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# Eglestonite, $[Hg_2]_3Cl_3O_2H$: Confirmation of the chemical formula by neutron powder diffraction

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## Abstract

To settle the discussion on the chemical formula of eglestonite, synthetic material was investigated by X-ray single crystal, neutron powder diffraction, and IR spectroscopic methods. The results show unequivocally that the chemical formula is $[Hg_2]_3Cl_3O_2H$, although no peaks attributable to the OH stretching vibration were observed in the powder IR absorption spectrum. From the good agreement between the structures of natural and synthetic eglestonite, as determined by X-ray single crystal methods, it is suggested that they have the same chemical formula. The formula of the Br-dominant isotypic mineral kadyrelite, for which $Hg_4(Br,Cl)_2O$ was recently proposed, should also probably be modified to $[Hg_2]_3(Br,Cl)_3O_2H$.

## Introduction

The rare cubic mercury mineral eglestonite was first described based on a sample from Terlingua, Brewster County, Texas, by Moses (1904), who proposed the chemical formula $Hg_6Cl_3O_2$. On the basis of another chemical investigation, Hillebrand and Schaller (1909, 1910) modified the formula to $Hg_4Cl_2O$. This formula was generally accepted for more than half a century, e.g., by Wolfe (Palache et al., 1951), who determined $a$ = 16.00(4) Å for probable space group *Ia3d,* by Hedlik (1950), who approximately located the Hg atoms in a subcell with $a/2$, and by Rouse (1975), who found $a$ = 16.0398(3) Å and space group *Ia3d.* Mereiter and Zemann (1976) determined the crystal structure on material from the same locality by X-ray methods [$a$ = 16.036(3) Å, space group *Ia3d*]. They found a cell content of 96 Hg, 48 Cl, and 32 O atoms, i.e., with a ratio Hg:Cl:O = 6:3:2, as given by Moses (1904). This stoichiometry, the presence of mercury as $Hg_2$ dumbbells characteristic of Hg(I), the presence of 16 O-O contacts per unit cell with O-O = 2.59(7) Å, and the location of the O atoms at the apices of trigonal $OHg_3$ pyramids caused the authors to postulate that the unit cell contains 16 H atoms at or near position 16(*a*) and to propose for eglestonite the chemical formula $[Hg_2]_3Cl_3O_2H$. This proposal was supported by analytical $H_2O$ determinations of eglestonite synthesized under hydrothermal conditions, yielding 0.62, 0.75, and 0.74 wt% $H_2O$, as compared with the theoretical value of 0.67 wt% for $[Hg_2]_3Cl_3O_2H$.

The formula of Mereiter and Zemann (1976) was rejected by Vershkovskaya et al. (1979) and by Kovaleva and Vasiliev (1987) because IR investigations of eglestonite powder from occurrences in the USSR did not show bands for the OH stretching vibration. From this observation, they decided to return to the formula $Hg_4Cl_2O$ of Hillebrand and Schaller (1910), which was also used for Br-bearing eglestonite (Vasiliev and Lavrentiev, 1986) and for the Br-dominant eglestonite analogue kadyrelite (Vasiliev, 1987).

The controversy regarding the formula of eglestonite thus concerns the H content as well as the ratio Hg:Cl:O. In this paper we present the results of new investigations of synthetic eglestonite, carried out in the hope of solving the problem. Extension of the neutron investigation to naturally occurring eglestonite was unfeasible because of the scarcity of the material.

## X-ray single crystal study of synthetic eglestonite

From the same lot of synthetic eglestonite used by Mereiter and Zemann (1976) for the analytical $H_2O$ determination mentioned above, a dodecahedron with a diameter of ~0.04 mm was selected for a structure determination on an X-ray four-circle diffractometer (Philips PW1100, Mo$K\alpha$ radiation, graphite monochromator). Space group *Ia*3*d* and $a$ = 16.036(4) Å were found, as for natural eglestonite from Terlingua (cf. Palache et al., 1951; Rouse, 1975; Mereiter and Zemann, 1976). Intensities of reflections (395) with $\theta$ = 2–25° were measured by $\omega$ scans with a scan range of 0.7°, corrected for absorption ($\mu$ = 898 cm$^{-1}$, transmission factors 0.151–0.176), and merged to 193 unique observed reflections

**TABLE 2.** Comparison of atomic parameters of natural and synthetic eglestonite

| Atom | | $x$ | $y$ | $z$ | $B_{iso}/B_{eq}$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Hg | NX | 0.17208(7) | 0.01365(9) | 0.00908(9) | 2.31 | 1.04(5) | 2.99(7) | 2.90(8) | −0.01(5) | 0.10(5) | 0.25(6) |
| | SX | 0.17220(7) | 0.01354(9) | 0.00911(10) | 2.30 | 1.04(5) | 3.08(7) | 2.77(8) | 0.04(5) | 0.17(5) | 0.12(6) |
| | SN | 0.17229(7) | 0.01331(10) | 0.00910(10) | 2.18 | 0.89(6) | 3.02(13) | 2.62(14) | −0.02(7) | 0.01(7) | 0.05(8) |
| Cl | NX | ⅛ | 0.36297(44) | ¼ − $y$ | 1.60(18) | | | | | | |
| | SX | ⅛ | 0.36416(46) | ¼ − $y$ | 1.96(19) | | | | | | |
| | SN | ⅛ | 0.36352(10) | ¼ − $y$ | 1.50(4) | | | | | | |
| O | NX | 0.0466(12) | $x$ | $x$ | 1.80(60) | | | | | | |
| | SX | 0.0446(11) | $x$ | $x$ | 1.13(60) | | | | | | |
| | SN | 0.0449(2) | $x$ | $x$ | 1.12(10) | | | | | | |
| H | SN | 0.0069(11) | $x$ | $x$ | 1.63(38) | | | | | | |

*Note:* NX = natural eglestonite, X-ray data of Mereiter and Zemann (1976). SX = synthetic eglestonite, X-ray data, this work. SN = synthetic eglestonite, neutron powder data, this work. Space group *Ia*3*d*, *a* = 16.036(3) Å, *Z* = 16 $Hg_6Cl_3O_2H$. H position statistically occupied by 16 H atoms per unit cell.

[$R_{merge}$ = 0.025, cutoff $I > 2\sigma(I)$]. Least-squares refinements were initiated with the atomic parameters of natural eglestonite (Mereiter and Zemann, 1976), and converged with weights $\omega = 1/[\sigma^2(F_o) + 0.0002 \cdot F_o^2]$ to $R$ = 0.044, $R_w$ = 0.038, and $S$ = 1.09, and resulted in only minor parameter shifts. Tests of the occupancy factors of Hg, Cl, and O did not indicate the presence of vacancies. All calculations were carried out with the program SHELX76 (Sheldrick, 1976), using neutral atom scattering functions with anomalous dispersion terms. Table 1[1] contains observed and calculated structure factors, and atomic parameters are given in Table 2. Table 4 contains interatomic distances for this refinement and for refinements of natural material and by neutron diffraction for comparison.

## NEUTRON POWDER DIFFRACTION STUDY OF SYNTHETIC EGLESTONITE

A 0.5-g sample of synthetic eglestonite from the same lot as that used by Mereiter and Zemann (1976) and contaminated by some $Hg_2Cl_2$ was sealed in a thin-walled V can, and a neutron powder diffraction pattern was taken at a nominal wavelength of 1.595 Å on the high-resolution neutron powder diffractometer D2B at the ILL, Grenoble, France. Diffraction data were measured in 0.025° steps over an angular range of 0–165°. The data were analyzed in the $2\theta$ range 12–150° with a multiphase powder neutron profile refinement program (Wiles and Young, 1981; Schneider, 1987). The refinement was initiated with the structure data of Mereiter and Zemann (1976), taking into account the $Hg_2Cl_2$ admixture, and converged at $R_p$ = 0.20 and $R_{wp}$ = 0.18. A Fourier synthesis calculated at this stage showed a distinct negative scattering density at or close to 0,0,0, which could be attributed only to the presence of a H atom at this location. Its introduction into the calculations caused a significant drop in $R$ values (by ≈0.05), but with little difference between placement of the H atom at the center of symmetry [0,0,0; position 16($a$), site symmetry $\overline{3}$] and placement nearby at $x = y = z \approx 0.006$ on the threefold axis [position 32($e$), site symmetry 3, half occupancy]. Both positions are located between a pair of closely spaced O atoms and correspond to a centered or an off-centered O-H-O H bond. Trial refinements showed that the O and the centered H position are fully occupied with an uncertainty of a few percent. Technical details of the final refinement were 22 varied parameters for eglestonite, consisting of one scale factor, Gaussian profile with three peak half-width parameters, asymmetry, angular zero, lattice constant $a$, six positional parameters, six anisotropic thermal parameters for Hg and isotropic thermal parameters for Cl, O, and H. Only the scale factor was varied for the $Hg_2Cl_2$ admixture, and peak shape, asymmetry, and zero point were the same as for eglestonite; structure and unit-cell data of $Hg_2Cl_2$ from Dorm (1971) were not varied. Scattering lengths Hg = 12.66, Cl = 9.5792, O = 5.805, and H = −3.7409 (in fm) according to Koester et al. (1981). Final agreement factors were $R_p$ = 0.142, $R_{wp}$ = 0.111,

**TABLE 4.** Interatomic distances (Å) and angles (°)

| | NX | SX | SN |
|---|---|---|---|
| Hg-Hg$^{a}$ | 2.516(2) | 2.512(2) | 2.509(3) |
| Hg-Cl$^{b}$ | 3.010(6) | 3.026(6) | 3.015(2) |
| Hg-Cl$^{c}$ | 3.030(2) | 3.025(2) | 3.025(2) |
| Hg-Cl$^{d}$ | 3.095(8) | 3.076(8) | 3.090(3) |
| Hg-O | 2.165(7) | 2.182(7) | 2.182(2) |
| O-O$^{e}$ | 2.59(7) | 2.48(7) | 2.494(11) |
| O-H | | | 1.055(32) |
| Hg$^{a}$-Hg-Cl$^{b}$ | 95.9(2) | 96.2(2) | 96.1(1) |
| Hg$^{a}$-Hg-Cl$^{c}$ | 108.1(1) | 108.3(1) | 108.3(1) |
| Hg$^{a}$-Hg-Cl$^{d}$ | 102.5(1) | 102.3(1) | 102.4(1) |
| Hg$^{a}$-Hg-O | 162.7(9) | 164.2(9) | 163.9(2) |
| Cl$^{b}$-Hg-Cl$^{c}$ | 78.9(1) | 79.1(1) | 79.1(1) |
| Cl$^{b}$-Hg-Cl$^{d}$ | 77.9(2) | 78.3(2) | 78.1(1) |
| Cl$^{c}$-Hg-Cl$^{d}$ | 143.1(2) | 143.6(2) | 143.3(1) |
| Cl$^{b}$-Hg-O | 100.9(9) | 99.1(9) | 99.6(2) |
| Cl$^{c}$-Hg-O | 79.1(3) | 78.5(3) | 78.7(1) |
| Cl$^{d}$-Hg-O | 77.6(3) | 77.3(3) | 77.2(1) |
| Hg-O-Hg$^{f}$ | 114.6(7) | 113.5(7) | 113.7(1) |
| Hg-O-H | | | 113.7(1) |

*Note:* NX = natural eglestonite, X-ray data of Mereiter and Zemann (1976). SX = synthetic eglestonite, X-ray data, this work. SN = synthetic eglestonite, neutron powder data, this work. Symmetry code: none *x, y, z*; (a) ½ − *x, y,* −*z*; (b) −*z, x, y* − ½; (c) ½ − *y, z,* −*x*; (d) *x,* ½ − *y,* −*z*; (e) −*x,* −*y,* −*z*; (f) *z, x, y*.

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[1] Copies of Tables 1 and 3 may be ordered as Document AM-92-501 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.

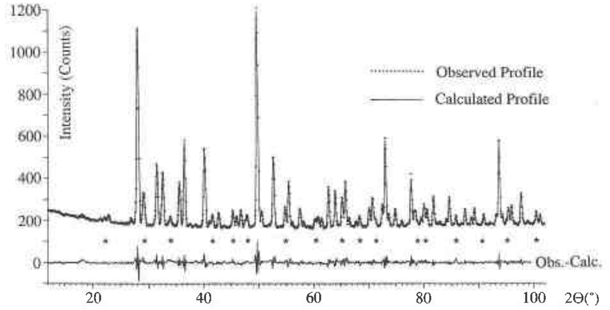

Fig. 1. Observed and calculated neutron diffraction profile of synthetic eglestonite contaminated with ~8 wt% $Hg_2Cl_2$. Only part ($2\theta = 12-102°$) of the complete pattern ($2\theta < 150°$) is shown. Stars indicate where $Hg_2Cl_2$ contributes significantly to the profile. A difference (observed-calculated) curve appears at the bottom of the figure.

and $R_1 = 0.065$. A plot of the profile is shown in Figure 1, numeric details and profile data are given in Table 3, and atomic parameters are given in Table 2. According to the refined scale factors the sample contained 8.5 wt% $Hg_2Cl_2$. The results of the neutron diffraction confirm that the analytical $H_2O$ content of synthetic eglestonite found by Mereiter and Zemann (1976) is due to the presence of structural H atoms.

## IR SPECTRA

Infrared spectra of pure hand-picked synthetic eglestonite were recorded in the range $\nu = 4000-300$ cm$^{-1}$ with a Perkin-Elmer grating spectrometer and the KCl pellet technique. The spectra agree with those published by Vershkovskaya et al. (1979) and by Kovaleva and Vasiliev (1987) in that they show no recognizable absorption band between 4000 and 500 cm$^{-1}$, the range in which OH valence vibrations are known to occur. The first observable band is at approximately 400 cm$^{-1}$ (very broad) and was attributed by Vershkovskaya et al. (1979) to Hg-O vibrations. A few additional bands were found below 300 cm$^{-1}$ by the authors mentioned above.

Part of our sample used for IR spectroscopy was heated in a closed tube, resulting in the formation of condensed $H_2O$, whereas blank tests with $Hg_2Cl_2$ were negative in that respect. This test demonstrated that routine powder IR spectroscopy failed to detect a significant amount of bonded H in the case of eglestonite.

## DISCUSSION

The structure of eglestonite consists of four interpenetrating cubic (10,3) nets (Wells, 1984) of composition $(Hg_2)_3O_2$ in which O atoms form three O-Hg bonds and are connected by Hg-Hg dumbbells situated along each link of the net. The nets are held together by short O-H-O bonds and by Cl ions coordinated to six Hg atoms in the form of a distorted octahedron (Fig. 2). The coordination figure of Hg, formed by one Hg atom, three Cl atoms, and one O atom, is irregular (cf. Mereiter and Zemann, 1976).

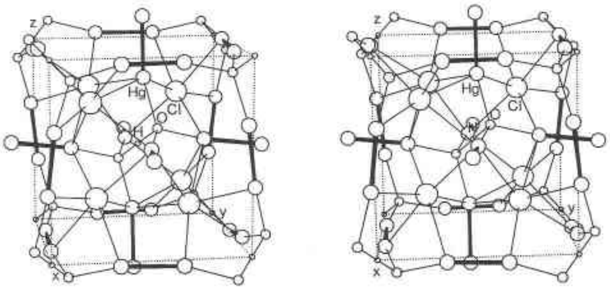

Fig. 2. Stereoscopic view of ½ × ½ × ½ of the unit cell of eglestonite. For simplicity, and in contrast to coordinates in Table 2, H atoms were drawn in centered positions ($x,y,z$ = 000 and equivalent positions).

The most important results of our present investigation are

1. In confirmation of the earlier X-ray investigation of natural eglestonite by Mereiter and Zemann (1976), the present X-ray single crystal and neutron powder diffraction study shows that in synthetic eglestonite the atomic ratio Hg:Cl:O is also 6:3:2 and not 4:2:1, as proposed by Hillebrand and Schaller (1910), Vershkovskaya et al. (1979), and Kovaleva and Vasiliev (1987) for natural material.

2. Neutron powder diffraction confirms that the analytical $H_2O$ content of synthetic eglestonite (Mereiter and Zemann, 1976) did not originate from intergranular $H_2O$ or from fluid inclusions but is due to structural H atoms that are bonded to O atoms. These H atoms are in positions previously derived from crystal chemical arguments and take part in the formation of short O-H-O type H bonds. Because all atomic positions are fully occupied within the limits of experimental accuracy, the chemical formula of synthetic eglestonite is confirmed to be $[Hg_2]_3Cl_3O_2H$, as proposed by Mereiter and Zemann (1976).

3. Synthetic and natural eglestonite show very good agreement in the structure data determined by X-ray single crystal methods (Table 2; differences between atomic parameters of NX and SX divided by their pooled estimated standard deviations vary between 0.2 and 1.9; no evidence exists for a partial occupancy of the Hg,Cl, and O sites). Therefore, we have to conclude that they both contain H atoms at the same location, as found by neutron powder diffraction from synthetic eglestonite. Omitting H from the chemical formula of natural eglestonite would induce valencies contradicting general experience and, further, O···O distances clearly less than all well-established Van der Waals distances (Zemann, 1986).

4. The O-H-O H bond in eglestonite, for which an O-O distance of 2.59(7) Å was found previously (X-ray data; Mereiter and Zemann, 1976), is only 2.49(1) Å in synthetic eglestonite (neutron data). This is one of the shortest known H bonds between two otherwise exclusively metal-bonded O atoms. Because of its length, which exceeds the shortest known types of O···O H bonds by approximately 0.05 Å, the O-H-O bond in eglestonite is

probably asymmetric, and not symmetric, as ideally required by the centrosymmetric space group *Ia*3*d*. The structure model preferred for the final neutron powder refinement is in agreement with this assumption, and the structure may be regarded as disordered in this respect.

5. Whereas the experimental results of our IR investigations on synthetic eglestonite agree very well with those of Vershkovskaya et al. (1979) and Kovaleva and Vasiliev (1987) on natural material, the conclusions are different. As the same material that gave IR spectra with no OH peaks gave rise to analytical $H_2O$ and resulted in H in the structure located through neutron diffraction studies, we must conclude that eglestonite is one of those compounds with short H bonds for which IR spectra are insensitive to OH stretching vibrations—at least for routine powder work. Another such example among minerals is pectolite, with a short H bond of $O \cdots O = 2.473(2)$ Å (Takéuchi and Kudoh, 1977), for which difficulties in detecting OH in the IR absorption spectra were reported (Ryall and Threadgold, 1966; Hammer, 1989).

6. As the chemical formulas of Br-bearing eglestonite and the Br-dominant analogue kadyrelite, determined by Vasiliev and Lavrentiev (1986) and Vasiliev (1987), respectively, are not in agreement with the well-established ratio of Hg:Cl:O = 6:3:2 for both natural and synthetic eglestonite, and as their methods for the determination of H were not adequate, we suggest that the general form of the chemical formula of eglestonite, $[Hg_2]_3Cl_3O_2H$, should also be applied to Br-bearing eglestonite and kadyrelite.

It is useful to emphasize the difficulties in recording signals of OH stretching vibrations by routine IR methods occur only if the corresponding H bond is very short. In the much more common cases with medium to long H bonds, say with $O \cdots O > 2.6$ Å, IR spectroscopy is very sensitive, as noted in the investigation of shakovite, $[Hg_2]_2SbO_3(OH)_3$ (Tillmanns et al., 1982).

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