Crystal structures of metallo–organo phosphates from X-ray powder diffraction data

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Abstract

The application of X-ray powder diffraction for the solution and refinement of unknown crystal structures is due to the recent developments in both computational and instrumental methods. While a good number of structures of simple to fairly complex inorganic compounds have been solved ab initio, by using powder diffraction data, application of such techniques to compounds containing organic groups is rare. By the use of laboratory and synchrotron X-ray powder diffraction data, we have successfully solved and refined a number of metallo–organic compounds containing both rigid and flexible carbon skeletons. In this paper we briefly describe our recent results on some complex metallo–organo phosphates. We also show the correctness of the powder structures by comparing the results of one such compound with its subsequent single crystal study.

Keywords: Phosphates; X-ray powder diffraction; Crystal structure

1. Introduction

One of the primary tools used for the determination of organometallic structures is single crystal X-ray diffraction. Of course, this technique requires compounds to be obtained in the form of suitable single crystals. Since the vast majority of organometallic compounds are molecular in nature, the practitioner can sooner or later find the proper solvent system for single crystal growth. In the 1970s structure determination by X-ray methods was not as much a push button science as it is today. Furthermore, not every laboratory had its own X-ray unit and crystallographer. Therefore, we were happy to collaborate with our honoree Marvin Rausch in determining the structure of a series of Π-complexes of several metals [1]. Every once in a while the structure turned out to be one that was unexpected, or a structure which yielded deeper insight into reaction pathways. If a powdered product was obtained for which single crystals could not be prepared, the practitioner had to rely on indirect spectroscopic methods. Structure solutions from powder data were almost never considered. Even simple indexing of the powder pattern to prove phase purity and derive unit cell constants was almost never attempted. In the past two decades improvements in instrumentation, theory and software have made it possible to not only extract this information but also solve the structure. Initially, the powder method was applied to solve the structures of relatively simple inorganic compounds [2]. Essential to the entire process was Rietveld's [3] development of the whole pattern refinement method.

One of the drawbacks of powder patterns is the overlap of reflections, particularly at high diffraction angle. Rietveld showed that a structure could be refined as to its atomic positions and thermal parameters without decomposing the pattern into individual reflections. Instead, a least-squares analysis is made between the observed X-ray pattern and one calculated from the model structure by minimizing the difference between them. The trick is to obtain the model structure. We were convinced early on that if the pattern were decomposed into its individual reflections, then single crystal methods could be applied to obtain a portion of the structure. The Rietveld method does lend itself to difference syntheses where a pattern calculated from a partial structure can be subtracted from the observed powder pattern and the difference used to locate missing atoms. Fortunately, at just that time several programs appeared aimed at abstracting intensities from the powder patterns by mathematically duplicating the peak shape and

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size [4]. At first we solved the structures of inorganic compounds that were of interest as ion exchangers [5,6], and then that of a molecular sieve using about 65 reflections for the initial "direct methods" solution [7]. This latter study represented the first structure solution of a zeolite-like compound ab initio from powder data.

A major thrust of our research program involves synthesis of extended structures containing organic groups. These compounds have potential for use as catalysts, ion exchangers and sorbents [8]. A variety of organic functional groups may be attached to the phosphonate ligand to vary the properties of the metal phosphonate. Depending upon the ligand and metal used to synthesize the compounds, we have obtained layered compounds [9], compounds with linear chains [10], double chains [11], and unusual porous structures [12]. In many cases only microcrystalline samples were obtained, and powder methods were used to determine their structures [9c,11–12]. Recently, we have been able to determine the structure of a uranyl phenylphosphonate containing 50 non-hydrogen atoms in the unique portion of the unit cell using conventional X-ray diffraction methods with intensities derived from X-ray powder data [12b].

In solving structures of organometallic compounds from powder data there are some inherent additional problems to those already mentioned. For example, our metallophosphonates yield only weak diffraction peaks and their intensities fall off very rapidly at higher scattering angles. Despite these difficulties, we have been able to locate and refine all the atoms, including the carbon atoms, in a large number of structures. In this paper we show that fairly complex metallo–organo phosphates can be structurally characterized from their powder diffraction data. The results thus obtained are highly satisfactory, and in one case we were able to compare the results with those obtained from a subsequent single crystal study (see below). Although the compounds described below are not organometallic compounds in the traditional sense, they contain both metal atoms and organic groups, the basic constituents of organometallic systems. Our experience would indicate that the structures of organometallic compounds could also be solved by similar methods. In fact, this has now been demonstrated in some cases [13].

2. X-ray powder structure of $Zr_2(O_3PCH_2CH_2-bi-pyridinium-CH_2-CH_2PO_3) \cdot F_6 \cdot 2H_2O(Zr-viologen)$

This compound exhibits very interesting photochemical behavior [14]. It was prepared by reacting $ZrOCl_2$ with the organophosphonic acid in the presence of HF. Initial preparations yielded only powder samples whose diffraction patterns were fairly well resolved. For data

collection, the powder sample was ground to a particle size of the order of 5–10 μ and loaded into a rectangular aluminum sample holder of dimensions 18×20 mm^2. The thickness of this holder is 1 mm. The sample was side-loaded to minimize preferred orientation effects. Step-scanned powder data for the sample were collected by means of a Rigaku computer controlled diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite monochromated radiation. Data were collected using the $2\theta/\theta$ mode between 2 and 80° in 2θ with a step size of 0.02° and a count time of 15 s per step. For indexing and structure solution, the data were stripped of the K $\alpha2$ contribution. However, both K $\alpha1$ and K $\alpha2$ contributions were used for Rietveld refinement. The powder pattern was indexed using both the trial and error [15a] and Ito [15b] methods. The best solution which indexed all the lines indicated a monoclinic cell with $a = 6.672$, $b = 12.6$, $c = 13.589$ Å, $\beta = 101.77°$. A least-squares refinement was then conducted with the program LSUCRE to obtain accurate unit cell parameters [16]. The systematic absences were consistant with the space group $P2_1/c$. Integrated intensities were extracted from the profile by decomposition methods as described earlier [17]. Several powder pattern decomposition programs for overlapping peaks are available [18,19]. These include methods that may or may not require structural information. The decomposition procedure over the range $8° < 2\theta < 60°$ in the present case yielded 74 reflections, of which 69 were non-overlapping. The intensities of the overlapping peaks were divided by the number of contributors and included in the data set. After appropriate corrections, the raw powder intensities were converted to structure factors (F_o and $\sigma(F_o)$) similar to those used for single crystal structure solution. Direct method attempts in TEXSAN [20] using these 74 structure factors revealed the positions of the Zr and P atoms. These positions were consistent with the peaks in the Patterson map, computed using the same data set. Difference Fourier maps yielded the coordinated atoms, but not those of the organic group. These C and N atoms, as well as the lattice water molecules, could be located from Fourier maps computed after Rietveld refinement [21] of the full powder pattern using the structural fragment obtained as described above. The structure was then refined against the full pattern using soft constraints for the bond lengths and angles. Initially, the weights of these constraints were kept at a high value to avoid the refinement from diverging. As the structure is completed and refinement is near completion, these constraints were assigned reduced weights. The weights could not be removed completely, even at the final stage of refinement, without reducing the stability of the refinement. These geometrical constraints play an important role in refining structures against X-ray powder diffraction data.
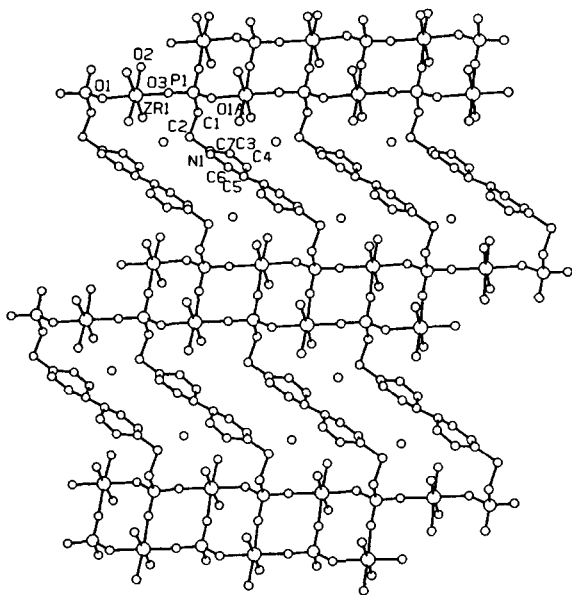
Fig. 1. Structure of $Zr_2(O_3PCH_2CH_2$-bipyridinium-CH_2-$CH_2PO_3) \cdot F_6 \cdot 2H_2O$ in the unit cell as viewed along the b-axis. The c-axis is vertical.

In addition to the conventional refinement of positional and thermal parameters, as is the case for single crystal structures, refinement of other parameters was also necessary in the case of powder structures. These include the lattice parameters, zero point error of the instrument, profile coefficients used to describe the shape (Gaussian or Lorentzian) of the peaks, background functions and preferred orientation effects.

The refinement converged leading to a satisfactory profile fit and an R-factor of 0.053 for 1366 (Cu Kα1 and Kα2) observed structure factors [22]. The structure of the compound along the b-axis is shown in Fig. 1. The results are surprising because a two-dimensional layer structure was expected similar to that found for α-$Zr(HPO_4)_2 \cdot H_2O$ [23]. On the contrary, the structure consists of double chains of metal octahedra and phosphate tetrahedra held together by P–O–Zr bonds. The octahedral coordination of Zr atoms is completed by three phosphonate oxygens and three F atoms. The double chains are then linked on either side to similar double chains by the organic group $-CH_2-CH_2-$bipyridinium-CH_2-CH_2-. This type of connectivity produces metal phosphonate sheets in the ac-plane. The water molecules reside between symmetry related sheets and hydrogen-bond to the coordinated F atoms.

3. Single crystal study of (Zr–Viologen)

Recently, Thompson and coworkers have obtained single crystals of the same compound by hydrothermal methods. In order to compare the results of powder structure with those obtained from single crystals in

general, we have now carried out structure solution and refinement of the above compound by using single crystal diffraction data.

A colorless crystal of dimensions $0.3 \times 0.2 \times 0.05$ mm^3 was mounted on a Rigaku AFC5R diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.71069$ Å) for data collection. Cell parameters were obtained from least-squares refinement of 25 carefully selected reflections, chosen from a 46.8–49.5° 2θ shell, immediately prior to data collection. Intensity data were collected up to a 2θ limit of 50° using the ω–2θ method. Of the 2226 reflections which were collected, 2043 were unique ($R_{int} = 0.014$). The data were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method using the TEXSAN system of programs [20]. The position of the Zr atom was derived from the three-dimensional Patterson map. Subsequent difference Fourier maps revealed the locations of all the other atoms in the structure. The data were corrected for absorption and secondary extinction effects. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. The final R and R_w factors are 0.054 and 0.065 respectively for 1397 reflections with $I > 4.00\sigma$. The maximum and minimum peaks on the final difference Fourier map were 1.17 and -1.14 e Å^{-3}.

Crystal data and atomic positions obtained from the single crystal study are given in Table 1 and the corresponding data derived from powder data are given in Ref. [22]. A comparison of the bond lengths derived from single crystal and powder data for this compound is given in Table 2. The atomic positions obtained in these two studies compare very well, including those of

Table 1
Positional parameters and B_{eq} for Zr–viologen compound

Atom	x	y	z	B_{eq}
Zr1	0.8003(1)	0.09218(6)	0.13335(5)	0.55(3)
P1	0.2903(3)	0.0276(2)	0.1087(1)	0.86(8)
F1	0.7591(8)	0.2231(4)	0.0517(4)	2.3(2)
F2	0.8370(7)	0.9566(4)	0.2109(4)	1.8(2)
F3	0.8593(7)	0.1777(4)	0.2580(4)	1.8(2)
O(W)	0.248(1)	0.2440(6)	0.3557(7)	4.4(4)
O1	0.480(1)	0.0899(4)	0.1421(4)	1.4(2)
O2	0.744(1)	0.0020(4)	0.0023(4)	1.3(2)
O3	0.120(1)	0.0933(4)	0.1312(4)	1.5(2)
N1	0.512(1)	0.9441(6)	0.3550(5)	1.3(3)
C1	0.303(1)	0.9069(7)	0.1816(7)	1.6(3)
C2	0.307(1)	0.9196(7)	0.2906(7)	2.1(4)
C3	0.646(2)	0.8647(8)	0.3808(7)	2.3(4)
C4	0.841(1)	0.8839(7)	0.4392(7)	1.9(4)
C5	0.898(1)	0.9869(7)	0.4677(6)	1.2(3)
C6	0.753(1)	0.0682(6)	0.4382(6)	1.4(3)
C7	0.563(1)	0.0437(7)	0.3820(6)	1.5(3)

Crystal data: $a = 6.651(2)$, $b = 12.550(3)$, $c = 13.486(7)$ Å, $\beta = 101.65(4)°$; space group $P2_1/c$; $R = 0.054$; $R_w = 0.065$; GOF = 2.26; no. of reflections ($I < 4.0$ $\sigma(I)$) 1397; no. of variables 154.

Table 2
Intramolecular distances

Atom	Atom	Distance	Distance *
ZR1	F1	1.966(5)	2.04(1)
ZR1	F2	1.986(5)	2.04(1)
ZR1	F3	1.966(5)	2.04(1)
ZR1	O1	2.157(6)	2.08(1)
ZR1	O2	2.068(5)	2.09(1)
ZR1	O3	2.130(7)	2.03(1)
P1	O1	1.476(6)	1.55(1)
P1	O2	1.514(6)	1.58(1)
P1	O3	1.483(6)	1.52(1)
P1	C1	1.80(1)	1.81(1)
C1	C2	1.47(1)	1.58(2)
N1	C2	1.50(1)	1.53(2)
N1	C3	1.34(1)	1.37(2)
N1	C7	1.33(1)	1.32(2)
C3	C4	1.40(1)	1.41(2)
C4	C5	1.38(1)	1.38(2)
C5	C5'	1.50(1)	1.51(2)
C5	C6	1.40(1)	1.38(2)
C6	C7	1.37(1)	1.42(2)

Prime indicates the C5 atom related by a center of symmetry.

* Bond lengths obtained from X-ray powder diffraction data (Ref. [16]).

the organic groups and lattice water oxygen. The bond parameters obtained from single crystal study are more accurate, but their values are very similar to those obtained from powder X-ray data, including those of the organic moiety. This lends confidence to the correctness of structures determined from powder data. The largest errors will appear in hydrogen bond distances. For example, the average O(W)—F hydrogen bonding distance in the powder and single crystal structures are 2.72 and 2.81 Å respectively. It should be noted, however, that the comparison is very good in this case, but larger errors are expected in structures derived from poor quality powder diffraction data. In general, a meaningful comparison of the results may be made if one considers the average values of the bond parameters in the case of structures derived from powder diffraction data. It has to be remembered that the atomic positions were refined against a limited number of powder diffraction data, and that some ideal geometrical values with allowable error limits were included for the refinement of powder structures. Nevertheless, one can get significant structural information which is otherwise unobtainable if the compound cannot be grown in the form of single crystals. In the case of X-ray powder structure refinement, however, only isotropic thermal parameters are used. In some cases a common parameter is used for one type of atom to reduce the number of refinable parameters. However, by the use of neutron diffraction data, the structure can be refined anisotropically. The GSAS program [21] allows simultaneous refinement of X-ray and neutron data as independent data

sets, greatly improving the accuracy of bond distances and angles and location of H atoms.

4. Structure of a complex tubular uranyl phosphonate $[UO_2]_3[HO_3PC_6H_5]_2[O_3PC_6H_5]_2 \cdot H_2O$ from powder diffraction data

The powder diffraction data were collected on a rotating anode X-ray source as described for the Zr–viologen compound above. The pattern was indexed on an orthorhombic cell (space group $P2_12_12_1$) with $a = 17.1966(2)$, $b = 7.2125(2)$, $c = 27.8282(4)$ Å and $Z = 4$. The intensities were extracted from the profile using the Le Bail method [19] in program GSAS [21]. A combination of direct methods and heavy atom method was used to derive the positions of the U, P, and some O atoms. The positions of the remaining oxygen atoms and those of 24 independent carbon atoms were derived by difference Fourier maps calculated following Rietveld refinement of the full pattern. This structure contains 50 non-hydrogen atoms in the asymmetric unit and represents the most complex structure solved so far using laboratory X-ray powder data [12b]. A total of 159 structural parameters were refined, which lead to a final R_F factor of 0.05. The structure is shown in Fig. 2.

5. Structure of a mixed phosphate/phosphonate layered compound containing a phosphonatomethyliminodiacetic acid (PMIDA) group

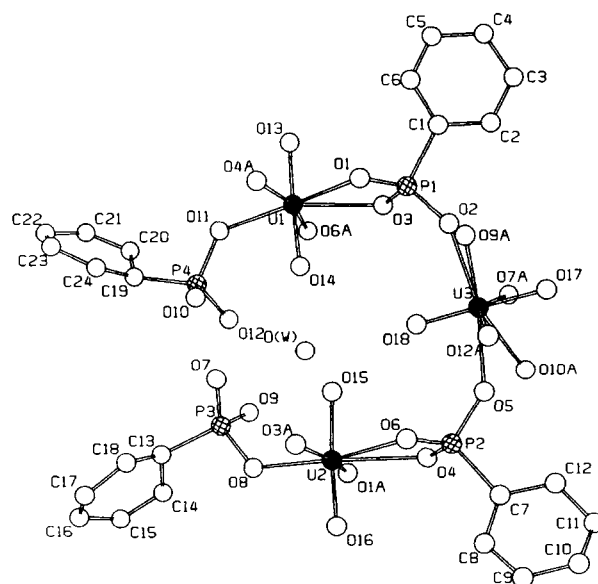This structure has a complex organic moiety unlike the other two structures described above [24]. The

Fig. 2. Structure of uranyl phenylphosphonate $[UO_2]_3[HO_3PC_6H_5]_2$-$[O_3PC_6H_5]_2 \cdot H_2O$.
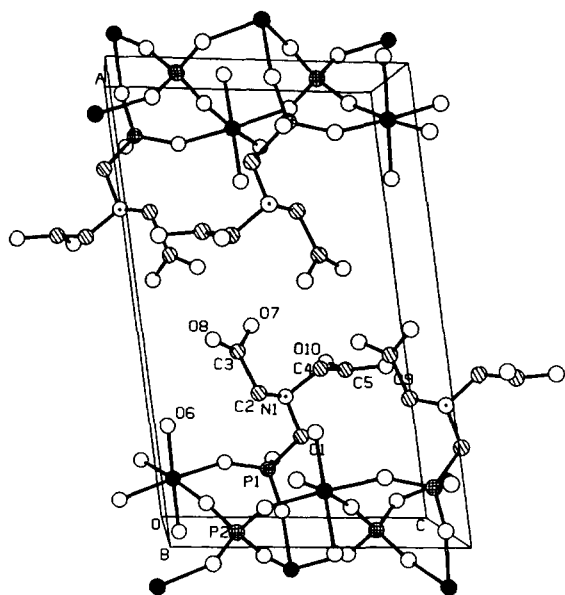
Fig. 3. Projection of the structure of Zr–PMIDA layer compound $[Zr_2(PO_4)\{O_3PCH_2N(CH_2CO_2H)_2\}\{O_3PCH_2N(CH_2CO_2H)(CH_2-CO_2)\} (H_2O)_2]$ along the b-axis.

PMIDA group does not have a rigid geometry like the phenyl groups or bipyridinium groups. The laboratory X-ray powder data were initially used to solve the structure. In this case, the crystals are monoclinic, space group $P2/c$, $a = 14.9010(3)$, $b = 8.6541(1)$, $c = 9.1367(1)$ Å, $\beta = 97.960(2)°$, and $Z = 2$. The positions of Zr and P were obtained by low angle Patterson map. Rietveld refinement and difference Fourier maps revealed the atoms of metal octahedra and phosphonate tetrahedra, but not those of the PMIDA group. To locate these atoms, it was necessary to obtain a synchrotron data set. For this purpose, the sample was finely ground and loaded into a 1 mm glass capillary. The data were collected at the National Synchrotron Light Source on a spinning sample using a monochromated X-ray radiation of wavelength 1.1487 Å in steps of 0.008° for the range $4° < 2\theta < 60°$. The counting time per step varied from 1 to 10 s. The synchrotron source yields intense high quality powder data, and by using the capillary method the data can be obtained with minimal preferred orientation effects. Using these data we were able to locate all the remaining atoms in the structure and refine them successfully. A view of the structure is shown in Fig. 3.

6. Conclusions

The use of X-ray powder data to solve structures ab initio is still in its formative stage. We have attempted to utilize only data obtained from diffractometers available in almost every chemistry department. However, synchrotron data were required to complete some of the

structures. For highest accuracy, neutron data can be combined with the X-ray data to increase the ratio of data to parameters to be determined and refined. Electron diffraction can be used to help determine the correctness of the space group and unit cell choice. All of this indicates that, at this stage of development, structure solutions by powder methods require the involvement of an experienced crystallographer. Thus, collaboration between the synthetic practitioner and a crystallographer, such as demonstrated by that of Professor Mark E. Thompson and the authors, is in order.

Acknowledgments

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