Precipitation of $\text{NH}_4\text{UO}_2\text{PO}_4\cdot3\text{H}_2\text{O}$—Solubility and Structural Comparison with Alkali Uranyl(2 +) Phosphates

Introduction

The formation of uranyl(2+) phosphates ($\text{UO}_2\text{HPO}_4\cdot4\text{H}_2\text{O}$ and ($\text{UO}_2)_3(\text{PO}_4)_2\cdot8\text{H}_2\text{O}$) and alkali uranyl(2+) phosphates ($\text{MUO}_2\text{PO}_4\cdot\text{nH}_2\text{O}$; $M=$Li, Na, K, Rb, Cs; $4\geq n > 2.5$) by spontaneous precipitation from supersaturated solutions and the stability of uranyl phosphate complexes has been described in some of our previous papers [1-5]. These compounds are important for the production of uranium from low-grade phosphate ores and in fuel reprocessing [6-8].

Precipitation conditions of ammonium uranyl(2+) phosphate can be of interest for the separation of uranium as a secondary product in the production of monoammonium phosphate (additive of fertilizers) [9]. Three polymorphs of $\text{NH}_4\text{UO}_2\text{PO}_4\cdot3\text{H}_2\text{O}$ are known [10,11]. The solubility product of one of these compounds has been

Volume 93 Number 4 July-August 1988

Journal of Research of the National Bureau of Standards

Precipitates formed in the system $\text{UO}_2(\text{NO}_3)_2\cdot2\text{NH}_2\text{OH}-\text{H}_2\text{PO}_4\cdot\text{H}_2\text{O}$, aged for 30 days at 298 K, were studied. The precipitates were characterized by chemical and thermogravimetric analyses, x-ray powder diffraction, infrared spectroscopy, polarized light microscopy, and by their fluorescent properties. The precipitation boundary was established tindallometrically and microscopically. On the basis of these measurements, the stability conditions, structural parameters, and solubility of the tetragonal polymorph of $\text{NH}_4[\text{UO}_2\text{PO}_4]\cdot3\text{H}_2\text{O}$ were determined. This compound shows a close structural relationship with $\text{H}_3[\text{UO}_2\text{PO}_4]\cdot3\text{H}_2\text{O}$ (space group $P4/ncc$) and alkali uranyl(2+) phosphates polyhydrates $\text{M}[\text{UO}_2\text{PO}_4]\cdot\text{nH}_2\text{O}$ ($\text{n=4 for M=Li;}$ $\text{n=3 for M=Na, K, Rb and n=2.5 for M=Cs}$). The unit-cell dimensions determined for $\text{NH}_4\text{UO}_2\text{PO}_4\cdot3\text{H}_2\text{O}$ are: $a=b=7.02$ Å, $c=18.08$ Å ($P4/ncc$).

The thermodynamic solubility product constant, $K_s=a(\text{NH}_4^+)\times a(\text{UO}_2^{2+})\times a(\text{PO}_4^{3-})$, for $\text{NH}_4\text{UO}_2\text{PO}_4\cdot3\text{H}_2\text{O}$ was determined: $\log K_s = -26.50\pm0.09$. The $K_s$ values of $\text{M}[\text{UO}_2\text{PO}_4]\cdot\text{nH}_2\text{O}$ (at ionic strength, $I=0.23$ mol dm$^{-3}$) calculated from previously published experimental data by using correct stability constants of uranyl(2+) phosphate complexes are: $\log K_s = -22.61\pm0.08$ for $\text{M=Na}$; $\log K_s = -23.92\pm0.12$ for $\text{M=K}$; $\log K_s = -24.13\pm0.19$ for $\text{M=Rb}$; $\log K_s = -23.80\pm0.20$ for $\text{M=Cs}$, and $\log K_s = -24.74\pm0.10$ for $\text{M=NH}_4$, showing that $\text{NH}_4\text{UO}_2\text{PO}_4\cdot3\text{H}_2\text{O}$ is less soluble than corresponding alkali uranyl(2+) phosphates.

Key words: alkali uranyl(2+) phosphates; ammonium uranyl(2+) phosphate; precipitation; solubility product; unit-cell dimensions; x-ray diffraction pattern.

Accepted: April 4, 1988

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formed by using classical analytical methods [12,13] and at an ionic strength of 0.23 mol dm$^{-3}$ [14] using inaccurate association and stability constants for phosphoric acid and uranyl phosphate complexes, respectively.

This paper describes the formation of different precipitates in the system UO$_2$(NO$_3$)$_2$-NH$_4$OH-H$_3$PO$_4$-H$_2$O at 298 K. These precipitates were characterized by chemical and physical methods. The stability region for the precipitated tetragonal structure of this polymorph was compared to that calculated in this paper using a proper set of constants as a function of reactant concentrations, and its solubility product constant was determined. The structure of this polymorph was compared to that of hydrogen uranyl(2+)phosphate [2,15] and alkali uranyl(2+)phosphates [3,4]. The solubility data for NH$_4$UO$_2$PO$_4$·3H$_2$O and MUO$_2$PO$_4$·nH$_2$O obtained by Vesely, Pekarek, and Abbrent [14] were recalculated in this paper using a proper set of constants to obtain solubility products, and they were compared with our data.

**Experimental Section**

Stock solutions were prepared by dissolving the following P.A. chemicals in triply distilled water: UO$_2$(NO$_3$)$_2$, H$_3$PO$_4$, and NH$_4$OH (Merck, Darmstadt). Standardization of solutions was performed by using classical analytical methods [16,17].

Precipitation in the system UO$_2$(NO$_3$)$_2$-NH$_4$OH-H$_3$PO$_4$-H$_2$O (at 298 K) was performed at constant uranyl(2+)nitrate concentration, 1×10$^{-3}$ mol dm$^{-3}$; the concentrations of NH$_4$OH varied from 5×10$^{-2}$ to 3.2 mol dm$^{-3}$ and phosphoric acid from 5×10$^{-3}$ to 1 mol dm$^{-3}$. The samples were prepared by mixing UO$_2$(NO$_3$)$_2$ solution with an equal volume of NH$_4$OH·H$_3$PO$_4$ solution. Approximately 400 samples were prepared to define precipitation and phase boundaries. One day and 30 days after mixing the reactant solutions, the samples were examined in detail. The pH was measured with the Radiometer equipment: electrode GK 2302 C and pH-meter Mo 26. The precipitation boundary (the line that separates the region of precipitation from the region of clear solutions) was determined tynndallometrically and microscopically. The morphology of the precipitates was examined in white, polarized and UV light under an Orthoplan microscope (Leitz, Wetzlar). Selected precipitates were characterized by means of chemical and thermogravimetric analyses (TGA), x-ray powder diffraction patterns (XRD) and infrared (IR) spectra. The phase boundaries (lines that separate the regions in which different solid phases precipitate) were determined on the basis of these data.

The solid phase was chemically analyzed for uranium, phosphorus and nitrogen. Uranium was precipitated with (NH$_4$)$_2$HPO$_4$ heated at 1373 K and weighed as U$_2$O$_3$P$_2$O$_7$ [18]. Phosphorus was determined gravimetrically by precipitation with ammonium molybdate [19] and spectrophotometrically as phosphovanadomolybdatoc complex [19]. Nitrogen was determined by chemical microanalysis. The water content was determined thermogravimetrically (Cahn RG recording electromicrobalance).

X-ray diffraction patterns were recorded on a Phillips x-ray diffractometer with a proportional counter, using graphite monochromated CuK$\alpha$ radiation. The x-ray patterns were calibrated with graphite as the internal standard [10] with a unitcell $a = 2.463$ Å, $c = 6.714$ Å ($\lambda = 1.54178$ Å). Relative intensities, $I_{rel}$ are given as peak heights. IR spectra (600 to 3600 cm$^{-1}$) were obtained using a Perkin-Elmer Mo-221 spectrophotometer and the standard KBr pellet technique.

**Results**

The concentration diagram of UO$_2$(NO$_3$)$_2$-NH$_4$OH-H$_3$PO$_4$-H$_2$O systems aged for 30 days is presented in figure 1. The precipitation and phase boundaries (full lines) and iso-pH curves (dotted lines) are shown. Only the experimental points representing samples in which solid phase was fully examined (XRD, IR, TGA, chemical analysis) are shown in figure 1 (filled circles). Chemical and TG analyses revealed that the solid phase was NH$_4$UO$_2$PO$_4$·3H$_2$O:

| % U   | % P   | % N   | % H$_2$O |
|-------|-------|-------|----------|
| Found: 54.28-54.60 | 7.06-7.12 | 3.16-3.25 | 12.30-12.40 |
| Theoretical: 54.46 | 7.09 | 3.20 | 12.36 |

TGA showed the loss of 2.4±0.2 mol H$_2$O up to 353 K and an additional 0.6±0.2 mol loss in the interval from 353 to 403 K. Transformation of anhydrous NH$_4$UO$_2$PO$_4$ to UO$_2$HPO$_4$ (loss of NH$_3$) starts at 450 K. The IR spectrum of

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2 Certain commercial materials and equipment are identified in this paper to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or the ADA Health Foundation or that the material or equipment identified is necessarily the best available for the purpose.
NH₄UO₂PO₄·3H₂O showed characteristic phosphate and uranyl vibrations [20].

In table 1 are given observed \( d \)-values \( (d_{\text{obsd}}) \) and the relative intensities \( (I_{\text{rel}}) \) for NH₄UO₂PO₄·3H₂O obtained by XRD. Comparison of the X-ray powder pattern of NH₄UO₂PO₄·3H₂O with those of the \( \text{H}_2\text{O}[\text{UO}_2\text{PO}_4]\)·3H₂O \( [2,15] \) confirms a close structural relationship among them \( (P4/ncc \text{ space group, structure: metatorbernite}) \); the \( (h00) \) and \( (00l) \) reflections were used to calculate the unit cell parameters for NH₄UO₂PO₄·3H₂O: \( a = b = 7.02(1) \text{ Å} \), and \( c = 18.08(4) \text{ Å} \). The \( hkl \) indices and \( d_{\text{calcd}} \) values (table 1) are calculated on the basis of unit cell parameters by using computer programs \( [21,22] \). The excellent agreement between observed and calculated \( d \) values (table 1) indicate a pure tetragonal polymorph NH₄UO₂PO₄·3H₂O.

NH₄UO₂PO₄·3H₂O crystallizes in the broad concentration range \( pH<2 \) (fig. 1). Its crystals were in the form of squarish platelets showing an intense green fluorescence. In the region where a small increase in the ratio \( c(\text{NH₄OH})/c(H₃PO₄) \) (at constant \( c(H₃PO₄) \)) causes a steep jump in the \( pH \) values of successive samples (from 2 to 9), stable colloidal particles obtained. At low concentrations

Table 1. X-ray powder pattern for NH₄UO₂PO₄·3H₂O \( (P4/ncc, a = 7.02 \text{ Å}, c = 18.08 \text{ Å}, Z = 4) \)

| \( h \) | \( k \) | \( l \) | \( d_{\text{obsd}} \) | \( d_{\text{calcd}} \) | \( I_{\text{rel}} \) |
|------|------|------|-----------|-----------|------|
| 0    | 0    | 2    | 9.08      | 9.04      | 100  |
| 1    | 0    | 2    | 5.56      | 5.54      | 20   |
| 1    | 1    | 0    | 4.97      | 4.96      | 12   |
| 0    | 0    | 4    | 4.53      | 4.52      | 12   |
| 1    | 1    | 2    | 4.35      | 4.35      | 14   |
| 1    | 0    | 4    | 3.80      | 3.80      | 51   |
| 2    | 0    | 0    | 3.51      | 3.51      | 17   |
| 1    | 1    | 4    | 3.34      | 3.34      | 1    |
| 2    | 0    | 2    | 3.28      | 3.27      | 20   |
| 2    | 1    | 1    | 3.09      | 3.09      | 1    |
| 0    | 0    | 6    | 3.02      | 3.01      | 1    |
| 2    | 1    | 2    | 2.97      | 2.97      | 9    |
| 2    | 1    | 3    | 2.78      | 2.78      | 29   |
| 2    | 1    | 4    | 2.58      | 2.58      | 8    |
| 2    | 2    | 2    | 2.39      | 2.39      | 5    |
| 3    | 0    | 2    | 2.27      | 2.27      | 14   |
| 3    | 1    | 0    | 2.22      | 2.22      | 6    |
| 3    | 1    | 1    | 2.21      | 2.20      | 3    |
| 2    | 2    | 4    | 2.18      | 2.18      | 12   |
| 3    | 1    | 2    | 2.16      | 2.16      | 15   |
| 3    | 1    | 3    | 2.08      | 2.08      | 6    |
| 3    | 0    | 4    | 2.07      | 2.08      | 3    |
| 1    | 1    | 8    | 2.06      | 2.06      | 9    |
| 2    | 1    | 7    | 1.998     | 1.995     | 1    |
| 2    | 0    | 8    | 1.901     | 1.900     | 4    |
| 3    | 0    | 6    | 1.849     | 1.848     | 4    |
| 2    | 1    | 8    | 1.834     | 1.834     | 5    |
| 0    | 0    | 10   | 1.808     | 1.808     | 5    |
| 3    | 2    | 4    | 1.788     | 1.788     | 4    |
| 4    | 0    | 0    | 1.754     | 1.755     | 1    |
| 1    | 0    | 10   | 1.751     | 1.751     | 1    |
| 4    | 0    | 2    | 1.723     | 1.723     | 1    |
| 1    | 1    | 10   | 1.699     | 1.699     | 12   |
| 4    | 1    | 1    | 1.695     | 1.695     | 6    |
| 2    | 2    | 8    | 1.672     | 1.671     | 1    |
| 3    | 3    | 0    | 1.655     | 1.655     | 1    |
| 4    | 0    | 4    | 1.636     | 1.636     | 4    |
| 3    | 0    | 8    | 1.626     | 1.626     | 3    |
| 2    | 0    | 10   | 1.608     | 1.607     | 6    |
| 4    | 1    | 4    | 1.595     | 1.593     | 2    |
| 3    | 1    | 8    | 1.585     | 1.584     | 4    |
| 4    | 2    | 0    | 1.570     | 1.570     | 1    |
| 4    | 2    | 2    | 1.547     | 1.547     | 1    |
| 0    | 0    | 12   | 1.508     | 1.507     | 2    |
| 2    | 4    | 4    | 1.484     | 1.483     | 3    |
| 3    | 2    | 8    | 1.475     | 1.475     | 3    |
| 2    | 2    | 10   | 1.462     | 1.461     | 2    |
| 1    | 1    | 12   | 1.442     | 1.442     | 6    |
| 4    | 2    | 5    | 1.439     | 1.440     | 3    |
of NH₄OH and H₃PO₄ mixtures of NH₄UO₂PO₄·3H₂O with H₂O[UO₂PO₄]·3H₂O and (UO₂)(PO₄)₂·8H₂O were found. At pH>9 mixtures of amorphous NH₄UO₂PO₄·3H₂O (prevailing solid phase) and an undefined compound (designated by X in fig. 1) precipitated. The chemical identification of X was not possible due to its extremely small presence (less than 5%).

In table 2 are given the concentrations of all components in the solutions equilibrated with NH₄UO₂PO₄·3H₂O(s) (points along the precipitation boundary). The ionic concentration product, 

$$K_s = c(UO_2^{2+})c(NH_4^+)c(PO_4^{3-})$$

expressed in greater detail form is

$$K_s = \frac{c(UO_2^{2+})c(NH_4^+)c(PO_4^{3-})}{K_{13}K_{12}K_1}\left(\frac{\beta_0 c(H_3PO_4)}{a(H^+)}\right)^{-1}.$$ 

In this equation c(UO₂⁺) and c(NH₄⁺) are the total concentrations of uranyl and ammonium species in the solution, respectively. K₁₃, K₁₂, and K₁ are the association constants of phosphoric acid [23-25] (table 3, equilibria 1-3) and β₀ are the stability constants of different uranyl phosphate complexes [5] (table 3, equilibria 4-7). The calculations were performed using a computer program de-

| System no. | $10^2 \times c(PO_4^{3-})/mol \ dm^{-3}$ | $10^4 \times c(NH_4^+)/mol \ dm^{-3}$ | pH | $10^4 / mol dm^{-3}$ | $10^5 \times I/ mol dm^{-3}$ | log Kₛ | log Kₛ(I=0) |
|------------|---------------------------------|---------------------------------|----|---------------------|---------------------|--------|----------------|
| 1          | 5.0                             | 2.25                            | 1.76 | 1.90                 | -26.03              | -26.83 |
| 2          | 6.0                             | 4.50                            | 1.71 | 2.13                 | -25.84              | -26.68 |
| 3          | 8.0                             | 9.00                            | 1.69 | 2.48                 | -25.63              | -26.52 |
| 4          | 10.0                            | 17.50                           | 1.61 | 2.89                 | -25.52              | -26.46 |
| 5          | 15.0                            | 40.00                           | 1.53 | 3.73                 | -25.40              | -26.43 |
| 6          | 20.0                            | 90.00                           | 1.43 | 4.69                 | -25.27              | -26.39 |
| 7          | 25.0                            | 125.00                          | 1.41 | 5.40                 | -25.24              | -26.42 |
| 8          | 30.0                            | 175.00                          | 1.33 | 6.26                 | -25.26              | -26.51 |
| 9          | 40.0                            | 350.00                          | 1.31 | 8.06                 | -25.09              | -26.44 |
| 10         | 50.0                            | 550.00                          | 1.30 | 9.95                 | -24.99              | -26.44 |
| 11         | 60.0                            | 1250.00                         | 1.23 | 15.88                | -24.89              | -26.54 |

*In all systems c(UO₂⁺) = 1×10⁻³ mol dm⁻³.

Table 3. Homogeneous and heterogeneous equilibria

| Ref. | log K(I=0) | log K(I=0.23 mol dm⁻³) |
|------|------------|------------------------|
| 1.   | 2.148      | 2.01                   |
| 2.   | 7.199      | 6.77                   |
| 3.   | 12.35      | 11.64                  |
| 4.   | 1.50       | 1.28                   |
| 5.   | 1.30       | 1.30                   | 5     |
| 6.   | 1.30       | 0.93                   |
| 7.   | 2.30       | 1.93                   |
| 8.   | 13.997     | 13.86                  |
| 9.   | -26.59±0.09| b                      |
| 10.  | -24.39     | b                      |
| 11.  | -25.70     | a                      |
| 12.  | -25.91     | a                      |
| 13.  | -25.59     | a                      |

*At 298 K.

This work.

Recalculated in this work from reference 14.

Recalculated in this work from reference 3.

Corrected from I=0 to I=0.23 mol dm⁻³.

Corrected from, I=0.23 mol dm⁻³ to I=0.
signed on the basis of the procedure published earlier (ref. [5], eqs 1–5). The input data for the program were the concentrations of all components in the solution (table 2) and the values of thermodynamic equilibrium constants at 298 K (table 3, equilibria 1–7). The ionic strength, I, defined as $I = 0.5 \sum c z^2$ (c and z are the concentration and valence charge of the ion, respectively) was calculated by an iterative procedure (iterations until the change was less than ±1%). Consequently, the values of the equilibrium constants at $I = 0$ were calculated from thermodynamic equilibrium constants by using the values of the activity coefficients (y) of the ions at corresponding ionic strengths. Activity coefficients (at 298 K) of all ions (except UO$_2^{2+}$) were calculated by using the Davies equation [26]: $\log y = -0.509z^2[\sqrt{I}/(\sqrt{I} + 1)] - 0.27$. For uranyl(2+) ions the activity coefficients determined by Brusilovsky [27] were used. In figure 2 is presented the dependence of the activity coefficients on the ionic strength: for the ions with valence charge 2 the curve was calculated by using the Davies equation (curve 1) and for the uranyl(2+) ions it was constructed by using the experimental values [27] (curve 2). The difference between these two curves is considerable.

![Figure 2](image-url)  
**Figure 2.** Calculated activity coefficients [26] for the ions with ±2 valence charge (curve 1) and experimentally determined activity coefficients for UO$_2^{2+}$ [27] (curve 2) as a function of the ionic strength.

The calculated values of the solubility products (log $K_s$) at the corresponding ionic strengths and the thermodynamic values [log $K_s$ ($I = 0$)] are presented in table 2; log $K_s$ ($I = 0$) has at 298 K an average value of $-26.50 \pm 0.09$ (table 3, equilibrium 9).

**Discussion**

Ammonium uranyl(2+)phosphate trihydrate precipitates as the only solid phase in a broad concentration range of the reactants (fig. 1). On the contrary, in the presence of alkali ions, mixtures consisting of hydrogen and alkali uranyl(2+)phosphates prevail [3,4]. These results can be explained by the greater sorption affinity of NH$_4^+$ on uranylhydrogen(2+)phosphate tetrahydrate as compared to that of alkali cations [28].

In order to compare the solubilities of ammonium and alkali uranyl(2+)phosphates we recalculated the solubility data of Vesely, Pekarek, and Abbrent [14] (experiments performed at $I = 0.23$ mol dm$^{-3}$) by using reported association constants of phosphoric acid [23–25] (table 3, equilibria 1–3) and stability constants of uranyl(2+)phosphate complexes [5] (table 3, equilibria 4–7) corrected from $I = 0$ to $I = 0.23$ mol dm$^{-3}$ (by using experimental activity coefficients of UO$_2^{2+}$ ions [27]). The average values of ionic activity and concentration products are listed (table 3, equilibria 9–13). The solubilities of different uranyl phosphate compounds depend on the cationic species in the structure. The ionic product constants ($K_s$) increase as follows: $K_s$(NH$_4$) < $K_s$(Rb) < $K_s$(K) < $K_s$(Cs) < $K_s$(Na).

Our experimentally determined $K_s$($I = 0$) values of NH$_4$UO$_2$PO$_4$·3H$_2$O and KUO$_2$PO$_4$·3H$_2$O [3] (table 3, equilibria 9 and 11) corrected to $I = 0.23$ mol dm$^{-3}$ shows an excellent agreement with the corresponding values recalculated from the data [14] originally determined at $I = 0.23$ mol dm$^{-3}$. This confirms the accuracy of the stability constants of the uranyl phosphate complex species [5] and the experimental precision of the solubility data [3,14]. The $K_s$ values determined and those recalculated in this work are in disagreement with the values given by Klygin et al. [13] and Muraveva et al. [29]. These authors did not consider the uranyl(2+)phosphate complex formation. The value of $K_s$ for KUO$_2$PO$_4$·3H$_2$O determined by Chukhlantsev and Stepanov [12] is a hundred times higher than ours, but their solubility product constant of NH$_4$UO$_2$PO$_4$·3H$_2$O (at undefined ionic strength) is similar, (log $K_s = -26.36$) [12], to the value determined in this work (at $I = 0$). It seems that (a) experimental uncertainties and (b) calculations which do not take into account complex species compensate each other, giving a value of $K_s$ for NH$_4$UO$_2$PO$_4$·3H$_2$O similar to the one we determined. Recalculation of their data [12] is not
possible because the analyses of the equilibrated solutions were incomplete.

The X-ray powder pattern of NH₄[⁺][UO₂P₂O₇]·3H₂O reveals a close structural relationship with the series M[UO₂P₂O₇]·nH₂O (n = 4 for M = Li; n = 3 for M = H₂O₂, Na, K, Rb; and n = 2.5 for M = Cs). The crystal structure of M[UO₂P₂O₇]·nH₂O (fig. 3, structure of H₂O[UO₂P₂O₇]·3H₂O [15]) reveals packing arrangements of infinite layers of octahedra and tetrahedra and water layers containing M (H₂O⁺, alkali or NH₄⁺) ions. Uranium exhibits an octahedral coordination. The PO₄ tetrahedron acts as a monodentate bridging group; each PO₄ group is coordinated to four UO₂⁺ ions. A striking structural feature is the arrangement of the water molecules. The size of the hydrogen, alkali and ammonium ionic species in particular compounds affects the content of the crystalline water in the unit-cell.

The unit-cell parameters of alkali uranyl(2⁺) phosphates are calculated [21,22] from our previously published XRD data [4] and are compared with those of NH₄[UO₂P₂O₇]·3H₂O (table 4). Calculated unit-cell dimensions of these compounds are in very good agreement with the values obtained from single-crystal data [30]. The increasing values of the unit-cell volumes of the trihydrates M[UO₂P₂O₇]·3H₂O, M = Na, K, NH₄, Rb (table 4), correlate with increasing ionic radii [31] of corresponding species: Na(r⁺ = 0.97 Å), K(r⁺ = 1.33 Å), NH₄(r⁺ = 1.43 Å), and Rb(r⁺ = 1.47 Å).

### Table 4. Unit-cell parameters (space group P4/nmc, Z = 4) of hydrogen, ammonium and alkali uranyl(2⁺) phosphates

| Compound         | a/Å  | c/Å  | V/Å³ |
|------------------|------|------|------|
| H₂O[UO₂P₂O₇]·3H₂O [15] | 6.995 | 17.491 | 855.84 |
| Li[UO₂P₂O₇]·4H₂O    | 7.04(2) | 18.28(7) | 906.0 |
| Na[UO₂P₂O₇]·3H₂O    | 7.01(2) | 17.52(4) | 860.9 |
| K[UO₂P₂O₇]·3H₂O     | 7.01(1) | 17.84(6) | 876.7 |
| NH₄[UO₂P₂O₇]·3H₂O   | 7.02(1) | 18.08(4) | 891.0 |
| Rb[UO₂P₂O₇]·3H₂O    | 7.00(1) | 18.36(3) | 899.6 |
| Cs[UO₂P₂O₇]·2.5H₂O* | 7.06(2) | 17.80(8) | 887.2 |

* Pseudo tetragonal (monoclinic) [4,30].

### Acknowledgment

The authors express their gratitude to Dr. B. Kojic-Prodic ("Rudjer Bošković" Institute, Zagreb) for fruitful discussion and help during the work. The authors also wish to thank Dr. W. E. Brown (ADAHF Paffenbarger Research Center, NBS) and Dr. W. Wong-Ng (Ceramics Division, NBS) for their suggestions during the final revision of this paper. This work was supported in part by the Self-Management Council for Scientific Research of S. R. Croatia, Yugoslavia, and by the National Bureau of Standards, Gaithersburg, MD (Project No. PP-776, NBS/G-39). One of the authors (M. Markovic) was on a Fulbright Scholarship at the ADAHF Paffenbarger Research Center, NBS, where this paper was finalized.

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![Figure 3. The infinite layers of [UO₂P₂O₇]⁻ (composed of octahedra and tetrahedra) and water layers in the structure of H₂O[UO₂P₂O₇]·3H₂O [15]. The water molecules in the water layer are designated by the open circles.](image-url)
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