

Application of X-ray Powder Diffraction Techniques to the Solution of Unknown Crystal Structures

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Introduction

The single most comprehensive tool for the structure determination of crystalline solids is the X-ray diffraction method. For this purpose a well-developed single crystal is necessary. However, not all crystalline solids yield the necessary single crystals but rather are obtained as microcrystalline powders that resist further crystal growth. Traditionally X-ray powder diffraction techniques have routinely been used for characterization of crystalline materials. For instance, the diffraction peaks (d spacings and relative intensities) in the powder pattern are characteristic fingerprints of a compound that can be used in the identification of new materials. However, it was recognized that the powder pattern contained much structural information but the data were difficult to transform into usable form. Many structures were solved by trial and error methods and calculated intensities compared qualitatively with the observed intensities. Obviously such methods have limited applicability and are prone to error.

An important development was the introduction of the Rietveld technique of whole pattern refinement.¹ This technique was originally applied to neutron diffraction data because the peaks have a nearly Gaussian shape whereas X-ray powder reflections do not. This feature

allows the powder pattern to be represented by a series of Gaussian functions. It is then possible to compare the powder pattern calculated from a model structure to the observed pattern and minimize their differences by whole pattern refinement. However, the Rietveld method requires prior knowledge of the structure which could be obtained either from modeling studies or from related known structures. In the recent past efforts have been made to derive this structural model directly from phasing the powder diffraction data using standard Patterson and "direct methods", as is routinely being done in single-crystal studies. Although the basic principles involved in these two methods are the same, structure solution from powder data is still a challenge. In the case of single crystal diffraction, the Bragg reflections are spatially resolved into three dimensions in reciprocal space while the powder data are confined to the one-dimensional 2θ axis. As a consequence the diffraction peaks overlap, either accidentally, or due to symmetry. Other factors which affect the powder data are preferred orientation effects leading to false intensities, reflection broadening, especially at high angles, and noise from counting statistics. These factors collectively reduce the number of single indexed reflections to only a minor fraction of the total possible diffraction data. Werner² for the first time showed that structures of simple inorganic compounds could be solved with the use of only a handful of such nonoverlapped reflections by standard Patterson and Fourier methods. Subsequently, some simple compounds were characterized using both Patterson^{3–5} and direct methods.⁶ In 1986, using direct methods, Rudolf et al.⁷ solved, for the first time, the structure of an aluminum phosphate molecular sieve containing 26 non-hydrogen atoms in the asymmetric unit, with the help of only 60 unambiguously indexed X-ray powder diffraction data.

To increase the success rate in powder structure solution and to attempt solutions of complex structures, it is necessary to decompose the entire powder pattern into individual reflections with reasonable certainty in their intensity estimation. This method yields a substantially larger number of reflections up to high scattering angles, making it possible to apply the principles of direct method techniques. Several methods^{8–13} have now been developed to extract individual intensities from powder diffraction data with or without the knowledge of a

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structural model. In the meantime, substantial advances were made in instrumentation techniques^{14,15} and computational aspects¹⁶ as well as in the use of high-resolution neutron¹⁷ and synchrotron X-ray¹⁸ diffraction for structure solution. These developments resulted in the solution of a number of crystal structures ab initio from powder data including recent successes involving some complex systems.^{19,20a} These results are significant for chemists because powder methods are the only techniques available to derive three-dimensional structural information of new compounds that can be prepared only in polycrystalline form or compounds obtained only under special conditions involving high pressure or temperature. This paper describes the use of powder diffraction data in solving unknown crystal structures and also highlights some of the difficulties present in this method which are far from trivial.

Basic Principles and Crystallographic Problems. The single-crystal reflections have characteristic spacial resolution leading to a three-dimensional array of diffraction spots. The intensities of these reflections can be accurately measured. When single crystals are crushed into microcrystals, as in polycrystalline samples, the diffraction from a particular lattice plane in different crystallites lies on a cone with a specific Bragg angle, characterized by 2θ . Using modern diffractometers, one can measure very accurately the intensities of these cones as a function of 2θ but the spacial information of individual reflections is lost. The other serious problem is the overlap of non-equivalent reflections either by symmetry-imposed degeneracy or by accidental degeneracy, especially at higher scattering angle. Although all the information of the single crystal is present in this powder diffraction pattern, the challenge in ab initio structure solution from powder diffraction data is to decompose the powder pattern into its individual constituents to obtain "single-crystal-type" data. This "single-crystal-type" data set is not used for structure refinement; instead, the refinement is carried out by Rietveld methods using the full powder diffraction profile.

The collapse of three-dimensional reciprocal space of the individual crystallites onto the one-dimensional axis, among others, results in preferred orientation of crystallites if they are nonisotropic. As a consequence, the intensities of the powder lines depend on the way the sample was prepared for measuring the data. This problem is found to be very serious for layered materials such as metal phosphates and phosphonates. These layers prefer to pack preferentially along the interlayer axis, resulting in orientational effects for the powder

intensities. Side loading into a flat sample holder, mixing the sample with amorphous spherical silica, and use of a suspension chamber²¹ significantly reduce the preferred orientation effects. The refinement of this parameter to reduce its effect is now available in standard Rietveld programs;²² however, it requires prior knowledge of the structure.

Experimental Section

The critical step in structure solution from powder data depends on the data acquisition. Synchrotron X-ray sources, because of their high-intensity radiation and excellent vertical collimation, can be used to obtain the best instrumental resolution for collecting powder data.¹⁵ The source tunability allows the selection of wavelength in order to diminish the effects of heavy absorbers. In addition the high flux provides excellent counting statistics in a short count time.

Neutrons are scattered by the nucleus, an essentially point source, and therefore, the scattering intensity is not angle dependent unlike scattering factors for X-rays which decrease with increasing scattering angle. Most importantly, nuclear scattering lengths show very little dependence on atomic number in contrast to X-ray scattering amplitudes which increase dramatically and systematically with atomic number. Because of this dependency, solving a crystal structure ab initio from neutron data is much more difficult than solving it from X-ray data. In an ideal approach, the integrated X-ray intensities, possibly from a synchrotron source, are used to solve the main features of the structure using either heavy atom methods or direct methods. The light atom positions, including hydrogen atoms, that are difficult to locate from X-ray data, are then obtained from the use of neutron diffraction data. The complete structure may then be refined using the two sets of data to obtain a realistic model for the structure. Such a combination of synchrotron X-ray and neutron diffraction was in fact used for the solution and refinement of some structures.^{19,23-26} However, it is not possible, given the limited number of facilities, to obtain synchrotron and neutron data for all the powder materials that have been synthesized, nor is it convenient to do so. The practicable method is to use a conventional X-ray source for the collection of powder data as is now done routinely for single-crystal data collection. Considerably higher intensity X-rays may be obtained by the use of rotating anodes in place of sealed tube generators. Our experience is that structures of moderately high complexity (up to 50 atoms in the asymmetric unit) can be solved and refined by using rotating anode X-ray data.²⁰ Only in some special cases was it necessary to obtain synchrotron data.

General Methods of Structure Solution from Powder Data. The initial step in this direction involves obtaining

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accurate peak positions and intensities that are then used in indexing²⁷ and unit cell parameter refinement. The intensities are also used to derive possible space groups. Since the latter step is highly dependent on the observed intensities of the peaks, it is very important that the weak reflections are properly measured and that the sample is free from any impurity phases.

Once the crystal system is correctly identified and the unit cell parameters are refined, the most critical step is full pattern decomposition to extract individual intensities of Bragg reflections from the powder pattern. These intensities are then converted to structure factors for use in structure solution by either Patterson methods or direct methods. Obviously the quality of the extracted structure factors depends heavily on the quality of the powder data which are associated with the nature of the sample and the source used for data collection. Currently a variety of pattern decomposition programs are available. Among them, the two commonly used programs are ALLHKL⁸ and the Le Bail method¹² developed by Pawley and Le Bail, respectively. The extraction of intensities in GSAS²² is based on the Le Bail method, which begins with a set of calculated structure factors based on a partial or dummy structure to obtain an initial set of structure factors. In the subsequent cycles of refinement, these initial structure factors are used as F_{calc} for the next cycle. These extracted structure factors then can be used as single-crystal data for calculation of Patterson maps or direct method E -maps.

It is generally understood that the application of direct methods requires all the possible Bragg reflections including the weak ones. For those of us who deal with single-crystal data, the rule of thumb is that the data should extend to 0.9–1.0 Å resolution and that the atom-to-reflection ratio should be on the order of 1/6–1/7. It is possible to satisfy these criteria for relatively simple inorganic compounds by getting high-quality powder diffraction data using a synchrotron source. However, for most of the compounds, the weak reflections are present in the background level and one gets data only up to a 2θ limit of about 80°. Even in such cases, and also in the absence of efficient decomposition programs such as those mentioned above, it was shown that direct methods can be applied successfully for the solution of relatively complex structures (see below).

In the following example, we show the application of the above-mentioned procedure for the solution of an unknown structure.²⁸ The compound is an ion exchanger of composition $\text{K}_2\text{ZrSi}_3\text{O}_9 \cdot \text{H}_2\text{O}$. The X-ray powder diffraction data were collected in our laboratory using a rotating anode (Cu target) generator operating at 50 kV and 180 mA. The sample was loaded on a flat aluminum sample holder, and the data were collected in the 2θ range 10–80°, using a step size of 0.01° and a time constant of 10 s/step. Initially the pattern was decomposed to get accurate peak positions using a locally written program, GRAPH.^{5b} The peaks were indexed using Ito's method^{27a}

and TREOR.^{27b} The solution which indexed all the peaks corresponded to a primitive orthorhombic cell with $a = 10.2977(2)$, $b = 13.3207(3)$, and $c = 7.1956(1)$ Å. Systematic absences were consistent with the space group $P2_12_12_1$. Unit cell refinement of the peak positions yielded 62 single indexed peaks and 11 peaks with two contributors. The intensities of the latter set of peaks were divided equally between the contributing Bragg peaks and included in the data set. This data set was converted into a single-crystal type data set (F_{hkl} , σ_{hkl}) and then input to a single-crystal structure package,²⁹ for application of direct methods (MITHRIL³⁰). A solution with the best figure of merit ($\text{FOM}_{\text{abs}} = 2$, $\psi_0 = 1.4$, and $\text{resid} = 19.39$) yielded the positions of Zr, two Si, two K, and three O atoms. These positions were used as a starting model for Rietveld refinement of the full powder pattern. Subsequent Fourier difference maps revealed all the atoms in the structure.

For better accuracy, the pattern was decomposed using the Le Bail method in GSAS. For this purpose the correct unit cell positions and space group were input along with a structure model consisting of a random atom position. The parameters refined include terms for background function, unit cell parameters, zero point error, and profile coefficients. The refinement converged with $R_{\text{wp}} = 0.075$ and $R_p = 0.053$ (Figure 1). Intensities of 467 $\text{K}\alpha_1$ reflections were extracted from the 2θ range 10–80°. This data set was input to MITHRIL for the calculation of an E -map. In this case a solution with $\text{FOM}_{\text{abs}} = 1.67$, $\psi_0 = 1.28$, and $\text{resid} = 30$ revealed positions of all the above-mentioned atoms obtained by using GRAPH extracted data, as well as two additional atom positions. Using these starting models the structure was completed by Fourier methods. The refinement converged with final agreement factors of $R_{\text{wp}} = 0.072$, $R_p = 0.051$, and $R_F = 0.042$ for 426 reflections. The corresponding Rietveld difference plot is shown in Figure 2, and a plot of the structure is shown in Figure 3. This experiment shows that even with a limited low-angle data set (60–70 reflections) it is possible to get a reasonable starting model which can then be completed and refined using the full pattern by the Rietveld method.

Structures from Conventional X-ray Powder Data. In recent years a number of crystal structures have been solved and refined successfully using laboratory X-ray data. In the earlier studies only single indexed reflections were utilized for solutions by Patterson or direct methods. Werner and co-workers were the first to adopt photometered film powder data for structure determination. They^{2–4} applied Patterson methods for the solution of the structures of $(\text{NH}_4)_4[\text{MoO}_2)_4\text{O}_3](\text{C}_4\text{H}_3\text{O}_5)_2 \cdot \text{H}_2\text{O}$, $\text{CaCl}_2(\text{NH}_3)_2$, and $\text{Cu}_2\text{HfO}_6 \cdot 2\text{H}_2\text{O}$. In the 1980s, direct methods⁶ were applied for the first time to the solution of simple structures such as MnP_4 and $\alpha\text{-ScOOH}$. Subsequently, Rudolf et al.,⁷ by the use of direct methods, solved the structure of an aluminum phosphate molecular sieve, $(\text{AlPO}_4)_3 \cdot (\text{CH}_3)_4\text{NOH}$. This compound contains 26 independent atoms in the asymmetric unit, and it represents the first zeolite structure solved by using direct methods. The powder data (Cu $\text{K}\alpha$, 8–80° in 2θ) were obtained

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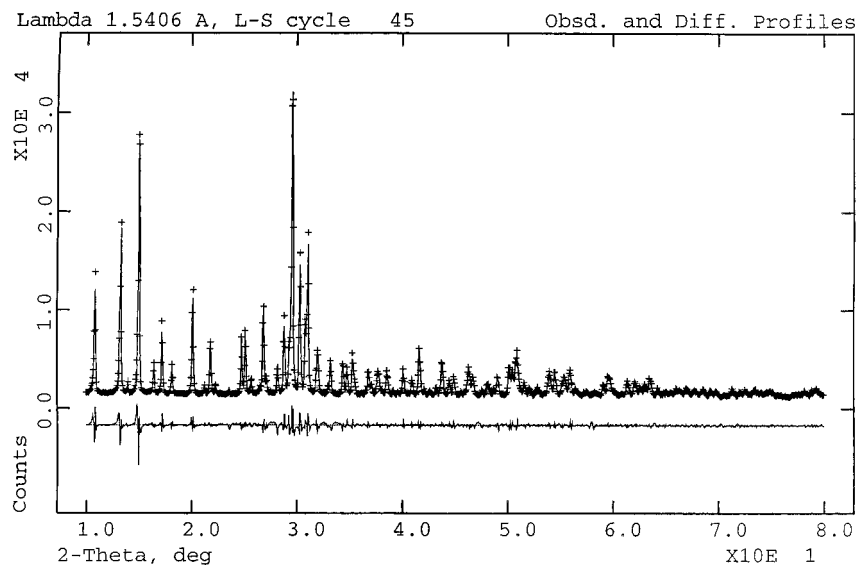


FIGURE 1. Observed, calculated, and difference profiles for the Le Bail Reitveld refinement of the titanium silicate compound. Note that no structural model is used for the refinement.

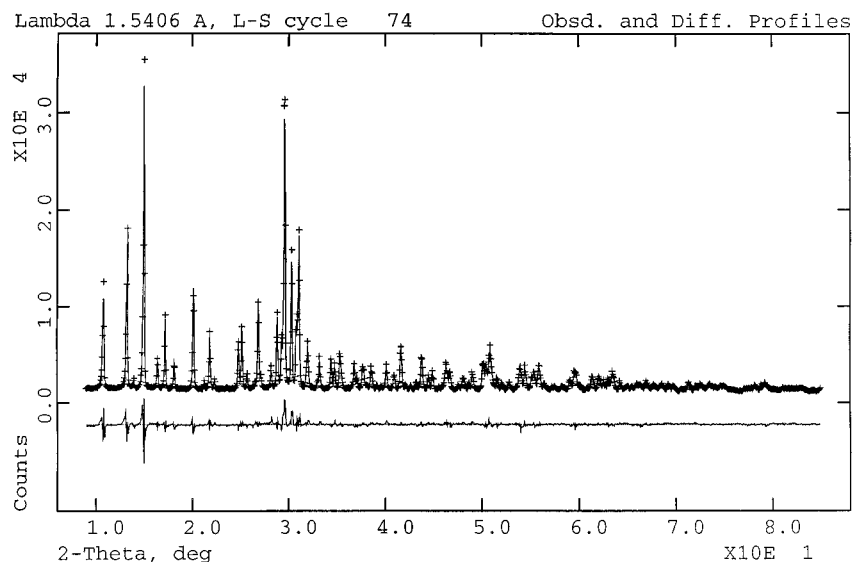


FIGURE 2. Final Rietveld difference plot for the refinement of the structure.

utilizing a conventional sealed tube generator. Only 60 unambiguously indexed reflections were used together with an equal number of null reflections with zero intensities to get a solution from direct methods. Due to the very limited number of reflections present it was necessary to draw contour maps at a very low electron density intervals in order to recognize structural features. Nevertheless, even the tetramethylammonium ion positions within the zeolite cavity could be determined. Following this study a number of structures from simple to complex nature were characterized both by heavy atom and direct method techniques.³²

When a graphite monochromator is used the radiation consists of the $K\alpha_1$ – α_2 doublet which results in doubling the number of diffraction lines in the X-ray pattern. Since the wavelengths of the doublet and their intensity ratio are well-known, the contribution of α_2 can be removed from the diffraction data. Such procedures are employed

in most cases. It is very convenient, however, to use monochromatic radiation so that the mathematical manipulation of the data can be avoided. For example, by the use of a germanium monochromator, the $K\alpha_2$ can be eliminated and data corresponding to only $K\alpha_1$ may be recorded. Such a method has been used for the solution of a number of structures.³³

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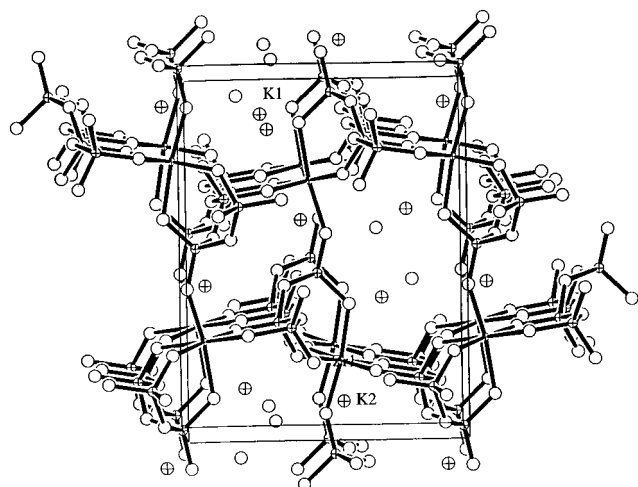


FIGURE 3. Portion of the structure of $K_2ZrSi_3O_9 \cdot H_2O$. The potassium ions in the smaller cavities (K2) can selectively be exchanged for other ions such as Cs^+ , K, Si, and Zr atoms are represented by large, medium, and small crossed circles, respectively. The oxygen atoms are represented by open circles.

The most complex structure solved thus far using laboratory data is that of a uranyl phosphonate compound, $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2 \cdot H_2O$.^{20a} The crystals belong to the orthorhombic space group $P2_12_12_1$ with $a = 17.1966(2)$, $b = 7.2125(2)$, $c = 27.8282(4)$ Å. The structure consists of 50 non-hydrogen atoms (Figure 4A) in the asymmetric unit, and it was solved by a combination of direct methods and Fourier methods using Cu $K\alpha$ data from a rotating anode source in the 2θ range of $7-85^\circ$. The structure consists of three independent uranium atoms, among which two are seven-coordinated and the third is eight coordinated. The metal atoms are connected by four distinct phosphonate groups to form a one-dimensional channel structure along the b -axis direction. The phenyl groups are arranged on the outer periphery of the channel, and their stacking forces keep the channel framework intact in the lattice. It is interesting to note that the arrangement of channels in the lattice, in this case, is very similar to that found for another uranyl phenylphosphonate compound, $UO_2(O_3PC_6H_5) \cdot 0.7H_2O$ ^{20b} (Figure 4B), which was also characterized by powder diffraction data. Recently Le Bail³⁴ has solved the structure of β - Ba_3AlF_9 (29 atoms) using a similar method. In both cases the intensity data were extracted using the Le Bail method. These examples demonstrate the power of conventional X-ray diffraction data in resolving complex structures.

One of our research interests, where powder techniques played a key role, is the chemistry of layered metal phosphates and phosphonates. These systems have potential applications in the areas of catalysis, absorption, ion-exchange, sensors, etc.³⁵ Most of these compounds cannot be obtained as single crystals, primarily due to their insolubility and also due to the very nature of the

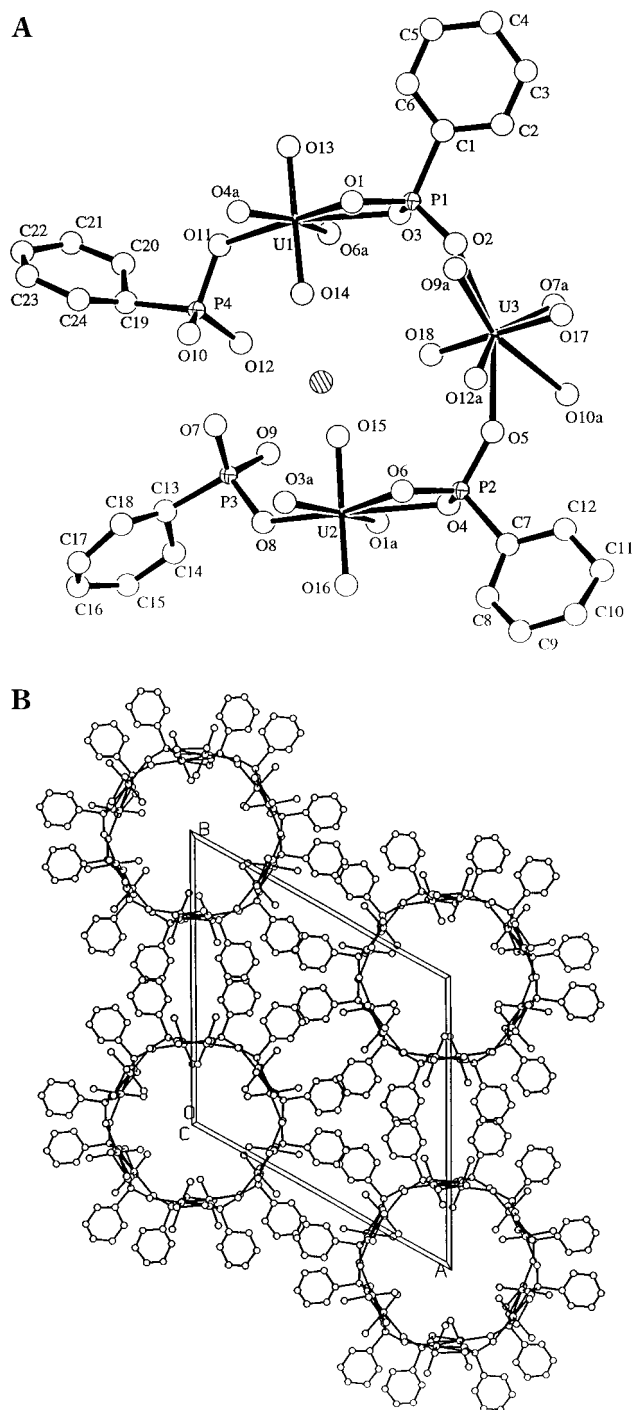


FIGURE 4. (A) Portion of the structure of $(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2 \cdot H_2O$. The phosphonate oxygens are involved in linking the uranyl groups along the projection axis leading to a porous one-dimensional structure. (B) Arrangement of uranyl phosphonate tubes in the structure of $UO_2(O_3PC_6H_5) \cdot 0.7H_2O$. The tube diameter is ~ 12.0 Å.

structure itself. The study of the metallophosphonates and other metalloorganic compounds is also of fundamental interest to show that powder data can in fact be used in the solution of the organometallic compounds³⁶ that constitute a major research branch in chemistry. Recently some conventional organometallic compounds were also structurally characterized by powder diffraction data.^{32n-p} Some of the metalloorganic compounds studied in our group are listed in Table 1.

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Table 1. Some Examples of Metallo-organic Structures Determined ab Initio from X-ray Powder Data

formula	space group	V (\AA^3)	no. of atoms	ref
$\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$	$C2/c$	1458	11 (syn)	37
$\text{Zr}(\text{O}_3\text{PCH}_2\text{Cl})_2$	$P2_1/c$	1024	13	38
$\text{MoO}_2(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}$	$P222$	958	14	39
$\text{Zr}_2\text{P}_2\text{O}_8\text{F}_6\text{N}_2\text{C}_{14}\text{H}_2\text{O}$	$P2_1/c$	1115	17	40
$\text{Zr}_2(\text{PO}_4)(\text{PMIDA})_2 \cdot 2\text{H}_2\text{O}$	$P2/c$	1167	19 (syn)	41
$\text{Pb}(\text{HO}_3\text{PC}_6\text{H}_5)_2$	$C2/c$	1476	11	42
$\text{UO}_2(\text{O}_3\text{PCH}_2\text{Cl})$	$P2_1/c$	623	9 (syn)	43
$\text{Zn}(\text{O}_3\text{PC}_6\text{H}_5)(\text{C}_n\text{H}_n + 3\text{NH}_2)$, $n = 3, 4, 5$	$P2_1/c$	1164–1377	15–17	44a
$\text{Zn}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3) \cdot 2\text{H}_2\text{O}$	$Pnmm$	526	7	45
$\text{Zn}(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3\text{H})$	$P\bar{1}$	665	21	45
$\text{Cu}(\text{HO}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3\text{H})$	$P\bar{1}$	307	11	46
$\text{Cu}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3) \cdot 2\text{H}_2\text{O}$	$C2/c$	1074	9	46
$\text{Cu}_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{PO}_3) \cdot 2\text{H}_2\text{O}$	$P2_1/c$	407	7	47
$\text{Zr}_2(\text{PO}_4)(\text{O}_3\text{P}(\text{C}_{14}\text{H}_{16}\text{N}_2\text{PO}_3)\text{F}_3 \cdot 3\text{H}_2\text{O})$	$P2/c$	1089	20 (syn)	48
$\text{Zn}_2(\text{O}_3\text{P}(\text{C}_6\text{H}_4)_2\text{PO}_3) \cdot 2\text{H}_2\text{O}$	$Pnn2$	761	12	47
$[\text{Cu}_2\text{Cl}_4(\text{bppz})]_n$	$C2/m$	503	12	49

The new chemistry that emerged from this study, which otherwise could not have been obtained, is worth mentioning. One example is a reaction involving the reversible binding of primary amines to layered metal phosphonates in the solid state.⁴⁴ Zinc phenylphosphonate monohydrate $\text{Zn}(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}$ takes up 1 mol of the amine by releasing the coordinated water molecule. Although the physicochemical data are very convincing for the product that has been formed, the uptake of amine results in a decrease of the interlayer spacing for the propyl and butyl members, a result unexpected for a simple substitution reaction. The host molecule was crystallized in the single-crystal form, and the structure was solved.^{44b} However, the intercalate could be obtained only in the polycrystalline form. By using powder diffraction data the structure of a number of the intercalates was recently solved.^{44a} Surprisingly, the intercalate phase no longer retains the layer structure of the host compound. Instead, the layer rearranges itself to provide room for the location of the bulky amine molecules. The six-coordinated zinc atoms adopt a tetrahedral geometry, and consequently, the layer expands to accommodate the incoming amine. On removal of the amine by acid treatment, the layer reverts to the structure it had before intercalation. The structure of the layers in the host and the intercalate is shown in Figure 5. This type of reversible binding of molecules may have applications in areas such as sensors.

The structure of an anion exchanger and catalytically active compound, $\text{Zr}_2(\text{PO}_4)_2(\text{O}_3\text{PC}_{14}\text{H}_{16}\text{N}_2\text{PO}_3)\text{F}_3 \cdot 3\text{H}_2\text{O}$,⁴⁸ determined from synchrotron X-ray powder data, is shown

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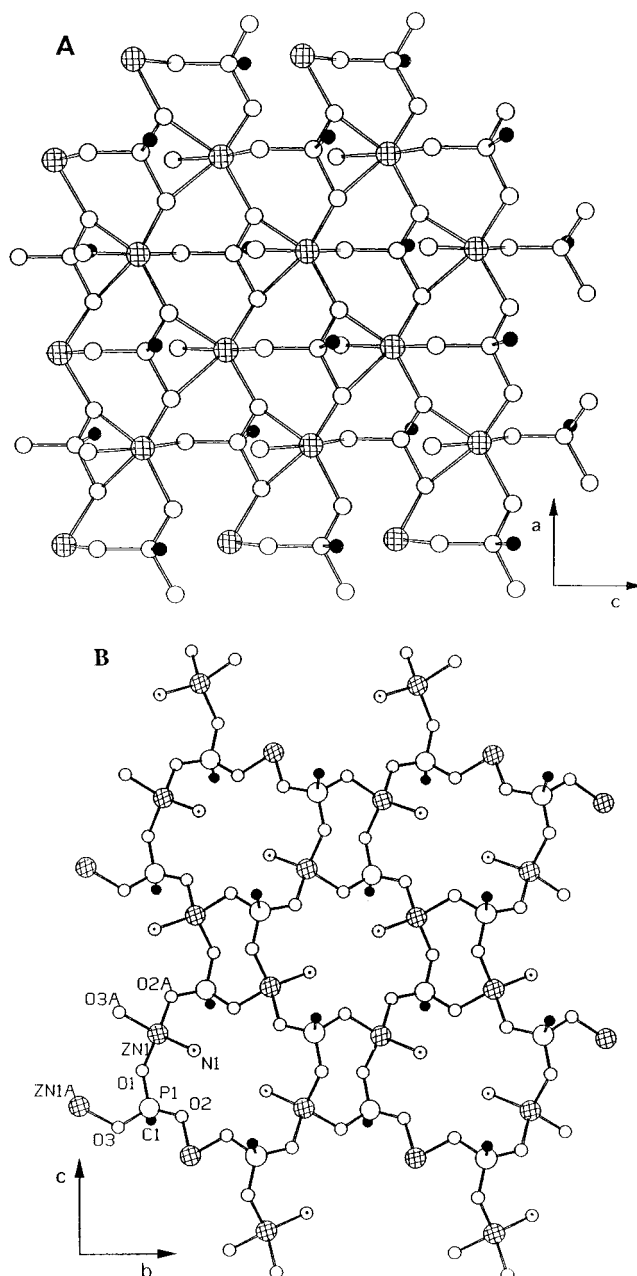


FIGURE 5. Metal phosphonate layer arrangements in (A) the structure of zinc phenylphosphonate monohydrate and (B) the structure of zinc phenylphosphonate-alkylamine intercalate. The structural changes are reversible and take place in the solid state.

in Figure 6. The structure consists of inorganic lamellae bridged by ethyldiolgen diphosphonate groups. The arrangement leads to large pores in the structure which contain the anions and water molecules. The compound is novel in that it contains an inorganic-organic mediated pore structure, and more importantly, the three-dimensional structure provides significant chemical insight into the catalytic and photocatalytic properties of this class of compounds. The free anions in the pore can be readily exchanged for PtCl_4^{2-} ions. It was found that the metal

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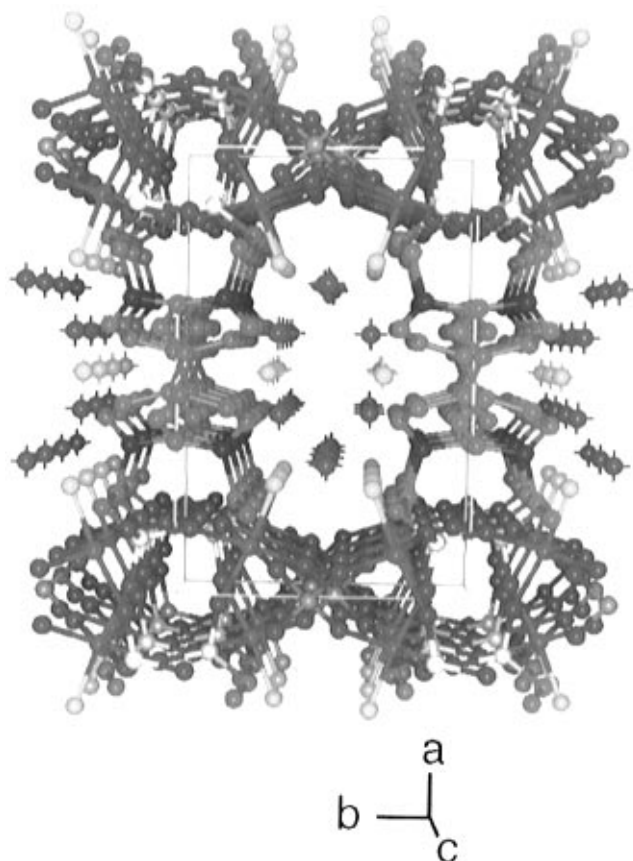


FIGURE 6. (top) Structure of $Zr_2(PO_4)_2(O_3PC_{14}H_{16}N_2PO_3)F_3 \cdot 3H_2O$ showing the pores filled with anions (light olive) and water molecules (red). Phosphate P atoms are shown in orange and phosphonate P atoms are shown in gray. (bottom) A schematic representation of the same structure is also shown for clarity.

particles inside the pore formed by reducing agents generate hydrogen photochemically from water and ultraviolet light.

Powder diffraction has played an important role in understanding the selectivity of cation binding in porous inorganic ion exchangers. These materials have pores similar to those found in zeolites and are capable of extracting specific ions from a bulk solution containing significant concentrations of other ions. This process is important in the selective absorption of radioactive species such as Cs^+ and Sr^{2+} from nuclear waste solutions.

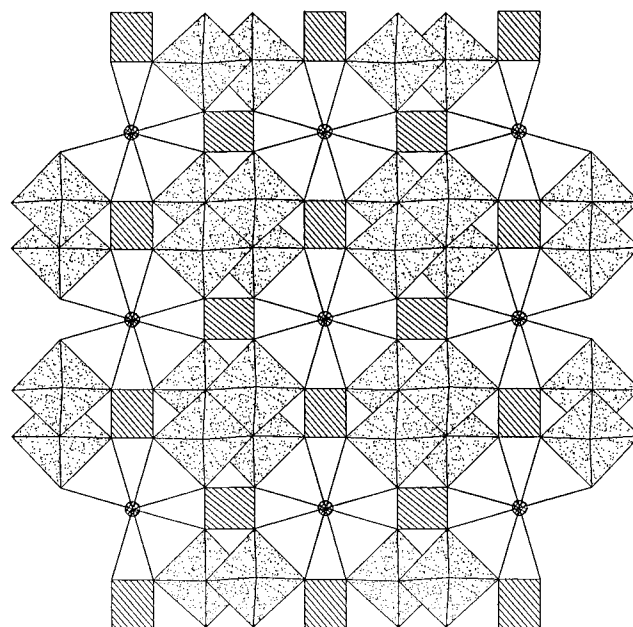


FIGURE 7. Polyhedral representation of the structure of a porous titanosilicate $Na_2Ti_2O_3SiO_4$. The cesium ions are shown by filled circles in the center of the tunnels. Stippled figures represent grouping of four titanium octahedra, the lined squares represent the silicate groups.

An example of such a compound is the zirconium silicate described earlier. Recently a titanosilicate having the ideal formula, $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$, was found to absorb Cs^+ ions selectively in 5.7 M sodium ion and 0.6 M hydroxide ion solutions.⁵⁰ This special property should be due to some subtle structural feature of the material. To understand the underlying principles of ion exchange, its structure was solved from laboratory X-ray powder data.⁵¹ The crystals belong to the tetragonal space group $P4_2/mcm$ with $a = b = 7.8 \text{ \AA}$ and $c = 11.97 \text{ \AA}$. The structure consists of $(TiO)_4$ cubes linked by silicate groups along the a and b directions to form an open cavity (Figure 7). The $(TiO)_4$ cubes are linked along the c direction by corner sharing, resulting in a one-dimensional channel along the c -axis. The channel dimensions obtained from the structural study indicate that they are ideally suited for the formation of optimal $Cs-O$ bonds. The Cs^+ ions can fit very well at the center of the cavity with very good bond lengths, while the sodium ions are distributed at sites away from the center. Although K^+ ions can occupy the same positions as Cs^+ , the $K-O$ bond lengths are longer than normal.⁵² This type of structural basis for ion selectivity has also been established for similar types of materials.⁵³

Application of Synchrotron X-ray and Neutron Diffraction Data. Excellent reviews have appeared recently on these topics.⁵⁴ As mentioned earlier, synchrotron radiation, due to high brightness and excellent vertical

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collimation, has the ability to provide high-resolution X-ray powder data with minimal peak overlap. These advantages over conventional sources would help in indexing the pattern and most importantly could provide a large number of singly indexed Bragg reflections for structure solution. In addition, the high quality of the data could improve the refinement, leading to precise structural parameters including thermal vibrational parameters. In some cases, it was found that synchrotron data were essential to resolve the atom positions, particularly those involving a labile carbon skeleton that could not be located using conventional X-ray data.⁴¹ It is easier to locate these light atoms by the use of neutron diffraction data, and such a combination of synchrotron X-ray and neutron diffraction data sets can be employed in the solution of complex structures.^{19,55} Neutron diffraction data may also be used for structure solutions;^{17,32i} however, its special advantage is in the location and refinement of light atoms in the structure and has been used for location of light atoms such as organic groups in zeolite cavities.⁵⁶

Structure Determination of Organic Molecules. Structures of purely organic compounds are difficult to solve *ab initio* due to the absence of strong scatterers. The presence of only light atoms reduces the number of high-angle reflections considerably, making the application of direct methods a difficult task. In the case where the crystals diffract to high angles it is possible to solve organic structures. Recently with the use of synchrotron data, Shankland et al.⁵⁷ were able to locate all 17 non-hydrogen atoms in the structure of chlorothiazide, a drug molecule. In cases where only limited data are available the structures were solved using the Patterson search method.⁵⁸ A known large fragment of the molecule whose structure is to be determined is used for the search against the low-angle diffraction data. Once a reasonable location of the fragment in the unit cell is established, the regular Rietveld method is employed to complete the structure and refinement by the rigid body method.

Monte Carlo and Maximum Entropy Methods. Recently a method which does not depend on the intensity extraction from powder pattern has been successfully applied for the solution of organic molecules.⁵⁹ The so-called Monte Carlo method is based on the standard Metropolis importance sampling algorithm.⁶⁰ The method in fact does not use the powder data at all. Instead it generates a series of trial structures in the given unit cell whose calculated powder patterns can then be compared with the observed pattern for acceptance or rejection. The crystal structure of $\text{Co}(\text{CN})_5\text{Li}_3\cdot 2\text{DMF}$ was solved by a

similar method.⁶¹ Models for the $\text{Co}(\text{CN})_5$ and two DMF moieties were placed randomly in the unit cell and a translation and rotation search was performed using a Monte Carlo method. Once a satisfactory agreement was obtained between the observed and calculated diffraction pattern, the structure was refined by the Rietveld method.

The problem of data overlapping in powder patterns is handled in a rational manner by entropy maximization and likelihood ranking. The method is based on maximum entropy algorithms⁶² and was used to solve some unknown crystal structures.⁶³

Conclusions

Obviously, the accuracy of the structure derived from powder data is not equal to that obtained from single-crystal data. However, this method can provide significant chemical knowledge for compounds that can be prepared only in polycrystalline form. In one case we have been able to compare the results derived from conventional X-ray powder data to those obtained from its single-crystal structure. We had earlier solved the structure of a photochemically active zirconium diphosphonate compound, $\text{Zr}_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{-bis}(\text{pyridinium})\text{-CH}_2\text{CH}_2\text{PO}_3)$ by using relatively low resolution (2θ , 8–80°) X-ray powder data.⁴⁰ Subsequently, the compound was obtained in single-crystal form by hydrothermal methods and it was characterized by single-crystal methods. The results compare very well, including the position of the lattice water.³⁶ The results from single-crystal study, however, are highly accurate, and the larger errors in the positions derived from powder data are obviously due to the availability of only a limited number of data. This drawback in powder data also affects the values of the thermal parameters of the atoms. When dealing with low-resolution X-ray powder data, such as the one described above for the zirconium compound, only isotropic thermal parameters are used, and in most cases, a common parameter is used for one type of atom to reduce the number of parameters to be refined. Nevertheless, the level of agreement is satisfactory and is even more comparable using synchrotron data.⁶⁴

Since the structure solution depends on the quality of the powder data, it is essential that the best possible data be collected for the sample. For example, the use of variable counting time data collection has been shown to improve the quality of data, resulting in better precision in structural parameters.⁶⁵ Use of Le Bail extracted data greatly aids in applying direct methods (MITHRIL,³⁰

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SIRPOW⁶⁶). Giocovazzo⁶⁷ in his latest review has described the potential of direct method applications to powder data. He and co-workers have developed programs to handle powder data in a systematic manner similar to that used for single-crystal data.⁶⁷ In addition, developments in areas such as maximization and likelihood ranking,⁶³ Patterson squaring,⁶⁸ and others⁶⁹ could help in tackling the difficult problems involved in powder structure solu-

tion particularly for organic molecules. However, given the success achieved so far, a wider usage of powder methods for structure solution is certainly in order.

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