

SrHg₂O₂Cl₂, the First Strontium Mercury Oxychloride. Crystal Structure Determination by *ab Initio* Powder Methods

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Little work has been reported on simple inorganic compounds containing Sr and Hg in combination.¹ Here, we report the synthesis and *ab initio* structure determination from powder data of SrHg₂O₂Cl₂, the first strontium mercury oxychloride.

SrHg₂O₂Cl₂ was prepared by the solid-state reaction of SrO₂ and Hg₂Cl₂, resulting in a rusty brown powder. An electron microprobe analysis indicated an Sr:Hg ratio of 1:1.96 (estimated uncertainty ±2%). We were unable to prepare single crystals of SrHg₂O₂Cl₂ for conventional structure determination; hence, the crystal structure was determined by *ab initio* methods^{2–4} using laboratory X-ray powder diffractometer data. A joint Rietveld refinement⁵ against X-ray powder data and neutron powder diffraction data allowed the light-atom positions (O and Cl) to be located to satisfactory precision.

SrHg₂O₂Cl₂ (Table 1, Figures 1 and 2) contains seven distinct atoms. The strontium cation is coordinated by three O atoms and five Cl atoms in irregular coordination. The two Hg atoms show approximately linear “dumbbell” O–Hg–O coordination [$d_{\text{av}}(\text{Hg–O}) = 2.07 \text{ \AA}$], which is characteristic of divalent mercury.⁶ Thus, during the synthesis, Hg^I was oxidized to Hg^{II}, with concurrent reduction of peroxide to oxide ions.⁷ Hg(1) also bonds to a third oxygen atom, resulting in an unusual T-shaped Hg(1)O₃ grouping. Three chlorine atoms complete the irregular Hg(1)O₃Cl₃ coordination polyhedron. Hg(2) bonds to four Cl atoms, in addition to its two O atom neighbors, resulting in a distorted Hg(2)O₂Cl₄ octahedron. Nonbonded Hg···Hg distances of >3.1 Å are found in SrHg₂O₂Cl₂, which are characteristic of Hg^{II}, as opposed to Hg^I, for which Hg–Hg bonding contacts of

Table 1. Atomic Positional/Thermal Parameters for SrHg₂O₂Cl₂

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (Å ²)
Sr(1)	0.3737(4)	0.6224(5)	0.7237(5)	0.006(1)
Hg(1)	0.3673(3)	0.1654(4)	0.4721(3)	0.0090(7)
Hg(2)	0.1038(3)	0.4349(4)	0.3711(3)	0.0096(6)
Cl(1)	0.1160(4)	0.1026(5)	0.1580(4)	0.012(1)
Cl(2)	0.3724(4)	0.3224(5)	0.9661(4)	0.0104(9)
O(1)	0.0041(5)	0.4253(8)	0.8326(6)	0.007(2)
O(2)	0.2307(5)	0.3214(8)	0.5782(6)	0.007(2)

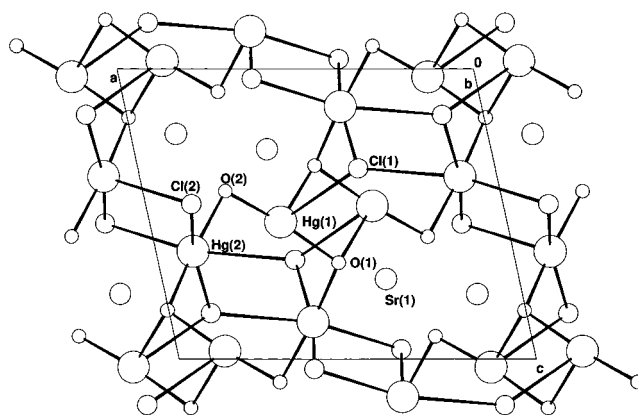


Figure 1. View down [010] of the SrHg₂O₂Cl₂ structure. Atoms are represented by spheres of arbitrary radius.

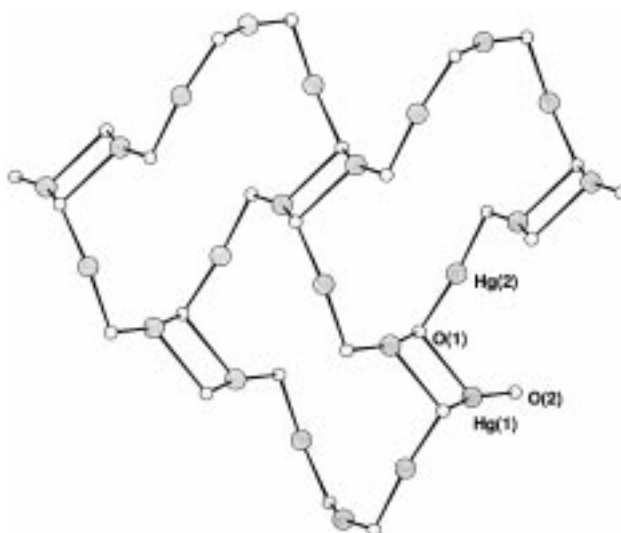


Figure 2. Detail of the SrHg₂O₂Cl₂ structure showing part of an infinite mercury/oxygen sheet.

~2.5 Å occur.⁶ The bond angles about the two distinct oxygen atoms are both approximately tetrahedral [O(1) bonds to 1 Sr + 3 Hg; O(2) bonds to 2 Sr + 2 Hg]. The Cl(1) atom bonds to two Sr and five Hg neighbors in irregular coordination. Cl(2) is coordinated to three Sr and two Hg atoms which form an

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- (4) Unit cell by autoindexing; space group of $P2_1/n$ by inspection; structure solution (Hg, Sr atoms) by intensity extraction followed by direct methods; Rietveld refinement and Fourier difference maps to locate O and Cl species. Full details and software references are given in the Supporting Information.
- (5) Neutron diffraction: ~10 g sample, cylindrical vanadium sample can, $T = 298$ (2) K, diffractometer HRNPD (Brookhaven National Laboratory), $\lambda = 1.8832(1) \text{ \AA}$. A joint X-ray/neutron Rietveld refinement resulted in a satisfactory solution ($R_p = 3.89\%$, $R_{wp} = 4.83\%$, X-ray $R(F^2) = 5.98\%$, neutron $R(F^2) = 8.77\%$, $\chi^2 = 3.21$, 4199 data points, 75 parameters, residuals defined in ref 7). Four regions containing peaks due to a small amount of an unidentified impurity phase were excluded from the neutron data ($d = 2.75, 2.48, 1.43, 1.24 \text{ \AA}$). A fixed absorption correction (μ_r effective = 0.5) was applied to the neutron data to account for the substantial absorption of mercury at this wavelength. Crystal data: SrHg₂O₂Cl₂, $M_r = 591.71$, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.9432(4) \text{ \AA}$, $b = 7.0226(3) \text{ \AA}$, $c = 8.2877(3) \text{ \AA}$, $\beta = 102.441(1)^\circ$, $V = 565.44(6) \text{ \AA}^3$, $Z = 4$.
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approximate square-based pyramid about this atom (Hg in the apical position). Bond valence calculations for the constituent atoms in $\text{SrHg}_2\text{O}_2\text{Cl}_2$ were in accordance with their expected values.⁸

$\text{SrHg}_2\text{O}_2\text{Cl}_2$ crystallizes as a new structure type with significant two-dimensional character. Infinite, formally neutral, sheets of stoichiometry $[\text{Hg}_2\text{O}_2]_\infty$ are arrayed normal to the $[\bar{1}01]$ direction (Figure 2). These sheets are built up from pairs of $\text{O}(1)\text{—Hg}(1)\text{—O}(2)$ dumbbell units, which fuse together *via* $\text{Hg}(1)\text{—O}(1)$ bonds to result in “4-rings” of alternating $\text{Hg}(1)$ and $\text{O}(1)$ atoms. The $\text{Hg}(2)$ cation makes a dumbbell link to $\text{O}(1)$ and $\text{O}(2)$ neighbors in adjacent 4-rings, resulting in highly puckered, infinite layers. The Sr^{2+} and Cl^- species then serve to “pillar” the $[\text{Hg}_2\text{O}_2]_\infty$ sheets into a three-dimensional structure. An alternative way to picture the structure (Figure 1) reveals a complex network of Hg, O, and Cl atoms surrounding one-dimensional channels propagating along $[010]$, which are occupied by the strontium cations. There is no suggestion, however, that the Sr species show any mobility in these channels.

The structure of $\text{SrHg}_2\text{O}_2\text{Cl}_2$ is completely different from that of $\text{BaHg}_2\text{O}_2\text{Cl}_2$, and its isostructure $\text{PbHg}_2\text{S}_2\text{I}_2$,⁹ in which isolated

Hg_4O_4 and Hg_4S_4 squares, respectively, are found. The T-shaped $\text{Hg}(1)\text{O}_3$ local coordination in $\text{SrHg}_2\text{O}_2\text{Cl}_2$ is rare. In one form of mercury oxychloride, $\text{Hg}_6\text{O}_4\text{Cl}_4$,¹⁰ some Hg^{II} atoms are three-coordinated to O but in flat pyramidal geometry, as opposed to the T-shape found here. The most common “isolated” O—Hg—O dumbbell coordination occurs in most mercury(II) compounds including high- T_c superconductor related phases such as $(\text{Hg}_{0.5}\text{Bi}_{10.5})(\text{Sr}_{1.5}\text{La}_{0.5})\text{CuO}_5$.¹¹

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Supporting Information Available: Text describing the synthesis and structure determination procedures, a listing of geometrical data, and figures showing final Rietveld difference profile plots (8 pages). Ordering information is given on any current masthead page.

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