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Determination of Crystal Structures from Limited Powder Data Sets: Crystal Structure of Zirconium Phenylphosphonate

BY M. D. POOJARY, H.-L. HU, F. L. CAMPBELL III AND A. CLEARFIELD

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

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Abstract

The structure of zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, was solved based on a combination of modeling techniques and Patterson methods and refined by Rietveld methods. Powder diffraction data were collected using synchrotron radiation ($\lambda = 1.3087 \text{ \AA}$). The crystals belong to the space group

$C2/c$ with $a = 9.0985 (5)$, $b = 5.4154 (3)$, $c = 30.235 (2) \text{ \AA}$ and $\beta = 101.333 (5)^\circ$. The reliability factors are $R_{wp} = 0.129$, $R_p = 0.095$, $R_F = 0.023$ and the statistically expected $R_{wp} = 0.02$. In the c -axis projection the structure resembles very closely that of α -zirconium phosphate. The phenyl groups are inclined by about 30° to the c axis and also tilted from the ab plane. The C -center-related phenyl

groups form rows along the a axis in such a way that the adjacent rings are not in the same plane. The neighboring row is similar to this but the orientation of the rings is different. The JCPDS file No. for $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$ is 44-2000.

Introduction

There are many crystalline compounds for which it has not been possible to grow macroscopic single crystals. The only alternative to single-crystal X-ray structure solutions is the use of powder data. Although the powder pattern contains all the single-crystal data, crystallographers have generally avoided using powder data for a number of reasons. The number of observed reflections in a powder pattern is likely to be no more than about 5–10% of the single-crystal data. This low output is the result of several factors. Diffraction from a powder yields cones of diffracted radiation of which the detector records only a small arc of the circular cone base. Thus, weak intensities are hidden in the background. Overlap of non-equivalent reflections is common and particularly severe in low-symmetry systems and at high scattering angles. However, very significant advances in hardware and software development have now made it possible to solve structures by *ab initio* crystallographic methods (Cheetham & Wilkinson, 1991; Hiraguchi, Hashizume, Fukunaga, Takenaka & Sakata, 1991; Rudolf, Saldarriaga & Clearfield, 1986). In a sense, it is felt that the problem of peak overlap is the 'factor which limits the complexity of structures that can be determined successfully by this method' (Tremayne *et al.*, 1992).

In addition to the problems inherent in structure analysis from powder data, we have faced additional limiting experimental factors. Our systems yield broadened reflections, the intensities of which rapidly diminish at high angles as a result of disorder inherent in the solid. In addition, the data suffer from severe preferred orientation because the structures are layered. Nevertheless we have been able to obtain significant structural information from such limited data sets.

Zirconium bis(monohydrogen orthophosphate) monohydrate, $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, abbreviated as α -ZrP, is of considerable interest because of its layered structure and more importantly it functions as an ion exchanger (Clearfield, 1982). In this layered structure the Zr atoms lie nearly in a plane and are bridged by phosphate groups. These phosphate groups alternate above and below the level of the plane. Three O atoms of each phosphate group are bonded to three different Zr atoms arranged in the form of a nearly equilateral triangle. The fourth O atom points away from this plane and carries an H atom. Exchange occurs by replacement of these H

atoms by cations which occupy positions between the layers. The adjacent layers in α -ZrP are held together by van der Waals forces, and therefore these layers can undergo easy expansion or contraction during ion exchange or intercalation processes (Clearfield, 1990). The structure of α -ZrP was solved by single-crystal methods (Clearfield & Smith, 1969; Troup & Clearfield, 1977). However, the crystals disorder so severely from the exchange process that single-crystal data were unusable for the ion-exchanged phases. Powder data sets were used to solve the crystal structures of $\text{ZrKH}(\text{PO}_4)_2$ (Clearfield, McCusker & Rudolf, 1984) and $\text{ZrNaH}(\text{PO}_4)_2$ (Rudolf & Clearfield, 1985a). In these structure solutions only 47 unambiguously indexed reflexions were used to complete a three-dimensional Patterson map. These maps revealed the presence of the Zr atom in both cases and the remaining atoms were located sequentially from Fourier difference maps. The correctness of the structures was substantiated by the ready location of the unexchanged proton from a subsequent neutron diffraction study (Rudolf & Clearfield, 1985b).

Direct methods were employed using the program *MITHRIL* (Gilmore, 1983) and 40 unambiguously indexed reflections to locate the Zr atom in $\text{ZrNaH}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Rudolf & Clearfield, 1989). The complete structure was then solved by a combination of Patterson-search and Fourier methods. This structure solution was not trivial since it had a different space group and layer arrangement from that of the anhydrous half-exchanged phases. Solution of these structures allowed us to deduce a plausible mechanism for the exchange reaction.

In recent years a large body of literature has developed describing the synthesis and properties of layered zirconium phosphonates (Clearfield, 1990; Alberti & Costantino, 1991). These compounds are poorly crystalline so that it has not been possible to obtain single crystals or to record more than a few powder reflections other than those of the 001 type. However, by hydrothermal treatment of the poorly crystalline zirconium phenylphosphonate, it was possible to obtain crystals which yielded about 30 reflections. Since a knowledge of the structure of a prototype organic derivative would greatly aid the development of model structures for related organic derivatives, we attempted a structure solution by powder methods. The results are presented here.

Data collection, structure solution and refinement

Room-temperature powder diffraction data for the sample were obtained at the National Synchrotron Light Source on beamline X7A using a wavelength of 1.3087 Å from a Ge(111) monochromator using a Ge(220) analyzer crystal. The data were collected

every $0.01^\circ 2\theta$ from 4 to $60^\circ 2\theta$ with a count time of 4 s per step.†

The raw data were transferred to the *GRAPH* format (Rudolf, 1988) for further processing. Initial attempts to index the pattern using the program *TREOR* (Werner, 1964) were not successful possibly because of the large c -axis cell dimension and small number of well resolved reflections. Since this structure is derived from that of α -ZrP, it was thought that the layer structure of α -ZrP would be a key in indexing the pattern. Electron diffraction patterns obtained down the c axis showed that the intensity distribution in this projection is closely similar to that in α -ZrP. A model for the layer consisting of Zr, P and O was constructed based on the observed dimension along the c^* axis and on the assumption that the dimensions along a and c are closely similar in these two structures. Powder diffraction patterns were calculated for this model in the space group $P2_1/c$ over a range of monoclinic angles β . Once a close match between this calculated pattern and observed data was obtained, the cell dimensions were then refined using least-squares procedures. This procedure led to successful indexing of the pattern.

The indexed reflections showed the systematic absences of the type hkl , $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$, indicating that the space group is either Cc or $C2/c$. The structure solution was attempted in the centrosymmetric space group $C2/c$. A total of 32 unambiguous reflections were present up to a 2θ limit of 41° . The intensities of these reflections were accurately measured by decomposition methods and were converted to the normal $F_o(hkl)$ and $\sigma(hkl)$ for structure solution. The Zr atom and the P atom were identified from the Patterson maps and these positions were close to those used in the above-mentioned model. In the present case the Zr atom was located on the center of symmetry while in α -ZrP it occupies a general position as required by the symmetry in space group $P2_1/c$. The positions of the three O atoms and the C atom bonded to P were derived on the basis of the known geometry of Zr octahedra and the layer structure of α -ZrP.

The positions of these six atoms were used as a starting model for the Rietveld refinement. Using a utility program *GRAPH*, the raw data were transferred to the *GSAS* program package (Larson & Von Dreele, 1988) for the full-profile refinement. The first reflection (002) had to be omitted from the refinement because it showed severe asymmetry. Additionally, *GSAS* allows the use of only one set of peak profile coefficients to describe the entire pat-

tern. Thus, the coefficients chosen for the remainder of the patterns did not describe this reflection very accurately. However, the integrated intensity of this reflection was checked against that calculated from the final model and was found to be satisfactory. Initial refinement of the scale, background, unit-cell parameters and the zero-point error led to an acceptable overall agreement between the observed and calculated patterns. A difference Fourier map computed at this stage allowed the location of the remaining atoms of the phenyl group. Atomic positions were refined with soft constraints consisting of Zr—O, P—O, P—C and C—C bond distances. The geometry around Zr and P was fixed by the appropriate distances between the bonded O atoms. Geometric constraints were also applied for the phenyl group. A total of 20 geometric constraints were included and initially their weight was kept high to maintain a reasonable geometry. As the refinement progressed the soft constraints were assigned less and less weight, but they could not be removed completely without reducing the stability of the refinement. In the last stages of refinement the atomic isotropic thermal parameters were refined. Attempts were made to include the contributions from the H atoms at the calculated positions, but this did not affect the refinement results. In the final refinement the shifts in all the parameters were less than their estimated standard deviations. A difference Fourier map computed at this stage was featureless. Neutral atomic scattering factors were used for all atoms. No corrections were made for anomalous dispersion, absorption or preferred orientation.

Results

Crystallographic data are given in Table 1. Final positional and thermal parameters are presented in Table 2. Table 3 lists the bond lengths and bond angles. The Rietveld refinement plot is shown in Fig. 1. Figs. 2 and 3 are the projections of the structure down the b and c axes, respectively, with atoms labeled in Fig. 3.

The layer structure of zirconium phenylphosphonate is essentially that of α -ZrP. In the present case, however, the layers are moved apart to accommodate the phenyl groups. The major difference in these two structures is their crystal symmetry. α -ZrP as well as its ion-exchanged forms crystallize in the space group $P2_1/c$ (or $P2_1/n$) and $P2/c$ (Rudolf & Clearfield, 1985*a,b*). In these structures the Zr atom lies in a pseudo-special position (0.76, 0.25, 0.51) and the two PO_4 groups are related by pseudo C -centering. Zirconium phenylphosphonate, on the other hand, crystallizes in the C -centered cell and the Zr atom occupies an ideal special position on the

† Powder diffraction data have been deposited with JCPDS and with the British Library Document Supply Centre as Supplementary Publication No. SUP 71273 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Crystallographic data for zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$

Wavelength (Å)	1.3087
Pattern range (2θ) (°)	4-60
Step-scan increment (2θ) (°)	0.01
Step-scan time (s)	4
Space group	C2/c
a (Å)	9.0985 (5)
b (Å)	5.4154 (3)
c (Å)	30.235 (2)
β (°)	101.333 (5)
Z	4
D _x (g cm ⁻³)	1.834
T (K)	296 (2)
No. of contributing reflections	356
No. of geometric observations	20
P—O distances and tolerance (Å)	1.53 (2)
Zr—O distances and tolerance (Å)	2.03 (3)
O—O distances for PO ₄ (Å)	2.55 (2)
C—C distances and tolerance (Å)	1.39 (2)
No. of structural parameters	41
No. of profile parameters	11
Statistically expected R _{wp} *	0.02
R _{wp} *	0.129
R _p †	0.095
R _F ‡	0.023

* $R_{wp} = [\sum w(I_o - I_c)^2 / \sum (wI_o^2)]^{1/2}$. Expected $R_{wp} = R_{wp}/(\chi^2)^{1/2}$ where $\chi^2 = \sum w(I_o - I_c)^2 / (N_{obs} - N_{var})$.
 † $R_p = \sum |I_o - I_c| / \sum I_o$.
 ‡ $R_F = (|F_o| - |F_c|) / (|F_o|)$.

center of symmetry. The asymmetric unit therefore consists of one Zr atom and one phenylphosphonate group.

The Zr atoms are situated in the planes at $z = 0$ and $\frac{1}{2}$. Three coplanar Zr atoms form an equilateral triangle and the P atoms are located at the center of these triangles approximately 1.7 Å above or below the plane. About a given Zr atom there are six such triangles. Among them three contain P atoms above the plane while the other three contain the centrosymmetrically related P atoms and thus they are situated below the plane. The three O atoms of the phosphonate group are involved in binding the three

Table 2. Positional and thermal parameters

$U_{iso} = B_{iso}/(8\pi^2)$.

	x	y	z	U_{iso} (Å ²)
Zr	0.75	0.25	0.5	0.008 (1)
P	0.9380 (8)	0.729 (2)	0.5567 (2)	0.011 (2)
O1	1.065 (1)	0.720 (3)	0.5298 (4)	0.011 (4)
O2	0.838 (2)	0.509 (2)	0.5471 (5)	0.018 (5)
O3	0.847 (2)	0.969 (3)	0.5436 (5)	0.025 (8)
C1	1.029 (2)	0.734 (4)	0.6159 (3)	0.03 (1)
C2	0.965 (5)	0.594 (8)	0.6467 (7)	0.33 (3)
C3	1.053 (4)	0.567 (4)	0.6903 (8)	0.40 (3)
C4	1.148 (2)	0.757 (4)	0.7081 (3)	0.08 (1)
C5	1.193 (2)	0.921 (3)	0.6782 (6)	0.07 (1)
C6	1.111 (2)	0.937 (2)	0.6340 (5)	0.01 (1)

Table 3. Bond lengths (Å) and angles (°)

Zr—O1	2.07 (1) 2 ×	O1—Zr—O1	180.0
Zr—O2	2.05 (1) 2 ×	O1—Zr—O2	89.5 (5) 2 ×
Zr—O3	2.09 (1) 2 ×	O1—Zr—O2	90.5 (5) 2 ×
		O1—Zr—O3	87.0 (5) 2 ×
		O1—Zr—O3	93.0 (5) 2 ×
		O2—Zr—O2	180.0
		O2—Zr—O3	89.9 (4) 2 ×
		O2—Zr—O3	90.1 (4) 2 ×
		O3—Zr—O3	180.0
P—O1	1.54 (1)	O1—P—O2	111 (1)
P—O2	1.49 (1)	O1—P—O3	108 (1)
P—O3	1.55 (1)	O1—P—C1	106 (1)
P—C1	1.82 (1)	O2—P—O3	110 (1)
		O2—P—C1	110 (1)
		O3—P—C1	110 (1)
C1—C2	1.42 (2)	C1—C2—C3	116 (2)
C2—C3	1.41 (2)	C2—C3—C4	119 (1)
C3—C4	1.38 (2)	C3—C4—C5	118 (1)
C4—C5	1.39 (2)	C4—C5—C6	119 (1)
C5—C6	1.40 (2)	C5—C6—C1	119 (1)
C6—C1	1.36 (2)	C6—C1—C2	116 (1)

Zr atoms of the triangle which leads to a regular octahedral geometry for the Zr atom. The Zr—O bond distances average 2.07 Å and the O—Zr—O bond angles are close to 90°. These values are in agreement with those observed for α-ZrP and other Zr—PO₄ structures. The phosphonate group displays

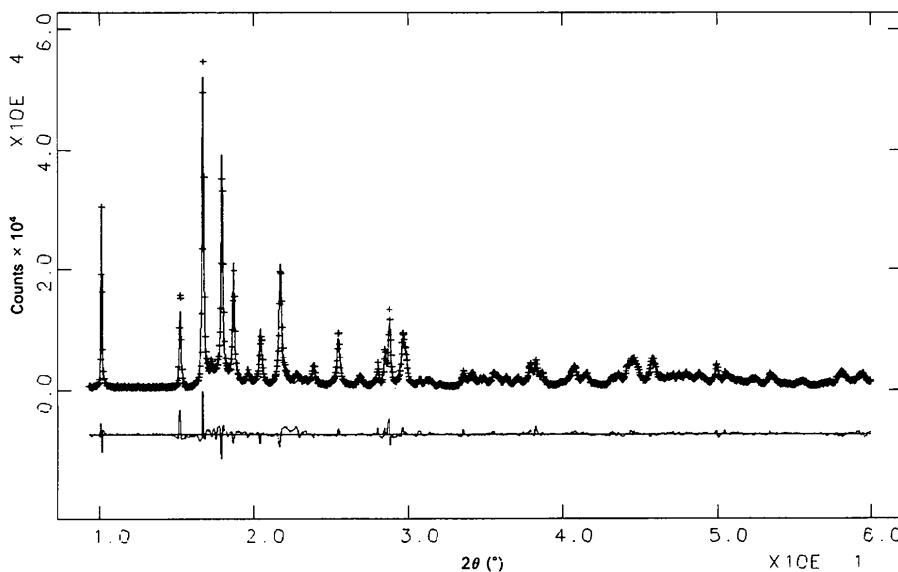


Fig. 1. Observed (+) and calculated (—) profiles (X-ray intensity versus 2θ) for the Rietveld refinement of zirconium phenylphosphonate. The diffraction data were collected using synchrotron radiation. The bottom curve is the difference plot on the same intensity scale.

normal bond lengths and angles. The P—C distance (1.82 Å) and the C—C distances (average = 1.39 Å) agree well with the values obtained for copper(II) phenylphosphate (Zhang & Clearfield, 1992) from a single-crystal study. The phenyl group is nearly planar as derived (average deviation = 0.1 Å) and shows the expected bond angles. The dihedral angle between the least-squares planes of glide-related phenyl groups is 74°, in other words, the plane of the phenyl rings is tilted by about 37° to the *ac* plane.

The arrangement of the phenyl groups is shown in Fig. 2. These groups are oriented away from the *ab* plane towards the adjacent such planes. They are inclined by about 30° to the *c* axis and also tilted from the *ab* plane. The *C*-center-related phenyl groups form rows along the *a* axis in such a way that the adjacent rings are shifted $\frac{1}{2}$ along the *b* axis. The neighboring row, which is shifted along the *c* axis, is related to this by the *c* glide and hence the orientation of the rings in these two rows is different. Unit-cell translations extend this arrangement along the *b* axis. This packing thus represents an efficient way of sharing the available space by the phenyl groups. It should be mentioned, however, that there are some contacts which involve the C atoms of the *C*-center-related phenyl groups. Among them the

shortest contact is C2...C5 (3.0 Å), while the other contacts, viz. C2...C6 (3.3 Å) and C3...C5 (3.3 Å), are within the allowed values. All other non-bonded contacts between the C atoms are above 3.8 Å. It appears that the large thermal parameters observed for the C atoms C2 and C3 are a consequence of the packing arrangement of the phenyl groups. Manganese (Cao, Lee, Lynch & Mallouk, 1988) and zinc phenylphosphonates (Martin, Squattrito & Clearfield, 1989) exhibit disordered structures in which two positions for the phenyl rings are observed. A similar situation holds for lanthanum phenylphosphonate, $\text{La}(\text{O}_3\text{PC}_6\text{H}_5)(\text{HO}_3\text{PC}_6\text{H}_5)$ (Wang, Zhang, Hu, Frausto & Clearfield, 1992). This disorder arises because the true unit cell has a doubled *c* axis, equivalent to the *b* axis in zirconium phenylphosphonate, arising from the phenyl rings being inclined at 58° in alternate rows in the *c* axis direction. Severe crowding would result without this freedom to tilt away from such repulsion interactions between the phenyl rings. The close approach of C2 and C3 to an adjacent ring may then result in some disorder in adjusting to positions which minimize repulsion effects between the rings. The C atom at the *para* position, C4, is well separated from the other atoms of the groups linked to the layers both at *Z* = 0 and $\frac{1}{2}$.

Other factors such as absorption, extinction and preferred orientation may also contribute to errors in the thermal parameters. Extinction errors should not be a major factor in the present case because of the very small crystallite size and poor crystallinity of the sample. Modifications to the *GSAS* program are in progress (Von Dreele, 1993) which will permit routine corrections for absorption and preferred orientation to be made and these will be applied in future work.

In summary, the main difficulty in solving the structure of zirconium phenylphosphonate involved obtaining the correct unit cell. The difficulty stemmed from the very long *c* axis. In-plane electron diffraction photographs indicated that the *a* and *b* axes were not too different from those in the parent α -ZrP (Troup & Clearfield, 1977) and the approximate *c* axis was obtained from the 002 reflection as approximately 30 Å. However, even with this information the program *TREOR* was unable to find the correct unit cell. Therefore, our own trial-and-error technique, as described in the experimental section, was utilized. The three-dimensional Patterson map was then able to locate both the Zr and P atoms using 32 unambiguously indexed reflections. This was sufficient to complete the structure solution. Earlier we had obtained a structure solution of an aluminium phosphate molecular sieve (23 atoms, 73 structural parameters) by direct methods from 60 unambiguously indexed reflections (Rudolf,

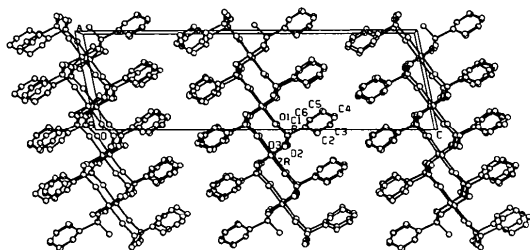


Fig. 2. Projection of the structure down the *b* axis showing the numbering scheme used in Table 2. The overlapping phenyl rings along the projection axis are separated by 5.415 Å (*b* dimension of the crystal).

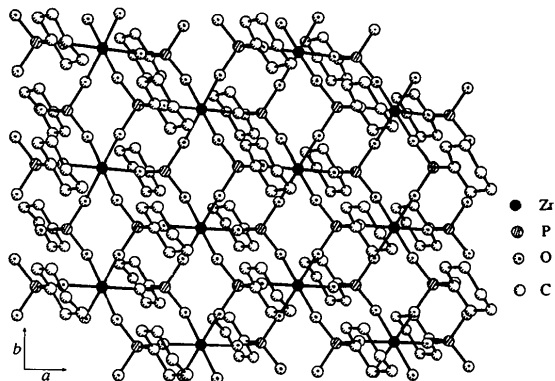


Fig. 3. A portion of the structure down the *c* axis showing the layer formed by Zr, P and O atoms. The phenyl groups are projected away from this plane.

Saldarriaga & Clearfield 1986). The Al, P and two O atoms were clearly revealed in contour maps prepared at a contour interval of $0.1 e \text{ \AA}^{-3}$. These results indicate that a great deal of structural information can be obtained from fairly limited data even when the reflections are broadened or subject to a certain amount of error as a result of preferred orientation as layered compounds surely must be.

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X-ray Analysis of Wavefunctions by the Least-Squares Method Incorporating Orthonormality. II. Ground State of the Cu^{2+} Ion of Bis(1,5-diazacyclooctane)-copper(II) Nitrate in a Low-Symmetry Crystal Field

BY KIYOAKI TANAKA

Chemistry Department, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

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Abstract

Analysis of the d wavefunctions of Cu^{2+} in $[\text{Cu}(\text{daco})_2](\text{NO}_3)_2$ ($\text{daco} = 1,5\text{-diazacyclooctane}$) was carried out successfully using the least-squares method incorporating orthonormality. The Cu^{2+} ion is coordinated square planarly by four N atoms which form the C_4 crystal field. The deformation

density after refinement with spherical scattering factors showed the hole orbital of Cu^{2+} in the Cu-N_4 coordination plane. The deformation density in the plane perpendicular to the coordination plane could not be represented well without introducing κ parameters, assigned to each d orbital, which took into account the expansion and contraction of each d orbital. The difference densities after d -orbital analy-