

Solid-State Water-Catalyzed Transformation at Room Temperature of a Nonluminescent Linear-Chain Uranyl Phenylphosphonate into a Luminescent One

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Abstract: Single crystals of a recently prepared, at room temperature non-luminescent, linear-chain α -uranyl phenylphosphonate (α -UPP), $[\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O})]_2 \cdot 8\text{H}_2\text{O}$, transform at room temperature and moderate humidity into a new strongly luminescent linear-chain β -uranyl phenylphosphonate (β -UPP), $\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$. Both compounds have also been synthesized separately and characterized by single-crystal methods. The α -phase crystallizes in the triclinic space group $P\bar{1}$, with $a = 11.724(4)$ Å, $b = 16.676$ Å, $c = 11.375$ Å, $\alpha = 101.61(5)^\circ$, $\beta = 106.76(3)^\circ$, $\gamma = 102.57(4)^\circ$, and $Z = 2$, whereas the β -phase crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.766(2)$ Å, $b = 11.255(2)$ Å, $c = 20.959(4)$ Å, $\beta = 100.38(3)^\circ$, and $Z = 4$. In both compounds, the coordination of the uranium atoms is pentagonal bipyramidal, and the metal-to-phosphonate ratio is 1:2. The most obvious difference between the two linear-chain compounds is the manner in which their phenyl rings are arranged. When viewed along the appropriate axes, phenyl rings of α -UPP arrange in two rows in a cis conformation, whereas those of β -UPP arrange in two rows in a trans conformation. The suggested mechanism of transformation consists of breaking a U–O_{equatorial} bond, followed by a rotation of a phenylphosphonate group. During this rotation, the protonated phosphonate oxygen is deprotonated by one of the lattice water molecules and the detaching phosphonate oxygen is protonated. The deprotonation appears to be the rate-determining step of the transformation, not the U–O_{equatorial} bond breaking. The linear uranyl phenylphosphonate chains remain uninterrupted during the phase transformation process, but they shift and rearrange to form a different lattice as their shape changes from cis to trans.

Introduction

Phase transformations in the solid state are an important area of materials science, because it is concerned with dynamic properties of new materials and with the dynamic processes influencing these properties.^{1,2} Some of the properties for which these solid-state materials are of interest are mechanical properties such as hardness, inertness to corrosion, thermoelasticity, conductivity, and magnetism³ among others. Among the materials studied are metals and metal alloys,⁴ oxides, salts, ceramic materials, binary and ternary halogenides, and chalcogenides.⁵ Such compounds have relatively simple structures which has enabled theoreticians to quantify many of the processes⁶ and to formulate generally accepted laws.⁷ Since most of the mentioned materials are kinetically (more than thermodynamically) relatively stable, studying the dynamic processes in these materials on a reasonable time scale often requires elevated temperatures or other extreme conditions.⁸ Measurable changes of properties occurring at ambient conditions on a reasonable time scale are generally quite rare.

The area of metal phosphonate chemistry has recently expanded considerably,⁹ and many different types of phosphonate compounds have been prepared: layered,^{10–24} porous,^{25–28} linear,^{14,29–31} and others.^{32–34} As a part of our ongoing

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investigations of solid uranyl phosphonates^{20,26,29,35} we present an interesting phenomenon during which single crystals of a recently prepared and characterized nonluminescent linear-chain uranyl phenylphosphonate transformed at room temperature into a new, strongly luminescent phase. Subsequently, we were able to grow single crystals of this new phase and to determine its structure. A series of measurements also allowed us to propose a pathway for this transformation. The suggested mechanism includes the rotation of a phenylphosphonate group about a pivotal U–O bond, and instead of controlling the reaction rate by temperature, it is rather controlled by the humidity of the environment.

Experimental Section

Materials and Methods. Chemicals of reagent grade quality were obtained from commercial companies. Uranyl nitrate hexahydrate was recrystallized from water, and other chemicals were used without further purification. Thermogravimetric analyses (TGA) were carried out on a DuPont thermal analysis unit Model No. 951 unit at a rate of 10 °C/min in air. X-ray powder patterns were measured on a Seifert-Scintag PAD-5 powder diffraction unit with a Cu K α radiation at a step scan of 0.02° and at a rate of 1° per min. Electronic absorption spectra were acquired on a Varian/Cary 219 spectrometer. For spectrum acquisition, Nujol mull suspension of a solid sample was soaked into Whatman #1 filter paper and placed in the path of the sample beam, and filter paper soaked with Nujol mull alone was placed in the path of the reference beam. Electronic emission spectra were measured on an SLM Aminco, Model 8100 spectrometer with a xenon lamp and a 90° angle between the excitation and emission beams at a rate of 0.5 nm/s. Solid-state ³¹P MAS NMR spectra were collected on a Bruker MSL 300 spectrometer. IR spectra were obtained on a BIO-RAD FTS-40 spectrometer in KBr in the range 4000–400 cm⁻¹ with 64 scans and 4-cm⁻¹ resolution.

Synthesis of [UO₂(HO₂PC₆H₅)₂(H₂O)]₂·8H₂O (α -UPP). A 2.00 g (4.0 mmol) amount of UO₂(NO₃)₂·6H₂O (Strem Chemicals) was dissolved in 40 mL of deionized water in a plastic beaker, and 1.20 mL (34 mmol) of 48% HF (Aldrich) was added to the mixture. Next, 5.06 g (32 mmol) of H₂O₃PC₆H₅ (Aldrich) was dissolved in 60 mL of deionized water and filtered into the uranyl solution. The U:P:F molar ratio was 1:8:8.5. The total volume was adjusted to approximately 140 mL, seeded with previously grown small crystals, and the beaker was covered with a plastic lid. The next day, blossoms of thin yellow needles appeared, and after three more days they were isolated, washed with deionized water, and air-dried (yield 0.55 g or 20%). This procedure is a slight modification of a procedure published earlier.²⁹ The less concentrated reactants used here yielded a better crystalline product. If the crystals of the α -phase are not isolated from the mother liquor in approximately 5 days after preparing the solution, the luminescent crystals of the β -phase start precipitating as well, thus contaminating the desired nonluminescent product. The mother liquor left standing for several days either at room temperature or at an elevated temperature (55 °C) produced block-shaped crystals of the β -phase.

Synthesis of UO₂(HO₂PC₆H₅)₂(H₂O)·2H₂O (β -UPP). A 2.00 g amount of UO₂(NO₃)₂·6H₂O (4.0 mmol) was dissolved in 40 mL of deionized water in a plastic beaker, and 1.40 mL (40 mmol) of 48% HF was added. Next, 5.06 g of phenylphosphonic acid, H₂O₃PC₆H₅

Table 1. Crystallographic Data for β -UPP

formula wt	638.25
<i>a</i> (Å)	7.766(2)
<i>b</i> (Å)	11.255(2)
<i>c</i> (Å)	20.959(4)
α (deg)	90.0
β (deg)	100.38(3)
γ (deg)	90.0
<i>V</i> (Å ³)	1802.0(7)
<i>Z</i>	4
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
ρ_{calc} (g/cm ³)	2.350
λ (Å)	0.71073
μ , (cm ⁻¹)	92.4
temp (°C)	-80
<i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>)]	0.042
<i>R</i> _w (<i>F</i> ₂) [<i>I</i> > 2 σ (<i>I</i>)]	0.105

$$^a R(F) = \frac{\sum(|F_o| - |F_c|)/\sum|F_o|}{\sum[F_o^2 - F_c^2]^{1/2}}, \quad R_w(F_o^2) = \left\{ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)]} \right\}^{1/2}$$

Table 2. Selected Bond Lengths (Å) for β -UPP

U(1)–O(1)	1.778(7)	P(1)–O(5)	1.483(8)
U(1)–O(2)	1.777(7)	P(1)–O(7)	1.586(8)
U(1)–O(3)	2.381(7)	P(1)–C(1)	1.79(1)
U(1)–O(4)	2.336(7)	P(2)–O(4)	1.510(7)
U(1)–O(5)	2.325(7)	P(2)–O(6)	1.499(8)
U(1)–O(6)	2.317(7)	P(2)–O(8)	1.592(7)
U(1)–O(W1)	2.518(7)	P(2)–C(7)	1.77(1)
P(1)–O(3)	1.515(7)		

(32 mmol), was dissolved in 60 mL of deionized water and filtered into the uranyl solution with stirring. The U:P:F ratio was 1:8:10. The solution was covered with a plastic lid, and the beaker was placed in an oven at 55 °C. The next day, tiny luminescent cube-like crystals appeared on the walls of the beaker and on the bottom. No nonluminescent needles of α -UPP were observed in the beaker. For a single-crystal analysis, small crystals were isolated after only about 2 days. After 10 days, this procedure yielded large (up to 3 mm), block-like crystals, which were stable in air over a long period of time.

X-ray Structure Analysis

The crystal structure determination of α -UPP was published earlier.²⁹

UO₂(HO₂PC₆H₅)₂(H₂O)·2H₂O (β -UPP). A yellow crystal of dimensions 0.4 × 0.4 × 0.3 mm was isolated from the solution, mounted on a glass fiber, and then transferred onto the diffractometer under a steady nitrogen stream at a constant temperature of -80° C. Data collection was carried out on a Siemens P4 diffractometer operating at 50 kV and 30 mA with Mo K α radiation ($\lambda = 0.71073$ Å), equipped with a Siemens LT-2 cryostat. Unit cell parameters were calculated from 25 reflections between 15 and 30°. Intensity data were collected at -80 °C by using the ω -2 θ scan mode to a maximum value of 2 $\theta = 50^\circ$. Three intensity standards were measured every 100 reflections, and their intensities were found to be constant within the entire data collection. A total of 3419 reflections were collected of which 3170 were independent. The total number of observed reflections (*I* > 2 σ) was 2466. Data were corrected for Lorenz and polarization effects.

The structure of β -UPP was solved by the Patterson method with use of the SHELXS-86 program and refined with use of the SHELXL-93 program. The position of the uranium atom was first located in the Patterson map, and the positions of the remaining atoms were obtained in difference Fourier maps. No hydrogen atoms were found, so they were placed on the phenyl groups in calculated positions and assigned fixed temperature factors. All atoms were refined anisotropically. The final cycle of full-matrix refinement was based on 3170 reflections and 236 parameters. The maximum and minimum residual peaks on the final difference Fourier map corresponded to +2.64 and -1.77 e/Å³, and the highest residual peaks were found close to the uranium atom. Crystallographic data for β -UPP are listed in Table 1, atomic coordinates and thermal parameters in Supporting Information, bond lengths in Table 2, and bond angles in Table 3.

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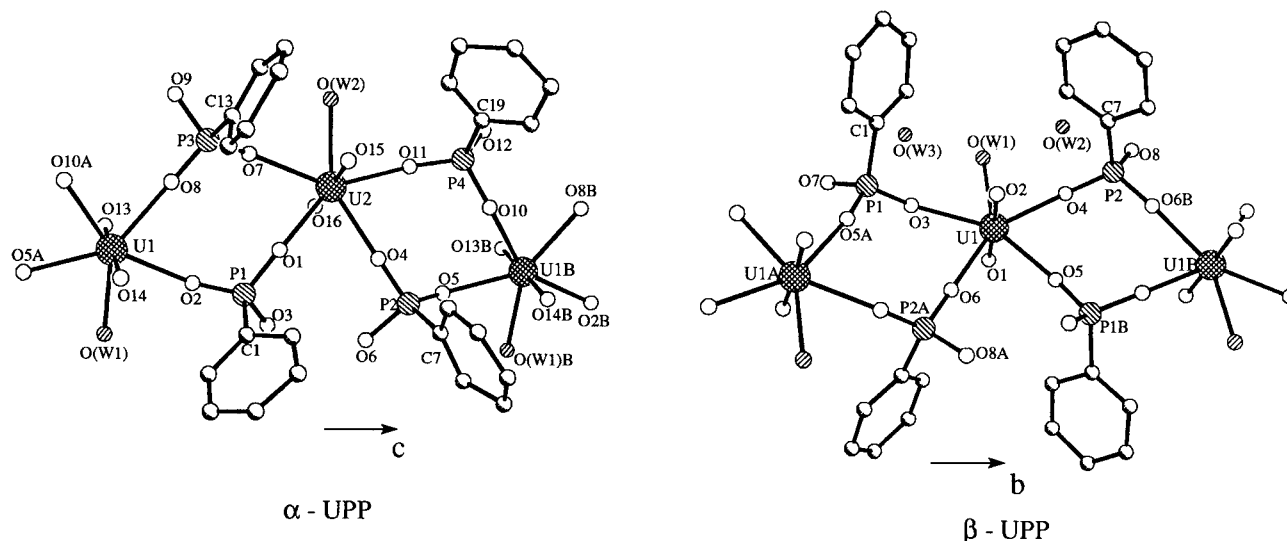


Figure 1. Coordination and bonding in nonluminescent α -UPP and in luminescent β -UPP. The linear chains of the two phases propagate along axes c and b , respectively.

Table 3. Selected Bond Angles for β -UPP

O(1)–U(1)–O(2)	177.9(3)	O(3)–P(1)–O(5)	115.3(4)
O(1)–U(1)–O(W1)	85.8(3)	O(3)–P(1)–O(7)	102.0(4)
O(1)–U(1)–O(3)	90.3(3)	O(5)–P(1)–O(7)	110.5(4)
O(1)–U(1)–O(4)	92.7(3)	O(3)–P(1)–C(1)	111.8(4)
O(1)–U(1)–O(5)	87.9(3)	O(5)–P(1)–C(1)	109.4(5)
O(1)–U(1)–O(6)	87.0(3)	O(7)–P(1)–C(1)	107.4(5)
O(2)–U(1)–O(W1)	94.9(3)	O(4)–P(2)–O(6)	117.6(4)
O(2)–U(1)–O(3)	88.1(3)	O(4)–P(2)–O(8)	107.7(4)
O(2)–U(1)–O(4)	89.4(3)	O(6)–P(2)–O(8)	106.7(4)
O(2)–U(1)–O(5)	93.0(3)	O(4)–P(2)–C(7)	109.3(4)
O(2)–U(1)–O(6)	91.2(3)	O(6)–P(2)–C(7)	109.6(5)
O(3)–U(1)–O(W1)	68.6(2)	O(8)–P(2)–C(7)	105.2(4)
O(W1)–U(1)–O(4)	66.5(2)	P(1)–O(3)–U(1)	141.5(4)
O(4)–U(1)–O(5)	73.6(2)	P(2)–O(4)–U(1)	147.2(5)
O(5)–U(1)–O(6)	76.4(3)	P(1)–O(5)–U(1)	162.0(5)
O(6)–U(1)–O(3)	75.3(2)	P(2)–O(6)–U(1)	170.8(5)

Results

Structures of α -UPP and of β -UPP. The structure of α -UPP consists of linear chains,²⁹ and β -UPP resembles the α -phase in many aspects (Figure 1).

In both compounds, the uranium atoms adopt a slightly distorted pentagonal bipyramidal geometry with the uranyl oxygen atoms at the apices. In the equatorial plane, each uranium is coordinated by four oxygen atoms of four different phosphonate groups and by an oxygen of a water molecule. The adjacent metal atoms are bridged by pairs of phenylphosphonate groups. Each phosphonate group, however, uses only two of its oxygen atoms for the purpose of bridging, and the third oxygen atom is protonated. The linear chains in the α - and β -phases propagate along the c -axis and b -axis, respectively. From the crystallographic viewpoint, the β -phase has a higher symmetry even on the atomic level. There are two crystallographically distinct uranium atoms and four distinct phenylphosphonate groups in α -UPP as opposed to only one unique uranium atom and two unique phenylphosphonate groups in β -UPP.

The analogous bonding distances and bonding angles in the α - and the β -phases are very similar as well. The U–O_{axial} bond lengths are very short, 1.74 to 1.84 Å in α -UPP and 1.78 Å in β -UPP, whereas the bridging U–O_{equatorial} bond distances are much longer, and they range from 2.29 to 2.38 Å for α -UPP and from 2.31 to 2.38 Å for β -UPP. The U–O distances involving the coordinating water molecule are 2.46 and 2.52 Å

in the α -phase and 2.52 Å in the β -phase. The O–U–O bond angles in the equatorial plane range between 68 and 74° for α -UPP and between 66 and 76° for β -UPP, which in both cases is reasonably close to the ideal 72° for a regular pentagonal arrangement.

The values found for the P–O_{bridging} bond distances range from 1.45 to 1.53 Å for the eight bonds of the α -phase and 1.48 to 1.51 Å for the four bonds of this type in the β -phase. The longer P–O_{terminal} distances (1.60–1.63 Å in α -UPP and 1.59 Å in β -UPP) confirm the P–OH bond.

The linear chains of the α - and β -phase uranyl phenylphosphonates propagate along the c -axis ($c = 11.375$ Å) and b -axis ($b = 11.255$ Å), respectively (Figure 2), and the phenyl rings of each chain form two rows standing nearly perpendicular to the chains.

In α -UPP the two rows of phenyl groups point in the same general direction of the uranyl phosphonate chain in a *cis* fashion (Figure 3), and the angle between the two rows, derived from the torsion angle C1–P1–P3–C13, is approximately 33°. The opposite, “open” side of each chain is hydrophilic, because the hydroxyl POH and the coordinated water molecules reside there. This side accommodates 8 lattice water molecules for every 2 uranium atoms. The adjacent chains also orient their hydrophobic phenyl sides to each other and their open hydrophilic sides to each other so as to form alternating hydrophobic and hydrophilic regions parallel to the a – c plane.

In contrast to the α -phase, in β -UPP the two rows of phenyl rings point in the opposite direction of the uranyl phosphonate chain in a *trans* fashion. As building blocks, the *trans* chains cannot form alternating hydrophobic and hydrophilic planes as was observed in α -UPP. Instead, the neighboring UP chains stack themselves along the a -axis to form a pseudo-layer in the a – b plane that is roughly an a -dimension in width and extends infinitely in the b -direction. These pseudo-layers are then translated along the c -axis, interlocking each other by means of their protruding phenyl rings. The space between the UP chains accommodates two lattice water molecules OW2 and OW3 that are hydrogen bonded to the water molecule OW1, coordinating the uranium atom at distances of 3.11 and 2.74 Å, respectively. In addition, water molecule OW2 is also hydrogen bonded to the protonated phosphonate oxygen atom O8 at a distance of 2.65 Å, and OW3 is similarly hydrogen bonded to O7 at a distance of 3.44 Å.

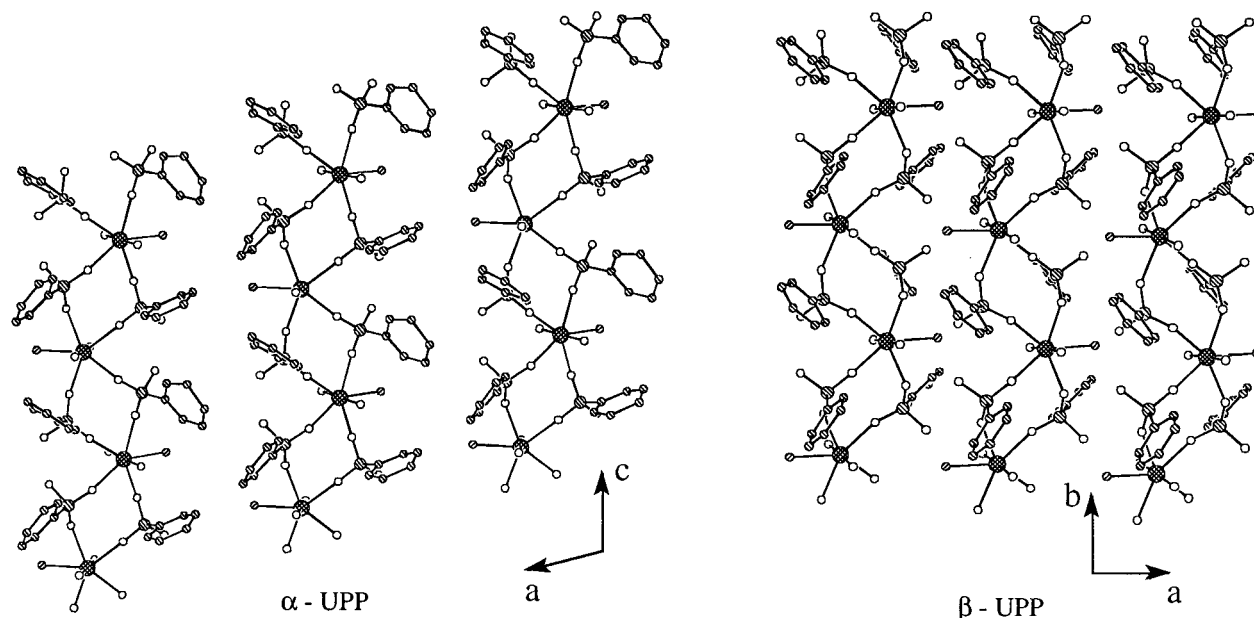


Figure 2. Arrangement of neighboring chains in uranyl phosphonates, α and β . Structures of the individual chains from this perspective appear very similar. However, the chains of the nonluminescent α -phase are more loosely arranged compared to the relatively tighter arrangement in the luminescent β -phase.

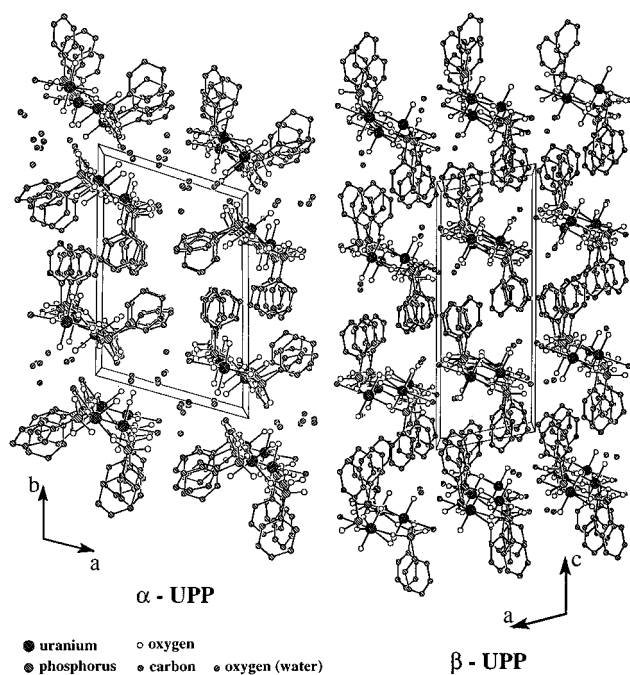


Figure 3. View of the unit cells of α -UPP and of β -UPP along the propagating linear chains. The α -phase arranges its phenyl rings in two rows in a cis fashion, whereas the β -phase arranges its phenyl rings in two rows in a trans fashion.

Electronic Absorption Spectra. Electron absorption spectra of both phases exhibit the vibronic progression typical for the uranyl ion, and both spectra appear very similar (Figure 4). In the spectrum of α -UPP the peaks and shoulders (sh) are found at 496, 479, 473, 464 (sh), 458, 448 (sh), 442 (sh), 435, 423, 411, 400, 389 (sh), 377, and 364 nm, and in the spectrum of β -UPP the peaks are positioned at 498, 482, 475, 466, 460, 453, 445 (sh), 439, 426, 414, 403, 392 (sh), 377, 367, and 357 nm. The α -UPP phase absorbs only at wavelengths shorter than 520 nm, and the baseline beyond this wavelength is virtually flat. The β -phase, however, shows a sloping shoulder ranging from the peak at 498 nm across the whole remaining portion of the visible spectrum. This slope is probably due to light scattering

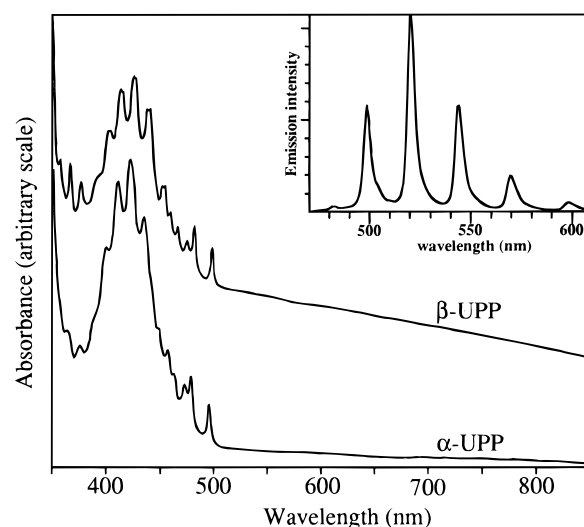


Figure 4. Electronic absorption spectra of α -UPP and of β -UPP, and the electronic emission spectrum of β -UPP (inset) at room temperature.

rather than to light absorption by a particular chromophore. Unlike in α -UPP, some peaks of β -UPP (at 453, 439, 426, 414, 403, and probably 392 (sh) nm) are split into two with the approximate spacings of 2 nm, which in this wavelength range corresponds to approximately 120 cm^{-1} .

IR Spectra. IR spectra of both compounds are almost identical, confirming all the important functional groups, which in fact are the same in both compounds. The IR spectrum of α -UPP has been published and bands assigned in detail earlier.²⁹

³¹P NMR Spectra. Both compounds exhibit very similar spectra. α -UPP shows a doublet of very sharp peaks in the 1:1 ratio at +21.1 and +18.5 ppm, and β -UPP shows a 1:1 doublet of equally sharp peaks at +23.8 and +19.8 ppm. The two signals correspond to two different kinds of phosphorus atoms in both structures.

Solid-State Transformation of α -UPP into β -UPP. When thin needles of α -UPP are enclosed in a vial and set aside at room temperature, they undergo a transformation into the β -phase. No visible change of the crystal shape is initially observed by the eye, but under the microscope, small hazy spots

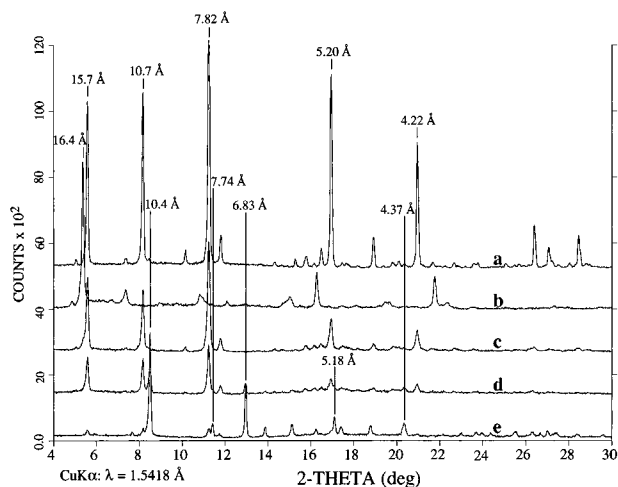


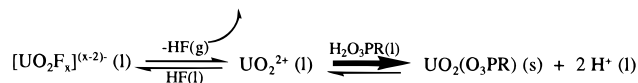
Figure 5. Transformation of α -UPP into β -UPP documented by X-ray powder patterns: (a) α -UPP, (b) α -UPP dehydrated in nitrogen gas stream for 10 h, (c) α -UPP rehydrated in 100% humidity for 2 days, (d) α -UPP rehydrated for 16 days, and (e) α -UPP rehydrated for 28 days.

appear on otherwise clear and transparent crystal surfaces. An inspection by a UV lamp reveals that the small nontransparent spots brightly luminesce in contrast to the remaining bulk of nonluminescent crystals. The amount of luminescent phase increases over time both visually and by X-ray powder patterns. After a year, between 90 and 100% of the single crystals of α -UPP are converted into β -UPP. The rate of transformation, however, depends on the size and the quality of the crystals. The identity of the transformed compound was confirmed by matching its X-ray powder pattern, electronic absorption spectrum, ^{31}P NMR spectrum, and TGA curve to the analogous measurements on freshly synthesized single crystals of β -UPP, and the match in all measurements was excellent.

This transformation process is significantly accelerated by increasing the humidity of the environment or by dehydrating the crystals of α -UPP and then rehydrating them in air saturated with water vapor. Passing dry nitrogen gas over the crystals of the α -phase causes them to collapse within seconds, and in approximately 10 h the compound loses up to 6 of the 8 uncoordinated lattice water molecules.²⁹ The X-ray powder pattern loses all peaks at $2\theta > 23$, indicating that the long-range ordering is lost. If the dehydrated powder is kept in a dry atmosphere, no transformation occurs, and the powder pattern remains unchanged (Figure 5). The dehydration process is reversible, and the exposure of the dehydrated sample to air saturated with water vapor leads to a complete rehydration (by TGA), and to an almost complete restoration of the original powder pattern of α -UPP within 2 days (Figure 5). The five strongest peaks of α -UPP are located at 15.7, 10.7, 7.82, 5.20, and 4.22 Å. Tiny luminescent dots start appearing in the powder under the UV light on the 5th day of rehydration, and peaks attributed to β -UPP appear in the powder pattern on the 10th day. Over the next several days the peaks of α -UPP diminish and the peaks of β -UPP grow. On the 28th day of rehydration, the peaks of the α -phase have mostly disappeared, and the powder pattern contains strong peaks of the β -phase; the five strongest peaks are located at 10.4, 7.74, 6.83, 5.18, and 4.37 Å (Figure 5). Grinding of the dehydrated sample before rehydration increased the rate of phase transformation about twice. An attempt to transform crystals of α -UPP into β -UPP by their immersion in pure water resulted in their visual decomposition within 2–3 days. The powder pattern of this residue was very poor, showing a high background with many broad, undefinable peaks.

Discussion

Reacting aqueous solutions of uranyl ions with phenylphosphonic acid immediately produces a precipitate of poorly defined composition and very low crystallinity. One way of preparing highly crystalline metal phosphonates is by first complexing the metal ion in solution by a ligand followed by slow removal of the ligand to ensure a very gradual precipitation of the product. The ligand used for the complexation of the uranyl ion here is fluoride ion supplied by the addition of HF. Several equilibria are involved in the overall reaction:



As fluoride is removed from the solution by evaporation in the form of HF, UO_2^{2+} becomes available to react with the phenylphosphonic anion, and single crystals or powder of high crystallinity is formed. This method was first used by Alberti et al.³⁶ to obtain single crystals of $\text{Zr}(\text{O}_3\text{POH})_2 \cdot \text{H}_2\text{O}$, and more recently it was used to obtain single crystals of α -UPP.²⁹ The mentioned equilibrium is very sensitive to the U/F ratio; adding slightly less HF leads to a product of very low crystallinity, whereas slightly more HF results in no precipitation. In addition, recent experiments have proven that both mentioned phases often precipitate out together, and preparing pure phases requires finding the conditions to favor the desired product. In this case, a slight change in the concentration of HF and in temperature produced such an effect. β -UPP is thermodynamically more stable than the α -phase, so it is easier to prepare without the presence of α -UPP by raising the temperature. However, it is more difficult to prepare α -UPP without contamination by β -UPP. Even if a pure batch of the nonluminescent crystals of α -UPP is successfully prepared, at room temperature these crystals start transforming into the luminescent β -phase within a few days. However, freezing the crystals to -20°C significantly inhibited the decay of crystals of α -UPP.

The results of the solid-state phase transformation pose two intriguing questions:

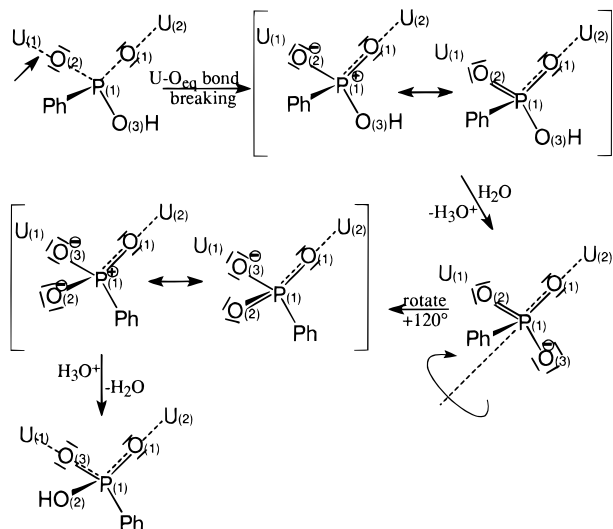
1. How does α -UPP transform at room temperature into β -UPP?
2. Why does β -UPP at room temperature luminesce so brightly whereas α -UPP with the same coordination environment around the UO_2^{2+} luminescence chromophore does not luminesce at the same conditions at all?

The answer to the first question can be divided into two parts. First, each of the chains must change their shape from cis to trans. Second, the transformed trans chains must shift so as to form a new lattice of the exact dimensions of β -UPP.

Inspection of the structure of α -UPP reveals that simple rotation of the phenylphosphonate group around its two bridging oxygens anchored by neighboring uranium atoms (Figure 1) cannot produce β -UPP. In such a case, the protonated terminal oxygen atom would end up on the inner side of the UP chain, not on the outer side. Clearly, the transformation cannot be accomplished without bond breaking and bond making. The crystal structure of α -UPP²⁹ revealed that all the U–O_{equatorial} bonds are significantly longer (approximately 2.35 Å) than the sum of the covalent radii of the uranium and oxygen atoms (2.15 Å). This suggests that the weak U–O_{equatorial} bond can be broken quite easily, possibly by the thermal vibration of the involved atoms. Upon such a bond breaking, the equatorial coordination of the uranyl ion would drop from 5 to 4, a quite

(36) Alberti, G.; Costantino, U.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113–1117.

Scheme 1



stable coordination environment of the uranyl ion.²⁹ The immediate local coordination deficiency of the uranium atom in place of the broken bond can be stabilized by the shift of the coordinating water molecule toward the coordination site vacated by the phosphonate oxygen. Therefore, it is more likely that the U–O_{equatorial} bond breaking affects oxygens adjacent to the coordinating water molecule; bonds likely to break during the α - to β -UPP transformation include U1–O2, U1–O5, U2–O7 and U2–O11, and bonds less likely to break include U1–O8, U1–O10, U2–O1 and U2–O4. An argument concerning the direction in which the infinite chains shift will be advanced later which shows that breaking of only two of the four mentioned bonds leads to the formation of the β -phase.

The rotation mechanism of a phosphonate group is described in Scheme 1 with the phosphonate group P1 as an example (compare with Figure 1). When the U1–O2 bond breaks, the hydrogen phenylphosphonate group is free to rotate around the U2–O1 axis. Rotation around the U2–O1 axis by 120° clockwise will cause O2 to move into the position occupied by C1, requiring C1 to move into the position occupied by the protonated O3, and O3 will move in place of O2. The oxygen atom O3, however, must be deprotonated before it can form a new bond with U1. The deprotonation of O3 and protonation of O2 is achieved by means of the unbound lattice water molecules which serve as proton carriers. The two intermediates are stabilized by resonance structures as depicted in Scheme 1.

The suggested mechanism is in accord with the experiments, indicating that dehydration of α -UPP stopped the transformation process, whereas increasing the humidity significantly sped up the reaction. Dehydration and rehydration caused the collapse of crystals, making them more porous and therefore more accessible to gaseous water molecules which catalyze the transformation. The significantly higher reaction rate at high humidity also suggests that deprotonation of the protonated oxygen atom is the rate-determining step of the cis-to-trans transformation, and not the U–O bond breaking.

Another hypothetical possibility would involve a deprotonation of the water molecule OW1 by the detaching oxygen O2 followed by the rotation and reprotonation of OW1 by O3. However, this mechanism is inconsistent with the observation during which the reaction stopped on exposing the crystals to dry nitrogen gas, because under such mild dehydrating conditions, the coordinated water molecules remain unaffected. In such a mechanism, there is no need for any unbound lattice water molecules, and the transformation rate would be expected to be independent of humidity.

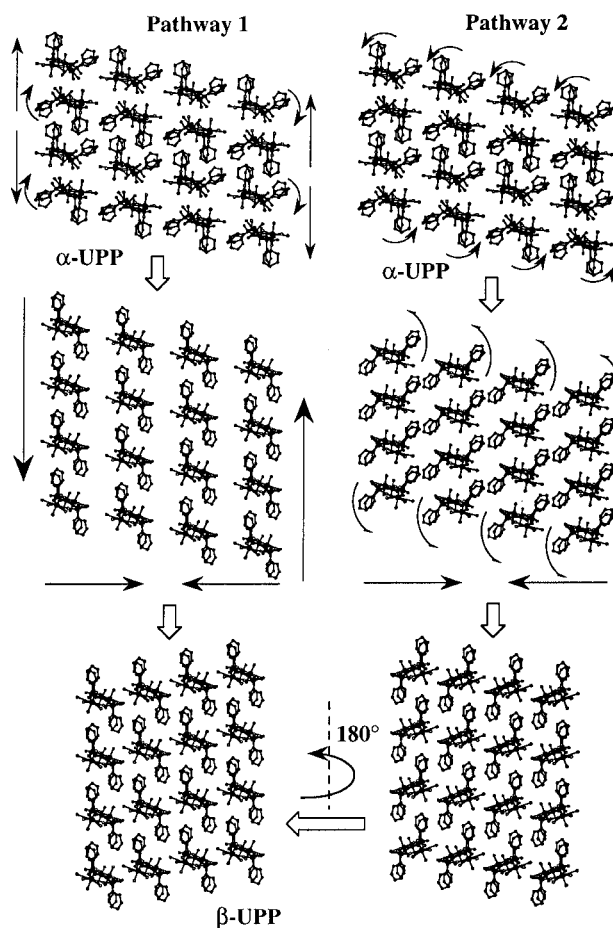


Figure 6. Two possible pathways of rearrangement of uranyl phenylphosphonate chains during the solid-state transformation of α -UPP into β -UPP. Pathway 2 is much more feasible than Pathway 1. For a detailed description, please see the text.

How do the newly formed trans chains rearrange to form a new lattice of β -UPP? Before attempting to answer this question, one must first realize that in α -UPP, the phenyl rings of phosphonate groups P1 and P2 are oriented parallel to the b -axis, whereas the phenyl rings of phosphonate groups P3 and P4 are tilted approximately 33° away from the b -axis (Figures 1 and 3). In β -UPP, all the phenyl rings are oriented parallel to each other and also parallel to the c -axis. After the rotation of the phosphonate groups all phenyl rings must be parallel to each other, so there are two possibilities of how this rearrangement of the chains occurs:

Pathway 1: The phenylphosphonate groups in α -UPP parallel to the b -axis, P1 and P2, remain in that orientation, and the tilted ones, P3 and P4, rotate to become parallel to the first half (Figure 6). During the rotation of the tilted phenylphosphonate groups, the chains would have to expand vertically to accommodate the increased size of the UPP chains in this direction (16.7 Å vs 21.0 Å). In the second step, the chains shift relative to each other in the vertical direction and they contract horizontally. In reality, these processes would be happening simultaneously, but the model in Figure 6 is helpful in understanding the direction of shifts of the UP chains.

Pathway 2: The phenylphosphonate groups tilted 33° from the b -axis, P3 and P4, remain in that orientation, and the ones parallel to the b -axis, P1 and P2, rotate. In the second step, the chains slightly rotate counterclockwise, and they contract horizontally. Even though the product looks like a mirror image of β -UPP, it should rather be understood as β -UPP viewed from the opposite direction of the b -axis.

In fact, only one of the two possible pathways is allowed, because mixing the chains produced by the first and the second pathways would not build a lattice of any sort. The presented data clearly favor Pathway 2 for at least two reasons: (1) In Pathway 1, the vertical expansion of chains in the first step is very unlikely to happen. This expansion would have to be driven by the phenylphosphonate groups rotating about the unbroken U–O_{equatorial} bond. Such a rotation is a very unlikely driving force for a lattice expansion, since the rotating phenylphosphonate group will accommodate in space requiring a minimum of energy rather than force the chains apart. In other words, rotation of a phenylphosphonate group is not a strong enough driving force for such an energetically demanding expansion. On the other hand, in Pathway 2 the rotating phenylphosphonate group does not experience any such steric obstacles and can rotate freely. (2) The second step of Pathway 1 is unlikely, especially the shifts of chains in the vertical direction relative to each other.

Now it is possible to determine, which U–O_{equatorial} bonds in α -UPP are most likely to break so as to initiate its transformation into the β -phase. Earlier, we have strongly favored the U–O bonds neighboring the coordinating water molecules, namely U1–O2, U1–O5, U2–O7, and U2–O11 (Figure 1). The reason was stabilization of the coordination sphere of the uranium atoms after such a bond breaking occurs. Of these four mentioned U–O bonds, it is possible to exclude those of the phenylphosphonate groups tilted 33° from the *b*-axis of α -UPP, because according to Pathway 2 these phenylphosphonate groups do not rotate. The only two U–O bonds remaining as likely candidates for the initial U–O_{equatorial} bond breaking thus are U1–O2 and U1–O5, and the pivotal bonds for the rotation are U2–O1 and U2–O4, respectively.

The second intriguing problem which arose during this research was determining what causes the sharply different luminescence behavior in the two phases in which the uranyl ion has virtually identical chemical environments. While β -UPP exhibits an intense emission with a spectrum very typical for the uranyl ion, the α -phase unexpectedly does not luminesce at room temperature at all. However, upon cooling to liquid nitrogen temperature, α -UPP does luminesce. In determining a possible cause for quenching of the α -phase at room temperature, it is possible to exclude electron transfer, because no suitable electron donor for the quenching of the uranyl luminescence is present in either of the two phases. Energy transfer of any sort can also be excluded, because there is no suitable chromophore to absorb the energy of the excited state of the uranyl ion. Since α -UPP luminesces upon cooling, lattice

vibrations, namely the thermal motion of the linear chains, are most likely responsible for a vibrational non-radiative decay. This suggestion also makes sense if one compares the structures and the distances between the chains in both compounds (Figures 2 and 3). The chains of α -UPP are packed much more loosely than those of β -UPP, and their additional vibrational freedom could reasonably cause a vibrational non-radiative decay of the uranyl luminescence in the α -phase. These investigations, however, are still in progress, and a more detailed explanation will be provided subsequently.

Conclusions

An interesting dynamic phase transformation process occurring in the solid state at room temperature has been studied. The transformation process of α -UPP into β -UPP was divided into two subsequent parts: the cis-to-trans transformation of the individual uranyl–phenylphosphonate chains, and rearrangement of the trans chains to form an entirely new lattice. By interpreting the results of experiments conducted at room temperature, it was possible to suggest a mechanism of the cis-to-trans transformation, as well as how the uranyl–phenylphosphonate chains rearrange. The described phase transformation process was accompanied by a drastic change of the luminescence properties for which a quantitative explanation has not been provided here. However, the nature of the different luminescence behavior of the two presented compounds has been suggested. We have shown that by a careful examination of limited data, it is possible to fairly accurately describe dynamic processes occurring even in an environment generally so unfavorable to mechanistic studies as the inorganic solid state.

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Supporting Information Available: Thermal ellipsoid figure of β -UPP, atomic coordinates of β -UPP, and anisotropic thermal parameters of β -UPP, non-essential intramolecular distances and bond angles of β -UPP (4 pages). See any current masthead page for ordering and Internet access instructions.

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