The structure of PbV$_2$O$_6$(II) differs from that of other MX_2O_6 systems. Most of the previously investigated metavanadates as for example β-CdV$_2$O$_6$ (Bouloux & Galy, 1969), MgV$_2$O$_6$ (Ng & Calvo, 1972), CoV$_2$O$_6$ (Sauerbrei, 1972), ZnV$_2$O$_6$ (Angenault & Rimsky, 1968; Andreetti, Calestani, Montenero & Bettinelli, 1984), and CuV$_2$O$_6$ (Calvo & Manolescu, 1973) have structures based upon, or derived from, the brannerite structure (Ruh & Wadsley, 1966) which can be considered a distortion of a hexagonal pseudo close-packed array of O atoms with both *M* and V atoms octahedrally coordinated. The distorted octahedral coordination around V atoms, characterized by five strong and one weak (~2·6 Å) V—O interactions, is present in other structures of metavanadates as for example in β-HgV$_2$O$_6$ (Angenault, 1970) and PbV$_2$O$_6$(I) (Jordan & Calvo, 1974).

The loss of the sixth weak interaction characteristic of the PbV$_2$O$_6$(II) structure was found in CaV$_2$O$_6$ and α-CdV$_2$O$_6$ (Bouloux, Perez & Galy, 1972). The structure of these compounds consists, as in PbV$_2$O$_6$(II), of columns of double chains parallel to the *b* axis, but the arrangement of the chains and consequently of the interspersed Pb atoms is different.

As concerns the transition between PbV$_2$O$_6$(I) and PbV$_2$O$_6$(II), four phenomena may be noted:

(*a*) the significant decrease of the density from 5·89 (I) to 5·30 Mg m^{-3} (II), which agrees with thermodynamic data;

(*b*) the decrease of the coordination number of lead from 9 to 8;

(*c*) the decrease of the vanadium coordination from 6 to 5 by loss of the weak V—O interaction present in PbV$_2$O$_6$(I);

(*d*) the formation in PbV$_2$O$_6$(II) of void channels parallel to the *b* axis between the double chains centered in the *xz* plane at $(0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2})$.

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Structures of Metastable Lead Metavanadates: the Orthorhombic PbV$_2$O$_6$(III) Modification

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Abstract. $M_r = 405{\cdot}7$, orthorhombic, $C222$, $a = 8{\cdot}273$ (2), $b = 12{\cdot}422$ (2), $c = 7{\cdot}685$ (1) Å, $V = 789{\cdot}8$ (3) Å^3, $Z = 6$, $D_x = 5{\cdot}11$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 35{\cdot}42$ mm^{-1}, $F(000) = 1056$, $T = 293$ K; final $R = 0{\cdot}042$ for 522 observed reflections. The structure of PbV$_2$O$_6$(III) differs from that of other MX_2O_6 systems and consists of zigzag chains of corner-sharing VO$_4$ tetrahedra, which cross on adjacent

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layers perpendicular to the *c* axis; Pb atoms lie in planes perpendicular to the *c* axis, which separate adjacent VO_4 chains.

Introduction. Continuing our studies (Calestani, Andreetti, Montenero & Bettinelli, 1985) on the structural modifications induced in PbV_2O_6 by the transition between the stable crystalline phase PbV_2O_6(I) (Jordan & Calvo, 1974) and the glassy state, we present here the crystal-structure determination of PbV_2O_6(III). Of the three possible PbV_2O_6 polymorphs this phase is thermodynamically the nearest to the vitreous state. It can normally be obtained by devitrification of equimolar $PbO.V_2O_5$ glass at $T \simeq 573$ K or by solidification of the melt at an extremely high cooling rate. The study of the crystal structure of PbV_2O_6(III) is interesting, since it can give information on the structure of the glass.

Experimental. Crystals of PbV_2O_6(III) were obtained imbedded in a vitreous matrix by quenching equimolar $PbO.V_2O_5$ melt on a copper plate. The separation of PbV_2O_6(III) single crystals from the quenched mass is, as in the case of PbV_2O_6(II), quite difficult but some small crystals could be isolated by repeatedly breaking the samples. The transparent PbV_2O_6(III) pale-brown-colored crystals present no well defined habit since they tend to break in a casual way so that the external aspect is not very different from that of the glass.

Diffraction intensities collected from a small crystal (0·14 × 0·10 × 0·05 mm), automated Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 1–30° θ range, max. range h,k,l: 11,17,10, ω–2θ scan, $(0{\cdot}90 + 0{\cdot}35\tan\theta)^\circ$ scan width, rate varying between 0·72 and 10·0° $\min^{-1}$. Lattice parameters obtained by least-squares refinement of 25 accurately centered reflections in range $5 < \theta < 11^\circ$. Crystal orientation checked on three standard reflections every 100 reflections and crystal stability every hour. 1360 collected reflections $(+h,+k,+l$ and $-h,-k,-l)$ corrected for Lorentz and polarization effects and for absorption using empirical-absorption-correction procedure based on nine reflections measured in ψ scan $(80 < \chi < 90^\circ)$ (North, Phillips & Mathews, 1968), calculated transmission-factor range 0·61 to 1·0. After merging $(R_{\rm int} = 0{\cdot}024)$, 522 unique reflections with $I > 3\sigma(I)$ used in crystal-structure analysis. All calculations performed on a PDP 11/34 computer with the Enraf–Nonius *SDP-PLUS* (1982) package of crystallographic programs. Structure solved by standard heavy-atom techniques. Final model [with isotropic thermal parameters for O(1) and O(2) and anisotropic for all other atoms] refined by least-squares ($\sum w\Delta F^2$ minimized) using scattering factors for neutral Pb, V and O including anomalous-scattering factors (*International Tables for X-ray Crystallography*, 1974) to give $R = 0{\cdot}042$, $R_w = 0{\cdot}055$; $w = [(\sigma F)^2 + (0{\cdot}02F)^2 + 13{\cdot}0]^{-1}$. $(\Delta/\sigma)_{\rm max} < 0{\cdot}01$. Max. height in final difference Fourier map 1·8 e Å^{-3} [at 1·23 Å from V(1)].

Discussion. Atomic coordinates and isotropic thermal parameters are shown in Table 1, selected bond distances and angles in Table 2.* Fig. 1 shows the structure of PbV_2O_6(III) projected onto the *ab* plane.

In the structure there are two types of V atom each bonded to four O atoms at short distances which form distorted tetrahedra, with two other longer V—O interactions. $V(1)O_4$ and $V(2)O_4$ groups form single chains sharing corner O atoms in the sequence ···V(1)—V(2)—V(2)··· which extend infinitely perpendicular to the *c* axis and cross on adjacent layers (Figs. 1 and 2). This chaining of VO_4 groups involves two longer V—O interactions [2·48 (2)–2·95 (2) Å] inside the same chain which cap two adjacent faces of the tetrahedra.

Concerning the cations in the structure, there are two types of interspersed Pb atom in PbV_2O_6 distributed in layers perpendicular to the *c* axis $(z = 0,\ z = \frac{1}{2})$; between these layers run the VO_4 chains. Pb(1) is bonded to eight O atoms of four of these chains. The Pb(1)—O distances range from 2·63 (2) to 2·66 (2) Å. Pb(2) is bonded to eight O atoms of two of these chains. Four of the O atoms lie at a distance ~2·5 Å, while the remaining four are significantly farther away [2·78 (2)–3·02 (2) Å]. It must be pointed out that while the average bond distance between V(2) and the four nearest O atoms [1·74 (2) Å] is in the range generally observed for tetrahedrally coordinated V^{5+} ions, the corresponding V(1)—O average bond distance is surprisingly short. This is only partially compensated by the two longer V(1)···O(4) [2·95 (2) Å] interactions [2·48 (2) and 2·94 (2) Å for V(2)···O(5)]. Moreover, the tetrahedral coordination around V(1) is extremely distorted, the O(3)—V(1)—O(3)′ angle between the two nearest O atoms being 167·6 (9)°.

This induced us to reconsider the crystal structure of PbV_2O_6(III) on the basis of a symmetry reduction from space group *C*222 to *C*2. New data were collected and half-normal probability tests (Abrahams & Keve, 1971), performed on sets of reflections not equivalent in the *C*2 case, showed no significant deviation from orthorhombic symmetry (correlation coefficient = 0·99). Moreover, refinements in *C*2 space group provided dubious results: on one hand one V(1)—O(3) bond distance was increased while on the other hand, the second V(1)—O(3) bond distance was shorter.

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* Lists of observed and calculated structure factors and of anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39820 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}/B$
Pb(1)	0	0	0	1·54 (3)
Pb(2)	0	0·18947 (9)	$\frac{1}{2}$	1·16 (1)
V(1)	$\frac{1}{4}$	$\frac{1}{4}$	0·0769 (7)	0·99 (9)
V(2)	0·1836 (5)	0·4319 (3)	0·2552 (5)	0·71 (5)
O(1)	0	$\frac{1}{2}$	0·226 (3)	1·6 (3)*
O(2)	0·166 (2)	0·013 (2)	0·704 (2)	2·0 (3)*
O(3)	0·245 (3)	0·131 (1)	0·056 (2)	1·8 (2)
O(4)	0·178 (2)	0·347 (1)	0·419 (2)	1·9 (3)
O(5)	0·088 (3)	0·246 (2)	0·197 (2)	2·3 (4)

* Refined isotropically.

Table 2. *Bond distances* (Å) *and selected bond angles* (°)

Pb(1)—O(2)	2·66 (2) ×4	V(1)—O(3)	1·49 (2) ×2
Pb(1)—O(3)	2·63 (2) ×4	V(1)—O(5)	1·63 (2) ×2
Pb(2)—O(2)	3·02 (2) ×2	V(1)···O(4)	2·95 (2) ×2
Pb(2)—O(4)	2·77 (2) ×2	V(2)—O(1)	1·75 (1)
Pb(2)—O(4)	2·53 (1) ×2	V(2)—O(2)	1·63 (2)
Pb(2)—O(5)	2·54 (2) ×2	V(2)—O(3)	1·82 (2)
		V(2)—O(4)	1·64 (1)
		V(2)···O(5)	2·48 (2)
		V(2)···O(5)	2·94 (3)
O(3)—V(1)—O(3)′	167·6 (9)	O(1)—V(2)—O(2)	112·8 (9)
O(5)—V(1)—O(5)′	110·9 (8)	O(1)—V(2)—O(3)	112·4 (6)
O(3)—V(1)—O(5)	96·6 (11)	O(1)—V(2)—O(4)	112·6 (6)
O(3)—V(1)—O(5)′	90·5 (11)	O(2)—V(2)—O(3)	100·3 (9)
O(3)′—V(1)—O(5)′	96·6 (11)	O(2)—V(2)—O(4)	105·7 (8)
O(3)′—V(1)—O(5)	90·5 (11)	O(3)—V(2)—O(4)	112·3 (6)
V(2)—O(1)—V(2)′	165·3 (3)	V(1)—O(3)—V(2)	109·1 (8)

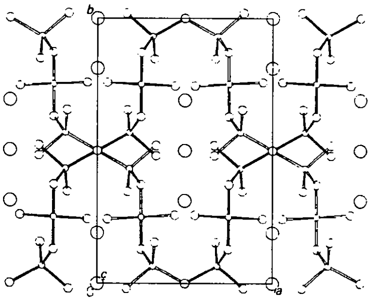

Fig. 1. Projection of the PbV_2O_6(III) structure onto the *ab* plane. The largest circles are Pb atoms and the smallest are V atoms. Open and filled bonds lie on adjacent layers.

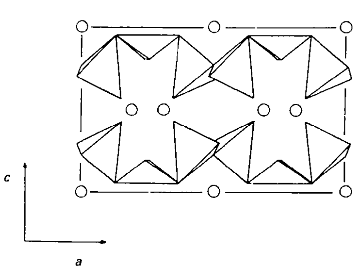

Fig. 2. An idealized view of the corner-shared VO_4 chains in PbV_2O_6(III).

The position of the O(3) atom was therefore considered on the basis of its interaction with the adjacent atoms. Displacements of the O(3) atom in the *xy* plane lead in two quadrants to a shortening of the V(1)—O(3) bond distance; in the other two they lead to an increase of the V(1)—O(3) bond distance but cause a significant shortening of the V(2)—O(3) and Pb(1)—O(3) interactions respectively. Displacement along *z* which tends to increase the V(1)—O(3) bond distance and to diminish the O(3)—V(1)—O(3)′ angle, tends at the same time to bring the O(3) atoms near to the plane of the Pb(1) atoms. The VO_4 chains are compressed between adjacent Pb-atom layers; this causes the anomalous behavior of the coordination around V(1) and is responsible for internal stress which can be detected for example in breaking PbV_2O_6(III) samples, for which fractures arise not along crystallographic planes, but casually as in the glass. In spite of this internal stress condition, the observed structure is probably that for which the resulting energy of the system is a minimum, leading displacements from the observed site to greater stress.

Moreover, it must be taken into account that PbV_2O_6(III) is a high-energy phase which is thermodynamically similar to the glass for which the possibility of disorder is not negligible. The observed structure could be an 'average' of energetically equivalent atomic arrangements.

The structure of PbV_2O_6(III) differs from that of the other MX_2O_6 systems. All the previously investigated metavanadate structures present the V atom in a distorted octahedral or square-pyramidal coordination (Calestani *et al.*, 1985).

The radical change of the vanadium coordination in PbV_2O_6(III) is revealed by the absence in the possible unit cells of a parameter of 3·6 Å (typical of the metavanadates and V_2O_5 structures) which is related to the layer structure of edge-shared VO_6 or VO_5 groups. The PbX_2O_6 series of compounds ($X \neq$ V) is generally based upon octahedra either corner- or edge-shared; only PbP_2O_6 (Jost, 1964) presents a structure based on corner-shared tetrahedra.

The study of the crystal structure of the metastable phases PbV_2O_6(II) and PbV_2O_6(III) confirms that they are intermediate crystalline phases in the transition between the stable PbV_2O_6(I) form and the glass. The transition occurs with a monotonic decrease of the density [5·89 (I) → 5·30 (II) → 5·11 Mg m^{-3} (III)] to a value [PbV_2O_6(III)] in the range generally observed for equimolar $PbO.V_2O_5$ glasses. The decrease of the density corresponds to an increase of the void space in the cell. In PbV_2O_6(II) the existence of void channels parallel to the *b* axis was pointed out; in PbV_2O_6(III) the void space is distributed in channels perpendicular to the *a* axis and centered in the *yz* plane at $(0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2})$ and in the layer of the chains, between adjacent chains.

The transition occurs with a gradual decrease of the coordination around V atoms from 6 to 4. This causes notable changes in the structure from columns of quadruple chains of edge-sharing octahedra (I), to columns of double chains of edge-sharing square pyramids (II), to zigzag single chains of corner-sharing tetrahedra (III). Spectroscopic measurements in the IR region (Baiocchi, Bettinelli, Montenero & Di Sipio, 1982; Calestani, Montenero, Pigoli & Bettinelli, 1984) showed analogies in the spectra of PbV_2O_6(III) and of equimolar $PbO.V_2O_5$ glass. The hypothesis of a similitude between their structures can be advanced, the structure of the glass consisting of disordered chains of VO_4 tetrahedra with Pb atoms interspersed.

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Conformational Aspects of *meso*-Tartaric Acid. VIII.* Structure of Sodium *meso*-Tartrate, $2Na^+.C_4H_4O_6^{2-}$

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Abstract. $M_r = 194{\cdot}05$, monoclinic, $P2_1/n$, $a = 4{\cdot}999$ (1), $b = 6{\cdot}348$ (2), $c = 10{\cdot}135$ (2) Å, $\beta = 97{\cdot}49$ (1)°, $V = 318{\cdot}9$ (1) Å^3, $Z = 2$, $D_x = 2{\cdot}021$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}32$ mm^{-1}, $F(000) = 192$, $T = 295$ K, $R = 0{\cdot}029$ for 2056 observed diffractometer data. The *meso*-tartrate anion adopts an unusual centrosymmetric conformation, imposed by the crystallographic centre of symmetry. This unfavourable conformation accompanies an appreciable distortion from planarity of the glycolic acid parts. The anions are joined together *via* a two-dimensional hydrogen-bonded network. The Na^+ ion is irregularly coordinated to six O atoms.

Introduction. It has been established that in solution *meso*-tartaric acid consists predominantly of enantiomeric rotamers (Kroon, 1982). These are also present in the crystal structures of three modifications of the free acid and of metal complexes studied so far. The first centrosymmetric conformation to be found in a crystal structure was in a complex of *meso*-tartaric acid with an optically active base (Kroon, Duisenberg & Peerdeman, 1984). Therefore it seemed worthwhile to extend our structural knowledge about salts of *meso*-tartaric acid with simple cations. The present crystal-structure determination contributes to that aim.

Experimental. Regularly formed block-shaped crystal, dimensions approximately 0·5 mm, grown from an aqueous solution. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, cell measurements with setting angles of 12 reflections in θ range from 14 to 17°; $\omega/2\theta$ scan mode, scan width 0·40° + 0·35°tanθ and variable speeds; $2\theta_{max} = 86°$, $h = 0$ to 9, $k = 0$ to 12, $l = -19$ to 19; no systematic fluctuations in standard reflections $11\bar{4}$ and $\bar{1}14$; 2364 independent reflections, 2056 considered observed [$I > 2{\cdot}5\sigma(I)$]. Lp corrections, but no absorption correction. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Refinement on F by full-matrix least squares (*SHELX*76; Sheldrick, 1976). H atoms located from a three-dimensional difference Fourier map and by stereochemical considerations; their positional and isotropic thermal parameters subsequently refined.

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* Part VII: de Vries & Kroon (1984).

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