In both N_2 and CO, the fact that an antibonding orbital is accepting electrons is more than balanced by the developing metal–ligand π-bond. The importance of this is underscored by considering the interaction of metal atoms with the noble gases. The ionization potential of argon is 15.76 eV, so that we might naively predict electron flow from the metal to argon. This does not happen, the bonding being only of van der Waals strength.[29] Clearly the accepting orbital of Ar cannot form a bond to the metal, since it is not in the valence shell of the atom. To be an electron acceptor, as G. N. Lewis pointed out years ago, an atom must have a vacant orbital in the valence shell. In a molecule there must also be a vacancy in the valence shell, though the vacant orbital may be antibonding.

It has been shown that any polar molecule with a dipole moment greater than 1.63 D must have a finite, though small, electron affinity.[30] However, the electron in cases such as HF or H_2O, is in a very diffuse, Rydberg-like orbital.[31] Such orbitals, presumably, cannot be used to form bonds to the electron donor. A value of $A = 0$ for such polar molecules is probably more useful.

Acknowledgment. This work was supported by a grant from the Department of Energy, Contract No. DEA503-765F00034. W. E. Palke and R. G. Parr are thanked for helpful discussions.

---

(29) McNab, T. K.; Micklitz, H.; Barrett, P. H. *Phys. Rev. B.: Solid State* **1971**, *4*, 3787. Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1355.

(30) Crawford, O. H. *Mol. Phys.* **1971**, *20*, 585; **1973**, *26*, 139.

(31) Lowe, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 5557. This reference has a good description of the electron affinities of small molecules.

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

Crystal Structures from Powder Data. 1. Crystal Structure of $ZrKH(PO_4)_2$

A. CLEARFIELD,* L. B. McCUSKER, and P. R. RUDOLF

Received June 4, 1984

The crystal structure of $ZrKH(PO_4)_2$ was solved from X-ray powder data. Initial positional parameters for the zirconium atom were obtained by solution of the Patterson map prepared with integrated intensities of 47 unambiguously indexed reflections. The remaining atoms were located by Fourier methods, and structure refinement was effected by the Rietveld method using the entire 10–80° data set. Final indicators were $R_F = 0.036$, $R_{wp} = 0.145$, and $R_{wr} = 0.024$. Unit cell parameters obtained from the Rietveld refinement are $a = 9.228$ (1) Å, $b = 5.336$ (1) Å, $c = 16.661$ (1) Å, and $\beta = 114.35$ (1)°. The space group is $P2/c$ with $Z = 4$. The structure can be described as consisting of α-zirconium phosphate layers in which adjacent layers are shifted by $^1/_2b$ with respect to the parent compound. Potassium ions lie halfway between the layers and are coordinated by eight oxygen atoms, four from P–O$^-$ and four from the Zr–O–P framework. Bond distances and angles for the non-potassium atoms were comparable to those in $Zr(HPO_4)_2{\cdot}H_2O$ while the K–O interatomic distances ranged from 2.76 (4) to 3.01 (5) Å. The unexchanged hydrogen atoms could not be located.

Introduction

During the past 15 years increasing sophistication in methods of solving the X-ray phase problem has combined with advanced instrumentation and computer software to make the solution of most small- and medium-sized crystal structures a relatively routine and rapid operation. The structural information that has accumulated through the use of X-ray diffraction studies has been fundamental to our understanding of matter on the molecular level. However, there are many crystalline substances for which single crystals suitable for X-ray structural studies are difficult, if not impossible, to grow. Therefore, the ability to solve structures from X-ray (or neutron) powder data without any prior knowledge of the structure is greatly to be desired.

Our interest in this problem dates back to 1970 when it became apparent that we would not be able to prepare suitable single crystals of ion-exchanged phases of zirconium phosphate. The structure of the α-phase, $Zr(HPO_4)_2{\cdot}H_2O$, has been solved[1,2] and shown to be a layered one. The monohydrogen phosphate protons can be exchanged singly, forming half-exchanged and fully exchanged phases, respectively, with alkali-metal cations.[3] Although large single crystals of the acid form can be prepared,[4,5] the crystals shatter and disorder as the layers expand to accommodate the cations. Only in the case of the ammonium ion form, $Zr(NH_4PO_4)_2{\cdot}H_2O$, were suitable single crystals obtained and was the structure solved.[6] This was possible because NH_3 intercalates between the layers rather than exchanges.[7]

In our first attempt[8] the integrated intensities were determined by cutting out the area under the peaks on the powder pattern and weighing them. Only umambiguously indexed reflections were treated in this way, yielding 40–50 usable pieces of data. In all cases tried, the position of the zirconium atom could be determined from the Patterson map, and in some instances, phosphorus atom positions could also be derived. The remaining atoms were found by Fourier methods and refinement carried out by a least-squares routine with employment of heavy damping. This work was never published because of the unsatisfactory bond distances and angles obtained. However, it was encouraging in that a starting model had been obtained from no, or little, prior knowledge of the structure.

Since that time great progress has been made in recognizing and overcoming the problems inherent in powder X-ray studies.[9-11] Since the advent of the Rietveld method for

---

(1) Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431.

(2) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311.

(3) Clearfield, A. In "Inorganic Ion Exchange Materials"; CRC Press: Boca Raton, FL, 1982; Chapter 1.

(4) Alberti, G.; Torracca, E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 317.

(5) Inoue, Y.; Yamada, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3528.

(6) Clearfield, A.; Troup, J. M. *J. Phys. Chem.* **1973**, *77*, 243.

(7) Alberti, G.; Bertrami, R.; Costantino, U.; Gupta, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1057.

(8) Duax, W. L.; Clearfield, A., unpublished results.

(9) National Bureau of Standards. "Accuracy in Powder Diffraction"; Block, S.; Hubbard, C. S.; Eds.; U.S. Government Printing Office: Washington, DC, 1980.

(10) Smith, D. K., Barret, C. S., Leyden, D. E., Predecki, P. K., Eds. "Advances in X-ray Analysis"; Plenum Press: New York, 1981; Vol. 24.

(11) Hubbard, C. S.; et al. "Advances in X-ray Analysis"; Plenum Press: New York, 1983; Vol. 26.

0020-1669/84/1323-4679$01.50/0

refinement of neutron powder data,[12,13] some 200 structures had been refined as of 1978.[14] Application of the Rietveld technique to X-ray data was slow to develop and only 20 some structures have been refined in this way since 1980.[15] However, the Rietveld method requires a good starting model before it can be applied. Where the structure is totally unknown, there are very few reports of structure solution and refinement from powder data. Refinements of structural isomorphs,[16] isostructural compounds,[17] or unknown structures[18,19] are rare. The structures of several zeolites have been solved by model building based on a knowledge of unit cell dimensions, symmetry, and sorption data as a guide.[20–25] In the case where the framework is known, the location of exchanged ions in zeolites has been determined.[26–28] However, no general method for solving crystal structures by diffractometer powder methods on a routine basis has yet been developed. In this and succeeding papers we will explore the evolution of such a method. In this paper we describe the structure of Zr(KPO$_4$)(HPO$_4$) as determined from X-ray powder data.

Experimental Section

Sample Preparation and Treatment. α-Zirconium phosphate, Zr(HPO$_4$)$_2$·H$_2$O, was prepared by refluxing a gel in 12 M H$_3$PO$_4$ for 2 weeks.[29] The gel had been prepared by slow addition of excess concentrated phosphoric acid (ACS reagent grade) to a 0.5 M solution of zirconyl chloride (ZrOCl$_2$·8H$_2$O recrystallized twice from 7–8 M HCl). The crystals were washed free of chloride and phosphate ions with deionized water and air-dried. Potassium ion exchange to the first end point (half-exchange) was carried out by potentiometric titration.[30] KOH was added slowly so as not to exceed a pH of 8 at any time. At the completion of the titration the samples were covered and stirred for several days. They were then washed and dried overnight at 120 °C. Identification was made via the X-ray powder pattern, which showed only the presence of Zr(KPO$_4$)(HPO$_4$)$_2$, and TGA (split-out of $^1/_2$ mol of H$_2$O at 450–550 °C).

X-ray Data Collection. The potassium-exchanged crystals were mixed with 5 wt % NBS standard-reference silicon powder (no. 640) as an internal calibrant and side-loaded to reduce preferred orientation. Intensity data were collected by step scanning between 5 and 80° in 2θ with a step size of 0.01° and a count time of 36 s/step. A computer-controlled powder diffractometer (Seifert-Scintag, PADII) with Cu Kα nickel-filtered radiation was used for data collection. The diffractometer was controlled by a microcomputer (Data General Corp. NOVA3) with 24 kbytes of memory and dual single-density 8-in. floppy disks ($^1/_3$ Mbyte each) as a temporary storage medium. A multiple I/O board was interfaced to the computer to allow the data to be transmitted from the floppy disks to a PDP 11/60 computer for further data reduction and analysis. The data were formatted, checked for spikes and excessive noise, and scaled with locally modified programs of the Nicolet powder package.[31] A detailed description of the programs and techniques will be presented elsewhere.[32] A full-profile analysis was then performed on the smoothed data, and the resulting peak positions were corrected by using the Si line positions. Indexing was performed by both the trial and error method[33] and Ito's method.[34] After indexing, the cells were critically evaluated, indices were assigned and a rigorous unit cell least-squares refinement was conducted. Peaks that could not be deconvoluted by the profile refinement were rejected, and the remaining starting set (h, k, l, $\int I$) was used to generated the normal $F_o(hkl)$ and $\sigma(F_o)$ used for input to the structure determination package.[35]

Table I. Crystallographic Data

pattern 2θ range, deg	10–80
step scan increment for processing (2θ), deg	0.02
std peak for peak shape function: hkl; 2θ, deg	002; 11.6
peak range (no. of half-widths)	20
space group	$P2/c$
a, Å	9.228 (1)
b, Å	5.336 (1)
c, Å	16.661 (1)
β, deg	114.35 (1)
no. of steps	3396
no. of contributing reflcns	391
no. of geometric observns	41
8 P–O distances, Å	1.53 (2)
6 Zr–O distances, Å	2.06 (2)
12 O–P–O angles, deg	109.5 (2.0)
12 O–Zr–O angles, deg	90 (2)
3 O–Zr–O angles, deg	180 (3)
no. of structural params	39
no. of profile params	8
statistically expected R_{wp}	0.124
$R_{wp} = \{\Sigma w_i[y_{io} - (y_{ic}/c)]^2/\Sigma w_i y_{io}^2\}^{1/2}$	0.145
$R_F = (\Sigma \lvert I_o^{1/2} - I_c^{1/2} \rvert)/(\Sigma I_o^{1/2})$	0.036
$R_{wr} = \{\Sigma w_i[c_i - c_i(x)]^2/\Sigma w_i c_i^{-2}\}^{1/2}$	0.024

Structure Solution and Refinement. A unit cell least-squares refinement led to the indexing of 47 unambiguous peaks in the angular range 5–60° in 2θ. The cell was found to be monoclinic with a = 9.222 (1) Å, b = 5.333 (1) Å, c = 15.348 (2) Å, and β = 98.82 (2)°. Systematic absences of the type ($h0l$) with $h + l = 2n + 1$ fixed the space group as $P2/n$. The calculated cell volume is 745.9 Å^3, which by analogy with α-zirconium phosphate (V = 721 Å^3, Z = 4)[2] contains 4 formula units. The position of the unique zirconium atom was found from the Patterson function calculated with the 47 reflections. These initial zirconium parameters were refined, and a three-dimensional Fourier map was prepared from the refined position. This map yielded the two phosphorus atom positional parameters while sucessive difference maps (three in all) yielded the remaining atomic positions. Least-squares refinement of the positional parameters and temperature factors could only be carried out with heavy damping and selective refinement of a few parameters per cycle. When R_F, defined as $\sum||F_o| - |F_c||/\sum|F_o|$, was 0.16, Rietveld refinement[36,37] was begun by using the entire pattern from 10–80° in 2θ.

An α_2-stripping program[38,39] was used to remove the Cu Kα_2 contribution to the X-ray diffraction pattern, and the Si calibration peaks were removed by hand. Values for background intensity were

---

(12) Rietveld, H. M. *Acta Crystallogr.* **1967**, *22*, 151.
(13) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.
(14) Cheetham, A. K.; Taylor, J. C. *Solid State Chem.* **1977**, *21*, 253.
(15) Young, R. A. Reference 9, p 143.
(16) Thomas, J. O. *J. Appl. Crystallogr.* **1980**, *13*, 605.
(17) Casado, P. G.; Mendiola, A.; Rasines, I. *Inorg. Chem.* **1982**, *21*, 2902.
(18) Werner, P.-E. *Chem. Commun., Univ. Stockholm* **1981**, *6*, 16.
(19) Smith, D. E.; Maskasky, J. E.; Spaulding, L. R. *J. Appl. Crystallogr.* **1982**, *15*, 488.
(20) Reed, T. B.; Breck, D. W. *J. Am. Chem. Soc.* **1956**, *78*, 5972.
(21) Broussard, L.; Shoemaker, D. P. *J. Am. Chem. Soc.* **1960**, *82*, 1041.
(22) Meier, W. M.; Kokotailo, G. T. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1969**, *128*, 352.
(23) Barrer, R. M.; Villiger, H. *Z. Kristallogr., Kristallgeom., Kristallophys., Kristallchem.* **1969**, *128*, 352.
(24) Robson, H. E.; Shoemaker, D. P.; Ogilvie, R. A.; Manor, P. C. *Adv. Chem. Ser.* **1973**, *No. 101*, 106.
(25) Kokotailo, G. T.; Chu, P.; Lawton, S. L.; Meier, W. M. *Nature (London)* **1978**, *275*, 119.
(26) Mortier, W. J.; Costenoble, M. L. *J. Appl. Crystallogr.* **1973**, *6*, 448.
(27) Costenoble, M. L.; Mortier, W. J.; Uytterhoeven, J. B. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1877; **1978**, *74*, 466,477; **1979**, *75*, 898. Pearce, J. R.; Mortier, W. J.; Uytterhoeven, J. B.; Lunsford, J. H. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 937. Gellens, L. R.; Mortier, W. J.; Uytterhoeven, J. B. *Zeolites* **1981**, *1*, 11.
(28) Gallezot, P.; Alarcon-Diaz, A.; Dalmon, J. A.; Imelik, B. *J. Catal.* **1975**, *39*, 334.
(29) Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 114.
(30) Clearfield, A.; Duax, W. L.; Garces, J. M.; Medina, A. S. *J. Inorg. Nucl. Chem.* **1972**, *34*, 329.
(31) Sparks, R. A. "Nicolet Powder Package"; Nicolet Instrument Corp.: Madison, WI, 1980 (modified by P. R. Rudolf).
(32) Rudolf, P. R.; Clearfield, A. *Acta Crystallogr., Sect. A: Found. Crystallogr.*, in press.
(33) Werner, P. E. *Z. Kristallogr., Kristallogeom., Kristallphys., Kristallchem.* **1964**, *120*, 375.
(34) Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89.
(35) Enraf-Nonius, "Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1975 (revised 1981).
(36) Baerlocher, Ch. "The X-ray Rietveld System", Institut für Kristallographie & Petrographie, ETH, Zurich, 1982.
(37) Baerlocher, Ch. "Proceedings of the 6th International Conference on Zeolites"; Butterworths: London, U.K., 1983.
(38) Ladell, J.; Zagofsky, A.; Pearlman S. *J. Appl. Crystallogr.* **1975**, *8*, 499.
(39) Mallory, C. L. "Cu Kα Elimination Subroutine", Alfred University, Alfred, NY, 1979 (modified by P. R. Rudolf).

Table II. Positional and Thermal Parameters for $Zr(HPO_4)(KPO_4)$

	x	y	z	U, Å^2
Zr	0.742 (2)	0.777 (10)	0.995 (1)	0.004 (2)
K(1)	$^1/_2$	0.059 (13)	$^1/_4$	0.042 (7)
K(2)	0	−0.038 (12)	$^1/_4$	0.042 (7)
P(1)	0.163 (2)	0.721 (6)	0.112 (2)	0.010 (4)
P(2)	0.664 (2)	0.277 (6)	0.111 (1)	0.010 (4)
O(1)	−0.021 (2)	0.752 (12)	0.078 (2)	0.019
O(2)	0.208 (6)	0.482 (11)	0.080 (4)	0.019
O(3)	0.229 (6)	0.944 (12)	0.082 (4)	0.019
O(4)	0.675 (5)	0.516 (11)	0.063 (4)	0.019
O(5)	0.512 (3)	0.779 (10)	0.910 (2)	0.019
O(6)	0.733 (5)	0.052 (11)	0.081 (4)	0.019
O(7)	0.242 (5)	0.715 (12)	0.214 (2)	0.019
O(10)	0.245 (6)	0.307 (11)	0.288 (2)	0.019

estimated in regions between well-separated peaks, and linear interpolation of these values yielded the background correction, which was applied at each step along the X-ray pattern. A single peak was selected and a peak-profile function calculated. This function is not based on an analytical function but is calculated from the experimental data, and consequently, any peak shape can be described quite accurately. The entire pattern was then analyzed for the dependence of peak width (WD_{estd}) and peak asymmetry (PA_{estd}) on 2θ. Additional details are given in Table I. It was necessary to convert the data to space group $P2/c$ as the Rietveld program requires the standard space group representation.

An important aspect of the Rietveld method is the refinement of profile (in addition to structural) parameters. in this case, eight such parameters were used: four for the lattice constants and four for the refinement of peak width and peak asymmetry as a function of 2θ. The equations for the latter can be expressed as

$$WD_{cor} = t(WD_{estd}) + u(2\theta)(WD_{estd}) \qquad (1)$$

$$PA_{cor} = v(PA_{estd}) + w(2\theta)(PA_{estd}) \qquad (2)$$

where t, u, v, and w are the variables (no zero-point correction for the 2θ values was necessary). These parameters were allowed to vary periodically throughout the refinement process.

Forty-one geometric observations in the form of known Zr–O and P–O bond distances and O–Zr–O and O–P–O bond angles were added to the X-ray data. The approximate atomic coordinates of the Zr, P, and O positions obtained in the structure determination procedure were refined by using these geometric observations (no X-ray data) to obtain an idealized geometry for the zirconium phosphate layers and a reasonable starting model. As structure refinement progressed, the geometric observations were given less and less weight with respect to the X-ray data, but they could not be removed completely without reducing the stability of the refinement.

The adjustment of the half-width and peak asymmetry parameters proved to be critical in the early stages. Once they were correct, the refinement of the structural parameters converged quickly. As the agreement between observed and calculated patterns improved, the preferred orientation factor decreased to zero. Apparently the side-sample-loading method effectively minimized the anticipated stacking of the flat crystallites.

Although the positional parameters refined well, the oxygen thermal parameters would not converge to sensible values, so they were fixed at an average value found in the α-zirconium phosphate structure.[1] Only one thermal parameter for each atom type was refined because atoms K(1) and K(2) and P(1) and P(2) were found to be highly correlated. All parameter shifts in the final cycle of refinement were less than 30% of their corresponding esd's. The final difference Fourier was featureless. Neutral-atomic scattering factors[40] were used for all atoms. No anomalous dispersion or absorption corrections were applied.

Results

Crystallographic details are summarized in Table I, final parameters in Table II, and selected bond distances and angles in Table III. The observed and calculated diffraction patterns are shown in Figure 1.

Table III. Selected Interatomic Distances (Å) and Angles (deg)

General Distances and Angles

	min/max	av
P–O	1.51 (7)/1.56 (4)	1.54
Zr–O	2.01 (3)/2.08 (7)	2.04
O–P–O	107 (3)/113 (3)	109
O–Zr–O	85 (2)/99 (2)	90
O–Zr–O	170 (2)/176 (2)	172

K–O Distances

K(1)–O(3)	2.95 (6)	K(2)–O(1)	3.01 (5)
K(1)–O(5)	2.76 (4)	K(2)–O(6)	2.92 (5)
K(1)–O(7)	2.87 (7)	K(2)–O(7)	2.86 (6)
K(1)–O(10)	2.99 (6)	K(2)–O(10)	2.78 (7)

Bond Angles for K(1) Coordination Sphere

O(10)–K(1)–O(10)′	127 (3)	O(10)–K(1)–O(5)	52 (1)
O(7)–K(1)–O(7)′	100 (3)	O(10)–K(1)–O(5)′	110 (2)
O(3)–K(1)–O(3)′	156 (3)	O(7)–K(1)–O(3)	51 (2)
O(5)–K(1)–O(5)′	143 (3)	O(7)–K(1)–O(3)′	112 (2)
O(10)–K(1)–O(7)	154 (2)	O(7)–K(1)–O(5)	96 (1)
O(10)–K(1)–O(7)′	71 (2)	O(7)–K(1)–O(5)′	108 (1)
O(10)–K(1)–O(3)	109 (2)	O(3)–K(1)–O(5)	58 (2)
O(10)–K(1)–O(3)′	82 (2)	O(3)–K(1)–O(5)′	132 (2)

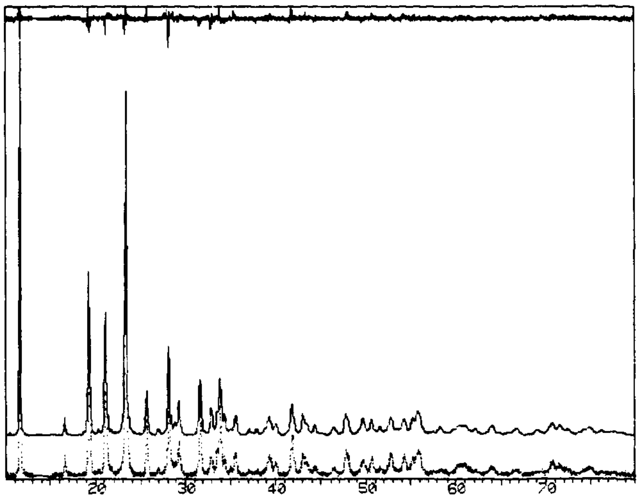

Figure 1. Observed (lower), calculated (middle), and difference (upper) profiles for α-$ZrHK(PO_4)_2$.

The unit cell parameters listed in Table I are derived from the Rietveld refinement and thus include contributions from the entire X-ray pattern. The $P2/n$ cell parameters obtained from the 47 resolved peaks are well within 3 standard deviations of the more accurate $P2/c$ cell parameters derived from the Rietveld refinement.

The half-exchanged potassium ion phase is a monohydrate, but the water of crystallization is immediately lost on removal of the solid from contact with the aqueous solution.[30] In the process, the interlayer distance shrinks from 7.95 to 7.59 Å. This distance is only slightly larger than the interlayer distance (7.55 Å) of the original hydrogen form.[2] The means by which this economy of space is effected is shown by reference to Figure 2.

The potassium ions reside on the 2-fold axes and are 8-coordinate. Four of the atoms in each coordination sphere are O(10) and O(7), which in the parent acid, $Zr(HPO_4)_2 \cdot H_2O$, were bonded to hydrogen atoms. The remainder of the coordination sphere is produced by close approach of framework oxygen atoms: O(5) and O(3) in the case of K(1); O(1) and O(6) for K(2). Bond distances and angles are given in Table III. The 2-fold axis requires that half of the oxygen atoms in each coordination sphere come from a layer above the potassium and the other half from the layer below. In order to effect this arrangement, the adjacent layers are shifted by $^1/_2 b$ relative to their positions in the unexchanged or protonic

---

[40] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 73–82.

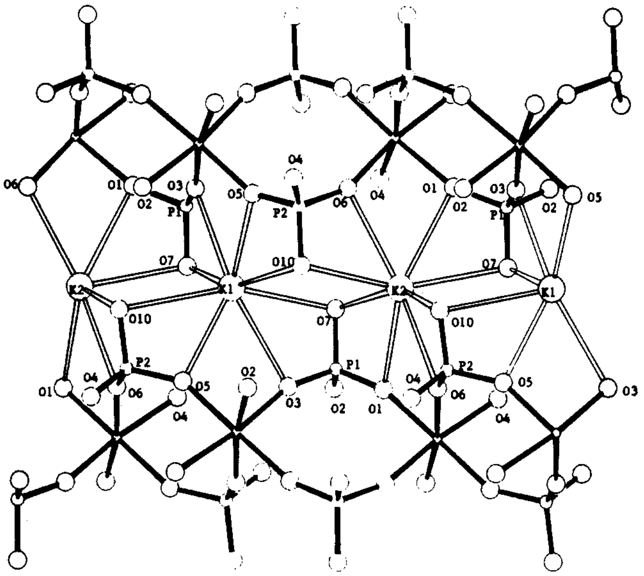

Figure 2. View of the α-$ZrHK(PO_4)_2$ structure showing the potassium coordination spheres (*a* across and *c* down).

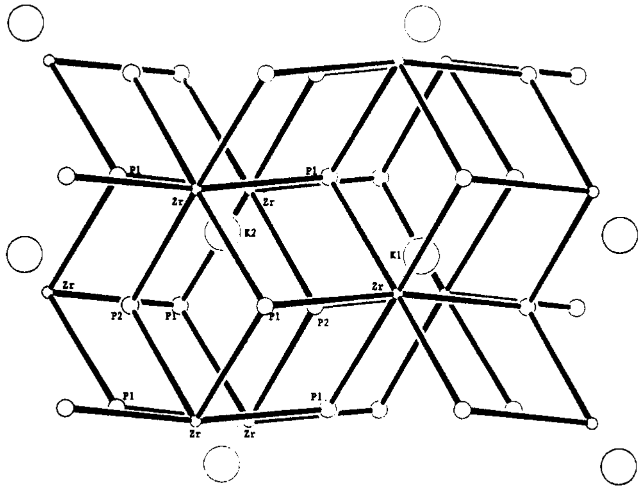

Figure 3. View of the α-$ZrHK(PO_4)_2$ structure showing two layers and their positions relative to one another. The corner atoms of one interlayer cavity are labeled (*a* across and *c* down).

form.[1] This creates a new cell origin at $^1/_2b$ relative to the origin in the parent acid α-zirconium phosphate.

This shifting of the layers destroys the 2_1 axis present in $Zr(HPO_4)_2 \cdot H_2O$ and creates a new six-sided interlayer cavity. The top and bottom are still capped by phosphate groups, but now they are either both P(2) or both P(1) (Figure 3). In the parent acid form the sequence was always P(1) top to P(2) bottom or vice versa. The K(2) ions lie on the 2-fold axis at $x = 0$ and y almost zero while the K(1) ions lie at $x = {}^1/_2$. This places the K^+ ions inside adjacent cavities but off-center toward corners as shown in Figure 3. Each K^+ is surrounded by four $P-O^-$ groups, and each O^- bridges two K^+. The remainder of the negative charge is neutralized by the two hydrogen atoms not displaced by K^+. These could not be located from the X-ray data. However in the *b* direction there is always an O(7) facing an O(10) at a distance of 3.38 Å. This distance is too long for hydrogen bonding so that the H atoms may be randomly distributed among half of the O(10) and O(7) atoms, making these oxygens 4-coordinate.

Discussion

The only other crystal structure determination of a cation-exchanged α-zirconium phosphate is that of the fully exchanged ammonium ion form.[6] In this structure there is no shifting of the layers relative to each other and the ammonium ions occupy positions within the type of cavity described for the parent acid.[1] Since the reaction is one of intercalation,[7] it appears that the ammonia diffuses into the lattice to produce the diammonium form in a single stage.[41] That is, no half-exchanged phase is formed. In the process the *c* axis, or interlayer distance, increases to accommodate the ions. That NH_4^+ exists within the lattice rather than NH_3 is deduced from the fact that each $P-O^-$ group is surrounded by four nitrogens and each nitrogen in turn is surrounded by four $P-O^-$ groups.

In the present structure each K^+ is also coordinated by four $P-O^-$ oxygens, and this would now seem to be the preferred means of bonding. If the fully exchanged Na^+ or K^+ forms are found to have structures similar to that of $Zr(NH_4PO_4)_2 \cdot H_2O$, then it means that another shift of $^1/_2b$ by the layers would be required. As yet no evidence for rotation of the layers, as has been postulated from EXAFS data for $ZrCu(PO_4)_2$, is forthcoming.[42] However, divalent ions may coordinate in a way that requires this rotation. We intend to examine the copper structures by powder methods.

The structure solution described in this paper may have implications for beyond the field of layered zirconium phosphates. If indeed it can be shown that Patterson and direct methods can be applied to limited powder data, then whole new areas of materials science become accessible to X-ray structure solution.

Acknowledgment. This work was supported by the National Science Foundation under Grants Nos. CHE 81-14613 and DMR 80-25184 and the Robert A. Welch Foundation under Grant No. A-673.

Registry No. $ZrKH(PO_4)_2$, 54408-13-8.

---

(41) Clearfield, A.; Hunter, R. A. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1085.

(42) Alagna, L.; Tomlinson, A. G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3009.