

## The crystal structure of kombatite, $\text{Pb}_{14}(\text{VO}_4)_2\text{O}_9\text{Cl}_4$ , a complex heteropolyhedral sheet mineral

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### ABSTRACT

The crystal structure of kombatite,  $\text{Pb}_{14}(\text{VO}_4)_2\text{O}_9\text{Cl}_4$ ,  $a = 12.682(2)$ ,  $b = 22.566(5)$ ,  $c = 11.279(2)$  Å,  $\beta = 118.11(1)^\circ$ ,  $V = 2847(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $C2/c$ , has been solved by direct methods and refined to an  $R$  index of 9.0% using  $\text{MoK}\alpha$  X-ray data. There is one unique V position tetrahedrally coordinated by four O atoms, and there are seven Pb positions with a variety of coordination geometries. Four Pb atoms are coordinated by three or four O atoms and three or four Cl atoms at the vertices of flattened square antiprisms, with the central Pb cations displaced strongly toward the O ligands. Three Pb atoms are coordinated by five or six O atoms but have four of the ligands to one side of the Pb cation. The behavior of all the Pb cations is compatible with the presence of a stereoactive lone-pair of electrons.

The structural unit of kombatite is a  $[\text{Pb}_{14}(\text{VO}_4)_2\text{O}_9]^{4+}$  double sheet, and adjacent sheets are linked by Cl anions. The structural unit consists of two sheets of the tetragonal PbO structure in which one-eighth of the Pb positions are replaced by V, with the addition of two apical O anions and the omission of one O anion within the Pb-O sheet. Thus the kombatite structure is strongly related to that of tetragonal PbO.

### INTRODUCTION

Kombatite is a lead vanadium oxy-chloride,  $\text{Pb}_{14}(\text{VO}_4)_2\text{O}_9\text{Cl}_4$ , from the Kombat mine, Namibia, and was first described by Rouse et al. (1986). It occurs as bright yellow anhedral crystals up to 0.2 mm in diameter and has a perfect cleavage parallel to (010). It is the V analogue of sahlinite,  $\text{Pb}_{14}(\text{AsO}_4)_2\text{O}_9\text{Cl}_4$  (Rouse and Dunn, 1985).

### EXPERIMENTAL METHODS

Rotation Laue photographs of equant crystals gave very weak diffraction patterns, irrespective of the size of the crystal, because of the very high X-ray absorption coefficient (841  $\text{cm}^{-1}$ ) of kombatite. However, a thin plate gave a good diffraction pattern, the result of low absorption orthogonal to the plate; consequently, intensity data were collected on a thin plate. The crystal was mounted on a Nicolet R3m automated four-circle diffractometer equipped with a Mo X-ray tube. Twenty-five reflections were measured on a random-orientation photograph and

aligned automatically on the diffractometer. From the resulting setting angles, least-squares refinement gave the cell dimensions listed in Table 1, together with the orientation matrix. Intensity data were collected according to the procedure of Hawthorne and Groat (1985). A total of 2738 reflections was measured to a maximum  $2\theta$  angle of  $60^\circ$ . Ten strong reflections uniformly distributed with regard to  $2\theta$  were measured at  $10^\circ$  intervals of  $\psi$  (the azimuthal angle corresponding to the rotation of the crystal about its diffraction vector). These data were used to calculate an absorption correction, modeling the crystal as a thin plate (minimum glancing angle =  $15^\circ$ ) and reducing the azimuthal  $R$  index from 25.5 to 2.4%; this correction was then used on the normal intensity data. Data were corrected for Lorentz and polarization effects and reduced to structure factors. A reflection was considered as observed if the magnitude of the structure factor exceeded that of 5 sd on the basis of counting statistics. Miscellaneous information pertaining to data collection and structure refinement is given in Table 1.

TABLE 1. Miscellaneous information for kombatite

$a$ (Å)	12.682(2)	crystal size (mm)	$0.23 \times 0.13 \times 0.02$
$b$	22.566(5)	radiation/monochromator	$\text{MoK}\alpha/\text{Gr}$
$c$	11.279(2)	no. of unique intensities	2738
$\beta$ ( $^\circ$ )	118.11(1)	no. of $ F_o  > 5\sigma$	2146
$V$ (Å <sup>3</sup> )	2847(1)	$R_{\text{azimuthal}}$ (%)	25.5 → 2.4
Space group	$C2/c$	$R_{\text{obs}}$ (%)	9.0
		$R_{w\text{ obs}}$ (%)	9.1
Cell content: $4[\text{Pb}_{14}(\text{VO}_4)_2\text{O}_9\text{Cl}_4]$			

TABLE 2. Final parameters for kombatite

Site	x	y	z	$U_{eq}$	$U_{11}^*$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pb1	0.1136(1)	0.0841(1)	0.1807(1)	113(5)	104(6)	128(12)	114(5)	-21(7)	58(4)	11(8)
Pb2	0.3706(1)	0.0876(1)	0.0761(1)	135(6)	114(6)	155(13)	135(6)	-25(7)	57(4)	-23(8)
Pb3	0.1271(1)	0.4219(1)	0.4547(1)	124(6)	146(6)	122(12)	122(6)	11(6)	77(5)	19(8)
Pb4	0.3780(1)	0.4174(1)	0.3074(1)	119(6)	132(6)	133(12)	106(5)	-16(7)	69(4)	40(8)
Pb5	0.3541(1)	0.1948(1)	0.3001(2)	127(6)	142(7)	101(12)	154(6)	-9(6)	82(5)	-7(8)
Pb6	0.1213(2)	0.1988(1)	0.4211(1)	133(6)	135(6)	136(12)	136(6)	-40(7)	70(5)	-39(8)
Pb7	0.3998(1)	0.3034(1)	0.0617(1)	116(6)	95(6)	119(12)	142(6)	3(6)	63(5)	8(7)
V	0.1360(6)	0.3214(5)	0.1765(6)	90(12)						
Cl1	0.372(1)	0.4957(8)	0.060(1)	204(20)						
Cl2	0.3739(9)	0.0134(7)	0.2982(9)	159(18)						
O1	0.238(3)	0.146(2)	0.114(3)	149(58)						
O2	0.253(3)	0.135(3)	0.381(3)	197(65)						
O3	0.476(2)	0.358(2)	0.487(2)	32(43)						
O4	0.010(3)	0.351(2)	0.045(3)	206(67)						
O5	0.251(2)	0.340(2)	0.143(3)	125(53)						
O6	0	0.145(3)	1/4	119(74)						
O7	1/2	0.145(3)	1/4	145(78)						
O8	1/2	0.368(4)	1/4	188(91)						
O9	0.172(3)	0.352(3)	0.328(3)	266(76)						
O10	0.104(6)	0.249(5)	0.172(7)	651(170)						

\*  $U_{ij} \times 10^4$ .

## STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with coefficients of anomalous dispersion, were taken from the *International Tables for X-ray Crystallography*, vol. 4 (Ibers and Hamilton, 1974).  $R$  and  $R_w$  indices are of the conventional form and are given as percentages.

The structure was solved by direct methods. The  $E$  statistics suggest that the structure is centrosymmetric, as required by the uniquely determined space group  $C2/c$ , and the solution with the highest combined figure of merit showed most of the Pb positions. The remaining atoms were located by successive cycles of refinement and difference-Fourier synthesis, and the final structure was refined to an  $R$  index of 10.1% for a model with isotropic displacements for all atoms. Anisotropic displacements on the Pb atoms produced convergence at an  $R$  index of 9.0%. Attempts to refine an anisotropic model for the remaining atoms produced no significant reduction in the  $R$  index and resulted in some negative displacements. These features, together with the high final  $R$  index, undoubtedly result from problems associated with the extreme absorption of X-rays by this material.

Final atomic positions and displacement factors are given in Table 2, selected interatomic distances are given in Table 3, observed and calculated structure factors are listed in Table 4,<sup>1</sup> and an empirical bond valence table is shown in Table 5.

## DISCUSSION

## Pb coordination

Details of the cation coordination polyhedra for the Pb atoms are shown in Figure 1 and Table 3. There are seven

distinct Pb positions, and they fall into two groups with regard to coordination geometry. Pb1 to Pb4 are sevenfold or eightfold coordinated by both O and Cl atoms;  $Pb\phi_8$  polyhedra ( $\phi$  = unspecified ligand) are flattened square antiprisms (Fig. 2), and  $Pb\phi_7$  polyhedra are diminished square antiprisms. Figure 1 shows an asym-

TABLE 3. Selected interatomic distances (Å) in kombatite

Pb1-O1	2.47(4)	Pb2-O1	2.33(4)
Pb1-O2	2.40(3)	Pb2-O4a	2.84(5)
Pb1-O3d	2.43(3)	Pb2-O5a	2.75(3)
Pb1-O6	2.38(4)	Pb2-O7	2.28(4)
Pb1-Cl1a	3.34(2)	Pb2-Cl1a	3.31(4)
Pb1-Cl1g	3.36(2)	Pb2-Cl2	3.00(1)
Pb1-Cl1h	3.47(2)	Pb2-Cl2c	3.31(1)
Pb1-Cl2	3.33(1)	(Pb2-O)	2.55
(Pb1-O)	2.42	(Pb2-Cl)	3.21
(Pb1-Cl)	3.38		
Pb3-O2b	2.18(4)	Pb4-O3	2.25(3)
Pb3-O4e	2.36(5)	Pb4-O5	2.51(4)
Pb3-O9	2.36(6)	Pb4-O8	2.24(4)
Pb3-Cl1i	3.33(2)	Pb4-O9	3.10(5)
Pb3-Cl2b	3.15(1)	Pb4-Cl1	3.27(2)
Pb3-Cl2j	3.51(1)	Pb4-Cl1c	3.31(1)
Pb3-Cl2k	3.52(1)	Pb4-Cl1i	3.49(2)
(Pb3-O)	2.30	Pb4-Cl2k	3.57(1)
(Pb3-Cl)	3.38	(Pb4-O)	2.53
Pb5-O1	2.22(3)	(Pb4-Cl)	3.41
Pb5-O2	2.32(5)	Pb6-O2	2.41(5)
Pb5-O4f	2.73(3)	Pb6-O3b	2.34(3)
Pb5-O7	2.45(3)	Pb6-O6	2.18(4)
Pb5-O10	3.06(8)	Pb6-O9b	3.04(4)
(Pb5-O)	2.56	Pb6-O10	2.95(9)
		Pb6-O10e	2.78(8)
		(Pb6-O)	2.62
Pb7-O1a	2.24(3)		
Pb7-O3c	2.26(3)	V-O4	1.73(3)
Pb7-O5	2.59(4)	V-O5	1.72(4)
Pb7-O8	2.39(5)	V-O9	1.70(4)
Pb7-O10a	2.87(9)	V-O10	1.67(1)
(Pb7-O)	2.47	(V-O)	1.71

Note: equivalent positions: a =  $\bar{x} + 1/2, \bar{y} + 1/2, \bar{z}$ ; b =  $\bar{x} + 1/2, \bar{y} + 1/2, \bar{z} + 1$ ; c =  $\bar{x} + 1, \bar{y}, \bar{z} + 1/2$ ; d =  $\bar{x} - 1/2, \bar{y} + 1/2, \bar{z} - 1/2$ ; e =  $\bar{x}, \bar{y}, \bar{z} + 1/2$ ; f =  $\bar{x} + 1/2, \bar{y} + 1/2, \bar{z} + 1/2$ ; g =  $\bar{x} - 1/2, \bar{y} - 1/2, \bar{z}$ ; h =  $\bar{x} + 1/2, \bar{y} - 1/2, \bar{z} + 1/2$ ; i =  $\bar{x}, \bar{y} + 1, \bar{z} + 1/2$ ; j =  $\bar{x} - 1/2, \bar{y} + 1/2, \bar{z}$ ; k =  $\bar{x} + 1/2, \bar{y} + 1/2, \bar{z} + 1/2$ .

<sup>1</sup> A copy of Table 4 may be ordered as Document AM-94-554 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 5. Bond valence\* values for kombatite

	Pb1	Pb2	Pb3	Pb4	Pb5	Pb6	Pb7	V	Total
O1	0.35	0.49			0.63		0.60		2.07
O2	0.41		0.70		0.50	0.40			2.01
O3	0.39			0.59		0.48	0.58		2.04
O4		0.16			0.20			1.19	2.00
O5		0.20	0.45	0.32			0.27	1.23	2.02
O6	0.43 <sup>x2</sup> →					0.70 <sup>x2</sup> →			2.26
O7		0.55 <sup>x2</sup> →			0.37 <sup>x2</sup> →				1.84
O8				0.60 <sup>x2</sup> →			0.42 <sup>x2</sup> →		2.04
O9			0.45	0.10		0.11		1.30	1.96
O10					0.11	0.18	0.15	1.43	2.00
Cl1	0.11	0.12	0.12	0.14					0.88
	0.11			0.12					
	0.08			0.08					
Cl2	0.12	0.28	0.19	0.06					0.91
		0.12	0.07						
			0.07						
Total	2.00	1.92	2.05	2.01	1.81	2.11	2.02	5.15	

\* Calculated from the parameters of Brown (1981) for Pb<sup>2+</sup>-O and Brese and O'Keeffe (1991) for Pb<sup>2+</sup>-Cl.

metry in the coordination of atoms Pb1 to Pb4. For each square antiprism (or diminished square antiprism), one square consists of O atoms and the other square consists of Cl atoms. Moreover, each central Pb atom is displaced from the center of the polyhedron toward the O ligands, with a ⟨Pb-O⟩ distance of 2.45 Å and a ⟨Pb-Cl⟩ distance of 3.35 Å. The coordination of the Pb5 to Pb7 atoms is quite different (Fig. 1). They bond only to O and are

fivefold or sixfold coordinated. However, the coordination is still one sided, with a square of O atoms to one side and one or two additional ligands to the other side of the central cation. These asymmetric coordinations for Pb<sup>2+</sup> are very characteristic of stereoactive lone-pair behavior, whereby the lone-pair electrons project outward on one side of the cation, forcing it to assume an asymmetric coordination.

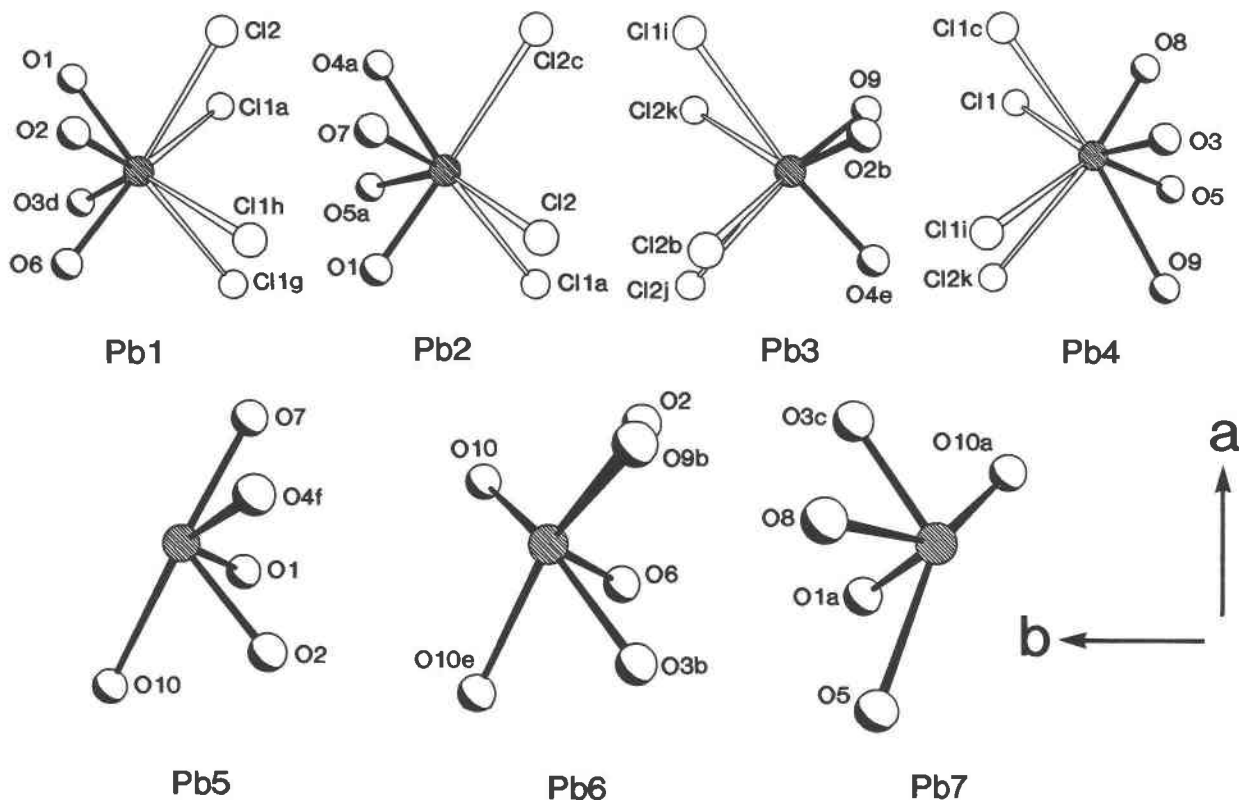


Fig. 1. Details of the coordination polyhedra in kombatite; Pb atoms are shaded circles.

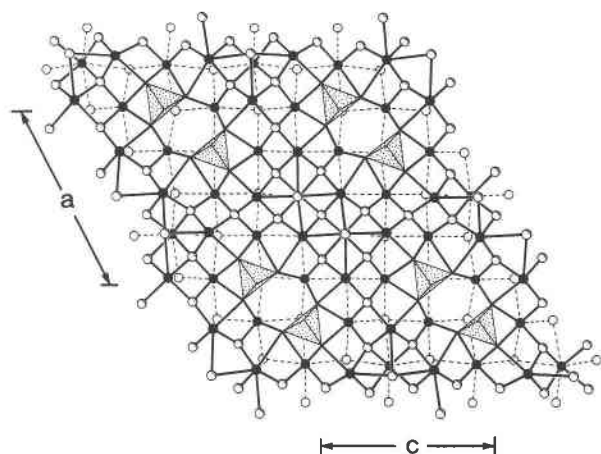


Fig. 2. Half of the structural unit (sheet) in kombatite, projected down [010];  $VO_4$  groups are dot shaded, Pb-O bonds are solid lines, Pb-Cl bonds are broken lines; Pb atoms are solid circles, O atoms are partly shaded, and Cl atoms are open circles.

### V coordination

There is one distinct V position coordinated by four O anions in a slightly distorted tetrahedral arrangement. The  $\langle V-O \rangle$  distance falls within the range observed for inorganic crystals (Hawthorne and Faggiani, 1979), and the observed variation in individual distances is compatible with the bond valence requirements of the individual anions (Table 4), despite the large standard deviations attached to the observed distances.

### Bond valence characteristics

The bond valence values for kombatite are shown in Table 5. They were calculated with  $Pb^{2+}-O$  parameters of Brown (1981) and the  $Pb^{2+}-Cl$  parameters of Brese and O'Keeffe (1991). By and large, the incident bond valence sums at each anion and cation are close to ideality. This was not the case when we used the  $Pb^{2+}-O$  parameters of Brese and O'Keeffe (1991), for which deviations of up to 0.65 vu were observed in the anion sums. The individual bond valence values emphasize the asymmetric coordination of the Pb cations, the bond valences of which range from 0.07 to 0.70 vu. The weaker values correspond to Pb-Cl distances of 3.51 Å, as compared with Pb-V distances of 3.48 Å. We cannot just ignore these longer distances as doing so would reduce the incident bond valence sums at Cl1 and Cl2 to 0.72 and 0.77 vu, respectively. We have two possible explanations: (1) there is a directional component to the Pb- $\phi$  bonding or (2) the  $Pb^{2+}-Cl$  bond valence parameters are slightly in error, that is, the interaction is stronger at shorter distances and falls off slightly more rapidly at longer distances.

### Structural topology

The structural unit of kombatite is a  $[Pb_{14}(VO_4)_2O_9]^{4+}$  double sheet that is constructed of two halves related by the  $n$  glide operation at  $y = 1/4$  and  $3/4$ . One-half of the

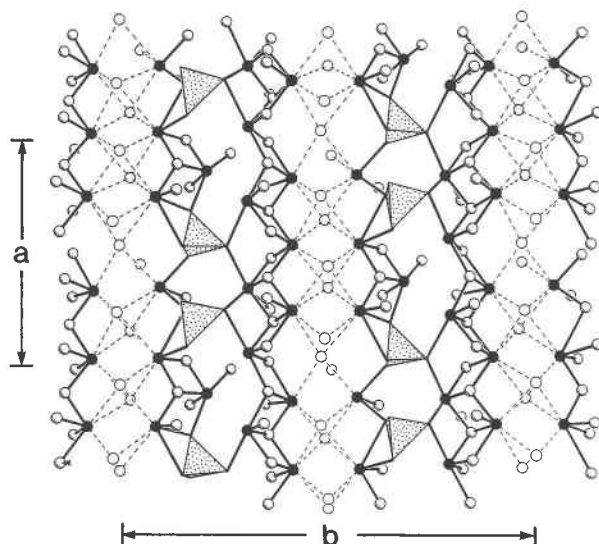


Fig. 3. The structure of kombatite projected onto (001), showing the intersheet linkage made by Cl atoms.

sheet is illustrated in Figure 2. It consists of a square array (in projection) of Pb and O atoms, with some atoms missing and replaced by V to form  $VO_4$  groups. Figure 3 shows the sheets edge on. Two of the sheets shown in Figure 2 link together primarily through the  $VO_4$  groups to form thick composite sheets that are then linked by layers of Cl atoms at  $y = 0$  and  $1/2$ . The Pb atoms on the outside of the composite sheets (Pb1-Pb4) bond weakly to the layers of Cl atoms, which can thus be considered interstitial anions. The general form of the structure of kombatite is rather interesting. A structure can be thought of as a strongly bonded structural unit (Hawthorne, 1983, 1992) linked by interstitial species. Usually the structural unit has anionic character and is linked by interstitial cations. In kombatite the structural unit  $[Pb_{14}(VO_4)_2O_9]^{4+}$  has cationic character and is linked by interstitial anions.

### Relationship to other structures

The structure of the tetragonal polymorph of PbO is shown in Figure 4. The similarity to the structural unit in kombatite is striking, to say the least. In both structures, we see a square array of Pb and O atoms (Figs. 2, 4a), and when viewed edge on (Figs. 3, 4b), the ladderlike appearance of the PbO sheets is very similar. In fact, we can derive the kombatite sheet very simply from the PbO sheets in the following way. A fragment of the PbO sheet is shown in Figure 5a. Two Pb atoms are replaced with V atoms and two O atoms, as shown in Figure 5b. The central O atom no longer has sufficient cation coordination (i.e., incident bond valence) and is not present. The resulting fragment (Fig. 5b) is easily identified in the kombatite sheet (Fig. 2). We may write this sequence in the following way:  $16 \times PbO \rightarrow Pb_{16}O_{16} \rightarrow Pb_{16}O_{16} + 2V + 2O - 2Pb - O \rightarrow [Pb_{14}(VO_4)_2O_9]^{4+} \rightarrow$  structural unit in kombatite. Thus kombatite may be considered as slabs of PbO structure in which alternate sheets interca-

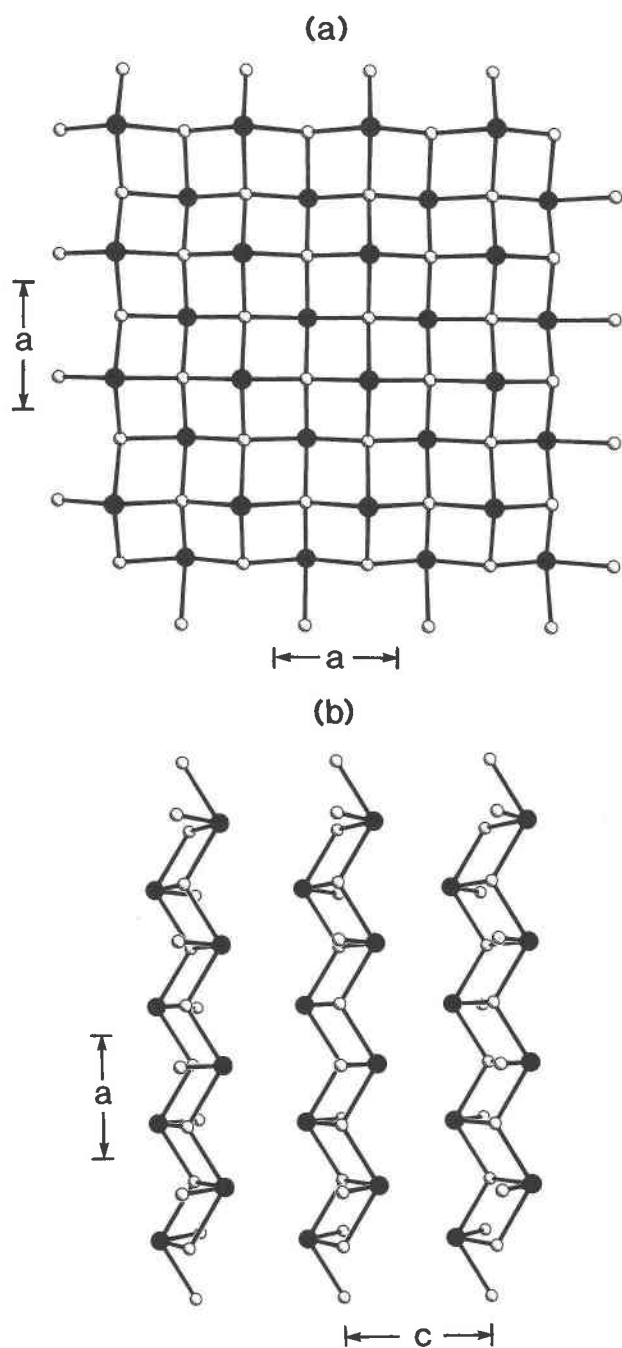


Fig. 4. The structure of tetragonal PbO (a) projected down [001] and (b) projected down [100]; legend as in Fig. 2.

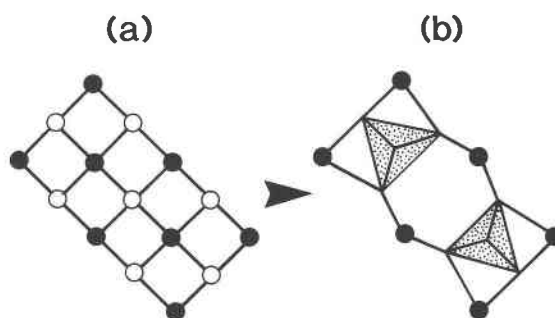


Fig. 5. (a) Fragment of the PbO structure; (b) replacement of two Pb atoms with two V atoms plus two O atoms, together with the omission of the central O atom of the fragment.

late  $\text{VO}_4$  groups and Cl atoms. For such a complex structure and formula, this is a pleasingly simple building principle.

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