Structure Determination of Uranium Halogenide Phosphates UXPO$_4 \cdot$ 2H$_2$O (X = Cl, Br) from Powder Diffraction Data

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The structure of the two isostructural uranium halogenide phosphates UClPO$_4 \cdot$ 2H$_2$O and UBrPO$_4 \cdot$ 2H$_2$O was determined from conventional monochromatic X-ray powder diffraction data. The crystal symmetry is tetragonal (space group *I4/m*, *Z* = 8) with lattice constants *a* = 14.631(2) and *c* = 6.662(1) Å for the chloride phase and *a* = 14.7480(7) and *c* = 6.6810(4) Å for the bromide compound. The structure solution was found from Patterson and Fourier syntheses and refinements by the Rietveld method (38 parameters, 760 reflections) converged to R_F = 0.03 for both examples. The configuration around uranium(IV) is derived from the typical pentagonal bipyramid formed by two water oxygen atoms, four phosphate oxygen atoms, and one halide atom. Due to steric considerations, the halide atom deviates from the pentagonal base, leading to a repulsion of the two apical oxygen atoms. The interatomic distances and angles are usual and agree with the values found from neutron diffraction in related compounds. The discrete UX$_1$O$_6$ (X = Cl, Br) polyhedra are linked together by phosphate tetrahedra which are viewed as the unique bonding units in the structure. This arrangement results in a 3D network based on two kinds of tunnels along [001]. The widest tunnel contains the X atoms, while half of the water molecules lie in the smallest tunnel. © 1997 Academic Press

INTRODUCTION

Uranium phosphates have been studied extensively in the past; however, significant clarifications on the chemistry of these compounds were reported only recently (1). This is the consequence of the structure determination of a few phases available only in a powder form, which was made possible with the advances of the powder diffraction method that have occurred in recent years (2). Indeed, modern powder diffraction has shed new light on the chemistry of uranium phosphates in revealing the crystal structure and the

chemical formula of two major phases: the mixed-valence uranium–uranyl phosphate U(UO$_2$)(PO$_4$)$_2$ (3) and diuranium oxide phosphate U$_2$O(PO$_4$)$_2$ (4). A thorough chemical study (1, 5) has shown that the preparation of these two materials results from an intermediate phase, uranium chloride phosphate tetrahydrate, whose behavior with temperature depends on the synthesis atmosphere. When it is heated in air at 1170°C, uranium–uranyl phosphate is obtained (3, 5); when heated at 1350°C in argon, the diuranium oxide phosphate is formed (4, 5). Additionally, the uranium chloride phosphate is transformed into an uranium hydroxide phosphate by hydrolysis, and the reaction is reversible (5).

Uranium chloride phosphate was originally formulated with four water molecules but it has been shown that three water molecules are lost easily in a dry atmosphere without a significant change in the powder diffraction pattern (5). This uranium halogenide phosphate, a compound important in the chemistry of uranium phosphates, has been obtained in powder form. The present study deals with the structure determinations of uranium chloride phosphate and the isostructural bromide phosphate.

EXPERIMENTAL

Sample Preparation

Chemical reagents were supplied by Merck, Aldrich, and Prolabo, except the uranium metal which was obtained from our own laboratory source. The uranium chloride phosphate hydrate was prepared at room temperature by soft chemistry methods, as described in detail elsewhere (5). The chemical analysis of this sample showed that the general chemical formula is UClPO$_4 \cdot n$H$_2$O, with $1 \leq n \leq 4$ depending on the vapor pressure of water present. However,

the structural study reported here reveals that the stable phase in air at 25°C is the dihydrate form.

A similar synthesis was applied for the preparation of uranium bromide phosphate hydrate. In this procedure about 10 g of metallic uranium was dissolved in 50 cm³ of concentrated hydrobromic acid. The solution was concentrated by evaporation and then centrifugated. Uranyl ion was not detected in the UV–visible spectrum of this solution. The concentration of uranium ($1.35\ M$), was determined by spectrophotometry. Phosphoric acid ($15\ M$) was added dropwise to a uranium(IV) hydrobromic solution in the molar ratio $U/PO_4 = 1$ (with 2–3% excess of phosphoric acid). In contrast to the synthesis of the uranium chloride phosphate, the formation of a gelatinous precipitate was observed with the bromide product. The material was evaporated on a sand bath at 80°C, the residue was then washed with ethanol to remove excess H_3PO_4 and HBr. It was then centrifuged and dried in air.

For the determination of the U(IV) content, the compound was dissolved in a 3-M solution of H_2SO_4 in the presence of hydrogen peroxide (6). The resulting uranyl solution was analyzed by spectrophotometry at $\lambda_{max} = 420$ nm (experimental: 47.6%). The bromine content was analyzed by conventional potentiometric titration with $AgNO_3$ (6), after dissolution of the sample in nitric acid ($1\ M$) (experimental: 16.0%). The phosphate content was found by a gravimetric method (experimental: 18.8%), and the water amount was calculated by difference (experimental: 17.3%). The results of the chemical analyses were in accordance with the formula $UBrPO_4 \cdot 5H_2O$, which corresponds to the calculated values: 47.22% for U, 16.07% for Br, 18.85% for PO_4, and 17.86% for H_2O. Nevertheless, uranium bromide phosphate was found to be sensitive to the ambient conditions. The structural study reported here reveals that the stable phase in air, at 25°C, is the dihydrated form.

Similar IR spectra, as well as absorption spectra in the UV–visible region, were observed for uranium bromide phosphate and uranium chloride phosphate. Figure 1 shows the analogies between the IR spectra of the two phases, recorded with an Hitachi I-2001 spectrophotometer (4000–400 cm⁻¹) using samples of 2–3 wt % in KBr. The assignment of the frequencies has been discussed for the chloride phase (Table 3 in Ref. 5).

Attempts to obtain the related iodide compound, using a similar synthesis method, were unsuccessful. In all of these cases, the uranium hydroxide phosphate was obtained.

X-Ray Powder Diffraction

For structure analysis, X-ray powder diffraction data were collected, at 25°C, with a Siemens D500 high-resolution diffractometer using the parafocusing Bragg–Brentano geometry. Monochromatic $CuK\alpha_1$ radiation ($\lambda = 1.5406$ Å)
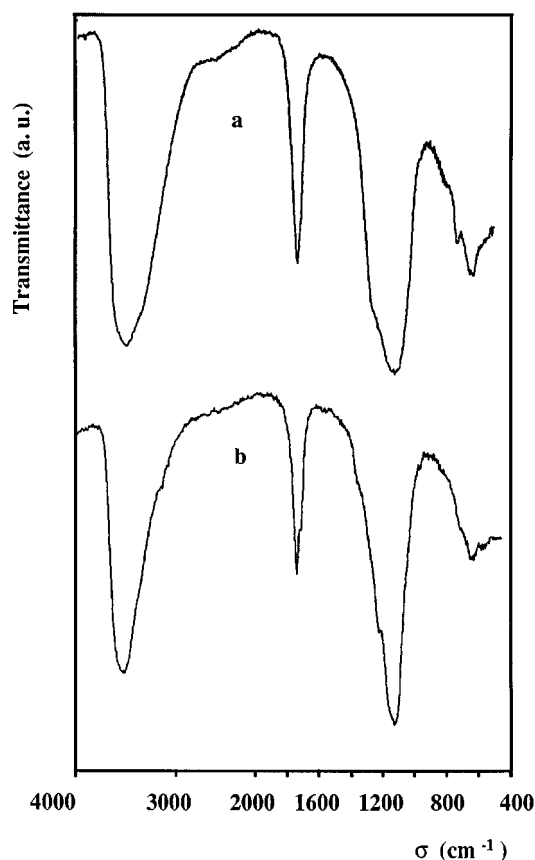

FIG. 1. Infrared absorption spectra of (a) $UClPO_4 \cdot 2H_2O$ and (b) $UBrPO_4 \cdot 2H_2O$.

was produced by means of an incident-beam curved-crystal germanium monochromator and asymmetric focusing. The characteristics of this powder diffractometer and its instrument resolution curve, $FWHM = 0.065°(2\theta)$ at $40°(2\theta)$), have been discussed elsewhere (7). The two diffraction patterns were scanned over the angular range $7–140°(2\theta)$ with a step length of $0.02°(2\theta)$ and a fixed counting time, $35\ sec \cdot step^{-1}$. The interrogation of the ICDD-PDF database (8) using the Socabim search/match program (PC software package DIFFRAC-AT supplied by Siemens) did not reveal isostructural chemically related compounds. The fitting program PROFILE, from Socabim, was used for the extraction of the angular positions of the Bragg reflections.

STRUCTURE DETERMINATION

Indexing

The powder diffraction patterns were indexed with the program DICVOL91 (9), using the first 20 lines, with an absolute error of $0.03°(2\theta)$ on peak positions. A tetragonal unit cell was obtained for both compounds, with the figures

of merit $M_{20} = 68$ and $F_{20} = 96(0.0048, 43)$ for $UClPO_4 \cdot 2H_2O$ and $M_{20} = 73$ and $F_{20} = 112(0.0042, 43)$ for $UBrPO_4 \cdot 2H_2O$. No isostructural material was found by interrogating the NIST-CDF database (10). The powder data available in the two patterns were reviewed from these solutions and the unit cell parameters were refined by a least-squares procedure (11). The final parameters are

$$UClPO_4 \cdot 2H_2O: a = 14.631(2), c = 6.662(1) \text{ Å},$$

$$V = 1426.1(3) \text{ Å}^3 [M_{20} = 50 \text{ and } F_{30} = 74(0.0126, 32)].$$

$$UBrPO_4 \cdot 2H_2O: a = 14.7480(7), c = 6.6810(4) \text{ Å},$$

$$V = 1453.1(1) \text{ Å}^3 [M_{20} = 122 \text{ and } F_{30} = 151(0.0052, 38)].$$

The powder diffraction data for both compounds have been deposited with the ICDD (12). Reflections hkl with $h + k + l = 2n + 1$ were not detected in the diffraction line list, which is in agreement with space groups $I4$, $I\bar{4}$, and $I4/m$.

Structure Solution and Refinement

The *ab initio* structure determination was carried out from the powder diffraction pattern of $UClPO_4 \cdot 2H_2O$ assuming the centrosymmetric space group $I4/m$. From pattern decomposition with the iterative procedure available in the program FULLPROF (13), 244 structure-factor moduli were extracted in the angular range $10–80°(2\theta)$. They were used as input data in the program SHELXS-86 (14) for the calculation of a three-dimensional Patterson synthesis from which the unique U atom (0.39, 0.18, 0) could be located in the special position $8m$. A subsequent Fourier map was generated with the crystal structure refinement program SHELXL93 (15) from which the positions of one chlorine atom, one phosphate group, and one water molecule were found. Surprisingly, the Cl atom is located on the general position $16i$, which is not in accordance with the formula $UClPO_4 \cdot 2H_2O$ if $Z = 8$. A Fourier calculation assuming space group $I\bar{4}$, in which the multiplicity of the general position is 8, showed also two sets of positions for Cl atom. In order to investigate further this observation it was decided to study the related bromide phase, where the contrast between U and halogen atoms is more similar. The latter analysis resulted in the same conclusion about the Br positions. Consequently, the structure of both phases was refined with the space group $I4/m$ assuming an occupation rate of 0.5 for X atoms ($X = Cl$, Br) in the Wyckoff position $16i$. At this stage, the structure still corresponded to a monohydrated uranium halide phosphate with an unusual sixfold coordination of U atom. The Rietveld refinements carried out over the complete angular range were characterized by the reliability factors $R_p = 0.114$, $R_F = 0.041$ and $R_p = 0.098$, $R_F = 0.042$ for the chloride and bromide compounds, respectively. However, a final difference Fourier

map, generated from the powder data up to $125°(2\theta)$, revealed an electron density residue, with low magnitude, consistent with the presence of one additional O atom around the U atom. This oxygen was identified as belonging to a water oxygen atom (Ow2) located roughly at 2.60 Å from the U atom in the mirror plane, similar to the water molecule already established (Ow1). This additional water molecule improved significantly the pattern profile fitting and provided a coordination of seven for the U atom, suggesting the formula $UXPO_4 \cdot 2H_2O$ ($X = Cl$, Br). Due to the high contrast between light atoms and U, soft-constraints were imposed on the distances within the phosphate groups in the final Rietveld refinements. Crystallographic details and agreement indices for the two studies are reported in Table 1. The final Rietveld refinements, based on the 760 reflections available in the range $10–140°(2\theta)$, involved 38 parameters including 1 scale factor, 18 atomic coordinates, and 5 isotropic temperature factors (thermal parameters for oxygen atoms having the same chemical function were constrained in the same manner). The 14 remaining refined parameters were the usual profile parameters. Figs. 2a and 2b display the final Rietveld plots for $UClPO_4 \cdot 2H_2O$ and $UBrPO_4 \cdot 2H_2O$, respectively. Final atomic positions and thermal displacement parameters are given in Table 2, and selected bond distances and angles are given in Table 3. It is worth noting that the precision of the results is comparable with those previously derived from X-ray powder diffraction studies of $U(UO_2)(PO_4)_2$ (3) and $U_2O(PO_4)_2$ (4), though the phosphate group is slightly more precise, as expected from the geometric constraints applied to the tetrahedron. In the structure refinement of the two final compounds, neutron powder diffraction data were used to obtain an improved precision on the atomic positions of the light atoms. Unfortunately, attempts to prepare completely deuterated phases of the hydrated uranium

TABLE 1
Details of Rietveld Refinements for $UClPO_4 \cdot 2H_2O$ (a) and $UBrPO_4 \cdot 2H_2O$ (b)

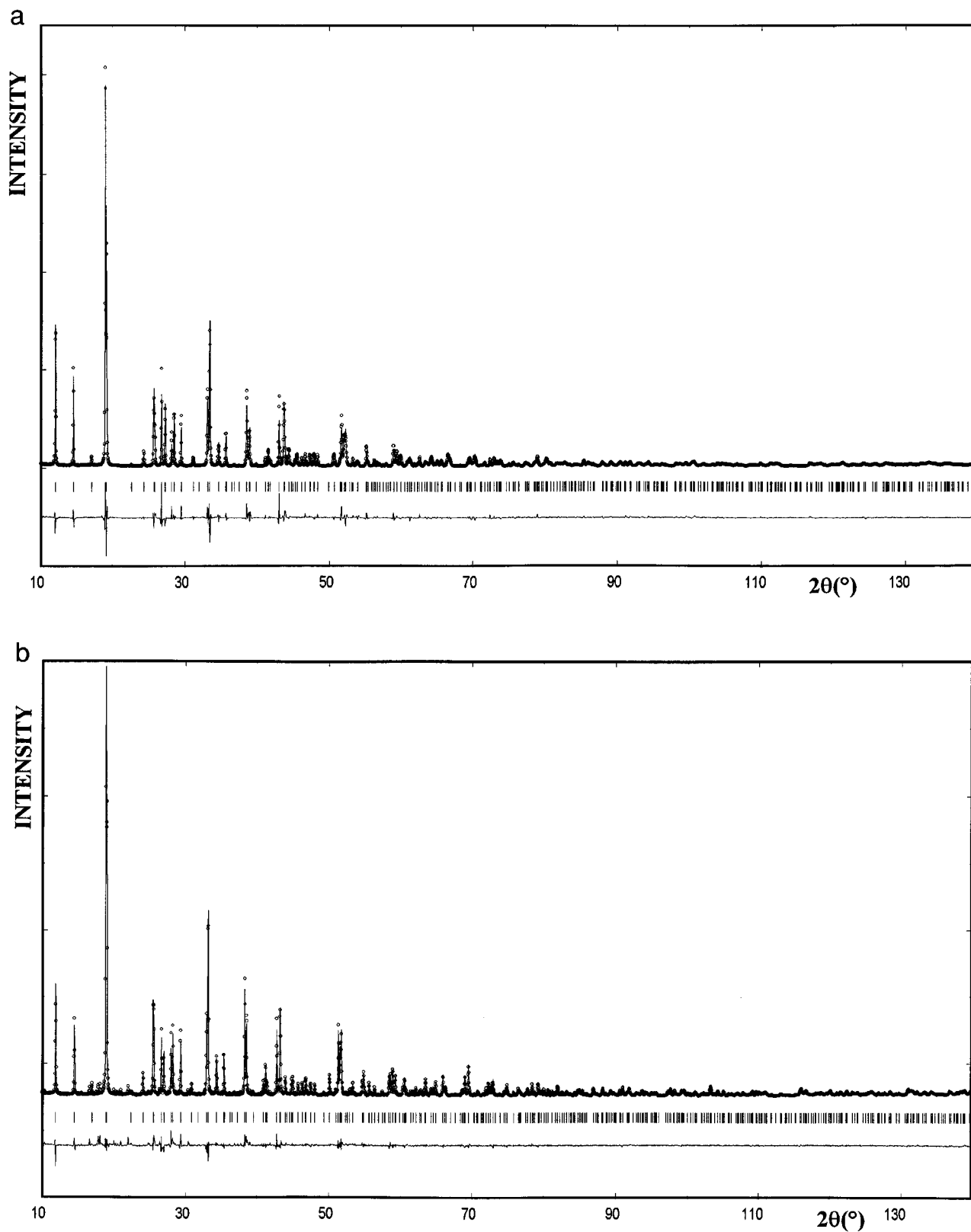|		
Space group	$I4/m$	
Z	8	
Wavelength (Å)	1.5406	
2θ range (°)	10–140	
Step scan increment (°2θ)	0.02	
Number of atoms	8	
Number of reflections	761	
Number of structural parameters	24	
Number of profile parameters	14	
	a	*b*
R_F	0.030	0.030
R_B	0.056	0.053
R_p	0.101	0.084
R_{wp}	0.132	0.119

FIG. 2. Final Rietveld plots for the two uranium halide phosphate dihydrates from monochromatic X-ray powder diffraction. The upper trace shows the observed data as dots, while the calculated pattern is shown by solid line. The lower trace is the plot of the difference (observed minus calculated): (a) $UClPO_4 \cdot 2H_2O$ (maximum intensity counts: 24000) and (b) $UBrPO_4 \cdot 2H_2O$ (maximum intensity counts: 13000).

TABLE 2
Fractional Atomic Coordinates and Thermal Isotropic Parameters for UClPO$_4 \cdot$ 2H$_2$O (a) and UBrPO$_4 \cdot$ 2H$_2$O (b)

Atom		x	y	z	B_{iso} (Å^2)
U	a	0.3896(1)	0.2178(1)	0	1.14(4)
	b	0.38869(9)	0.21647(9)	0	1.18(3)
P	a	0.6375(7)	0.1837(7)	0	1.8(2)
	b	0.6387(6)	0.1807(6)	0	1.1(2)
X^*	a	0.4631(9)	0.3552(8)	0.255(2)	1.0(2)
	b	0.4616(5)	0.3602(4)	0.2681(7)	2.0(1)
O1	a	0.375(1)	0.161(1)	0.316(2)	3.1(3)^a
	b	0.3721(9)	0.164(1)	0.307(2)	2.3(3)^c
O2	a	0.534(2)	0.183(1)	0	3.1(3)^a
	b	0.535(1)	0.178(2)	0	2.3(3)^c
O3	a	0.278(2)	0.322(2)	0	3.1(3)^a
	b	0.276(2)	0.319(1)	0	2.3(3)^c
Ow1	a	0.244(2)	0.122(2)	0	1.9(5)^b
	b	0.243(2)	0.118(2)	0	3.5(2)^d
Ow2	a	0.409(2)	0.042(2)	0	1.9(5)^b
	b	0.409(2)	0.038(2)	0	3.5(5)^d

Note. Atom marked with * has an occupation number of 0.5.

$^{a-d}$ Some parameters were allowed to vary in the same manner.

halide phosphates by isotopic exchange (H$_2$O/D$_2$O) for neutron diffraction were unsuccessful.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 3 is a projection of the structure of UXPO$_4 \cdot$ 2H$_2$O (X = Cl or Br) along [001]. All atoms, except O1 and X, lie on the mirror plane (001) (O1 and X are then superimposed with their symmetric equivalent with respect to m). The four vertices of the phosphate tetrahedron are linked to four uranium atoms (Fig. 4). Two vertices, O2 and O3, connect the discrete UX_1O$_6$ polyhedra in the plane, while O1 and O1^I ensure their connection along the c axis. From this arrangement, which involves PO$_4$ tetrahedra as bonding units, two types of tunnels result along [001] (Fig. 3). The widest tunnel, centered on the coordinates 0, 0 and 1/2, 1/2, contains the X atoms. Four U–O2, four U–O3, and four O2–O3 edges display a dodecahedral section (effective diameter $\approx$ 4 Å). The smallest tunnel, centered on 1/2, 0 and 0, 1/2, is characterized by a pseudo-square section (edge $\approx$ 2.3 Å) and contains the bonded water molecules Ow2.

Figure 5 represents the environment of the sevenfold coordinated uranium atom (Table 3). The phosphate oxygens, O2 and O3, and the water molecules, Ow1 and Ow2, form four independent metal–oxygen bonds. The three remaining bonds involve the atoms located out of the mirror plane (i.e., O1, O1^I) and one halogen atom X. The U–O distances range from 2.18(2) to 2.59(2) Å for X = Cl, and from 2.20(1) to 2.65(5) Å for X = Br. As expected, the longest distances are related to U–Ow1 and U–Ow2 bonds. The

TABLE 3
Selected Bond Distances (Å) and Angles (°) with Their Standard Deviations for UClPO$_4 \cdot$ 2H$_2$O (a) and UBrPO$_4 \cdot$ 2H$_2$O (b)

Within the UX_1O$_6$ polyhedra		
	a	b
U–O1	2.28(1)	2.20(1)
U–O1^I	2.28(1)	2.20(1)
U–O2	2.18(2)	2.23(2)
U–O3	2.23(2)	2.25(2)
U–Ow1	2.55(3)	2.60(3)
U–Ow2	2.59(2)	2.65(3)
U–(X, X^I)	2.84(1)	2.98(6)
O1–U–O1^I	135(2)	137(2)
O3–U–Ow1	76(1)	76(1)
Ow1–U–Ow2	63(1)	62(1)
Ow2–U–O2	70(1)	69(1)
(X, X^I)–U–O2	78(8)	80(6)
(X, X^I)–U–O3	78(8)	78(7)

Within the PO$_4$ groups		
	a	b
P–O1^{II}	1.53(2)	1.55(1)
P–O1^{III}	1.53(2)	1.55(1)
P–O2	1.51(2)	1.53(2)
P–O3^{IV}	1.51(2)	1.53(2)
O1^{II}–P–O1^{III}	106(2)	112(2)
O1^{II}–P–O2	103(2)	103(2)
O1^{III}–P–O2	103(2)	103(2)
O1^{II}–P–O3^{IV}	115(2)	111(3)
O1^{III}–P–O3^{IV}	115(2)	111(3)
O2–P–O3^{IV}	113(3)	115(4)

Possible hydrogen bonds		
	a	b
Ow2—Ow2^{VII}	2.94(3)	2.92(4)
U–Ow2—Ow2^{VII}	121(2)	119(2)
Ow1—$X^{V,VI}$	3.19(3)	3.17(3)
U–Ow1—$X^{V,VI}$	141(2)	144(2)

Note. Symmetry code: I, x, y, $-z$; II, $0.5 + y$, $0.5 - x$, $0.5 - z$; III, $0.5 + y$, $0.5 - x$, $z - 0.5$; IV, $1 - y$, x, z; V, $0.5 - y$, $x - 0.5$, $0.5 - z$; VI, $0.5 - y$, $x - 0.5$, $z - 0.5$; VII, $1 - x$, $-y$, z.

corresponding mean values, 2.35 and 2.36 Å, respectively, are very close to those found from neutron diffraction for the UO$_7$ polyhedra in the structure of uranium phosphates containing U(IV), e.g., U(UO$_2$)(PO$_4$)$_2$ (2.32 Å) and U$_2$O (PO$_4$)$_2$ (2.33 Å) (3, 4). The unique U–Cl and U–Br distances are 2.84(1) and 2.98(6) Å, respectively. Although very few structures of uranium(IV) halides are known, these values may be compared to both those found for the seven-coordinated U^{IV} in UOCl$_2$ (16), where the U–Cl distances spread from 2.70 to 2.86 Å, and for the two sets of U–Cl distances in the coordination dodecahedron observed in UCl$_4$ (17) (2.87 and 2.64 Å). In uranium tetrabromide UBr$_4$
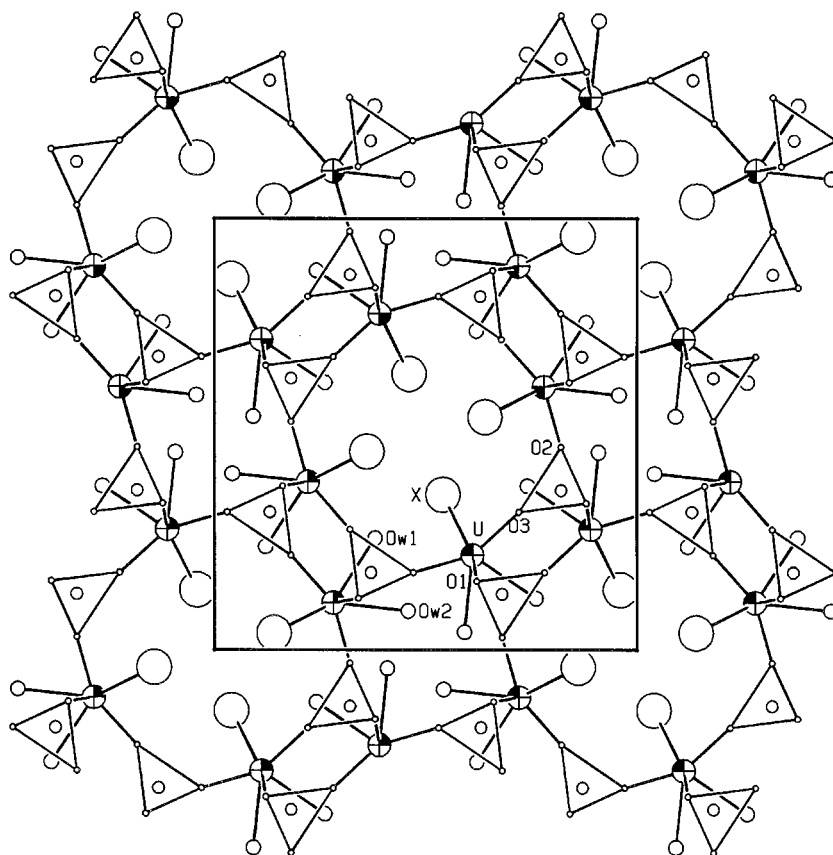
FIG. 3. Representation of the structure of $UXPO_4 \cdot 2H_2O$ ($X =$ Cl, Br) projected along [001].

(18), whose structure has been described by UBr_7 pentagonal bipyramid units, the equatorial U–Br distances range from 2.85 to 2.95 Å, whereas the distances from U to apical bromines are shorter, with the values 2.61 and 2.78 Å.

As clearly displayed in Fig. 5, the environment of the heavy atom may be viewed as a distortion of the known pentagonal bipyramidal arrangement (D_{5h}) found in a number of well-defined uranium (IV, VI) compounds, e.g., UBr_4
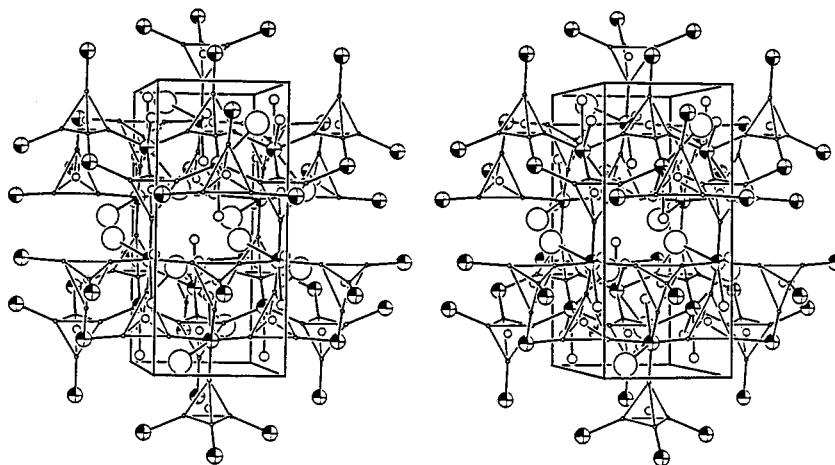

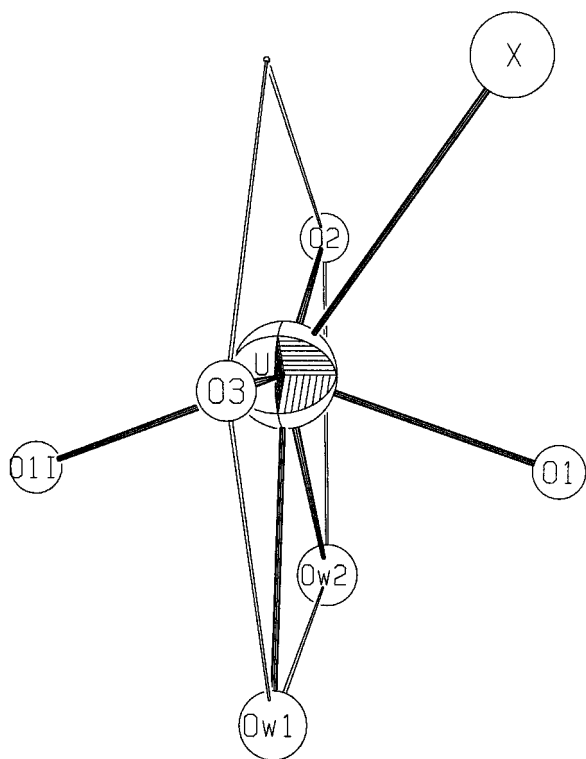**FIG. 4.** ORTEP stereoscopic view of $UXPO_4 \cdot 2H_2O$ ($X =$ Cl, Br) showing the phosphate coordination.

FIG. 5. Representation of the seven-fold coordination environment around the uranium atom in the structure of $UClPO_4 \cdot 2H_2O$ and $UBrPO_4 \cdot 2H_2O$ emphasizing the distortion of the polyhedron from the ideal bipyramidal pentagonal shape.

From the Ow—O distances smaller than 3.1 Å (and the U–Ow—O angles greater than 95°, it is possible to suggest possible hydrogen bonds, according to Baur criteria (22), in the mirror plane involving only Ow2 (2.94 and 2.92 Å for $X = Cl$ and Br, respectively) and then running inside the small tunnels. The O–H—X ($X = Cl$, Br) bonds are as found in $UOCl_2 \cdot H_2O$ (23), they involve only Ow1 and they may be taken as being weak hydrogen bonds since the Ow1—Cl and Ow1—Br distances are 3.19 and 3.17 Å, respectively (24).

As reported above, the phosphate group is a major bonding unit in this new structure type of uranium(IV) phosphates, since there is no additional connection between the discrete UX_1O_6 polyhedra except for the hydrogen bonding. Indeed, by comparison with three structures recently reported (i.e., $U(UO_2)(PO_4)_2$ (3), $U_2O(PO_4)_2$ (4), and $CaU(PO_4)_2$ (25), in which bidentate phosphate groups are observed) the four corners of the PO_4 tetrahedron in $UXPO_4 \cdot 2H_2O$ are also shared with four U polyhedra.

The crystal structure of uranium chloride and bromide phosphates $UXPO_4 \cdot 2H_2O$ ($X = Cl$, Br) presents an interesting topology which explains both the reversible ionic exchange properties (chloride/hydroxyl group) reported elsewhere (5) and the variation in the degree of hydration found for different partial pressure of water vapor. These two features arise from the presence of tunnels in the c axis direction, which provide a way for the reversible migration of ions or water molecules.

(18), UO_2Cl_2 (19), $U(UO_2)(PO_4)_2$ (3), $U_2O(PO_4)_2$ (4), β-UO_2SO_4 (20), and $UO_2C_2O_4 \cdot 3H_2O$ (21). This distortion is a consequence of the larger size of the halogen atom with respect to the four oxygen atoms that lie in the same plane. In fact, too-short X–O (O2, O3) distances (2.72, 2.75 Å ($X = Cl$) and 2.89, 2.81 Å ($X = Br$)) would be obtained if the halogen atom was located in the pentagonal plane (shown in Fig. 5). However, it should be noted that these hypothetical values agree well with the O–O bond lengths found in the U^{IV} pentagonal bipyramid of $U(UO_2)(PO_4)_2$ (2.77 Å) (3). Similarly, the U–X distances would become too short (2.28 Å ($X = Cl$) and 2.37 Å ($X = Br$)), but would be in accordance with the mean U^{IV}–O values calculated from the equatorial oxygens of $U^{IV}O_7$ polyhedra in $U(UO_2)(PO_4)_2$ (2.376 Å) (3) and $U_2O(PO_4)_2$ (2.404 Å). Consequently, the halogen atom is logically deviated to one or the other side of the plane (distances normal to the plane are 1.70 and 1.79 Å for $X = Br$ and Cl, respectively). Similarly, for steric considerations, the two apical O atoms (O1 and O1^I) are repulsed by the X atom; consequently, the angle O1–U–O1^I is far from 180° (135° and 137°). This characteristic angle is 176.5° for the "ideal" geometry observed in $U(UO_2)(PO_4)_2$ (3) or $U_2O(PO_4)_2$ (4).

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