(3)	As(1)-O(4)	1.674(3)	As(1)-O(9)	1.675(3)
As(1)-O(1)	1.683(3)	As(1)-O(9)	1.679(3)	As(1)-O(4)	1.680(3)
As(1)-O(9)	1.684(3)	As(1)-O(5)	1.679(3)	As(1)-O(5)	1.681(3)
As(1)-O(5)	1.688(3)	As(1)-O(1)	1.690(3)	As(1)-O(1)	1.683(3)
<As(1)-O>	1.68	<As(1)-O>	1.68	<As(1)-O>	1.68
As(2)-O(7)	1.679(3)	As(2)-O(7)	1.675(3)	As(2)-O(6)	1.679(3)
As(2)-O(6)	1.683(3)	As(2)-O(6)	1.676(3)	As(2)-O(12)	1.682(3)
As(2)-O(12)	1.685(3)	As(2)-O(12)	1.680(3)	As(2)-O(7)	1.684(3)
As(2)-O(8)	1.689(3)	As(2)-O(8)	1.692(3)	As(2)-O(8)	1.687(3)
<As(2)-O>	1.68	<As(2)-O>	1.68	<As(2)-O>	1.68
Mn(1)-O(16)W	2.147(4)	Fe(1)-O(17)W	2.084(4)	Co(1)-O(14)W	2.039(3)
Mn(1)-O(14)W	2.149(4)	Fe(1)-O(16)W	2.091(4)	Co(1)-O(17)W	2.040(3)
Mn(1)-O(17)W	2.155(4)	Fe(1)-O(14)W	2.100(4)	Co(1)-O(16)W	2.045(3)
Mn(1)-O(15)W	2.170(4)	Fe(1)-O(15)W	2.102(4)	Co(1)-O(15)W	2.064(3)
Mn(1)-O(13)W	2.186(4)	Fe(1)-O(13)W	2.141(4)	Co(1)-O(13)W	2.118(3)
Mn(1)-O(10)	2.320(3)	Fe(1)-O(10)	2.284(3)	Co(1)-O(10)	2.245(3)
<Mn(1)-O>	2.19	<Fe(1)-O>	2.13	<Co(1)-O>	2.09

approximately square-planar sets. Hydrogen bonds extend from these sets to the anions at the equatorial vertices of uranyl square bipyramids that are also shared with tetrahedra, to the H₂O groups at the equatorial positions of the octahedra, and connect these square sets together (Fig. 8).

As expected, the mean bond-lengths of the octahedra in the interlayers of all of the compounds (Tables 17 to 20) show a nearly linear correlation with the effective ionic radii of their divalent elements as tabulated by Shannon (1976).

DISCUSSION

Polymorphism in the decahydrates

In the structures of the decahydrates, two different polymorphs were refined: the *I2/m* polymorph (*MnUP10*), and the *P2₁/n* polymorph (*CoUP10*, *NiUP10*, *MgUAs10*, and saléeite: Miller & Taylor 1986). These structures are not polytypic modifications, *i.e.*, compounds built up by stacking layers of identical structure and composition, where the modifications differ *only* in the stacking sequence (Guinier 1984). Rather, the differing arrangements of the H₂O groups in the interlayers (both the H₂O groups coordinating the divalent cation and those held only by hydrogen bonds) are responsible for the difference in structure. The uranyl phosphate (or uranyl arsenate) sheets in the two polymorphs are geometrically indistinguishable and, in general, are stacked in an identical fashion.

TABLE 21. BOND VALENCE SUMS FOR THE CATIONS

<i>MnUAs12</i>	sum (vu)	<i>MnUP10</i>	sum (vu)	<i>MnUAs8</i>	sum (vu)
U(1)	6.27	U(1)	6.06	U(1)	6.05
As(1)	5.17	P(1)	4.99	U(2)	6.07
Mn(1)	2.09	Mn(1)	1.99	As(1)	5.02
				As(2)	5.01
<i>CoUAs12</i>	sum (vu)	<i>CoUP10</i>	sum (vu)	Mn(1)	2.07
U(1)	6.15	U(1)	6.12		
As(1)	5.06	P(1)	5.03	<i>FeUAs8</i>	sum (vu)
Co(1)	1.97	Co(1)	1.97	U(1)	6.15
				U(2)	6.16
<i>MgUAs12</i>	sum (vu)	<i>NiUP10</i>	sum (vu)	As(1)	5.05
U(1)	6.21	U(1)	6.08	As(2)	5.05
As(1)	5.02	P(1)	4.98	Fe(1)	2.07
Mg(1)	2.13	Ni(1)	1.97		
				<i>CoUAs8</i>	sum (vu)
<i>NiUAs12</i>	sum (vu)	<i>MgUAs10</i>	sum (vu)	U(1)	6.18
U(1)	6.13	U(1)	6.18	U(2)	6.17
As(1)	5.03	As(1)	4.86	As(1)	5.06
Ni(1)	2.00	Mg(1)	2.11	As(2)	5.02
				Co(1)	2.07
<i>NiUP12</i>	sum (vu)				
U(1)	6.11				
P(1)	4.95				
Ni(1)	1.99				

A single large difference-Fourier peak is present in the refinements of both *CoUP10* and *NiUP10* (Tables 11, 12). It is probable that these peaks arise from the Đurovič effect, in which difference-Fourier residues corresponding to "virtual atoms" are caused by the presence of stacking faults in an otherwise ordered matrix (Nespolo & Ferraris 2001). This effect is observed commonly in the difference-Fourier maps of order-disorder structures composed of two polytypes, such as are found in certain micas and complex titanosilicates (Ferraris *et al.* 2001, Krivovichev *et al.* 2003). The peaks in *CoUP10* and *NiUP10* are unlikely to result from systematic errors in the absorption correction, as they are located at rather suspicious distances: ~1.53 Å from U, and ~2.3 Å from P, the reverse of the regular bond-distances. The average P–O distance in tetrahedra is 1.53(1) Å, and the normal U–O_{eq} distance in uranyl square bipyramids is 2.29(1) Å (Tables 18, 19). It is doubtful that the similarities of these distances are accidental. In the decahydrates studied herein, it is likely that the stacking faults arise from the occurrence of alternative orientations of the uranyl phosphate sheet during crystal growth. Interestingly, the refinement of the structure of saléeite does not show large difference-Fourier peaks (Miller & Taylor 1986). The largest difference-Fourier peaks in the low-precision structure of *MgUAs10* are all within 1 Å of the U position, and are attributed to the poor quality of the diffraction data and possibly to systematic errors in the absorption correction.

Why is *MnUP10* a different polymorph than the other decahydrates? An explanation simply involving cation size is more suitable than one based on crystal-field theory, as all of the divalent cations involved are approximately in octahedral coordination, and neither Mn²⁺ nor Mg²⁺ have any net crystal-field stabilization energy (Jaffe 1988, Burns 1993). The effective ionic radius of ⁶Mn²⁺ is 0.830 Å, 20% larger than that of ⁶Ni²⁺, 0.690 Å (Shannon 1976). The larger size of Mn

TABLE 22. BASAL SPACINGS FOR REFINED STRUCTURES

Mineral	Chemical Formula	CS	SG	<i>d</i> (Å)	<i>hkl</i>
	Mn[(UO ₂)(AsO ₄) ₂](H ₂ O) ₈	A	<i>P</i> $\bar{1}$	8.76	011
metakahlerite	Fe[(UO ₂)(AsO ₄) ₂](H ₂ O) ₈	A	<i>P</i> $\bar{1}$	8.66	011
metakirchheimerite	Co[(UO ₂)(AsO ₄) ₂](H ₂ O) ₈	A	<i>P</i> $\bar{1}$	8.61	011
	Mn[(UO ₂)(PO ₄) ₂](H ₂ O) ₁₀	M	<i>I2/m</i>	10.19	020
	Co[(UO ₂)(PO ₄) ₂](H ₂ O) ₁₀	M	<i>P2₁/n</i>	9.97	020
saléeite ¹	Mg[(UO ₂)(PO ₄) ₂](H ₂ O) ₁₀	M	<i>P2₁/n</i>	9.97	020
	Ni[(UO ₂)(PO ₄) ₂](H ₂ O) ₁₀	M	<i>P2₁/n</i>	9.91	020
nováčekite II	Mg[(UO ₂)(AsO ₄) ₂](H ₂ O) ₁₀	M	<i>P2₁/n</i>	10.04	020
	Mn[(UO ₂)(AsO ₄) ₂](H ₂ O) ₁₂	A	<i>P</i> $\bar{1}$	11.12	001
"kirchheimerite"	Co[(UO ₂)(AsO ₄) ₂](H ₂ O) ₁₂	A	<i>P</i> $\bar{1}$	11.04	001
nováčekite I	Mg[(UO ₂)(AsO ₄) ₂](H ₂ O) ₁₂	A	<i>P</i> $\bar{1}$	11.06	001
	Ni[(UO ₂)(AsO ₄) ₂](H ₂ O) ₁₂	A	<i>P</i> $\bar{1}$	11.01	001
	Ni[(UO ₂)(PO ₄) ₂](H ₂ O) ₁₂	A	<i>P</i> $\bar{1}$	10.95	001

NOTE: CS = crystal system (A: triclinic, M: monoclinic); SG = space group; *d* = basal *d*-value; ¹ data for natural material from Miller & Taylor (1986); all other data are from synthetic materials, equivalent or analogous to minerals.

appears to entail a different arrangement of H₂O groups and a different network of hydrogen-bonds, thus producing a different structure. This effect is not observed in the dodecahydrates or octahydrates, in which the manganese uranyl arsenate compounds are isostructural with the Fe, Co, Mg and Ni compounds. Whether this disparity of behavior with respect to polymorphism in the decahydrates is a result of the greater adaptability of the triclinic dodecahydrate or octahydrate structures, or influenced by the substitution of As for P, is not clear, as manganese uranyl phosphate structures with these hydration states (8, 12) were not refined.

States of hydration in autunite-type compounds of divalent transition metals and Mg

The results presented are consistent with the presence of three separate hydration states in compounds with the autunite-type sheet that have either Mn, Fe, Co, Ni or Mg in the interlayer. The dodecahydrates are triclinic (pseudomonoclinic) and have basal spacings of ~11 Å, the decahydrates are monoclinic (pseudo-orthorhombic) and have basal spacings of ~10 Å, and the octahydrates are triclinic with basal spacings of ~8.7 Å (Table 22). We emphasize that each hydration state corresponds to a different structure-type; the H₂O content in these compounds does not vary as in zeolites, but rather is required to maintain the integrity of the hydrogen-bonding network. Changes in hydration state, whether through dehydration or rehydration, give rise to separate structures. In this connection, the ferroan saléeite studied by Vochten & Van Springel (1996) is considered, on the basis of powder X-ray-diffraction data (Tables 1, 22), to be isostructural with the material investigated by Miller & Taylor (1986). The low apparent H₂O content of the ferroan saléeite is interpreted to be a result of dehydration induced by the conditions of the electron-microprobe analysis, and not to represent the actual H₂O content of the material.

The literature is not in agreement on the symmetry of the uranyl phosphate octahydrates (Table 1). On the basis of Guinier and Debye-Scherrer film data, lehrnerite is monoclinic, pseudo-orthorhombic, space group $P2_1/n$ (Mücke 1988, Vochten *et al.* 1990). From diffractometer data, bassetite also is monoclinic, pseudo-orthorhombic, space group $P2_1/m$ (Vochten *et al.* 1984, Vochten 1986). Oxidation of the ferrous iron in bassetite gives rise to the mixed ferric-ferrous species vochtenite: (Fe²⁺,Mg)Fe³⁺[UO₂/PO₄]₄(OH)(H₂O)₁₂₋₁₃ (De Grave & Vochten 1988, Zwann *et al.* 1989). From Weissenberg and precession data, Vochten *et al.* (1981) derived triclinic cells for Co[(UO₂)(PO₄)₂](H₂O)₇ and its Ni equivalent, but the volumes and densities reported for these two chemical analogues differ by 15%, rather than the expected ~0.4% (Table 4). From the basal *d*-values of these compounds (Table 1), it is likely that the Co

compound was the octahydrate, and the Ni compound, the decahydrate (equivalent to *NiUP10*).

On the basis of the common isotypy of uranyl phosphates and uranyl arsenates (*e.g.*, *NiUP12* and *NiUAs12*), it is probable that the uranyl phosphate octahydrates lehrnerite, bassetite, metasaléeite and their Co equivalent, as well as the uranyl arsenate octahydrates metanováčekite and *UM1997-41*, are isostructural with *MnUAs8*, *FeUAs8* and *CoUAs8* (Tables 1, 22). Correspondingly, we can predict that metalodèveite also is isostructural with these octahydrate compounds because of its similar basal spacing (Table 1) and the close size of Zn and Co (effective ionic radii of 0.740 and 0.745 Å, respectively; Shannon 1976). In the same fashion, kahlerite is probably isostructural with the dodecahydrates presented herein (Table 22).

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