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# $U(UO_2)(PO_4)_2$, a New Mixed-Valence Uranium Orthophosphate: *Ab Initio* Structure Determination from Powder Diffraction Data and Optical and X-ray Photoelectron Spectra

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A mixed-valence uranium phosphate, $U(UO_2)(PO_4)_2$, has been synthesized through dry and wet chemical processes. The crystal structure has been solved *ab initio* from conventional monochromatic X-ray powder diffraction. The unit cell is triclinic (space group $P\bar{1}$, $Z = 2$) with the cell dimensions $a = 8.8212(4)$ Å, $b = 9.2173(5)$ Å, $c = 5.4772(3)$ Å, $\alpha = 102.622(4)°$, $\beta = 97.748(4)°$, $\gamma = 102.459(5)°$, and $V = 416.55(3)$ Å$^3$. Initial positional parameters for two independent uranium atoms were obtained by solution of the Patterson map resulting from 509 integrated intensities. Phosphorus and oxygen atoms were localized by Fourier methods. The final indicators from the Rietveld refinement was $R_F = 0.039$ and $R_{wp} = 0.144$. The overall quality of the structure was improved from the refinement of atomic coordinates from neutron diffraction data ($R_F = 0.029$, $R_{wp} = 0.057$). The structure consists of $PaCl_5$-type chains based on a $[U(1)_2–U(2)_2]_n$ sequence running along [110] through edge-sharing bipyramidal pentagons around each uranium atom. The identification of a linear uranyl entity $(O–U–O)^{2+}$ with two terminal oxygens in the U(2) coordination sphere allows one to attribute a +6 oxidation state for U(2) and consequently U(1) should formally be called U(IV), in accordance with the green color of the sample. The remaining apices of each polyhedron are occupied by oxygen atoms from bidentate phosphate groups, which serve to connect the chains together, generating a complex tridimensional network. Moreover, the presence of two distinct valences for uranium atoms has been confirmed by additional chemical, optical, and X-ray photoelectron spectroscopy analyses. From redox reactions the ratio U(IV)/U(VI) was found to be one; absorption spectrum in the UV–visible range qualitatively revealed the presence of both oxidation states and the $4f_{7/2}$ peak of uranium observed by XPS has shown an asymmetric form which has been interpreted with two different binding energies arising from U(IV) and U(VI).

## Introduction

Uranium and thorium orthophosphates have been reported a long time ago,[1–3] but no structural data are available for these materials whose potential applications in the field of nuclear wastes are important.[4] These solids were obtained in a polycrystalline form, and the powder X-ray diffraction method has played a central role in their characterization and identification, but the reported data appear nowadays of moderate quality and improvement is certainly required. Moreover, the number of compounds found in these systems and the frequent polymorphism are responsible for a certain confusion concerning some reported chemical formulas. As part of an active research program related to radioactive wastes, based on the uranium and thorium phosphate systems, a pure polycrystalline uranium phosphate phase has been prepared. The interrogation of the powder diffraction database from its diffraction pattern has revealed some similarities with those of two previously reported compositions, i.e., $U_3(PO_4)_4$[2] and $(U_2O_3)P_2O_7$.[3] The last chemical formula was also reported in other studies.[4,5] As a consequence of the uncertainty about the chemical formula of the new phase and the absence of crystallographic data, a structural investigation was needed. The present study is intended to analyze carefully how specific chemical reactions coupled with modern powder crystallography could be able to clarify and to help the understanding of these complex systems. The synthesis of the pure phase of uranium phosphate, and its crystal structure solved *ab initio* from conventional X-ray powder diffraction and refined from neutron powder diffraction data, are reported. In addition, a complementary investigation based on chemical, optical, and X-ray photoelectron spectroscopy (XPS) analyses is presented. Results and discussion about the valence of uranium in this new uranium phosphate phase are also reported.

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## Experimental Procedures

**Preparation of Uranium Orthophosphate.** In previous studies,[2–4] uranium phosphate syntheses were based on both dry and wet chemistry. In dry chemistry the phosphating agent is the mono- or the dihydrogen ammonium phosphate, uranium is introduced through the tetravalent oxide $UO_2$, and the usual thermal treatments are applied. The amount of each reactant is chosen according to the stoichiometry of the expected compound, e.g., a uranium/phosphate ratio 3/4 for the formula $U_3(PO_4)_4$. These conditions were strictly reproduced in air or argon atmospheres. The sample was heated in an alumina crucible at a heating rate of 5 °C $min^{-1}$ up to 210 °C. This temperature was kept constant for 20 h and, finally, increased to 1350 °C. The weight loss measured at 210 °C was in good agreement with the value corresponding to the elimination of $NH_3$ and $H_2O$ molecules. At the end of the reaction at 1350 °C, it was noted that the mass of the sample was less than expected for the synthesis of $U_3(PO_4)_4$. This observation was indicative that the chemical reactional mechanism was different from that initially expected. This feature was confirmed by the significant differences observed in the powder diffraction pattern of the final product by comparison with results already published.[2] To clarify this point, different chemical synthesis routes described in detail elsewhere,[6] essentially based on soft chemistry, were also used.

The general process involved the following steps: (i) The preparation of solutions (1 M) of tetravalent uranium ions in hydrochloric acid medium (4–5 M) either by reduction of uranyl chloride ($UO_2Cl_2$) solution by hydrazine or by dissolution of uranium metal in HCl solution. To prevent any oxidation of tetravalent uranium, the solutions were always kept under argon atmosphere. (ii) The concentration of the U(IV) solutions up to 1.6 M at 80 °C by evaporating HCl and $H_2O$. (iii) The addition, at room temperature, of concentrated phosphoric acid ($\sim$15 M) with respect to the expected stoichiometry ($U/PO_4 = 3/4$), giving rise to a bulky green precipitate, which was then dried at 80 °C. Chemical analyses showed that the major part of the uranium was contained in this solid phase.

Whatever the chemical reaction used to obtain the tetravalent uranium solutions ($UO_2Cl_2$ or metallic uranium), the precipitate was then subjected to the same heating treatment described above in the dry chemical process, except for the upper temperature which was limited to 1170 °C. The diffraction pattern of this sample was similar to the one obtained for the phase prepared from solid-state chemistry.

Finally, whatever the chemical route employed, it was clear that a uranium phosphate compound different from $U_3(PO_4)_4$ was synthesized. Furthermore, the successful indexing of its powder diffraction pattern described below demonstrated the purity of this new phase. Its density was measured with a helium pycnometer Accupyc 1330 from Micromeritics. The average value from five measurements was 5.602 ± 0.015 g $cm^{-3}$. The green powder analyzed by SEM gave a mean grain diameter of 10–15 $\mu$m with particles not well shaped, connected by round and smooth surface bridges.

**X-ray Diffraction.** Diffraction data were collected with a Siemens D500 high-resolution powder diffractometer using monochromatic Cu $K\alpha_1$ X-rays ($\lambda = 1.540\,598$ Å) obtained with an incident-beam germanium monochromator. The alignment of the instrument was checked by means of the $00l$ reflections of fluorophlogopite mica (NIST SRM 675),[7] and the error on the zero point was estimated less than 0.005° ($2\theta$). Characteristics of the diffractometer and its instrument resolution curve, characterized by a shallow minimum at about 40° ($2\theta$), have been described elsewhere.[8] The diffraction pattern was scanned over the angular range 9–120° ($2\theta$), with a step length of 0.02° ($2\theta$). The counting times were 25 s $step^{-1}$ to 80° and 50 s $step^{-1}$ from 80.02° to the end of the scan. Then, the full pattern was scaled to the lower counting time. Such a procedure improves significantly the counting statistics at high angles. After data collection the stability of the X-ray source was checked by recording the first lines of the pattern. For pattern indexing, the precise determination of peak positions was carried out by means of the Socabim fitting program PROFILE, available in the PC software package DIFFRAC-AT supplied by Siemens. After collecting the diffraction data, the ICDD PDF database[9] was interrogated using the DIFFRAC-AT search/match program constraining the search to the chemical elements involved in the synthesis. As indicated in the introductory section a partial match with the patterns of the two uranium compounds $(U_2O_3)P_2O_7$ [File No. 13-0064][3] and $U_3(PO_4)_4$ [File No. 16-0225][2] was found. The diffraction pattern of the last compound is indexed with a monoclinic cell[2] ($V = 1023$ Å$^3$); however, the corresponding figure of merit $F_{18} = 2(0.059, 200)$ indicates the low quality of the data and suggests that the proposed unit cell must be considered as doubtful.

**Neutron Diffraction.** Powder neutron diffraction data were collected with the high-resolution multidetector powder diffractometer D1A ($\lambda = 1.9842$ Å) of the Laboratoire Léon Brillouin (Laboratoire commun CEA-CNRS). The pattern was scanned over the range 10–159.50° ($2\theta$) with a step length of 0.05°.

**Spectroscopic Measurements.** Absorption spectra in the UV–visible region were carried out with a VARIAN DMS 300 spectrophotometer. A powder sample of uranium phosphate was deposited on a silica plate which was previously scratched to provide good adhesion; the thickness of the sample was a few hundredths of a micrometer. For the near-IR range a CARY 5 spectrophotometer was used. All spectra were recorded at room temperature. X-ray photoelectron spectroscropy (XPS) measurements were conducted with a Perkin-Elmer PHI 5500 spectrometer using a nonmonochromatic X-ray beam from a Mg $K\alpha$ source. The anode operated at 350 W and the spot diameter was 3 mm. The spectrometer was calibrated using the 1s level of carbon traces on the sample. XPS experiments were performed at ambient conditions on pellets of pure uranium phosphate (8 mm diameter, 1 mm thick) pressed at 1 GPa.

## *Ab Initio* Structure Determination

**Indexing.** The X-ray pattern indexing was performed by means of the program DICVOL91[10] from the first 20 lines with an absolute error of 0.03° ($2\theta$) on peak positions. A triclinic solution was found with the figures of merit $M_{20} = 92$ and $F_{20} = 163(0.0037, 33)$. The correctness of this solution was subsequently confirmed from a review of the complete powder diffraction data, using the evaluation program NBS*AIDS83.[11] After a least-squares refinement, the unit-cell dimensions were $a = 8.8212(4)$ Å, $b = 9.2173(5)$ Å, $c = 5.4772(3)$ Å, $\alpha = 102.622(4)°$, $\beta = 97.748(4)°$, $\gamma = 102.459(5)°$, and $V = 416.55(3)$ Å$^3$, with $M_{20} = 71$ and $F_{30} = 120(0.0047, 54)$. The powder diffraction data are given in Table 1. At this stage, it was clear from the unit cell volume and observed density that the formula $[U_3(PO_4)_4]$, initially expected from the sample preparation, was not correct. On the other hand, assuming a global formula $UOPO_4$ and $Z = 4$, the calculated density is 5.56 g $cm^{-3}$, which may be compared to the observed value, 5.60(2) g $cm^{-3}$. Also, it should be noted that from the solution found, an approximate indexing of the pattern of $(U_2O_3)P_2O_7$[3] can be proposed, with some angular discrepancies greater than 0.30° ($2\theta$). The corresponding figures of merit for this pattern [$M_{20} = 3$ and $F_{30} = 3(0.068, 132)$] indicate the very low quality of the data. Finally, the interrogation of the NIST-CDF database[12] did not reveal

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**Table 1. X-ray Powder Diffraction Data for $U(UO_2)(PO_4)_2$**

| *h k l* | $2\theta_{obs}$ (deg) | $2\theta_{calc}$ (deg) | $d_{obs}$ (Å) | $I_{obs}$ |
|---|---|---|---|---|
| 0 1 0 | 10.149 | 10.159 | 8.71 | 1 |
| 1 1 0 | 16.346 | 16.354 | 5.42 | 35 |
| 0 0 1 | 16.880 | 16.886 | 5.25 | 28 |
| 0 $\bar{1}$ 1 | 17.335 | 17.347 | 5.11 | 1 |
| $\bar{1}$ 0 1 | 18.095 | 18.102 | 4.90 | 1 |
| $\bar{1}$ $\bar{1}$ 1 | 19.950 | 19.957 | 4.447 | 100 |
| 0 2 0 | 20.393 | 20.398 | 4.351 | 29 |
| 1 $\bar{1}$ 1 | 20.623 | 20.629 | 4.303 | 32 |
| 2 0 0 | 20.991 | 20.997 | 4.229 | 26 |
| $\bar{1}$ 1 1 | 21.602 | 21.611 | 4.111 | 24 |
| 0 1 1 | 21.893 | 21.890 | 4.057 | 1 |
| 1 $\bar{2}$ 1 | 24.446 | 24.448 | 3.638 | 2 |
| $\bar{2}$ 2 0 | 25.360 | 25.362 | 3.509 | 70 |
| 2 1 0 | 25.632 | 25.636 | 3.473 | 1 |
| $\bar{1}$ $\bar{2}$ 1 | 26.100 | 26.098 | 3.411 | 4 |
| 1 1 1 | 26.759 | 26.759 | 3.329 | 12 |
| 2 0 1 | 29.535 | 29.535 | 3.022 | 41 |
| 0 2 1 | 29.827 | 29.823 | 2.993 | 35 |
| 1 3 0<br>2 $\bar{2}$ 1 | 29.919 | 29.905<br>29.924 | 2.984 | 11 |
| $\bar{3}$ 1 0 | 30.743 | 30.743 | 2.906 | 6 |
| $\bar{2}$ 2 1 | 31.316 | 31.314 | 2.854 | 4 |
| 1 $\bar{3}$ 1 | 31.412 | 31.412 | 2.846 | 25 |
| 3 0 0 | 31.726 | 31.723 | 2.818 | 2 |
| $\bar{2}$ $\bar{2}$ 1 | 32.634 | 32.637 | 2.742 | 6 |
| 2 2 0<br>3 0 1 | 33.051 | 33.053<br>33.056 | 2.708 | 3 |
| $\bar{3}$ 1 1 | 33.508 | 33.519 | 2.672 | 17 |
| $\bar{1}$ 0 2 | 33.770 | 33.759 | 2.652 | 1 |
| 0 0 2 | 34.152 | 34.152 | 2.623 | 3 |
| $\bar{1}$ $\bar{3}$ 1<br>2 2 1 | 34.433 | 34.433<br>34.441 | 2.603 | 10 |
| 2 $\bar{3}$ 1<br>1 3 0 | 35.130 | 35.118<br>35.138 | 2.553 | 21 |
| $\bar{3}$ $\bar{1}$ 1 | 35.783 | 35.784 | 2.507 | 6 |
| 3 1 0 | 35.868 | 35.867 | 2.502 | 12 |
| 1 $\bar{1}$ 2 | 35.943 | 35.940 | 2.4966 | 8 |
| $\bar{1}$ $\bar{2}$ 2 | 36.331 | 36.338 | 2.4708 | 9 |
| $\bar{2}$ 0 2 | 36.674 | 36.677 | 2.4485 | 9 |
| 3 $\bar{1}$ 1 | 36.966 | 36.964 | 2.4298 | 2 |
| 1 $\bar{2}$ 2<br>$\bar{1}$ 1 2 | 37.130 | 37.118<br>37.129 | 2.4194 | 10 |
| $\bar{2}$ $\bar{1}$ 2 | 37.202 | 37.194 | 2.4149 | 1 |
| $\bar{1}$ 3 1 | 37.437 | 37.435 | 2.4003 | 2 |
| 0 1 2 | 38.255 | 38.255 | 2.3508 | 1 |
| $\bar{2}$ 3 1 | 38.826 | 38.831 | 2.3176 | 1 |
| $\bar{1}$ 4 0<br>1 $\bar{4}$ 1 | 40.071 | 40.066<br>40.076 | 2.2484 | 1 |
| $\bar{2}$ $\bar{2}$ 2 | 40.549 | 40.553 | 2.2230 | 18 |
| 0 $\bar{4}$ 1 | 40.593 | 40.599 | 2.2207 | 4 |
| 1 $\bar{3}$ 2 | 41.081 | 41.079 | 2.1954 | 2 |
| 3 $\bar{3}$ 1<br>0 4 0 | 41.473 | 41.470<br>41.481 | 2.1756 | 11 |
| 2 4 0<br>2 2 1 | 41.577 | 41.563<br>41.582 | 2.1703 | 22 |
| 2 3 0 | 41.974 | 41.976 | 2.1507 | 1 |
| 1 1 2 | 42.270 | 42.265 | 2.1364 | 13 |
| $\bar{4}$ 2 0 | 42.512 | 42.511 | 2.1248 | 8 |
| 4 0 0 | 42.747 | 42.743 | 2.1136 | 1 |
| $\bar{4}$ 0 1<br>1 2 2 | 42.928 | 42.932<br>42.961 | 2.1051 | 2 |
| $\bar{3}$ 3 1 | 43.053 | 43.050 | 2.0993 | 6 |
| 1 3 1 | 43.572 | 43.571 | 2.0755 | 2 |
| 3 1 1 | 43.670 | 43.671 | 2.0711 | 1 |
| $\bar{3}$ 1 2 | 43.802 | 43.804 | 2.0651 | 1 |
| 2 0 2<br>$\bar{1}$ $\bar{4}$ 1 | 43.926 | 43.922<br>43.931 | 2.0596 | 1 |
| $\bar{2}$ 2 2 | 44.048 | 44.044 | 2.0542 | 1 |
| 0 2 2 | 44.637 | 44.633 | 2.0284 | 1 |
| $\bar{2}$ $\bar{3}$ 2<br>$\bar{4}$ 3 0 | 46.238 | 46.237<br>46.252 | 1.9618 | 1 |
| 4 1 0 | 46.690 | 46.686 | 1.9439 | 1 |
| 0 $\bar{4}$ 2 | 46.914 | 46.908 | 1.9351 | 7 |
| $\bar{3}$ $\bar{2}$ 2<br>4 $\bar{1}$ 1 | 47.082 | 47.088<br>47.096 | 1.9286 | 1 |
| 4 $\bar{2}$ 1 | 47.177 | 47.174 | 1.9250 | 13 |
| $\bar{3}$ 2 2<br>$\bar{2}$ 4 1 | 47.758 | 47.731<br>47.753 | 1.9029 | 1 |
| $\bar{3}$ $\bar{3}$ 1 | 48.445 | 48.445 | 1.8775 | 1 |
| 3 $\bar{2}$ 2 | 48.959 | 48.970 | 1.8590 | 1 |
| 0 4 1<br>3 $\bar{1}$ 2 | 49.267 | 49.244<br>49.283 | 1.8481 | 8 |
| 4 0 1 | 49.431 | 49.427 | 1.8423 | 6 |
| $\bar{2}$ $\bar{4}$ 1 | 49.628 | 49.619 | 1.8355 | 4 |
| 1 $\bar{5}$ 1 | 49.795 | 49.790 | 1.8297 | 3 |
| $\bar{4}$ 0 2 | 49.932 | 49.933 | 1.8250 | 6 |
| 2 $\bar{4}$ 2 | 50.110 | 50.107 | 1.8189 | 5 |
| 0 $\bar{1}$ 3<br>3 3 0 | 50.514 | 50.489<br>50.515 | 1.8053 | 7 |
| $\bar{1}$ 3 2 | 50.566 | 50.580 | 1.8036 | 7 |
| $\bar{3}$ 4 1 | 50.786 | 50.783 | 1.7963 | 6 |
| $\bar{4}$ $\bar{2}$ 1 | 50.905 | 50.905 | 1.7924 | 4 |
| 3 $\bar{3}$ 2<br>0 $\bar{2}$ 3 | 51.015 | 51.007<br>51.015 | 1.7888 | 11 |
| 2 4 0<br>3 0 2 | 51.883 | 51.879<br>51.914 | 1.7609 | 1 |
| $\bar{2}$ $\bar{1}$ 3<br>$\bar{4}$ 4 0 | 52.092 | 52.065<br>52.086 | 1.7543 | 8 |
| 0 0 3 | 52.273 | 52.267 | 1.7486 | 4 |
| $\bar{5}$ 1 0 | 52.392 | 52.394 | 1.7450 | 8 |
| $\bar{2}$ 0 3<br>0 3 2 | 52.638 | 52.635<br>52.654 | 1.7374 | 4 |
| $\bar{5}$ 1 1<br>$\bar{3}$ $\bar{3}$ 2 | 52.785 | 52.778<br>52.803 | 1.7329 | 6 |

chemically related materials with known crystal structure. Consequently, an *ab initio* structure determination was undertaken from the X-ray powder diffraction data assuming the space group $P\bar{1}$.

**Structure Solution and Refinement.** The X-ray powder diffraction pattern of uranium orthophosphate is strongly dominated by the scattering contributions from the metal atoms since the ratio of atomic scattering factors of uranium and oxygen atoms is greater than 11.5, which is the ratio of atomic numbers. The extraction of the integrated intensities has been carried out by means of the Le Bail iterative procedure[13] implemented in the Rietveld refinement program FULLPROF,[14] a version derived from the DBW3.2S (8804) Rietveld program.[15] This rapid and efficient approach of pattern decomposition, based on equipartition of overall intensity for strongly overlapping reflections, was applied to the range 10–80° ($2\theta$) and gave a list of 509 observed structure factors. They were introduced in the structure determination package MolEN, supplied by Enraf-Nonius, in order to generate a Patterson map, from which two independent uranium atoms in the asymmetric unit were localized [U(1) 0.29, 0.05, 0.35, and U(2) 0.80, 0.55, 0.34]. It can be seen that U(2) differs from U(1) by a translation close to $(^1/_2, ^1/_2, 0)$. This property explains the fact that a pattern indexing solution with half the cell volume was first obtained [$V$ = 208 Å$^3$, $M_{20} = 33$, $F_{20} = 59(0.014, 24)$] when the few lines with an intensity close to one (see Table 1) were omitted. The refinement of the U atomic positions lead to an $R_F$ factor of 0.16. The calculation of a first Fourier map gave the approximate coordinates of two phosphorus atoms.

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**Table 2. Details of Rietveld Refinements for $U(UO_2)(PO_4)_2$[a]**

| | | |
|---|---|---|
| space group | $P\bar{1}$ | |
| $Z$ | 2 | |
| no. of atoms | 14 | |
| | X-rays | neutrons |
| wavelength (Å) | 1.5405981 | 1.98420 |
| step scan increment (°2$\theta$) | 0.02 | 0.05 |
| 2$\theta$ range (°) | 9–120 | 10–159.50 |
| no. of reflections | 1240 | 853 |
| no. of structural parameters | 49 | 51 |
| no. of profile parameters | 18 | 18 |
| $R_F$ | 0.039 | 0.029 |
| $R_B$ | 0.052 | 0.044 |
| $R_p$ | 0.106 | 0.049 |
| $R_{wp}$ | 0.144 | 0.057 |
| $R_{exp}$ | 0.073 | 0.032 |

[a] The $R$ factors are defined as $R_F = (\sum|I(\text{“obs”})^{1/2} - I(\text{calc})^{1/2}|)/\sum I(\text{“obs”})^{1/2}$. $R_B = (\sum|I(\text{“obs”}) - I(\text{calc})|)/\sum I(\text{“obs”})$. $R_p = (\sum|y_i(\text{obs}) - (1/c)y_i(\text{calc})|)/\sum y_i(\text{obs})$. $R_{wp} = [(\sum\omega_i[y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2)/\sum\omega_i[y_i(\text{obs})]^2]^{1/2}$. $R_{exp} = [(N - P)/\sum\omega_i[y_i(\text{obs})]^2]^{1/2}$.

By increasing the upper limit of the angular range, the location of 10 additional oxygen atoms was revealed from a somewhat laborious analysis (except for four O atoms) of Fourier and difference Fourier syntheses alternating with least-squares Rietveld refinements. Finally, a total of 14 atoms was found in the asymmetric unit cell, describing a correct trial structure model based on two bridging phosphate groups acting as bidentate groups with respect to two 7-fold coordinated uranium atoms. In the final Rietveld refinement 67 parameters were involved: a scale factor, 48 atomic parameters including 6 isotropic thermal parameters, the zero-point and 6 cell parameters, 3 coefficients to describe the angular dependence of diffraction line half-widths, 1 asymmetry parameter and 2 parameters to describe the angular variation of the mixing factor of the pseudo-Voigt function fitted to the observed line profiles. In addition, five coefficients were used to describe the functional dependence of the background. Crystallographic details are reported in Table 2. Figure 1 shows the best fit between calculated and observed diffraction patterns, corresponding to satisfactory structure and profile indicators $R_F = 0.039$ and $R_{wp} = 0.144$. The final positional and temperature parameters obtained from the X-ray diffraction dataset are given in Table 3. The results of the structural investigation from X-ray diffraction show that the asymmetric unit cell contains 14 atoms (2 U, 2 P, and 10 O) which would correspond to a global formula $U_2P_2O_{10}$. The identification of two isolated phosphate groups combined with the fact that no incoherent scattering background was detected by neutron diffraction, as usually found when hydrogen atoms are present, allows a more precise formula to be given, i.e., $U_2O_2(PO_4)_2$. At this stage, the problem of oxidation state of uranium atoms should be discussed. The green color of the sample indicates the likely presence of U(IV). Moreover, an uranyl group in the unit cell is clearly evidenced, since a pentagonal bipyramidal polyhedron with two significant, though not accurate, short axial bond lengths (1.65 and 1.76 Å) are observed. Consequently, a more descriptive ionic model for uranium phosphate must be proposed, $U^{4+}(UO_2)^{2+}(PO_4)_2{}^{6-}$.

The accuracy on the atomic positions of the lighter atoms derived from X-ray diffraction data cannot be high, as shown by the spread of P–O distances in the phosphate groups (1.46–1.62 Å). To improve the overall quality of the crystal structure determined from X-ray diffraction, neutron diffraction data were used to refine the atomic coordinates. In this case the appropriate scattering lengths of uranium and oxygen atoms have a ratio of 1.45. The complete structure found from X-ray diffraction was used as starting structural model and the refinement of 75 parameters for 853 reflections converged immediately to the agreement factors $R_F = 0.029$ and $R_{wp} = 0.057$. A small improvement of the accuracy on the U–O and P–O distances, without any modification of the $R$ factors, was observed when the positions of the U atoms were kept fixed to the precise positions derived from the X-ray diffraction data (69 refined parameters). Crystallographic details are given in Table 2, and the final Rietveld plot is shown in Figure 2. Atomic coordinates are reported and compared to those derived from X-ray diffraction in Table 3. Interatomic distances and angles are listed in Table 4.

**Description of the Structure.** Figure 3 is a stereoscopic view of the structure, and Figure 4 a projection along the [001] direction. They show that the structure of $U(UO_2)(PO_4)_2$ is built from infinite $PaCl_5$-type chains running along [110]. A chain is formed by pentagonal bipyramidal polyhedra around the U atoms sharing two opposite edges involving the independent oxygen atoms O(3), O(7), O(9), and O(10). It consists of an alternation of two distinct polyhedra pairs based on $UO_7$ groups characterized by U(1) in one pair and U(2) in the following one. The cross-linkage of two identical chains proceeds via bidentate $PO_4$ tetrahedra in the [001] direction. The second function of each phosphate group is to bridge the chains in planes parallel to (001). This arrangement generates “channels” running along [001]; their approximate rectangular section is limited by two short edges arising from phosphate groups and two longer edges of U(1) or U(2) polyhedra. The $P(1)O_4$ and $P(2)O_4$ tetrahedra are bidentate with regards to U(1) and U(2) polyhedra through the O(3)–O(7)$^{I}$ and O(9)$^{III}$–O(10)$^{II}$ edges respectively as displayed in Figure 5. The two corresponding oxygen–oxygen distances are the shortest [2.371 and 2.409 Å] in the U polyhedra; they contribute to the deviation from an ideal pentagonal bipyramidal shape as well as four other short O–O distances which concern the common edges O(7)–O(7)$^{I}$ (2.673 Å), O(9)–O(9)$^{III}$ (2.773 Å), O(3)–O(10), and O(3)$^{II}$–O(10)$^{II}$ (2.690 Å). The remaining O–O bond lengths of edges approximate 3 Å. One of the most noticeable features of the structure is the existence of two different pentagonal bipyramidal environments for U. It may be pointed out that the U(1)–O and U(2)–O distances in the respective ranges 2.219–2.543 Å (mean value of 2.376 Å) and 2.267–2.573 Å (mean value of 2.436 Å) display two irregular pentagons. O(4) and O(6) atoms which occupy the apices of the U(1) bipyramid [$d$(U(1)–O) = 2.177, 2.171 Å and O(4)–U(1)–O(6) = 176.5°] belong to phosphate groups, while the two apical oxygen O(5) and O(8) are terminal atoms of U(2) polyhedra with shorter bond lengths [$d$(U(2)–O) = 1.764, 1.767 Å]. The distortion of the pentagonal ring system from planarity can be estimated by means of a determination of the best plane through each uranium atom U(1) and U(2) and their respective five equatorial oxygen neighbors. The equations of the planes, in perpendicular form with absolute coordinates, are $0.5674X + 0.7326Y - 0.3758Z = 0.0863$ for U(1) and $0.7300X + 0.3610Y - 0.5803Z = -6.2496$ for U(2). The individual deviations from the first plane are 0.089(3), −0.0194(7), 0.155(7), 0.243(7), −0.316(7), and 0.024(7) Å for the successive U(1), O(1), O(3), O(7), O(7)$^{I}$, and O(10) atoms. For the second plane, they are −0.001(3), 0.121(7),

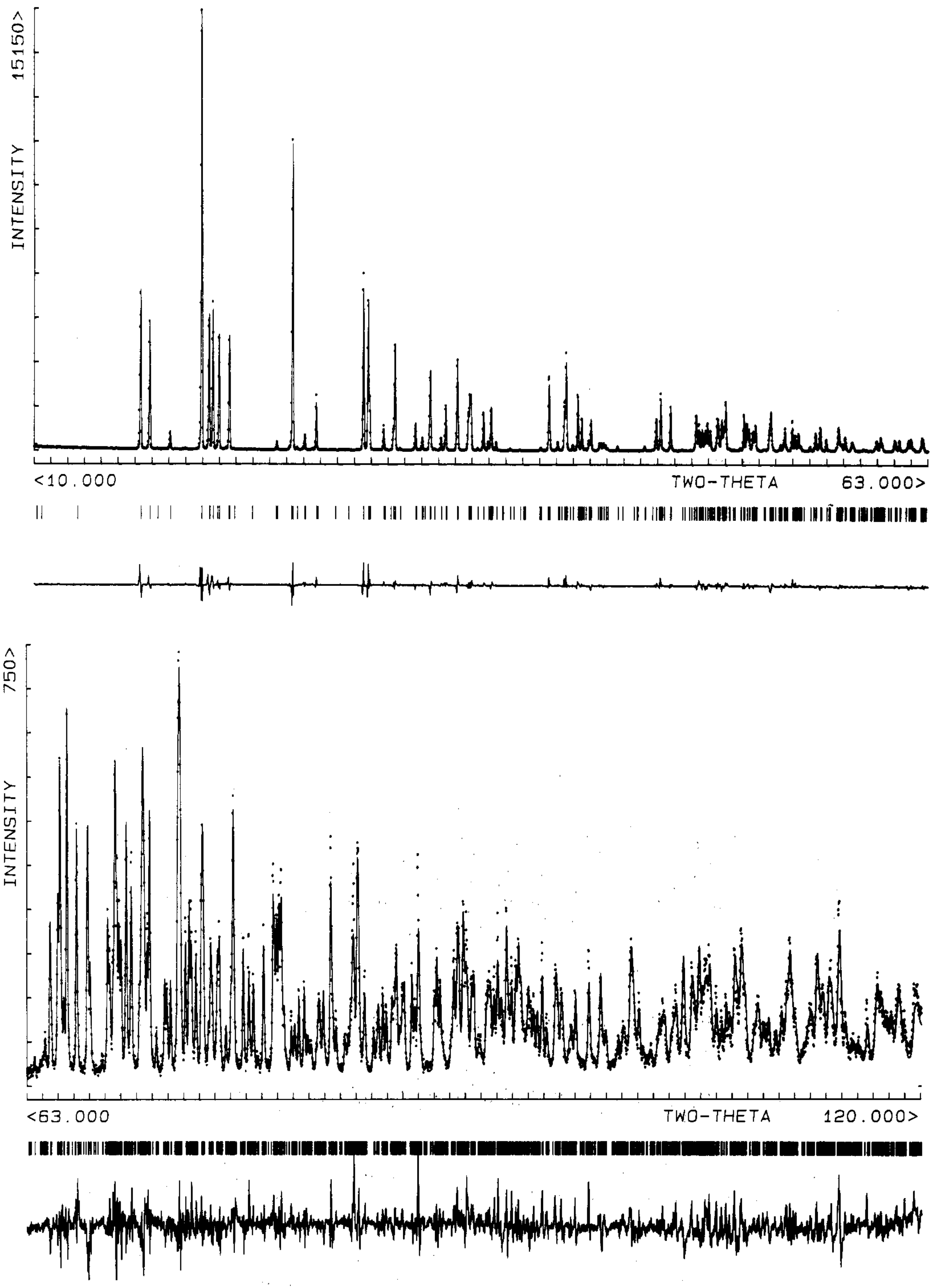

**Figure 1.** Final Rietveld plot of $U(UO_2)(PO_4)_2$ from monochromatic X-ray powder diffraction. The upper trace shows the observed data as dots, while the calculated pattern is shown by solid line. The lower trace is a plot of the difference: observed minus calculated. Note that the intensity scale is different for the high angle range.

−0.190(7), 0.208(7), −0.030(7), and −0.108(7) Å for U(2), O(2), O(9), O(9)$^{III}$, O(3)$^{II}$, and O(10)$^{II}$ atoms. The value of the dihedral angle between the two planes is 26.3(3)°.

The two short U(2)–O(5) and U(2)–O(8) distances, combined with an axial O(5)–U(2)–O(8) angle of 176.1°, are consistent with the symmetric linear bonding usually found in an uranyl group $(UO_2)^{2+}$. This situation corresponds to a +6 oxidation state for U(2) and, consequently, a +4 state must be attributed to U(1), since U(1) is as abundant as U(2) in the structure. Two distinct uranium species in two separated sites are also observed in the crystal structure of some compounds belonging to the complex uranium oxide system; this has been interpreted in terms of mixed valence structures and a significant example is $U_3O_8$ [$^1/_3$(+4), $^2/_3$(+6)].[17] Moreover, the short lengths of axial U–O bonds of less than 2 Å, considered as forming an uranyl unit [1.63–1.85 Å], along with a mean length of the five equatorial bonds ranging from 2.35 to 2.50 Å, can be usually seen in other well-defined uranyl compounds with pentagonal bipyramidal coordination for uranium atoms, e.g., β-$UO_2SO_4$ [U–2O 1.77 Å, –5O 2.38 Å],[18] $UO_2(HCOO)_2{\cdot}H_2O$ [U–2O 1.76 Å,

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(17) Loopstra, B. O. *Acta Crystallogr.* **1964,** *17,* 651.

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**Table 3. Fractional Atomic Coordinates and Thermal Isotropic Parameters from X-ray (RX) and Neutron (N) Powder Diffraction for $U(UO_2)(PO_4)_2$**

| atom | | $x$ | $y$ | $z$ | $B_{iso}$ (Å$^2$) |
|---|---|---|---|---|---|
| U(1) | RX | 0.2965(3) | 0.0493(3) | 0.3543(4) | 1.2(4) |
| U(2) | RX | 0.8040(3) | 0.5523(3) | 0.3375(4) | 1.5(4) |
| P(1) | RX | 0.484(2) | 0.240(2) | 0.894(2) | 1.6(4)[a] |
| | N | 0.4841(7) | 0.2376(7) | 0.910(1) | 2.2(1) |
| P(2) | RX | 1.078(2) | 0.817(2) | 0.724(2) | 1.6(4)[a] |
| | N | 1.0752(7) | 0.8202(6) | 0.728(1) | 1.6(1) |
| O(1) | RX | 0.130(4) | −0.104(4) | 0.002(7) | 1.8(5)[b] |
| | N | 0.1324(6) | −0.1124(6) | 0.0135(9) | 1.4(1) |
| O(2) | RX | 0.626(4) | 0.376(4) | 0.016(7) | 1.8(5)[b] |
| | N | 0.6266(6) | 0.3748(6) | 0.0145(9) | 1.7(1) |
| O(3) | RX | 0.361(4) | 0.272(3) | 0.727(6) | 2.3(7)[c] |
| | N | 0.3589(6) | 0.2736(6) | 0.724(1) | 1.4(1) |
| O(4) | RX | 0.179(3) | −0.112(3) | 0.555(6) | 1.8(5)[b] |
| | N | 0.1834(7) | −0.0922(6) | 0.582(1) | 2.1(1) |
| O(5) | RX | 0.690(4) | 0.512(4) | 0.566(6) | 3.2(7)[d] |
| | N | 0.6941(6) | 0.4982(6) | 0.564(1) | 2.2(1) |
| O(6) | RX | 0.416(3) | 0.174(3) | 0.115(6) | 1.8(5)[b] |
| | N | 0.4169(6) | 0.1797(6) | 0.120(1) | 2.3(1) |
| O(7) | RX | 0.470(3) | −0.109(3) | 0.263(5) | 0.1[e] |
| | N | 0.4728(6) | −0.1047(6) | 0.277(1) | 1.7(1) |
| O(8) | RX | 0.905(4) | 0.600(4) | 0.122(6) | 3.2(7)[d] |
| | N | 0.9145(7) | 0.6196(6) | 0.120(1) | 2.8(1) |
| O(9) | RX | 0.929(3) | 0.356(3) | 0.351(5) | 0.1[e] |
| | N | 0.9298(7) | 0.3518(6) | 0.352(1) | 1.7(1) |
| O(10) | RX | 0.096(4) | 0.160(3) | 0.365(6) | 2.3(7)[c] |
| | N | 0.0972(6) | 0.1772(6) | 0.357(1) | 1.3(1) |

[a–d] Some thermal parameters were allowed to vary in the same manner. [e] Parameters not refined.

−5O 2.41 Å],[19] $UO_2(C_2O_4)\cdot 3H_2O$ [U−2O 1.63 Å, −5O 2.49 Å][20] and $LiBUO_4$ [U−2O 1.795 Å, −5O 2.344 Å].[21] A number of additional geometrical parameters for uranyl groups in related compounds have been reported by Denning.[22]

Phosphate groups are well-defined by regular dimensions as shown by reasonable P−O distances in the range 1.510–1.565 Å. The mean values of 1.534 and 1.533 Å for P(1)O4 and P(2)O4, respectively, are in accordance with the average of 1.539 Å for P−O distances as found in some metal–orthophosphates.[23] According to the theory by Pauling[24] and Baur,[25] it is established that the length of O−O edges from a tetrahedra like $PO_4$ shared with a cationic polyhedra is expected shorter than those of edges which are not shared. The corresponding O−P−O angles should also be found shorter. The two bidentate phosphate groups in the structure of $U(UO_2)(PO_4)_2$ follow this rule, since it was clearly evidenced that one O−O distance of the six defining each tetrahedron and the corresponding O−P−O angle are especially low. The values 2.371 Å and 99.6° are observed for P(1)O4 and 2.409 Å and 103.1° for P(2)O4.

On the basis of the bond valence theory described by Brown,[26] the bond strengths have been calculated from all U(1)−O and U(2)−O bond lengths found from the neutron diffraction dataset. The sum of these bond strengths allows one to approximate the valence of each independent uranium atom. Values of 4.3 and 6.4 have been obtained for U(1) and U(2), respectively. These results confirm the accuracy of atomic parameters which is sufficiently high to distinguish two oxidation states. This way, it is clearly demonstrated that the structure contains two ionic uranium species in equal proportions located in two distinct sites. One uranium atom, U(1), is formally of oxidation number +4, whereas the other one, U(2), should formally be called U(VI) and is related with the formalism of an uranyl ion.

**Chemical Formula of Uranium Phosphate.** The structure determination of the uranium phosphate showed that the chemical formula was $U(UO_2)(PO_4)_2$. This unexpected result when preparing the material has further been confirmed by subsequent chemical analyses carried out after the structure was known. Since tetravalent uranium is sensitive to oxidation, special chemical processes have been developed to determine the amount of uranium and phosphate. For the determination of the tetravalent uranium content, uranium phosphate was dissolved in a medium $H_2SO_4$ (1 M)–$H_3PO_4$ (1 M) with an excess of a known volume of titrated $K_2Cr_2O_7$. After dissolution, the remaining dichromate ion was determined with a Mohr's salt solution. Thus, the part of dichromate reduced was representative of the part of U(IV) which was oxidized. The total amount of uranium was found by dissolving uranium phosphate in a mixture of $H_2SO_4$ (18 M) and $(NH_4)_2S_2O_8$ to oxidize U(IV) into U(VI). These solutions were adjusted to approximately $10^{-2}$–$10^{-3}$ M in $UO_2^{2+}$ and 4 M in $H_2SO_4$. The concentration of uranyl ions was determined by spectrophotometry at 420 nm. The content in phosphate ion was obtained by gravimetry after precipitation of ammonium phosphomolybdate.[27]

These analytical procedures were applied to different samples prepared by the wet and solid-state procedures described above. Finally, the results obtained for [U(IV)], [$U_{total}$], and [$PO_4^{3-}$] are better expressed from the following ratios:

$$\frac{[\mathrm{U(IV)}]}{[\mathrm{U(VI)}]} = 1.00 \pm 0.07 \qquad \frac{[\mathrm{U_{total}}]}{[\mathrm{PO_4^{3-}}]} = 0.99 \pm 0.03$$

These results are in agreement with the formula $U(UO_2)(PO_4)_2$ derived from the powder diffraction investigation. Consequently, it is clear that the expected orthophosphate $U_3(PO_4)_4$ is not prepared in the experimental conditions described above despite the initial selected proportion of reactants. To explain this feature, the following overall reaction scheme of the synthesis of uranium orthophosphate from ammonium hydrogenophosphate and $UO_2$ can be proposed:

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(21) Gasperin, M. *Acta Crystallogr.* **1990**, *C46*, 372.

(22) Denning, R. G. *Gmelin Handbuch Anorg. Chem.* **1983**, *A6*, 55.

(23) (a) Nord, A. G. In *Stoichiometry of Organometallic and Inorganic Compounds*, Bernal, I., Ed; Elsevier: Amsterdam, 1986; Vol. 1, pp 50–145. (b) Baur, W. H. *Acta Crystallogr.* **1974**, *B30*, 1195.

(24) Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; p 547.

(25) Baur, W. H. *Am. Mineral.* **1972**, *57*, 709.

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(27) Charlot, G. In *Les Méthodes de la Chimie Analytique*; Masson: Paris, 1966, p 847.

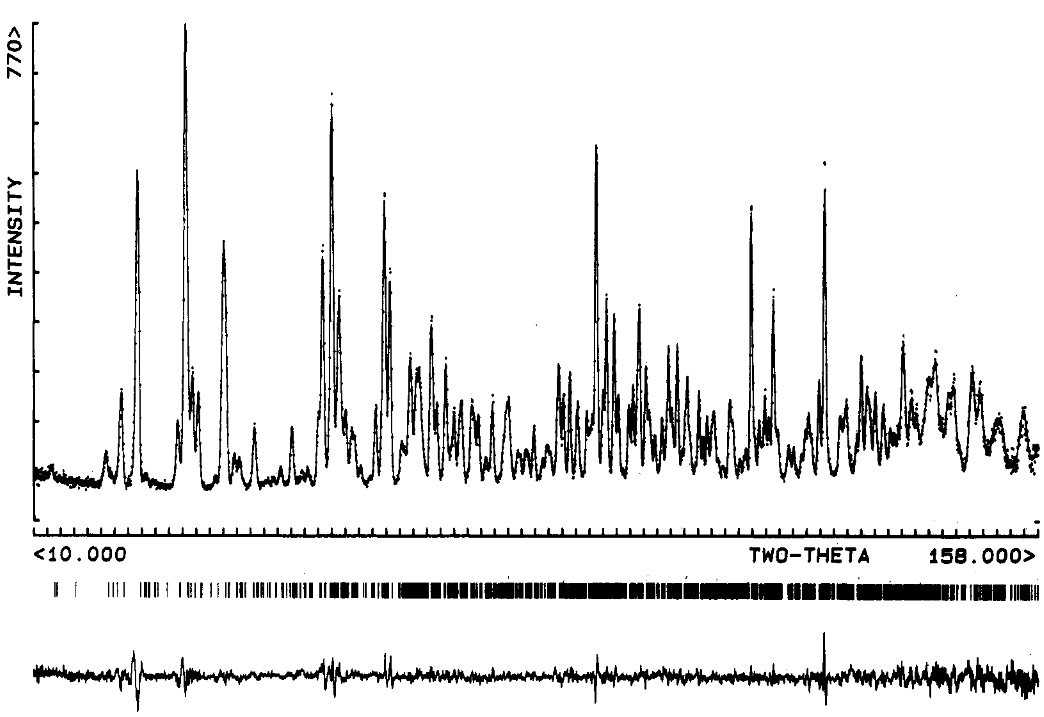

**Figure 2.** Final Rietveld plot of $U(UO_2)(PO_4)_2$ from neutron powder diffraction.

**Table 4. Selected Bond Distances (Å) and Angles (deg) with Their Standard Deviations for $U(UO_2)(PO_4)_2$ from Neutron Powder Diffraction**[a]

| | | | |
|---|---|---|---|
| | Uranium Atoms Coordination | | |
| U(1)–O(1) | 2.219(5) | U(2)–O(2) | 2.267(6) |
| U(1)–O(3) | 2.460(6) | U(2)–O(3)$^{\mathrm{II}}$ | 2.419(6) |
| U(1)–O(4) | 2.177(6) | U(2)–O(5) | 1.764(6) |
| U(1)–O(6) | 2.171(6) | U(2)–O(8) | 1.767(6) |
| U(1)–O(7) | 2.341(6) | U(2)–O(9) | 2.362(6) |
| U(1)–O(7)$^{\mathrm{I}}$ | 2.543(6) | U(2)–O(9)$^{\mathrm{III}}$ | 2.561(6) |
| U(1)–O(10) | 2.318(6) | U(2)–O(10)$^{\mathrm{II}}$ | 2.573(6) |
| O(4)–U(1)–O(6) | 176.5(2) | O(5)–U(2)–O(8) | 176.1(3) |
| | Phosphate Groups | | |
| P(1)–O(2)$^{\mathrm{IV}}$ | 1.520(8) | O(2)$^{\mathrm{IV}}$–P(1)–O(3) | 111.2(5) |
| P(1)–O(3) | 1.540(8) | O(2)$^{\mathrm{IV}}$–P(1)–O(6)$^{\mathrm{IV}}$ | 111.8(5) |
| P(1)–O(6)$^{\mathrm{IV}}$ | 1.510(8) | O(2)$^{\mathrm{IV}}$–P(1)–O(7)$^{\mathrm{I}}$ | 110.9(5) |
| P(1)–O(7)$^{\mathrm{I}}$ | 1.565(8) | O(3)–P(1)–O(6)$^{\mathrm{IV}}$ | 112.6(5) |
| | | O(3)–P(1)–O(7)$^{\mathrm{I}}$ | 99.6(4) |
| | | O(6)$^{\mathrm{IV}}$–P(1)–O(7)$^{\mathrm{I}}$ | 110.1(5) |
| P(2)–O(1)$^{\mathrm{V}}$ | 1.521(7) | O(1)$^{\mathrm{V}}$–P(2)–O(4)$^{\mathrm{VI}}$ | 109.9(4) |
| P(2)–O(4)$^{\mathrm{VI}}$ | 1.535(8) | O(1)$^{\mathrm{V}}$–P(2)–O(9)$^{\mathrm{III}}$ | 112.0(4) |
| P(2)–O(9)$^{\mathrm{III}}$ | 1.539(8) | O(1)$^{\mathrm{V}}$–P(2)–O(10)$^{\mathrm{III}}$ | 111.9(4) |
| P(2)–O(10)$^{\mathrm{II}}$ | 1.537(7) | O(4)$^{\mathrm{VI}}$–P(2)–O(9)$^{\mathrm{III}}$ | 109.4(4) |
| | | O(4)$^{\mathrm{VI}}$–P(2)–O(10)$^{\mathrm{II}}$ | 110.3(4) |
| | | O(9)$^{\mathrm{III}}$–P(2)–O(10)$^{\mathrm{II}}$ | 103.1(4) |

[a] Symmetry code: (I) $1 - x, -y, 1 - z$; (II) $1 - x, 1 - y, 1 - z$; (III) $2 - x, 1 - y, 1 - z$; (IV) $x, y, 1 + z$; (V) $1 + x, 1 + y, 1 + z$; (VI) $1 + x, 1 + y, z$.

(i) From room temperature to 280 °C, the reaction is endothermic and volatile products are eliminated.

(ii) From 280 to 500–600 °C, the reacting mixture is amorphous and the initial stoichiometry ($U/P = {}^3/_4$) is not conserved.

(iii) From 500–600 to 1100 °C several reactions take place, giving a partly crystallized diphosphate phase ($UP_2O_7$), which then disappears to form an orthophosphate. At the end of this process, 33% of the total phosphate amount is decomposed, and simultaneously 50% of U(IV) is oxidized into the hexavalent state.

It is quite unusual to observe the decomposition of phosphate at temperature below 800 °C. To explain this feature, the redox properties of the couple U(IV)/U(VI) can be evoked. Tetravalent uranium is oxidizable and through its oxidation the thermal degradation of phosphate is induced. This reaction stops when exactly (at 1100 °C) half the amount of uranium is the +4 state. This feature can be attributable to the crystal lattice energy of uranium phosphate, which stabilizes both oxidation states of uranium in a strong phosphate matrix. Besides the phosphate disappearance during synthesis, it has been observed that air is needed to obtain a pure uranium phosphate phase. In several attempts carried out in an argon atmosphere, the sample obtained had an X-ray powder diffraction pattern corresponding to a mixture of uranium(IV) diphosphate and a dominating orthophosphate $U(UO_2)(PO_4)_2$ phase. This observation emphasizes how phosphate decomposition is necessarily connected to tetravalent uranium oxidation. However, syntheses starting with a stoichiometry of $U/P = 1/1$ leads to pure final product only in air.

## Spectroscopic Measurements

**Optical Absorption.** The absorption spectrum of uranium phosphate powder in the UV–visible is shown in Figure 6. Optical properties of U(IV) and U(VI) in various types of matrices are well known.[28] Fortunately, ranges of energy where absorption takes place for each uranium ion are not overlapping. Main absorption lines due to tetravalent uranium spread from about 450 nm up to 1.3 μm, while uranyl ions absorb only below 450 nm. An assignment of the absorption bands in terms of the corresponding multiplets is then possible. This can be done when, for a given ion and a given symmetry, the positions in energy of the crystal field levels are already known. In addition, it is considered that the crystal field in the uranium phosphate is of the same order of magnitude than in $ThBr_4$ and in $ThCl_4$.[29] With these assumptions, the analysis of the uranium phosphate spectrum is quite simple.

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(29) Hubert, S.; Chong Li Song; Genet, M.; Auzel, F. *J. Solid State Chem.* **1986,** *61,* 252.

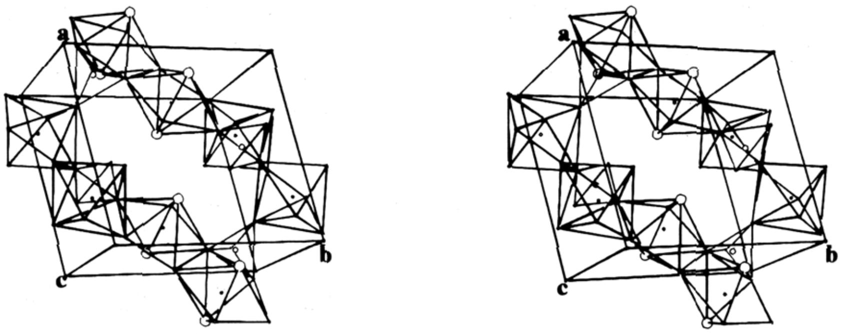

**Figure 3.** ORTEX[16] stereoscopic view of $U(UO_2)(PO_4)_2$ with U in small circles, O(5) and O(8) at the apices of the U(2) bipyramid are in large circles.

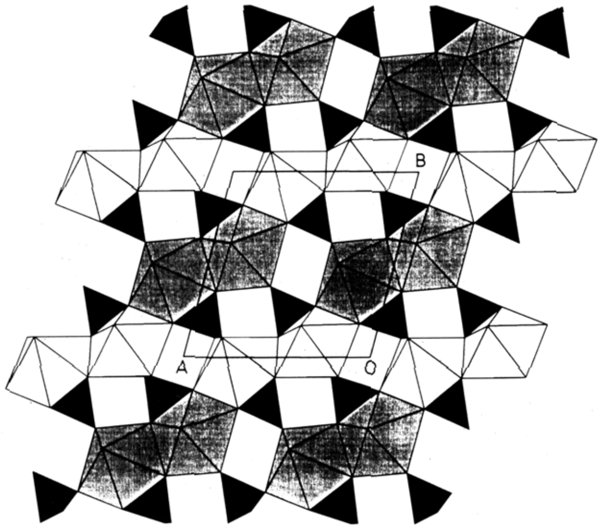

**Figure 4.** Projection of the structure of $U(UO_2)(PO_4)_2$ along [001] in terms of pairs of edge-sharing bipyramidal pentagons around uranium atoms. Note that the $U(2)O_7$ polyhedra are more shaded than the $U(1)O_7$ groups.

In the visible, four intense bands are seen at about 470, 480–520, 530–570, and 580–650 nm. They respectively correspond to the multiplets $^3P_2$, $^1I_6$, and $^3P_1$ and, for the broad and intense band in the red, to a mixture of several levels, $^1G_4$, $^1D_2$, and $^3P_0$. The weak absorption at around 750 nm is assigned as $^3H_6$. All these absorption lines are in good agreement with what is expected for $U^{4+}$ ions in a crystal[28]. Furthermore, it was checked that the appearance of intense absorption in the region 0.9–1.2 μm ($^3F_3$, $^3F_4$) definitely confirmed the existence of $U^{4+}$ ions in $U(UO_2)(PO_4)_2$.

In the ultraviolet domain, down to 450 nm, the spectrum exhibits the characteristic absorption shape of uranyl ions; it consists of four main lines regularly spaced and located at 444, 429, 416, and 404 nm. Their intensity smoothly decreases towards shorter wavelengths. This spectrum, known for a long time, has never been interpreted with any conflict.[22,28] The more recent results and calculations imply a molecular model where the atomic levels of oxygen (2s,2p) are combined with the 5p, 5f, and 6d atomic orbitals of uranium.[30,31]

It is worth noting that the spectroscopic properties of molecular uranyl ions are not very sensitive to the environment of the ions; thus, a simple comparison of the absorption spectrum of $U(UO_2)(PO_4)_2$ with any other uranyl compound is sufficient to determine that there is no great difference.

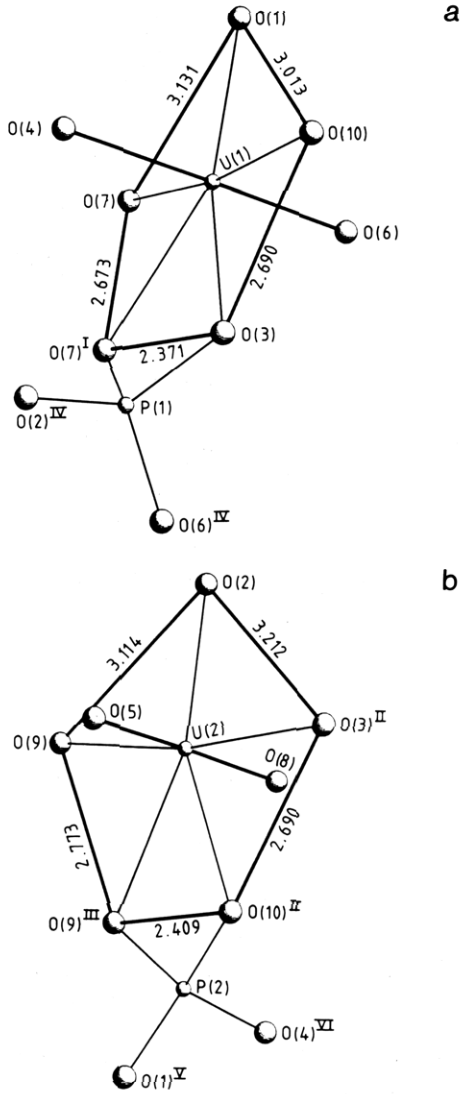

**Figure 5.** Coordination polyhedron of (a) U(1) and (b) U(2) atoms in $U(UO_2)(PO_4)_2$.

*From the optical absorption of our uranium phosphate,* it clearly appears that the presence of $U^{4+}$ and $UO_2^{2+}$ ions is unambiguous. Further studies at low temperature and in the far-infrared region are in progress.

A special remark needs to be made. Uranyl ion is usually strongly fluorescent under UV excitation with a mercury lamp, whatever the medium, liquid or solid state. Pres-

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[30] Denning, R. G. *Struct. Bonding* **1992**, *79*, 215.

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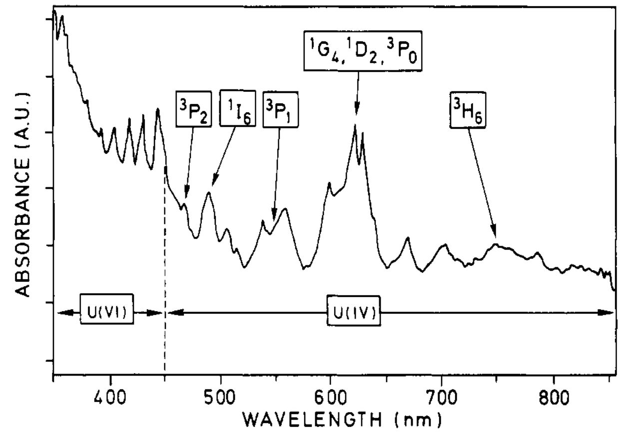

**Figure 6.** UV-visible absorption spectrum for $U(UO_2)(PO_4)_2$.

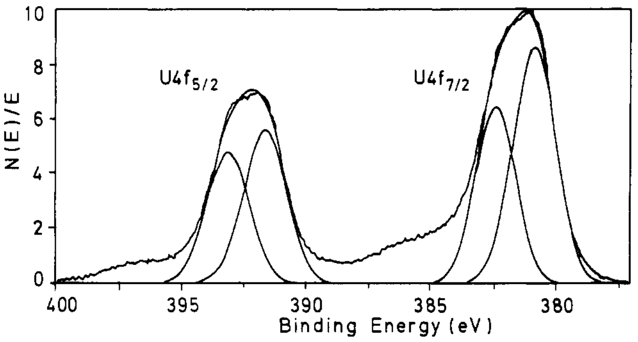

**Figure 7.** X-ray photon spectroscopy spectrum for $U(UO_2)(PO_4)_2$.

ently, this fluorescence has not been observed, even at liquid nitrogen temperature. This quenching effect is rare but has already been reported.[32] In uranium phosphate, it could be due to an energy transfer from U(VI) to U(IV) or to a pair effect between two adjacent U(VI).

**X-ray Photoelectron Spectroscopy.** The XPS spectrum is shown on Figure 7. Bands associated to the uranium $4f_{7/2}$ and $4f_{5/2}$ are broad and asymmetric. Their decomposition leads to two components for each band. For the $4f_{7/2}$ level, energies 380.7 and 382.2 eV with a full width at half-maximum height of about 2 eV are in agreement with values already published for $U_3O_8$.[33] The energy difference between the two peaks (~1.5 eV) is much greater than in $U_3O_8$ (~0.9 eV).[33] Analysis of the $4f_{5/2}$ gives the same difference in energy, but the peaks are a little bit broadened (~2.1 eV). Earlier data on $UO_3$, which is a U(VI) compound, have mentioned two low-intensity satellites located at 3.7 and 10.6 eV on the high binding energy side.[34] It should be noted that between the doublets 5/2 and 7/2 a weak shoulder is present at around 386 eV with a different energy of 3.8 eV to the 382.2-eV peak of the $4f_{7/2}$ band. The other satellite must be masked under the $4f_{5/2}$ band. A more detailed investigation of the XPS data is needed to confirm these satellites. The assignment of the two peaks of each doublet (5/2 and 7/2) can be done by comparison with $U_3O_8$ (see below). The low binding energy peak of $4f_{7/2}$ (380.7 eV) is attributed to tetravalent uranium while those at 382.2 eV corresponds to the hexavalent state. The 5/2 doublet behaves similarly. In $U_3O_8$ the peak areas are in the ratio U(IV)/U(VI) = 1/2 according to the chemical composition given to this mixed oxide: $U^{IV}U_2{}^{VI}O_8$. In $U(UO_2)(PO_4)_2$ the proportion of U(IV) should be equal to that of U(VI). In fact, in Figure 7, the area of the U(IV) band is greater than that for U(VI). That is likely due to a reduction effect produced by the flux of electrons emitted together with the X-rays from the Mg K$\alpha$ source. These electrons are not screened and interact with the uranium phosphate surface, inducing the transformation of U(VI) into U(IV). Other effects could also be responsible for such a reduction. They have already been observed by Allen *et al.* for $U_3O_8$,[33] and they imply chemical reactions taking place under a high vacuum, and they also involve the radiation chemistry induced by the X-ray beam. The longer the exposure time of the samples, the greater is the reduction. In our case, it has been verified that for a short acquisition time (within a minute), the decomposed spectrum of any component of the doublet fits roughly with equal amounts of U(IV) and U(VI).

**Table 5. Energy Binding of Uranium $4f_{7/2}$ Level**

| compound | *E* (eV) | ref |
|---|---|---|
| $UO_2$ | 380.2 | 39 |
| $U_2O_5$ | 380.9<br>379.7 | 41 |
| $\alpha$-$U_3O_8$ | 380.6<br>379.7 | 33 |
| $\gamma$-$UO_3$ | 381.9 | 40 |
| $UF_4$ | 382.0 | 41 |
| $U(UO_2)(PO_4)_2$ | 382.2<br>380.7 | this work |

## Discussion

Uranium oxidation states are numerous: III, IV, V, VI, but two of them, III and V, are very unstable, especially in aqueous solutions. The tetravalent state is oxidizable, and thus the potentiality of uranium to exist in two different valence states in a same material is small and it explains why only a few compounds contain a mixed valence. There are two types of uranium compounds which belong to the mixed valence category, the uranium oxides ($U_3O_8$, $U_2O_5$, $U_4O_9$, ...), uranium chalcogenides,[35,36] and the intermetallic materials, like uranium silicides.[37] The latter type represents new kinds of chemical products for which most of the results concern their conductivity properties, and it is not easy to say from these measurements how they could be classified in terms of mixed-valence compounds. This controversial field is widely open to discussion. Concerning uranium oxides, they have been intensively studied for the past 2 decades. The uranium-oxygen system is very complex and it is often assumed that from $UO_2$ to $UO_3$, instead of defined compounds, a continous solid solution of oxygen in uranium is obtained. Nevertheless, compounds whose stoichiometry corresponds to $U_4O_9$, $U_3O_8$, and $U_2O_5$ were analyzed by XPS. $U_4O_9$ shows a spectrum difficult to interpret where the main part of the uranium is tetravalent, and the rest might be pentavalent.[38] In Table 5 are reported the XPS results of $U_3O_8$, $U_2O_5$, and $U(UO_2)(PO_4)_2$ together with additional references on $UO_2$ , $UO_3$, and $UF_4$. Each oxide $U_3O_8$ and $U_2O_5$ is sometimes considered respectively as a mixture of $UO_2 + 2UO_3$ and $UO_2 + UO_3$ with a ratio U(IV)/U(VI) of 1/2 and 1/1.[41]

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From a chemical point of view, comparing the same atomic level of an element with different oxidation states, the highest one has the highest binding energy. Thus, for a given doublet the lowest binding energy is representative of U(IV) and the highest of U(VI). Therefore, the 380.7- and the 382.2-eV levels of uranium in the phosphate matrix have been attributed to U(IV) and U(VI). On the other hand, for the same oxidation state, the binding energy increases as the bond becomes more ionic. Thus, for the U(IV) $4f_{7/2}$ level, an increase of the binding energy is observed for the sequence: $UO_2$, $U_3O_8$, $U(UO_2)(PO_4)_2$, $U_2O_5$, and $UF_4$ (uranium tetrafluoride being considered as the more ionic compound of this series).

The absorption spectrum of $U(UO_2)(PO_4)_2$ does not show any evidence of a charge-transfer band to convert $U^{4+}$ to $UO_2^{2+}$. This conversion seems difficult to realize, since the two-electron exchange would be associated with an important structural change because of the breakdown of two double oxygen bonds for the uranyl ion. The needed energy should be high, and this transition should be in the ultraviolet. Such a band is not really observed, though the absorbance value increases of an order of magnitude from 380 to 200 nm.

As uranium is present in $U(UO_2)(PO_4)_2$ in two different valence states without any possible conversion between them, this compound might be classified in class I according to the Robin and Day proposition,[42] while $U_3O_8$ and $U_4O_9$ belong to the class II owing to their semiconducting properties.[38–42] The electrical conductivity of uranium phosphate has not yet been studied; however, phosphates, except the Nasicon type, are generally considered as insulators as is expected for a class I compound.

As indicated in the Introduction, the chemistry of uranium phosphates reported until now in the literature was on the whole confused, with suggested chemical formulas containing phosphate and diphosphate groups. This structural work has clearly demonstrated that phosphate groups are contained in $U(UO_2)(PO_4)_2$. From some distant apparent analogies between its diffraction pattern and those of the compounds previously reported, $U_3(PO_4)_4$[2] and $(U_2O_3)P_2O_7$,[3] it is likely that those two last chemical formulas are not correct. Nevertheless, it is interesting to note that in the diphosphate material, the presence of uranium with mixed valence was observed as well as uranyl groups, but the ratio P/U was found to be 1.15.[4] The present study has revealed that a new orthophosphate, $U(UO_2)(PO_4)_2$, exists in the $UO_2$–$P_2O_5$ system; this result should contribute to clarify the chemistry of this system.

To conclude, from the application of modern powder crystallography techniques, the crystal structure of uranium phosphate has been solved. It is worth noting that the result has been obtained with a high-resolution system using a conventional X-ray source. Since no structural data was known for the phases described in the system $UO_2$–$P_2O_5$, the novel structure reported here sheds new light on the crystal chemistry of uranium phosphates. From the neutron powder diffraction, an accurate description of the structure has been reported. This *ab initio* structure determination has demonstrated that the material has the chemical formula $U(UO_2)(PO_4)_2$ with two oxidation states for uranium.

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