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THE CRYSTAL STRUCTURES OF $X(NpO_2)(PO_4)(H_2O)_3$ (X = K^+, Na^+, Rb^+, NH_4^+) AND THEIR RELATIONSHIP TO THE AUTUNITE GROUP

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Abstract

Four Np^{6+} phosphates with compositions $X(NpO_2)(PO_4)(H_2O)_3$, $X = K^+, Na^+, Rb^+, NH_4^+$, have been synthesized by mild hydrothermal methods, and their structures have been determined. Single-crystal X-ray-diffraction data were collected using Mo$K\alpha$ radiation and an APEX CCD detector. The Np^{6+} structures containing K^+, Na^+, Rb^+, and NH_4^+ (*KP1*, *NaP1*, *RbP1*, *NH₄P1*) were refined to agreement indices R_1 0.042, 0.051, 0.066, and 0.023 calculated for 831, 856, 798, and 857 unique observed reflections, respectively. *KP1* crystallizes in space group $P4/ncc$, with a 6.9564(8), c 17.826(4) Å, V 862.6(2) Å^3, $Z = 4$. *NaP1* also is tetragonal, $P4/ncc$, with a 7.005(1), c 16.986(4) Å, V 833.6(3) Å^3, $Z = 4$. *RbP1* is tetragonal, $P4/ncc$, with a 7.031(4), c 17.87(2) Å, V 884(1) Å^3, $Z = 4$. *NH₄P1* crystallizes in space group $P4/ncc$ with a 6.9843(6), c 18.023(3) Å, V 879.2(2) Å^3, $Z = 4$. Each of these structures contains sheets of composition $[(NpO_2)(PO_4)]^-$ consisting of Np^{6+} in square bipyramidal coordination and phosphate tetrahedra. These sheets are topologically identical to the well-known uranyl phosphate sheets of the autunite group. The monovalent cations and H_2O group are located in the interlayer, where they balance the charge on the sheets and provide linkages between the sheets.

Keywords: neptunium phosphate, synthetic compounds, crystal structure, neptunyl phosphate sheets, autunite group.

Sommaire

Nous avons synthétisé quatre phosphates de Np^{6+} de composition $X(NpO_2)(PO_4)(H_2O)_3$, $X = K^+, Na^+, Rb^+, NH_4^+$, par méthodes hydrothermales douces, et nous en avons déterminé la structure. Les données en diffraction X ont été prélevées sur monocristal avec rayonnement Mo$K\alpha$ et un détecteur de type APEX CCD. Les structures à Np^{6+}, contenant les ions K^+, Na^+, Rb^+, et NH_4^+ (*KP1*, *NaP1*, *RbP1*, *NH₄P1*) ont été affinées jusqu'à un résidu R_1 de 0.042, 0.051, 0.066, et 0.023, calculé en utilisant 831, 856, 798, et 857 réflexions uniques observées, respectivement. *KP1* cristallize dans le groupe spatial $P4/ncc$, avec a 6.9564(8), c 17.826(4) Å, V 862.6(2) Å^3, $Z = 4$. *NaP1* aussi est tétragonal, $P4/ncc$, avec a 7.005(1), c 16.986(4) Å, V 833.6(3) Å^3, $Z = 4$. *RbP1* est tétragonal, $P4/ncc$, avec a 7.031(4), c 17.87(2) Å, V 884(1) Å^3, $Z = 4$. *NH₄P1* cristallise dans le groupe spatial $P4/ncc$, avec a 6.9843(6), c 18.023(3) Å, V 879.2(2) Å^3, $Z = 4$. Chacune de ces structures contient des feuillets de composition $[(NpO_2)(PO_4)]^-$ contenant le Np^{6+} en coordinence bipyramidale carrée et des tétraèdres phosphatés. Ces feuillets sont topologiquement identiques aux feuillets bien connus à uranyle et phosphate du groupe de l'autunite. Les cations monovalents et le groupe H_2O sont situés dans l'interfeuillet, où ils balancent les charges des feuillets et assurent la cohésion entre feuillets.

(Traduit par la Rédaction)

Mots-clés: phosphate de neptunium, composés synthétiques, structure cristalline, feuillets à phosphate et neptunyle, groupe de l'autunite.

Introduction

More than 40 species of uranyl phosphates and arsenates have been described that are members of the autunite and meta-autunite groups (Finch & Murakami 1999). The relatively low solubility of the uranyl phosphates of these groups in groundwater has important implications for the mobility of uranium in phosphate-bearing systems (Murakami *et al.* 1997). Precipitation of these minerals can be achieved at emplaced reactive barriers in the subsurface that are designed to limit the mobility of uranium in groundwater systems (Sowder *et al.* 1996). Soils contaminated by actinides, such as those at the Fernald site in Ohio where uranium ore was processed (Buck *et al.* 1996), and the K1300 locality of the DOE–K 25 site at Oak Ridge, Tennessee (Roh

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et al. 2000), have been found to contain minerals of the autunite group.

The fate and transport of ^{237}Np are important for the safe, permanent disposal of nuclear waste in a geological repository contained in the unsaturated zone (Lieser & Muhlenweg 1988, Silva & Nitsche 1995). With a half-life of 2.14×10^6 years, ^{237}Np is a significant contributor to the total potential dose of radiation associated with such a repository system (Silva & Nitsche 1995). Expected conditions in a geological repository within the unsaturated zone suggest that Np will be most mobile in the pentavalent state. Pentavalent Np exhibits a higher solubility than Np^{4+} and could be transported as a dissolved constituent of groundwater. Engineered systems that limit the mobility of ^{237}Np may be important in the design components of a repository (Kaszuba & Runde 1999). The mobility of Np in a repository could also be influenced by the precipitation of Np-rich phases, adsorption of Np onto mineral surfaces or colloids, or through the incorporation of Np into secondary uranyl phases (Silva & Nitsche 1995, Burns *et al.* 1997b, 2004). The formation of uranyl and neptunyl phosphates in or near a repository could decrease the release of ^{237}Np from the repository.

The crystal-chemical characteristics of U^{6+}, Np^{5+}, and Np^{6+} are generally similar, as all usually exist as nearly linear dioxo cations [$(UO_2)^{2+}$, $(NpO_2)^+$, and $(NpO_2)^{2+}$] with typical bond-lengths of 1.79(4), 1.83(2) and 1.75(2) Å, respectively (Burns *et al.* 1997a). The actinyl ion in crystal structures is further coordinated by four, five, or six equatorial ligands, giving square, pentagonal, and hexagonal bipyramids that are capped by the O atoms of the actinyl ions. Given the similar size of cations Np^{6+} and U^{6+} and geometries of polyhedra, it is reasonable to expect that analogous Np^{6+} and U^{6+} compounds will be isostuctural. Furthermore, $(NpO_2)^{2+}$ should substitute readily for $(UO_2)^{2+}$ within the structures of uranyl minerals (Burns *et al.* 1997b). We are conducting a detailed study of the crystal chemistry of Np^{5+} and Np^{6+}, and are delineating relationships with the crystal chemistry of U^{6+} (Forbes & Burns 2005, 2006, Forbes *et al.* 2006). Here, we present the details of the synthesis and structures of the Np^{6+} phosphates $X(NpO_2)(PO_4)(H_2O)_3$ ($X = K^+, Na^+, Rb^+, NH_4^+$) and compare them to their analogous uranyl mineral structures.

PREVIOUS WORK

Hexavalent Np compounds with the formula $X(NpO_2)(PO_4)(H_2O)_{3–4}$, $X = H_3O^+, NH_4^+, Li^+, Na^+, K^+$, and $X[(NpO_2)(PO_4)]_2(H_2O)_{6–9}$, $X = Mg^{2+}, Ca^{2+}, Sr^{2+}$, and Ba^{2+}, have been synthesized (Weigel & Hoffmann 1976). These syntheses yielded violet powders for the monovalent cations and light brownish powders for the divalent cations. The identity of these materials was established by X-ray powder diffraction, but their structures have not been reported. The compounds presented here appear to be identical to some of those synthesized by Weigel & Hoffmann (1976), on the basis of comparison of their calculated and observed X-ray powder-diffraction patterns.

EXPERIMENTAL METHODS

Hydrothermal synthesis

The reagents KCl (Fisher Scientific Lot #78390), NaCl (Aldrich Chemical Lot #12926EN), RbCl (Acros Chemical Lot #A011718701), and NH_4Cl (J.T. Baker Lot #30960) were used as received. Apatite, $Ca_5(PO_4)_3F$, from the Liscombe deposit, Ontario, or a 1.6 M H_3PO_4 solution (Baker Scientific Lot #350820), were used as the source of phosphate in each experiment. A stock solution was prepared by dissolving Np^{5+} in a 1 M HCl solution. *CAUTION: ^{237}Np represents a serious health risk due to the emission of alpha and gamma radiation. All studies were conducted in the hot laboratories of Argonne National Laboratory, which has appropriate equipment and personnel for handling such materials.* All reactions took place in 7 mL Teflon cups with screw-top lids. After loading the reactants, the tightly closed Teflon cups were placed in 125 mL Teflon-lined Parr reaction vessels. Fifty mL of ultrapure water was added to each vessel to provide counter-pressure during heating. The reactions took place in a gravity convection oven for one to two weeks. The vessels were allowed to cool slowly to room temperature before removal from the oven. In each case, red platy crystals with maximum diameters of approximately 200 to 800 μm and a dark green precipitate resulted. Additional details of the syntheses are given in Table 1.

Structure solutions and refinements

Single crystals of Np^{6+} phosphates containing K^+, Na^+, Rb^+, and NH_4^+ (*KP1, NaP1, RbP1, NH_4P1*) were mounted on glass fibers and placed on a Bruker three-circle X-ray diffractometer equipped with either an APEX or APEX II CCD detector. A sphere of three-

TABLE 1. DETAILS OF THE SYNTHESES OF $X(NpO_2)(PO_4)(H_2O)_3$, $X = K^+, Na^+, Rb^+, NH_4^+$

	KP1	*NaP1*	*RbP1*	*NH_4P1*
XCl ($X = K^+, Na^+, Rb^+, NH_4^+$)	0.0898 g	0.0249 g	0.1373 g	0.0256 g
Phosphate source	$Ca_5(PO_4)_3F$		1.6 M H_3PO_4	
	0.0254 g	0.0249 g	0.75 mL	0.75 mL
Np^{5+}	0.025 M	0.025 M	0.025 M	0.025 M
pH	0.48	0.31	0	0.15
Temperature (°C)	150	150	115	150
Reaction time (weeks)	2	2	1	1

dimensional data was collected at room temperature for each crystal using graphite-monochromatized Mo$K\alpha$ radiation and frame widths of 0.3° in ω for *KP1, RbP1,* and *NH$_4$P1* and 0.6° in ω for *NaP1*. The X-ray data were collected with count-times per frame of 60 seconds for *NaP1* and 10 seconds for *KP1, RbP1,* and *NH$_4$P1*. Unit-cell parameters were refined by least-squares techniques using the Bruker Smart or Apex II software. The Bruker Saint software was used for data integration as well as correction for Lorentz and polarization. Semi-empirical corrections for absorption were applied by modeling the crystals as plates using the Bruker program Xprep. Reflections with plate-glancing angles less than 3° were discarded. Selected crystallographic data and refinement information are provided in Tables 2 and 3.

All structures were solved by direct methods and refined on the basis of F^2 for all unique data using the Bruker Shelxtl Version 5 system of programs (1998). Scattering factors for each atom were taken from International Tables for X-ray Crystallography (Ibers & Hamilton 1974). In each case, the Np^{6+} cation was located in the direct-methods solution. The other cations and anions were located in difference-Fourier maps calculated following refinement of the partial structure-models. Compounds *KP1, NaP1, RbP1* and *NH$_4$P1* crystallizes in space group *P*4/*ncc*.

The final structure-model for *KP1* includes anisotropic displacement parameters for the cations, and isotropic parameters for the lighter anions. In the case of *NaP1*, anisotropic displacement parameters were refined for Np and P only, owing to positional disorder present at the Na site. The final structure-models of *RbP1* and *NH$_4$P1* include anisotropic displacement parameters for all atoms.

The occupancies for the Na site in *NaP1* and the NH_4 site in *NH$_4$P1* were constrained to provide an electroneutral structure. The H_2O groups occupy 75% of these sites, and the cation accounts for the remaining 25%. The H atom positions of the interlayer H_2O group were refined with the constraint that O–H bonds be ~0.96 Å for *KP1*. In the case of *NaP1*, the electron density around the O(4) atom, which corresponds to the H_2O group, is distributed over two closely spaced sites. The O atom was modeled as two sites with O(4A) 25% occupied and O(4B) 50% occupied, with a Na^+ cation accounting for the remaining 25%. The O(4A) and O(4B) sites are separated by 1.04(3) Å, indicating that both cannot be occupied locally. Atomic positional parameters are given for all atoms in Tables 4 for *KP1, NaP1, RbP1,* and *NH$_4$P1*. Table 5 contains selected interatomic distances for *KP1, NaP1, RbP1,* and *NH$_4$P1*, respectively. Tables of structure factors have been sent to the Depository of Unpublished Data on the MAC web site [document Np phosphates CM45_471].

Descriptions of the Structures

The compounds *KP1, NaP1, NH4P1,* and *RbP1* contain sheets of neptunyl square bipyramids and phosphate tetrahedra. Topologically identical sheets

TABLE 2. MISCELLANEOUS CRYSTALLOGRAPHIC INFORMATION FOR *KP1* AND *NaP1*

	KP1	*NaP1*
Formula	$K(NpO_2)(PO_4)(H_2O)_3$	$Na(NpO_2)(PO_4)(H_2O)_3$
Formula weight (g)	457.07	440.96
Space group	*P*4/*ncc*	*P*4/*ncc*
a (Å)	6.9564(8)	7.005(1)
c (Å)	17.826(4)	16.986(4)
Volume (Å^3)	862.6(2)	833.6(3)
Z	4	4
Calculated density (g/cm^3)	3.659	3.466
Absorption coefficient (mm^{-1})	12.75	12.73
F(000)	860	764
Crystal size (mm)	0.10 × 0.075 × 0.01	0.05 × 0.05 × 0.005
Theta range for data collection	3.72 to 33.15°	3.77 to 34.39°
Limiting indices	$-10 < h < 10$, $-10 < k < 10$, $-27 < l < 26$	$-10 < h < 10$, $-11 < k < 10$, $-26 < l < 26$
Reflections collected / unique	11966 / 831	12204 / 856
Data / restraints / parameters	831 / 2 / 32	856 / 0 / 23
Goodness-of-fit on F^2	1.137	0.910
Final R indices [$I > 2\sigma_I$]	$R_1 = 0.0421$ $wR_2 = 0.1146$	$R_1 = 0.0508$ $wR_2 = 0.1004$
Largest diff. peak and hole	2.316 and -2.000 Å^{-3}	2.365 and -2.726 Å^{-3}

TABLE 3. MISCELLANEOUS CRYSTALLOGRAPHIC INFORMATION FOR *RbP1* AND *NH$_4$P1*

	RbP1	*NH$_4$P1*
Empirical formula	$Rb(NpO_2)(PO_4)(H_2O)_3$	$(NH_4)(NpO_2)(PO_4)(H_2O)_3$
Formula weight (g)	503.44	435.98
Space group	*P*4/*ncc*	*P*4/*ncc*
a (Å)	7.031(4)	6.9843(6)
c (Å)	17.87(2)	18.023(3)
Volume (Å^3)	884(1)	879.2(2)
Z	4	4
Calculated density (g/cm^3)	3.740	3.218
Absorption coefficient (mm^{-1})	17.43	12.02
F(000)	868	748
Crystal size (mm)	0.11 × 0.09 × 0.01	0.15 × 0.12 × 0.005
Theta range for data collection	3.69 to 32.42°	3.69 to 33.35°
Limiting indices	$-10 < h < 10$, $-10 < k < 10$, $-26 < l < 26$	$-10 < h < 10$, $-10 < k < 10$, $-27 < l < 27$
Reflections collected / unique	11165 / 798	13102 / 857
Data / restraints / parameters	798 / 0 / 32	857 / 0 / 30
Goodness-of-fit on *F*2	0.842	1.099
Final R indices [$I > 2\sigma_I$]	$R_1 = 0.0666$, $wR_2 = 0.1549$	$R_1 = 0.0236$ $wR_2 = 0.0594$
Largest diff. peak and hole	4.312 and -3.516 Å^{-3}	3.394 and -1.416 Å^{-3}

containing uranyl polyhedra are well known from minerals of the autunite group (Locock & Burns 2003a, b, Locock *et al.* 2004, 2005). The single symmetrically independent Np^{6+} cation in each structure is strongly bonded to two O atoms, giving linear dioxo $(NpO_2)^{2+}$ cations. The bond lengths of the neptunyl ion in the four structures range from 1.73(2) to 1.77(2) Å, consistent with those in other Np^{6+} compounds. The average bond-length for Np^{6+}–O_{Np} (*Np* = neptunyl) is 1.75(2) Å, whereas Np^{5+}–O bonds are longer, with an average of 1.83(2) Å (Burns *et al.* 1997a). The $(NpO_2)^{2+}$ cation is further coordinated by four atoms of oxygen arranged at the equatorial vertices of a square bipyramid that is capped by the neptunyl ion O atoms. The Np–O_{eq} (*eq*: equatorial) bond-lengths range from 2.273(8) to 2.30(1) Å. One symmetrically independent phosphate tetrahedron is present in each structure, with P–O bond lengths ranging from 1.537(9) to 1.56(1) Å. The autunite-type sheet results from the sharing of vertices between neptunyl square bipyramids and the phosphate tetrahedra, giving the sheet composition $[(NpO_2)(PO_4)]^-$ (Fig. 1).

The K^+, Na^+, and Rb^+ cations are located at sites in the interlayer region, where they are coordinated by O atoms of the neptunyl ions in the sheets on either side, as well as by the H_2O groups located in the interlayer (Fig. 2). In the case of *NH₄P1*, the NH_4^+ cations are held in place by H bonds extending from the NH_4 group to O atoms of the H_2O groups. The K(1) site in *KP1* is coordinated by six atoms of O with bond lengths ranging from 2.87(2) to 3.13(3) Å. In the structure of *NaP1*, the Na^+ cation is bonded to interlayer H_2O groups and O_{Np} atoms, with interatomic distances ranging from 2.34(4) to 2.97(3) Å. The Rb(1) site in *RbP1* exhibits a similar coordination-polyhedron to that of the K(1) site, but the bond lengths are longer owing to the larger size of Rb^+ (Table 5).

DISCUSSION

Compound *KP1* is the Np^{6+} analogue of meta-ankoleite, $K(UO_2)(PO_4)(H_2O)_3$ (Gallagher & Atkin 1966). Meta-ankoleite crystallizes in space group *P*4/*ncc* with *a* 6.99379(2) Å, *c* 17.78397(7) Å, and *V* 869.87 Å^3 (Fitch & Cole 1991). Uramphite, $(NH_4)(UO_2)(PO_4)(H_2O)_3$, is a recognized species (Nekrasova 1957). X-ray

TABLE 4. ATOM COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR *KP1*, *NaP1*, *RbP1* AND *NH₄P1*

	KP1	*NaP1*	*RbP1*	*NH₄P1*
Np(1) *x*	¼	¼	¼	¼
Np(1) *y*	¼	¼	¼	¼
Np(1) *z*	0.2983(1)	0.4478(1)	0.0492(1)	0.0476(1)
Np(1) U_{iso}	0.017(1)	0.021(1)	0.022(1)	0.007(1)
P(1) *x*	¾	¾	¾	¾
P(1) *y*	¼	¼	¼	¼
P(1) *z*	¼	½	0	0
P(1) U_{iso}	0.018(1)	0.029(1)	0.022(2)	0.008(1)
X(1) *x*	0.8420(40)	-0.4820(40)	0.5222(13)	0.5218(4)
X (1) *y*	0.0310(40)	0.1940(30)	0.1761(14)	0.1629(4)
X (1) *z*	0.4183(13)	0.6933(11)	-0.1854(5)	-0.1841(2)
X (1) U_{iso}	0.062(7)	0.075(7)	0.069(4)	0.022(1)
O(1) *x*	¼	¼	¼	¼
O(1) *y*	¼	¼	¼	¼
O(1) *z*	0.3954(10)	0.5500(11)	-0.0494(13)	-0.0501(2)
O(1) U_{iso}	0.025(4)	0.041(4)	0.029(4)	0.014(1)
O(2) *x*	¼	¼	¼	¼
O(2) *y*	¼	¼	¼	¼
O(2) *z*	0.1993(11)	0.3462(11)	0.1475(17)	0.1449(3)
O(2) U_{iso}	0.028(4)	0.041(4)	0.042(6)	0.014(1)
O(3) *x*	0.6840(20)	-0.2560(40)	0.5754(17)	0.5750(4)
O(3) *y*	0.0230(30)	0.4227(13)	0.2826(16)	0.2775(3)
O(3) *z*	0.4418(9)	0.5568(5)	0.0524(7)	0.0507(1)
O(3) U_{iso}	0.044(4)	0.045(2)	0.030(4)	0.010(1)
O(4) *x*	0.7774(17)		0.5222(13)	0.5218(4)
O(4) *y*	0.0755(12)		0.1761(14)	0.1629(4)
O(4) *z*	0.1982(5)		-0.1854(5)	-0.1841(2)
O(4) U_{iso}	0.025(2)		0.069(4)	0.022(1)
O(4A) *x*		-0.482(40)		
O(4A) *y*		0.194(30)		
O(4A) *z*		0.6933(11)		
O(4A) U_{iso}		0.075(7)		
O(4B) *x*		0.8480(30)		
O(4B) *y*		0.2600(70)		
O(4B) *z*		0.1996(11)		
O(4B) U_{iso}		0.049(5)		

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF *KP1*, *NaP1*, *RbP1* AND *NH₄P1*

	KP1	*NaP1*	*RbP1*	*NH₄P1*
Np(1)-O(1)	1.73(2)	1.74(2)	1.76(2)	1.759(4)
Np(1)-O(2)	1.77(2)	1.73(2)	1.76(2)	1.754(5)
Np(1)-O(3) × 4	2.273(8) $^{a, b, c, d}$	2.295(9) $^{e, f, g, h}$	2.30(1) $^{i, j, k}$	2.279(3) $^{l, m, n}$
P(1)-O(3) × 4	1.537(9) $^{c, o, p}$	1.547(9) $^{e, q, r}$	1.56(1) $^{j, s, t, u}$	1.538(2) $^{m, v, w, x}$
K(1)-O(3)	2.87(2) ^{y}			
K(1)-O(2) × 4	2.94(3) $^{a, b, c, d}$			
K(1)-O(3)	3.13(3) ^{p}			
Na(1)-O(4B)		2.34(4) ^{z}		
Na(1)-O(4B)		2.50(4) ^{aa}		
Na(1)-O(4A)		2.59(4) ^{bb}		
Na(1)-O(4B)		2.63(4) ^{cc}		
Na(1)-O(4A)		2.72(3) ^{dd}		
Na(1)-O(4A)		2.72(3) ^{ee}		
Na(1)-O(3)		2.97(3) ^{q}		
Rb(1)-O(1) × 3			3.14(2) $^{i, j, k}$	
Rb(1)-O(2) × 4			3.46(1) $^{o, ff, gg, hh}$	

Symmetry transformations used to generate equivalent atoms1/: a = x - 1/2, -y, -z + 1/2; b = -y, -x + 1, -z + 1/2; c = y + 1/2, x - 1/2, -z + 1/2; d = -x + 1, y + 1/2, -z + 1/2; e = y - 1/2, -x, -z + 1; f = -x, -y + 1, -z + 1; g = x + 1/2, y - 1/2, -z + 1; h = -y + 1, x + 1/2, -z + 1; i = x, -x + 1/2, z; j = -x + 1/2, -y + 1/2, z; k = -y + 1/2, x, z; l = -y + 1/2, x, z; m = -x + 1/2, -y + 1/2, z; n = y, -x + 1/2, z; o = -y + 1, -x + 1, -z + 1/2; p = -x + 3/2, -y + 1/2, z; q = -x - 1/2, -y + 1/2, z; r = -y, x + 1/2, -z + 1; s = -y, x - 1/2, -z; t = y - 1/2, -x + 1, -z; u = x - 1, y, z; v = x - 1, y, z; w = x + 1, y, z; x = -y, x - 1/2, -z; y = -y + 1, x - 1/2, -z + 1; z = -x + 1/2, y, z + 1/2; aa = x - 1, -y + 1/2, z + 1/2; bb = y - 1/2, -x + 1, -z + 1; cc = y - 1/2, x + 1/2, -z + 3/2; dd = -y, x - 1/2, -z + 1; ee = y - 1, -x - 1/2, z; ff = -x + 1, -y, -z; gg = y + 1/2, -x + 1, -z; hh = x - 1/2, y + 1/2, -z.

powder-diffraction data for synthetic uramphite gave the unit-cell parameters *a* 7.02 Å, *c* 18.08 Å, *V* 890.99 Å^3 and space group *P*4/*ncc* (Marković *et al.* 1988). The structure determination of *NH$_4$P1* gives similar unit-cell parameters and space group.

A solid-solution series has been hypothesized among uramphite, meta-ankoleite, and chernikovite, $(H_3O)(UO_2)(PO_4)(H_2O)_3$ (Ross & Evans 1965). The H_3O^+, NH_4^+, and K^+ play similar structural roles in these compounds. All occur randomly distributed over the four general interlayer sites. Similarities of the ionic radii of these species allow the K^+ cation to substitute into the H_2O sites with little strain or disturbance to the structure (Ross & Evans 1965). Structural data obtained for the synthetic analogue of meta-ankoleite indicate a disordered structure at room temperature, with K^+ randomly occupying four of the 16 general sites that are otherwise filled with H_2O groups (Fitch & Cole 1991). Similar disorder of the interlayer cations is found in all four compounds presented here.

The X-ray powder-diffraction patterns for the Np^{6+} phosphates synthesized by Weigel & Hoffman (1976) were indexed and gave unit-cell dimensions that are smaller than the compounds reported here. Powder X-ray-diffraction patterns of the monovalent compounds yielded a tetragonal symmetry with lattice constants *a* 6.93(3) to 6.96(2) Å, *c* 8.76(6) to 9.16(7) Å, *V* 421.2 to 439.9 Å^3 and *Z* = 2. The single-crystal X-ray-diffraction data for the K^+, Na^+, NH_4^+, and Rb^+ compounds require doubling of the unit cell in the *c* direction.

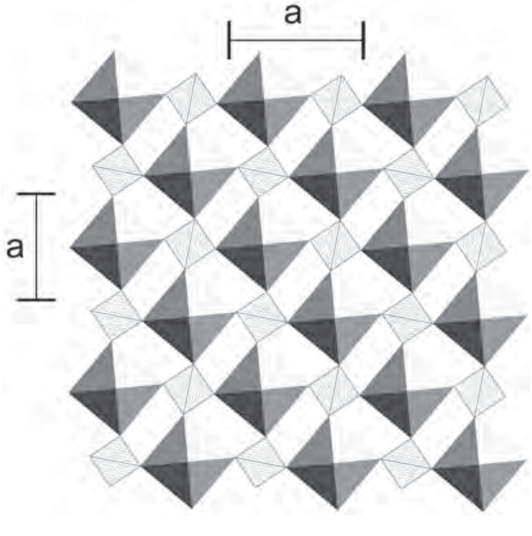

FIG. 1. Polyhedral representation of the neptunyl phosphate sheets in $X(NpO_2)(PO_4)(H_2O)_3$, $X = K^+, Na^+, Rb^+, NH_4^+$. The neptunyl polyhedra (shown in gray) share corners with the phosphate tetrahedra to form the autunite-type sheet.

The compounds synthesized by Weigel & Hoffman (1976) were formed by the reaction of $Np^{6+}O_2(NO_3)_2$ with a H_3PO_4 solution. Our synthesis began with $Np^{5+}O_2^+$ in 1 M HCl solution combined with apatite or H_3PO_4 as the phosphate source. The oxidation of Np^{5+} to Np^{6+} most likely occurred by the disproportionation reaction:

$$2\ NpO_2^+ + 4\ H^+ \rightarrow Np^{4+} + NpO_2^{2+} + 2\ H_2O.$$

The equilibrium of the disproportionation reaction is strongly dependent on the acid concentration, with K = 4 × 10^{-7} in 1 M perchloric acid (Fahey 1986). Our compounds were synthesized in solutions with a pH of 0 to 0.5, indicating that the disproportionation reaction is likely. In addition, the presence of complexing agents of Np in solution may further shift the equilibrium of this reaction. Substitution of 1 M $HClO_4$ for 1 M H_2SO_4 shifts the equilibrium constant from 4 × 10^{-7} to 2.4 × 10^{-2} (Fahey 1986). In studies concerning the electrode reaction-kinetics of NpO_2^+/NpO_2^{2+}, Yamamura *et al.* (2005) found that the reaction is irreversible in sulfuric

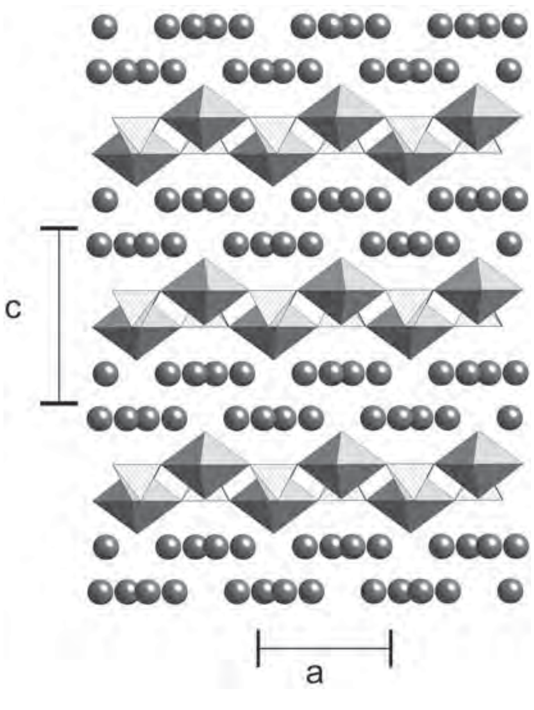

FIG. 2. Projection of the structure of $X(NpO_2)(PO_4)(H_2O)_3$, $X = K^+, Na^+, Rb^+, NH_4^+$ along [100] showing the interlayer sites (illustrated as spheres). The interlayer cations (K^+, Na^+, Rb^+, or NH_4^+) occupy 25% of the sites, and the remainder is occupied by H_2O groups.

and acetic acid and reversible in perchloric, nitric and hydrochloric acid. The redox behavior of Np in phosphoric acid has not been studied, but may also shift the equilibrium of the reaction and affect the disproportionation of Np^{5+} in solution.

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