

## The Structure of Twinned Manganese(III) Hydrogenbis(orthophosphate) Dihydrate

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### Abstract

$\text{MnH}_3\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  is monoclinic, space group  $P2_1/b$ , with  $a = 7.618$  (1),  $b = 8.839$  (1),  $c = 6.703$  (2) Å,  $\gamma = 125.46$  (4)°,  $V = 735.5$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $M_r = 251.9$ ,  $D_x = 2.27$ ,  $D_m = 2.24$  Mg m<sup>-3</sup>. The crystal used for structure determination was a twin with coinciding orthogonal reciprocal lattices; the twin fraction is  $\alpha = 0.366$  (4). The structure was refined to  $R = 0.049$  for 903 reflections. It contains distorted octahedra with central Mn atoms and two phosphite anions.

### Introduction

The study of the title compound was undertaken as part of the investigation of systems containing poly-(orthophosphate) anions (Ebert & Čipera, 1966). Crystals were prepared in the Department of Inorganic Chemistry of Charles University (Podlaha, 1963).

### Experimental

The red-violet crystals are stable in air and to X-rays. Preliminary lattice parameters and space group ( $P2_1/b$ ) were obtained from diffraction photographs (Mo  $K\alpha$  radiation). Refined cell parameters were obtained by a least-squares method (Shoemaker, 1970) from 30 reflections centred on the diffractometer. The lattice of the structure exhibits a centred orthorhombic arrangement due to

$$(2a + b) \cdot b = 0 \quad (1)$$

which hold in the limits of the error of measurement. But the 'non-orthorhombic' systematic extinction as well as the observed differences in intensities of a few 'orthorhombic-equivalent' reflections (see Fig. 1) exceeding the measuring error led to the conclusion that the crystallographic system and the space group are as

mentioned above. A crystal of approximately  $0.1 \times 0.1 \times 0.2$  mm was used for intensity measurements on a Hilger & Watts four-circle diffractometer with Mo  $K\alpha$  radiation. The  $\omega$ - $2\theta$  scan technique was used to measure 1078 independent reflections with  $2\theta \leq 60^\circ$ . The scan speed varied from 1 to 4° min<sup>-1</sup> determined from a rapid prescan. The scanning interval was 2°. 175 reflections were classified as unobserved on the criterion  $I < 1.96\sigma_1(I)$  where  $I = (TC - B_1 - B_2)R$  and  $\sigma_1(I) = R\sqrt{(TC + B_1 + B_2)}$  ( $TC$  = total count,  $R$  = scan speed,  $B_1$  and  $B_2$  = background counts measured at each end of the scan for half the scan time). All unobserved reflections were used in the refinement with  $F_{\text{unobs}} = \frac{1}{2}F_{\text{min}}$  and  $\sigma_1(F_{\text{unobs}}) = (1/\sqrt{12})F_{\text{min}}$  ( $F_{\text{min}}$  = the minimum observable value of  $|F|$ ). The intensities of one standard reflection measured after every ten reflections showed no significant variation. The data were corrected for Lorentz and polarization effects, but not for absorption or extinction.

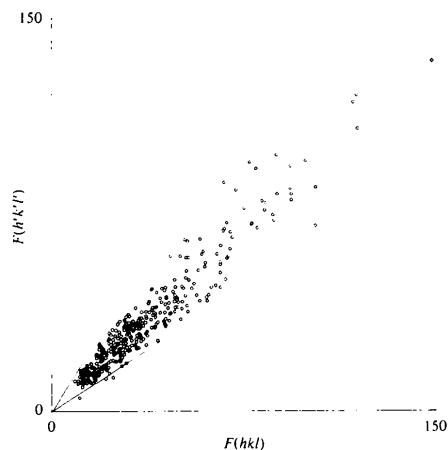


Fig. 1. Diagram of  $F_o(h'k'l')$  plotted against  $F_o(hkl)$ ;  $h'k'l'$  are related to  $hkl$  by the twin operation. The straight lines limit the area of occurrence of points.

## Structure determination and refinement

The structure was solved by the heavy-atom method. The positions of the Mn and P atoms were determined from a three-dimensional Patterson synthesis: Mn in special position (a) (0,0,0), P in general position (e) ( $\frac{1}{4}, \frac{3}{8}, \frac{1}{4}$ ). A Fourier  $\gamma'$ -synthesis (Ramachandran & Srinivasan, 1970) based on these input parameters provided the positions corresponding to the vertices of the two  $\text{HPO}_3$  pyramids symmetrically related by a (non-space-group) twofold rotation axis normal to the (100) plane and passing through the mid-point of two neighbouring Mn atoms, *i.e.* ( $0, \frac{1}{4}, \frac{1}{4}$ ). We tried to refine this structure using this non-space-group twofold axis on the assumption that the positions of the  $\text{HPO}_3$  tetrahedra indicated by the six peaks found in the Fourier maps are randomly occupied. However, the final value of  $R = \sum |F_o| - |F_c| / \sum |F_o|$  was not satisfactory ( $R = 0.121$ ).

The consequence of relation (1) is that the point symmetry of the lattice is  $2/m 2/m 2/m (D_{2h})$  and therefore higher than the point symmetry of the structure, which is  $2/m (C_{2h})$ . This means, that the necessary condition for twinning with superimposed reciprocal lattices is fulfilled. No sample investigated exhibited any signs of disorder, such as splitting of the diffraction spots or diffuseness either on the Weissenberg photographs or in the diffractometer measurements. For this reason we assumed the existence of two individuals related by the twofold axis described above (this rotation is the twinning operation).\* These two individuals contribute independently to each measured intensity  $I_{hkl}$  (Catti & Ferraris, 1976). Thus we have:

$$I_{hkl} = (1 - \alpha) J_{hkl} + \alpha J_{h'k'l'} \quad (2)$$

where  $J_{hkl}$  and  $J_{h'k'l'}$  are the intensities which an untwinned crystal of the same total volume would give,  $\alpha$  is the fraction of the smaller individual and  $h' = h + k$ ,  $k' = -k$ ,  $l' = -l$ . The refinement was carried out with a local modification of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962) which was adapted for coincidence of reflections following relation (2) in a similar way to the Kennicott (1963) method. The program enables us to refine directly the twin fraction and all positional and vibrational parameters. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/\sigma^2(F_o)$  derived from  $\sigma_2(I) = [\sigma_1^2(I) + (0.06I)^2]^{1/2}$ .

The initial scale and overall temperature factor were estimated from the Wilson plot. The initial twin fraction was chosen as 0.5 and the refined value was 0.366 (4) which is in satisfactory agreement with the value 0.28

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Hamilton, 1959)

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
Mn	0	0	0	0.91 (3)
P	0.2421 (2)	0.3624 (2)	0.2615 (2)	0.84 (3)
O(1)	0.4739 (6)	0.4667 (5)	0.1783 (7)	1.4 (1)
O(2)	0.0787 (6)	0.2316 (5)	0.1065 (7)	1.4 (1)
O(3)	0.2033 (6)	0.5056 (5)	0.3297 (6)	1.3 (1)
O(4)	0.7486 (6)	0.3567 (6)	0.2635 (7)	1.6 (1)

Table 2. Interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

Symmetry code	(i)	(ii)	(iii)	
	$1 - x, 1 - y, -z$	$x, y - \frac{1}{2}, \frac{1}{2} - z$	$1 - x, \frac{1}{2} - y, z - \frac{1}{2}$	
Mn—O(2)	1.907 (4)		O(4)—O(1 <sup>ii</sup> )	2.836 (6)
—O(3 <sup>ii</sup> )	1.902 (5)			
—O(4 <sup>iii</sup> )	2.229 (5)		O(2)—Mn—O(3 <sup>ii</sup> )	90.2 (2)
P—O(1)	1.546 (5)		O(2)—Mn—O(4 <sup>iii</sup> )	91.4 (2)
—O(2)	1.515 (5)		O(3 <sup>ii</sup> )—Mn—O(4 <sup>iii</sup> )	89.6 (2)
—O(3)	1.527 (5)		O(1)—P—O(2)	110.9 (3)
O(1)—O(1 <sup>i</sup> )	2.438 (7)		O(1)—P—O(3)	108.5 (2)
O(4)—O(1)	2.831 (7)		O(2)—P—O(3)	111.7 (3)

estimated from the angle of the straight lines in the  $F_{hkl}$  vs  $F_{h'k'l'}$  plot (Murray-Rust, 1973), see Fig. 1.

Refinement with isotropic temperature factors converged to  $R = 0.062$ ; the same procedure employing anisotropic temperature factors converged to  $R = 0.049$  (for observed reflections). We tried unsuccessfully to locate the H atoms using a difference synthesis based on the structure factors corrected for twinning (Zachariasen & Plettinger, 1965). We were also unsuccessful in our attempts to refine the positions of the H atoms starting from their theoretical positions.

The final coordinates of the nonhydrogen atoms are given in Table 1 and the interatomic distances, bond angles and symmetry code in Table 2.\* Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out on a TESLA 200 computer.

## Results and discussion

The Mn, O (from  $\text{H}_2\text{O}$ ) and P atoms form a framework common to both individuals. The symmetry of this

\* Observation with the polarizing microscope did not determine whether the samples investigated consisted of two individuals or were polysynthetic twins, because the samples were not transparent.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36664 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

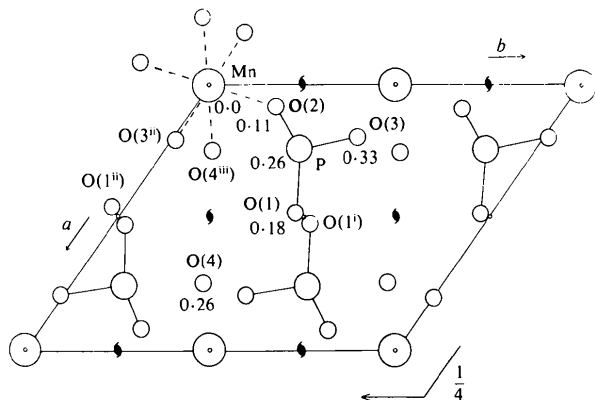


Fig. 2. Schematic projection of the structure along  $c$ . Symmetry elements are indicated and atoms are identified in accordance with Tables 1 and 2 with their approximate  $z$  coordinates given.

framework is in good approximation to  $C2/c2/m2_1/b$  (where the orthorhombic axes  $a_{\text{ortho}}$ ,  $b_{\text{ortho}}$ ,  $c_{\text{ortho}}$  are chosen as  $2a + b$ ,  $b$ ,  $c$  respectively). The presence of the phosphite oxygens reduces this symmetry to the subgroup  $P112_1/b$ . The phosphite oxygens fit this framework in two ways such that their positions {related by the [2..] at  $(0, \frac{1}{4}, \frac{1}{4})$ , in orthorhombic notation} yield geometrically equivalent patterns, since the corresponding rotation transforms the framework into itself. Because of the high symmetry of the framework the same twinning may be explained using other equivalent symmetry elements, enlarging the monoclinic subgroup to the orthorhombic group.

In the structure (Fig. 2) there are octahedra of O atoms with a central Mn atom. Two of these atoms belong to the crystalline water, O(4), and the remaining four to the  $\text{HPO}_3^{2-}$  anions. The distance Mn–O(4) is significantly longer by  $0.324 \text{ \AA}$  than the mean of the remaining Mn–O distances. Hence the octahedra are tetragonally distorted which is in accordance with the supposed Jahn–Teller effect for the electron configuration  $3d^4$  and was independently confirmed by splitting of the bands in the reflectance

diffuse spectra. In the neighbourhood of the P atoms the P–O distances agree with the literature data (Johansson & Lindqvist, 1976; Loub, Podlahová & Ječný, 1978; Colton & Henn, 1971). Although we did not locate the H atoms, we assume that two phosphite anions are connected into an  $\text{H}_3\text{P}_2\text{O}_6^{3-}$  anion by a linear symmetric hydrogen bond\* in accordance with the distance O(1)–O(1') which is  $2.438(7) \text{ \AA}$  (Braun, 1976).

\* The corresponding H atom is supposed to occupy the site  $(d)$   $(\frac{1}{2}, 0, 0)$ .

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