

THE CRYSTAL STRUCTURE OF ORLANDIITE, $\text{Pb}_3\text{Cl}_4(\text{SeO}_3)\cdot\text{H}_2\text{O}$, A COMPLEX CASE OF TWINNING AND DISORDER

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ABSTRACT

The crystal structure of orlandiite, $\text{Pb}_3\text{Cl}_4(\text{SeO}_3)\cdot\text{H}_2\text{O}$, has been determined and refined to $R = 0.042$. Orlandiite is triclinic, space group $P\bar{1}$ (no. 2), with a 8.136(3), b 8.430(6), c 9.233(7) Å, α 62.58(7), β 71.84(4), γ 75.13(4)°, and $Z = 2$. The unit cell can be referred to a pseudomonoclinic C -centered setting using the transformation $[-2 \frac{1}{2} 0 / 0 -\frac{1}{2} 0 / 0 -\frac{1}{2} 1]$, leading to a 15.727, b 4.215, c 8.196 Å, β 103.03°. The crystals so far examined are twinned on the $\{0 1 0\}$ plane in the pseudomonoclinic reference-frame, in cases closely simulating monoclinic symmetry. Besides twinning-induced apparent disorder, especially involving the position of a lead atom, there is also actual disorder involving the selenite anion. Owing to disorder of the selenite group, two independent Pb atoms in the structure can be either nine-fold or eight-fold coordinated. In the first case, they are surrounded by six chlorine and three oxygen atoms of the selenite anion (tricapped trigonal prismatic coordination); in the second case, one of the bonded oxygen atoms is missing. These coordination polyhedra are linked together to form sheets normal to $[1 0 0]$. A third nine-fold coordinated Pb atom, showing apparent signs of disorder (actually caused by twinning) is located between these sheets, together with the SeO_3^{2-} anion and the H_2O molecule.

Keywords: orlandiite, crystal structure, selenite, twinning, lead, chlorides.

SOMMAIRE

Nous avons déterminé et affiné la structure cristalline de la orlandiite, $\text{Pb}_3\text{Cl}_4(\text{SeO}_3)\cdot\text{H}_2\text{O}$, jusqu'à un résidu R de 0.042. Il s'agit d'un minéral triclinique, groupe spatial $P\bar{1}$ (no. 2), a 8.136(3), b 8.430(6), c 9.233(7) Å, α 62.58(7), β 71.84(4), γ 75.13(4)°, et $Z = 2$. La maille élémentaire peut être transformée en maille pseudomonoclinique à C centré au moyen de la transformation $[-2 \frac{1}{2} 0 / 0 -\frac{1}{2} 0 / 0 -\frac{1}{2} 1]$, ce qui donne les paramètres a 15.727, b 4.215, c 8.196 Å, β 103.03°. Les cristaux que nous avons examinés sont maclés sur le plan $\{0 1 0\}$ dans le système de coordonnées pseudomonocliniques, et dans certains cas simulent très bien une symétrie monoclinique. En plus d'un désordre apparent dû au développement de macles, impliquant surtout la position d'un atome de plomb, il y a aussi un désordre réel impliquant la position de l'anion sélénite. A cause de ce désordre, deux atomes indépendants de Pb peuvent avoir une coordinence neuf ou huit. Dans le premier cas, le Pb est entouré de six atomes de chlor et trois d'oxygène d'un groupe sélénite (en coordinence prismatique trigonale à trois sommets); dans le second, un des atomes d'oxygène est absent. Ces polyèdres de coordinence sont liés l'un à l'autre pour former des feuillettes perpendiculaires à $[1 0 0]$. Un troisième atome de Pb, à coordinence neuf, aussi sujet à un désordre apparent dû au développement de macles, est situé entre ces feuillettes, avec l'anion SeO_3^{2-} et la molécule de H_2O .

(Traduit par la Rédaction)

Mots-clés: orlandiite, structure cristalline, sélénite, maclage, plomb, chlorures.

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INTRODUCTION

Orlandiite, a hydrated chloride selenite of lead with formula $\text{Pb}_3\text{Cl}_4(\text{SeO}_3)\cdot\text{H}_2\text{O}$, is a recently discovered mineral species named in honor of Prof. Paolo Orlandi of the University of Pisa (Campostrini *et al.* 1999). The mineral was found in a selenium-rich part of the oxidation zone at the old lead–arsenic mine of Baccu Locci, near Villaputzu, Sardinia, Italy, where it is associated with chalcocite and an impressive number of other secondary selenium minerals, among which another lead chloride selenite containing copper, $\text{Pb}_4\text{CuCl}_3(\text{SeO}_3)_3(\text{OH})$ (Campostrini *et al.* 1999). The association of these rare selenium oxysalts is very interesting (Pasero & Perchiazzi 1989, Campostrini & Gramaccioli 2001). No natural chloride selenites of lead have been discovered so far at other localities. A further area of interest concerns the possible relationships with other oxygenated chlorides of lead, either natural or synthetic. A crystal-structure investigation of orlandiite has been undertaken to clarify the nature of the new species.

COLLECTION OF X-RAY DATA
AND STRUCTURE REFINEMENT

A small fragment having approximate dimensions $0.02 \times 0.03 \times 0.08$ mm was mounted on a glass fiber in a random orientation. A preliminary examination and data collection were performed with $\text{MoK}\alpha$ radiation (0.71073 \AA) on an Enraf–Nonius CAD4 kappa axis diffractometer equipped with a graphite crystal monochromator on the incident beam. The unit-cell parameters are reported in Table 1, together with some relevant crystallographic details. The cell constants were obtained from a least-squares refinement, using the setting angles of 25 reflections in the range $8 < \theta < 20^\circ$. Using the matrix $[-2 \frac{1}{2} 0 / 0 -\frac{1}{2} 0 / 0 -\frac{1}{2} 1]$ to transform the unit cell, a pseudomonoclinic C-centered cell with a 15.727, b 4.215, c 8.196 \AA , β 103.03° is obtained; such a marked pseudo-symmetry accounts for the ubiquitous

presence of twinning on the $\{0 1 0\}$ plane (in the monoclinic setting).

The data were collected at room temperature, using the ω -scan technique, up to a maximum 2θ of 54° . On the basis of the occupancy results obtained from the structure refinement, the crystal fragment used was found to consist of two different individuals in a twin relationship in the proportion of 75 and 25%. The only other crystal suitable for X-ray data collection was found also to be a twin consisting of two individuals in equal amounts and perfectly simulating monoclinic symmetry. Owing to the complexity of the situation, the absence of extra reflections was accurately checked using a Siemens diffractometer equipped with a SMART CCD area-detector. This procedure has also shown the absence of peak splitting. Details of the data-collection procedure and structure refinement also are reported in Table 1.

Lorentz and polarization corrections were applied to the data, as well as an empirical absorption correction, as described in Demartin *et al.* (1991). The structure was solved by direct methods [SHELXS 86, Sheldrick (1990)] and difference-Fourier synthesis. In the refinement, full-matrix least-squares were used [SHELXL 97, Sheldrick (1997)]. Scattering factors of neutral atoms were assumed for Pb, Se, Cl, and O; anomalous dispersion effects were included in Fc. Site occupancies affected by disorder and twinning were first refined separately for each atom, to account for a reasonable interpretation of such effects; in the final steps, they were kept fixed in order to minimize the number of parameters to be refined.

Observed and calculated structure-factor tables are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A general picture

The mineral displays a layered structure similar to those observed in cotunnite, PbCl_2 [Nozik *et al.* 1976], and in lead oxyhalide compounds, such as barstowite $\text{Pb}_4\text{Cl}_6(\text{CO}_3)\cdot\text{H}_2\text{O}$, in which complex anions play the same structural role as halide ions (Kutzke *et al.* 2000). A perspective view of the crystal structure, as seen almost along $[001]$, in which such layers are evident, is shown in Figure 1.

The positions of the significant electron-density peaks are reported in Table 2, together with their interpretation in terms of atom positions and occupancies. Such an interpretation implies the simultaneous presence of disorder in the selenite group, which is distributed over two positions of equal weight, and twinning; the problem was rendered complex by the overlap of most positions related by both such processes, with the only exception of those involving Pb(3) and Se, which

TABLE 1. CRYSTALLOGRAPHIC DATA FOR ORLANDIITE

Molecular formula	$\text{Pb}_3\text{Cl}_4(\text{SeO}_3)\cdot\text{H}_2\text{O}$	Formula weight	908.35 amu
Crystal system	triclinic	Space group	$P\bar{1}$ (no. 2)
a (\AA)	8.136(3)	b (\AA)	8.430(6)
c (\AA)	9.233(7)	α ($^\circ$)	62.58(7)
β ($^\circ$)	71.84(4)	γ ($^\circ$)	75.13(4)
V (\AA^3)	529.3(7)	Z	2
D_{calc} (g cm^{-3})	5.699		
μ ($\text{MoK}\alpha$) (cm^{-1})	520.1	Scan mode	ω
Scan speed ($^\circ \text{ min}^{-1}$)	0.5–2	Scan width ($^\circ$)	$1.5+0.35 \tan \theta$
θ range ($^\circ$)	3–27	Measured refl.	2430
Independent refl.	2287	Observed refl.	
Transmission factors	0.45–1.00	$[I > 2\sigma(I)]$	1311
Parameters refined	128	Final R and R_w indices ⁵	0.047, 0.104
Largest diff. peak and hole ($e \text{\AA}^{-3}$)	2.53, –3.99		

$$^5 R = [\sum (F_o - k |F_c|) / \sum F_o] \quad R_w = [\sum w (F_o - k |F_c|)^2 / \sum w F_o^2]^{1/2}$$

do not overlap. This apparently surprising situation accounts for the very presence and ease of twinning (see below).

For the sake of clarity, in Table 2 and elsewhere in the paper, the two different sites occupied by the corresponding atoms of the disordered selenite anion are denoted by *a* and *b*, respectively; on the other hand, the primes refer to the less abundant (25%) individual in the twin.

Interatom distances and angles are reported in Table 3. Here, together with the bond distances around Pb(3) and the Se atoms, the corresponding distances between Pb'(3) or Se' and their neighbors in the minor portion (25%) of the twin are also reported for comparison. The differences between the two sets are hardly significant, in spite of the low values of the estimated standard deviation, because there are considerable systematic errors due to partial overlap of some electron-density peaks. Such a similarity of the corresponding portions provides one of the proofs in favor of the presence of twinning (see also below).

The asymmetric unit of the mineral corresponds to the formula $\text{Pb}_3\text{Cl}_4(\text{SeO}_3)\cdot\text{H}_2\text{O}$, and completely agrees with the results of chemical analyses (Campostrini *et al.* 1999). Refinement of the positional, displacement and site-scattering parameters indicates full occupancy of the two lead sites, A and B. However, this "full" occupancy actually derives from overlap of the corresponding electron-density peaks in the twin, [*i.e.*, 0.75 Pb(1) + 0.25 Pb'(1) for A, and 0.75 Pb(2) + 0.25 Pb'(2) for B]. Because of twinning, a third lead site is instead apparently split into two subsites, designated as Pb(3) and Pb'(3), with an occupancy of 0.75 and 0.25, respectively. It may be helpful to note that there is no significant difference between the corresponding equivalent values of *U* of these Pb(3) and Pb'(3) atoms in the list

of atomic displacement parameters (Table 2); instead, the differences that can be seen in the anisotropic U_{ij} parameters are only due to the different orientation of such atoms.

As disorder and twinning act jointly in this structure, the selenium atom gives rise to four distinct peaks, of different weight. The two positions of selenium in the dominant individual (75%), which are related by disorder, are indicated by Se(a) and Se(b), respectively; the two corresponding alternative configurations of the SeO_3^{2-} anion involve the atoms Se(a), O(1a), O(2a), O(3a) on one hand, and Se(b), O(1b), O(2b), O(3b) on the other. The same refined value of occupancy (0.375) for both these positions, Se(a) and Se(b), which are not overlapping, indicates that such configurations occur in

TABLE 2a. ORLANDIITE: FRACTIONAL COORDINATES AND TOTAL OCCUPANCY

Site	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	Occupancy
Pb(3)	0.5689(2)	0.6062(3)	0.7553(2)	0.75
Pb'(3)	0.5689(7)	0.1048(9)	0.7543(6)	0.25
Se(a)	0.4904(6)	0.8685(8)	0.3860(7)	0.375
Se(b)	0.4926(6)	0.7532(9)	0.3850(7)	0.375
Se'(a)	0.5042(24)	0.6413(31)	0.6178(26)	0.125
Se'(b)	0.5128(23)	0.7443(30)	0.6167(24)	0.125
A**	0.11376(11)	-0.00862(14)	0.71741(12)	1.00
B	0.12075(11)	0.48200(15)	0.71678(12)	1.00
C	0.19243(70)	0.09558(86)	0.96161(71)	1.00
D	0.19225(63)	0.60008(82)	0.95409(68)	1.00
E	-0.13721(69)	0.33192(82)	0.65464(69)	1.00
F	0.13242(66)	0.16944(84)	0.34662(68)	1.00
G	0.4992(27)	0.7555(36)	0.9967(37)	1.00
J	0.6710(22)	0.7415(25)	0.4332(22)	1.00
Ka	0.5742(40)	1.0638(48)	0.3343(41)	0.50
Kb	0.5657(32)	0.5653(39)	0.3347(33)	0.50
La	0.3685(37)	0.8144(42)	0.5799(37)	0.50
Lb	0.3661(39)	0.6707(46)	0.5796(39)	0.50

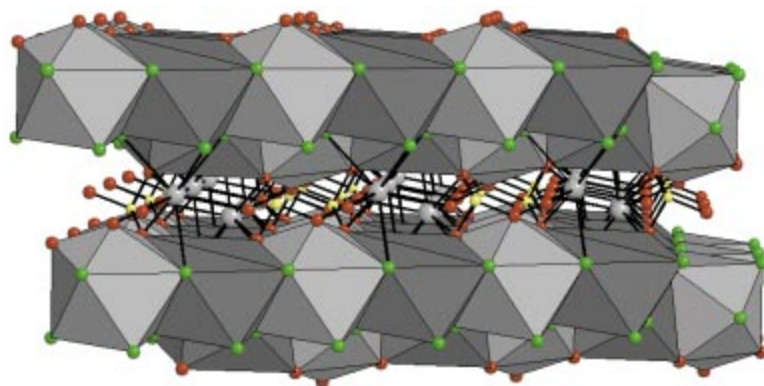


FIG. 1. View of the structure of orlandiite as seen almost along [001]. Color code: Pb(1): dark gray polyhedra, Pb(2): light gray polyhedra, Pb(3): light gray spheres, Cl: green spheres, Se: yellow spheres, and O: red spheres.

TABLE 2b. ORLANDITE: DISPLACEMENT PARAMETERS

Site	U_{11}/U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Pb(3)	0.0106(5)	0.0730(12)	0.0149(6)	-0.0077(7)	-0.0021(4)	-0.0004(5)	0.0384(4)
Pb'(3)	0.0441(23)	0.0829(44)	0.0173(20)	0.0007(23)	-0.0180(17)	-0.0036(24)	0.0549(15)
Se(a)	0.0117(22)	0.0105(27)	0.0101(25)	-0.0037(21)	-0.0010(18)	-0.0008(19)	0.0115(11)
Se(b)	0.0094(22)	0.0217(31)	0.0079(24)	-0.0065(21)	-0.0016(18)	-0.0028(20)	0.0128(12)
Se'(a)	0.0253(44)						
Se'(b)	0.0218(41)						
A	0.0220(4)	0.0242(6)	0.0243(5)	-0.0086(4)	-0.0074(3)	-0.0017(4)	0.0238(3)
B	0.0237(4)	0.0260(6)	0.0249(5)	-0.0109(5)	-0.0078(3)	-0.0009(4)	0.0247(3)
C	0.240(25)	0.0274(37)	0.0215(29)	-0.0086(27)	-0.0035(22)	-0.0045(24)	0.0251(13)
D	0.0161(22)	0.0258(35)	0.0187(27)	-0.0072(26)	0.0003(20)	-0.0026(22)	0.0222(13)
E	0.0240(25)	0.0212(35)	0.0202(30)	-0.0076(26)	-0.0023(21)	0.0010(23)	0.0237(13)
F	0.0210(24)	0.0287(37)	0.0191(29)	-0.0087(26)	-0.0060(20)	-0.0081(23)	0.0221(13)
G	0.0350(94)	0.0533(117)	0.1313(195)	-0.0633(131)	0.0000(110)	-0.0115(84)	0.0668(65)
J	0.0362(41)						
Ka	0.0267(75)						
Kb	0.0118(57)						
La	0.0239(65)						
Lb	0.0281(70)						

* The temperature factor is of the form: $T_i = \exp(-2\pi^2(U_{11}h^2(a^*)^2 + \dots + 2U_{12}hka^*b^* + \dots))$

** For the sites A to L, the populations are the following (the symbols a and b refer to the different orientations of the selenite anion owing to disorder, and the primes refer to the less abundant individual (25%) of the twin):

A = 0.75 Pb(1) + 0.25 Pb'(1), no a-b disorder B = 0.75 Pb(2) + 0.25 Pb'(2), no a-b disorder
 C = 0.75 Cl(1) + 0.25 Cl'(2), no a-b disorder D = 0.75 Cl(2) + 0.25 Cl'(1), no a-b disorder
 E = 0.75 Cl(3) + 0.25 Cl'(4), no a-b disorder F = 0.75 Cl(4) + 0.25 Cl'(3), no a-b disorder
 G = 0.75 OW + 0.25 OW' J = 0.375 O(1a) + 0.375 O(1b) + 0.125 O'(1a) + 0.125 O'(1b)
 Ka = 0.375 O(2a) + 0.125 O'(2b) Kb = 0.375 O(2b) + 0.125 O'(2a)
 La = 0.375 O(3a) + 0.125 O'(3a) Lb = 0.375 O(3b) + 0.125 O'(3b)

equal amounts, in agreement with our expectation from thermodynamic considerations (see below). A further important detail supporting our interpretation is that the sum of such occupancies ($2 \times 0.375 = 0.75$) equals the corresponding refined value for Pb(3), which is not affected by actual disorder and belongs to the larger component (75%) of the twin. A corresponding situation occurs for Se'(a), Se'(b), and Pb'(3) in the other individual (25%) of the twin, *i.e.*, there are again two alternative orientations of the selenite anion, each having an occupancy of 0.125, involving the atoms Se'(a), O'(1a), O'(2b), O'(3a) on one hand, and Se'(b), O'(1b), O'(2a), O'(3b) on the other, and the sum ($2 \times 0.125 = 0.25$) equals the occupancy of Pb'(3).

For both the (a) and the (b) sites of the non-overlapping "disordered" atoms, such as Se, a value of 0.5 is attained if the corresponding occupancies in the two individuals of the twin are summed [*i.e.*, Se(a) plus Se'(a), *etc.*]. A similar situation can be observed for the overlapping "disordered" oxygen atoms O(2) and O(3), for which, owing to such overlap [*e.g.*, O(2b) with O'(2a)], the occupancy of the corresponding sites (Ka, Kb, La, Lb) is equal to 0.5. For the "J" site, a total occupancy of 1.00 is attained because it is common to all the four O(1) atoms of the split selenite groups.

Disorder or twinning?

There are good "thermodynamic" reasons for supporting the idea that this structure involves both actual disorder (of the selenite anion) and twinning [especially evident considering the Pb(3) atom]. For example, we examined the atom-atom distances in the corresponding configurations of the disordered selenite group, and also those around Pb(3) and Pb'(3). For the selenite anion, there is no significant difference in length not only between the Se(a)-O bonds and the Se(b)-O bonds, but also between these oxygen atoms and Pb. Accordingly, the two configurations (a) and (b) have the same energy, and disorder with equal population (50%) in the crystal indeed becomes the most plausible situation, in order to attain maximum entropy, *i.e.*, thermodynamic stability.

On the other hand, both Se(a) and Se(b) are incompatible with the presence of a lead atom at the Pb(3) site, otherwise the contact distances would be too short [*e.g.*, Pb(3)-Se(a) and Pb'(3)-Se(b) = 1.42 Å]. Therefore, the splitting between Pb(3) and Pb'(3) cannot be ascribed to disorder, and a similar argument holds concerning the "mirror" case concerning Pb(3) and either Se'(a) or Se'(b). In any case, since the corresponding distances concerning Pb(3) and Pb'(3) within the same

part of the twin are the same, there would be no reason why their population would depart from 50%. Therefore, the only possibility is that of having two portions of a twinned crystal examined together. Such a conclusion is supported by the occurrence of the same geometry within the two parts of the twin (see above and Table 3) and by the existence of crystals with variable proportions of the two individuals. The possibility of partial ordering of the selenite group is ruled out by the absence of extra peaks in the diffraction pattern (see above).

The Pb(1) and Pb(2) sites

The coordination polyhedra of the Pb(1) and Pb(2) atoms are shown in Figure 2. Each of these lead atoms is invariably coordinated by six chlorine atoms (green). The number of bound oxygen atoms (red) depends upon the orientation of the selenite anion, of which only one

possibility is shown in the figure, for sake of clarity. The bond distances around the Pb atoms are shown in Table 3: for these two atoms, all the possible bonds with the disordered oxygen atoms, labeled as "a" and "b", respectively, are reported, and such bonds actually exist or not depending upon the arrangement of the selenite anion. A fundamental point is that where Pb(1) is [9]-coordinated, an adjacent Pb(2) atom should be [8]-coordinated [six chlorine atoms, plus O(3a) and O(1), the latter being common to both orientations of the selenite anion], otherwise the Se(a)...Se(b) distance would be too short (0.98 Å).

In other words, each Pb atom is actually linked to either "a" or "b" oxygen atoms, but it is never linked to "a" and "b" atoms at the same time. For this reason, the coordination of Pb(1) is either nine-fold with trigonal tricapped prismatic geometry (TTP) [if it is bonded to "a" atoms, corresponding to the selenite group Se(a) O(1), O(2a) and O(3a)] or eight-fold [if it is bonded to O(3b), corresponding to the group Se(b), O(1), O(2b) and O(3b)]. Similarly, the coordination of Pb(2) is either nine-fold (if it is bonded to "b" atoms) or eight-fold (with "a" atoms). Both these coordination geometries are commonly observed in other lead oxysalts; for instance, the TTP polyhedron of composition $PbCl_6O_3$ is similar to that displayed by Pb(3) in barstowite (Kutzke *et al.* 2000), although it is more distorted. A similar asymmetric [8]-fold coordination for lead has also been observed in freedite, $Pb_3Cu(AsO_3)_2O_3Cl_5$ (Pertlik 1987). The Pb(1) and Pb(2) polyhedra alternate along [010] to form structural columns by sharing the triangular bases of the tricapped trigonal coordination prism or a triangular base of the bicapped trigonal coordination prism. The shortest distances occurring between Pb(1) and Pb(2) atoms within the columns are 4.147 and 4.284 Å, and they are similar to those found in barstowite (4.204 Å) (Kutzke *et al.* 2000). All lead-anion distances are within the usual ranges found for lead halide compounds [see, for instance Kutzke *et al.* (2000), Nozik *et al.* (1976)]. Columns containing the Pb(1) and Pb(2) atoms are connected along [001] through the sharing of faces and edges to form sheets normal to [100]. The shortest Pb-Pb distances occurring between the columns are about 4.84 Å.

The PbSeO₃•H₂O layer

The third independent Pb(3) atom is located between the sheets containing Pb(1) and Pb(2), together with the selenite anion and the H₂O molecule. The coordination geometry is shown in Figure 3 where, for the sake of clarity, only the situation relative to the Pb(3) atom belonging to the dominant individual in the twin (75%) is reported [the corresponding situation concerning Pb'(3) is analogous]. These lead atoms display nine-fold coordination, being surrounded by four chlorine atoms, three oxygen atoms of the selenite anion and two symmetry-related H₂O molecules (OW); they are arranged in a zig-

TABLE 3. INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN ORLANDIITE*

Lead polyhedra			
Pb(1)-Cl(1)	3.046(9)	Pb(2)-Cl(1)	3.021(6)
Pb(1)-Cl(1) ^a	3.140(6)	Pb(2)-Cl(2)	3.038(8)
Pb(1)-Cl(2) ^b	3.035(6)	Pb(2)-Cl(2) ^c	3.216(5)
Pb(1)-Cl(3)	2.991(6)	Pb(2)-Cl(3)	3.019(8)
Pb(1)-Cl(4)	3.009(6)	Pb(2)-Cl(3) ^f	3.018(6)
Pb(1)-Cl(4) ^e	3.011(8)	Pb(2)-Cl(4) ^f	3.046(6)
Pb(1)-O(1a,b) ^d	2.77(2)	Pb(2)-O(1a,b) ^d	2.76(2)
Pb(1)-O(2a) ^b	2.40(3)	Pb(2)-O(2b) ^d	2.40(2)
Pb(1)-O(3a) ^b	2.58(3)	Pb(2)-O(3b)	2.51(4)
Pb(1)-O(3b)	3.44(4)	Pb(2)-O(3a)	3.40(4)
Pb(3)-Cl(2)	3.041(5)	Pb'(3)-Cl(1)	3.063(7)
Pb(3)-Cl(2) ^j	3.349(7)	Pb'(3)-Cl(1) ^e	3.304(9)
Pb(3)-Cl(3) ^h	3.111(7)	Pb'(3)-Cl(3) ^h	3.096(10)
Pb(3)-Cl(4) ^d	3.109(7)	Pb'(3)-Cl(4) ^j	3.131(9)
Pb(3)-OW	2.88(4)	Pb'(3)-OW ^b	2.83(3)
Pb(3)-OW ^a	2.91(2)	Pb'(3)-OW ^c	2.91(2)
Pb(3)-O(1)	2.58(2)	Pb'(3)-O(1) ^d	2.69(2)
Pb(3)-O(2b) ^d	2.54(4)	Pb'(3)-O(2b) ^d	2.55(3)
Pb(3)-O(2a) ^h	2.57(3)	Pb'(3)-O(2a) ^d	2.56(5)
Pb(3)-O(3a)	2.43(3)	Pb'(3)-O(3a) ^d	2.74(3)
Pb(3)-O(3b)	2.46(4)	Pb'(3)-O(3b) ^d	2.74(3)
The selenite anion			
Se(a)-O(1a)	1.63(2)	Se(b)-O(1b)	1.61(2)
Se(a)-O(2a)	1.75(4)	Se(b)-O(2b)	1.76(4)
Se(a)-O(3a)	1.66(3)	Se(b)-O(3b)	1.68(3)
O(1a)-Se(a)-O(2a)	92(1)	O(1b)-Se(b)-O(2b)	95(1)
O(1a)-Se(a)-O(3a)	98(1)	O(1b)-Se(b)-O(3b)	99(1)
O(2a)-Se(a)-O(3a)	106(2)	O(2b)-Se(b)-O(3b)	104(2)
Se'(a)-O'(1a)	1.81(2)	Se'(b)-O'(1b)	1.79(3)
Se'(a)-O'(2b) ^d	1.79(4)	Se'(b)-O'(2a) ^h	1.79(5)
Se'(a)-O'(3a)	1.55(3)	Se'(b)-O'(3b)	1.66(5)
O'(1a)-Se'(a)-O'(2b) ^d	122(2)	O'(1b)-Se'(b)-O'(2a) ^h	126(2)
O'(1a)-Se'(a)-O'(3a)	95(2)	O'(1b)-Se'(b)-O'(3b)	93(2)
O'(2b)-Se'(a)-O'(3a)	118(2)	O'(2a) ^h -Se'(b)-O'(3b)	113(2)

Symmetry codes: a = -x, -y, 2-z; b = x, y-1, z; c = -x, -y, 1-z; d = 1-x, 1-y, 1-z; e = -x, 1-y, 2-z; f = -x, 1-y, 1-z; g = 1-x, -y, 2-z; h = 1+x, y, z; i = 1-x, -y, 1-z; j = 1-x, 1-y, 2-z; k = 1-x, 2-y, 1-z. * Bond distances and angles belonging to the less abundant individual (25%) in the twin are reported in italics.

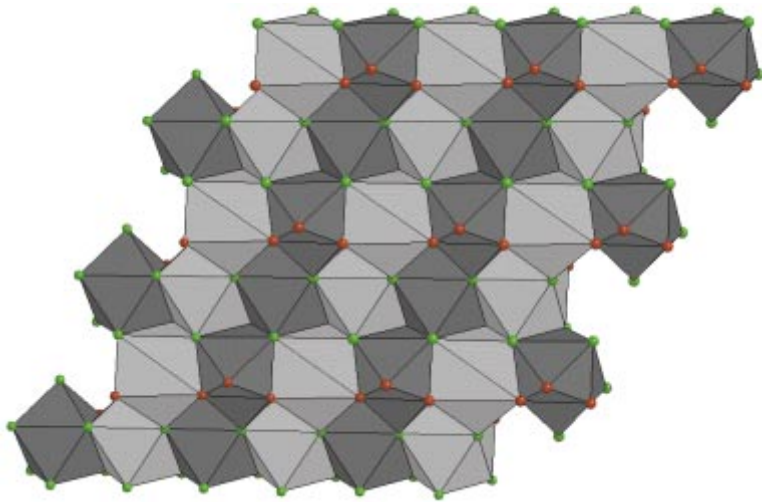


FIG. 2. View of the layer containing atoms Pb(1) (dark gray polyhedra) and Pb(2) (light gray polyhedra), as seen along [100].

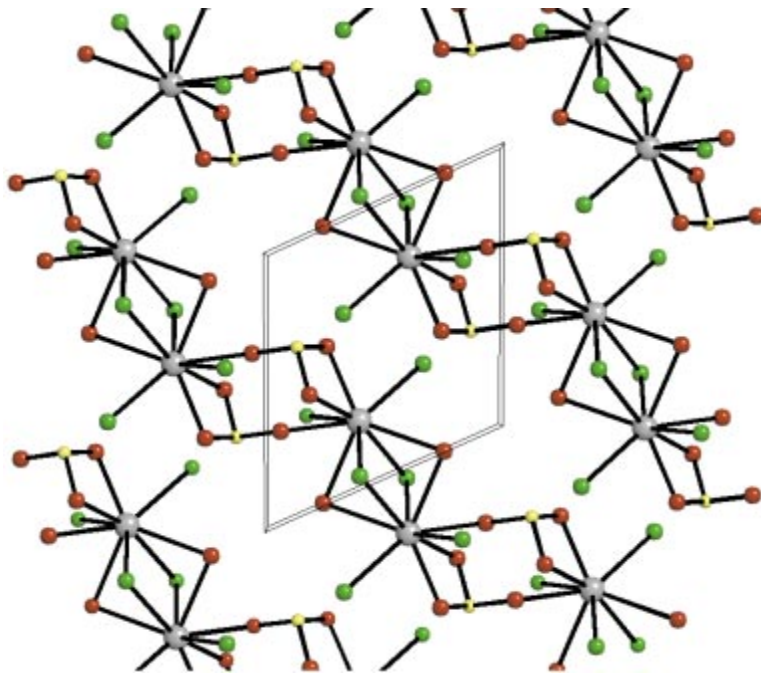


FIG. 3. View of the layer containing Pb(3), the selenite anion and the H₂O molecule. Color code: Pb: gray, Cl: green, Se: yellow, and O: red.

zag way and alternatively bridged either by selenite anions or by two chlorine atoms and two H₂O molecules. The shortest Pb(3)...Pb(3) interaction occurs where the symmetry-related Pb ions are bridged by H₂O molecules (3.911 Å). The selenite anion displays the expected trigonal pyramidal geometry.

The origin of twinning in orlandiite

Orlandiite is a lead chloride selenite related to a wide group of natural and synthetic lead oxychlorides. In addition, the structure of orlandiite provides a particularly clear explanation of the mechanism of twinning. Here, in fact, the situation almost accounts for the existence of a mirror plane, and nearly all the atoms actually coincide with their "mirror" images or with that of other atoms; the disordered Pb(3) and Se atoms, which are incompatible with such mirror images, constitute the only exceptions. For this reason, a true mirror plane does not exist.

Owing to this "quasi-monoclinic" symmetry, the existence of twinning is highly favored by the possibility of sharing most atoms in the composition plane between the two individuals. That such a composition plane (and twin plane) is indeed {010} in a monoclinic setting is certainly not surprising. Rather more surprising is the fact that the structure can actually be referred to a really "monoclinic" set of axes with $\alpha = \gamma = 90^\circ$ exactly. For the twin where the two individuals are present in equal amounts, such a geometry causes the usual crystallographic procedures to end up with a C-centered cell of apparently monoclinic *Cm* symmetry; such a structure was perfectly refinable up to a final *R* value of 0.056 on 870 independent reflections, of which 730 have an intensity $I > 2\sigma(I)$. This result caused considerable confusion at the beginning; the possibility of dimorphism was seriously considered, until it was definitely ruled out on the above grounds.

The triclinic primitive unit cell considered here for orlandiite conforms with the IUCr standards. Use of centered cells is instead only accepted on the strict basis of symmetry, in order to choose a set of axes that is the most appropriate reference for the symmetry operations. For this reason, reference to such cells is not recommended in the triclinic system, although they are currently used for some minerals (*e.g.*, triclinic feldspars). However, at least in the present case, where the α and γ angles are exactly 90° , a physically significant suggestion is apparent to justify the choice of centered cells, even for such a pseudosymmetrical structure.

ACKNOWLEDGEMENTS

The authors are indebted to Mr. Italo Campostrini for kind assistance in selecting the crystals used here. Financial contribution from MURST 40% 2001: "Cristallochimica dei minerali metallici e loro alterazione" is gratefully acknowledged by C.M. Gramaccioli. Drs. A. Pring, A.D. Rae, M. Snow and R.F. Martin provided considerable help in revising the manuscript.

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- Received January 8, 2003, revised manuscript accepted July 30, 2003.*