Synthesis and Crystal Structure of a New Layered Zirconium Phosphate Compound, $Zr(PO_4)F(OSMe_2)$

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The crystal structure of a layered zirconium phosphate compound $Zr(PO_4)F(OSMe_2)$ was solved *ab initio* by using X-ray powder diffraction data and refined by the Rietveld method. It crystallizes in the tetragonal space group *P4/n* with $a = 6.6093(2)$, $c = 9.2371(3)$ Å and $Z = 2$. The positions of the metal and the phosphorus atoms were derived from a three-dimensional Patterson map computed using 50 unambiguously indexed powder diffraction intensities. The remaining atoms were located from Fourier-difference maps. The final agreement factors are $Rwp = 0.109$, $Rp = 0.082$ and $R_F = 0.059$. The structure is layered in which the metal atoms and the phosphate groups are located nearly in a plane. All the oxygen atoms of the phosphate group are involved in metal co-ordination. The axial sites of the metal octahedra are occupied by the charge-neutralizing fluoride ion and the oxygen atom of a dimethyl sulfoxide molecule.

Recently there has been growing interest in the chemistry of layered metal compounds. Our work has been mainly devoted to Group IV metal phosphates, particularly those of zirconium compounds.[1] The zirconium phosphate compounds are ion exchangers and studies have shown that there are in fact two major types of crystalline materials: $Zr(HPO_4)_2{\cdot}H_2O$, referred to as α-zirconium phosphate which is the more stable phase;[2,3] and $Zr(PO_4)(H_2PO_4){\cdot}2H_2O$, γ-zirconium phosphate.[4,5] Crystal structures of these compounds formed the basis not only for understanding the ion-exchange mechanism but also in preparing the corresponding metal phosphonates. These phosphonates, when properly functionalized, may serve as hosts for a variety of intercalation reactions and have potential applications in the areas of catalysis, ion exchange and sorption.[1,6] Many other layered forms of zirconium phosphate have been prepared[7] but their structures are unknown.

Zirconium phosphate compounds are difficult to crystallize because of their great insolubility, and in fact only the α phase was characterized by single-crystal diffraction data. The crystals of the parent zirconium phosphate become highly disordered during ion exchange or intercalation as the layers separate to accommodate the ions or guest molecules. Thus, these phases can be obtained only in microcrystalline form, which in most cases yield broad reflections with decreasing intensities at high scattering angles. Nevertheless, we were able to determine the structures of some of the ion-exchanged phases,[8–11] phosphonates[12,13] and amine intercalates[14,15] from their powder diffraction patterns.

In this paper we report the synthesis and structure of a new zirconium phosphate layer compound. The crystal structure of the compound was solved by conventional methods using X-ray powder diffraction data. This is the first example of a layer compound having a Zr:P ratio of 1:1. We also discuss some preliminary results obtained on the reaction of this compound with phosphates and phosphonates.

Experimental

Synthesis and Characterization.—The chemicals were of reagent-grade quality obtained from commercial sources and used without further purification. The compound $ZrOCl_2{\cdot}8H_2O$ (0.05 mol) was dissolved in 49% HF (43 cm^3; Zr:F ratio 1:25) and doubly distilled water (5 cm^3). This solution was then mixed with H_3PO_4 (85%, 0.1 mol, 6.8 cm^3) in dimethyl sulfoxide (dmso) (60 cm^3) and heated at 120 °C in a plastic beaker covered with Parafilm for several days. The product was filtered off, washed with water and dried at 100 °C for 2 d. Thermogravimetric analysis showed that the sample loses 27% of its weight up to 1000 °C. The ^{31}P NMR spectrum indicated a single phosphorus site (δ −20.8) in the structure. The IR spectrum showed the characteristic bands of dmso (3023, 3005, 1425, 1325 and 1016 cm^{-1}) as well as those of the phosphate group [Found: C, 8.6; H, 1.9. Calc. for $Zr(PO_4)F(dmso)$: C, 8.5; H, 2.1%].

Data Collection, Structure Solution and Refinement.—Step-scanned X-ray powder data for the sample (packed on a flat aluminium sample holder) were collected for a finely ground sample by means of a Rigaku computer-automated diffractometer. A 0.5° divergence and scatter slits together with a 0.15° receiving slit were employed. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. The sample was side-loaded to minimize preferred orientation effects. Data were collected between 5 and 80° in 2θ with a step size of 0.02° and a count time of 20 s per step. Data were mathematically stripped of the $K\alpha_2$ contribution and peak picking was conducted by a modification of the double-derivative method.[16] The powder pattern was indexed by Ito methods[17] on the basis of the first 20 observed lines (figure of merit = 24). The best solution which indexed all the lines indicated a tetragonal unit cell with lattice parameters $a = 6.609$ and $c = 9.237$ Å. The indexed reflections showed systematic absences of the type $hk0$, $h + k = 2n + 1$ which is consistent with the space group *P4/n*.

Integrated intensities were extracted from the profile over the range $7 < 2\theta < 78°$ by decomposition (maximum likelihood estimation) methods as described earlier.[18] This procedure produced 50 unambiguously indexed reflections. These peaks were used to generate the normal $F_o(hkl)$ and $\sigma(F_o)$ and input to the single-crystal structure-determination package.[19] The positions of the Zr and P atoms were located from a three-dimensional Patterson map computed using this data set. These atomic positions were used for Rietveld profile refinement in GSAS.[20] The positions of the remaining atoms in the structure were located from three successive Fourier-difference maps. The atomic positions were then refined using soft constraints which define the expected geometries of the metal atom and the phosphate group within some allowable error limits. All the atoms were refined isotropically. In the final cycles of refinement the shifts in all the parameters were less than their estimated standard deviations. Neutral atomic scattering factors were used for all atoms. No corrections were made for anaomalous dispersion, absorption or preferred orientation. The strong (001) reflection is asymmetric and affected by the preferred orientation to a great extent. Therefore this peak was not included in the final Rietveld difference plot, however it was used in the calculation of the R_F factor.

Results and Discussion

Crystallographic data are given in Table 1, final positional parameters in Table 2 and bond lengths and angles in Table 3. The Rietveld refinement plot is shown in Fig. 1. Figs. 2 and 3 are projections of the structure down the *a* and *c* axis, respectively.

The Zr atoms are located on a four-fold axis with their *z* coordinate approximately ±0.1. The P atoms are situated on a $\bar{4}$ axis and they lie exactly in a plane at $z = 0$. They are surrounded by the four Zr atoms, among which two are above the plane while the other two are shifted below the plane to the same extent. Similarly, each Zr atom is surrounded by four P atoms and this arrangement produces a two-dimensional layer structure as shown in Figs. 2 and 3. The in-plane co-ordination of the metal is through the four symmetry-related positions of the phosphate oxygen O(2). The fluoride ion is shifted away from the plane and occupies one of the axial sites of the Zr atom. The other axial site is occupied by the oxygen atom of the dmso molecule. The fluoride ion and the dmso both lie on the four-fold axis thus forming a perfect F–Zr–O 180° angle. Since the dmso molecule lies on the 4 axis, the carbon atoms of the methyl groups are disordered over two positions each with 50% occupancy. The dmso and the fluoride ions are disposed into the interlayer space in such a way that the methyl groups are positioned directly above or below the F atom of the adjacent layer. The distance between the mean plane of the disordered carbon atoms of a dmso molecule and the F atom is about 3 Å. The corresponding C $\cdots$ F distance between these groups is about 3.5 Å. Apart from this there are no other interactions between the zirconium phosphate layers. The bond parameters involving the zirconium octahedra and the phosphate group are normal. The C–S–C bond angle (85°) is slightly smaller than the normal value which may be due to symmetry-imposed disorder of the dmso molecule.

Table 1 Crystallographic data for $Zr(PO_4)F(dmso)$

Formula	$C_2H_6FO_5PSZr$
Pattern range, 2θ/°	15–80
Step scan increment, 2θ/°	0.02
Step scan time/s	20
Space group	*P*4/*n* (no. 85)
a/Å	6.6093(2)
c/Å	9.2371(3)
Z	2
D_c/Mg m^{-3}	2.33
No. of contributing reflections	256
No. geometric observations	25
P–O distances and tolerance/Å	1.53(2)
Zr–O distances and tolerance/Å	2.03(3)
O $\cdots$ O distances for PO_4/Å	2.55(2)
O $\cdots$ O distances for ZrO_6, *cis*/Å	2.90(2)
Zr–F/Å	1.99(2)
No. structural parameters	17
No. profile parameters	11
Statistically expected *Rwp*	0.03
Rwp	0.109
Rp	0.082
R_F	0.059

$Rwp = [\Sigma w(I_o - I_c)^2/\Sigma(wI_o{}^2)]^{\frac{1}{2}}$, $Rp = \Sigma|I_o - I_c|/\Sigma I_c$, $R_F = \langle|F_o| - |F_c|\rangle/\langle|F_o|\rangle$; expected $Rwp = Rwp/(\chi^2)^{\frac{1}{2}}$, $\chi^2 = \Sigma w(I_o - I_c)^2/(N_{obs} - N_{var})$, N_{obs}, N_{var} = numbers of observations and variables.

Table 2 Positional parameters for $Zr(PO_4)F(dmso)$

Atom	*x*	*y*	*z*
Zr	0.25	0.25	0.1015(2)
P(1)	0.25	0.75	0
O(1)	0.25	0.25	0.8734(9)
O(2)	0.2277(21)	0.9412(5)	0.0982(5)
F(1)	0.25	0.25	0.3171(8)
S(1)	0.25	0.25	0.7061(8)
C(1)*	0.0176(15)	0.1671(21)	0.6513(13)

* Occupancy 0.5.

The structure described here is different from that of α- and γ-zirconium phosphates although all are layered. Unlike the present case, α and γ phases have a Zr : P ratio of 1 : 2. In the α phase the metal atom binds to three oxygen atoms of each phosphate group. The fourth oxygen of both the phosphate groups carries the proton and points away from the layers. The P atoms are located alternately above and below the metal plane. The metal atoms are arranged in the form of an equilateral triangle. The metal phosphate layer structure in the present case, however, is similar to that observed for the γ phase despite the difference in Zr : P ratio in these systems. In the γ phase one of the phosphate groups is located almost in the metal plane and all four of its oxygens are involved in metal binding. This situation is similar to that described for the present compound although in the γ phase the in-plane dimensions (*a* and *b*) are not equal and the layers are shifted relative to one another. The second phosphate exists as a dihydrogenphosphate group, $H_2PO_4{}^-$, and it bridges the metal atoms through two of its oxygen atoms. In the absence of such phosphate oxygens, dmso and F atoms complete the metal co-ordination in $Zr(PO_4)F(dmso)$.

Recently, we determined the structure of a photochemically active zirconium viologen phosphonate compound,[21] $Zr_2[O_3PCH_2CH_2(NC_5H_4C_5H_4N)CH_2CH_2PO_3]F_6{\cdot}2H_2O$ from powder diffraction data. This compound also has a Zr : P ratio of 1 : 1, however the structure is a different layer type. Three of the phosphonate oxygens and three fluorine anions complete the octahedral co-ordination of the zirconium atom. The phosphate-bridged metal atoms are arranged in the form of isolated double chains which are connected to each other by the bifunctional ethylviologen groups.

The axial disposition of the fluoride ion and dmso molecule together with high thermal vibration and disorder of the latter indicate that these groups may be substituted by other ligands. Reaction of this compound with an excess of aqueous (0.1 mol dm^{-3}) phosphoric acid resulted in conversion into highly crystalline α-$Zr(HPO_4)_2{\cdot}H_2O$. Similar reaction with phenylphosphonic acid yielded zirconium phenylphosphonate along

Table 3 Bond lengths (Å) and angles (°) for $Zr(PO_4)F(dmso)$

Zr–O(1)	2.107(8)		Zr–F(1)	1.991(7)	
Zr–O(2)	2.046(3)	(4 ×)			
O(1)–Zr–O(2)	89.1(2)	(4 ×)	O(2)–Zr–F(1)	90.87(15)	(4 ×)
O(1)–Zr–F(1)	180		O(2)–Zr–O(2)^a	178.3(3)	(2 ×)
O(2)–Zr–O(2)^a	89.987(4)	(4 ×)			
P(1)–O(2)	1.563(3)	(4 ×)			
O(2)–P(1)–O(2)^b	109.1(3)	(2 ×)	O(2)–P(1)–O(2)^b	109.7(2)	(4 ×)
S(1)–O(1)	1.546(8)		S(1)–C(1)	1.708(8)	(2 ×)
O(1)–S(1)–C(1)	107.2(5)	(2 ×)	C(1)–S(1)–C(1)^a	85.0(3)	(2 ×)
P–O(2)–Zr	144.0(4)		S–O(1)–Zr	180	

^{a} Like atoms related by four-fold symmetry. ^{b} Like atoms related by $\bar{4}$ symmetry.

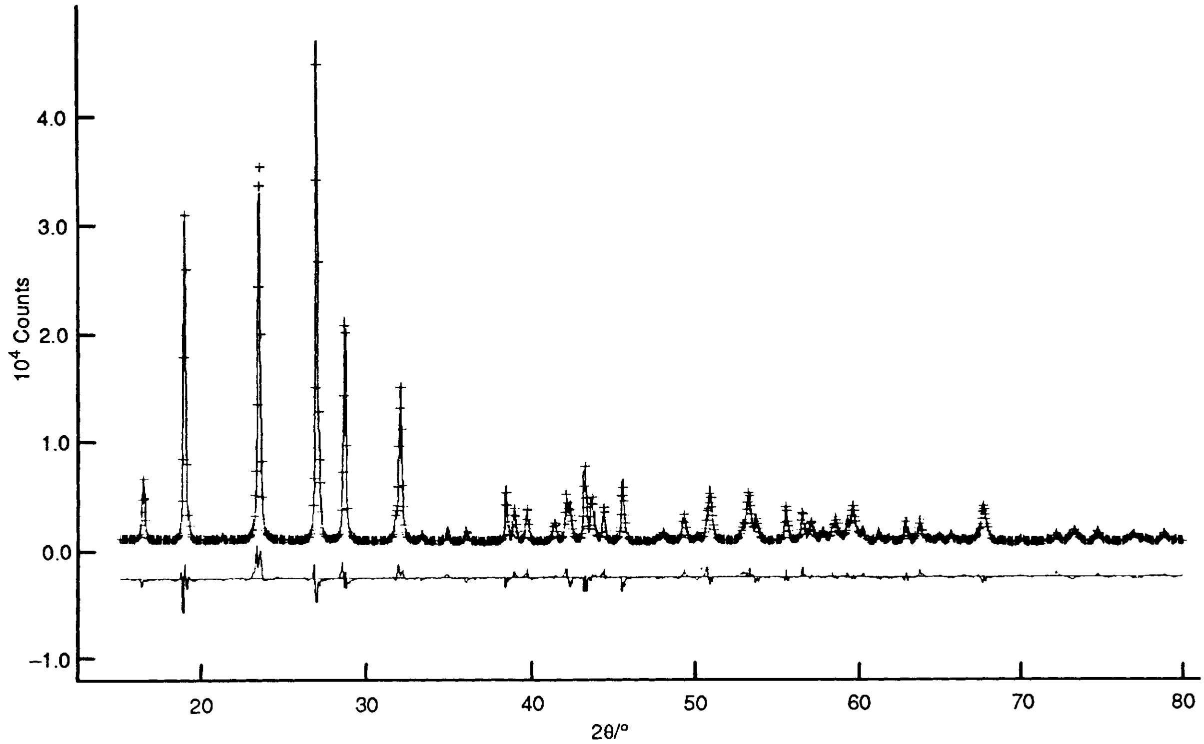

Fig. 1 Observed (+) and calculated (—) profiles (X-ray intensity *versus* 2θ) for the Rietveld refinement. The lower curve is the difference plot on the same intensity scale

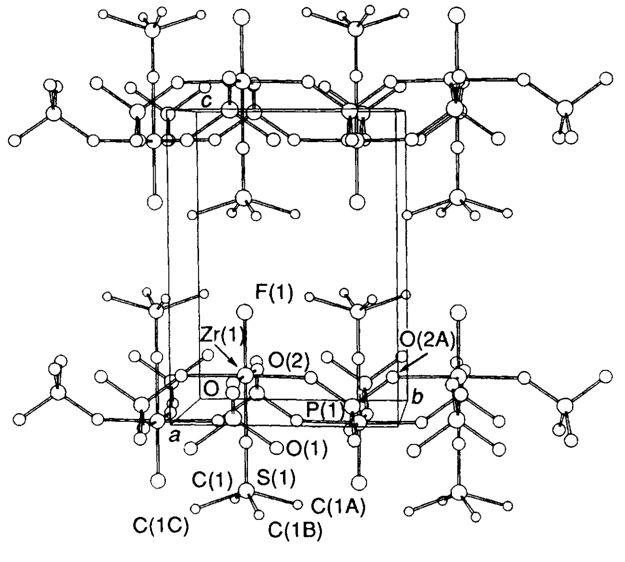

Fig. 2 Projection of the structure down the *a* axis showing the positioning of the dmso and F atoms in the interlayer space

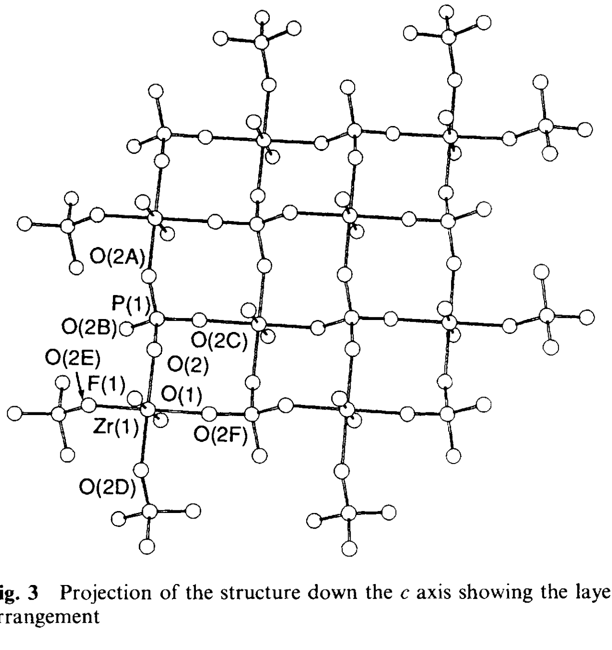

Fig. 3 Projection of the structure down the *c* axis showing the layer arrangement

with some unreacted Zr(PO$_4$)F(dmso). Refluxing with ammonium phosphate, on the other hand, resulted in a γ-type structure, Zr(PO$_4$)(NH$_4$HPO$_4$). We are now attempting to improve the crystallinity of this material and if successful the procedure described above may be an efficient way of preparing γ-Zr(PO$_4$)(H$_2$PO$_4$)·2H$_2$O.

Converting the structure to α-Zr(HPO$_4$)·H$_2$O involves a complete rearrangement of the layers as the phosphate group has to bridge three metal atoms instead of four in the present case. Forming a γ-type structure, however, is relatively simple. Both in the present compound and γ-Zr(PO$_4$)(H$_2$PO$_4$)·2H$_2$O, one of the phosphates bridges four metal atoms. Inspection of Fig. 2 shows that within a layer the adjacent dmso and F atoms are oriented in the same direction. Some of the important contacts between these groups and the associated Zr atoms are C···F ≈3.3, C···Zr ≈4.0, S···F ≈4.7 and S···Zr ≈5.0, Zr···Zr ≈5.0 Å. When dmso and F atoms are replaced by a phosphate group, the two nearest Zr atoms (≈5.0 Å) are bridged by two oxygens from this group. In this process the Zr atoms move slightly apart (about 5.3 Å), the in-plane dimensions become non-equivalent, and consequently the symmetry is reduced to monoclinic. The structure of γ-Zr(PO$_4$)(NH$_4$HPO$_4$) will be published elsewhere.[15]

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