

## The crystal structure of pinchite, $\text{Hg}_5\text{Cl}_2\text{O}_4$

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### ABSTRACT

The crystal structure of pinchite,  $\text{Hg}_5\text{O}_4\text{Cl}_2$ ,  $a = 11.619(3)$ ,  $b = 6.105(2)$ ,  $c = 11.710(3)$  Å,  $V = 830.6(4)$  Å<sup>3</sup>, space group *Ibam*, has been solved by direct methods and refined to an *R* index of 3.0% using *MoK $\alpha$*  X-ray data. There are three distinct Hg positions: Hg1 is coordinated by two O and four Cl atoms in a distorted octahedral arrangement; Hg2 is coordinated by four O and two Cl atoms in a bi-diminished, Siamese dodecahedral arrangement; and Hg3 is coordinated by four O atoms in a distorted tetrahedral arrangement. The structure consists of layers of HgCl and  $\text{Hg}_5\text{O}_4$  composition and is closely related to the structure of terlinguaite,  $\text{Hg}^+\text{Hg}_2^{2+}\text{O}_2\text{Cl}_2$ .

### INTRODUCTION

Pinchite,  $\text{Hg}_5\text{O}_4\text{Cl}_2$ , is a mercury oxy-chloride from Terlingua, Texas, and was first described by Sturman and Mandarino (1974); it was named after William W. Pinch of Rochester, New York, who first discovered the unique character of this material. Pinchite occurs as blocky or platy crystals up to 1 mm in maximum dimension and is associated with montroydite and terlinguaite.

### EXPERIMENTAL METHODS

The crystals used in this work were supplied by Bill Pinch. The high absorption proved to be somewhat of a problem, and several X-ray intensity data sets were collected before an adequate structure was derived. A crystal was mounted on a glass disk and was ground to a thin plate (20  $\mu\text{m}$  thick); the plate was then detached from the disk, attached to a glass fiber, and mounted on a Nicolet *R3m* automated four-circle diffractometer equipped with a Mo X-ray tube. Thirty-five reflections were found using a random-search method 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 1391 reflections were measured to a maximum  $2\theta$  angle of 60°. Ten strong reflections uniformly distributed with regard to  $2\theta$  were measured at 10° intervals of  $\psi$  (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector). These data were used to calculate an absorption correction, modeling the crystal as a thin plate

and reducing the  $R_{\text{azimuthal}}$  index from 33.9 to 3.5%; this correction was then used on the normal intensity data. Data were corrected for Lorentz and polarization effects, averaged, and reduced to structure factors. A reflection was considered as observed if its magnitude exceeded that of 5 sd on the basis of counting statistics. Information pertaining to data collection and structure refinement is given in Table 1.

### 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. IV (Ibers and Hamilton, 1974). *R* and  $R_w$  (statistical weights) indices are of the conventional form and are given as percentages.

The structure was solved by direct methods. The *E* statistics indicated that the structure was centrosymmetric, and the solution with the highest combined figure of merit showed all the Hg positions. The remaining atoms were located by successive cycles of refinement and difference-Fourier synthesis, and the final structure refined to an *R* index of 3.0% for a model with anisotropic displacements for all atoms. Final atomic positions and displacement factors are given in Table 2; selected interatomic distances are given in Table 3; observed and

TABLE 1. Crystal and refinement information for pinchite

<i>a</i> (Å)	11.619(3)	Crystal size (mm)	0.21 × 0.17 × 0.02
<i>b</i> (Å)	6.105(2)	Radiation/mono	MoK $\alpha$ /graphite
<i>c</i> (Å)	11.710(3)	No. of $ F $	465
<i>V</i> (Å <sup>3</sup> )	830.6(4)	No. of $ F_o  > 5\sigma$	386
Space group	<i>Ibam</i>	$R_{\text{azimuthal}}$ (%)	33.9 → 3.5
Cell content	4[Hg <sub>5</sub> O <sub>4</sub> Cl <sub>2</sub> ]	$R_{\text{obs}}$ (%)	3.0
$\mu$ (cm <sup>-1</sup> )	929	$R_w$ (obs) (%)	3.2

† Deceased, August 4, 1992.

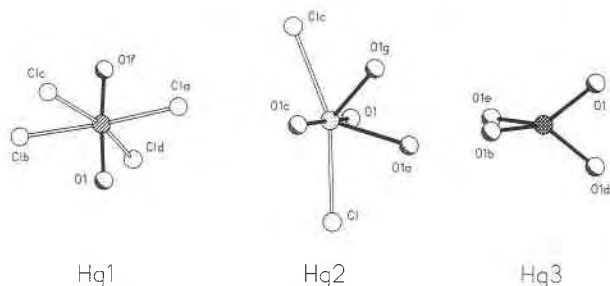


Fig. 1. The coordination of the three crystallographically distinct Hg positions in pinchite. Hg atoms are shaded, O atoms are shadowed spheres, and Cl atoms are open spheres. Hg-O bonds are solid lines, and Hg-Cl bonds are open lines.

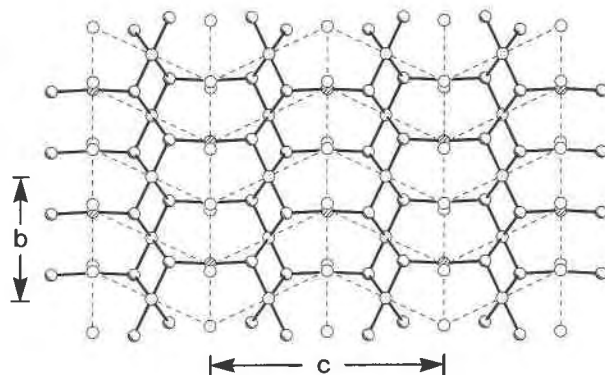


Fig. 2. The crystal structure of pinchite projected down the *a* axis. Legend as in Fig. 1, except Hg-Cl bonds are shown as dashed lines.

calculated structure factors are listed in Table 4;<sup>1</sup> and an empirical bond-valence table is shown in Table 5.

## DISCUSSION

### Hg coordination

Details of the coordination polyhedra for the three crystallographically distinct Hg atoms are shown in Figure 1 and Table 3. Hg1 is coordinated by two O atoms and four Cl atoms in a distorted octahedral arrangement. The two O atoms are in a trans arrangement, and the  $\langle \text{Hg1-O} \rangle$  and  $\langle \text{Hg1-Cl} \rangle$  distances are 2.06 and 3.00 Å, respectively; the resulting octahedron is flattened in the O-Hg1-O axial direction. Hg2 is coordinated by four O atoms and two Cl atoms, with  $\langle \text{Hg2-O} \rangle$  and  $\langle \text{Hg2-Cl} \rangle$  distances of 2.38 and 3.29 Å, respectively. The coordination polyhedron thus formed is a bi-diminished, Siamese dodecahedron (Johnson, 1966), the one-sided nature of which is very apparent in Figure 1. This is very characteristic of stereoactive lone-pair behavior, which plays an important role in the pinchite structure. Hg3 is coordinated by four O atoms in a distorted tetrahedral arrangement, with  $\langle \text{Hg3-O} \rangle = 2.24$  Å. Both electroneutrality requirements and incident bond-valence sums at the Hg atoms show them all to be in the divalent state.

Should the long Hg2-Cl distances of 3.29 Å be considered as bonds? The bond-valence table (Table 5) suggests

that this must be the case. The bond-valence sums around the three Hg atoms are  $\sim 2$  vu, in accord with the (long-range) electroneutrality requirements, although the sum around Hg3 is somewhat low. The sum around the Cl atom is low (0.70 vu), and omission of the Hg2-Cl interaction reduces this sum even further; this indicates that the Hg2-Cl interaction must be included as a chemical bond. The results of Table 5 suggest that the current Hg-O and Hg-Cl bond-valence curves are too strong at short distances and too weak at long distances, although the curves do give sums close to ideal for  $\text{HgCl}_2$ .

### Structure topology

The structure of pinchite, projected down the *a* axis, is shown in Figure 2. There is a very prominent compositional layering to the structural arrangement, the layers being parallel to (001). At  $z = 0$  and  $1/2$ , there are HgCl layers of Hg1 and Cl atoms; at  $z = 1/4$  and  $3/4$ , there are  $\text{Hg}_3\text{O}_4$  layers of Hg2, Hg3, and O atoms. These layers are linked by Hg1-O bonds and by Hg2-Cl bonds (Fig. 2). Inspection of the sheet at  $z = 0$  (Fig. 3a) shows a slightly distorted square array of Hg1 and Cl atoms. Comparison with Figure 1 shows this sheet to be an array of edge-sharing octahedra that link to adjacent layers by means of Hg1-O bonds orthogonal to the sheet. The sheet at  $z = 1/4$  (Fig. 3b) is more complex. The  $\text{Hg}_2\text{O}_4\text{Cl}_2$  polyhedra share edges to form chains extending along the *b* axis, and these chains are cross-linked in the *a* direction by the Hg3 atoms (the  $\text{Hg}_3\text{O}_4$  tetrahedra) to form the Hg-O sheet.

<sup>1</sup> A copy of Table 4 may be ordered as Document AM-94-570 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 2. Final atom parameters for pinchite

Site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Hg1	0.1405(1)	0.2145(1)	0	151(2)	170(5)	171(4)	112(3)	0	0	1(5)
Hg2	0.1618(1)	1/2	1/4	163(2)	222(5)	112(4)	153(3)	-25(2)	0	0
Hg3	0	0	1/4	228(4)	117(6)	186(7)	379(7)	0	0	0
Cl	0.1082(7)	0.275(1)	1/2	132(6)	88(29)	275(26)	272(28)	0	0	27(28)
O1	0.144(1)	0.199(2)	0.1754(6)	193(31)	300(79)	163(42)	114(33)	6(37)	-37(44)	-66(62)

\*  $U_i$  values have been multiplied by  $10^4$ .

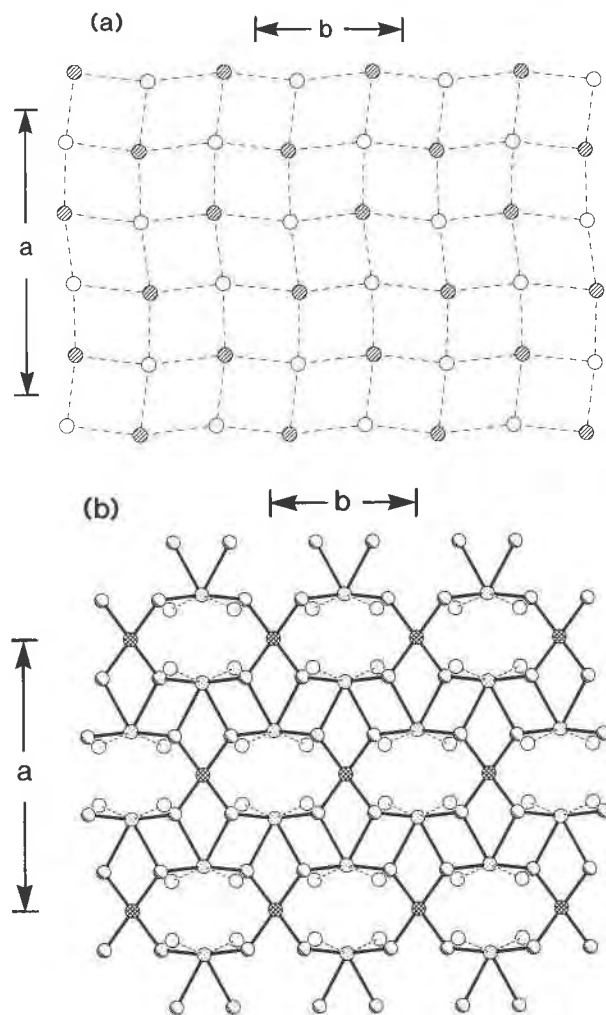


Fig. 3. The sheet elements in the crystal structure of pinchite projected down the *c* axis: (a) the sheet at  $z = 0$ ; (b) the sheet at  $z = 1/4$ ; legend as in Fig. 2.

TABLE 3. Selected interatomic distances (Å) and angles (°) in pinchite

Hg1-O1f	2.058(8) × 2	O1-Hg1-Cl <sup>b</sup>	89.0(4) × 2
Hg1-Cl <sup>a</sup>	2.917(8)	O1-Hg1-Cl <sup>b</sup>	91.3(4) × 2
Hg1-Cl <sup>b</sup>	2.916(8)	O1-Hg1-Cl <sup>c</sup>	92.7(3) × 2
Hg1-Cl <sup>c</sup>	3.142(6)	O1-Hg1-Cl <sup>d</sup>	87.6(3) × 2
Hg1-Cl <sup>d</sup>	3.008(6)	Cl <sup>b</sup> -Hg1-Cl <sup>c</sup>	95.5(2)
<Hg1-O>	2.06	Cl <sup>b</sup> -Hg1-Cl <sup>d</sup>	98.4(2)
<Hg-Cl>	3.00	Cl <sup>b</sup> -Hg1-Cl <sup>e</sup>	76.0(2)
		Cl <sup>b</sup> -Hg1-Cl <sup>f</sup>	90.1(2)
		O1 <sup>a</sup> -Hg2-O1 <sup>g</sup>	67.0(5)
Hg2-O1 <sup>c</sup>	2.04(1) × 2	O1-Hg2-O1 <sup>g</sup>	110.6(4) × 2
Hg2-O1 <sup>h</sup>	2.71(1) × 2	O1-Hg2-O1 <sup>g</sup>	79.6(5)
Hg2-Cl <sup>f</sup>	3.294(3) × 2	O1-Hg2-Cl	89.1(3) × 2
<Hg2-O>	2.38	Cl-Hg2-Cl <sup>f</sup>	158.3(3)
<Hg2-Cl>	3.29	Cl-Hg2-O1 <sup>g</sup>	71.5(2) × 2
		Cl-Hg2-O1 <sup>h</sup>	88.7(2)
		Cl-Hg2-O1 <sup>h</sup>	129.1(2) × 2
Hg3-O1 <sup>b,d,e</sup>	2.24(1) × 4	O1-Hg3-O12	134.2(4) × 2
<Hg3-O>	2.24	O1-Hg3-O1 <sup>d</sup>	114.3(6) × 2
		O1-Hg3-O1 <sup>e</sup>	83.7(7) × 2

Note:  $a = \bar{x} + 1/2, \bar{y} + 1/2, \bar{z} + 1/2$ ;  $b = \bar{x}, y, \bar{z} + 1/2$ ;  $c = x, \bar{y} + 1, \bar{z} + 1/2$ ;  $d = x, \bar{y}, \bar{z} + 1/2$ ;  $e = \bar{x}, y, z$ ;  $f = x, y, \bar{z}$ ;  $g = \bar{x} + 1/2, y + 1/2, z$ .

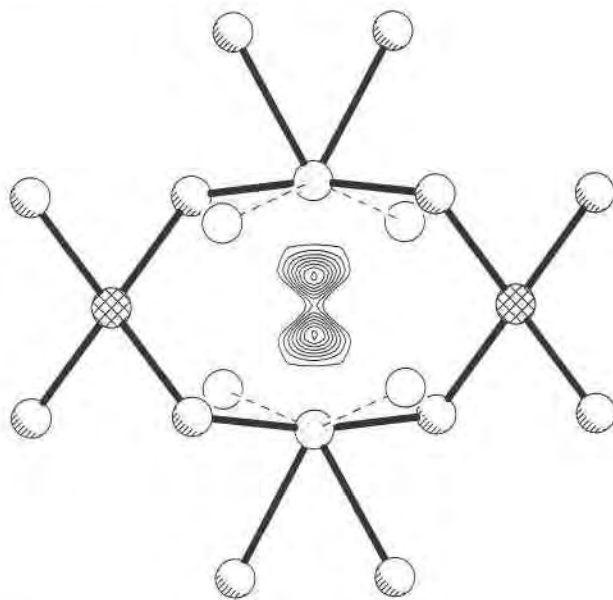


Fig. 4. Difference-Fourier map around the Hg2 atoms within the Hg-O plane in pinchite. The contours are from 1 to 2.4 e/Å<sup>3</sup>, and the contour interval is 0.2 e/Å<sup>3</sup>. Legend as in Fig. 1.

Also shown in Figure 3b are the Hg2-Cl bonds that link this sheet to the sandwiching Hg1-Cl sheets.

#### Lone-pair effects in pinchite

Divalent Hg is commonly lone-pair stereoactive. This typically results in a very asymmetrical (one-sided) coordination, with the lone pair positioned on the opposite side of the atom to the coordinating anions. Inspection of Figure 1 shows that Hg2 has the very one-sided coordination typical of stereoactive lone-pair behavior. As shown in Figure 3b, there are large interstices within the Hg-O layer, and Hg2 atoms occur on either side of these interstices, the lone pair of electrons presumably projecting out into this cavity. Figure 4 shows a difference-Fourier map through this cavity in the plane of the layer. There are two prominent maxima within the cavity, lying approximately 1.3 Å from the Hg2 positions; possibly these represent the lone pairs of electrons, although the distance of 1.3 Å seems large compared with distance of 0.6 Å, which is common for the lone pair of Pb<sup>2+</sup>.

TABLE 5. Bond-valence\* table for pinchite

	Hg1	Hg2	Hg3	Total
O	0.79 <sup>x21</sup>	0.83 <sup>x21</sup>	0.45 <sup>x41</sup>	2.20
Cl	0.16	0.13 <sup>x21</sup>		0.69
	0.16	0.07 <sup>x21</sup>		
	0.10			
	0.13			
Total	2.13	2.06	1.80	

\* Curves from Brown (1981).

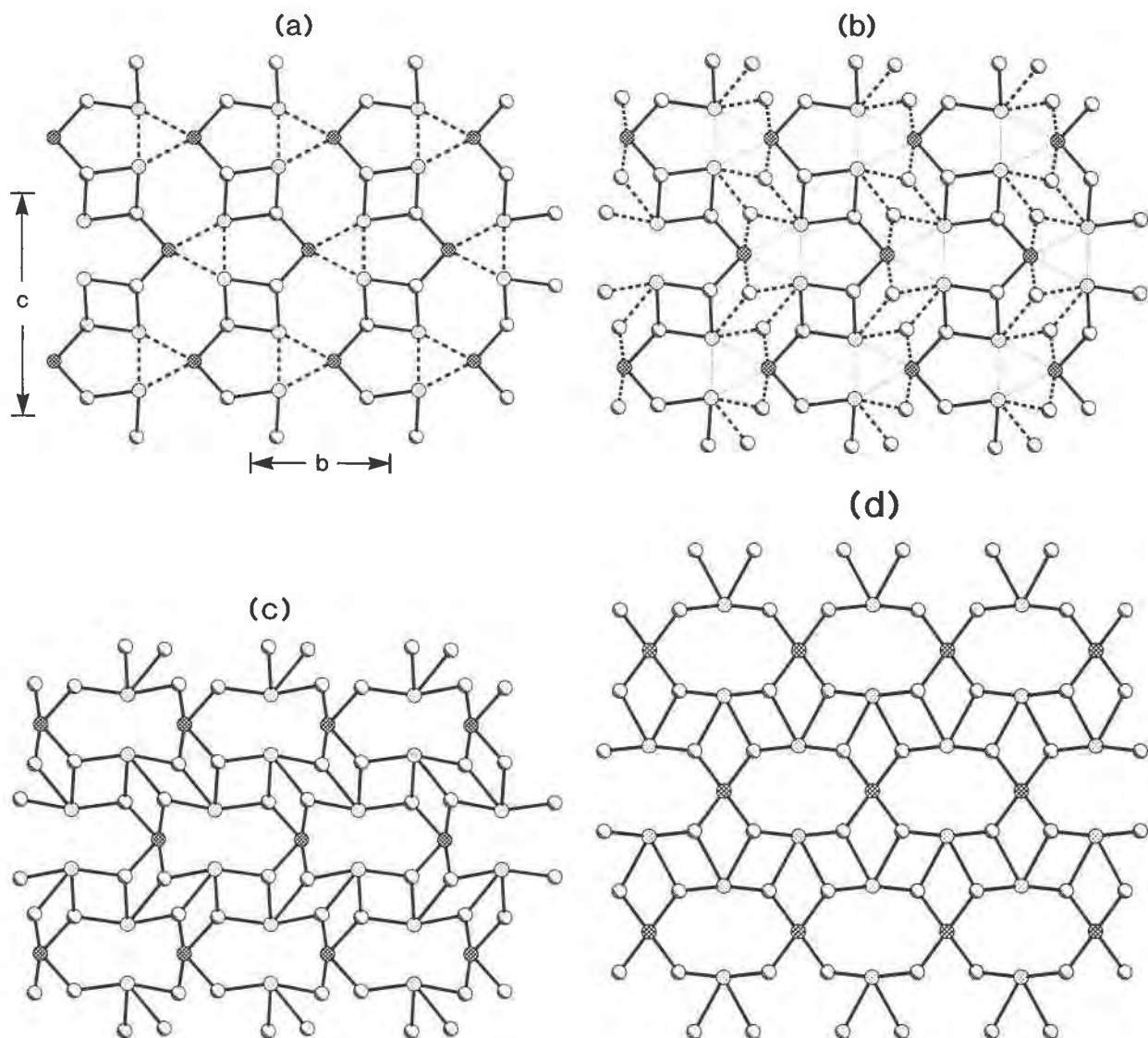


Fig. 5. The structural relationship between terlinguaite and pinchite: (a) the  $\text{Hg}_3\text{O}_2$  layer in terlinguaite;  $\text{Hg}^+-\text{Hg}^+$  bonds are shown as broken lines; (b) the addition of  $\text{O}^{2-}$  to a; previous  $\text{Hg}^+-\text{Hg}^+$  bonds are shown by dotted lines, and new  $\text{Hg}-\text{O}$  bonds are shown as broken lines; (c) the  $\text{Hg}-\text{O}$  layer resulting from this conceptual oxidation of a; note the fourfold coordination of all the Hg atoms within the plane; (d) adjustment of the layer in c to maximal symmetry; compare with Fig. 3b.

The  $\text{Hg}_3\text{O}_4$  tetrahedron shows extreme angular distortion (Table 3). Inspection of Figure 3b shows that, in principle, the atomic arrangement could exist with regular tetrahedral coordination of Hg3. However, the structure cannot relax in this way because of the opposing stereoactive lone pairs of electrons that project into these interstices (Figs. 3b and 4), and the  $\text{Hg}_3\text{O}_4$  tetrahedra are consequently very distorted.

#### Relationship to terlinguaite

Pinchite,  $\text{Hg}_3^+\text{O}_4\text{Cl}_2$ , is associated with terlinguaite,  $\text{Hg}_2^+\text{Hg}_3^+\text{O}_2\text{Cl}_2$ , the structure of which was described by Brodersen et al. (1989). Despite the difference in oxida-

tion state for some of the Hg atoms in pinchite and terlinguaite, their structures are closely related, both consisting of interleaved Hg-O and Hg-Cl layers. Figure 5a shows the Hg-O layer in terlinguaite. The dominating feature of this layer is the  $\text{Hg}_3^+$  trimer, in which there is a bonding interaction between adjacent  $\text{Hg}^+$  cations. Within the plane,  $\text{Hg}_3^+$  trimers are arranged at the nodes of a  $6_3$  net, and intertrimer linkage is provided by O atoms. Each  $\text{Hg}^+$  links to two O atoms, and each O atom is coordinated by three Hg atoms. The resulting arrangement has the stoichiometry  $\text{Hg}_3^+\text{O}_2$  and interleaves with HgCl layers (like pinchite, Fig. 3a). Thus the difference between pinchite and terlinguaite lies in the structure of

the Hg-O layers (Figs. 3b, 5a). The relationship between these two layers can be illustrated by a conceptual oxidation process, as depicted in Figure 5. The Hg-O layer of terlinguaite has six-sided interstices (Fig. 5a). If we introduce a pair of O atoms into each of these interstices, the arrangement of Figure 5b results. Each of these additional O atoms is threefold coordinated by Hg atoms and promotes the oxidation of  $\text{Hg}^+$  to  $\text{Hg}^{2+}$ , which breaks the  $\text{Hg}^+-\text{Hg}^+$  interaction (shown diagrammatically by dotted lines in Fig. 5b). The resulting arrangement is shown in Figure 5c. The linkage in Figure 5c is topologically identical to that in pinchite; allowing the Hg-O network in Figure 5c to flex to its maximal symmetry (Fig. 5d) results in the Hg-O layer of the pinchite structure. Thus an epitaxial relation between terlinguaite and pinchite seems possible, with terlinguaite overgrown by pinchite, with progressively oxidizing conditions of crystallization.

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