Synthesis and Crystal Structure of Zirconium Chloromethylphosphonate

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The crystal structure of zirconium chloromethylphosphonate, $Zr(O_3PCH_2Cl)_2$, has been solved and refined using powder diffraction data. The crystals belong to the space group $P2_1/c$ with $a = 9.3402(7)$ Å, $b = 5.3926(3)$ Å, $c = 21.374(2)$ Å and $\beta = 107.892(5)°$. The reliability factors are $R_{wp} = 0.155$, $R_p = 0.115$, $R_F = 0.04$ and expected $R_{wp} = 0.035$. The layer arrangement in the structure resembles very closely that in α-zirconium phosphate. The chlorine atoms on both the methyl groups are disordered, in such a way that the disordered positions are displaced along the *b* axis of the crystal.

Zirconium bis(monohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP) is of considerable interest because of its layered structure and more importantly its function as an ion exchanger.[1,2] We have been involved in the synthesis and structural studies of zirconium as well as di- and trivalent layered metal phosphonates.[3–7] One can prepare functionalized derivatives, particularly those of Group 4 metal phosphonates[8–10] which in turn exhibit interesting complexing and sorption behaviour. Since these are layered compounds, they can also act as hosts in intercalation reactions.[11–14] An example of this type of reaction was demonstrated for copper phosphonate systems,[15] where alkylamines were intercalated into the anhydrous metal phosphonate layers. The crystal structures[5] of these copper phosphonates showed that the metal is in an unusual five-coordinate environment in which the water molecule is bonded in the equatorial position of the square-pyramidal geometry. On dehydration the vacant site created on the copper coordination sphere is responsible for the intercalation of the amines. Thus it is important to obtain three-dimensional structural information on the model phosphonates in order to understand the reactions involved in these layered compounds. However, there is a dearth of structural information on Group 4 layered phosphonates because of the difficulty in obtaining highly crystalline samples. Recently we were able to solve the crystal structure of zirconium phenylphosphonate.[3] In this paper we describe the synthesis and X-ray powder structure of zirconium chloromethylphosphonate.

Experimental

Synthesis

Chloromethylphosphonic acid (3.7 g) was dissolved in 10 ml of deionized water and 10 ml of ethanol. A 0.64 mol l^{-1} solution of $ZrOCl_2 \cdot 8H_2O$ (4.15 g in 10 ml of deionized water and 10 ml of ethanol) was added to the above phosphonic acid solution which resulted in the formation of a gel. This gel was placed in a high-pressure bomb and 2.1 ml of 12% hydrofluoric acid was added. The bomb was kept in an oven at 130 °C for 24 h. The white product was centrifuged, washed with water and dried in the oven at 65 °C overnight. Found: P, 17.42%, Cl, 20.3%. Calculated for $Zr(O_3PCH_2Cl)_2$: P, 17.8%, Cl, 20.37%. TG showed a negligible weight loss up to 900 °C. At 911 °C the compound lost 21.76% of its weight. The expected value on the assumption that the final product of combustion in ZrP_2O_7 is 24.03%. The slightly low value observed is probably due to incomplete combustion since the solid was still black. The solid-state ^{31}P NMR spectrum of the sample showed a single resonance at -4.8 ppm.

Data Collection, Structure Solution and Refinement

Step-scanned X-ray powder data for the finely ground sample (packed on a flat aluminium sample holder) were collected by means of a Rigaku computer-automated diffractometer. 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 2 and 80° in 2θ with a step size of 0.02° and a count time of 12 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]

Initial attempts to index the pattern by auto-indexing programs were not successful, possibly due to severe overlapping of the diffraction peaks. The method adopted for indexing is similar to that described for the zirconium phenylphosphonate structure.[3] A model for the layer consisting of Zr, P and O was constructed based on the observed dimension along the c^* axis and the in-plane dimensions of α-ZrP. 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.[17]

A Patterson map was computed using the low-angle diffraction data extracted from the powder pattern. The positions of the Zr and the P atoms derived from this vector map were consistent with those used in the model for indexing. A model consisting of Zr, two P atoms and six oxygen atoms were then used as a starting model for the Rietveld refinement in the GSAS program package.[18] After the initial refinement of the scale, background, unit-cell parameters and positional parameters a difference Fourier map was computed, which allowed the positioning of the methyl carbon atoms. A subsequent Fourier map revealed two positions for the Cl atoms at bonding distances (*ca.* 1.7 Å) from the methyl carbon atoms. Chemical analysis and TG results, however, show that the compound contained one chlorine atom for each of the methyl groups. Therefore, it was assumed that the Cl atoms were disordered in the structure. These disordered Cl positions were included with equal occupancy for the two positions in the next cycles of refinement. Atomic positions were refined with soft constraints consisting of Zr—O, P—O, P—C and C—Cl bond distances. All the atoms were refined isotropically. The occupancies of the disordered chlorine positions were refined close to 0.5. In the final 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 anomalous dispersion, absorption or preferred orientation.

Results and Discussion

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. Fig. 2 and 3 are the projections of the structure down the a and b axes, respectively.

The layer structure of Zr chloromethylphosphonate as well as that of zirconium phenylphosphonate[3] is essentially that of α-ZrP.[19] These studies show that isostructural derivatization in α-ZrP has very little effect on its layer structure. The only changes that are seen in these derivatives are on the interlayer spacing and the relative orientation of the layers in the unit cell. The extent of layer separation depends on the bulkiness of the substituted groups. In the present case the interlayer spacing is 10.17 Å compared to 7.6 Å in the parent compound. Note that in the case of phenylphosphonate, the metal atoms lie exactly on the layers at $z=0$ and $z=1/2$ (centres of symmetry), which results in a higher symmetry space group, $C2/c$, for the crystals than for the parent and the present

Table 1 Crystallographic data for zirconium chloromethylphosphonate

molecular formula	$ZrP_2O_6C_2Cl_2H_4$
pattern range, 2θ/degrees	5–75
step scan increment, 2θ/degrees	0.02
step scan time/s	12
space group	$P2_1/c$
a/Å	9.3402(7)
b/Å	5.3926(3)
c/Å	21.374(4)
β/degrees	107.892(5)
Z	4
D_c/mg m^{-3}	2.25
no. of contributing reflections	1061[a]
no. geometric observation	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–Cl distances and tolerance/Å	1.83(2)
no. structural parameters	41
no. profile parameters	11
expected R_{wp}	0.035
R_{wp}	0.155
r_p	0.115
R_F	0.04

[a] Includes data for both $K\alpha_1$ and $K\alpha_2$ radiation.
$R_{wp} = (\Sigma_w(I_o - I_c)^2/\Sigma[wI_o^2])^{1/2}$; $R_p = (\Sigma|I_o - I_c|/\Sigma I_c)$;
$R_F = \langle|F_o| - |F_c|\rangle/\langle|F_o|\rangle$. Expected $R_{wp} = R_{wp}/(\chi^2)^{1/2}$;
$\chi^2 = \sigma_w(I_o - I_c)^2/(N_{obs} - N_{var})$.

Table 2 Positional and thermal parameters for zirconium chloromethylphosphonate

atom	x	y	z	U_{iso}/Å^2
Zr	0.2458(8)	0.750(1)	0.9991(5)	0.008(1)
P(1)	0.9855(10)	0.741(2)	0.0825(5)	0.011(2)
P(2)	0.4658(11)	0.260(2)	0.0784(5)	0.011(4)
O(1)	0.111(1)	0.756(5)	0.0554(8)	0.018(5)
O(2)	0.871(2)	0.965(3)	0.0589(10)	0.025(8)
O(3)	0.893(2)	0.496(2)	0.0654(8)	0.03(1)
C(1)	0.050(3)	0.766(4)	0.1721(4)	0.03(3)
O(4)	0.385(2)	0.007(2)	0.0589(9)	0.04(3)
O(5)	0.369(2)	0.472(2)	0.0513(8)	0.08(1)
O(6)	0.618(1)	0.253(5)	0.0621(8)	0.07(1)
C(2)	0.520(2)	0.274(3)	0.1690(5)	0.01(1)
Cl(1A)[a]	0.184(5)	0.008(6)	0.197(2)	0.03(3)
Cl(1B)[a]	0.118(5)	0.496(5)	0.212(1)	0.04(2)
Cl(2A)[a]	0.611(3)	0.570(4)	0.191(1)	0.04(3)
Cl(2B)[a]	0.648(4)	0.031(5)	0.200(1)	0.04(2)

[a] Occupancy = 0.50.

Table 3 Bond lengths (Å) and angles (degrees) for zirconium chloromethylphosphonate

|			
Zr–O(1)	1.991(8)	O(1)–Zr–O(6)	178.4(6)
Zr–O(2)	2.066(8)	O(2)–Zr–O(3)	88.3(5)
Zr–O(3)	2.056(9)	O(2)–Zr–O(4)	89.4(8)
Zr–O(4)	2.057(10)	O(2)–Zr–O(5)	176.1(6)
Zr–O(5)	2.006(7)	O(2)–Zr–O(6)	86.7(6)
Zr–O(6)	2.085(8)	O(3)–Zr–O(4)	176.7(7)
		O(3)–Zr–O(5)	91.4(5)
O(1)–Zr–O(2)	91.9(4)	O(3)–Zr–O(6)	87.4(7)
O(1)–Zr–O(3)	91.8(4)	O(4)–Zr–O(5)	90.7(5)
O(1)–Zr–O(4)	90.5(5)	O(4)–Zr–O(6)	90.2(6)
O(1)–Zr–O(5)	92.0(5)	O(5)–Zr–O(6)	89.4(4)
P(1)–O(1)	1.462(8)	O(1)–P(1)–O(2)	112(1)
P(1)–O(2)	1.585(9)	O(1)–P(1)–O(3)	114(1)
P(1)–O(3)	1.562(9)	O(1)–P(1)–C(1)	111(1)
P(1)–C(1)	1.826(9)	O(2)–P(1)–O(3)	107(1)
		O(2)–P(1)–C(1)	105(1)
		O(3)–P(1)–C(1)	107(1)
P(2)–O(4)	1.552(9)	O(4)–P(2)–O(5)	113(2)
P(2)–O(5)	1.464(8)	O(4)–P(2)–O(6)	109(1)
P(2)–O(6)	1.564(9)	O(4)–P(2)–C(2)	106(1)
P(2)–C(2)	1.847(9)	O(5)–P(2)–O(6)	115(1)
		O(5)–P(2)–C(2)	109(1)
		O(6)–P(2)–C(2)	105(1)
C(1)–Cl(1A)	1.77(2)	P(1)–C(1)–Cl(1A)	110(1)
C(1)–Cl(1B)	1.71(2)	P(1)–C(1)–Cl(1B)	114(1)
		Cl(1A)–C(1)–Cl(1B)	111(2)
C(2)–Cl(2A)	1.80(2)	P(2)–C(2)–Cl(2A)	106(1)
C(2)–Cl(2B)	1.76(2)	P(2)–C(2)–Cl(2B)	108(1)
		Cl(2A)–C(2)–Cl(2B)	111(1)
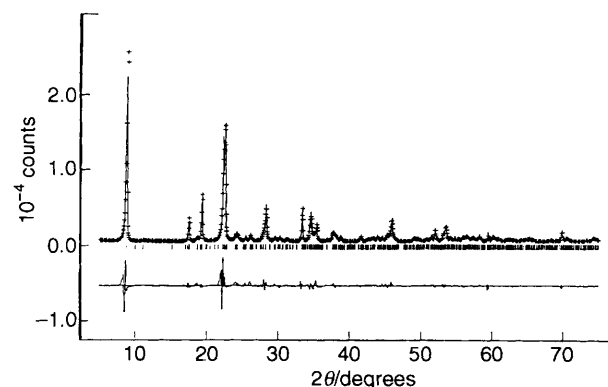
Fig. 1 Observed (+) and calculated (—) profiles (X-ray intensity *versus* 2θ) for the Rietveld refinement. The bottom curve is the difference plot on the same intensity scale.

compound. The last two compounds crystallize in the space group, $P2_1/c$ in which the metal atoms are shifted slightly above and below the planes.

The Zr atoms are situated in the *ab* planes at z close to 0 and 1/2. Any three Zr atoms in this plane form an equilateral triangle and the P atoms are located approximately at the centres of these triangles. The three oxygen atoms of each phosphonate group are involved in binding the three Zr atoms of the triangle, leading to a regular octahedral geometry for the Zr atom. The coordination about Zr atom and the geometry surrounding the P atoms are similar to those observed for α-ZrP and other Zr-PO_4 structures.[19,20] The Zr–O–P angles range from 153 to 169° with an average of 160°. The chloromethyl groups occupy the interlayer space. The bond parameters involving the carbon atom in these groups, *viz.* P–C, C–Cl and the corresponding angles agree
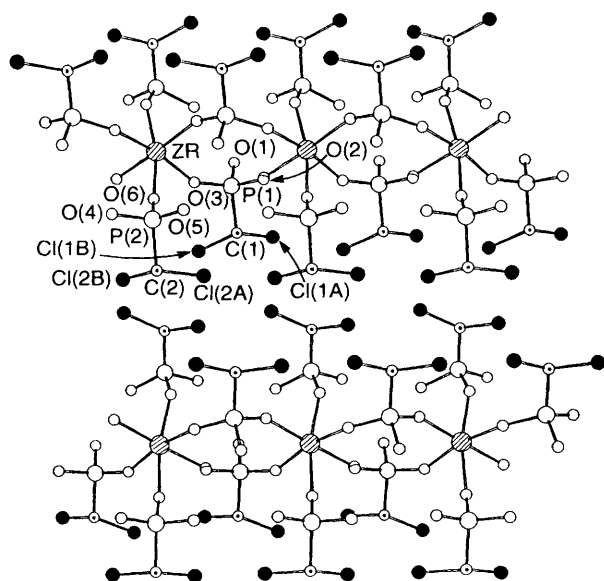
Fig. 2 Portion of the layer structure along the *a* axis showing the numbering scheme used in Table 2. The *b* axis is horizontal and the *c* axis vertical.
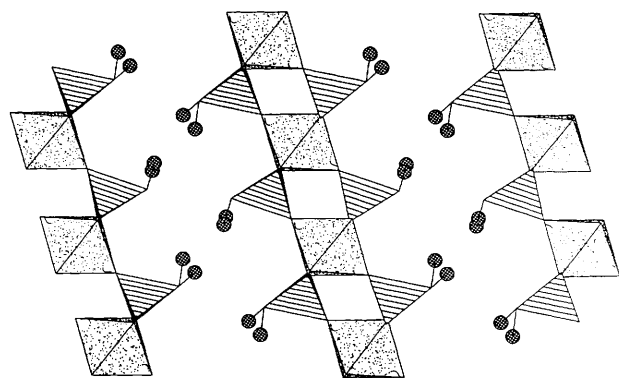

Fig. 3 Polyhedral representation of the structure along the *b* axis. The *a* axis is vertical and the *c* axis horizontal. Note that the adjacent methyl carbon atoms and the disordered chlorine atoms bonded to them are displaced half-way along the projection axis.

well with those obtained from single-crystal data for related structures.[7]

The chlorine atoms bonded to the methyl carbons are disordered. These disordered positions have the same *x* and *z* coordinates, but their *y* coordinates are separated by 1/2. In the structure, the carbon atoms have *y* coordinates closer to either 1/4 or 3/4 and the chlorine atoms are located at *y* closer to 0 and 1/2. In the absence of disorder and if we assume the same orientation of the two independent chloromethyl groups, the two ideal positions for the chlorine atoms would be either Cl(1A) and Cl(2A) or the other pair, Cl(1B) and Cl(2B). Both these sets of positions satisfy the geometry of the chloromethylphosphonate group. If we take one of these sets, for example, Cl(1A) and Cl(2A), then the glide related Cl(2B) is 2.6 Å from Cl(1A). Similar contacts are found for the other pair of disordered positions. In the case of Zn[7] and uranyl[21] chloromethylphosphonates the symmetry-related chlorine atoms are separated by *ca.* 3.3 Å. The unacceptably short contact between the chlorine atom positions in the present case thus leads to the disorder which is described above. To overcome these contacts the chlorine atoms in the two methyl groups are oriented in different ways. In other words, some unit cells would contain positions Cl(1A) and

Cl(2B) only while the others contain Cl(1B) and Cl(2A) and *vice versa*. In this orientation the symmetry-related positions are well separated from each other. For example, Cl(1A) is 3.6 and 3.4 Å from the glide related positions of Cl(2B). The arrangement of disordered positions observed in the present study indicates a possible superlattice along the *b* axis of the crystal. Since the disorder is not apparent in the layers and due to the limited number of available powder data, no attempts have been made to refine the structure in the supercell.

It is interesting to compare the coordination behaviour of the title compound to the zinc and uranyl chloromethyphosphonates. Unlike the zirconium compound, the zinc[7] and uranyl[21] systems contain one phosphonate group for each of the metals. This composition difference is basically due to the charge requirement of the metal atoms. In spite of this difference, all these compounds are layered. Depending upon the preparation conditions, Zn formed three types of compounds.[7] In $Zn(O_3PCH_2Cl)\cdot H_2O$, the metal atoms are octahedrally coordinated by phosphonate oxygens and water molecules. Since the structure contains only four oxygens for coordination, the phosphonate oxygens are involved both in chelation and bridging interactions. In the structure containing three water molecules, $Zn_2Cl(O_3PCH_2Cl)$ $(HO_3PCH_2Cl)\cdot 3H_2O$, zinc atoms are both tetrahedrally and octahedrally coordinated. In this case the phosphonate oxygens are involved in bridging only while the other coordination sites are occupied by water oxygens and a chlorine atom other than that of phosphonate groups. In the urea adduct, the tetrahedral sites of the Zn atoms are occupied by three phosphonate oxygens and one from urea. Similar types of layer structures were also found for methylphosphonates[13] of divalent metals such as Zn, Co and Mg as well as the ethylphosphonate[22] of Fe. In these structures the coordination behaviour of the metals is essentially identical to that of $Zn(O_3PCH_2Cl)\cdot H_2O$. The uranium atom in $UO_2(O_3PCH_2Cl)$, is seven-coordinate and the uranyl oxygens are in the *trans* orientation. The other five coordination sites are occupied by the phosphonate oxygens. Two of the phosphonate oxygens are involved both in chelation and in bridging the adjacent metal atoms to form four-membered rings. Therefore it appears that the binding modes of the phosphonate oxygens in these layer structures depends on the requirement of the metal to acquire its preferred coordination geometry.

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