

REDETERMINATION OF THE CRYSTAL STRUCTURE OF HANAWALTITE

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ABSTRACT

The crystal structure of hanawaltite, $\text{Hg}_6\text{Hg}^{2+}\text{O}_3\text{Cl}_2$, a 11.796(4), b 13.890(6), c 6.471(2) Å, V 1060.2(6) Å³, space group $Pbma$, $Z = 4$, has been refined to an R index of 0.049 on the basis of 662 merged, observed reflections. The crystal structure has two distinct layers; a $\text{Hg}^+-\text{Cl}-\text{O}$ layer consisting of ribbons of $[\text{Hg}-\text{Hg}]^{2+}$ dimers resembling the configuration in the calomel structure and a $\text{Hg}^{2+}-\text{Hg}^+-\text{Cl}-\text{O}$ layer with alternating mercurous and mercuric oxychloride chains.

Keywords: hanawaltite, crystal structure, mercurous, mercuric, oxychloride.

SOMMAIRE

La structure cristalline de la hanawaltite, $\text{Hg}_6\text{Hg}^{2+}\text{O}_3\text{Cl}_2$, a 11.796(4), b 13.890(6), c 6.471(2) Å, V 1060.2(6) Å³, groupe spatial $Pbma$, $Z = 4$, a été affinée jusqu'à un résidu R de 0.049 en utilisant 662 réflexions observées regroupées. La structure est faite de deux couches distinctes: la couche $\text{Hg}^+-\text{Cl}-\text{O}$ contient des rubans de dimères $[\text{Hg}-\text{Hg}]^{2+}$ tout comme dans la structure du calomel, tandis que la couche $\text{Hg}^{2+}-\text{Hg}^+-\text{Cl}-\text{O}$ montre une alternance de chaînes d'oxychlorures mercureux et mercurique.

(Traduit par la Rédaction)

Mots-clés: hanawaltite, structure cristalline, mercureux, mercurique, oxychlorure.

INTRODUCTION

Hanawaltite, $\text{Hg}_6\text{Hg}^{2+}\text{O}_3[\text{Cl}(\text{OH})]_2$, was first described by Roberts *et al.* (1996). Although this was a very complete description of this new mineral species, the authors admitted that the crystal-structure determination was of poor quality. The poor refinement was attributable to the poor quality of the crystal available at the time. Recently, another sample was discovered at the type locality, in the lower workings of the Clear Creek claim, San Benito County, California. The present refinement of the structure does not refute the original description in any way, but the improved R index and related improved standard deviations of the atomic positions are worth recording.

EXPERIMENTAL

For the intensity-data measurements, a crystal fragment ($0.12 \times 0.10 \times 0.05$ mm) of hanawaltite was used. Intensity data were collected on a fully automated Siemens P3 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated $\text{MoK}\alpha$ radiation.

A set of 28 reflections was used to orient the crystal and to subsequently refine the cell dimensions. Two asymmetric units of intensity data were collected (*i.e.*, $+h \pm k + l$) up to $2\theta = 60^\circ$ using a $\theta:2\theta$ scan-mode with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. Information relevant to the data collection and structure determination is given in Table 1. Reduction of the intensity data, structure determination and initial refinement were accomplished by means of the SHELXTL (Sheldrick 1990) package of computer

TABLE 1. HANAWALTITE: DATA-COLLECTION INFORMATION

| | | | |
|--|--------------------|---|-------------|
| Space Group | <i>Pbma</i> (#57) | Measured reflections | 3016 |
| a (Å) | 11.796(4) | Merged reflections | 1619 |
| b (Å) | 13.890(6) | Observed reflections [$> 8\sigma(F)$] | 662 |
| c (Å) | 6.471(2) | $R(\text{int})$ | 0.094 |
| V (Å ³) | 1060.2(6) | Min/Max transmission | 0.047/0.010 |
| Radiation | $\text{MoK}\alpha$ | Refined parameters | 64 |
| μ (mm ⁻¹) | 102 | R index | 0.049 |
| Unit-cell contents: $4 \times \text{Hg}_6\text{Hg}^{2+}\text{O}_3[\text{Cl}(\text{OH})]_2$ | | | |

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TABLE 2. HANAWALTITE: ATOMIC PARAMETERS ($U_s \text{ \AA}^2 \times 10^4$) AND BOND-VALENCE SUMS

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} | U_{eg} | BVS |
|-----|-----------|-----------|-----------|----------|----------|----------|----------|----------|----------|----------|------|
| Hg1 | 0.1163(1) | 0.5831(1) | 0.4705(3) | 220(7) | 293(8) | 312(9) | 0(8) | -85(7) | -29(8) | 275(5) | 0.86 |
| Hg2 | 0.2915(2) | 0.6290(2) | 0.6751(3) | 265(7) | 369(10) | 314(10) | -10(9) | -89(7) | -86(8) | 316(5) | 0.81 |
| Hg3 | 0.0388(2) | ¾ | 0.1336(4) | 164(9) | 263(13) | 347(14) | 0 | 3(10) | 0 | 258(7) | 0.75 |
| Hg4 | 0.2457(2) | ¼ | 0.1495(5) | 174(9) | 440(17) | 397(15) | 0 | -3(1) | 0 | 337(8) | 0.95 |
| Hg5 | 0 | ½ | 0 | 193(9) | 294(11) | 268(12) | -6(1) | -18(9) | 17(10) | 252(6) | 1.54 |
| Cl1 | ¼ | ½ | 0.078(3) | 289(69) | 562(115) | 296(80) | 0 | 0 | 57(84) | 382(52) | 0.6 |
| Cl2 | 0.446(1) | ¾ | 0.335(3) | 167(58) | 589(108) | 262(77) | 0 | -4(6) | 0 | 339(48) | 0.79 |
| O1 | 0.360(3) | ¾ | -0.132(9) | 95(171) | 372(280) | 942(417) | 0 | -9(24) | 0 | 470(17) | 1.79 |
| O2 | -0.030(2) | 0.555(2) | 0.297(4) | 317(144) | 389(168) | 49(115) | 7(11) | 11(11) | 15(15) | 252(8) | 1.7 |

The bond-valence sums (BVS) were calculated from the constants of Brese & O'Keeffe (1991).

programs. For the ellipsoidal absorption correction, 12 intense diffraction-maxima in the range 8 to 57° 2 θ were chosen for Ψ diffraction-vector scans after the method of North *et al.* (1968). The merging *R* for the Ψ -scan data set (396 reflections) decreased from 18.3% before the absorption correction to 7.75% after the absorption correction.

The initial model for this structure was reported in Roberts *et al.* (1996). The final residual electron densities were +3.1 and -4.3 $e/\text{\AA}^3$. Calculation of the bond-valence sums, using the constants of Brese & O'Keeffe (1991), yield consistently low values for all of the anions and cations. It is evident that in minerals with a high degree of metallic bonding, these calculations are of limited use, but they helped substantiate the valence assignment to the O-atomic sites.

Table 2 contains the final positional and anisotropic displacement parameters and bond-valence sums, and Table 3, the selected interatomic distances. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada Ottawa, Ontario, Canada K1A 0S2.

DISCUSSION OF THE CRYSTAL STRUCTURE

Hanawaltite is one of the few minerals containing both valences of mercury, Hg⁺ and Hg²⁺. The Hg⁺ is typically in distinct [Hg-Hg]²⁺ dimers. The two crystallographically different dimers have Hg-Hg distances of 2.536 and 2.544 Å (Table 3). In addition to the Hg-Hg bond, each Hg in the pair is bonded to additional O and Cl atoms. In Table 3, one can see that the coordination varies for each Hg. The Hg-O bond is generally shorter than the Hg-Cl bond, the Hg4-Cl2 being an exception. Figure 1 shows additional O and Cl ligands as end-extensions to the dimer; they do not lie within the area

TABLE 3. HANAWALTITE: SELECTED BOND-DISTANCES (Å)

| | | | |
|-------------|----------|----------|----------|
| Hg1-Hg2 | 2.536(3) | Hg2-Hg1 | 2.536(3) |
| Hg1-O2 | 2.10(3) | Hg2-O1 | 2.27(5) |
| Hg1-O2a | 2.65(3) | Hg2-O2 | 2.34(3) |
| Hg1-Cl1 | 3.21(1) | Hg2-Cl1 | 3.20(1) |
| Hg1-Cl2 | 3.32(1) | Hg2-Cl2 | 3.34(3) |
| (Hg1-O) | 2.375 | (Hg2-O) | 2.305 |
| (Hg1-Cl) | 3.26 | (Hg2-Cl) | 3.27 |
| Hg3-Hg4 | 2.544(3) | Hg4-Hg3 | 2.544(3) |
| Hg3-O1 | 2.10(4) | Hg4-O1 | 2.18(7) |
| Hg3-O2 × 2 | 3.01(3) | Hg4-Cl2 | 2.56(2) |
| Hg3-Cl2 | 3.23(3) | | |
| Hg5-O2 × 2 | 2.10(3) | | |
| Hg5-Cl1 × 2 | 2.992(3) | | |

between the two Hg atoms. The result of this elongate aspect to the coordination is that the dimers form undulatory ribbons parallel to [100], with O and Cl atoms cross-linking the ribbons (Fig. 1a). There is one Hg²⁺ ion (the Hg5 site) and it has rhombic-planar coordination. Mercury, in its ground state, has the outer electronic configuration $5d^{10}6s^2$. This rather stable electronic configuration, referred to as the "inert pair" in books on inorganic chemistry, makes mercury relatively non-reactive, like Tl, Pb and Bi. When mercury does form compounds, the *d* shell remains full, leaving the *s* and *p* orbitals available for bonding. This ligand field is satisfied by linear, covalent bonds for Hg²⁺, as in the HgO chain structure. This near-linearity in the stereochemistry of Hg²⁺ can be seen in the structure of hanawaltite, with two, short Hg-O bonds of 2.10 Å being linear and cross-linked by two longer Hg-Cl bonds

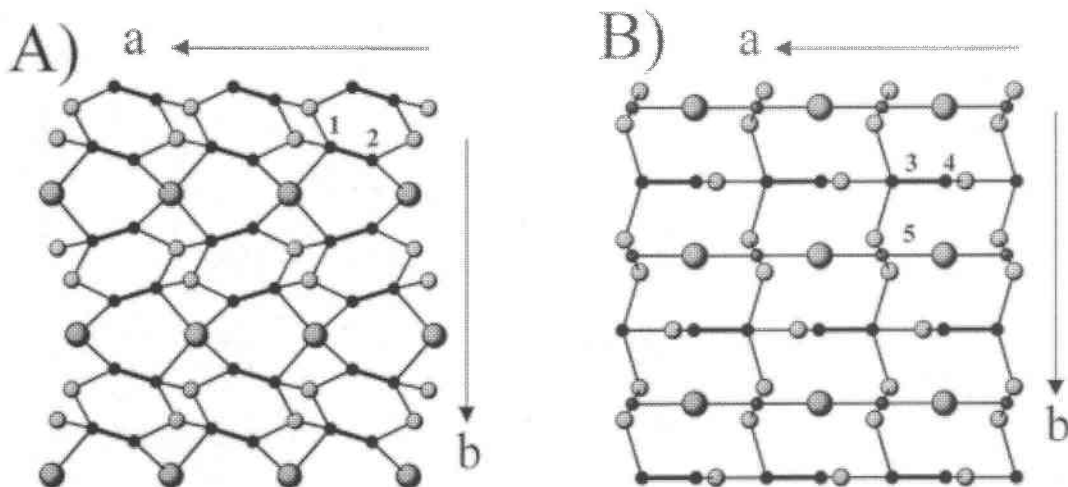


FIG. 1. The structure of hanawaltite projected on (001), showing: A) the $\text{Hg}^{2+}\text{-Cl-O}$ layer, and B) $\text{Hg}^{2+}\text{-Hg}^{2+}\text{-Cl-O}$ layer. The $[\text{Hg-Hg}]^{2+}$ dimers, represented as small, black circles with a solid bond, form undulating ribbons parallel to (100), whereas the Hg^{2+} atoms are single, small filled circles. The Cl atoms are larger and of a darker shade than the O atoms. The unit cell is indicated by vectors, and the integers refer to the Hg atom numbers given in Table 2.

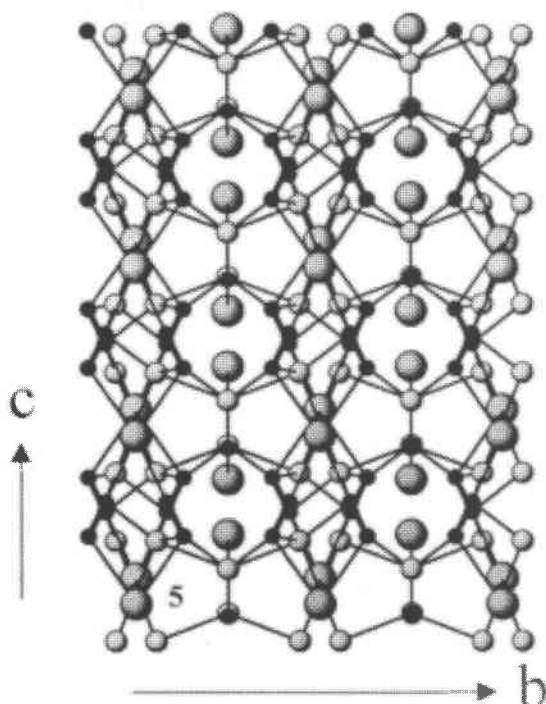


FIG. 2. The structure of hanawaltite projected on (100), showing the voids in the structure adjacent to the $\text{Hg}5$ site. Atom sizes and shading are as given in Figure 1. The unit cell is indicated by vectors, and the integer refers to the Hg atom number given in Table 2.

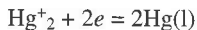
of 2.99 Å to complete the rhombic-planar coordination. An interesting feature of this stereochemistry is the apparent void space within the structure either side of the $\text{Hg}5$ atomic site (Fig. 2). This effect was interpreted as due to a stereoactive lone pair of electrons in the structure of pinchite, $\text{Hg}_5\text{O}_4\text{Cl}_2$ (Hawthorne *et al.* 1992).

The structure of hanawaltite consists of two chemically distinct layers. The $\text{Hg}^{2+}\text{-Cl-O}$ layer has ribbons of $[\text{Hg-Hg}]^{2+}$ dimers cross-linked by Cl and O atoms (Fig. 1). The configuration of this layer is much like that in the structure of calomel, with some of the Cl atoms replaced by O atoms. The second layer, $\text{Hg}^{2+}\text{-Hg}^{2+}\text{-Cl-O}$, is unique, as none of the other mercury oxychlorides have a mixed mercuric-mercurous layer (Fig. 1b). Here again the linear aspect of Hg coordination is evident, with alternating Hg^{2+} and $[\text{Hg-Hg}]^{2+}$ chains parallel to [100] and cross-linked parallel to [010]. Terlinguaite, the only other mercury oxychloride having both mercury ions, as established by crystal-structure analysis, has separate mercuric and mercurous layers: the mercuric layer with alternating Hg^{2+} and Cl^- ions as in the NaCl structure, and the mercurous layer with its distinctive Hg^+ trimer (Brodersen *et al.* 1989).

INSTABILITY OF MERCUROUS MINERALS

During the initial crystal-structure analysis of hanawaltite, the experiment was delayed owing to instrumental problems. For an entire year, the crystal remained in a glass vial on open shelving. At the time of the second collection of data, it became evident that the crystal had begun to decrepitate. Evidence of this

decrepitation was a 40% decrease in intensity measurements from the first dataset, formation of a small globule of native mercury on the surface of the crystal, and fracturing of the crystal. This decrepitation is attributed to photolysis:



In fact, in the presence of oxygen, the mercurous ion oxidizes so readily to Hg(l) and HgO that it is impossible to obtain mercurous oxide or hydroxide. Stabilization of oxychlorides is due to the halogen. In mercurous halides, the dissociation of the Hg–Hg bond decreases with decreasing electronegativity of the ligand anion. It is well known that calomel, Hg₂Cl₂, darkens upon exposure to sunlight, with decomposition into HgCl₂ and Hg(l) taking place. Other mercurous minerals that seem to photodecrepitate are terlinguaite, eglestonite and poyarkovite. Special precautions must be taken to preserve specimens believed to contain mercurous ions.

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