

Crystal Structure of Dilead Tritellurate(IV)

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The crystal structure of the title compound has been determined by the heavy-atom method from 1 059 reflections, measured with a diffractometer and refined by full-matrix least-squares methods to R 0.105. Crystals are orthorhombic, space group $Amam$, with unit-cell dimensions $a = 18.83(2)$, $b = 7.14(1)$, $c = 19.37(2)$ Å, and $Z = 12$. In the structure two of the crystallographically independent tellurium atoms are linked into endless chains parallel to the a axis by bridging oxygen atoms, and the other two are linked into isolated $[Te_3O_8]^{4-}$ ions. The co-ordination of the tellurium atoms can be considered to be based on a tetrahedral arrangement of three oxygen atoms and a lone pair of electrons, or a trigonal-bipyramidal arrangement of four oxygen atoms and the lone pair. The irregular co-ordination of the lead atoms can also be attributed to lone-pair effects.

DILEAD tritellurate(IV) was first grown in large single-crystal form by Robertson *et al.*¹ who supplied the material for this study. The pale yellow transparent crystal shows a tendency to cleave on a major growth face, and was shown to be biaxial with a $2V$ of *ca.* 72°. Only a few compounds of this stoichiometry have been reported in the literature, and since the lead compound did not appear to be related to any previously observed materials the crystal-structure analysis was undertaken.

EXPERIMENTAL

Approximate cell dimensions were determined from oscillation, Weissenberg, and precession photographs. The

photographs indicated orthorhombic symmetry and systematic absences corresponded to the space groups $Amam$, $A2_1am$, or $Ama2$.

Final cell dimensions were measured on a Stoe two-circle computer-controlled diffractometer with graphite-monochromated Mo- K_α radiation and a scintillation counter. Intensity data were collected from a crystal fragment of dimensions $0.12 \times 0.08 \times 0.30$ mm mounted about the direction of elongation (c). The ω -scan technique was employed with a stepping interval of 0.01° and a step time of 0.25 s; this corresponds to a scan rate of 2.4° min⁻¹. For layers $hk0-6$, $\Delta\omega$ was taken as 2.0°, and for the seventh and higher layers (equi-inclination angle, $\mu > 7^\circ$) a variable scan range was employed, $\Delta\omega$ being calculated

¹ D. S. Robertson, N. Shaw, and I. M. Young, *J. Phys. (D)*, 1976, **9**, 1257.

from $[A + (B \sin \mu / \tan \phi')]\phi'$, where $2\phi'$ is the azimuth angle² and A and B were assigned values of 1.0 and 0.5, respectively. The background for all the reflections was measured for 10 s at each end of the scan. Of 1355 reflections scanned within the range $0.1 < (\sin \theta)/\lambda < 0.65$, 1059, for which $I > 3\sigma(I)$, were considered to be observed and were used in the structure solution and refinement. Data were corrected for Lorentz and polarisation factors as well as for absorption, using a numerical integration method.

Crystal Data.— $\text{O}_8\text{Pb}_2\text{Te}_3$, $M = 925.2$, Orthorhombic, $a = 18.83(2)$, $b = 7.14(1)$, $c = 19.37(2)$ Å, $U = 2604.2$ Å³, $D_m = 7.16 \times 10^3$ kg m⁻³, $Z = 12$, $D_c = 7.08$, $F(000) = 4608$. Systematic absences: hkl when $k + l$ is odd, $h0l$ when h is odd, space group Amm (D_{2h}^{17} , in a non-standard setting), $A2_1am$ (C_{2v}^{12} , in a non-standard setting), or $Ama2$ (C_{2v}^{16}); Amm established as a result of the structure analysis. Mo- K_α radiation (λ 0.710 7 Å, $\mu = 465.6$ cm⁻¹).

Structure Determination.—The Patterson map was successfully solved in the centrosymmetric space group Amm yielding the co-ordinates of the two independent Pb atoms. Subsequent difference-Fourier maps were used to locate the Te and O atoms. The choice of space group has been vindicated by the successful solution and refinement of the structure. In addition, electrical measurements indicated the presence of a centre of symmetry.² Initial refinement was by full-matrix least-squares methods with layer scale factors refined separately, and all the atoms vibrating isotropically. Refinement was continued with layer scale factors held constant and with the introduction of anisotropic thermal parameters, for all the Pb and Te atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$. Scattering factors employed were those for the neutral atoms,³ with corrections for the effects of anomalous dispersion⁴ applied to those for Pb and Te. The weighting scheme used in the final cycles was⁵ $w = [\sigma^2(F_o) + (0.07|F_o|)^2]^{-1}$, chosen to give approximately constant values of $\Sigma w(|F_o| - |F_c|)^2$ in groups of increasing $|F_o|$ and $(\sin \theta)/\lambda$. The refinement of the isotropic secondary extinction co-

Fourier map showed no significant features. The final R for all the 1059 observed amplitudes is 10.5%. The high R value for this structure is probably a result of its high lead content and the difficulty of defining the crystal for absorption corrections.

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Distances			
Te(1)—O(1)	2.24(5)	Te(2)—O(1)	1.89(5)
Te(1)—O(7)	1.88(7)	Te(2)—O(6)	1.81(5)
Te(3)—O(2)	2.01(2)	Te(2) ... O(2 ¹)	3.00(3)
Te(3)—O(4)	2.38(3)	Te(4)—O(4)	1.83(3)
Te(3)—O(3)	1.78(4)	Te(4)—O(8)	1.71(7)
Te(3)—O(5)	1.98(4)	Te(4) ... O(6)	2.87(5)
Te(3) ... O(1 ^{III})	2.92(5)	Te(4) ... O(7 ^{IV})	2.82(7)
Te(3) ... O(6 ^{III})	3.12(6)	Pb(1) ... O(3)	2.73(4)
Te(3) ... O(7 ^{IV})	3.30(7)	Pb(1) ... O(4)	2.87(4)
Pb(2) ... O(4)	3.33(3)	Pb(1) ... O(8)	3.05(7)
Pb(2) ... O(8)	2.93(7)	Pb(1) ... O(3 ^V)	2.39(4)
Pb(2) ... O(4 ^{VI})	2.74(4)	Pb(1) ... O(3 ^{VI})	3.03(4)
Pb(2) ... O(5 ^{VI})	2.49(4)	Pb(1) ... O(5 ^{VII})	2.42(4)
Pb(2) ... O(7 ^{VIII})	2.28(7)	Pb(1) ... O(5 ^{VI})	2.88(4)
Pb(2) ... O(8 ^{VIII})	2.64(7)	Pb(1) ... O(6 ^{III})	2.47(4)
O(1) ... O(7)	2.85(6)	O(1) ... O(6)	2.85(7)
O(7) ... O(7 ^{IX})	2.96(10)	O(6) ... O(6 ^{IX})	2.68(6)
O(3) ... O(5)	2.87(6)	O(2) ... O(3)	2.75(5)
O(4) ... O(5)	2.84(6)	O(2) ... O(5)	2.89(6)
O(4) ... O(3)	2.84(5)	O(4) ... O(8)	2.55(7)
O(4) ... O(4 ^{III})	2.59(5)		
(b) Angles			
O(1)—Te(1)—O(1 ^{III})	169.7(1.9)		
O(7)—Te(1)—O(7 ^{IX})	103.6(3.3)		
Te(1)—O(1)—Te(2)	120.4(2.5)		
O(1)—Te(1)—O(7)	86.8(0.9)		
O(4)—Te(4)—O(8)	91.9(2.0)		
O(4)—Te(4)—O(4 ^{III})	90.2(1.5)		
Te(3)—O(4)—Te(4)	123.3(1.7)		
O(3 ^V)—Pb(1)—O(5 ^{VII})	87.6(1.4)		
O(3 ^V)—Pb(1)—O(6 ^{III})	93.5(1.4)		
O(5 ^{VII})—Pb(1)—O(6 ^{III})	90.5(1.5)		
O(5 ^{VI})—Pb(2)—O(5 ^{XI})	162.6(1.3)		
O(1)—Te(2)—O(6)	100.9(1.9)		
O(6)—Te(2)—O(6 ^{IX})	95.2(2.2)		
O(2)—Te(3)—O(3)	92.6(1.6)		
O(2)—Te(3)—O(4)	172.6(1.8)		
O(2)—Te(3)—O(5)	93.0(1.6)		
O(3)—Te(3)—O(5)	99.3(1.7)		
O(4)—Te(3)—O(5)	80.8(1.5)		
O(4)—Te(3)—O(3)	84.5(1.4)		
Te(3)—O(2)—Te(3 ^X)	146.2(3.3)		
O(7 ^{VIII})—Pb(2)—O(8 ^{VIII})	90.4(2.5)		
I $\frac{1}{2} - x, -1 + y, z$	II $\frac{1}{2} - x, 1 + y, z$		
III $\frac{1}{2} - x, y, z$	IV $x, 1 + y, z$		
V $1 - x, 1 - y, z$	VI $x, -\frac{1}{2} + y, \frac{1}{2} - z$		
VII $x, -1 + y, z$	VIII $x, \frac{1}{2} + y, \frac{1}{2} - z$		
IX $x, y, 1 - z$	X $1 - x, 2 - y, z$		
XI $\frac{1}{2} - x, \frac{3}{2} - y, \frac{1}{2} - z$			

TABLE 1

Final atomic positional parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Pb(1)	0.409 8(1)	0.368 6(3)	0.307 4(1)
Pb(2)	$\frac{1}{4}$	0.510 1(5)	0.191 6(2)
Te(1)	$\frac{1}{4}$	0.110 7(10)	$\frac{1}{2}$
Te(2)	0.073 0(3)	0.297 9(8)	$\frac{1}{2}$
Te(3)	0.416 4(2)	0.844 7(5)	0.386 5(2)
Te(4)	$\frac{1}{4}$	0.564 4(7)	0.387 9(3)
O(1)	0.131 4(26)	0.082 5(74)	$\frac{1}{2}$
O(2)	$\frac{1}{2}$	1	0.416 7(31)
O(3)	0.468 6(19)	0.713 9(56)	0.326 7(19)
O(4)	0.318 9(18)	0.680 7(50)	0.336 7(18)
O(5)	0.380 7(22)	1.041 9(60)	0.323 9(20)
O(6)	0.113 1(26)	0.432 3(74)	0.430 9(23)
O(7)	$\frac{1}{4}$	-0.052 5(111)	0.423 6(36)
O(8)	$\frac{1}{4}$	0.373 7(103)	0.334 3(36)

In the non-standard setting of the space group, general equivalent positions are: x, y, z ; $\bar{x}, \bar{y}, \bar{z}$; \bar{x}, \bar{y}, z ; x, y, \bar{z} ; $\frac{1}{2} - x, y, z$; $\frac{1}{2} + x, \bar{y}, \bar{z}$; $\frac{1}{2} - x, y, \bar{z}$; and $\frac{1}{2} + x, \bar{y}, z$.

efficient,⁶ g , converged at 5.7(4). No parameter shift, at convergence, was greater than 0.001 σ and a final difference-

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

² M. J. Buerger, 'X-Ray Crystallography', Wiley, New York, 1942.

³ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

⁴ D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

⁵ G. H. Stout and L. H. Jensen, 'X-Ray Structure Determination', Macmillan, London, 1969, p. 456.

⁶ A. C. Larson, *Acta Cryst.*, 1967, **23**, 664.

Most of the computations were carried out on the CDC 7600 at the University of Manchester Regional Computer Centre using the 'X-RAY '72' system of programs; SHELX-76 on the ICL 1906A at the University of Birmingham Computer Centre was used for the absorption corrections. Final atomic co-ordinates with estimated standard deviations are listed in Table 1, interatomic distances and angles in Table 2. Observed and calculated structure amplitudes ($\times 10$) and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22306 (5 pp.).*

RESULTS AND DISCUSSION

The structure is illustrated in Figure 1 and can best be described in terms of separate Pb^{2+} cations and complex tellurate(IV) anions. The anions are of two types, those defined by Te(1) and Te(2) and those defined by Te(3) and Te(4). Te(1) in a four-fold and Te(2) in an eight-fold special position, with O(1), O(6), and O(7) in eight-, sixteen-, and eight-fold positions respectively, give four separate $[\text{Te}_3\text{O}_8]^{4-}$ anions in the unit cell. Te(3) in a sixteen-fold and Te(4) in an eight-fold position, with their associated oxygen atoms, form endless-chain anions parallel to the a axis, with eight $[\text{Te}_3\text{O}_8]$ units in the unit cell.

In the separate anion the central tellurium atom Te(1) forms two bonds to terminal oxygen atoms, O(7), of

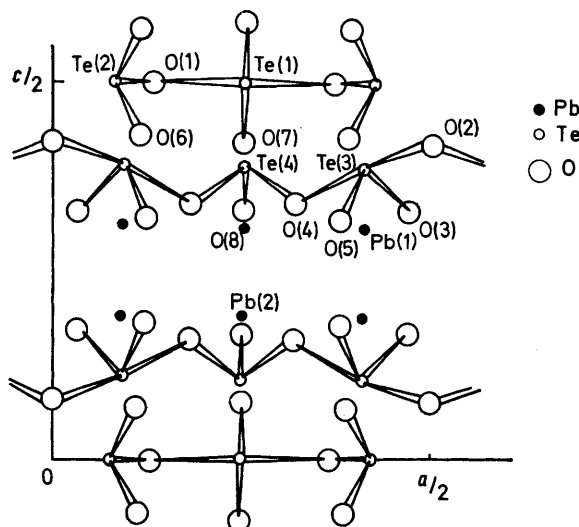


FIGURE 1 Projection of $\frac{1}{2}$ of the unit cell down $[010]$ showing the atom numbering

1.88 Å and two to bridging oxygen atoms, O(1), of 2.24 Å. The co-ordination geometry can best be described in terms of a trigonal-bipyramidal arrangement, on valence-shell electron-pair repulsion (VSEPR) theory,⁷ with the lone pair occupying the fifth co-ordination position. The O(7)–Te(1)–O(7^{II}) angle of 103.6° and the O(1)–Te(1)–O(1^{III}) angle of 169.7° are in line with the theoretical angles of 120 and 180°, when lone pair–bond pair interactions are taken into account.

The outer tellurium atoms Te(2) form two bonds to terminal oxygen atoms O(6) of 1.81 Å and one bond to the bridging oxygen atom O(1) of 1.89 Å. The pyramidal arrangement of the three oxygen atoms, with an average O–Te–O angle of 99°, can be correlated with a tetrahedral arrangement around tellurium, including the lone pair of electrons.

The Te(1)–O(1)–Te(2) bridge is asymmetric, and O(1) is more closely associated with Te(2), which suggests a contribution to the structure from the form TeO_3^{2-} –

TeO_2 – TeO_3^{2-} with two pyramidal ions linked by a neutral TeO_2 molecule.

In the chain anion Te(4) has three short bonds to oxygen of 1.83 Å ($\times 2$) to O(4) and 1.71 Å to O(8). The distance of 1.71 Å is extremely short, but the estimated standard deviation is high, and it is not significantly different from the other Te–O terminal bonds. The O–Te–O angles average 91°, giving a similar pyramidal co-ordination to that of Te(2), again on VSEPR theory based on a tetrahedral arrangement including the lone pair. Te(3) has two short terminal bonds to O(3) and O(5) of 1.78 and 1.98 Å, and a short symmetric bridge bond to O(2) of 2.01 Å, with an average O–Te–O angle of 95°, to give a similar pyramidal co-ordination to those of Te(4) and Te(2).

The chain is completed by the long asymmetric bridge bond Te(3)–O(4) of 2.38 Å. This gives a four-co-ordinate arrangement around Te(3) which is similar to that around Te(1), and can again be described in terms of a trigonal-bipyramidal co-ordination, including the lone pair of electrons. The O(3)–Te(3)–O(5) and O(2)–Te(3)–O(4) angles of 99.5 and 173.6° are very similar to the corresponding angles at Te(1) described above. The asymmetric bridge again suggests a contribution to the structure from the ionic form $[\text{TeO}_3]^{2-} + [\text{Te}_2\text{O}_5]^{2-}$, with the ions linked through the weak bond.

The tellurate(IV) anions in the present structure thus contain tellurium atoms which can be described as three- and four-co-ordinated by oxygen atoms. These two configurations have been found previously; for example, teinite,⁸ $\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$, contains a three-co-ordinate pyramidal unit with an average Te–O distance of 1.95 Å and average angles of 95°. Both the paratellurite⁹ and tellurite¹⁰ forms of TeO_2 contain four-co-ordinate units, with very similar geometries, based on the trigonal-bipyramidal model, to those described here. Average values for Te–O (axial) are 2.10 and for Te–O (equatorial) 1.85 Å, and corresponding angles *ca.* 100 and 150–180°.

TABLE 3

Parameters of some trigonal-bipyramidal co-ordinated TeO_4 units

Compound	Te–O bond/Å		O–Te–O Angle/°		Ref.
	apical	axial	apical	axial	
Theoretical model	2.23	1.88	162	102	11
$\text{Zn}_2\text{Te}_3\text{O}_8$ [Te(1)]	2.10	1.83	175	106	13
TiTe_3O_8	2.12	1.85	159	102	<i>a</i>
$\text{Fe}_2\text{Te}_4\text{O}_{11}$ [Te(4)]	2.17	1.96	150	99	14
$\text{Pb}_2\text{Te}_3\text{O}_8$ [Te(1)]	2.24	1.88	170	104	<i>b</i>
[Te(3)]	2.20	1.88	173	99	<i>b</i>

^a G. Meunier and J. Galy, *Acta Cryst.*, 1971, **B27**, 602.

^b This work.

Some values for both three- and four-co-ordinate species are given in Table 3, together with values from a theoretical model due to Galy *et al.*¹¹

⁷ R. J. Gillespie, 'Molecular Geometry,' Van Nostrand-Reinhold, London, 1972.

⁸ A. Zemmann and J. Zemmann, *Acta Cryst.*, 1962, **15**, 698.

⁹ J. Leciezewicz, *Z. Krist.*, 1961, **116**, 345.

¹⁰ H. Beyer, *Z. Krist.*, 1967, **124**, 228.

¹¹ J. Galy, G. Meunier, A. Anderson, and A. Åström, *J. Solid State Chem.*, 1975, **13**, 142.

The asymmetric arrangement found for Te(3) has been described¹¹ as (3 + 1) co-ordination, and is a feature of a number of tellurate(IV) structures, e.g. denningite¹²

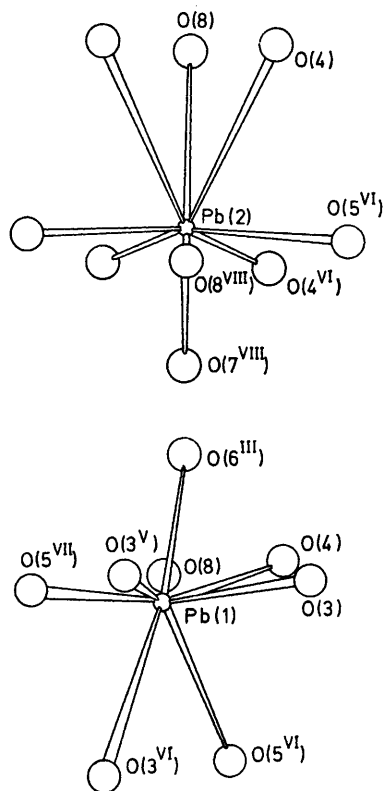


FIGURE 2 Projection down [100] of the co-ordination sphere of Pb(1) and down [010] of the co-ordination sphere of Pb(2), showing the atom numbering

(Mn,Ca,Zn)Te₂O₅ with Te–O distances of 2.04 and 2.36, Zn₂Te₃O₈ with distances¹³ of 1.98 and 2.41, and Fe₂Te₄O₁₁ with distances¹⁴ of 2.08 and 2.25 Å.

In addition to the near-neighbour co-ordination described above, there are some longer contacts to the tellurium atoms, a feature of structures containing Te^{IV} bonded to either oxygen or fluorine. These long contacts have been included in a consideration of the total co-ordination by Brown,¹⁵ who has calculated bond valences for many examples and has tabulated structures in terms of three different configurations. These are based on a six-co-ordinate arrangement, with either two strong, two intermediate, and two weak bonds (\mathcal{A}), or three strong and three weak bonds (\mathcal{C}), or the transitional case where the two intermediate bonds are unequal (\mathcal{B}).

In the present case the arrangements are not exactly comparable with Brown's configurations except for Te(4). Thus Te(1) has no further bonding [the nearest contacts to O(6) and O(8) are at 3.72 Å] and must be

considered four-co-ordinate (although it would be assigned to configuration \mathcal{A}). Te(2) has only two contacts to O(2) of 3.00 Å, and can be regarded as five-co-ordinate, best assigned to configuration \mathcal{C} . Te(3) has contacts of 2.92 Å to O(1), 3.12 Å to O(6), and 3.30 Å to O(7), and can therefore be considered to be seven-co-ordinate, although the interactions with O(6) and O(7) are obviously very weak. The arrangement is best assigned to configuration \mathcal{A} . Te(4) has contacts of 2.82 Å to O(7) and 2.87 Å ($\times 2$) to O(6) and is therefore six-co-ordinate and equivalent to configuration \mathcal{C} .

The lead atoms, although formally regarded as Pb²⁺ ions, also have a significant co-ordination by oxygen atoms. Thus Pb(1) has three nearest neighbours at an average distance of 2.42 Å, with an average O–Pb–O angle of 90.5°. This pyramidal arrangement can be considered on VSEPR theory in terms of a tetrahedral arrangement including the lone pair of electrons, similar to that for Te(2) and Te(4) above. A similar arrangement has been found in lead(II) oxide,¹⁶ lead(II) zinc silicate,¹⁷ and lead(II) germanate.¹⁸ There are five further contacts to the lead atom, as shown in Figure 2, giving a rather irregular arrangement, but grouped around the assumed lone-pair position.

For Pb(2) the situation is more difficult. However, the nearest neighbours are all on the same side of the lead atom, leaving space for the lone pair. Four oxygen atoms at an average distance of 2.48 Å, with the lone pair, form a distorted trigonal-bipyramidal arrangement with O–Pb–O (equatorial) of 90.4 and O–Pb–O (axial) of 162.6°. The Pb(2)–O(7^V) distance (2.28 Å) is extremely short but the estimated standard deviation is high and this is not considered significantly different

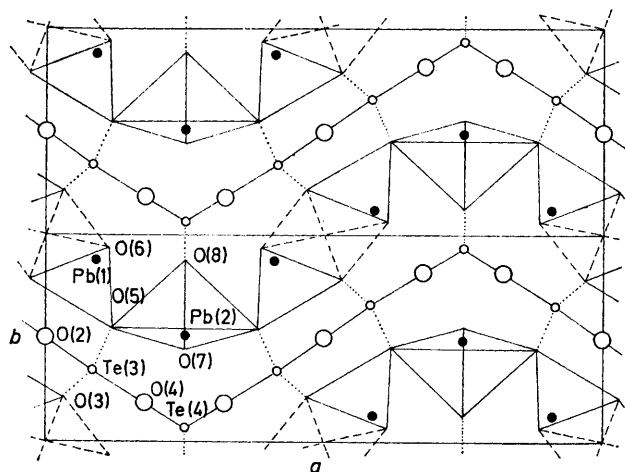


FIGURE 3 Projection of two adjacent cells along [001], showing the primary lead co-ordination polyhedra, in relation to the [Te₃O₆]⁴⁻ chain network for atoms with *z* co-ordinates between 0.065 and 0.195. Key as in Figure 1

from the other nearest-neighbour distances. This type of co-ordination has also been found in the structures of

¹² E. M. Walitzi, *Tschermaks Min. Petro. Mitt.*, 1965, **10**, 241.

¹³ K. Hanke, *Naturwiss.*, 1966, **53**, 273.

¹⁴ F. Pertlik, *Tschermaks Min. Petro. Mitt.*, 1972, **18**, 39.

¹⁵ I. D. Brown, *J. Solid State Chem.*, 1974, **11**, 214.

¹⁶ A. F. Wells, 'Structural Inorganic Chemistry,' 3rd edn., Oxford University Press, Oxford, 1962, p. 476.

¹⁷ C. T. Prewitt, E. Kirchner, and A. Preisinger, *Z. Krist.*, 1967, **124**, 115.

¹⁸ M. I. Kay, R. E. Newnham, and R. W. Wolfe, *Ferroelectrics*, 1975, **9**, 1.

orthorhombic lead(II) oxide¹⁹ and lead(II) zinc silicate.¹⁷ The longer contacts to the lead atom again form a rather irregular arrangement and are grouped around the lone-pair position.

The nearest-neighbour polyhedra around Pb(1) and Pb(2) link to give Pb_3O_8 units which are illustrated in Figure 3. It can be seen from Figure 1 that the lead atoms are arranged with their lone pairs directed parallel to the *c* axis, and there is clearly a weak structural

interaction in this direction, reflected in the long $\text{Pb} \cdots \text{O}$ contacts. This feature can be correlated with the pronounced tendency of the crystals to cleave on the {001} face.

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¹⁹ M. I. Kay, *Acta Cryst.*, 1961, **14**, 80.