Inorganic Ion Exchangers

VI. The Unit-Cell Dimensions of Crystalline Zirconium Phosphate

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In two preceding papers of this series [1,2] some references were made to a crystal structure proposed for zirconium bis(mo-nohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$, by Clearfield.[3] The complete molecular and crystal structure has now been determined by Clearfield and Smith[4] from three-dimensional X-ray intensity data. They have also discussed the relations between the crystal structure and the ion exchange properties of crystalline zirconium phosphate.[5]

The crystals are monoclinic with space group $P2_1/c$ (No. 14).[6] Using the unit cell dimensions determined by Clearfield and Smith the powder lines in Table 1 of Ref. 1 have been reindexed. The powder photographs were taken in a Guinier focusing

Table 1. Observed lines in the powder photograph of $Zr(HPO_4)_2 \cdot H_2O$ (Guinier focusing camera, intensities from a Philips commercial diffractometer).

h k l	$\sin^2\theta \times 10^4$ obs	calc	I_{obs}	h k l	$\sin^2\theta \times 10^4$ obs	calc	I_{obs}
0 0 2	102	103	73	2 1 4	1225	1226	4
1 1 0	293	294	38	0 2 4	1257	1258	5
2 0 −2	299	300	21	3 1 −6	1283	1279	4
0 1 2 } 1 1 −2 }	323	314 } 330 }	2	2 2 −4	1316	1319	6
0 0 4	412	414	2	4 0 0 } 1 1 −7 }	1326	1324 } 1325 }	5
1 1 2	465	465	100	1 2 −5 } 4 1 −4 }	1407	1404 } 1410 }	10
2 0 −4	476	475	50	1 1 6 } 4 1 −1 }	1432	1427 } 1427 }	7
2 0 2	570	570	7	2 0 −8 } 4 0 −6 }	1446	1445 } 1446 }	6
0 1 4	621	625	4	1 0 −8 } 1 2 4 }	1472	1467 } 1476 }	3
3 0 −2	642	646	2	0 5 2 }		1490 }	
3 0 0	744	745	1	3 2 −2 } 3 1 3 }	1494	1490 } 1493 }	2
2 1 2	784	781	1	3 0 4	1566	1564	2
1 1 4 } 0 2 0 }	842	842 } 844 }	24	3 0 −8 } 3 2 0 }	1588	1589 } 1590 }	2
3 1 −2 } 2 0 −6 }	856	857 } 857 }	26	0 0 8 } 1 2 −6 } 2 1 −8 }	1649	1654 } 1655 } 1656 }	6
3 1 −1	880	881	1	1 1 −8	1676	1678	6
1 2 0 } 0 0 6 }	930	927 } 930 }	3	4 1 1 } 4 0 2 } 2 2 −6 }	1700	1697 } 1699 } 1701 }	8
0 2 2	949	948	3	0 2 6 } 3 1 4 }	1775	1775 } 1775 }	—
3 1 0	956	956	4	3 1 −8	1801	1801	—
3 1 −4	967	965	4	2 2 4 } 0 1 8 }	1863	1859 } 1865 }	—
2 0 4	1016	1015	10	4 0 −8	1903	1899	—
1 2 −3 } 2 1 −6 } 3 0 −6 }	1062	1058 } 1068 } 1068 }	4	1 3 0	1981	1982	—
0 2 3	1074	1077	3				
3 1 1	1082	1084	3				
3 1 −5 } 1 2 2 }	1098	1096 } 1098 }	1				
0 1 6 } 2 2 −2 }	1140	1141 } 1144 }	2				
2 2 0	1176	1175	2				
4 0 −4	1200	1199	2				

camera with $CuK\alpha$-radiation and $Pb(NO_3)_2$ as a standard. The unit cell parameters were refined by a least squares treatment minimizing $\sum w(\sin^2\theta_0 - \sin^2\theta_c)^2$ with weights $w = 1/\sin^2 2\theta_0$. The following cell dimensions with estimated standard deviations were obtained:

$a = 9.097 \pm 0.005$ Å; $\beta = 111.38 \pm 0.01°$;
$b = 5.307 \pm 0.001$ Å; $V = 732.0 \pm 0.5$ Å³;
$c = 16.284 \pm 0.003$ Å;

Even if the values of a and c are somewhat higher than those published by Clearfield and Smith [4] there are no great difference between the two sets of lattice parameters. The observed and calculated values of $\sin^2\theta$ are listed in Table 1. The X-ray diffraction pattern of crystalline zirconium phosphate is shown in Fig. 1. Both the
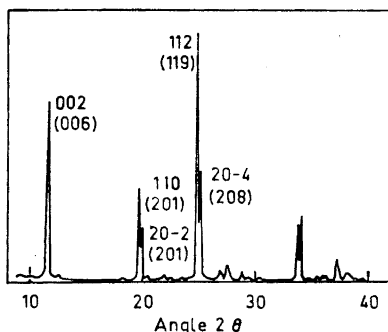

Fig. 1. X-Ray diffraction pattern of crystalline $Zr(HPO_4)_2 \cdot H_2O$. The indices used in Refs. 1 and 2 are put within brackets.

new and earlier indices of the strongest reflexions are given.

The (wrong) structure of $Zr(HPO_4)_2 \cdot H_2O$ referred to in the preceding papers [1,2] had a hexagonal unit-cell with $a = b = 10.5$ Å and $c = 45.6$ Å. The zirconium atoms were assumed to occupy the positions (0,0,0; 1/3,2/3,2/3; 2/3,1/3,1/3) in a rhombohedral centered pseudocell of half the cell dimensions. However, Clearfield and Smith [4] have pointed out that in their finally obtained monoclinic structure the zirconium atoms occupy positions very close to (0,0,0; 1/3,2/3,1/3; 2/3,1/3,2/3) in a pseudo-hexagonal cell which is related to the true unit cell as follows: $a_h = a_m/\sqrt{3} = 5.25$ Å, $b_h = b_m = 5.31$ Å, $c_h = (3c_m \cos 21.4°)/2 = 22.74$ Å; c_h is parallel to c_m^*. The conclusions reached in Refs. 1

and 2 are thus correct in their essential parts even if they to some extent are based upon a wrong hexagonal crystal structure for zirconium phosphate.

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2. Ahrland, S., Albertsson, J., Alnås, Å., Hemmingsson, S. and Kullberg, L. *Acta Chem. Scand.* **21** (1967) 195.
3. Clearfield, A. *Private communication.*
4. Clearfield, A. and Smith, G. D. *Inorg. Chem.* **8** (1969) 431.
5. Clearfield, A. and Smith, G. D. *Inorg. Chem. To be published.*
6. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1952, Vol. 1.

The Use of Carbon-13 Shifts in the Structural Determination of α,β-Unsaturated Acids

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This paper describes a straightforward ¹³C-NMR technique by which geometric assignments can be made for a wide variety of di- and trisubstituted α,β-unsaturated acids. The only information required is the ¹³C chemical shifts for the olefinic carbons of the compound under study. The technique complements existing methods for assigning structures to monosubstituted acrylic acids and *cis* and *trans* disubstituted ethylenes based on the magnitude of coupling constants in ¹H-NMR spectra,[1] and it is also a complement to the method

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