through a bridging H_2O or indeed directly by a base N to form a "macrochelate".[2] We reasoned that crystals could be grown when M′ = a metal ion with an intermediate O/N preference and where solution studies suggest an open coordination mode (>50%) (Co, Zn, Cd), if the $[M(H_2O)_6]^{2+}$ site needed for crystallization consists of Mg^{2+} or Ca^{2+}. Our rationale includes the following: (a) metals with a N preference would preferably coordinate to N rather than occupy the $[M(H_2O)_6]^{2+}$ site; (b) an open configuration suggested by solution data was that found in the crystals;[6,7] (c) the d-outer-shell metal ions have a greater preference for phosphate coordination over H_2O coordination; (d) Mg^{2+} and particularly Ca^{2+} appear to have a distorted $[M(H_2O)_6]^{2+}$ coordination sphere possibly especially suited for H bonding.[6]

By the use of two metal salts, crystals could be obtained that contained the two metal species, as analyzed by atomic absorption. For example, concentration of an aqueous ca. pH 4.5 solution of $Cd(NO_3)_2$, $Ca(NO_3)_2$, Na_2H_2ATP, and BPA in the molar ratio 1:1:2:2 afforded crystals of I. X-ray and elemental analyses of these crystals agreed with the formulation $[Ca(H_2O)_6][Cd(HATP)_2]\cdot 2HBPA\cdot 9H_2O$. The site occupation factor for Cd was determined by constraining its isotropic thermal parameter U to the reasonable value of 0.05 Å^2 and assuming that Ca fully occupied the $[M(H_2O)_6]^{2+}$ site. For this formulation, the analytical data calculated for I (2.26% Ca, 6.33% Cd) were in very good agreement with the values found (2.07% Ca, 6.10% Cd). The $[Cd(HATP)_2]^{4-}$ unit is depicted in Figure 1.

In an analogous experiment using $ZnSO_4$ and $MgSO_4$, crystals II were obtained and analyzed as above. However, the $[M(H_2O)_6]^{2+}$ site gave two peaks on the same C_2 axis with a total of 15 electrons. If we assume that there is a statistical disorder with Zn occupying the minor site, II can be formulated as $[Mg(H_2O)_6]_{0.72}[Zn(H_2O)_6]_{0.28}[Zn(HATP)_2]\cdot 2HBPA\cdot 12H_2O$ based on the X-ray data. This formulation (Anal. Calcd: Mg, 0.98; Zn, 4.70) is in excellent agreement with the analysis (Found: Mg, 1.02; Zn, 4.70). Although a consistent picture emerges for both I and II, we cannot rule out some deviation from these site occupations.

From solution studies, Mg^{2+} forms slightly more stable adducts than Ca^{2+} with triphosphate chains.[2] In direct competition experiments where crystals were grown in the presence of equimolar Mg^{2+} and Ca^{2+}, the Ca molar content exceeded the Mg content. Since it appears that $[Ca(H_2O)_6]^{2+}$ has a greater preference for the $[M(H_2O)_6]^{2+}$ site than does $[Mg(H_2O)_6]^{2+}$, we grew Mg/Zn crystals with the same amounts of all components used to grow crystals II, except for $MgSO_4$, which was doubled. The resulting material gave the following analytical data: 1.34% Mg, 3.76% Zn. These data agree with those expected for $[Mg(H_2O)_6][Zn(HATP)_2]\cdot 2HBPA\cdot 12H_2O$ (1.38% Mg, 3.70% Zn). If 10 equiv of $MgSO_4$ are present initially, the resulting crystals have analyses consistent with a ca. 40:60 Mg/Zn occupancy of the $[M'(HATP)_2]^{4-}$ site. This result is consistent with solution studies[2,3] which demonstrate a ca. 6-fold greater stability for triphosphate complexes with Zn^{2+} over Mg^{2+}.

Although Fe^{2+} and Fe^{3+} ATP complexes have not received detailed study, ATP is implicated in Fe biochemistry.[8] We have been able to obtain, to our knowledge, the first ATP crystals containing Fe. Using methods described above with a 2-fold amount of $MgSO_4$, we obtained crystals that can be formulated as $[Mg(H_2O)_6][Fe(HATP)_2]\cdot 2HBPA\cdot 12H_2O$ (Anal. Calcd: Mg, 1.38; Fe, 3.18. Found: Mg, 1.38; Fe, 3.29). These crystals oxidize slowly in air but are as yet too small for X-ray analysis.

The stability constants that guided our experiments are for 1:1 complexes and do not necessarily define the binding mode of the triphosphate chain. The parallels between our results and solution properties are most easily understood if the triphosphate chain is bound directly to the metal as a tridentate ligand. We believe that the small dependence of the stability constants on the M^{2+} species, which have prompted suggestions of outer-sphere phosphate complexes,[11] could, instead, reflect the remarkably similar conformation of the folded α, β, γ-coordinated triphosphate chain found in all tridentate ATP structures.[6,7,10,12] This folding is characterized by a P-P-P angle of ca. 90° in all previous structures and in I (86 (1)°) and II (85 (1)°). In all the structures, $M-O_\gamma$ is shorter than $M-O_\beta$ and $M-O_\alpha$.

In I, a relatively large ion, Cd, is bound to the triphosphate (M-O α, β, and γ distances are 2.27 (1), 2.28 (1), and 2.23 (1) Å for Cd and 2.14 (1), 2.084 (8), and 2.040 (9) Å for Zn, respectively). The major consequence appears to be in some of the sugar torsion angles not in the triphosphate conformation. For example, II has fairly typical values[6,7] for the C(3′)-C(4′)-C(5′)-O(5′) and C(4′)-C(5′)-O(5′)-P(1) torsion angles of 58 (1) and 166.9 (9)°, respectively. However, in I these angles are 47 (2) and 175 (1)°, respectively.

MgATP is arguably the most important coordination complex in nature. Our knowledge of its structure relies on indirect methods. It is reassuring that the fundamental understanding of metal binding to ATP in solution[2,3] provided by these methods appears to explain our findings. Furthermore, our studies suggest that such solution information can be exploited to direct metal centers to particular sites even in crystals of labile metals containing complex organic species.

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Supplementary Material Available: Tables of positional and thermal parameters, bond distances, and bond angles (15 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Inclusion Tuning of Nonlinear Optical Materials: Sorbates in the KTP Structure

Sir:

Potassium titanyl phosphate, $KTiOPO_4$ (KTP)[1,2] is a relatively new nonlinear optical material that has recently attracted considerable attention because of its high nonlinear optical coefficient, high optical damage threshold and low phase matching temperature sensitivity.[3] These properties make KTP the premier material used for second harmonic generation (SHG) of the 1.06 μm YAG laser. In addition, recent studies have shown that large single crystals may make excellent wave guides and electrooptic modulators,[4] which can be used effectively in fiber optic telecommunications. Large, high-quality, single crystals of KTP can

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(1) Masse, R.; Grenier, J. C. *Bull. Soc. Fr. Mineral. Cristallogr.* **1971**, *94*, 437.

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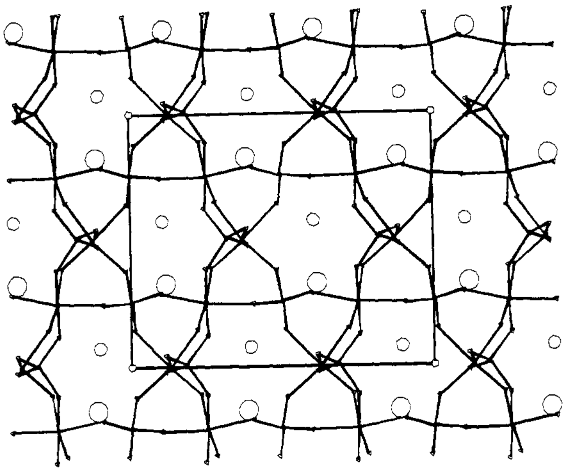

Figure 1. Channel structure of ammonium titanyl phosphate.

Table I. Unit Cell Dimensions and Selected Bond Distances (Å) for NTP, NOTP, NHTP, and KTP[a]

	KTP	NTP	NHTP	NOTP
a, Å	12.814 (6)	12.915 (2)	12.822 (1)	12.9154 (1)
b, Å	6.404 (2)	6.492 (1)	6.2835 (5)	6.4946 (1)
c, Å	10.616 (5)	10.597 (2)	10.5978 (8)	10.5886 (1)
V, Å^3	871.16	888.57	853.81	888.18
Ti(1)–O(9)	1.993 (4)	1.967 (3)	2.012 (4)	2.04 (2)
Ti(1)–O(10)	1.718 (4)	1.717 (3)	1.901 (4)	1.70 (2)
Ti(2)–O(9)	1.738 (4)	1.742 (4)	2.114 (5)	1.79 (2)
Ti(2)–O(10)	2.101 (4)	2.096 (4)	1.764 (5)	2.04 (2)

[a] Space group $Pna2_1$, No. 33. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.

be grown with appropriate mechanical and chemical stability.

An important crystallographic property with respect to the optical, chemical, and solid-state behavior of KTP is that there are two formula units in the asymmetric unit so that the proper solid-state formula is $K_2(TiOPO_4)_2$. The structure of KTP[5] is composed of helices of TiO_6 octahedra linked via phosphate bridges. This leads to an open framework structure in which the charge balancing cations are incorporated within the channels (Figure 1). The open nature of the $TiOPO_4$ host framework suggested the possibility that modification of the internal structural characteristics, and hence the electrooptic properties might be achieved by gas-phase absorption and desorption.

Large crystals (as large as 5 mm in the smallest dimension) of the ammonium analogue of KTP, $(NH_4)_2(TiOPO_4)_2$ (NTP), were synthesized by hydrothermal techniques. Initial studies utilizing TGA, DSC, and a controlled environment θ–θ X-ray powder diffractometer showed loss of ammonia, with retention of crystallinity up to 250 °C. Selective deammoniation of NTP to $NH_4H(TiOPO_4)_2$ (NHTP) is achieved under a vacuum of 10^{-5} mm at 223 °C. The second ammonia molecule is lost above 250 °C to give $H_2(TiOPO_4)_2$. Above 400 °C NTP goes through a reconstructive phase transition, and at 800 °C a new phase of $Ti_2P_2O_9$ recrystallizes. SHG measurements on the original NTP and NHTP showed SHG signals 2400 and 40 times that of quartz.[6]

Reammoniation of NHTP (200 °C) restored the SHG signal (2100) and crystallographic structure. In addition, gas-phase hydration of NHTP (200 °C) gave $(NH_4/H_3O)(TiOPO_4)_2$ (NOTP), a material with an SHG of 650. Thus, gas-phase sorbate tuning or switching of this nonlinear optic host is clearly demonstrated.

The structure/electrooptic relationship that defines the tuning of the SHG signal in NTP, NHTP, and the sample of NHTP which had been rehydrated was studied by single-crystal and high-resolution X-ray synchrotron powder diffraction techniques. The framework of NTP[7] is essentially identical with that of KTP (Table I). Along each Ti–O–Ti helical chain there are alternating long (1.967, 2.096 Å) and short (1.717, 1.742 Å) Ti–O bonds with the NH_4^+ cations located in the K^+ sites of KTP.

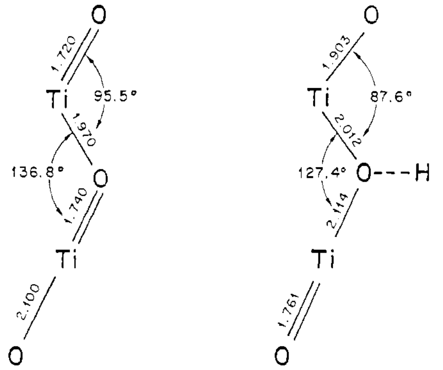

Figure 2. Change of helical (Ti–O) chain structure with deammoniation.

Single-crystal X-ray studies show that the bond length alternation in NHTP[8] is reduced (Table I and Figure 2). This is the result of an increase in the bond lengths at one of the bridging Ti–O–Ti oxygen atoms (O(9)) from 1.742/1.967 Å (NTP) to 2.012/2.114 Å (NHTP). The bond valence[9] of O(9) decreases

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(7) For $(NH_4)_2(TiOPO_4)_2$, a clear, colorless crystal of dimensions 0.4 × 0.35 × 0.2 mm was mounted on a glass fiber. Thirty-four reflections were computer centered on the diffractometer and the cell parameters refined by least squares to the values a = 12.915 (2) Å, b = 6.492 (1) Å, and c = 10.597 (2) Å. Intensity data were collected at room temperature by the $\theta/2\theta$ scan method using Mo Kα radiation on a Huber four-circle diffractometer with a graphite-crystal monochromator. Several ω scans showed typical peak widths of 0.2°. Data were collected (only in the octant containing $+h,+k,+l$) by using a scan rate of 6°/min from 1.3° below Kα_1 to 1.6° above Kα_2. Measurements were made up to $2\theta = 65°$, giving a total of 1938 reflections, of which 1878 were independent. With the use of the criterion $F_o^2 > 3\sigma(F_o^2)$, 1600 reflections were considered observed. Three standard reflections were measured every 100 reflections and showed no systematic variations. Intensities were corrected for Lorentz and polarization effects, absorption by using the method of Busing and Levy (Busing, W.; Levy, H. *Acta Crystallogr.* **1957**, *10*, 180) (μ = 21.8 cm^{-1}) and extinction (Larsen, A. C. *Acta Crystallogr.* **1967**, *23*, 664). The structure was refined by using the model taken from ref 5 in the space group $Pna2_1$. No hydrogen atoms could be located. Scattering factors were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. The function minimized during the least squares refinement was $w(|F_o| - |F_c|)^2$, where w was taken as $1/\sigma(F)$ and $\sigma(F) = [\sigma(I^2) + 0.003(I^2)]^{1/2}$. Refinement of the positional parameters using anisotropic thermal parameters for all atoms gave $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ = 4.0% and $R_2 = \sum(w(||F_o| - |F_c||))/\sum|F_o|$ = 5.5%. The final values of the positional and anisotropic thermal parameters are given in the supplementary material.

(8) For $(NH_4,H)(TiOPO_4)_2$, a clear, colorless crystal of dimensions 0.26 × 0.29 × 0.32 mm was mounted on a glass fiber. Twenty-seven reflections were computer centered on the diffractometer and the cell parameters refined by least squares to the values a = 12.822 (1) Å, b = 6.2835 (5) Å, and c = 10.5978 (8) Å. Intensity data were collected at room temperature by the $\theta/2\theta$ scan method using Mo Kα radiation on a Huber four-circle diffractometer with a graphite-crystal monochromator. Several ω scans showed typical peak widths of 0.2°. Data were collected (only in the octant containing $+h,+k,+l$) by using a scan rate of 6°/min from 1.3° below Kα_1 to 1.6° above Kα_2. Measurements were made up to $2\theta = 65°$, giving a total of 1869 reflections, of which 1812 were independent. With the use of the criterion $F_o^2 > 3\sigma(F_o^2)$, 1454 reflections were considered observed. Three standard reflections were measured every 100 reflections and showed no systematic variations. Intensities were corrected for Lorentz and polarization effects, absorption by using the method of Busing and Levy (Busing, W.; Levy, H. *Acta Crystallogr.* **1957**, *10*, 180) (μ = 22.6 cm^{-1}) and extinction (Larsen, A. C. *Acta Crystallogr.* **1967**, *23*, 664). The structure was refined by using the model taken from ref 5 in the space group $Pna2_1$. No hydrogen atoms could be located. The function minimized during the least squares refinement was $w(|F_o| - |F_c|)^2$, where w was taken as $1/\sigma(F)$ and $\sigma(F) = [\sigma(I^2) + 0.003(I^2)]^{1/2}$. Refinement of the positional parameters using anisotropic thermal parameters for all atoms gave $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ = 4.9% and $R_2 = \sum(w(||F_o| - |F_c||))/\sum|F_o|$ = 6.8%. The final values of the positional and anisotropic thermal parameters are given in the supplementary material.

from 1.70 (NTP) to 1.07 (NHTP) without including the hydrogen atom. These observations and the bond angle changes shown in Figure 2 suggest that the hydrogen atom in NHTP is coordinated to O(9).[10] Low-temperature neutron diffraction studies of the deuteriated NDTP are being carried out to verify this.

Hydrated NHTP was characterized by Rietveld analysis of high-resolution synchrotron X-ray powder diffraction data.[11] In this material H_3O^+ and NH_4^+ are located in the sites occupied by potassium in KTP. The long–short alternation is recovered (2.16/1.79 Å and 2.04/1.70 Å) along with the increased SHG signal.

The data confirm that protonation of every other oxygen atom in the helical –Ti–O–Ti–O–Ti– chain and the resultant reduction in bond asymmetry in the TiO_6 octahedra in NHTP are responsible for drastically lowering the SHG signal from that observed in NTP. This is consistent with recent localized bond charge models[12–15] of bulk nonlinear optical susceptibilities. The relative contributions of O–Ti–O asymmetry and changes in bond polarizability with Ti–O distance are presently being examined in the context of these models.

This study clearly demonstrates that gas-phase sorption and desorption into and out of inorganic acentric open-host frameworks such as that found in the KTP structure can be used to chemically modify nonlinear optical properties. The ability to fine tune nonlinear behavior in this manner has obvious implications for waveguides and electrooptic materials.

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Supplementary Material Available: Tables SI, SII, and SIII, listing refined atomic positions and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(10) Figure made with Chemx, developed and distributed by Chemical Design, Ltd, Oxford, England.

(11) For $(NH_4,H_3O)(TiOPO_4)_2$, high-resolution X-ray powder data were collected on the powder diffractometer at beam line X13a at the Brookhaven National Synchrotron Light Source. A perfect Ge(111) crystal scattering in the horizontal plane was used to monochromate the incident X-ray beam. The sample and LiF(400) scatter vertically. For a full description of the diffractometer geometry see ref 16. The wavelength was determined to be 1.536 68 Å by calibration with a Si standard. The sample was packed into a flat aluminum holder and data collected by step scanning from 5 to 73° in intervals of 0.01° for periods of 2–10 s. The cell parameters were refined to the values $a = 12.9154$ (1) Å, $b = 6.4946$ (1) Å, and $c = 10.5886$ (1) Å. The structure was refined by using the model taken from ref 5 in the space group $Pna2_1$. No hydrogen atoms could be located. The function minimized during the least-squares refinement was $\sum w(|y_o| - 1/c|y_c|)^2$, where w was taken as $1/y_o$. Refinement of the positional parameters gave $R_1 = 100\sum(||I_o| - 1/c|I_c||)/\sum|I_o| = 6.0\%$, $R_2 = 100\sum(||y_o| - 1/c|y_c||)/\sum|y_o| = 13.7\%$ and $X^2 = 1.8$. The final values of the positional and thermal parameters are given in the supplementary material.

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