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# Crystal structure of barstowite ($3PbCl_2 \cdot PbCO_3 \cdot H_2O$)

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## ABSTRACT

The crystal structure of barstowite ($3PbCl_2 \cdot PbCO_3 \cdot H_2O$, $P2_1/m$, $a = 4.2023(5)$, $b = 9.2020(7)$, $c = 16.6608(6)$ (Å), $\beta = 91.829(9)°$) from Bounds Cliff, St Endellion, Cornwall, has been determined to an R = 0.036. The structure can be described in terms of three layers stacked along [001] in the sequence ...CACBCACBC... to give a 16.7 Å repeat. Layer A consists of face-sharing $PbCl_8$ distorted square antiprisms. Layer B is composed of Pb coordinated to 5 Cl and 2 O each with two H to form $H_2O$ groups. Layer C is formed by Pb coordinated to 5 Cl and 3 O which are from $CO_3$ groups. The H positions are deduced and are H-bonded to O from carbonates. The structural details were in agreement with previous deductions based on infrared spectra.

**KEYWORDS:** barstowite, phosgenite, crystal structure, Bounds Cliff, Cornwall.

## Introduction

LEAD forms a wealth of compounds with various anionic species including $CO_3$, $SO_4$, OH, Cl, $H_2O$, and O; commonly two or more anion species may be incorporated into a structure adding to the chemical diversity. Barstowite was described by Stanley *et al.* (1991) and represents a combination of Pb with $CO_3$, Cl and $H_2O$, which clearly formed by the action of sea water on cerussite. The conversion of one Pb mineral to another by alteration of a primary Pb mineral to secondary Pb mineral(s) is a common phenomenon. However, there are additional processes which are possibly more common as they occur in the environment, or are industrially useful where Pb forms similar compounds. The natural occurrences which are amenable to careful examination may provide insight as to what compounds and reactions may occur on particles (e.g. Pb pollutants in soils) or surfaces which are difficult to characterize. Likewise, Pb compounds are used extensively in some commercial applications (e.g. stabilizers for polyvinyl chloride) and undergo reactions where anion exchange occurs ($3PbO \cdot PbSO_4 \cdot H_2O \rightarrow 3PbO \cdot PbSO_4 \cdot Cl_2$).

The ways in which Pb interacts with the environment are important. By characterizing natural compounds in extensive detail, the knowledge of possible reactions, coordinations and structural elements increase our understanding of the stereochemistry of Pb compounds forming on much smaller scales. We describe here, a further way in which Pb can combine with several anion units, as elucidated in the structure of barstowite.

## Experimental details and structure solution

The occurrence of barstowite and its properties have been described by Stanley *et al.* (1991). A small, polycrystalline fragment was obtained from the Natural History Museum sample (BM 1990,25) and from this, crystals were selected for single crystal studies. The fine, sub-parallel intergrowth prevented easy separation of a single crystal and only after numerous attempts was a suitable single crystal obtained.

The sample selected for single crystal data collection was irregular; its dimensions are given in Table 1. The crystal was mounted and oriented on an automated Picker-Krisel 4-circle diffract-

TABLE 1. Experimental details and crystallographic data for barstowite

| | |
|---|---|
| (A) Crystal-cell data | |
| *a* (Å) | 4.2023(5) |
| *b* (Å) | 9.2020(7) |
| *c* (Å) | 16.6608(6) |
| β (°) | 91.829(9) |
| *V* (Å$^3$) | 643.94(9) |
| Space group | $P2_1/m$ |
| Z | 2 |
| Formula | $3PbCl_2 \cdot PbCO_3 \cdot H_2O$ |
| $D_{calc}$ (g cm$^{-3}$) | 5.774 |
| μ (mm$^{-1}$) | 53.36 |
| (B) Intensity measurements | |
| Crystal size | 30 × 50 × 105 μm |
| Diffractometer | Picker, Krisel control |
| Monochromator | Graphite |
| Radiation | Mo-*K*α, λ = 0.71069 Å |
| Scan type | ω |
| 2θ range | 3.5–55.0 |
| Diffractions measured | 6999 |
| Unique diffractions | 1586 |
| (C) Refinement of the structure | |
| *R* 0.036 | $R = \Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$ |
| $R_w$ 0.086 | $R_w = [\Sigma w(\|F_o^2\|-\|F_c^2\|)^2/\Sigma w\|F_o^2\|^2]^{1/2}$ |
| Variable parameters | 80 |
| 'Goodness of fit' (GOF) | 1.20 |

ometer with *a* offset by 4° from the ϕ axis. Scanning of several diffractions showed symmetrical peaks and only on the most intense was a small adjacent peak recognized with an intensity of ~2% of the main peak. Refinement using 24 diffractions (14<2θ<28°: λ = 0.7093 Å), each the average of automatic centering of eight equivalent settings gave the final cell parameters (Table 1) consistent with those given by Stanley *et al.* (1991) and Kutzke *et al.* (1997). In total, 6,999 intensities were collected with ω step scans, 0.02° steps, 1 s/step, and a scan width of 1.8° for a 2θ range of 3.5–55°. Merging yielded 1586 intensities ($R_{int}$ = 0.029), all of which were used in refinements: the data collection range was $h \pm 5$, $k \pm 11$, $l \pm 21$; the mean intensity variation of three standard diffractions was 4%. An absorption correction using an analytical method was attempted, but was not applied to the data because of the poor fit of ϕ scans for test diffractions. This was the result of the inability to describe the irregularly shaped crystal. Therefore no absorption correction was applied. Systematic absences indicated space group $P2_1/m$, consistent with deductions by Stanley *et al.* (1991) and Kutzke *et al.* (1997). The initial model was derived from the direct methods program in SHELXTL (Trademark of Siemens Energy and Automation, Inc., Analytical Instrumentation, Madison, WI, USA). All Pb atoms were included in a least squares refinement using anisotropic temperature factors, and the Cl, O and C positions were located in subsequent difference-Fourier maps and included in the refinement. Subsequent analysis resulted in postulated positions of the H atoms (see discussion).

In the final model, 80 variables were refined: scale factor, extinction parameter positions for 11 atoms, and anisotropic displacement factors. The computer programs used included both local data reduction routines as well as SHELXTL with neutral scattering factors. The final least-squares refinement minimized all $F^2$ values, with $\sigma_F{}^2$ computed from $\sigma I$, the square root of [total counts + (2% of total counts)$^2$], $w = (\sigma_{F2})^{-2}$, $R(F) = 0.036$, $R_w(F^2) = 0.086$, $S = 1.20$; largest shift/e.s.d. ≈ 0.001 for all parameters; and maximum and minimum heights on final difference-Fourier map of +3.5 and −2.0 eÅ$^{-3}$. The final atomic coordinates and isotropic displacement parameters are given in Table 2, anisotropic displacement parameters in Table 3, and interatomic distances in Table 4.

## Structure

The barstowite structure can be most easily represented as a stacking of three layer types: Layer A – Pb-chloride; Layer B – Pb-chloride-$H_2O$; Layer C – Pb-chloride-carbonate. These layers are stacked in the [001] direction as ...CACBCACBC... to give a 16.7 Å *c* repeat (Fig. 1). Layer A is possibly the simplest and is composed of $PbCl_8$ distorted square antiprisms as shown in Fig. 2. The Pb(2)–Cl distances range from 2.84 to 3.20 Å. Similar coordination about Pb was described in laurionite (Venetopoulos and Rentzeperis, 1975) where Pb is coordinated to 5 Cl and 3 O in a distorted square antiprism. In this case, in contrast to barstowite, the antiprism is highly distorted because of the two types of anions.

Layer B, illustrated in Fig. 3, is composed of a sequence of Pb(1) with five Cl atoms located on one side of the Pb and two O(2) atoms opposite these Cl atoms. The two O atoms are actually $H_2O$ groups. The location of the H atoms was obtained by assuming that the coordination about O(2) was idealized tetrahedral with the position of the two

TABLE 2. Positional and isotropic displacement parameters for barstowite

| Atom | $x$ | $y$ | $z$ | $^*U_{eq}$ |
|---|---|---|---|---|
| Pb (1) | 0.2609(2) | 0.75 | 0.0415(1) | 0.0273(2) |
| Pb (2) | −0.7458(2) | 0.75 | 0.5116(1) | 0.0285(2) |
| Pb (3) | −0.1900(1) | 0.5096(1) | 0.2682(1) | 0.0189(2) |
| Cl (1) | 0.2892(8) | 0.75 | 0.2189(2) | 0.0187(7) |
| Cl (2) | −0.2310(6) | 0.5309(3) | 0.0879(2) | 0.0208(5) |
| Cl (3) | −0.2557(9) | 0.75 | 0.3957(2) | 0.0195(7) |
| Cl (4) | −0.2382(6) | 0.5502(3) | 0.5858(2) | 0.0214(5) |
| O (1) | −0.325(2) | 0.25 | 0.2875(7) | 0.021(2) |
| O (2) | 0.753(3) | 0.75 | −0.0632(6) | 0.019(2) |
| O (3) | 0.293(2) | 0.3729(7) | 0.2229(4) | 0.018(1) |
| C | −0.584(3) | 0.25 | 0.2457(9) | 0.016(3) |
| #H | 0.7492 | 0.6640 | −0.0969 | |

$^*U_{eq}$ is defined as $1/3 \sum_{i=1}^{3} \sum_{j-1}^{3} U_{ij}a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$

# H position deduced from geometry (see text).

Pb(1) atoms defining vertices and two H positions completing the tetrahedron with proper geometry. The derived positional parameters for H are given in Table 2. This resulted in H−O(2) distances of ~0.97 Å and a H−O(2)−H angle of 109.5°. A similar conclusion was made for the H position in penfieldite (Merlino *et al.*, 1995) where the coordination of 3 Pb atoms about a central O could be completed by the addition of a H atom to give tetrahedral geometry and an O-H···Cl bond.

Layer C is illustrated in Fig. 4 and shows Pb(3) coordinated to 5 Cl atoms, again all located one one side of the central Pb. On the other side, Pb(3) is coordinated to 3 O atoms from two different carbonate groups. The C−O(3) bond length is slightly longer than the C−O(1) length because O(3) is also H-bonded to the water molecule H−O(3) at 2.12 Å.

The similarity of barstowite to phosgenite, $Pb_2Cl_2(CO_3)$, based on IR spectra was noted by Stanley *et al.* (1991). Indeed, phosgenite is a layered structure with one layer based on $PbCl_5O_4$ polyhedra (Giuseppetti and Tadini, 1974) analogous to the $PbCl_8$ polyhedra in barstowite (Layer A) although phosgenite has nine coordinated Pb. Likewise, the carbonate group in

TABLE 3. Anisotropic displacement parameters for barstowite

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Pb (1) | 0.0223(3) | 0.0329(4) | 0.0266(3) | 0.0 | 0.0003(2) | 0.0 |
| Pb (2) | 0.0224(3) | 0.0336(4) | 0.0296(3) | 0.0 | 0.0010(2) | 0.0 |
| Pb (3) | 0.0187(2) | 0.0134(2) | 0.0246(2) | −0.0018(1) | −0.0009(1) | −0.0008(1) |
| Cl (1) | 0.019(2) | 0.016(2) | 0.021(2) | 0.0 | −0.002(1) | 0.0 |
| Cl (2) | 0.023(1) | 0.020(1) | 0.019(1) | 0.0014(9) | 0.0008(9) | 0.001(1) |
| Cl (3) | 0.025(2) | 0.017(2) | 0.016(2) | 0.0 | 0.001(1) | 0.0 |
| Cl (4) | 0.024(1) | 0.018(1) | 0.022(1) | 0.0007(9) | −0.0037(9) | 0.003(1) |
| O (1) | 0.014(5) | 0.015(5) | 0.034(6) | 0.0 | −0.005(4) | 0.0 |
| O (2) | 0.022(5) | 0.017(5) | 0.016(5) | 0.0 | −0.001(4) | 0.0 |
| O (3) | 0.020(3) | 0.010(3) | 0.024(4) | 0.002(3) | −0.000(3) | 0.003(3) |
| C | 0.013(6) | 0.012(6) | 0.023(7) | 0.0 | 0.015(5) | 0.0 |

TABLE 4. Bond lengths (Å) for barstowite ($3PbCl_2 \cdot PbCO_3 \cdot H_2O$)

| | | | | | |
|---|---|---|---|---|---|
| Pb (1) – O (2) | 2.714(11) | Pb (2) – Cl (3) | 2.838(4) | Pb (3) – O (1) | 2.479(3) |
| – O (2) | 2.747(11) | – Cl (3) | 2.867(4) | – O (3) | 2.523(7) |
| – Cl (1) | 2.954(4) | – Cl (4) | 3.048(3) | – O (3) | 2.602(7) |
| – Cl (2) | 3.006(3) | – Cl (4) | 3.048(3) | – Cl (2) | 3.010(3) |
| – Cl (2) | 3.006(3) | – Cl (4) | 3.059(3) | – Cl (4) | 3.029(3) |
| – Cl (2) | 3.020(3) | – Cl (4) | 3.059(3) | – Cl (3) | 3.086(2) |
| – Cl (2) | 3.020(3) | – Cl (4) | 3.203(3) | – Cl (1) | 3.120(3) |
| | | – Cl (4) | 3.203(3) | – Cl (1) | 3.201(3) |
| C (1) – O (1) | 1.271(18) | | | | |
| – O (3) | 1.296(10) | | | | |
| – O (3) | 1.296(10) | | | | |

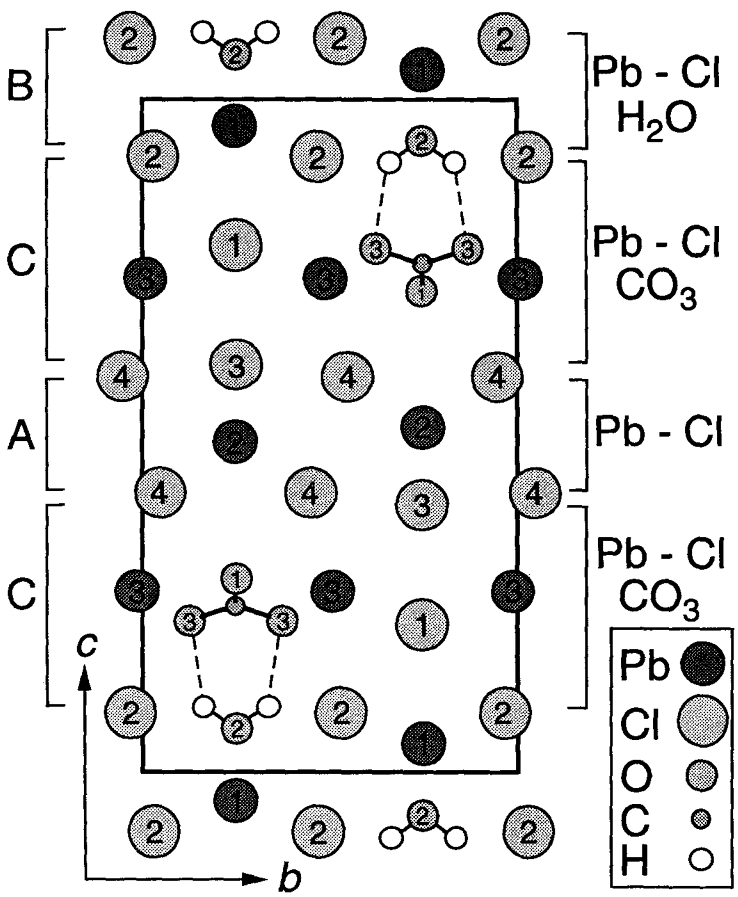

FIG. 1. Projection of barstowite structure onto (001). Three layer types are noted which are stacked along [001] in the sequence ...BCACBCA... as indicated on the left. Layer A includes Pb(2) and Cl(3) and Cl(4). Layer B includes Pb(1), Cl(1), Cl(2), and O(2) which is attached to 2 H atoms. Layer C is composed of Pb(3), Cl(1), Cl(2), Cl(3), Cl(4), and $CO_3$. H–bonding is indicated by dashed lines between H atoms and two O atoms of the $CO_3$ group (see discussion).

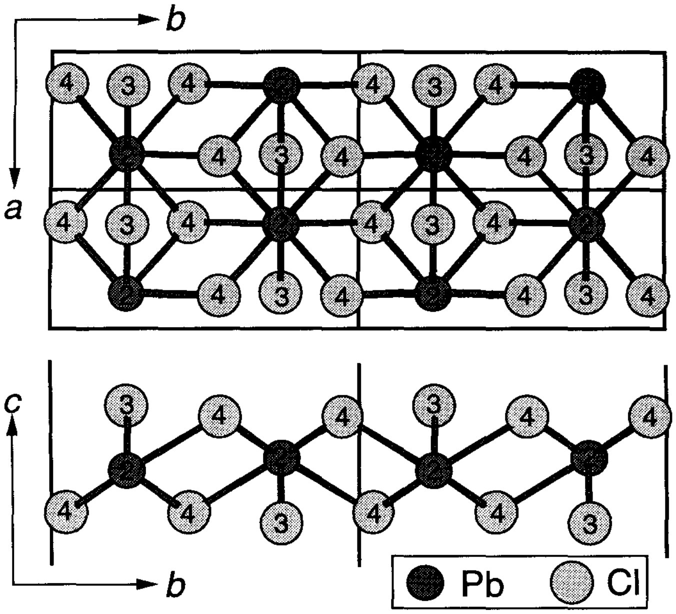

FIG. 2. Projection of Layer A onto (001) (top) and onto (100) (bottom). Pb(2) is coordinated to eight Cl atoms forming a slightly distorted square antiprism.

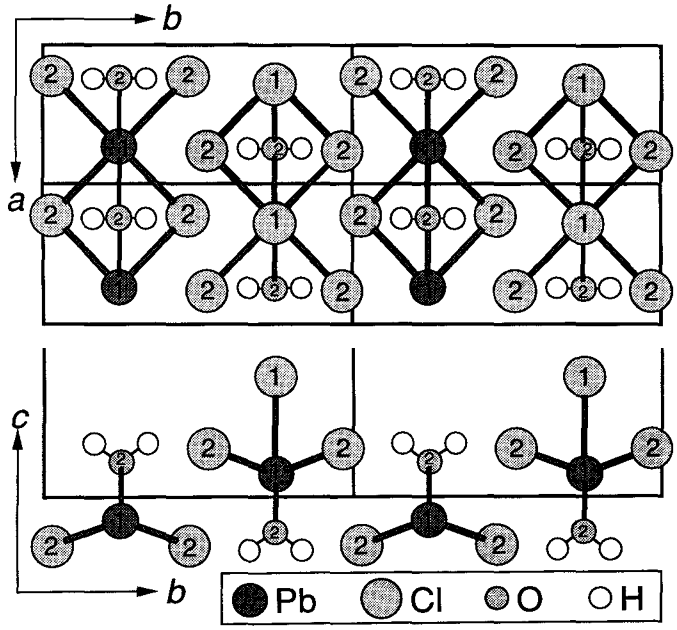

FIG. 3. Projection of Layer B onto (001) (top) and onto (100) (bottom). Pb(1) is coordinated to 5 Cl atoms and 2 O atoms from $H_2O$ groups. For each Pb(1) labelled in the upper figure, an O(1) below is not shown as they would superimpose.

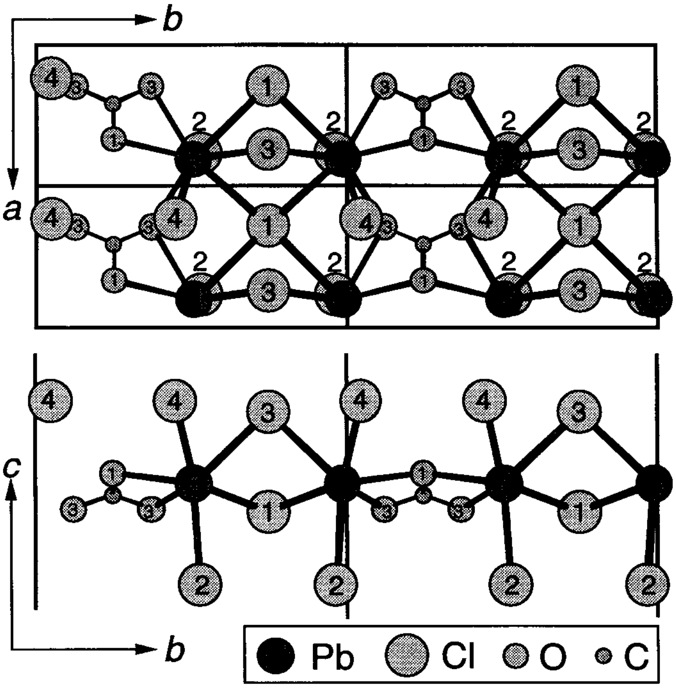

FIG. 4. Projection of Layer C onto (001) (top) and onto (100) (bottom). Each Pb(3) is coordinated to 5 Cl atoms and 3 O atoms of the $CO_3$ groups.

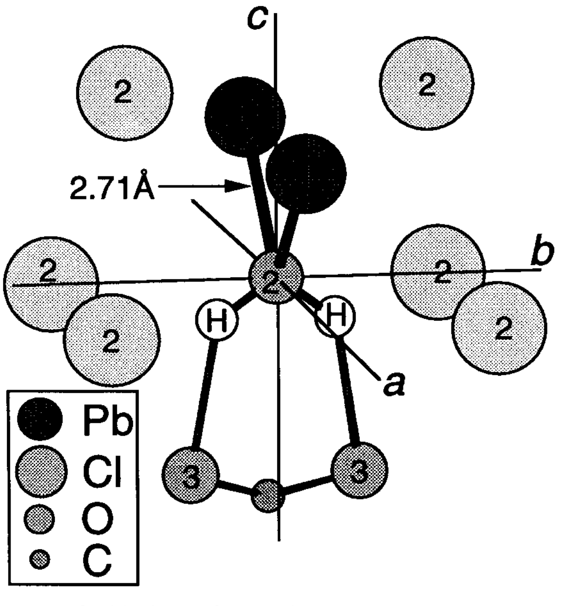

FIG. 5. Illustration of environment of O(2), the O of $H_2O$. The coordination about O(2) is formed by 2 Pb(1) and 2 H atoms shown in tetrahedral geometry. The O(2)–H distances are ~1.0 Å while the H–O(3) distances are ~2.10 Å, consistent with H-bonding.

phosgenite and barstowite has one short bond as in aragonite resulting in similar IR spectra (Stanley *et al.*, 1991). The inferred geometry of H necessary to satisfy the coordination about O(2) confirms the presence of $H_2O$ groups as deduced again from the IR spectra.

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