

Alkali-Ion-Catalyzed Transformation of Two Linear Uranyl Phosphonates into a Tubular One

Daniel Grohol and Abraham Clearfield*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received July 1, 1997

Uranyl ion UO_2^{2+} is widely known for its photochemical and photocatalytic redox behavior^{1–5} and for its interesting luminescence properties^{6,7} and rich spectroscopy.^{8–10} However, seldom is this linear ion thought to be capable of forming extended lattices of a variety of covalently bound structure types^{11,12} and, least of all, of undergoing transformations of these structures at room-temperature. Several recent investigations into how the uranyl ion interacts with alkyl- and arylphosphonic anions has led to the synthesis of a variety of structure types, linear-chain, layered, and tubular.^{13–16} This is somewhat surprising given the fact that the uranyl ion can bind ligands only in its equatorial plane. This axial anisotropy should lead to a limited number of possibilities in which this cation can interact with anionic ligands to form extended lattices compared with the isotropic cations of the M^{2+} type, but the opposite is true.

Very recently, we have synthesized two linear-chain structures, *cis*- α -uranyl phenylphosphonate (α -UPP), $[\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$,¹⁴ and *trans*- β -uranyl phenylphosphonate (β -UPP), $[\text{UO}_2(\text{HO}_3\text{PC}_6\text{H}_5)_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ ¹³ (Figure 1). Single crystals of α -UPP slowly transformed in air and at room temperature and moderate humidity into β -UPP.¹³ A mechanism for explaining the transformation was suggested, and it involved breaking of the $\text{U}-\text{O}_{\text{phosphonate}}$ bond and a rotation of the phenylphosphonate group about another, unbroken $\text{U}-\text{O}_{\text{phosphonate}}$ bond.

Upon attempting to investigate the ion-exchange properties of the two new compounds α -UPP and β -UPP, we have found that in the presence of the sodium or calcium ions in the form of NaCl , $\text{NaH}(\text{O}_3\text{PC}_6\text{H}_5)$, or CaCl_2 in an aqueous environment, both the linear-chain α -UPP and β -UPP transformed into another form, which has been structurally characterized earlier,¹⁷ the tubular $\text{UO}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot 0.7\text{H}_2\text{O}$ (γ -UPP). (Figure 2). The transformation was followed by X-ray powder patterns (Figure 3) which showed that a ground sample of α -UPP transformed

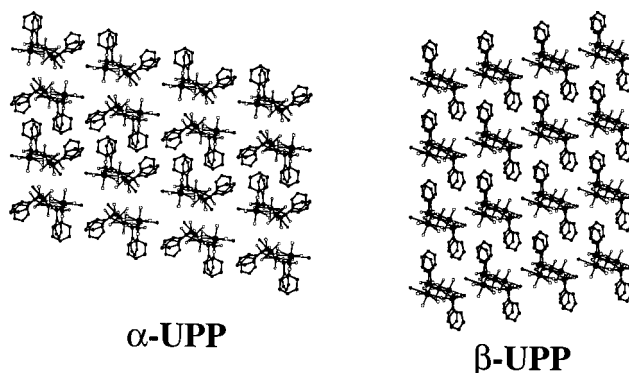


Figure 1. Structures of α -UPP and of β -UPP (view along the infinite linear chains).

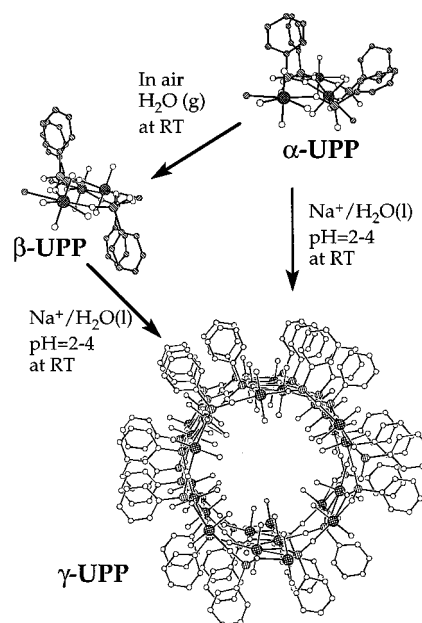


Figure 2. Transformations occurring between three uranyl phenylphosphonates at room-temperature conditions.

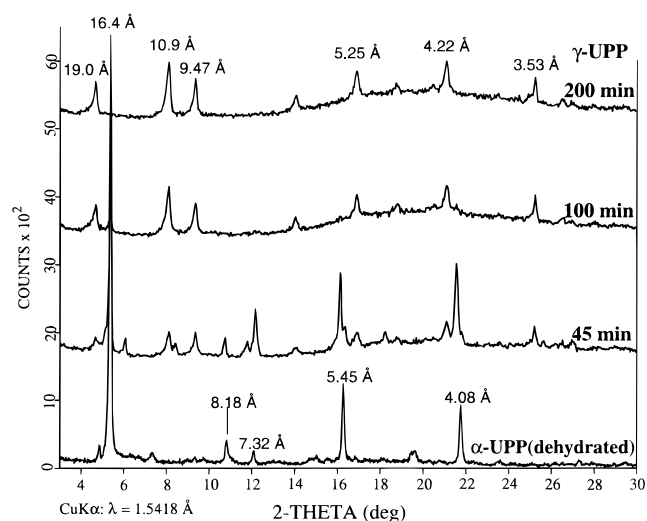


Figure 3. XRD powder patterns monitoring the transformation of *cis*- α -UPP into tubular γ -UPP.

into γ -UPP within 3 h, whereas a ground sample of β -UPP transformed under identical conditions into γ -UPP in approximately 7 h. Only a very small trace of the sodium ion was detected in the produced γ -UPP by atomic absorption spectroscopy. The transformation proceeded only in an acidic

- (1) Rabinowitch, E.; Belford, R. L. *Spectroscopy and Photochemistry of Uranyl Compounds*; Pergamon Press: Oxford, U.K., 1964.
- (2) Burrows, H. D.; Kemp, T. J. *Chem. Soc. Rev.* **1974**, *3*, 139–165.
- (3) Matsushima, R. *J. Am. Chem. Soc.* **1972**, *94*, 6010–6016.
- (4) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 1730–1735.
- (5) Suib, S. L.; Tanguay, J. F.; Occelli, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 6972–6977.
- (6) Hunsberger, L. R.; Ellis, A. B. *Coord. Chem. Rev.* **1990**, *97*, 209–224.
- (7) Brittain, H. G.; Perry, D. L. *J. Phys. Chem.* **1981**, *85*, 3073–3078.
- (8) Denning, R. G. *Struct. Bonding* **1992**, *79*, 215–276.
- (9) *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, 1982; Vol. A5.
- (10) Thorne, J. R. G.; Denning, R. G.; Barker, T. J.; Grimley, D. I. *J. Lumin.* **1985**, *34*, 147–165.
- (11) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements*, 2nd ed.; Chapman and Hall: London, 1986; Vol. 2.
- (12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons, Inc.: New York, 1988.
- (13) Grohol, D.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 4662–4668.
- (14) Grohol, D.; Subramanian, M. A.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5264–5271.
- (15) Poojary, D. M.; Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 1468–1473.
- (16) Poojary, D. M.; Grohol, D.; Clearfield, A. *J. Phys. Chem. Solids* **1995**, *56*, 1383–1388.
- (17) Poojary, D. M.; Grohol, D.; Clearfield, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1508–1510.

